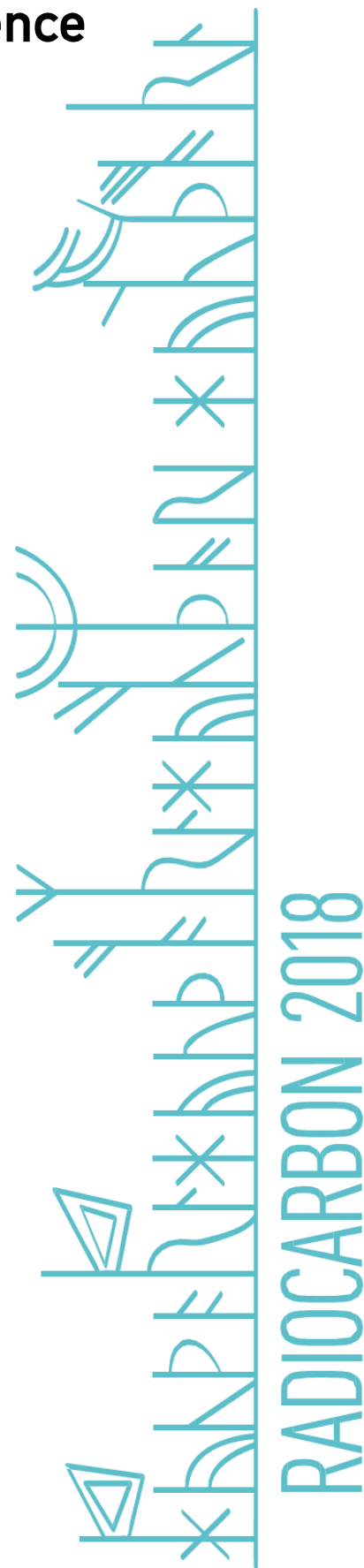


**23<sup>rd</sup> International Radiocarbon Conference**  
**June 17-22 2018**  
**Trondheim**

**Book of Abstracts**



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## Oral Presentations

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17:30			Poster Session 1	Poster Session 1	Poster Session 1	
18:00			Poster Session 1	Poster Session 1	Poster Session 1	
18:30			Poster Session 1	Poster Session 1	Poster Session 1	
19:00	Ice breaker	Registration	Pub of the Night: Kiegelkroa	City Tour		
19:30			Pub of the Night: Kiegelkroa	City Tour		
			Pub of the Night: Den Gode Nabo			

Updated program, 2018-06-15							
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16:30	Poster Session 2			Poster Session 2			
17:00	Poster Session 2			Poster Session 2			
17:30							
18:00							
18:30							
19:00	Pub of the Night: Lille London			Organ concert and conference dinner		Walk of the Night: Ladekaia	
19:30	Pub of the Night: Lille London			Organ concert and conference dinner		Walk of the Night: Ladekaia	

Monday 18-Jun-18 - 9:15 - Sansiro 1

## Archaeological Chronology: a Challenging Research Field

Elisabetta Boaretto<sup>1</sup>

<sup>1</sup> Kimmel Center for Archaeological Science and D-REAMS Radiocarbon Laboratory Weizmann Institute of Science.

Radiocarbon analysis is a very powerful tool for obtaining ages of strata within an archaeological site. In the words of William Libby “The determination of the chronology of ancient civilizations may be said to be the main archeological problem and task of radiocarbon dating.” This field of research, based on radiocarbon dating, has indeed changed several fundamental paradigms in archaeology, including the use of typology for synchronization between sites.

Chronological research in archaeology is limited by the relatively few materials that can be used for high resolution dating. Therefore the development of several new materials for dating such as ash, aragonite and phytoliths is underway, and research aimed at using mortar and plaster for dating, is still ongoing. Dating of single molecules and specific organic fractions in the material is also moving forward and radiocarbon researchers are looking for new materials for dating in order to improve chronological resolution.

**What next?** First step for solving challenging chronological problems in archaeology that relate to cultural changes is in the excavation; understanding the formation of the archaeological record. The excavation is where a chronology student should start integrating and applying other analytical methods, in addition to radiocarbon, to understand the archaeological record and its chronology.

Radiocarbon 2018 schedule: session color scheme	
M1	Developments in measurement techniques
M2	Developments in sample pretreatment
M3	Compound specific radiocarbon analysis
M4	New and updated facilities, status reports
M5	Laboratory management and organization
M6	Calibration and calibration records
M7	Statistical analysis and modelling
A1	Hydrology, limnology, oceanography, reservoir effects
A2	Terrestrial environment, sedimentology, plant, landscape etc.
A3	Climate studies
A4	Soil dynamics
A5	Archaeology
A6	Dendrochronology and single-year analysis
A7	Diet studies
A8	Anthropogenic impacts
A9	Forensics application of radiocarbon
A11	Other radiocarbon applications
O1	Other cosmogenic nuclides

Monday 18-Jun-18 - 10:30 - 11:30 - Sansiro 1

## Confessions of a Serial Polygamist: the reality of radiocarbon reproducibility in archaeological samples

Alex Bayliss<sup>1</sup>, Peter Marshall<sup>1</sup>

<sup>1</sup> Historic England, London, United Kingdom.

Since 1993 Historic England (and its predecessor English Heritage) has commissioned over 8000 radiocarbon measurements on archaeological samples. Over 80% of these have been interpreted within formal Bayesian statistical models. The multiple strands of reinforcing evidence incorporated in these models provide precise chronologies that make stringent demands on the accuracy of the radiocarbon results included in the analysis. Inter-laboratory replication is consequently a routine part of model validation and construction.

We report an analysis of replicate measurements from at least two laboratories on over 1000 archaeological samples. It is clear that laboratory reproducibility accounts for only part of the observed variation. The type of material dated is also critical to the reproducibility of measurements, with some sample types proving particularly problematic.

Monday 18-Jun-18 - 10:30 - 11:30 - Sansiro 1

## Detailed uncertainty analysis based on the first year of MICADAS in an experienced AMS group.

Anita Aerts-Bijma<sup>1</sup>, Harro Meijer<sup>1</sup>, Dipayan Paul<sup>1</sup>, Mike Dee<sup>1</sup>, Sanne Palstra<sup>1</sup>

<sup>1</sup> University of Groningen, Groningen, Netherlands.

After 25 years of loyal service, our High Voltage 2.5 MV Tandetron AMS was decommissioned when we moved our laboratories to our new building in spring 2017. As successor, we received an IonPlus "MICADAS" AMS instrument.

Compared to the previous machine, the most important innovation the Micadas brought to our lab is a substantially increased efficiency, resulting in much higher count rates and thus, at least in principle, significantly increased precision.

For our previous AMS facility, we used calculated "best estimates" for uncertainties that were based on all error sources in the measurements (next to the Poisson counting error also the standard deviation of the backgrounds, error in the mean of the calibration standards, and the uncertainty in the <sup>13</sup>C correction). Over the years, we verified that these uncertainties were indeed a good measure for the spread of the measurements [1].

With the Micadas we want to follow the same approach, that is, quantifying uncertainties as well as possible, instead of using (more or less) an educated guess. As the Poisson uncertainty is much lower than before (often close to 1‰ compared to almost 3‰ previously for 100% activity), several other uncertainty sources that were overwhelmed previously become visible, such as the spread caused by the combustion process (carry-over, incomplete combustion,...), chemical pretreatment variability, and others.

We will present the first results (based on one full year of operation) for the uncertainty budget of our <sup>14</sup>C measurements, for samples with need for various pretreatment steps: from just one -graphitization- to the full sequence including chemical pretreatments, extractions, combustion etc. The current result for a pure CO<sub>2</sub> sample with a 100% activity is 1.6 ‰ as the lowest possible uncertainty, with the graphitization step only. As this uncertainty is not limited by Poisson statistics, a longer measurement time will not reduce this number further.

[1] M. de Rooij et al., Radiocarbon 2008, 50, 413.

Monday 18-Jun-18 - 11:30 - 12:30 - Sansiro 1

## LASIS enhancements of C<sup>-</sup> currents from CO<sub>2</sub> samples

John Vogel<sup>1</sup>

<sup>1</sup> University of California (retired), Ukiah, CA, United States.

Ion-pair production from colliding neutral atoms is proposed as the dominant mechanism for creating negative ions in the cesium sputter ion source. The process depends on the electron donor atom having an ionization potential slightly greater than the electron affinity of the negative ion. That is the only requirement: ionization is possible between any two atoms if one has a positive electron affinity. The mechanism is better known in molecular chemistry than in elemental physics. Aside from the halogens, pair production has been quantified for only calcium (Ca) and rubidium (Rb) atoms, the first in collisions with excited neon and the second with excited Rb. Competition between sputtered products for specific excited Cs states as well as increased C<sup>-</sup> upon laser excitation of Cs(7p) are known. A model of the Ca-Ne\* collision has been generalized to predict the excited state energy for creating any elemental anion. This model explains the competition between sputtered O atoms and C atoms for the Cs(5d) state for CO<sub>2</sub> samples and allows speculative solutions for the low C<sup>-</sup> output. The most obvious solution from the model is to use Rb as the primary ion beam with 421 nm laser excitation of secondary Rb<sup>0</sup> to the Rb(6p) state. Poster discussions may reveal other solutions.

Monday 18-Jun-18 - 11:30 - 12:30 - Sansiro 1

## New radiocarbon mass spectrometry

Stewart Freeman<sup>1</sup>, Richard Shanks<sup>1</sup>, Cameron McIntyre<sup>1</sup>, Gabriel Gaubert<sup>2</sup>, Pierre Salou<sup>2</sup>, Kenny Kearney<sup>3</sup>, Thilo Hauser<sup>3</sup>, Mark Sundquist<sup>3</sup>

<sup>1</sup> SUERC, East Kilbride, United Kingdom.

<sup>2</sup> Pantechnik S.A., Bayeux, France.

<sup>3</sup> NEC, Middleton, WI, USA.

Positive-ion mass spectrometry (PIMS) is a recently invented and rapidly developing variant of accelerator mass spectrometry (AMS) that simplifies and extends radiocarbon measurement [1].

PIMS suppresses the interferences to C<sup>14</sup> detection with a hydrocarbon reaction cell that both dissociates mass 14 molecules and converts positive-ions negative to reject the N<sup>14</sup> isobar. This reversal of the usual AMS ion charging scheme eliminates the need for a particle accelerator and renders the new technique inherently more compatible with established sample speciation and preparation automation.

SUERC, Pantechnik & NEC have jointly developed a new PIMS instrument recently installed at SUERC, where the mass spectrometer complements the tandem & single-stage accelerator mass spectrometers already there. SUERC PIMS is done with an electron cyclotron resonance plasma ion source producing large C<sup>+</sup> beams from convenient gas samples. The new instrument is for diverse experimentation in tracer and natural-abundance radiocarbon science, and serves as the prototype for commercial spectrometers to follow.

PIMS performance and implications for radiocarbon metrology will be discussed.

[1] Freeman et al. (2015) Nucl. Instr. Meth. B 361 229–232.

*Monday 18-Jun-18 - 11:30 - 12:30 - Sansiro 1*

## HVE Sub-MV AMS based on vacuum insulated accelerators

Matthias Klein<sup>1</sup>, Dirk Mous<sup>1</sup>

*1 High Voltage Engineering Europa B.V., Amersfoort, Netherlands.*

HVE has included vacuum insulated tandem accelerators into its range of products. A 300 kV model was built for a sub-MV multi-element AMS test system. A smaller 210 kV model is applied in a dedicated <sup>14</sup>C radiocarbon system for biomedical and dating applications. This new system is characterized by a high level of automation that makes traditional beam tuning not necessary. The <sup>14</sup>C system is anticipated having a background level comparable to larger AMS systems. To minimize the energy cost of operation, permanent magnets are used for mass analysis. Technical details and system layout will be presented.

*Monday 18-Jun-18 - 11:30 - 12:30 - Sansiro 2*

## Big site, big data - Experiences and new possibilities with big data from a field archaeologist's point of view.

Magnar Mojaren Gran<sup>1</sup>, Ingrid Ystgaard<sup>1</sup>

*1 NTNU University Museum, Department of Archaeology and Cultural History, Trondheim, Norway.*

The Ørland project is one of the largest excavations of its kind in Norwegian archaeology. Covering an area of over 100 000 m<sup>2</sup>, along a narrow ridge on the Ørland peninsula at the mouth of the Trondheim fjord, it unearthed the remains of farmer-fisherman settlements spanning more than a millennium, from c. 700 BC – AD 1250.

The scale of the project has left us with a large amount of radiocarbon samples. With over 600 samples analyzed, we now find ourselves sitting on the largest dataset ever recorded on a single excavation in Norway.

Working with such big data has enabled us to interpret our site with more confidence, ask new questions, and even question old truths.

We would therefore like to share our experiences, and seek new possibilities within this dataset.



Monday 18-Jun-18 - 11:30 - 12:30 - Sansiro 2

## Systematic radiocarbon dating of human remains from the Late Neolithic collective dolmen burial of Oberbipp (Switzerland)

Noah Steuri<sup>1</sup>, Inga Siebke<sup>2</sup>, Anja Furtwängler<sup>3</sup>, Sönke Szidat<sup>4</sup>, Sandra Lösch<sup>2</sup>, Albert Hafner<sup>1</sup>

*1 Department of Prehistory, Institute of Archaeological Sciences and Oeschger Centre for Climate Change Research (OCCR), University of Bern, Switzerland.*

*2 Department of Physical Anthropology, Institute of Forensic Medicine, University of Bern, Switzerland.*

*3 Institute for Archaeological Sciences, Archaeo- and Palaeogenetics, University of Tübingen, Germany.*

*4 Department of Chemistry and Biochemistry and Oeschger Centre for Climate Change Research (OCCR), University of Bern, Switzerland.*

Collective megalithic burials of the Late Neolithic are found in the western parts of Europe between Southern Scandinavia and the Iberian Peninsula, however the discovery of undisturbed sites are extremely rare. The dolmen of Oberbipp is one of the few collective megalithic burial sites including human remains in Switzerland. The site therefore provides a unique opportunity for multidisciplinary research. Morphological analysis indicates, that approximately 40 individuals are buried in the grave chamber. It was not possible archaeologically to determine different occupation periods within the inhumations. Since dolmen graves were often reused over hundreds of years, this question could only be addressed with radiocarbon dating.

All the inhumations need to be dated individually. Since the evaluation of different burial sequences depends on precise dating, the same bony element (right femora) was analyzed by two (in some cases three) different laboratories. The aim of this systematical radiocarbon dating was therefore threefold: a) determine the total occupation time of the dolmen; b) evaluate the sequence of the burials; c) compare the results of the same skeletal element from different laboratories.

In total 73 radiocarbon dating results from three different laboratories (LARA Bern, CEZA Mannheim and RAU Oxford) of the right femora (n=31) are available to approach the question of the chronology of the burials.

The total occupation time of the dolmen was between 3350 and 2650BC. Only the application of systematical radiocarbon dating allowed determining two occupation periods within the burial.

In addition, the comparison between results shows that the dating of the same skeletal element varies little between laboratories, but in several cases, the difference was rather substantial and could have led to a different interpretation of the whole site.

The presentation will highlight the necessity of large serial dating of archaeological inhumations, especially from prehistoric collective burials of the Neolithic.

Monday 18-Jun-18 - 11:30 - 12:30 - Sansiro 2

## Pivotal Sites of Early Russia Radiocarbon Dated to the Exact Year

Margot Kuitems<sup>1</sup>, Andrei Panin<sup>2,3</sup>, Veronica Murasheva<sup>4</sup>, Elya Zazovskaya<sup>3</sup>, Yury Kononov<sup>3</sup>, Irina Arzgantseva<sup>5</sup>, Michael W. Dee<sup>1</sup>

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<sup>2</sup> Lomonosov Moscow State University, Russia.

<sup>3</sup> Institute of Geography RAS, Russia.

<sup>4</sup> State Historical Museum, Russia.

<sup>5</sup> Institute of Ethnology and Anthropology RAS, Russia.

Recent measurements on known-age (dendrochronological) tree-rings have revealed that the production of radiocarbon increased dramatically in the years 3372 BCE, 775 CE and 994 CE. These rapid increases in radiocarbon concentration, which are thought to result from intense bursts of cosmic radiation, can be used as the basis for a dating method capable of annual resolution. By detecting such a signal in a growth-ring from wood with the bark preserved, one simply has to count the number of rings to the edge to know the felling year of the tree. In this way, radiocarbon dating can achieve much higher precision than ever possible using traditional approaches. Recently, we applied this method to wood from Gnezdovo, near the Russia-Belarus border, which is one of the largest Viking sites of Europe, and a key centre of the early Slavic polities. Likewise, we dated 8th century wood from Por-Bajin in Tuva, on the Russia-Mongolia border. The function of this imposing fortress-like building, on an island in Lake Tere-Khol, has long been debated. We endeavoured to find the 775-signal in a number of wooden remains - with preserved bark - from the two sites. The first step, used to identify where the 775 CE (~15‰) uplift occurred, involved sampling every second tree-ring from the timbers obtained, and then combusting and directly measuring the samples as gas in the accelerator. Afterwards, once the point of uplift had been identified, the rings either side could be rigorously pretreated to alpha-cellulose and remeasured as graphite. The dates we have obtained are of unprecedented accuracy and precision and will allow new assessments to be made of the geochronological and archaeological significance of these sites. The results also demonstrate the suitability and potential of the novel methodology applied in this study.

Monday 18-Jun-18 - 13:40 - 15:20 - Sansiro 1

## The status report of AMS facility at CIAE

Ming He<sup>1</sup>, Qingzhang Zhao<sup>1</sup>, Yiwen Bao<sup>1</sup>, Qubo You<sup>1</sup>, Shengyong Su<sup>1</sup>, Shan Jiang<sup>1</sup>, Yueming Hu<sup>1</sup>, Yijun Pang<sup>1</sup>, Yuxuan Zhang<sup>1</sup>, Kangning Li<sup>1</sup>, Xiaoming Wang<sup>1,2</sup>, Shaoyong Wu<sup>1</sup>, Fangfang Wang<sup>1</sup>, Qi Meng<sup>1,3</sup>

<sup>1</sup> China Institute of Atomic Energy, Beijing, China.

<sup>2</sup> China Institute for Radiation Protection, Taiyuan, China.

<sup>3</sup> Guangxi Normal University, Guilin, China.

There are two AMS system now is using for AMS measurement. One is HI-13 AMS system, the another is single stage AMS. The HI-13 AMS system is based on a big accelerator which can working at terminal voltage of 12MV. There are two beam lines for AMS measurement. Base on the HI-13 AMS system more than 10 radionuclides such as <sup>10</sup>Be, <sup>36</sup>Cl, <sup>41</sup>Ca, <sup>53</sup>Mn, <sup>60</sup>Fe have been measured. The single stage AMS (SSAMS) system is a homemade AMS system which working at terminal of 200KV. Based on the SSAMS system, the measurement technique of <sup>14</sup>C and <sup>3</sup>H have been established. Beside the two system, a terminal voltage of 0.35MV AMS system is developing. This system is dedicated for the heavy nuclides (such as <sup>129</sup>I, <sup>236</sup>U, <sup>239</sup>Pu) measurement. The detail information for the three system and some applications will be introduced.

This work is supported by the national natural Science foundation of China under grant number of 11175266,11575296,11675269

Monday 18-Jun-18 - 13:40 - 15:20 - Sansiro 1

## Effect of $^{12}\text{C}$ beam saturation on the accuracy of $\delta^{13}\text{C}$ measurements from AMS

Gurazada Prasad<sup>1</sup>, Alex Cherkinsky<sup>1</sup>, Randy Culp<sup>1</sup>

<sup>1</sup> University of Georgia, Athens, GA, United States.

Compact AMS accelerators made possible the post-acceleration measurement of  $^{12}\text{C}$ ,  $^{13}\text{C}$  isotopes and hence determination of  $\delta^{13}\text{C}$ . Some labs do use the AMS derived  $\delta^{13}\text{C}$  for pMC correction. How accurate are the AMS derived  $\delta^{13}\text{C}$  values is the topic of our study. Our data for known standards showed that using  $\delta^{13}\text{C}$  values from IRMS consistently produced accurate pMC values. In this paper, we discuss the  $\delta^{13}\text{C}$  data from two AMS units at CAIS: an NEC 500kV CAMS and a 250kV SSAMS.

Analysis of samples measured on the CAMS unit shows that the mean difference between the  $\delta^{13}\text{C}$  values determined from AMS and IRMS instruments is less than 2 ‰. Fewer than 10% of the samples deviated from the IRMS values by more than 8 ‰.

However for SSAMS, the AMS  $\delta^{13}\text{C}$  values showed positive shift by about 10 ‰ and unusable for pMC correction. To address this issue, we need to look at the beam transmission of SSAMS and CAMS units, which is 32% and 42% respectively. To compensate for low beam transmission on SSAMS, we extract higher beam currents from the ion-source to achieve better statistical precision for  $^{14}\text{C}$  data. The  $^{13}\text{C}+/^{12}\text{C}+$  ratio on CAMS varies linearly with beam currents but high beam currents on SSAMS led to suppression of  $^{12}\text{C}+$  beam and even saturation beyond a certain value, resulting in a skewed  $^{13}\text{C}+/^{12}\text{C}+$  ratio. The SSAMS operating parameters for best  $^{14}\text{C}$  statistics differed from the parameters for optimal  $^{13}\text{C}/^{12}\text{C}$  ratio measurement. Beam current dependence of transmission has been previously reported in the literature, but there are not many detailed studies on its effect on the accuracy of AMS derived  $\delta^{13}\text{C}$  values. On the other hand, even at high currents,  $^{14}\text{C}+/^{13}\text{C}+$  ratios of the samples remained unaffected and when used with IRMS  $\delta^{13}\text{C}$  data, the pMC values obtained were in excellent agreement with consensus values for known standards.

On SSAMS, for pre-acceleration  $^{12}\text{C}^-$  current exceeding about 90  $\mu\text{A}$ , the post-acceleration  $^{12}\text{C}^+$  current is found to saturate. Since the  $^{12}\text{C}^+$  is not linear with  $^{12}\text{C}^-$  beam current, we explored if pre-acceleration  $^{12}\text{C}^-$  is linear with  $^{13}\text{C}^+$  beam current. It turned out these two beam currents are indeed linear with each other and suitable for  $\delta^{13}\text{C}$  calculation. This relationship may seem obvious given the beam saturation effect, but the linearity between  $^{12}\text{C}^-$  and  $^{13}\text{C}^+$  beams holds only for SSAMS and not for the CAMS tandem accelerator. We found dramatic improvement in the SSAMS  $\delta^{13}\text{C}$  data when  $^{13}\text{C}^+/^{12}\text{C}^-$  ratio was used for calculation and the positive shift in  $\delta^{13}\text{C}$  values was eliminated. As for the precision of  $\delta^{13}\text{C}$  from both machines, poorer precisions are thought to be primarily due to instabilities or variations in  $^{12}\text{C}$  beam current due to factors such as terminal fluctuations due to high beam current, short bounce times, suppression of beam transmission etc and need further investigation. This study is ongoing with the aim to improve the accuracy and precision of  $\delta^{13}\text{C}$  for both CAMS and SSAMS units.

Monday 18-Jun-18 - 13:40 - 15:20 - Sansiro 1

## Developments in AMS technology for biomedical applications

Daniele De Maria<sup>1</sup>, Simon Fahrni<sup>2</sup>, Lukas Wacker<sup>1</sup>, Frédéric Lozach<sup>3</sup>, Caroline Welte<sup>1</sup>, Hans-Arno Synal<sup>1</sup>

<sup>1</sup> Laboratory of Ion Beam Physics, Zurich, Switzerland.

<sup>2</sup> Ionplus AG, Dietikon, Switzerland.

<sup>3</sup> Novartis pharma, Basel, Switzerland.

Radiocarbon (<sup>14</sup>C) analyses by accelerator mass spectrometry (AMS) have great potential for biomedical applications, especially in pharmacokinetic studies using <sup>14</sup>C-labeled pharmaceutical compounds as a tracer. A major advantage compared to decay counting techniques is the high sensitivity of AMS that allows an innovative microtracer approach to ADME (Adsorption, Distribution, Metabolism and Excretion) studies, reducing significantly the administered radioactive dose. The applicability of AMS was investigated in a validation study conducted in collaboration with Novartis (Basel, Switzerland) in order to evaluate the performance of the MICADAS, the compact AMS facility used for routine gas measurements at ETH Zurich, Switzerland. The results of this study as well as technical improvements required to make AMS technology more competitive will be presented. Based on the experience gained through the validation study, a new gas handling system was developed to achieve a faster measurement process for applications where low precision but higher sample throughput is required. The design of the new interface will be discussed, focusing in particular on the strategies to overcome the time consuming cleaning procedure of the system required after each sample to avoid cross-contamination.

Monday 18-Jun-18 - 13:40 - 15:20 - Sansiro 1

## Investigation on the one-tube combustion and graphitization method for preparing AMS targets from organic materials

Xiaomei Xu<sup>1</sup>, Jennifer Walker<sup>1</sup>, Carla Mendez<sup>1</sup>, Dachun Zhang<sup>1</sup>, Guaciara Santos<sup>1</sup>

<sup>1</sup> University of California, Irvine, Irvine, California, United States.

Elder et al. (2017) presented a single step production of graphite from organic samples at the 14th International Conference on Accelerator Mass Spectrometry [1]. The method combines sample combustion and graphitization in a single process, using the modified sealed tube graphitization method [2], i.e., organic samples are placed inside a Pyrex tube containing zinc, titanium hydride and iron catalyst, evacuated and heated at 500-550°C for 7 hours. This removes the entire CO<sub>2</sub> purification step and thus is truly an easy and high-throughput method. Elder et al. demonstrated that this method works with a variety of organic samples including pure compounds, wood, peat, collagen and humics. However, very little is known about how the chemical compositions of the organic matter could affect the processes controlling this combined combustion and graphitization, or how such graphite targets will perform, regarding beam current intensities and backgrounds. In this work, we test a suit of organic materials with different oxygen/carbon (O/C) and nitrogen/carbon (N/C) ratios. We also investigate the possibility of adding CuO to organics with little or no natural amounts of oxygen. We attempt to optimize the graphitization yield and beam currents, access the precision and backgrounds vs. sample size, as well as examine the limitations of the method.

### References:

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Monday 18-Jun-18 - 13:40 - 15:20 - Sansiro 1

## Advances in Hydropyrolysis for <sup>14</sup>C measurement: Isolating Carbon, Reducing backgrounds, and Increasing Throughput.

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As fields such as chemistry and engineering advance, new opportunities open up in radiocarbon pretreatment. These enable us to more effectively isolate particular carbon species, answer new scientific questions, and improve precision and accuracy. Pyrogenic carbon (PyC), the polyaromatic compounds that fingerprint burning, are highly resistant over millennia, and relate to a clearly defined event (e.g. time of plant growth). These are therefore very valuable for dating, source apportionment, and carbon cycle studies. In some circumstances, PyC is relatively easy to isolate, and contaminants are acceptably removed by wet chemistry. But in many others, PyC samples are very small, ancient, dispersed in a matrix (e.g. soil), or contaminated. A method to tackle the latter problems, Hydropyrolysis (HyPy), has been developed and implemented at James Cook University and SUERC. We have been involved in a recent joint program to significantly advance and optimize the HyPy method for PyC isolation and radiocarbon dating. This has resulted in backgrounds for the process as low as <0.10 pMC, and the prospect of at least doubling or tripling throughput. Here we will discuss these advances, and give an overview of studies in which HyPy has been successfully applied to answer a range of questions, from providing reliable PyC chronologies where other sample types have failed, to understanding facets of soil carbon cycling by isolating specific compound classes.

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## Can multi-species annual <sup>14</sup>C explain controversy over dating the Thera eruption?

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Dating the Minoan eruption of Thera (Santorini) in the mid-second millennium BC has been a subject of interdisciplinary debate for decades. The eruption provides an environmental marker which could be used to synchronize archaeological chronologies of the Aegean, Egypt and the Near East and to anchor paleoenvironmental records in ice-cores, speleothems and lake sediments. As such, establishing a precise and accurate date is of critical importance to a range of disciplines. Debate has focused on a discrepancy between radiocarbon dating, which places the event in the late 17th century BC, and archaeologically based dating which places the eruption in the late 16th or early 15th century BC. In 2016 we began a program of annual <sup>14</sup>C data collection across the period 1700-1500 BC to see if an annually derived record could improve or verify existing calibrations, or if <sup>14</sup>C marker events could be located to serve as temporal anchors in this time period. Here we present multi-species annual-data which indicate the presence of an offset from the international radiocarbon calibration curve (IntCal13) between c.1660 and 1540 cal BC. Re-calibration of samples from key Thera eruption contexts using a calibration curve based on the annual data moves the most likely date range for Thera into the 16th century BC.

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## Radiocarbon dating of lead carbonates to identify and date cosmetics synthesized in Antiquity

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Cosmetics were of primary importance in everyday life in ancient Egypt and Greece [1-3]. Various colored compounds and mixtures were used as eye paint, kohl, blush and foundation. Black powder for eye make-up was mainly composed of galena and face-whitener was based on white chalk or cerussite (PbCO<sub>3</sub>). A large range of grays were obtained by mixing galena with cerussite and other lead-based compounds such as laurionite and phosgenite (Pb<sub>2</sub>Cl<sub>2</sub>CO<sub>3</sub>) [4]. These two compounds are considered as the earliest synthesized cosmetics [5] and cerussite exists in both natural and synthesized forms.

In this study, we use the radiocarbon method to date cosmetics by dating the based-lead carbonate ingredients. We performed radiocarbon measurements on ancient Egyptian and Greek make-up kept at the Louvre museum and dated from the 3<sup>rd</sup> millennium to the 3<sup>rd</sup> century before Christ. We show that atmospheric carbon dioxide was incorporated during the synthesis of some cosmetics. In this way, the <sup>14</sup>C was fixed in the mineral matrix through the carbonate ion and makes radiocarbon dating possible. We present the results obtained on cerussite and phosgenite measured by accelerator mass spectrometry (AMS) at the LMC14/ARTEMIS facility [6,7]. We found that cerussite was synthesized in 353-57 calBC by ancient Greeks to produce white make-up and we confirm that phosgenite was synthesized in about 1500 BC by the Egyptians.

In addition, the ratio <sup>14</sup>C/<sup>12</sup>C can be used to discriminate natural and synthesized lead carbonates. We show that during the Egyptian Kingdom, cerussite in cosmetics was a natural mineral associated to galena whereas phosgenite was artificially produced. More than one millennium later, Greeks manufactured cerussite to satisfy the demand for white cosmetics. These results will be discussed and compared to the ancient recipes written in Antiquity for the production of lead carbonates [8].

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[4] Martinetto P. et al., *Nucl. Instr. and Meth. B* 181, 744-748 (2001).

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[6] Dumoulin J.-P. et al., *Radiocarbon* 59, 713-726 (2017)

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[8] Theophrastus (4<sup>th</sup> c. BC), Dioscorides and Pliny the Elder (1<sup>st</sup> c. AD).

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## Going further with Egyptian Chronology : In-situ developments

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The Ifao radiocarbon laboratory in Cairo offers the possibility of performing dating in Egypt, where the exportation of archaeological samples is forbidden. It still remains the only active laboratory in the country, using the conventional method [1]. Following previous studies [2, 3], a wide multidisciplinary research program on Egyptian chronology has been initiated in 2017, based on excavation sites samples and covering all the ancient Egyptian periods. It combines analytical, archaeological, methodological and statistical approaches, working closely with instrumental developments of the laboratory.

- From an analytical point of view, several excavation sites have been selected because of their archaeological contexts to conduct individually radiocarbon dating projects.

o In the Baharya oasis, analytical studies have been initiated to constraint a climatic change identified by sedimentological analyses. A first complex chronological model combining archaeological data as well as radiocarbon dates is currently elaborated to detail the roman occupation in the Qasr Allam cultural complex.

o More than 80 human mummies possibly linked to the start of the 18th dynasty have been excavated in the KV40 tomb (King Valley, Luqсор). Portable FTIR analyses have been undertaken to evaluate the dating potential of such human remains and, contrary to common belief, the collagenous state-of-preservation was good enough to consider AMS dating. It definitively opens new prospects about the possibility of dating Egyptian archaeological bones, as very little has been done till now.

o Specific historical and radiocarbon investigations are engaged to constraint the Old Kingdom chronology, because of the large plateau-age which makes challenging to separate the 3th to 5th dynasties. In particular, a sharp chronological study is currently led for the Ouadi el-Jarf site, where archaeological evidences closely relate to the reign of Cheops.

- From a methodological point of view, the calibration curve in Egypt has to be refined in the continuation of the work engaged in [4], because of the peculiarity of the Nile flood. The Natural History Museum in Paris holds over 70 specimens collected by the botanist A. Raffeneau-Delile during Bonaparte's expedition to Egypt at the end of the 18th century. Evaluation of their <sup>14</sup>C ratio will help modeling possible offsets according to location in the Egyptian area (desert, valley, delta, red sea...).

- From a statistical point of view, a chronological model based on an innovative MCMC framework is under development to integrate the precise historical state-of-knowledge for each Egyptian king (attestations, most probable lengths of reigns...).

Results obtained so far clearly demonstrate the necessity to provide the Ifao laboratory with an AMS preparation line, which currently constitutes the main planned lab development. After a short presentation of the Ifao laboratory, the Egyptian chronology project will be outlined with its limitations and future perspectives. This will sketch a wide overview of archaeological dating projects in Egypt.

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2. Bronk Ramsey et al. 2010, Science 328, 2010, p.1554-1557.
3. Quiles et al., 2013, JAS 40, 2013, p. 423-432.
4. Dee et al., 2010, JAS 37, p. 687-693.



*Monday 18-Jun-18 - 13:40 - 15:20 - Sansiro 2*

## Radiocarbon dating of Late Bronze Age sites in the Shephelah region (Israel), and a re-evaluation of synchronisations with Egypt

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The chronology of the Late Bronze Age (LBA; ca. 1550-1150 BCE) – of all periods in the history of the southern Levant – is most closely tied to Egypt. Because the region has no historical chronology of its own in this timeframe, the structure and dating of the LBA were established with close reference to the reigns of Egyptian kings and their activities in the Levant. While the contemporary chronology of Egypt (the so-called New Kingdom) is now supported by radiocarbon dating, there is much uncertainty inherent in the use of material culture (imported finds and pottery) to tie Levantine archaeological remains to the Egyptian historical chronology. Even in the LBA, few Egyptian items are found that can precisely date strata, and the use of imported pottery as fossil directors is problematic. Further, slow changes in local pottery styles limit our dating resolution. These difficulties in the traditional dating approach underscore the need for direct dating of LBA sites using radiocarbon, which would also enable an independent check on the synchronization with Egypt.

The Shephelah – a lowland region of southwest Israel – was of considerable significance during the Late Bronze Age: it was among the more densely populated regions of the southern Levant and the rulers of its city-states were in regular contact with Egypt, as attested in the Amarna Letters. Thus the Shephelah is undeniably an important region for synchronizing the history of the southern Levant with Egypt.

A concerted effort is currently being made to develop and expand radiocarbon sequences for LBA occupation levels at key sites in the Shephelah, including Azekah, Gezer and Lachish. Short-lived samples have been obtained from active excavations, and by sampling baulks left exposed by previous excavations. This paper will present new datasets and Bayesian chronological models, with particular focus on Lachish, a dominant Late Bronze city-state of this region. An important outcome of radiocarbon work at this site is the identification of occupation evidence from the time of Thutmose III to Amenhotep II – evidence that has been missing until now, in contrast to the witness of textual sources (Papyrus Hermitage 1116A). The new results thus provide an excellent example of how radiocarbon dating can – and should – be more widely applied to date LBA strata, and used to independently check the synchronization of Levantine and Egyptian histories.



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## Setting the Clock in Jerusalem: Radiocarbon project update, working methods and a case-study from Wilson's Arch excavations

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The relatively detailed historical record of Jerusalem and the importance of the city throughout history, make Jerusalem a key site for the history and archaeology of the Near East. However, despite the 150 years of excavation in Jerusalem, less than 10 radiocarbon measurements were published prior to our study, and the chronology of the site has been entirely based on relative dating of material finds, such as pottery or coins. Even during the well recorded historical periods, many of the chronological questions regarding architectural remains are left unanswered or lack precision, due to the difficulty in establishing a secure connection with the “chronological items” used for their dating.

Since 2014, systematic radiocarbon research has been undertaken in Jerusalem excavations. Ongoing excavations and remaining sections from previous excavations have been sampled for radiocarbon dating, applying microarchaeological tools to identify secure in-situ contexts for dating and reliable stratigraphic sequences, in order to enable Bayesian modeling of the dates.

To date, over 100 dates have been undertaken, from scores of contexts around Jerusalem. In the following paper, the dates from a particular excavation – that of the excavations beneath Wilson's Arch – shall be presented as an example of the far-reaching implications of the radiocarbon project in Jerusalem. The excavations beneath Wilson's Arch have unearthed remains spanning a period of some 1500 years, including monumental and historically significant structures built at the foot of the Temple Mount. The radiocarbon dating of the different stratigraphic stages has helped narrow and fine tune the dating of these structures, which have been at the focus of archaeological debate. One such instance is the dating of the arch itself, which prior to excavation was debated, with a date ranging between the 1st Century BC and the 7th Century AD. Through the application of radiocarbon dating, the arch can now be securely dated, along with the other features discovered, such as the small theatre complex built beneath the arch. The precise dating of these features advances our understanding of Jerusalem's urban development in the various periods of its history. In this manner, the radiocarbon methodology applied allows for accuracy and precision required for a historical reconstruction of the Wilson's arch excavation complex and architectural sequence from the 1st century BC to the 15th century AD, allowing for “who built what” in Jerusalem's colorful past, while integrating these finds into a larger picture encompassing the entire settlement and rebuilding its urban fabric in a precise manner.

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## The use of radiocarbon in marine paleoclimate research

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Physical and chemical data that record past changes in climate and the ocean do hardly extend beyond the last 170 years. However, major and far more dramatic events of climate change occurred farther back, over the last 20 to 40 thousand years, where most evidence is based on proxy data obtained from ice cores, terrestrial and marine sediment archives. Here, radiocarbon (<sup>14</sup>C) ages of planktic foraminifera and other carbonate shells in marine sediments evolved as a key stratigraphic dating tool over the last 60 yr, especially since the onset of AMS analyses in the mid 1980s. It proved crucial for correlating centennial-millennial-scale climate signals in marine sediment records on a global scale, moreover, for estimating past changes in the rate of biogeochemical transfer.

However, many authors have increasingly become aware of a number of factors that influence and modify marine <sup>14</sup>C ages derived from marine microfossils, here to be discussed in detail. Besides processes of marine sediment displacement, bioturbation, and deep-reaching burrows problems arise from the absence of a generally accepted reference record of atmospheric <sup>14</sup>C concentration beyond ~14 ka, the lower end of tree ring calibration. On top of age control on the basis of radioactive decay, marine <sup>14</sup>C signals primarily reflect the spatial and temporal variation of local <sup>14</sup>C reservoir ages in surface and deep waters, that is the difference between coeval atmospheric and marine <sup>14</sup>C concentrations, now constrained by means of the technique of <sup>14</sup>C plateau tuning. Vice versa, <sup>14</sup>C reservoir ages form a valuable tracer of past water mass geometries and, most important, of the amount of carbon dissolved in the deep ocean during past climatic regimes.

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## Radiocarbon and Ocean Circulation

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Stable and radiocarbon isotopes in dissolved inorganic carbon (DI<sup>13</sup>C and DI<sup>14</sup>C, respectively) provide powerful information about the ocean carbon cycle, circulation and decadal changes. Historical measurements of these isotopes in the Southern Ocean are scarce, but we are currently participating in some of the Southern Ocean Carbon and Climate Observations and Modeling (SOCCOM) cruises to increase the measurement density. We are currently collecting approximately 480 samples each year.

The GLODAPv2 data product contains more than 850 DI<sup>14</sup>C measurements collected on samples south of 35°S between 1972 and 2013. Here, we present a synthesis of these and new data collected in the last five years. Direct time-series comparisons can now be made for 4 separate transects. For one transect, we have data from 1973, 1990, and 2010. Other transects compare time intervals between 1992 and 2005, 1993 and 2008, and 2005 and 2013.

Circulation patterns in the Southern Ocean are complex and present challenges for understanding the radiocarbon signal. In general, Southern Ocean sections show decreasing DI<sup>14</sup>C in surface waters as the bomb-produced component has moved into the interior or been advected away as well as increasing DI<sup>14</sup>C in intermediate and mode waters. These changes are obvious by comparing results from multiple occupations of the same area. The bottom water radiocarbon signals in this area are much more subtle, but indicative of new bottom water formation.

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## Towards an absolute chronology of the Middle-Upper Palaeolithic biocultural shift along the Danube fluvial corridor

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Recent research has shown the need for a reliable, high-resolution chronology to understand the complexity of the spatio-temporal distribution of Neanderthals and anatomically modern humans (AMH) during the transitional period between the Middle to Upper Palaeolithic. One region that has yet to benefit from the developments in dating sciences and the application of Bayesian modelling approaches is eastern Europe. Our research focuses on producing a more robust chronological framework for this region, especially the key area of the Danube fluvial corridor, which has been suggested as one of the conduits for early modern humans on their dispersal route into western Europe (e.g. Conard and Bolus 2003). We present new radiocarbon data and models that expand the picture that has emerged from recent studies conducted in western Europe. These results place the chronology for AMH dispersal on more secure footing, thereby refining our understanding of the regional variability and complexity of the Middle to Upper Palaeolithic biocultural shift.

This work is the result of four years of intensive doctoral research within the University of Oxford's PalaeoChron ERC project. We applied recent improvements in radiocarbon dating methodologies and analysis, such as ultrafiltration (Brock et al. 2010), single amino acid dating (Devièse et al. 2017), and KDE modelling (Bronk Ramsey 2017). Two strategies were pursued for sample selection. First, key sites with a deep stratigraphic record were targeted, e.g. Kozarnika and Temnata (Bulgaria), to initially establish site specific high resolution chronologies using Bayesian modelling. Second, type fossils, such as osseous spear points (e.g. from Dzeravá Skala in Slovakia, Istállóskő and Jankovich in Hungary) and human remains (both Neanderthal and AMH), were directly dated to establish regional spatio-temporal boundaries, i.e. dating the appearance and disappearance of an industry or species. Furthermore, published dates from Eurasian sites were evaluated, and, where deemed reliable, used as comparisons and incorporated into larger regional models.

The resulting chronology paints a picture of complex spatio-temporal biocultural distributions, with instances of possible alternating occupations. It indicates several surprising temporal consistencies over large geographical areas, marking the period around 43–41k cal BP as crucial to AMH cultural appearance. At the same time, our research questions some of the previous assumptions made about cultural units (e.g. the Szeletian) in the region, and proposes to investigate osseous points as a chronological indicator in their own right – independent from lithic industries.

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## The Yarkon-Taninim aquifer (Judea Group, Israel): continuous or discontinuous – verdict by Radiocarbon

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The Yarkon- Taninim (Y-T) carbonate aquifer of the Judea Group (of Cenomanian - Turonian age), is an important fresh water source in Israel. For efficient exploitation of the aquifer, hydrological parameters such as flow direction, flow rate, as well as determining if the aquifer is a single hydrological unit or not are needed. The current hydrological model was put forth over half a century ago. Mandel (1961) noted that static water levels of two major springs, at Rosh HaAayen in the south was +18m (MASL) and the Taninim springs in the north was +11 to +8 m MASL. In the absence of other visible outlets, he considered this to be the drainage from the confined aquifer. The dominant flow to the drainage was thus considered to be south to north, parallel to the Mediterranean coast. Later, the Beersheba area having water levels of approximately +25m MASL was added to make it one continuous aquifer. The model envisages water recharging in the Judea and Hebron Hills to the east, flowing downhill before encountering an impermeable facies change (Talme-Yafo Formation) in the Judea Group. These shales prevent drainage seawards, forcing the groundwater flow to swing northwards to discharge at the springs. Over the intervening years this hydrological model has been “verified” by computer modeling. The  $\delta^{2}\text{H}$  and  $\delta^{18}\text{O}$  values of the groundwater confirm that they are all from recharge of Eastern Mediterranean rains. Yet, much significant geochemical and isotopic data has been largely ignored, particularly radiocarbon.

Radiocarbon analyses have been measured in the aquifer waters from ~1970 to 2018. Aquifer radiocarbon activity values above 62 pMC can be considered of young age, having a “fall-out” component. Using the Darcy equation, and conservative transmissivity values, the flow from the Yarkon to the Taninim springs should take ~ 40,000 years. Water flowing from Beersheba should take even longer. Yet, the Taninim springs discharge contained tritium and radiocarbon values of ~60 pMC. The confined Beersheba- region groundwater does show a consistent decrease in radiocarbon activity along a flow path that starts at >60 pMC and terminates at 8 pMC. Northwards, the radiocarbon in groundwater increases sharply. We conclude that:

- a. The confined Beersheba aquifer is separated from the Y-T aquifer to the north of it.
- b. That the Taninim and Yarkon springs are not the total drainage. There must be fresh water loss to the sea, westwards via the Miocene-Pliocene erosional channels that had cut through the Talme-Yafo aquiclude.
- c. The supposed single aquifer is divided vertically, into at least two aquifers separated by aquicludes. The lower aquifer flow rapidly thorough karst. The flow in the upper part of the aquifer is slower through fractures in the host rock.
- d. The radiocarbon data suggests that a different hydrological approach is warranted.

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## Results from Accelerator Mass Spectrometer Facility from PRL-AURiS: Sedimentation rate in the Andaman basin

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A compact 1 MV Accelerator Mass Spectrometer has been recently installed at Physical Research Laboratory (PRL), Ahmedabad, India and has been named Accelerator Unit for Radioisotope Studies (PRL-AURiS). PRL-AURiS has been tuned for measurement of <sup>14</sup>C, <sup>10</sup>Be and <sup>26</sup>Al. Results of first few measurements from PRL-AURiS would be presented. Measurement of various radiocarbon inter-calibration standards from PRL-AURiS has shown very encouraging results similar to consensus values. A sediment core (SK/304B-18) from the northern Andaman Sea was dated using radiocarbon dating of planktonic forams and their radiocarbon ages were used to determine the sedimentation rate of the region. The sediment core dates back up to 7108 ± 88 yr. The sedimentation rate in the northern Andaman Sea ranges between 10.7-39.0 cm/kyr during last 7 kyr. The reduced sedimentation rate around 4000 yr suggests shift from wetter to drier climate condition over the region. This shift in climate has been ascribed to weakening of summer monsoon. The productivity and upwelling in the region persists because of winter monsoon and winds. The preliminary observation suggests that the sedimentation in the northern Andaman Sea is a function of summer monsoonal activity.

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## Reservoir age: A name both convenient and misleading

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The <sup>14</sup>C concentration in the oceans and in fresh water reservoirs is generally lower than in the atmosphere. The difference in <sup>14</sup>C concentration between atmosphere and aquatic reservoir is generally expressed as a “reservoir age”, that is the time it would take <sup>14</sup>C decay to reduce the atmospheric <sup>14</sup>C concentration to the one observed in the reservoir. The name reservoir age, though easy to use, creates the impression that the “age” is a property of the reservoir, while in reality it expresses the relative offset in the <sup>14</sup>C concentration in the reservoir from that of the atmosphere, resulting from the mixing of atmospheric carbon with <sup>14</sup>C depleted carbon from different sources in the reservoir. Reservoir age variability may thus be quite large and fast, depending on differences in contemporaneous <sup>14</sup>C fluctuations in atmosphere and reservoir. For large deep ocean reservoirs turnover times are long and the changes in their reservoir age may largely mirror fast fluctuations in atmospheric <sup>14</sup>C concentration. Fresh water reservoirs are generally small and in direct exchange with the atmosphere, so local geology, hydrology, and climate may play an important role in determining their offset from the atmospheric <sup>14</sup>C concentration.

The prospects for a global Marine calibration in analogy to IntCal, fostered by the name marine reservoir age, thus are grim, as already indicated by the differences in marine reservoir ages with time and geographic location that are increasingly being reported. The variability, inherent in the offset between the <sup>14</sup>C concentration in the atmosphere and that in an aquatic reservoir, means a considerable uncertainty in the conversion of a marine <sup>14</sup>C age into calendar age unless the local reservoir age associated with the sample is known. To reduce the uncertainty in marine calendar ages based on radiocarbon, we need a model that captures the internal heterogeneity of the oceans and the varying dynamics of the meridional overturning circulation with time and geographical location to derive in detail oceanic <sup>14</sup>C concentrations, and thus reservoir ages, as a function of time and location. This type of modeling is being developed. As an alternative, local reservoir ages over time can be determined independently via chronostratigraphic markers, correlation with independently dated records, or detailed correlation with the atmospheric <sup>14</sup>C record via plateau tuning.

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## Marine radiocarbon reservoir age simulations for the past 50000 years

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Radiocarbon dating prior to the tree-ring period (about 14000 calibrated years before present) largely relies on cross-dated marine <sup>14</sup>C records. These records have to be corrected by the Marine Radiocarbon Ages of surface waters (MRAs) because marine <sup>14</sup>C reservoirs are isotopically depleted with respect to the atmosphere. Here, we present simulations of the spatiotemporal MRA evolution during the past 50000 years. Using a three-dimensional ocean general circulation model forced with various climatic boundary conditions, we find that low- to mid-latitude MRAs have varied between 400 and 1200 <sup>14</sup>C years, with values of about 800 <sup>14</sup>C years at the Last Glacial Maximum. In the polar oceans we find MRAs exceeding 2000 <sup>14</sup>C years. Our model results agree reasonably well with reconstructions and can be used for <sup>14</sup>C chronologies.

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## Reservoir ages for seaweeds and seagrasses along the Kelp Highway

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We measured radiocarbon ages for known-age prebomb seaweed and seagrass samples from Pacific Coast locations of North and South America, from Puget Sound, USA (48°N) to Punta Arenas, Chile (53°S). The results show that without exception, these organic materials have reservoir ages similar to those of marine carbonate. This is true even for species that primarily photosynthesize dissolved CO<sub>2</sub> rather than bicarbonate and therefore have stable isotope signatures ( $\delta^{13}\text{C}$ ) similar to those of terrestrial C3 plants. Our results have clear implications for <sup>14</sup>C dating of marine or estuarine seaweeds and seagrasses, including calibration of the dates with global and regional marine reservoir corrections. Kelp forests and seaweeds were important habitats and resources for some of the First Americans, who may have traversed Pacific Rim coastlines relatively rapidly, following a Kelp Highway route entirely at sea level and without major obstructions, with a diverse array of terrestrial and marine resources.

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## Using stable carbon isotopes of bivalve shells to infer their radiocarbon reservoir age offset – a Black Sea case study

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Constraining radiocarbon reservoir age offsets is critical to deriving accurate calendar-age chronologies from radiocarbon (<sup>14</sup>C) dating of materials, which did not draw carbon directly from the atmosphere. The application of <sup>14</sup>C dating to such materials is severely limited in hydrologically-sensitive environments like the Black Sea because of an inability to quantify reservoir age offsets, which can vary quickly and significantly through time, due to the dynamics of the biogeochemical cycling of carbon. Here we reconstruct reservoir age offsets of Holocene bivalve shells from the coastal Black Sea. We show that the <sup>14</sup>C reservoir age offset and the stable carbon isotope composition of bivalve shells are linearly correlated. From a biogeochemical standpoint, this suggests that inorganic stable carbon isotope and radiocarbon compositions of Black Sea coastal waters are controlled by the balance between autochthonous primary productivity and heterotrophic respiration of allochthonous pre-aged terrestrial organic matter supplied by rivers. This provides an important implication for Black Sea geochronology as the reservoir age offset of any <sup>14</sup>C-dated shell can be inferred from its carbon stable isotope composition. Our results provide a fundamental geochemical tool which will improve the accuracy of Holocene calendar-age chronologies of Black Sea sediment archives. As an example, we present the calendar age-depth model of a sediment core that records the sedimentary evolution of the Danube delta over the last 10000 years.

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## Absolute dating of iron reinforcements in French gothic cathedrals

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The Gothic period that begins in the twelfth century in the north of France brought many changes in the architecture of cathedrals and churches. This new style is mainly characterized by achievements in the use of stone and glass but it also represents a great change in the use of metal for the construction of medieval buildings. Several tons of iron or steel reinforcements such as clamps, chains and tie-rods were used for each of the largest churches of the French kingdom for this period. These elements are of great interest to study the evolution of technical processes involved in the production and transformation of iron all along the medieval times. Nevertheless, cathedrals were built over several architectural phases, modified and repaired with iron elements potentially added at any of the numerous steps of this long history. As there is often no stylistic evidence that allows differentiating between the metallic reinforcements from different periods, it is only by absolute dating that a chronology of these elements can be drawn.

The aim of this presentation is to show how radiocarbon dating of iron can participate, by giving time points, to a multidisciplinary approach (archaeology, history, materials science) that tries to understand the work of craftsmen from the production of iron to the introduction of the ferrous artefacts in these medieval monuments.

After a description of the iron radiocarbon dating protocol, we will present the dates obtained on ferrous elements collected in seven gothic cathedrals among the most important in the development of French gothic architecture. We will discuss the dating results against the archaeological study and the metallographic and chemical analysis of the ferrous alloys.



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## Oxalate minerals for rock art dating: new developments and applications

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Development of AMS allowed targeting oxalate minerals – whewellite and wedellite as a dating material for rock art. Further studies have demonstrated that carbon in oxalates is not derived from the substrate on which they grow but most probably originate from bacteria and other microbiota residing on rock surfaces utilising atmospheric source. The other rock surface objects which potentially carry oxalates are the remnants of mud dauber nests. Oxalates could form post-construction from bacterial activity utilising favourable conditions in the nest stump. One more recognised source of oxalates associated with rock art is the use of plant sap as a binder for mineral pigments. In all instances oxalates on the rock surface exist in a mixture with other materials which could be carbon bearing contaminants. Hence the study of a bulk sample ends in radiocarbon concentrations of an average of all carbon compounds with unknown source and relationship with the inferred art. Therefore, chemical pretreatment methods were developed to isolate and target the compound of interest - calcium oxalate, and successfully applied to establish age constraints for some Australian rock art (Jones et al, 2017). We present and discuss some methodological data of studying oxalate crusts from various objects following the oxalate specific pretreatment approach, including dating of oxalate crusts on the objects with known age. Some applications to date rock surface deposits and oxalate minerals associated with Australian and African rock art objects are also shown and discussed. The presence of whewellite and mineral skins compositions were also investigated with X-ray diffraction, scanning electron microscopy and infrared spectroscopy methods. Selectiveness of the method and planned studies are considered.

### References

Jones, T., Levchenko, V., King, P. L., & Nayingull, A. (2017). Radiocarbon age constraints for a Pleistocene-Holocene transition rock art style: The Northern Running Figures of the East Alligator River region, western Arnhem Land, Australia. *Journal of Archaeological Science: Reports* 11, 80–89.



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## Radiocarbon Dating Animal Bones: When are the Dates “Too Old”?

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Sources of carbon in wetlands and calcareous areas represent unique challenges for interpreting the accuracy of radiocarbon ages. Atmospheric carbon dioxide is assumed to be the only carbon source for photosynthesis. However, dating modern and historic reference fish and modern reference wild rice indicates the presence of ancient carbon in bones and plant material. After dating four fish caught in 1939 in the Mississippi River in southeastern Minnesota that yielded four distinctly different, non-overlapping dates, we turned our attention to the question of which land animal bones yield similarly ancient dates. The fish bones spanned 1223 to 307 BP, leading to the conclusion that dissolved inorganic carbon (DIC) and perhaps other ancient carbon contributes to a freshwater reservoir effect. Trophic level of the fish (and their diet) is implicated in this date range since they were caught during the same fishing expedition in the same river. Adding additional reference fish, including northern pike, caught elsewhere in the state, returned differential offsets implicating geology and DIC as sources of ancient carbon. Wild rice harvested in 2015 yielded similar age offsets to the highest trophic level fish, suggesting both high trophic level fish and wild rice take in carbon from both the freshwater reservoir and the atmosphere.

Dating land animals also is affected by the diet of the land animals. Previous radiocarbon analysis of a moose (*Alces alces*) from Denmark (Philipsen 2015) indicates land animals are not immune to the problem of accumulating ancient carbon. Moose are known to eat aquatic plants, which can contribute ancient carbon, transferring the freshwater reservoir effect into their bones. What about land animals not known to eat aquatic diets, such as bison, and other herbivores? This presentation examines primarily dates on reference animals distributed from fish to animals living along waterway shores such as muskrats to land animals such as bison.

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## Is AAA-pretreatment sufficient to obtain reliable <sup>14</sup>C dates on food residues?

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Direct radiocarbon dating of charred food residue has become popular in archaeology due to its direct association with pottery use. Hence, it is generally expected that charred food residue yields reliable <sup>14</sup>C dates. It was noticed that some charred food residue dates from Mesolithic sites are older than the dates obtained on terrestrial organic material and their archaeological context, suggesting that a reservoir effect caused by the processing of fish might be the cause.

Food residues were included in a dating program for the early Neolithic of southern Britain, combining new and existing <sup>14</sup>C dates and applying a series of Bayesian chronological models (Bayliss et al. 2011). Around 15% of the food residue dates were judged to be inaccurate on archaeological grounds and there were some large offsets between replicate pairs of food residue dates from the same sherd. Molecular and isotopic analysis of residues from early Neolithic sites in southern Britain (e.g. Copley et al. 2005) have provided no evidence of the processing of aquatic resources in pottery vessels, so the issues highlighted in this study are likely to be the result of different sample pretreatment protocols as the <sup>14</sup>C analyses were conducted in different laboratories. Prior to dating, food residues are most commonly subjected to acid-alkali-acid (AAA) pretreatment to remove carbonates and humic and fulvic acids. The impact of sample pretreatment on the composition of food residues has not been investigated in detail. This study compares <sup>14</sup>C dates obtained with different pre-treatment methods on food residues and <sup>14</sup>C dates performed on reference material (e.g. bone, charcoal etc.) from the same archaeological context.

Bayliss A, van der Plicht J, Bronk Ramsey C, McCormac G, Healy F, Whittle A. 2011. Towards generational time-scales: the quantitative interpretation of archaeological chronologies. In: Whittle A, Healy F, Bayliss A, editors. *Gathering Time: Dating the Early Neolithic Enclosures of Southern Britain and Ireland*. Oxford: Oxbow Books. p 17–59.

Copley MS, Berstan R, Mukherjee AJ, Dudd SN, Straker V, Payne S, Evershed RP. 2005. Dairying in antiquity. III. Evidence from absorbed lipid residues dating to the British Neolithic. *Journal of Archaeological Science* 32(4):523–46.

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## An improved radiocarbon methodology (AOx-SC) for the reliable dating of old charcoal

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Radiocarbon dating Pleistocene-aged charcoal is challenging and systematic research during the past 20 years has shown that the routine Acid-Base-Acid (ABA) method does not decontaminate old charcoals (>20 ka BP) sufficiently and often results in significant age underestimates. The development of the Acid-Base-Oxidation with stepped combustion protocol (ABOx-SC) (Bird et al. 1999) has been shown to be a more rigorous approach that produces not just older, but more accurate age estimates when compared to independently dated markers (e.g. Douka et al. 2010; Wood et al. 2012). However ABOx-SC is highly destructive and can result in significant sample loss and often in failure to produce sufficient material to date, usually at the alkaline step. For this reason large starting weight of >50–150 mg of well-preserved charcoal is required.

Here we present a modified ABOx-SC protocol that excludes the “base” wash, which we considered chemically unnecessary, and involves Oxford’s pre- and full combustion steps at 630oC and 900oC respectively (rather than a proper stepped combustion originally described by Bird et al). The protocol is called AOx-SC and was also used recently by Tomiyama et al. (2016) in an experimental setting.

Our new results from about 20 paired ancient samples, as well as artificially contaminated and aged charcoals, treated with (ABA-)ABOx-AOx prior to AMS measurement reveal that AOx produces determinations comparable to ABOx in age but requires much less material, more similar to that required for ABA treatments (20-50mg) and it also results in significantly fewer sample fails.

Since mid-2015, AOx-SC has become the protocol of choice when dating Late Pleistocene-age charcoal (>20 ka) at the Oxford Radiocarbon Accelerator Unit. During this time we have observed significant improvement in the number of samples able to be measured with the protocol. Although some preliminary work has been undertaken, further work is required to understand and better assess charcoal degradation and decontamination mechanisms.

### References

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## Towards a pretreatment for radiocarbon dating dental enamel

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Radiocarbon dating of bone of more than c.2000 years in Australia and South East Asia is hampered by the rapid degradation of collagen. In the best-case scenarios, a few bones with a little collagen can be found when large numbers of bones are screened. However, more often no collagen remains. This means that in many contexts the only samples available to date are poorly associated with the event of interest, such as charcoal from burial contexts, resulting in low quality chronologies.

Enamel may provide an alternative skeletal material to radiocarbon date, but little work has examined diagenesis mechanisms, or how contaminating carbon can be removed. Routine protocols employed include reacting the enamel in either acetic acid or HCl, either as large pieces or a hand-ground powder. However, dates are rarely accurate: typically at least 5-10% of the carbon in enamel is a contaminant after routine pretreatment.

Using teeth known to be more than 50 ka, this presentation will show that:

1. of a range of acids tested, weaker acids produce older ages than strong acids, and acetic acid produces the oldest dates.
2. the smaller the grain size, the older the date produced, presumably because the majority of contamination lies in the pores between the apatite crystallites, or on their surface. This section builds on Wood, et al. (2016), who showed that leaching after mechanical grinding increases the age of enamel in comparison to handground enamel. It will demonstrate that the use of SelfFrag (selective fragmentation by high voltage pulsed electric current) to further fragment enamel once again provides older ages.

Although ages are greatly improved, accurate dates are not obtained. Typically the equivalent of 1- 2% of the carbon in enamel is modern in age after the most successful pretreatment attempted. FTIR and XRD are used in an attempt to identify whether this is due to 'recrystallisation' of the phosphate minerals during burial.

Wood, R., Duval, M., Mai Huong, N.T., Tuan, N.A., Bacon, A.M., Demeter, F., Durringer, P., Oxenham, M., Piper, P., 2016. The effect of grain size on carbonate contaminant removal from tooth enamel: Towards an improved pretreatment for radiocarbon dating, *Quaternary Geochronology* 36, 174-187.

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## Carbon source and production rate drive carbon sequestration in an alkaline lake eutrophic lake: analysis of bulk sediment using stepped combustion radiocarbon analysis.

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Rostherne Mere, UK, is an alkaline lake with a significant Freshwater Reservoir Offset (FRO). The lake is eutrophic due to considerable inputs of phosphorus and nitrogen during the operation of a sewage treatment works (STW) upstream from the lake between the 1930s and 1991 when it became overloaded and was closed. The lake remains eutrophic despite restoration works since the closure of the STW as phosphorus is stored in sediment and is remineralised, maintaining high nutrient levels and resulting eutrophication. The lake is dominated by autochthonous (within-lake) organic carbon due to high primary production rates. As such, its FRO is of a magnitude of  $>1600$  <sup>14</sup>C years.

This study used stepped combustion radiocarbon analysis to characterise carbon sources in a 55cm sediment core. High performance liquid chromatography was used to measure phytoplankton pigments and, along with standard diatom analyses, reconstructed algal populations and quantified production in the lake. Carbon accumulation rates were also determined from diatom valve accumulation with a chronology obtained from <sup>210</sup>Pb.

This multi-proxy approach characterised organic carbon pools in Rostherne Mere sediment. Labile and recalcitrant carbon sources were identified from bulk sediment samples. The proportion of each changed over the operation of the STW. Increased production rates and abundance of diatom and algal pigments were linked to elevated carbon accumulation rates. Recalcitrant carbon made up a higher proportion of carbon at the time of peak accumulation rate. In addition,  $\Delta^{14}\text{C}$  values became enriched, clearly identifying the operation of the STW. Results indicate that the relative importance of terrestrial/autochthonous carbon.

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## Radiocarbon (<sup>14</sup>C) Constraints On The Fraction Of Refractory Dissolved Organic Carbon In Primary Marine Aerosol From The Northwest Atlantic

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Nearly all organic carbon in seawater is dissolved (DOC), with more than 95% considered refractory based on modeled average lifetimes (~16,000 yr) and characteristically old bulk radiocarbon (<sup>14</sup>C) ages (4000 – 6000 yr) that exceed the timescales of overturning circulation. Although this refractory dissolved organic carbon (RDOC) is present throughout the oceans as a major reservoir of the global carbon cycle, its sources and sinks are poorly constrained. Recently, RDOC was proposed to be removed from the oceans through adsorption onto the surfaces of rising bubble plumes produced by breaking waves, ejection into the atmosphere via bubble bursting as a component of primary marine aerosol (PMA), and subsequent oxidation in the atmosphere (Kieber et al. 2016). To test this mechanism, we used natural abundance <sup>14</sup>C to trace the fraction of RDOC in PMA produced in a high capacity generator at two biologically-productive and two oligotrophic hydrographic stations in the Northwest Atlantic Ocean during a research cruise aboard the R/V Endeavor (Sep – Oct 2016). The <sup>14</sup>C values of PMA generated day and night from near-surface (5 m) and deep (2500 m) seawater were compared with corresponding <sup>14</sup>C signatures in seawater of near-surface dissolved inorganic carbon (DIC, a proxy for recently produced organic matter), bulk deep DOC (a proxy for RDOC), and near-surface bulk DOC. The  $\Delta^{14}\text{C}$  value of PMA (-891 ‰) generated directly from 2500 m seawater was depleted relative to DOC from the same depth (-451 ‰), suggesting deep organic matter is a heterogeneous mixture that contains and even older, aerosolizable fraction. Assuming this material also represents the aerosolizable fraction of RDOC in the surface ocean, then RDOC comprised 19 – 25 % of the PMA mass generated from surface waters in the Sargasso Sea and Georges Bank ( $-208 \text{‰} \leq \Delta^{14}\text{C} \leq -150 \text{‰}$ ), but only 4 – 8 % of the PMA mass from surface coastal waters near Block Island, NY ( $-54 \text{‰} \leq \Delta^{14}\text{C} \leq -16 \text{‰}$ ). Alternatively, assuming aerosolizable RDOC in the surface ocean could range from being purely fossil (-1000 ‰) to compositionally identical to bulk deep DOC (-451 ‰), then it could comprise between 17 – 45 % of PMA generated from Sargasso Sea and Georges Bank, and 4 – 16 % of PMA from Block Island. These results constrain the selectivity of PMA formation from RDOC in natural mixtures of bulk DOC comprised of recently produced and refractory organic matter. The implications of these results for PMA formation and RDOC biogeochemistry will be discussed.

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## The DIC isotopic characteristics of natural waters in Iceland. Comparison with isotope geochemical model simulations

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In recent years extensive measurements on dissolved inorganic carbon (DIC) isotope ( $\delta^{13}\text{C}$  and  $^{14}\text{C}$ ) in Icelandic waters (surface, as well as cold and thermal groundwater) have been performed in order to evaluate the carbon sources and reactions that possibly influence the carbon isotopic systematics of the water. The dataset spans geographically all parts of Iceland and reflects different temperature, pH, and DIC concentration. The results indicate a wide range in both  $^{14}\text{C}$  (0 to 130 pMC) and  $\delta^{13}\text{C}$  (+4 to -26‰). Three major carbon sources have been identified for the groundwater, i.e. 1) dissolution of partially degassed basaltic rocks formed at the surface or shallow depth 2) atmospheric  $\text{CO}_2$  through air-water exchange at surface, and 3) input of gas of mantle origin at depth into the groundwater systems (Stefánsson et al., 2016). The present study focuses on the carbon sources in cold ( $T < 15^\circ\text{C}$ ) waters in Iceland. The samples are surface waters (rivers, streams and soil waters) and from cold springs and shallow wells. The measured range in  $\delta^{13}\text{C}$  is large, from +4.0‰ to -21.5‰ (mean =  $-7.56 \pm 5.93$ ‰). The range in  $^{14}\text{C}$  concentration is also large, from 0 to 130 pMC, though most of the samples lie in the range from 70 to 110 pMC. Seasonal variation can be detected in the carbon isotopes of the glacial rivers, with spring samples being the youngest and least depleted in  $^{13}\text{C}$ , and the August samples being oldest and most  $^{13}\text{C}$  depleted. The cold groundwater samples (springs and shallow wells) show similar range in the carbon isotopes as the surface samples but without clear correlation between  $\delta^{13}\text{C}$  and the  $^{14}\text{C}$  content. Most of the samples collected from the soil zone are bomb influenced (110-117 pMC) with  $\delta^{13}\text{C}$  values in the range from -16‰ to -25‰. A few soil samples show older  $^{14}\text{C}$  ages presumably due to organic carbon from old vegetation. The results suggest that the carbon isotopic systematics of cold natural waters in Iceland outside volcanic areas can mainly be explained by 1) difference in  $\text{CO}_2$  air-water saturation and 2) influence of  $\text{CO}_2$  from both modern and older vegetation.

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Tuesday 19-Jun-18 - 13:40 - 15:20 - Sansiro 1

## Longevity of the Greenland shark, Black Dogfish and Humpback whales using eye lens radiocarbon dating

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The Greenland shark (*Somniosus microcephalus*) and the Black Dogfish (*Centroscyllium fabricii*) are deep water sharks, which are abundant throughout Northern Atlantic waters. Nevertheless, little is known about their habitats, biology and life history strategies; not least their longevity. Here we use radiocarbon dating on eye lenses for age determination. An adult Greenland shark has been shown to be around 400 years and the Black Dogfish has a minimum age of 50 years. We will compare the radiocarbon based age estimate with counting of annuli in the dorsal fin spines for the Black Dogfish. Similarly, humpback whale (*Megaptera novaeangliae*) age estimates are compared with ages determined by amino acid racemization. Because the rise of the radiocarbon bomb-pulse in the ocean is temporally stable and a robust indicator of age we conclude that annuli counting and amino acid racemization are inaccurate for age determination.

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## Radiocarbon on shells as a tool for paleoclimate research – a study from SE-Arabia

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Marine shells are a special challenge for radiocarbon. Compared to terrestrial material, shells usually seem shifted in age and older than its contemporary terrestrial counterparts. Thus, the marine reservoir correction is generally performed based on measurements of pre-bomb live collected shells found in museum collections and the mean value of several different species taken. In our research we noticed that this approach is not useful for paleoclimate studies, or for building tight chronologies, especially when other datable material is missing. We had found a species specific reservoir effect that also changes over time (Lindauer et al., 2016). In comparison to other paleoclimate proxies we noticed that changes are linked to climatic events and environmental changes (Lindauer et al., 2017).

This work was conducted at the United Arab Emirates (UAE) and Oman, between the Neolithic and Bronze Age. We also evaluated several other proxies (e.g. stalagmite data from UEA and Oman as well as the Dead Sea), in order to determine local and global factors that could influence our site and results. We managed to correlate possible changes through time and local mollusk species diversity to important factors, such as changes in ocean circulation and food resources. Further comparisons to shell literature data from Oman allow us to trace back seasonal ocean circulation patterns.

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Tuesday 19-Jun-18 - 13:40 - 15:20 - Sansiro 2

## Redating Palaeolithic human bones using the compound specific approach and the implications in understanding the Middle to Upper Palaeolithic transition in Eurasia

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Sample pre-treatment using HPLC has been operational at the Oxford Radiocarbon Accelerator Unit since 2006. Using preparative HPLC column(s) and non-carbon based eluents, this technique allows for the separation of underivatized amino acids liberated from the hydrolysis of collagen. A particular focus has been the isolation of hydroxyproline for compound specific AMS dating.

Our first aqueous-only mobile phase HPLC separation method involved 2 steps. The first one separated essential amino acids on a reversed-phase chromatographic column and the second separated the non-essential amino acids on a mixed-mode chromatographic column. Here, we report significant improvements that have been made to the method to enable faster preparative separation of amino acids from bone collagen, making the method suitable for routine AMS radiocarbon dating of contaminated bone samples.

This presentation will also show a selection of case studies from the ERC-funded project 'PalaeoChron' which is exploring the dispersal and chronology of early anatomically modern humans outwards from Africa and into Eurasia between 60-40,000 years ago. The study of this key period, during which Neanderthals and other archaic humans disappeared to extinction, relies on the power of radiocarbon dating for the chronological framework underpinning it. There is a huge onus on reliable dating, but this is extremely challenging due to the overwhelming effects of even trace (~<1%) amounts of carbon contamination on archaeological bone samples. To overcome this, as part of the project, we have been (re)dating human bone samples by AMS after isolating hydroxyproline from the collagen using preparative liquid chromatography. This has seen a dramatic improvement in our ability to decontaminate samples and obtain accurate results on Palaeolithic human bones.

Tuesday 19-Jun-18 - 13:40 - 15:20 - Sansiro 2

## Radiocarbon dating the archaeological site of Anzick: the influence of sample pre-treatment chemistry

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Found in 1968, the archaeological site of Anzick (24PA506), Montana, contains the only known Clovis burial (Lahren and Bonnicksen, 1974; Wilke et al., 1991; Owsley et al., 2001; Rasmussen et al., 2014). Here, the partial remains of a male infant, Anzick-1, were found in association with a Clovis assemblage of over 100 lithic and osseous artifacts—all red-stained with ochre. The incomplete, unstained cranium of an unassociated, geologically younger individual (Stafford et al., 1991, 1987), Anzick-2, was also recovered. Previous chronometric work has shown an age difference between Anzick-1 and the Clovis assemblage (represented by dates from two antler rod samples; Stafford et al., 1991, 1987; Morrow and Fiedel, 2006; Waters and Stafford, 2007; Rasmussen et al., 2014). This discrepancy has led to much speculation, with some discounting Anzick-1 as Clovis. To resolve this issue, we present the results of a comprehensive radiocarbon dating program that utilized four different pre-treatment methods on osseous material from the site. This comparative approach has allowed us to obtain robust chronometric data for a key site in First Americans research.

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*Tuesday 19-Jun-18 - 13:40 - 15:20 - Sansiro 2*

## **Big site, big data - Experiences and new possibilities with big data from a field archaeologist's point of view.**

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The Ørland project is one of the largest excavations of its kind in Norwegian archaeology. Covering an area of over 100 000 m<sup>2</sup>, along a narrow ridge on the Ørland peninsula at the mouth of the Trondheim fjord, it unearthed the remains of farmer-fisherman settlements spanning more than a millennium, from c. 700 BC – AD 1250.

The scale of the project has left us with a large amount of radiocarbon samples. With over 600 samples analyzed, we now find ourselves sitting on the largest dataset ever recorded on a single excavation in Norway.

Working with such big data has enabled us to interpret our site with more confidence, ask new questions, and even question old truths.

We would therefore like to share our experiences, and seek new possibilities within this dataset.

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## Carbon isotopes in shell carbonate and conchiolin of marsh periwinkle (*Littorina irrorata*): applications for coastal archaeology

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Radiocarbon dates on marine molluscs shells from estuaries are problematic because the inorganic carbon reservoirs from which shell carbonates are derived may vary significantly in radiocarbon content over multiple spatial and temporal scales. The mineral-bound organic matter within the carbonate shell matrix (“conchiolin”) is of dietary origin. Marsh periwinkle (*Littorina irrorata*) conchiolin was expected to reflect the atmospheric rather than marine carbon reservoir, thereby avoiding problems related to marine reservoir offsets, because they are generally found in marshes above the water line feeding on terrestrial marsh grasses, fungi, and algae.

In this study we compared <sup>14</sup>C ages of archaeological *Littorina* shell carbonate and conchiolin samples against dates for archaeologically associated terrestrial radiocarbon samples. The study included two specimens from Ossabaw Island, Georgia, on the Atlantic coast, and one specimen from Bayou St. John, Alabama, on the northern Gulf of Mexico. The inorganic shell fraction (carbonate) was sampled by reacting approximately 10 mg of powdered shell with 100% H<sub>3</sub>PO<sub>4</sub> in evacuated reaction vessels to produce CO<sub>2</sub>. A separate subsection of 100–200 mg of powdered shell was treated for analysis of the insoluble organic shell fraction, which consists predominately of conchiolin. Powdered shell was acidified with 85% H<sub>3</sub>PO<sub>4</sub>, thereby removing the carbonate phase, then reacted with Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> under vacuum to oxidize the organic phase to produce CO<sub>2</sub>. Archaeological *Littorina* shells yielded approximately 0.1% organic carbon, and <sup>14</sup>C activity was measured by AMS.

We demonstrate that: (1) conchiolin from archaeological periwinkles can be isolated successfully by the wet oxidation method; (2) as expected, stable carbon isotopes ( $\delta^{13}\text{C}$ ) in shell conchiolin (~ -20‰) and shell carbonate (~ -1‰) reflect dietary carbon and DIC, respectively; and (3) radiocarbon ages of shell carbonates are consistently older than the associated terrestrial samples by 100–150 <sup>14</sup>C yr. However, radiocarbon ages of conchiolin samples are different from associated terrestrial ages. Conchiolin from Atlantic coast specimens were younger than the expected by ca. 140 <sup>14</sup>C yr, while conchiolin from the Gulf coast specimen was ca. 150 <sup>14</sup>C yr older than expected.

There are several possible explanations for the discrepancies between observed and expected <sup>14</sup>C ages of archaeological conchiolin samples, including variability in radiocarbon content of *Littorina* diet; isotopic alteration of conchiolin due to diagenetic processes or sample recovery methods; and/or possibly contextual problems with associated terrestrial samples. Ongoing research includes analysis of modern, live-collected *Littorina* specimens, as well as environmental samples, to discriminate among the various sources of carbon in *Littorina* hard tissues.

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## Extraction of high-quality $^{14}\text{C}$ data from terrestrial sediments containing pollen fossils: High-efficiency pollen $^{14}\text{C}$ analysis using next-generation cell sorter

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Fossil pollen grains, which are commonly found in various types of sediments, have great potential for radiocarbon chronological research. If measurable amounts of fossil pollen grains can be extracted readily from sediment matrices, then  $^{14}\text{C}$  age determination could be performed at any depositional depth, regardless of with or without plant macrofossils, and the quality of the deposition age model can be considerably increased. Thus far, several lake sediments have been tested for pollen  $^{14}\text{C}$ . However, technical issues such as complex preparation procedures, collection rate, and purity of concentrated sample persisted and pollen  $^{14}\text{C}$  analysis has not been applied routinely. A novel pollen concentration method is developed herein using a next-generation cell sorter to quickly prepare pure concentrates of fossil pollen grains suitable for  $^{14}\text{C}$  dating, with a relatively simple preparation procedure.

Cell sorter was originally developed for biomedical researches to instantaneously identify and separate cells of specific fluorescence and shape. Some of the latest model machines can perform machine tuning and sample preparation semi-automatically, and it is designed to solve most issues via the exchange of replacement parts. In the proposed method of pollen purification, pollen-enriched suspension is introduced into cell sorter, which can separate more than a million grains of fossil pollen in half a day.

The pollen  $^{14}\text{C}$  analysis was conducted using a SG06 sediment core from Lake Suigetsu, which has one of the most reliable age models that we can use as reference. Pollen fossil samples equivalent to 50–100  $\mu\text{gC}$  were extracted from ca. 25–30 g of wet sediment and were measured using a compact AMS system (NEC 0.5 MV 1.5SDH-1) of LRD.UMUT. The  $^{14}\text{C}$  data of the pure pollen samples agreed well with the Suigetsu's  $^{14}\text{C}$  dataset on terrestrial plant leaf fossils. This result shows that accurate  $^{14}\text{C}$  data can be obtained from any depth of the core, even at depths at which plant remains are not present. Using the proposed method, the Suigetsu's  $^{14}\text{C}$  data can be enhanced for data density and evenness of the data intervals, both of which would directly contribute to the accuracy of the age model. We also believe that the proposed method can be applied to various sediment types from both marine and terrestrial realms, and will assist high-precision chronological study as well as quantification of marine reservoir age.

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## Radiocarbon Calibration using Atlantic Cold-Water Corals

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Combined U-series and radiocarbon dating of cold-water corals provides measures of the paleo seawater radiocarbon content, which is driven by air-sea gas exchange and advection and mixing pathways of differently aged water masses in the interior. Framework forming cold-water corals generally occupy habitats within the upper thermocline ocean (300 – 1000m) in the Atlantic influenced by the recirculation of mostly well ventilated mid-depth water masses. Thus, such corals provide an opportunity to reconstruct the reservoir age history of the upper mid-depth Atlantic, were previous studies had partly inferred large reservoir age changes. Here, we present a preliminary compilation of mid-depth radiocarbon reservoir ages spanning 30000 years. In addition to classical age quality control we further consider the growth history of coral mounds (i.e. the activity of coral growth and/or weathering potential). This compilation spatially spans data from the temperate northeast, southeast and southwest Atlantic. From 13000 years to present we observe a near perfect match with the IntCal13 adjusting to a mean pre-bomb and regional <sup>14</sup>C offset between atmosphere and thermocline ocean. From 30000 to 19000 years, i.e. during the last glacial thermocline water aging is recorded leading to more variable and higher offsets from IntCal13, i.e. reduced ventilation. However, glacial thermocline water aging rarely exceeds an increase of the regional reservoir age by more than a few hundred years.

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## Radiocarbon variability in northeast Atlantic intermediate waters during the past six decades recorded in cold-water corals

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The radiocarbon content of northeastern Atlantic upper intermediate water is intimately linked to cross thermocline exchange and advection of water masses along the basin scale re-circulation pathways. These water masses mainly result from the mixing of the subpolar and subtropical Atlantic intermediate water masses. With the introduction of bomb <sup>14</sup>C produced by atmospheric nuclear weapon testing in the 1950s and early 1960s, radiocarbon time series in intermediate ocean can provide unique information on the variability of intermediate ocean circulation.

Here, four cold water corals collected alive have been investigated in order to reconstruct high resolution time series of pre- and post-bomb radiocarbon for intermediate waters in three locations of northeastern Atlantic. Continuous <sup>14</sup>C records were obtained from long-lived specimens of the branching scleractinian cold-water corals *Madrepora oculata* and *Lophelia pertusa*. The studied corals were collected from the Norwegian Sea (67°N, 9°E, 350 m water depth), from the Bay of Biscay (46°54'N, 05°19'W, 691 m water depth) and from Rockall Trough (55°27'N, 15°03'W, 773 m water depth).

These time series provide new constraints on the age and growth rate of two of the most important framework-building cold-water coral species. Moreover, the coral <sup>14</sup>C records reveal a previously undocumented Delta <sup>14</sup>C dynamic for the eastern Atlantic intermediate waters over the past 60 years, most likely related to the cross thermocline exchanges and variations through time of the Atlantic mid-depth gyre circulation.

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## Cracked it! Dating archaeological pottery using compound-specific radiocarbon analysis (CSRA) of adsorbed lipids

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Radiocarbon dating of pottery vessels is challenging. It relies on obtaining sufficient carbon, free of contamination, which originates either from the use or from the manufacture of the pot. Invisible food residues preserved within vessel walls are of particular interest because of they are close in age to the time of the deposition due to fast metabolic turnover, and their preservation and relative immobility in the burial environment(1). Degraded animal fats, distinguished by their high content of C16:0 and C18:0 fatty acids, are often recovered in high concentrations in archaeological potsherds(2). Therefore, compound-specific radiocarbon dating (CSRA) of individual fatty acids is theoretically possible and highly desirable(1,3,4), rather than the analysis of carbonised residues or total lipid extracts, which are more prone to contamination from burial, handling, storage and extraction.

Preparative Capillary Gas Chromatography (PCGC) isolation has proven to be a powerful technique for isolating single compounds from environmental matrices for radiocarbon dating(3), however, improvements were required to achieve the accuracy and precision required for the dating of archaeological materials(1,4). Recent investigations identified and quantified sources of contamination associated with the isolation procedure(5). Based on this modified laboratory protocols were designed to minimize and/or eliminate the contamination. The new protocol has now been successfully applied to date a range archaeological materials.

Initial tests focussed on a corpus of bog butters spanning a 3000-year range. The tests were then further applied to a range of pottery vessels from well-dated archaeological contexts. We carefully selected pottery vessels of different ages and burial environments. Compound-specific radiocarbon dates obtained from the lipids showed good agreement with the pre-existing dates available either from dendrochronology or from Bayesian chronological modelling of radiocarbon dates. These results demonstrate the application of our enhanced CSRA methodology to archaeological pottery vessels, and, significantly, represent the first radiocarbon measurements obtained from lipids preserved in pottery vessels with equivalent accuracy to other commonly dated sample types.

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## Development of a novel solventless trapping system and PC-GC cleaning method for the isolation and recovery of compounds for reliable, high-precision CSRA

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Preparative capillary gas chromatography (PC-GC) has been widely adopted for the isolation of single compounds for compound-specific radiocarbon analysis (CSRA) since the inception of the technique in 1996<sup>1</sup>. Previous attempts at the CSRA of absorbed lipids from archaeological potsherds showed great promise but ultimately failed to attain the degree of accuracy or precision demanded by high-precision archaeological dating<sup>2 3</sup>. Thus, whilst PC-GC has proven to be highly effective for the isolation of a wide range of compounds from complex mixtures, a number of areas of concern existed relating to: i) the incorporation of exogenous carbon during the trapping procedure ('column bleed'), ii) the cross-contamination of samples isolated in subsequent trapping sequences, and iii) the incomplete removal of organic solvents used in the recovery of isolated compounds from traps.

We have previously reported the development of an NMR-based method for the direct quantification of exogenous carbon arising from GC column bleed and concluded that this did not represent a level of contamination which would significantly affect radiocarbon determinations<sup>4</sup>. However, concerns relating to solvent removal and sample cross contamination, remain. In this study, we quantify exogenous C within isolated samples arising from these sources and demonstrate that this has the potential to significantly affect the accuracy and repeatability of radiocarbon determinations.

Subsequently, the efficacy of a simple heat-based cleaning procedure for preventing cross-contamination between samples isolated in subsequent trapping sequences was assessed; and, after developing a simple, cost-effective and solvent-free compound trapping and recovery system, we present the result of tests demonstrating its reliability and the accuracy and precision of CSRA in which it was employed. Comparison of CSRA dates obtained using our new methods and 'bulk' <sup>14</sup>C determinations on modern reference materials and samples of archaeological fats (bog butters) demonstrate the efficacy and reliability of the heat-based cleaning and solventless trapping systems for the generation of high-precision, accurate radiocarbon determinations for archaeological applications.

1. Eglinton, T. I., Aluwihare, L. I., Bauer, J. E., Druffel, E. R. M. & McNichol, A. P. Gas Chromatographic Isolation of Individual Compounds from Complex Matrices for Radiocarbon Dating. *Anal. Chem.* 68, 904–912 (1996).

2. Stott, A. W. et al. Radiocarbon Dating of Single Compounds Isolated from Pottery Cooking Vessel Residues. *Radiocarbon* 43, 191–197 (2001).

3. Berstan, R. et al. Direct dating of pottery from its organic residues: New precision using compound-specific carbon isotopes. *Antiquity* 82, 702–713 (2008).

4. Casanova, E., Knowles, T. D. J., Williams, C., Crump, M. P. & Evershed, R. P. Use of a 700 MHz NMR Microcryoprobe for the Identification and Quantification of Exogenous Carbon in Compounds Purified by Preparative Capillary Gas Chromatography for Radiocarbon Determinations. *Anal. Chem.* 89(13) 7090-7098 (2017).

Wednesday 20-Jun-18 - 8:30 - 10:00 - Sansiro 1

## A preview of the IntCal19 radiocarbon calibration curves

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Radiocarbon calibration curves have been revised and extended many times over the past decades, but the more sophisticated geoscience and archaeological research becomes, the greater the need for improved curves. Fortunately, there has been an explosion of calibration quality data in the last few years as well as considerable progress on statistical methods for curve construction. New <sup>14</sup>C data sets include those from Hulu cave speleothems back to 55ka BP, late glacial tree-rings from Europe and New Zealand and decadal and single year tree-rings from around the globe. Improved understanding of natural fluctuations in <sup>14</sup>C concentration, their causes, magnitude and timing, will enable a better synthesis of calibration data from different sources. For example, the inclusion of modelled marine reservoir ages derived from a three-dimensional ocean circulation model (Butzin et al. 2017), allows us to apply more appropriate reservoir corrections to the marine <sup>14</sup>C data rather than the constant regional offsets from the atmosphere previously used.

The IntCal Working Group, with valuable input from focus group members, is in the final stages of constructing new curves for the Northern and Southern Hemisphere terrestrial and marine carbon reservoirs with a planned publication date of 2019. A preview of the data that are to be included and a preliminary Northern Hemisphere terrestrial calibration curve will be presented.

Butzin M, Köhler P, Lohmann G. 2017. Marine radiocarbon reservoir age simulations for the past 50,000 years. *Geophysical Research Letters* 44(16):8473-80.

Wednesday 20-Jun-18 - 8:30 - 10:00 - Sansiro 1

## Ocean ventilation and benthic-planktonic radiocarbon ages evolution over the last termination; a coupled climate model study.

Anne Mouchet<sup>1</sup>, Uwe Mikolajewicz<sup>2</sup>, Virna Meccia<sup>2</sup>, Eric Deleersnijder<sup>3,4</sup>, Veronika Gayler<sup>2</sup>, Marie Kapsch<sup>2</sup>, Thomas Riddick<sup>2</sup>, Florian Ziemen<sup>2</sup>

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Ocean circulation plays an essential role in Earth's climate and the global carbon cycle. A prerequisite for improving confidence in future climate projections is the accurate numerical modeling of past deep ocean circulation changes. Unfortunately our understanding of such changes in terms of transport pathways and transit times is impeded by ambiguities in data-based reconstructions which heavily rely on radiocarbon. Indeed, interpreting the temporal evolution of the deep-sea radiocarbon signal over the last deglaciation is far from straightforward since it is the result of simultaneous changes in atmospheric levels, air-sea exchange rates, and ocean circulation.

Here, we investigate how deep-sea radiocarbon ages scale to the actual ventilation timescales during transient experiments over the last termination with focus on periods characterized by significant changes in the AMOC.

For this purpose we take advantage of a set of transient simulations performed with the Max Planck Institute Earth System Model (MPI-ESM) including the newly developed adaptive bathymetry and river routing components. The experiments, starting at 26 ka BP, are constrained with prescribed time varying ice sheets and topography. Changes in ice sheet volume naturally result in freshwater surges which affect the Atlantic Meridional Overturning Circulation (AMOC).

Ocean radiocarbon is included in the model. The atmospheric <sup>14</sup>C follows the INTCAL13 reconstruction while the impacts of varying wind speed, sea-ice cover, and atmospheric CO<sub>2</sub> on air-sea exchange rate are explicitly included. The model also includes a set of age and dye tracers documenting the role of specific surface areas in the deep ocean ventilation as reported by radiocarbon and ideal age, respectively.

Our experiments put forward that the multiplicity of transit pathways in the ocean combined with the slow exchange at the air-sea interface prevents radiocarbon to carry unique regional surface signatures to depth.

Further, radiocarbon based ages exhibit large departures from the actual ventilation time scales which are not fully explained by the atmospheric signal.

These results put limitations on the use of radiocarbon as a ventilation proxy.

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## The demise, or the dawn, of the radiocarbon age in the Anthropocene?

Timothy Eglinton<sup>1</sup>

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Since the adoption of fossil fuels as a source of energy, humans set in motion profound changes to Earth's carbon cycle that have led to a build-up of CO<sub>2</sub> in the atmosphere and accompanying changes in climate, ecosystems and biogeochemical cycles. Assessing human perturbations to the carbon cycle, and predicting future responses, has become a pressing scientific challenge.

One clear signature of carbon cycle change stemming from burning of fossil fuels is a decrease in the radiocarbon content of atmospheric CO<sub>2</sub> and active surface carbon pools – the so-called “Suess effect” (Suess, 1955). Superimposed on this relatively gradual change is the abrupt shift to positive  $\Delta^{14}\text{C}$  values resulting from above-ground nuclear weapons testing in the mid-20th century. This <sup>14</sup>C “bomb spike” coincides with numerous trajectory changes in our environment due to human activity, leading some to propose this ominous milestone as the formal beginning of the Anthropocene (Steffen et al., 2015).

Atmospheric CO<sub>2</sub> concentrations have continued their inexorable climb upwards in concert with fossil fuel utilization, and now  $\Delta^{14}\text{C}$  values of CO<sub>2</sub> are returning to negative territory. Graven (2015) modeled future changes in <sup>14</sup>C contents of different carbon reservoirs through the 21st Century adopting different emission projections, and concluded that by the year 2100 under a “business as usual” scenario, atmospheric CO<sub>2</sub> would carry a <sup>14</sup>C age of ca. 2000 years. While this presents complications in the context of <sup>14</sup>C dating, it highlights the sensitivity of radiocarbon as a tracer of carbon cycle processes in the Anthropocene, and in particular for assessment of inputs and subsequent redistribution of fossil [fuel] carbon. Global carbon cycle models are increasingly able to incorporate isotopic information, providing powerful constraints and yielding testable outcomes. However, carbon cycle processes remain under-constrained from a radiocarbon perspective due to a paucity of observational data, particularly in a time-series context, for key carbon reservoirs (e.g., soil, riverine and oceanic dissolved and particulate organic matter).

While radiocarbon has generally been used relatively sparingly due to limitations of cost, sample throughput, sensitivity and selectivity, with the advent of increasingly versatile instrumentation for natural-abundance <sup>14</sup>C analysis there is enormous potential for expansion of the scope of <sup>14</sup>C studies. This marked increase in measurement capacity places us on the verge of a new era in radiocarbon-centric research that can shed new light on the workings and vulnerabilities of Earth's carbon cycle in the Anthropocene at unprecedented spatial and temporal resolution, and from the global scale to the molecular level.

The goal of this presentation is to (a) provide examples of the types and density of measurements that could inform isotope-enabled carbon cycle models, (b) highlight key areas of uncertainty spanning different carbon reservoirs that would benefit from in-depth radiocarbon investigations, and (c) outline a vision for a comprehensive global radiocarbon observation program that would require broad and sustained engagement by our community.

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Steffen W. et. al., 2015 The Anthropocene Review 2, 81-98.

Suess H.E. 1955. Science 122 415-417.

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## Dating monospecific and single-shell benthic foraminifera samples with a gas ion source: implications for the hypothetical release of <sup>14</sup>C-depleted CO<sub>2</sub> from ocean mid-waters into the atmosphere

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The evidence for very old intermediate waters during the glacial and deglaciation periods and their relationship with the evolution of atmospheric pCO<sub>2</sub> are still debated issues. The <sup>14</sup>C-depletion of intermediate waters may be linked to the Dansgaard-Oeschger (DO) and Heinrich (H) events abrupt climatic changes, which affected the stratification and dynamics of the global ocean during the last glacial period.

As shown by various proxies measured in ocean sediments, intermediate waters also experienced large variations of dissolved oxygen content, which may have affected the carriers of the geochemical signals, notably mixed benthic foraminifera used for <sup>14</sup>C reconstructions. A key aspect is therefore the ability to measure <sup>14</sup>C in high sedimentation rate cores and to analyze separately samples composed of monospecific benthic foraminifera adapted to oxic or suboxic conditions. Perturbing processes such as bioturbation should also vary with oxygen content, and it is also advisable to date single shells in order to evaluate their age spectrum at selected depths in the sediment.

We will present our progress in dating benthic foraminifera from a high sedimentation rate core from the northern Indian Ocean. The sediments located within the present oxygen minimum zone are partly laminated and we first measured several independent geochemical records to reconstruct hydrological and oxygen conditions over the last 50 kyr. Collectively, these proxies show marked variations that are in stratigraphic agreement and correlate precisely with DO and H events, independently dated in Greenland ice cores and in Chinese stalagmites.

For <sup>14</sup>C measurements of small samples we used the gas ion source of the AixMICADAS facility (Bard et al. 2015 NIMB) equipped with the gas interface system coupled to the carbonate handling system (CHS). Our method is based on the online leaching of ca. 30 % of the sample mass with HCl using the CHS, followed by complete hydrolysis of the residual carbonate with phosphoric acid. The precision, accuracy and blank levels have been tested extensively with IAEA C1 and C2 reference materials and internal standards, including old (>100 kyr BP) foraminifera.

We applied these techniques to the Indian Ocean core on 12 different species of benthic foraminifera adapted to various dissolved oxygen conditions. For sections corresponding to DO events, the <sup>14</sup>C age difference between benthic and planctonic foraminifera is broadly similar to that observed in the modern ocean (around 500 yr).

Surprisingly, large <sup>14</sup>C deviations are observed during the transition into the H1 period with all suboxic species systematically 2 kyr older than benthic foraminifera adapted to oxic conditions. The significant <sup>14</sup>C difference between benthic foraminifera picked at the same depth could be explained by bioturbation and migration in the sediment.

Our results suggest that care should be taken at the abundance variations of individual benthic foraminifera and that monospecific benthic samples should be used to reconstruct <sup>14</sup>C reservoir ages of intermediate waters. This will be crucial to settle the debate about the existence of large residence time in mid-ocean layers and on the hypothetical consequence of abrupt release of <sup>14</sup>C-depleted CO<sub>2</sub> into the atmosphere.

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## High resolution radiocarbon dated sediment core record of Nitrogen cycling in northern Arabian Sea during the last 35 ka

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Understanding the nitrogen cycle in marine environments is very important as it influences the global climate through its ability to modulate biological pump and nitrous oxide production (denitrification). Arabian Sea provide a unique marine setting to study the nitrogen cycle as it accommodates one of the world largest water column denitrification and high surface productivity. Here we reconstruct a long term productivity and nitrogen isotopic record from a high resolution radiocarbon dated sediment core retrieved from northern Arabian Sea. The reconstructed productivity record shows multi-millennial scale variations during 35-23 cal. ka BP, 23-16 cal. ka BP, 16-10 cal. ka BP and 10-1.3 cal. ka BP. Accordingly, the Last Glacial Maximum (LGM; 23-16 ka BP) was the most productive period in the study area followed by the Holocene (last 11.7 ka). However the cause for the high productivity observed during LGM and Holocene periods stem from diverse processes. The productivity during LGM was triggered by convective mixing of water column and atmospheric deposition of nutrients, whereas, the lateral advection of nutrients from upwelling centres during southwest monsoon was responsible for Holocene productivity. The nitrogen isotopic record give clues about the denitrification intensity and productivity in the study area. The  $\delta^{15}\text{N}$  data show low values during 35-16 ka BP than 16-1.3 ka BP. The increase in  $\delta^{15}\text{N}$  at 16 ka BP resulted due to the intensified pelagic denitrification and the de-glacial onset of southwest monsoon. The comparison of present  $\delta^{15}\text{N}$  record with coastal records shows the presence of an offshore gradient in  $\delta^{15}\text{N}$  during the last 16 ka, probably caused by the partial nutrient utilization and lateral advection of upwelled waters. The  $\delta^{15}\text{N}$  gradient increased during the Holocene from 1‰ at 10 ka BP to more than 2‰ at 1.3 ka BP. Increased nutrient utilization along the transport of upwelled waters from the Oman margin due to decline in the intensity of lateral advection may be the causative factor for the increase in  $\delta^{15}\text{N}$  gradient during Holocene. This study demonstrate the influence of surface processes along with denitrification on the nitrogen isotopic record.

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## Using the Suess effect on the stable carbon isotope to distinguish the future from the past in radiocarbon

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The depletion of <sup>14</sup>C due to the emission of radiocarbon-free fossil fuels (<sup>14</sup>C Suess effect) might lead to similar values in future and past radiocarbon signatures potentially introducing ambiguity in dating. I here use the global carbon cycle model BICYCLE and perform computer simulations to test if a similar impact on the stable carbon isotope via the <sup>13</sup>C Suess effect might help to distinguish between ancient and future carbon sources. To analyze a wide range of possibilities, I add to future emission scenarios (RCP2.6, RCP4.6, RCP6.0, RCT8.5, all extended until year 2500) some scenarios with carbon dioxide reduction (CDR) mechanisms, which partly enhance the depletion of atmospheric D<sup>14</sup>C already caused by the <sup>14</sup>C Suess effect. These CDR approaches include direct air capture (DAC), enhanced weathering (EW) and bioenergy with carbon capture and storage (BECCS), which all have different effects on the carbon isotopes.

The <sup>13</sup>C Suess effect leads in the simulated future to unprecedented depletion in δ<sup>13</sup>C shifting the carbon cycle to a phase space in D<sup>14</sup>C-δ<sup>13</sup>C in which the system has not been during the last 50 000 years and therefore the similarity in past and future D<sup>14</sup>C (the ambiguity in <sup>14</sup>C dating) induced by fossil fuels can in most cases be overcome by analyzing <sup>13</sup>C. Only for slow changing reservoirs (e.g. deep Indo-Pacific Ocean) or when CDR scenarios are dominated by BECCS the effect of anthropogenic activities on <sup>13</sup>C does not unequivocally identify between past and future carbon cycle changes.

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Wednesday 20-Jun-18 - 10:30 - 12:30 - Sansiro 1

## Is the dome leaking? Reconstruction of seawater <sup>14</sup>C from Porites coral outside of the Runit Island Dome.

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After the WWII, Enewetak Atoll was used to test nuclear weapons; the program ran from 1948 to 1958. After an intermittent use from 1958 to 1972 it was decided to return Enewetak Atoll to the Marshallese after the establishment and completion of the clean-up operations. The island of Runit (on Eastern side of Atoll). A cleanup plan was devised to remove all radioactive and non-radioactive debris (equipment, concrete, scrap metal), soil that exceeded 1.48Bq of plutonium per gram of soil and depositing it into the Cactus test crater on Runit Island. Approximately 73,000 cubic meters of surface soil from 6 islands were removed and deposited into the crater. All soil and large debris were bulldozed into place and mixed with concrete. A dome was constructed from 370 individual concrete panels averaging ca. 45cm thick to cover the crater. Tidal measurements suggest the potential for the release of contaminated groundwater from beneath the dome. This project uses a Porites coral collected in 2003 from the lagoon side of Runit Island to reconstruct the radiocarbon history. The coral core covers the years 1982-2003 with radiocarbon measurements every two months. Preliminary results suggest slightly elevated radiocarbon measurements when compared to external coral datasets. At this point it is unknown if the slightly elevated measurements are due to the dome or the much higher inventory of radionuclides in the atoll lagoon sediments.

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## Fifty years of atmospheric radiocarbon studies in Slovakia: NPP and fossil fuel impacts

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Two main sources of radiocarbon variations in the atmosphere of Slovakia have been identified: radiocarbon releases from the Jaslovské Bohunice nuclear power plant (NPP), and carbon dioxide from combustion of fossil fuels.

Both Bratislava and Žilkovce (5 km from the Jaslovské Bohunice NPP) sampling stations have been influenced by radiocarbon emissions from the Jaslovské Bohunice NPP, although in recent years the annual release rates decreased almost by a factor of 5. A correlation has been found between the Bratislava and Žilkovce atmospheric radiocarbon data when the NE transport of air masses from Jaslovské Bohunice to Bratislava dominated. The radiocarbon concentrations in the heavily polluted atmosphere of Bratislava were during eighties by about 10% and at Žilkovce by about 5% lower than the European clean air represented by the Jungfrauoch radiocarbon data. After 1993 the radiocarbon concentrations were similar at both sites, and from 2000 they were close to the European clean air levels. The observed radiocarbon behavior in the atmosphere provides a unique evidence of decreased fossil fuel carbon dioxide emissions in the region, as well as the long-term effect of the Jaslovské Bohunice NPP on the atmosphere of the SW Slovakia.



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## A comprehensive study on $^{14}\text{C}$ in the 10 MW High Temperature Gas-Cooled Reactor

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Owing to its high mobility in the environment and important radiological impact on human beings, increased attention has been paid to carbon-14 ( $^{14}\text{C}$ ) during the environmental impact assessment of nuclear power plants (IAEA 2004). The 10 MW high temperature gas-cooled reactor (HTR-10) is the first pebble-bed gas-cooled test reactor in China that adopted helium as primary coolant and graphite spheres containing tristructural-isotropic (TRISO) coated particles as fuel elements (Wu et al. 2002). Recently, a series of experiments on radioactive source terms in HTR-10 have been conducted: (1) measurement of specific activity and distribution of typical nuclides in irradiated graphite spheres from the core (Liu et al. 2017; Li et al. 2017), (2) measurement of radioactive dust concentration in the primary loop (Xie et al. 2017), (3) measurement of  $^3\text{H}$  activity concentration in the primary loop (Xie et al. 2018a), and (4) measurement of  $^{14}\text{C}$  activity concentration in the primary loop (Xie et al. 2018b). The specific activity and distribution of  $^{14}\text{C}$  in the four irradiated graphite spheres have been determined. The  $^{14}\text{C}$  activity concentration in the primary loop of HTR-10 has been obtained using the newly sampling system which can sample  $^{14}\text{C}$  from the coolant at three locations: 1) upstream of the copper oxide bed, 2) downstream of the copper oxide bed, and 3) downstream of the molecular sieve absorber. All the experimental data about  $^{14}\text{C}$  available in HTR-10 will be summarized and analyzed with theoretical calculations. The key issues on  $^{14}\text{C}$  research in HTGRs will be presented and discussed.

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Wednesday 20-Jun-18 - 10:30 - 12:30 - Sansiro 2

## Statistical Methodology for the IntCal19 radiocarbon calibration curves

Timothy J. Heaton<sup>1</sup>, Maarten Blaauw<sup>2</sup>, Paul G. Blackwell<sup>1</sup>, Christopher Bronk Ramsey<sup>3</sup>, Paula J. Reimer<sup>2</sup>, Marian Scott<sup>4</sup>

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A high-quality radiocarbon calibration curve requires not only high-quality calibration data but also a rigorous and reliable way to combine that data into a curve. The calibration data we use typically have several unique features that we need to both recognise and incorporate if we want to produce the best curve possible. For example:

- 1) The radiocarbon measurements of tree rings may not relate to single years but rather blocks of between 5-20 years;
- 2) for older periods, the calendar ages of our calibration data are often somewhat uncertain being themselves estimated (e.g. U/Th dating, varve counting, climate tie-pointing to otherwise dated archives ...);
- 3) offsets may exist between sets of radiocarbon measurements in different materials due to reservoir ages or dead carbon fractions which may also be unknown.

If we ignore these aspects of the data then the result would be a final curve that is neither robust nor accurate and which underestimates the variability. However, at the same time we also wish to have a method that is neither so complex nor slow to run that it does not allow us to investigate the robustness of the curve to individual data points, data sets or modelling assumptions.

In this talk we present the new methodology used for the creation of the IntCal19 calibration curves. Our approach aims to address all the features described above while also enabling us to investigate the sensitivity of the curve to changing assumptions. The curve itself is estimated using Bayesian regression splines with the addition of bespoke modelling to incorporate the uncertain calendar ages, blocking and offsets. Curve creation is performed within an MCMC sampler using parallel tempering to improve mixing.

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## Comparison records and their value for improving the <sup>14</sup>C calibration curve

Raimund Muscheler<sup>1</sup>, Florian Adolphi<sup>1,2</sup>, Timothy J. Heathon<sup>3</sup>, Johannes van der Plicht<sup>4,5</sup>, Anders Svensson<sup>6</sup>, Christopher Bronk Ramsey<sup>7</sup>, Paula J. Reimer<sup>8</sup>

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<sup>5</sup> Faculty of Archaeology, Leiden University, Leiden, The Netherlands.

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Connecting calendar ages to <sup>14</sup>C ages (i.e. constructing a calibration curve) is mainly based on <sup>14</sup>C samples that can also be dated via independent methods. However, comparison of <sup>14</sup>C data to other records such as cosmogenic radionuclide data from ice cores can provide tests of the quality of the <sup>14</sup>C data and its calendar age determinations. Here we will discuss how such additional information can aid the identification of uncertainties in <sup>14</sup>C records and the improvement of the calibration curve. We will discuss how high-resolution 10Be data can help to support short-term variations seen in the emerging annually resolved <sup>14</sup>C records or point to potential biases in the older part of the calibration curve.

The direct incorporation of such information into the calibration curve is challenging as it delivers only partial information (e.g. the placement of a floating tree ring sequence within a section of non tree ring data) possibly leading to an inhomogeneous calibration record. We will discuss how this issue will be addressed in the upcoming IntCal update.

The comparison of radionuclide records (mainly <sup>14</sup>C and 10Be) via common production rate changes has the additional benefit that it places ice core records into the context of very well absolutely dated <sup>14</sup>C records. This allows us to test the proposed synchronicity of rapid climate changes or, alternatively, the accuracy and precision of "climate wiggle matched" time scales that underlie part of the records entering the Intcal calibration curve.

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## Accounting for Reservoir Effects in Marine Radiocarbon Calibration

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The radiocarbon dating method is supported by highly refined calibration data empirically obtained from environmental archives. Nevertheless, marine calibration remains problematic due to the Marine Reservoir Effect (MRE), which is spatiotemporally variable. The currently accepted curve for radiocarbon calibration in the ocean is a global curve, partly derived by numerical modelling from its atmospheric counterpart. As such, this curve cannot account for the effects of local phenomena that are strongly correlated with <sup>14</sup>C signatures in seawater (e.g., ocean dynamics and continental runoff). Although the radiocarbon community has suggested the use of regional calibration curves that would better represent the heterogeneous ocean reservoir, a reasonable method for their construction has not yet been proposed. We directly address this longstanding issue in radiocarbon research by combining the output of a model for the temporal evolution of the MRE worldwide with the existing calibration curves.

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## Chronological significance of <sup>14</sup>C spike and precise age determination of the B-Tm Tephra, China/ North Korea

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The eruption age of Baitoushan-Tomakomai (B-Tm) tephra has been measured by various methods such as dendrochronology, varve chronology and <sup>14</sup>C wiggle-matching (Sun et al. 2014). The discovery of AD 774-775 <sup>14</sup>C spike (M12 peak, Miyake et al. 2012) provides a new special technique to obtain precise date (Wacker et al. 2014). Recently, the <sup>14</sup>C spike matching revealed the eruptive year as late AD 946 without error (Hakozaiki et al. 2018; Oppenheimer et al. 2017). Such <sup>14</sup>C spike (Güttler et al. 2015; Jull et al. 2014; Park et al. 2017; Usoskin et al. 2013) also shows the regional offsets of <sup>14</sup>C concentration (D<sup>14</sup>C) within the atmosphere of the northern hemisphere (Hong et al. 2013a, b; Imamura et al. 2007; Nakamura et al. 2013; Sakamoto et al. 2017) more clearly. These facts imply that simply comparing the <sup>14</sup>C concentrations with the calibration curve such as IntCal13 (Reimer et al. 2013) in the <sup>14</sup>C wiggle-matching may occur inconsistency. In dendrochronology, fluctuations of annual-ring width match the master curve, but the original width values are not used directly. To cancel regional offset including laboratory offset, in the <sup>14</sup>C wiggle-matching, the fluctuations of <sup>14</sup>C concentration also should be used to fit the calibration curve.

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Wednesday 20-Jun-18 - 10:30 - 12:30 - Sansiro 2

## New speleothem radiocarbon calibration records from Hulu Cave, China.

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Currently, few reliable <sup>14</sup>C calibration datasets are available beyond the limit of the dendro-dated tree-ring record at ~14 kyr BP, and the uncertainties of the <sup>14</sup>C calibration derived from these older data remain large and complex. For speleothem records, a major source of uncertainty comes from the so-called Dead Carbon Fraction correction (DCF) that compensates for incorporation of <sup>14</sup>C-free geologic carbonate (Genty et al., 1971) and/or aged subsurface soil carbon (Noronha et al., 2015) into the groundwater that eventually precipitates the speleothem carbonate. Speleothem H82 from Hulu cave near Nanjing in eastern China, spanning 26.8 - 10.6 kyr BP, demonstrated a notably small and stable DCF (5–6%) across major deglacial climate shifts (Southon et al., 2012), raising the possibility of using Hulu samples to extend the <sup>14</sup>C calibration further back in time with unprecedented precision and accuracy. Here, we present high-resolution 230Th-dated <sup>14</sup>C records from Hulu speleothems MSD (18.5–51 ka BP) and MSL (36–53 ka BP). Both speleothems are formed from hard, clean, void-free calcite and corrections for detrital thorium are low throughout. Furthermore, we now know that the small and stable DCF for these speleothems is due to their unusual geologic setting, which strongly suggests that it remained constant within tight bounds across the entire record.

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*Wednesday 20-Jun-18 - 10:30 - 12:30 - Sansiro 2*

## Reassessment of the Chronology of the Lake Suigetsu 2006 record in light of new analysis of the varves and other new radiocarbon datasets

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The varved Suigetsu 2006 (SG06) radiocarbon record covers the period ~10-50 ka cal BP and, because it is based on measurements on terrestrial plant macrofossils, it provides direct information on atmospheric levels of the radioisotope. For these reasons, the record is of considerable importance for radiocarbon calibration. The calendar chronology of SG06 is based on evidence from a number of sources. Firstly, we have a varve chronology using both microscopic analysis and micro XRF scanning; this has recently been extended to 50 ka and updated with new mathematical methods for interpolation and integration (Scholaut et al. in review). The other control on the chronology of the Suigetsu record, as it was included within the IntCal13 calibration curve, was comparison to the existing long speleothem records which, although having a dead-carbon-fraction (DCF), we expect to exhibit much of the same high-frequency components. For the next version of the calibration curve, we need to update this analysis to take account of the new speleothem records that are available and the new varve chronology. This paper considers the implications of this reassessment both in terms of the chronology of the record itself and for radiocarbon calibration.

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## A modified Wet Chemical Oxidation Method for Fresh Water DOC <sup>14</sup>C Analysis

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Radiocarbon (<sup>14</sup>C) analysis on dissolved organic carbon (DOC) in fresh water is very helpful for studying carbon cycles in the terrestrial environment. Lang et al (2016)[1] has presented a rapid and economic method for DOC <sup>14</sup>C analysis using wet chemical oxidation inside 12-ml Labco Exetainer<sup>®</sup> vials. Since this method yields tens of microgram carbon, it is only suitable for gas ion source AMS measurement. To get high precision measurement using the solid ion source AMS, a larger volume of water sample is required. Here we present a modified wet chemical oxidation method for ~500 ml fresh water samples. About 2 gram re-precipitated sodium persulfate was added as an oxidant into fresh water samples in a 1L glass Duran<sup>®</sup> bottles which was then sealed and heated to 100 °C for 1 hour. An evacuated 2 L stainless steel canister was used to extract the CO<sub>2</sub> from the headspace in the reaction bottle. CO<sub>2</sub> from the canister was purified cryogenically and quantified in a vacuum system, then graphitized using the sealed tube Zn reduction method [2]. We examined the yields and blanks of the method with both modern carbon and dead carbon (<sup>14</sup>C-free) standards. The oxidation yield is closed to 96-100%, but the headspace extraction yields is about 48-50% of the total oxidized carbon, and the total processing blank is about 7±1 µg C. We also compared Suwannee River natural organic matter standard (2R101N) and several fresh water samples to DOC measurements by UV photochemical oxidation [3]. Our isotopic standards show comparable results with those measured by the UV oxidation method, and are consistent with the consensus values after the blank corrections. The headspace extraction, however, leads to about 0.5‰ positive shift in DOC δ<sup>13</sup>C values. The advantage of this modified method over the method of Lang et al (2016) that is that it generates hundreds of microgram carbon, which yields a more precise AMS measurement. It also provides a higher throughput over the UV oxidation method: 4 samples and 4 processed standards can be prepared and graphitized in one day. An alternative CO<sub>2</sub> extraction method using N<sub>2</sub> sparging is under development as well, which will hopefully get close to 100% extraction of the CO<sub>2</sub> oxidized in the water.

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## UV photochemical extraction of marine dissolved organic carbon for concentration and isotopic measurements at UC Irvine: status, surprises, and recommendations

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The first ultraviolet photochemical oxidation (UVox) extraction method for isolation of marine dissolved organic carbon as CO<sub>2</sub> gas was first established in 1966 [1]. Subsequent, and considerable refinement of the UVox technique has co-evolved with the need for high-precision isotopic ( $\Delta^{14}\text{C}$ ,  $\delta^{13}\text{C}$ ) analysis and smaller sample size requirements for AMS <sup>14</sup>C measurements. The UVox line at UC Irvine was first established in 2004 and the instrument's UVox reaction kinetics and efficiency for isolating DOC as CO<sub>2</sub> gas rigorously tested with the goal of quantitatively isolating 1mgC for AMS <sup>14</sup>C measurements [2]. We have learned much over the past decade and have made considerable improvements to our sampling, storage and UVox methods to increase our overall efficiency [3-5]. Here we present a synthesis of our progress, discussing key parameters to consider when developing a UVox system for optimum precision, accuracy, and efficiency, and common pitfalls to avoid. This presentation will highlight the following key parameters: 1) Ocean to reactor: filtration, storage and transfer of DOC samples, 2) cryogenic trap design, efficiency and quantification of CO<sub>2</sub> breakthrough, 3) lamps, geometry, and parameterizing UVox kinetics and efficiency, and 4) Use of isotopic standards, blanks and small sample graphitization techniques for the correction of DOC concentrations and  $\Delta^{14}\text{C}$  measurements with propagated uncertainties.

New DOC UVox systems are now in use at many institutions and universities. However, without rigorous assessment of quantitative UVox DOC yields and blank contributions, DOC concentrations and carbon isotopic values from different UVox systems may not be comparable. We highlight the need for an inter-comparison study as a community-wide priority.

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## To leach or not? A method study on sample treatment for radiocarbon dating applied during Marine Isotope Stage 3 in the Nordic Seas

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Radiocarbon (<sup>14</sup>C) underpins much of our understanding of marine environmental change over the past 50 ka (thousand years), not only as a chronometer to determine the timing of important climatic events. Due to the radiocarbon decay time the oldest dates that can be reliably measured by this process date to around 50 ka. That implies that analysis towards the limit of the dating method, for example during Marine Isotope Stage 3, becomes more challenging. We present a radiocarbon pre-treatment method study from samples of a marine sediment core MD99-2284 (1500m water depth) located on the northeastern flank of the Faeroe-Shetland Channel (Dokken et al., 2013). A set of 67 radiocarbon dates on planktic foraminifera *Neogloboquadrina pachyderma* (sinistral) and 29 mixed benthic measurements (excluding milliods) have been performed in this time interval throughout Greenland interstadial (GI) 9 till 5 (40.4-32 ka BP).

On a subset of 10 samples and two (radiocarbon-dead) background samples four different ways of treatment were performed in order to evaluate the leach efficiency on the sample material: a) no leach applied, b) weak HCL (0.02M) leach removing 150 µg of foraminiferal material, c) strong HCL (0.06M) leach removing 450 µg of foraminiferal material and d) crushed and applying a clay removal using weak HCL (0.02M) removing 150 µg of foraminiferal material. The leach fractions (where available) were also measured. The results show that leached samples are up to 2300 years older than their non-leached counterparts. Background samples show higher deviations of up to 4200 years age difference between aliquots. In general, over the entire record we find that the majority of samples not treated with a weak HCL leach is appearing “younger” (beyond analytical error and INTCAL 09/13 uncertainty) than the assumed contemporary atmosphere hinting at a modern radiocarbon contamination on the foraminiferal shell material. This biases ages to appear younger than they originally were. Our study highlights that radiocarbon dating on marine sediment core material from the Nordic Seas during MIS 3 should undergo weak acid leach pre-treatment in order to represent reliable results.

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## Earthworm granules, a reliable support for <sup>14</sup>C dating of Dansgaard-Oeschger events in Last glacial loess sequences

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The characterization of Last Glacial millennial-timescale warming phases, known as interstadials or Dansgaard-Oeschger events, requires precise chronologies for the study of paleoclimate records. On the European continent, such chronologies are only available for several Last Glacial pollen and rare speleothem archives principally located in the Mediterranean domain. Farther north, in continental lowlands, numerous high-resolution records of loess and paleosols sequences show a consistent environmental response to stadial-interstadial cycles. However, the limited precision and accuracy of luminescence dating methods commonly used in loess deposits preclude exact correlations of paleosol horizons with Greenland interstadials. To overcome this problem, a radiocarbon dating protocol has been developed to date earthworm calcite granules. Here we present why earthworm granules constitute reliable dating support of loess-derived paleoclimate records and illustrate our approach by applying it on the reference loess sequence of Nußloch (Germany).

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## Validation and application of radiocarbon-based source apportionment of carbonaceous aerosols with the EnCan-total-900 protocol

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Carbonaceous aerosols are important components of fine airborne particulate matter (PM<sub>2.5</sub>), originating from natural and anthropogenic sources and impacting on human health and climate forcing. Thus, characterizing the sources of carbonaceous aerosols is vital for evaluating the effectiveness of mitigation policies.

Carbonaceous in PM ranges from less refractory organic carbon (OC) to highly- refractory elemental carbon (EC, or black carbon). For radiocarbon (<sup>14</sup>C) analysis, protocols must be capable to physically separate OC and EC mass fractions from its complex mixtures, before further processing (e.g. graphitization) and <sup>14</sup>C measurements. Thermal-optical analyses are common procedures used for the physical separation in source apportionment of PM. Since the separation of OC and EC mass fractions is operationally-defined, if OC is inadvertently transferred into the EC fraction, OC can be wrongly interpreted as combustion-related EC.

Here, <sup>14</sup>C measurements of a suit of OC and EC reference materials were used to validate the EnCan-total-900 method [1] for radiocarbon-based source apportionment studies. The EnCan-total-900 method, which was originally developed for carbon isotope analysis of OC and EC, involves three temperature-dependent steps. The first two steps occur under a pure helium condition at 550°C for the detection of OC and at 870°C for the detection of pyrolysis OC (POC) and carbonate carbon (CC). EC is detected at 900°C under helium and 10% oxygen. To investigate the ability of this method on identifying and partitioning OC and EC fractions from individual filters, several aliquots of single and mixed carbonaceous reference materials were produced, and discrete fractions of OC and EC were resolved and measured by <sup>14</sup>C. Once the effectiveness of the EnCan-total-900 method was evaluated and a total blank of approximately  $1.2 \pm 0.6 \mu\text{gC}$  was attained, we had applied the method to aerosols samples collected from Alert, Canada, at a latitude of 82°30'05" north, 817 kilometers (508 mi) from the North Pole. Those results will be briefly discussed here.

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## The influence of calibration curve construction methodology and composition on the accuracy and precision of radiocarbon wiggle-matching of tree-rings.

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The precision associated with <sup>14</sup>C wiggle-matching of tree-rings is impacted by the non-monotonic form of the <sup>14</sup>C calibration curve, the accuracy and precision of component datasets, and the statistical approach to producing the curve.

Assessing the ability of a particular calibration data set to produce accurate calendar information, especially for radiocarbon wiggle-matching, can be a difficult process. The primary focus of this paper is to investigate the factors that can impact upon the accuracy and precision of <sup>14</sup>C date calibration, including wiggle-matching short tree-ring sequences. These factors include accuracy of the unknown-age tree-ring measurements, calibration data set reproducibility, resolution and biases, method of curve construction and calibration curve structure. The current explosion of annual tree-ring AMS calibration data by a few laboratories make a study of this nature urgent.

We present here a new method for curve construction and test the method on extant and new Southern Hemisphere (SH) data sets for the post-LIA interval AD 1500-1950. The new method of construction allows calculation of component data offsets, permitting identification of laboratory and geographic biases. We assess the 5 existing and 6 new SH data sets, examining their dendrochronology, pretreatment and mean offsets. Campbell Island measurements exemplify a <sup>14</sup>C data set with a clear geographic offset, probably due to its high latitude location in the Southern Ocean. Lake Tāy measurements from *Callitris columellaris* trees provide an example of the difficulties associated with pretreating highly resinous species with the possibility of tree-ring <sup>14</sup>C data being influenced by sap translocation across ring boundaries.

Analysis by the new curve fitting regime as applied to the 10 suitable SH <sup>14</sup>C data sets suggests that the total offset ranges for component data sets should be less than ~15-20 yrs, with individual offsets of less than ~10 yrs. Data sets with offset ranges or individual offsets larger than this need to be carefully assessed before selection for calibration purposes.

The new method of curve construction and new SH curve produced similar wiggle-matching results when compared with OxCal using SHCal13, despite some evidence for biased high-resolution measurements in SHCal13. This suggests that high-resolution data sets need to be measured by at least two different laboratories to mitigate the impact of individual laboratory biases distorting the calibration curves.

Simulations using OxCal and the new SH curve suggest that wiggle-matching short sequences (e.g. less than ~60-rings) can produce high levels of precision (e.g. ranges of less than ~10 yrs) in the AD 1650-1850 interval. Earlier and later time periods in the time interval AD 1500-1950 containing <sup>14</sup>C plateaux or repeating structures may produce lower levels of precision, with ranges of 20-30 yrs or more.

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## Are there systematic offsets in the Northern Hemisphere tree-ring calibration data, and if so, what is their impact?

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Northern Hemisphere radiocarbon calibration dataset is essential to using radiocarbon as a chronometer throughout the Holocene. However, already in the early 1990s concerns emerged as to whether there might be systematic offsets between some of the measurements within the IntCal data set (McCormack et al. 1995). This paper revisits these concerns for a range of Holocene contexts. Combination of close visual assessment and the beta-binomial conjugate prior technique highlights a number of periods when systematic offsets between the Irish and German calibration data sets can be observed. Furthermore, in one of these, periods, 900-700 cal BC, the systematic offsets observed between the German and Irish calibration data correspond to a systematic offset observed in Anatolian tree-rings (Manning et al. 2001). This suggests that some of these offsets might represent divergences between atmospheric radiocarbon archives, rather than inter-laboratory differences. While such offsets had little effect when the calibration data sets were first constructed, they might begin introducing systematic error, as precision of measurements on unknown samples improves and large chronological models are constructed.

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## An Audit of Radiocarbon Measurements on Known-age Tree-rings from the Northern Hemisphere (AD 1950 – 5000 BC)

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IntCal13 contains 2951 measurements on known-age tree-rings dating to after 5000 BC. These results come from eight laboratories. Just over half are on decadal samples, with the remainder being on single-year samples (28%), 2- to 9-year blocks (9%) and bidecadal or lower resolution samples (12%).

In preparation for construction of the IntCalNH19 curve, an audit of existing published and unpublished measurements on known-age tree-rings has been undertaken. This has so far identified over 2000 published measurements that are not currently in IntCal, and over 3000 unpublished measurements that could potentially be included in a revised curve. These come from 35 laboratories, 17 of whom have produced more than 100 relevant results. Over 80% of these new measurements are on single-year samples. These new data are not spread evenly across the centuries, however, with more than 80% of measurements (almost 95% of them on single-year samples) dating between AD 1950 and 1000 BC.

Assessing this number of measurements against the published criteria for IntCal (Reimer et al. 2013) is a non-trivial task. It may be possible to construct a high-precision, single-year calibration curve for at least part of this timeframe that will accurately capture fine structure in the atmospheric concentration of radiocarbon that is masked by the coarser resolution of IntCal13. Issues of laboratory accuracy, inter-laboratory bias, and contemporary variations in atmospheric radiocarbon (derived from growing-season, local factors, regional factors, or latitude), however, are all material considerations in the construction of such a curve. We will provide a status report on our investigations into the available data and these issues.

Wednesday 20-Jun-18 - 13:40 - 15:20 - Sansiro 2

## High precision radiocarbon ages in the Younger Dryas

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The onset of the Younger Dryas (YD) is marked by an abrupt cooling in the northern hemisphere around 12 700 cal BP. The cause of the cooling is widely debated, in part due to low resolution, incomplete or insufficiently synchronized paleoclimate, paleoenvironmental and archaeological records. The northern hemisphere YD <sup>14</sup>C record is no exception. The longest absolutely dated tree-ring chronology, the Preboreal Pine Chronology (PPC), extends back to 12 325 cal BP with only 12 decadal radiocarbon measurements between 12 325- 11 900 cal BP. Overlapping floating tree-ring chronologies exist until 14 200 BP with decadal radiocarbon dates spread sporadically through time.

Here we present a new set of high precision annual to quinquennial radiocarbon dates of Swiss and German trees, dendrochronologically linked to the PPC between 12 325 - 11 900 cal BP. We also present annual to biennial <sup>14</sup>C dates for floating chronologies throughout the YD between 12 900 and 12 350 cal. BP. We demonstrate that even the floating chronologies can be calendar dated precisely and reliably when wiggle-matched to high precision southern hemisphere <sup>14</sup>C data from kauri trees. This new northern hemisphere <sup>14</sup>C record with over 1300 <sup>14</sup>C dates improves radiocarbon calibration throughout the YD and highlights significantly more variability in  $\Delta^{14}\text{C}$  than the current northern hemisphere record, thus yielding new insights into solar activity and carbon cycle changes during the YD.

Wednesday 20-Jun-18 - 13:40 - 15:20 - Sansiro 2

## Pushing research boundaries: New technologies to determine isotope ratios of bulk samples and compound specific isotope ratios.

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This presentation will focus on three newly developed instruments that have been developed by Thermo Fisher Scientific as tools to precisely and accurately determine the isotope ratio of a bulk sample and isotope ratios of molecules of different origin.

First presented is data and the technology behind the benchtop Thermo Scientific Delta Ray Isotope Ratio Infrared Spectrometer (IRIS) that enables scientists to determine accurate  $\delta^{13}\text{C}$ . Data will be presented from measurements of carbonate  $\delta^{13}\text{C}$  values in samples containing 200-300  $\mu\text{g}$  NBS 18. Calcite was measured with accuracy better than 0.03‰ VPDB on three instruments.

Second will be discussed the advantages of using temperature ramped gas chromatography to separate gases in EA-IRMS. The Thermo Scientific EA Isolink elemental analyzer isotope ratio mass spectrometer (EA-IRMS) employs a temperature ramped GC column that improves peak separation, peak fidelity, analysis of very small sample amounts and precision of replicate measurements. Data and the technology behind the Thermo Fisher Scientific EA Isolink will be presented.

Finally presented is chromatographic IRMS peripherals that enable scientists to measure compound specific isotope ratios. The GC IsoLink II is a solution that combines the separation capabilities of gas chromatography (GC) with the superior detection power of IRMS.  $\delta^{13}\text{C}$ ,  $\delta^{15}\text{N}$ ,  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  in complex mixtures can be determined on a compound level. The working principle of the GC Isolink II will be presented as well as workflow and data examples. The LC Isolink liquid chromatography IRMS system can be used to determine  $\delta^{13}\text{C}$  in sugars and amino acids without the need for derivatization. The liquid chromatography system can be a high pressure liquid chromatography system (HPLC) or an ion chromatograph (IC). The recent innovations in IC include high pressure systems, 4 micron columns and capillary systems that facilitate the possibility to use the IC to separate samples of complex nature. Working principle and example data will be presented focusing on IC-IRMS.

Thursday 21-Jun-18 - 8:30 - 10:00 - Sansiro 1

## Better understanding of the climatic and environmental factors that affect soil carbon biodegradation and stabilization

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Understanding the dynamics of soil carbon is a major challenge, especially as the IPCC pointed out the large uncertainty on soil carbon stock and its potential impact on future climate change. The increase in soil carbon stock is foreseen as a solution to mitigate global warming but this is relevant only if the storage is perennial. Therefore, <sup>14</sup>C content is used as an indicator of sustainability of soil carbon stock. Our aim in this study is to identify the climatic and environmental factors that affect the most the soil <sup>14</sup>C dynamics, although the many sources of uncertainty blurring the <sup>14</sup>C response. For this purpose, we investigate a statistical model selection procedure.

Our starting point is the Mathieu et al.'s (2015) profile, that describes the <sup>14</sup>C soil dynamics as a parametric function of depth ( $z$ ) and we applied to carbon content and  $F^{14}C$ :

$$C_{org} = H_1 + H_2 \exp(-z/ H_3) + \varepsilon \quad \text{and}$$

$$F^{14}C = \Theta_1 + \Theta_2 \exp(-z/ \Theta_3)\Theta_4 + \varepsilon$$

In this study, the estimation of the latent variables,  $H_i$  and  $\Theta_i$ , is performed using Bayesian inference via MCMC algorithms. This approach has the advantage to take into account parameter uncertainties as well as experimental errors.

To improve the statistical model reliability, we restricted the number of variables within the climatological, soil and environmental available variables. As part of variables are quantitative and part are categorical, we combined two bayesian variable selection procedures: the Stochastic Search Variable Selection (George and McCulloch, 1993) and the Bayesian Effect Fusion (Pauger and Wagner, 2017).

We here present the results of the variable selection applied to both <sup>14</sup>C and carbon content profiles: what are the variables that show the highest probability to impact <sup>14</sup>C or carbon content? are these selected variables in agreement with the conceptual views of soil carbon dynamics? what is the efficiency of the resulting model to mimics both <sup>14</sup>C and carbon content profiles?

Thursday 21-Jun-18 - 8:30 - 10:00 - Sansiro 1

## Annual cosmic ray events shown in carbon-14 data from the BC 10th to AD 14th century

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In recent years, <sup>14</sup>C measurements of annual resolution have been advanced. Annual cosmic ray increase events were found in AD 775 and AD 994 from such <sup>14</sup>C measurements. It is considered that the origin of these events is an extreme SPE (or several extreme SPEs) because of the following reasons: (1) annual increments of <sup>14</sup>C concentration are extremely large, (2) two events are recorded in many tree-ring samples from all over the world, and (3) there are sharp peaks in quasi-annual data of <sup>10</sup>Be concentrations in ice cores from Antarctica and Greenland for the periods around AD 775 and AD 994. Apart from two events, other rapid <sup>14</sup>C increases have been reported in ~660 BC, 3371 BC, and ~5480 BC, whose origins are considered as sudden increases of cosmic-ray intensities.

It is possible that other <sup>14</sup>C increase events exist in the past because of a lack of annual <sup>14</sup>C data for most periods in the past. The purpose of this research is to measure <sup>14</sup>C concentrations with annual resolution over the past long-term, and to clarify when such cosmic-ray events occurred and the occurrence rate of the events.

In order to investigate similar cosmic-ray increase events, we measured <sup>14</sup>C concentrations in annual rings (Japanese trees and North American tree) at biennial interval, for the period from 989 BC to AD 1424. Although <sup>14</sup>C data of this period has been almost continuously obtained, there are decades of deficiency. We obtained continuous <sup>14</sup>C data for most of the past 3000 years if we account for previous studies, finding that the AD 775 event has the largest <sup>14</sup>C increment in the period.



Thursday 21-Jun-18 - 8:30 - 10:00 - Sansiro 1

## High-precision chronologies by <sup>14</sup>C wiggle matching on laminated lake sediments

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Radiocarbon dating is a widely applied technique for the establishment of robust lake sediment chronologies. However, the quality of these chronologies strongly depends on a plethora of important parameters such as the material used for radiocarbon dating, the sampling resolution, the size of the samples or even the choice of the coring site. Only short-lived (e.g. needles, bud scales, periderms, leaves, and seeds), taxonomically identified (e.g. terrestrial plants and invertebrates), and well-preserved remains should be used as sample material in order to avoid reservoir age effects or even uncorrectable biases caused e.g. by charcoal pieces or bulk sediment analyses. Furthermore, the choice of a thoughtful sampling resolution and the application of an appropriate Bayesian deposition model for data evaluation (Bronk Ramsey, 2008) are both crucial. A stringent selection of the dating material and a high sampling resolution often requires the analysis of small remains (<5 mg). Sometimes, the usage of a gas ion source is helpful for samples <0.2 mg (Szidat et al., 2014).

In the current work, we investigated two varved lake sediment sequences from Moossee and Burgäschisee, both located on the Swiss Plateau (Rey et al., 2017) to test the ideal sampling strategy for high-precision dating. Constant-year sampling (e.g. always ca. 10 years within one sample) instead of constant-depth sampling (e.g. every cm) revealed to be important to reduce the age uncertainties (Rey et al., 2018). Radiocarbon dating was performed at the LARA laboratory at the University of Bern (Szidat et al., 2014). The mean  $2\sigma$  age uncertainties were reduced to  $\pm 19$  cal years for Moossee and to  $\pm 54$  cal years for Burgäschisee over the entire period of 3000 years, with  $2\sigma$  uncertainties of only  $\pm 13$  cal years and  $\pm 18$  cal years, respectively, for shorter time intervals (Rey et al., 2018). These results imply that a sophisticated subsampling strategy and a careful selection of short-lived and well-defined terrestrial plant remains are essential for the establishment of high-precision chronologies.

Bronk Ramsey, C. (2008), *Quaternary Science Reviews* 27, 42-60.

Rey, F., et al. (2017), *Vegetation History and Archaeobotany* 26, 571-586.

Rey, F., et al. (2018), *Radiocarbon* 60, in review.

Szidat, S., et al. (2014), *Radiocarbon* 56, 561-566.

Thursday 21-Jun-18 - 10:30 - 12:30 - Sansiro 1

## Radiocarbon as a tracer for past and modern atmospheric oxidizing capacity and global methane budget

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OH is the main tropospheric oxidant and determines the lifetime of methane and most other trace gases in the atmosphere, thereby controlling the amount of greenhouse warming that these gases can produce. Changes in [OH] in response to large changes in reactive trace gas emissions (which may occur in the future) are uncertain. Measurements of <sup>14</sup>C-containing carbon monoxide (<sup>14</sup>CO) over the last  $\approx$  25 years have been successfully used to help monitor changes in average OH concentration ([OH]), but little data exists prior to this time. We will describe a new project which aims to constrain the change in southern hemisphere [OH] since the preindustrial via measurements of <sup>14</sup>CO in ice cores from Law Dome, Antarctica. We will also show new measurements of <sup>14</sup>CO at the Mauna Loa atmospheric observatory, which are part of an effort to resume global <sup>14</sup>CO monitoring.

While <sup>14</sup>CO provides information about the variability of the main sink of atmospheric methane, <sup>14</sup>C of methane itself (<sup>14</sup>CH<sub>4</sub>) can place tight constraints on the magnitude of methane emissions from old carbon reservoirs. New ice core <sup>14</sup>CH<sub>4</sub> measurements from the last deglaciation, early Holocene and the preindustrial all indicate an almost entirely contemporaneous methane source. These measurements show that natural geologic methane emissions are much lower than previously believed, and that old carbon reservoirs such as marine methane hydrates and permafrost did not release a detectable amount of methane into the atmosphere during the global warming of the last deglaciation. This has important implications both for estimating the magnitude of today's anthropogenic emissions of fossil methane and for projecting future methane-climate feedbacks.

Thursday 21-Jun-18 - 10:30 - 12:30 - Sansiro 1

## Will ancient C in deep permafrost deposits be quickly respired upon thaw?

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Deep permafrost deposits that developed in unglaciated areas of the circum-arctic region (northeastern Russia, Arctic and boreal Alaska) during the Pleistocene store a substantial part (>25%) of the perennially frozen C inventory, while covering only a small area (8 %) of the continuous Arctic permafrost zone. These so-called Yedoma deposits are up to 40 m thick and consist of plant remnant, paleosols and ice-wedges. Ongoing global warming will intensify the thawing of these sediments and expose the organic matter (OM) to microbial decomposition, which will ultimately be released to the atmosphere as CO<sub>2</sub> and CH<sub>4</sub>. Predicting decomposition rates and future greenhouse gas emissions is difficult because the degradability of the OM stored in these heterogeneous deposits is highly uncertain. Presently, most information on decomposition rates is based on laboratory incubation experiments that do not consider natural field conditions.

Using a comprehensive set of methods, we evaluated the OM degradability of deep permafrost C by analyzing its composition (lipid biomarker, <sup>14</sup>C of n-alkanes), potential organo-mineral stabilization (<sup>14</sup>C of density fractions), and microbial respiration (CO<sub>2</sub> fluxes and <sup>14</sup>CO<sub>2</sub>) in northeastern Siberia. We found that the OM in the silty-sandy deposits was only slightly degraded before it was freeze-locked for millennia. The <sup>14</sup>C contents of density-fractionated sediments and of plant wax-derived n-alkanes reveal little protection of the OM against degradation by aggregate formation or interaction with the silty mineral material. Thus, deep permafrost OM is supposedly quickly degradable upon thaw. Our analyses of CO<sub>2</sub> flux and their <sup>14</sup>C content on a thawing Yedoma outcrop, however, demonstrate that predicting future CO<sub>2</sub> emission is more complicated and not possible using compositional and flux measurements alone due to the complexity of natural conditions: Upon thaw, the ancient OM may be mixed with overlaying sediments due to thermokarst formation and erosional processes. In addition, new vegetation will start growing on the exposed, bare sediments both introducing younger, more easily degradable organic components, which were found to fuel the degradation of the ancient OM. Using an isotopic mass balance based on <sup>14</sup>CO<sub>2</sub> and bulk sedimentary <sup>14</sup>C data, we calculated that up to 50% of the ancient sedimentary OM may be released, in particular from sediments with OM inputs from fresh roots and their exudates. In summary, our results stress that significant proportions of the ancient OM may be rapidly degraded with ongoing permafrost thaw because of its 'fresh' character and little protection within the mineral matrix.

Thursday 21-Jun-18 - 10:30 - 12:30 - Sansiro 1

## No evidence for 20th century acceleration in mobilization of fossil carbon from thawing permafrost in the Lena River catchment

Gesine Mollenhauer<sup>1</sup>, Maria Winterfeld<sup>1</sup>, Jens Hefter<sup>1</sup>, Hendrik Grotheer<sup>1</sup>, Laura Kattein<sup>1</sup>, Daniela Pittauer<sup>2</sup>

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Release of carbon from thawing permafrost in high northern latitudes is a potential positive feedback in a warming climate, particularly since large quantities of carbon-rich organic matter have been stored in the permafrost soils for many millennia. Thawing of permafrost is expected to make this ancient organic matter bioavailable resulting in increased emissions of greenhouse gases. Thawing of permafrost may also result in increased transport of particulate organic matter through river systems to the ocean, where parts of this organic matter may escape remineralization and will be buried in marine sediments. This process might have accelerated over the past century in a warming Arctic with more frequent thaw slumping and increased river discharge leading to increased mobilization of ancient terrestrial organic matter previously freeze-locked in permafrost.

We therefore studied short sediment cores that were recovered off two of the main branches of the Lena River Delta, receiving the suspended matter transported from the mainly permafrost covered catchment of this great Russian Arctic river. The cores were recovered in 2013 from water depths of approximately 15 m and dated using <sup>210</sup>Pbxs and <sup>137</sup>Cs. The sediment records cover the past 70 to 120 years. By direct combustion of isolated analytes using an elemental analyser (EA) directly coupled to the accelerator mass spectrometer (MICADAS, Ionplus) via a Gas Interface System, we obtained compound-specific radiocarbon ages for a suite of n-alkanoic acids. We studied C16 to C28 even carbon number n-alkanoic acids, a homologous series containing both aquatic (C16 and C18 n-alkanoic acids) and terrigenous (C26 and C28 n-alkanoic acids) biomarkers. Besides, we analysed biomarker concentrations and the geochemical composition of the sediment.

Our results reveal that throughout the records' length, the age at deposition of the terrigenous biomarkers remained constant, while that of the aquatic biomarker decreased in the most recent decades. We will discuss these findings in context of the increases in Lena River discharge observed since the late 1980ies. The results allow estimation of the rapidly cycling biospheric contribution to each biomarker.

Thursday 21-Jun-18 - 10:30 - 12:30 - Sansiro 1

## Carbon sequestration in a re-established wetland

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This study shows how radiocarbon dating can be used to monitor the success of a wetland restoration program and its impact on global climate.

The Danish River Odense Å was channelized in the years 1944-1950 and the surrounding riparian wetlands drained to provide land for agriculture. In 2003, it was brought back to its original meandering course (between Brobyværk and Lyndelse, 4.6 km of straight channel were remeandered to 6 km of natural channel with 16 meander bows) and 125 ha of wetlands were restored. One of the expected benefits of this operation is the increased sequestration of carbon in the sediments accumulating around the river. This would result in reduced CO<sub>2</sub> emissions, thus be an advantage for global climate and reduce Denmark's carbon footprint.

We measured the radiocarbon ages of the bulk organic sediment from different distances to the river and at different depths below surface. Furthermore, we analysed reference samples of surface soil, which had been collected immediately before the start of the restoration project. The radiocarbon ages of sediments accumulating after the restoration are decreasing: The deepest sediment samples, which had accumulated just after the restoration, have the highest ages. Today's surface samples have the youngest ages. This shows that increasing amounts of young carbon are sequestered in the wetland, while the amounts of old, redeposited carbon are decreasing. However, these observations also show that the radiocarbon age of bulk sediment samples does not yield the time of deposition, but rather indicate the source of the carbon.

A complicating factor are reservoir ages of plants contributing to the sediment organic matter. Therefore, we also radiocarbon dated aquatic and terrestrial vegetation. Surprisingly, not only aquatic, but also meadow plants such as soft rush, rough bluegrass and meadowsweet have considerable reservoir effects. CO<sub>2</sub> from decaying vegetation seems to be an important carbon source for some meadow plants, mimicking a canopy effect in the open land.

Thursday 21-Jun-18 - 10:30 - 12:30 - Sansiro 1

## Developing a preconcentration and purification setup for <sup>14</sup>C measurements of atmospheric methane

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Methane contributes substantially to global warming as the second most important anthropogenic greenhouse gas. Its sources are diverse and remain poorly quantified and not well understood [1]. The radiocarbon (<sup>14</sup>C) content of these emissions is of growing interest since it can be used as a tool for a methane source apportionment [2]. Indeed, contemporary methane (e.g. agriculture, biomass burning) contains present-day <sup>14</sup>C levels, whereas fossil methane (e.g. fossil fuels, geologic sources) is <sup>14</sup>C-free. However, this task is challenging given the very large amounts of methane required and its very low concentration in the atmosphere. Methane is usually separated from other trace gases in a stepwise process: first CO<sub>2</sub> is cryogenically removed, then CO is oxidized to CO<sub>2</sub> and also cryogenically removed, before methane can finally be oxidized and isolated as CO<sub>2</sub>. For this simplified process, cross contamination of CO<sub>2</sub> from one fraction to the next remains an issue difficult to overcome [3].

Our research aims at enabling the extraction of pure methane from atmospheric air and performing <sup>14</sup>C measurements with the accelerator mass spectrometer MICADAS in our laboratory [4]. We have developed a methane preconcentration and purification setup (MPPS). Here, we combine a methane preconcentration line with a preparative gas chromatography technique [5] to obtain pure methane samples from the atmosphere.

The MPPS accepts flasks or aluminum bags filled with 50-100 liters of dry atmospheric air, where the whole sample is pumped through a glass and stainless steel line. First, CO<sub>2</sub> is cryogenically removed in a custom-made Russian Doll trap [6]. Then, two successive preconcentration stages [7] enable the removal of most of bulk air before the sample enters the GC column, where methane is chromatographically separated from remaining bulk air and other trace gases and collected in an individual trap. The purity of the methane is verified before it is transferred to a copper oxide oven, where it is converted into CO<sub>2</sub> and finally recovered in a sealed glass ampoule, ready for a <sup>14</sup>C-AMS gas measurement. In this work, we present details of the setup, the evaluation of the methane isolation procedure and first <sup>14</sup>C results of methane extracted from ambient air.

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Thursday 21-Jun-18 - 10:30 - 12:30 - Sansiro 1

## Seasonal changes in the flux and source of CO<sub>2</sub> released during oxidative weathering of sedimentary rocks investigated using stable carbon isotopes and radiocarbon

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The amount of carbon contained in sedimentary rocks is vast compared to that of the atmosphere. These rocks can be exposed to Earth's oxygenated surface and the resulting oxidative weathering leads to a release of carbon dioxide (CO<sub>2</sub>) from the lithosphere to the atmosphere. CO<sub>2</sub> can be released immediately to the atmosphere in the case of i) the oxidation of the rock-derived organic matter, or ii) when one mole of sulfuric acid (produced by the oxidation of sulphide minerals (e.g., pyrite)) reacts with one mole of carbonate minerals. The combined CO<sub>2</sub> flux should impact the CO<sub>2</sub> budget of the atmosphere over centennial to millennial timescales and hence potentially Earth's climate. Despite being an important component of the global carbon cycle, the magnitude of and the biogeochemical processes governing these CO<sub>2</sub> emissions are currently poorly constrained.

Here we monitored bulk CO<sub>2</sub> production during oxidative weathering of sedimentary rocks in the Laval catchment (Draix, Alpes de Haute Provence, France) from December 2016 to May 2018, using 10 newly-designed in situ headspace chambers (Soulet et al., in review). In order to partition the source of the CO<sub>2</sub> emissions between CO<sub>2</sub> derived from dissolution of carbonate minerals and that from the oxidation of the rock organic matter, we sampled the CO<sub>2</sub> using zeolite traps and measured its stable carbon isotope ( $\delta^{13}\text{C}$ ) and radiocarbon ( $F^{14}\text{C}$ ) content. This allowed us to examine possible seasonal changes in both the flux and source of CO<sub>2</sub> released during oxidative weathering of rocks.

Measured bulk CO<sub>2</sub> fluxes ranged widely between ~10 and ~1200 gC.m<sup>-2</sup>.yr<sup>-1</sup> depending on the chambers and seasons. In all of the chambers, we found a ~10-fold increase in the bulk CO<sub>2</sub> emissions from winter months to summer months. Preliminary  $\delta^{13}\text{C}$ - $F^{14}\text{C}$  results suggest that the proportion of CO<sub>2</sub> derived from the dissolution of carbonate minerals is higher (~80%) than that derived from the oxidation of the rock organic matter (~20%), and appears to change over time. These first measurements which show seasonal changes in both the magnitude and source of the CO<sub>2</sub> emissions during weathering will help in understanding the biogeochemical processes underlying oxidative weathering of sedimentary rocks. Temperature and precipitation are likely to govern the reaction kinetics, alongside the role of microbial communities in the oxidative weathering of sedimentary rocks.

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## New annual radiocarbon measurements based on oak from the Danish Dendrochronology

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Since the publication of the 775 AD cosmic-ray event in 2012 there has been an increased focus world-wide on producing annual high precision <sup>14</sup>C measurements. At the Aarhus AMS Centre (AARAMS), a project has been initiated in close collaboration with astronomers and geoscientists to investigate the 11-year solar cycle during low solar activity periods in particular. So far, our focus has been on the Spörer (AD 1450 – 1550) and Oort (AD 1040 – 1080) grand solar minima. We have also, however, investigated the AD 775 and AD 994 cosmic-ray events; the latter at sub-annual resolution by <sup>14</sup>C dating both early and late wood fractions from single years. Additionally, we have produced annual <sup>14</sup>C data covering the periods from AD 650 – 750 and AD 800 – 900. The presented annual records are all made on the late-wood fraction from Danish oak trees only to ensure univocally a single year origin of the carbon. We will discuss the data in relation to published annual data as well as the existing data integrated in IntCal13. We believe that our datasets will provide a valuable contribution for updating the international calibration curve to annual resolution for the last 2000 years. Further, we will report on the laboratory procedures used at AARAMS for producing the annual <sup>14</sup>C data.

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## Two high resolution <sup>14</sup>C tree-ring records of the 4th and 5th century AD: applications for archaeology, astrophysics and dendrochronology

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The wide availability of accelerator mass spectrometry – AMS – as a standard tool for <sup>14</sup>C analysis is opening the way to generate larger numbers of high resolution <sup>14</sup>C tree-ring data. Only small amounts of sample material is needed for AMS compared to the decay-counting technique that has predominantly been used for measuring tree-ring datasets in the past allowing the reconstruction of high resolution tree-ring data.

We present a continuous record of over 100 years of annually resolved <sup>14</sup>C tree-ring data from the 4th and 5th century AD. Using two parallel tree-ring records from the high and mid latitudes we demonstrate the applicability of tree-ring records to reconstruct fluctuations in the atmospheric carbon-production due to the 11-year solar cycle. Using those high frequency fluctuations in tree-ring records may allow the synchronization of tree-ring data. These records also illustrate benefits for radiocarbon dating for archeological samples by improving accuracy and precision of the calibration dataset INTCAL, that is mainly based on radiocarbon data with a 10-year resolution.



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## Is there any evidence for atmospheric <sup>14</sup>C offset within the Northern Hemisphere? Searching for an answer in massive bald cypress deposits in the Southeastern U.S.

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Tree-ring chronologies have long been employed to calibrate radiocarbon dates to calendar years. These chronologies provide the absolute time reference for atmospheric <sup>14</sup>C content during the last 12 ka and led to the identification of the well-known offset in <sup>14</sup>C concentration between the Northern and Southern Hemispheres. Intrahemisphere offsets likely due to growing season differences based on elevation (e.g., between stone pine growing in the Alps at ~2250m asl and the low-altitude German and Irish oak chronology used for INTCAL98 (Dellinger et al. 2004)) and differences between species (e.g., the different growing season of juniper as compared to the INTCAL98 oaks and pines (Kromer et al. 2001)) have also been identified. Currently no tree-ring <sup>14</sup>C data exist for the southeastern United States. We have located a site at the mouth of the Altamaha River in Georgia where ancient remnant trees, mostly bald cypress (*Taxodium distichum*) are regularly recovered. The Altamaha Wildlife Management Area (WMA) comprises a series of islands managed by the state for waterfowl hunting, consisting of large, rectangular ponds, each surrounded by deep canals, with ponds linked by elevated earthen roadways. During maintenance work at the Altamaha WMA, which is largely continuous due to erosion as well as the impact of strong storms, numerous stumps and trunks of trees are hauled up from the canals, which can be up to 30 feet in depth. We have obtained samples from 41 bald cypress trees from the WMA. 52 radiocarbon dates at inner and outer rings of 26 of these trees indicate that the trees at the WMA span a wide temporal range, from a few hundred to about 6 ka <sup>14</sup>C years before present. 70 additional trees at the site were recently located and marked; these trees also will be sampled. We have started to build a ringwidth chronology, connecting our trees to the chronology from the same locale constructed by Stahle (1985), which extends from 929 A.D. to 1985 A.D. We have obtained samples from individual rings from three trees with the goal of determining the best technique for pretreatment. The <sup>14</sup>C ages of these rings are, respectively, 600–800 years, 3500–3650 years, and 4850–5050 years. These samples were treated with traditional ABA treatment and extraction of hemicellulose and  $\alpha$ -cellulose fractions. The results show no significant differences among the pretreatments (<1 sigma), thereby suggesting that ABA pretreatment is sufficient for building a high-resolution <sup>14</sup>C tree-ring chronology based on bald cypress.

We invite all laboratories to participate in the analysis of this unique tree ring collection to find out if there is any regional offset for the southeastern United States.

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## From Decadal to Annual: Examining the Substructure of the Calibration Curve

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There has recently been a resurgence of interest in tree-ring archives as records of the past activity of radiocarbon in the atmosphere. The reasons for this are both technical and theoretical. Investigations have certainly been aided by the fact AMS instruments can now routinely achieve precisions that are comparable with the calibration record itself. However, an equally important factor has been the realisation that annual features in the radiocarbon record can be both distinct and globally synchronous. One growing area of research involves the detection of single-year rises in radiocarbon concentration, or Miyake Events, which are indicative of past solar, and potentially galactic, radiation events. Furthermore, the prospect of tracking such events around the globe may also make this research relevant for atmospheric carbon cycling. Finally, the transition from decadal to annual resolution also presents the tantalising possibility of exact-year radiocarbon dating. As part of the ECHOES project, we are examining the past atmospheric record in order to reveal the relationship between the decadal curve and corresponding annual data, and to uncover any further single-year features that may have astronomical or chronological significance. Here, we discuss a number of new data sets that we have obtained on periods of interest in the late Holocene. On some occasions, it appears as though the decadal record inheres too much structure, and on other it seems as though important annual information is currently being obscured.

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## Structure of carbon-14 excursions in tree-rings at 800BC

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<sup>14</sup>C excursions on a short time scale have been found in Holocene tree-ring records and have generated widespread interest. These excursions at AD 774-775 and AD 993-994 are usually explained as due to extreme solar proton events (SPE) and have been reproduced in as many as 47 different trees and locations (Buentgen et al. 2018). In addition, a larger event has also been reported at 5480 BC (Miyake et al. 2017) as well as another at 660 BC (Park et al. 2017). Other events have been reported such as at 3371-3371BC (Wang et al. 2017). Clearly, other events must exist, but could be the result of diverse processes affecting the cosmic-ray flux including solar events, gamma-ray bursts and geomagnetic phenomena. Dee et al. (2017) searched for supernova effects but this was so far inconclusive. In order to detect other possible events, we have identified periods when the <sup>14</sup>C increase rate is rapid and large in the international radiocarbon calibration (IntCal) data. We identify a new possible excursion starting at ~814BC, which may be connected to the beginning of a solar minimum associated with the beginning of the Hallstatt period (approx. 800-400BC). We compare results of annual <sup>14</sup>C measurements from tree rings of giant sequoia (California) and cedar (Japan) for the period 835-778BC, using the AMS laboratories at Debrecen and Nagoya. We note that the structure of the increase from 814 BC is similar to the increase at 5480 BC, suggesting a related origin. We consider whether there are different kinds of events, which may be observed that are consistent with different types of solar phenomena, geomagnetic events or other explanations. We also highlight the potential importance of these annual data to improve the IntCal international radiocarbon calibration curve.

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## Radiocarbon dating of the oldest living tree in Europe: methodology, results, and opportunities

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We present the combined application of dendrochronology and AMS (Accelerator Mass Spectrometry) radiocarbon analyses for dating extremely old trees. We applied our methods to a living tree named Italus, growing in the Pollino massif in Southern Italy. This Heldreich's pine (*Pinus heldreichii*) has a diameter at breast height of 160 cm and is located on a steep rocky slope with cliff ledges.

A significant limit to dendrochronological dating is that old trees can be hollow. Indeed, our sampled tree lacked the innermost part of the trunk. For this reason, the age (955 CE) obtained by dendrochronology on increment cores extracted from the stem could only be considered a terminus post quem. A first, preliminary estimation of the tree age could be obtained by estimating the missing rings (205-227) from considerations related to average ring width and the distance between the end of the core and the stem centre. In this way an age of 727-749 CE could be presumed.

In order to obtain a more accurate estimation of tree age, a novel approach was developed using AMS radiocarbon analysis of tree rings sequences extracted from exposed roots of the tree. Four root tree-ring sequences were cross-dated between them and allowed to establish a floating chronology of ~320 years.

Radiocarbon ages were then wiggle matched to the INTCAL13 calibration curve and allowed to absolutely date the oldest 10 rings to  $793 \pm 11$  CE. Thanks to the radiocarbon dates, a tree-ring match was then found between the stem and root samples, which placed the first root tree-ring to 789 AD, resulting in an estimated age of the tree of 1229 years in 2017. This age makes Italus the oldest tree living in Europe.

The identification in the root sequences of the 993-994 CE large excursion of the atmospheric radiocarbon concentration allows also to further improve the achievable chronological resolution to the level of a single year.

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## The Application of Sedimentary Geology, Geochemistry, and Geochronology to Interpret Radiocarbon Dates of Quaternary Fossils and Stratigraphic Sequences

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Radiocarbon measurements from fossils recovered in late Quaternary deposits can be useful in attempts to constrain the age of sedimentary sequences and infer landscape evolution processes and biogeographic patterns, if there is an assessment of the sedimentary/taphonomic context and the analytical factors that contribute to the accuracy and precision of age estimates. Fossils in sedimentary contexts where they could be redeposited (and thus older than the deposits) and fossils that directly represent the age of the deposit can be effective stratigraphic controls. In western North America, mammoth fossils recovered from gravels in the Glendive 12-15 m terrace along the Yellowstone River may be older than the gravels, yet a measurement of about 20,500 radiocarbon years before present (RCYBP) can be applied to help constrain the age of overlying silts. These silts have been interpreted as glacial lake deposits formed by blocking of the Yellowstone drainage by the Laurentide Ice Sheet; the radiocarbon measurement provides a maximum age for the overlying sediments and the related ice margin within the Yellowstone valley.

In addition, laboratory chemical pretreatments used to obtain the organic fraction of bone and the methods applied to measure the sample and calculate the precision of the measurement are important factors to consider. For example, a variety of analytical techniques applied to samples from a mammoth from upland silts within the Yellowstone valley resulted in a set of radiocarbon determinations that can be used to constrain the age of the mammoth, and the overlying buried soil. Different pretreatment procedures, ranging from application of HCl and NaOH to ultrafiltration, were used to remove possible exogenic organics, resulting in the isolation of different components of the organic (or total acid insoluble) fraction. In general, two groups can be distinguished by their values and techniques of measurement; younger values consist of radiometric (beta decay) measurements, while most older values are from AMS measurements. The oldest radiocarbon determinations are from bone treated using dilute HCl and dilute NaOH or with HCl, NaOH and ultrafiltration and have a range of about 14,000-15,000 cal BP. An ultrafiltered sample with a value centered on about 14,600 cal BP suggests the mammoth might be associated with the warmer climate of the Bølling interstadial and is several thousand years older than the Younger Dryas.

If the radiocarbon determinations older than 12,000 RCYBP provide accurate estimates, then the most likely range is 14,000-15,000 cal BP. If this is the case, the mammoth is: 1) older than the Younger Dryas and Clovis artifact assemblages and 2) possibly associated with the Bølling climate event (or within the the Oldest Dryas-Bølling-Older Dryas sequence, or early Bølling-Allerød interstadial). In addition, the age of the mammoth implies that the overlying buried soil could have formed as a result of local climate conditions associated with the Younger Dryas. Interpretations of biogeographic and landscape dynamics from vertebrate remains rely on understanding both sedimentological (taphonomic) depositional contexts and the geochemical procedures applied to obtain radiocarbon values that are used to estimate the ages of fossils in stratigraphic sequences.

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## Reconstruction of the karst Quaternary environment in Croatia based on radiocarbon results

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Interdisciplinary multi-proxy study of paleoclimate and paleoenvironment in the Croatian karst region was performed within the project “Reconstruction of the Quaternary environment in Croatia using isotope methods”. Dinaric karst occupies about half of the Croatian territory, encompassing continental and coastal areas and different climate zones, and is characterized by intensive carbonate precipitation in form of tufa, speleothem, lake sediment and algal rims. Various carbonate sediments were studied (speleothems from 3 caves, lake sediments from the Plitvice Lakes, tufa deposits from the Zrmanja River area, marine algal rims from several locations along the eastern Adriatic coast) with the aim of estimation of the regional response of the karst environment to global changes during the Quaternary, and to determine specificities of each carbonate system. A summary of the project results will be presented here.

Radiocarbon dating revealed two groups with the <sup>14</sup>C ages <11,000 BP (all types of sediments) and >30,000 BP (speleothem and tufa). The speleothem and tufa samples from the latter group were dated by the U-Th series method up to MIS 10 and MIS 5 stages, respectively. The Holocene ages ranged from about 11,000 BP (speleothems) to the Anthropocene (top lake sediments). The response of carbon isotope composition of lake sediments to the global <sup>14</sup>C variation was observed by a<sup>14</sup>C peaks in both organic matter and carbonates. Variations in composition of sediments from shallow, coastal lake areas enabled identification of extreme hydrological events.

Monitoring of modern environmental settings in three caves revealed variable atmospheric influences and specific hydrological behaviour of each drip site. However, homogenized stable isotope composition of drip water and stable cave environmental settings give confidence for calcite deposition under isotope equilibrium conditions enabling retrieval of paleoclimate and paleoenvironmental information.

Algal rims (*Lithophyllum byssoides*) are good and precise sea-level indicators and their morphology, age and stable isotope composition could be linked to climate changes. Two main goals of algal rims study were to determine the marine reservoir effect essential for accurate calculation of the algal rim <sup>14</sup>C ages, and to reconstruct relative sea-level changes along the eastern Adriatic coast beginning at 5th century. Similarly, study of freshwater reservoir effect along the Zrmanja and Krupa rivers included water chemistry analyses and isotope analyses of DIC and active freshwater carbonates.

Mosses are important fragments in the karst environment and they play an active role in tufa formation. Submerged mosses use carbon from two sources: atmospheric CO<sub>2</sub> and dissolved inorganic carbon (DIC). It was found that certain species of mosses incorporate carbon only from dissolved inorganic carbon (DIC), while certain aquatic moss species show higher <sup>13</sup>C fractionation if the share of atmospheric CO<sub>2</sub> is higher or if the flow velocity is higher. Understanding the source partition can help understanding formation of secondary carbonates that constitute tufa barriers.

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## From Fractions to Fluxes: The International Soil Radiocarbon Database (ISRaD)

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**Introduction:** The response of the terrestrial carbon sink to anthropogenic perturbation of the global carbon cycle and associated climate change is highly uncertain. Radiocarbon observations of soils are a powerful tool for resolving this uncertainty and improving our understanding of the rates and drivers of soil organic carbon (SOC) stock change. Building on previous efforts to synthesize the available soil radiocarbon data into a single global database, the International Soil Radiocarbon Database (ISRaD) will provide both a benchmark for tracking ongoing SOC stock changes as well as a means of testing hypotheses for what controls these rates of change.

**Methods:** ISRaD is specifically designed to accommodate a wide range of soil radiocarbon data including bulk soil layers, soil fractions, profile fluxes, interstitial measurements, and laboratory incubations, as well as associated data to aid in interpretation, i.e. concentrations, stocks, and flux rates of C and other nutrients, soil properties, and other climatic and ecological data. ISRaD is open source, allowing for community contribution and facilitating easy access to data while enabling the flexibility to accommodate new data types and future growth. Data in ISRaD will be annually ingested into the International Soil Carbon Network (ISCN) database to leverage the strengths of both databases and to avoid redundancy. ISRaD consists of two parts: the database itself, and an integrated R package consisting of tools for data ingestion and quality control, querying, and generating reports. Data in ISRaD is structured as a list of entries, with each entry defined as a published study with a unique DOI. Each entry is itself a list of hierarchically linked data tables corresponding to different measurement dimensions, e.g. metadata (source citation), site (geographic coordinates), layer (bulk soil data), etc. Controlled vocabulary is implemented for key data fields to standardize units and streamline analysis. Documentation and an entry template (Excel workbook) are available at ISRaD's website: (<https://github.com/powellcenter-soilcarbon/soilcarbon>).

**Results and Discussion:** While we are actively seeking more data, ISRaD already contains data from > 300 studies, >600 sites, and > 4000 radiocarbon measurements. The wealth of data in ISRaD has the potential to provide powerful constraints for improving both the mechanistic understanding of SOC dynamics and the performance of global carbon models.

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## Preparation of bulk mortar samples and lime lumps for radiocarbon dating. Sequential dissolution of fine-grained material with phosphoric acid

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Reliable radiocarbon dating of lime mortars requires careful and selective sample preparation procedures. Since the sixties several different protocols have been developed, some relying on good mechanical separation of the carbonates carrying the relevant <sup>14</sup>C signal and others on different dissolution procedures with hydrochloric (HCl) and phosphoric (H<sub>3</sub>PO<sub>4</sub>) acid. As long as radiometric methods were used in radiocarbon dating HCl was used to dissolve the mortar samples. Our research group shifted to AMS dating already in the early 90's and developed preparation procedures based on existing H<sub>3</sub>PO<sub>4</sub> hydrolysis routines for analyzing stable carbon and oxygen isotopes in geological carbonate. Only later did we realise that H<sub>3</sub>PO<sub>4</sub> is actually more selective when dissolving different carbonates and we started exploring the possibility to identify contaminating carbonates based on dissolution rate and carbon isotope signature. Dating several CO<sub>2</sub> fractions extracted during phosphoric acid hydrolysis of well-defined grain size components of mortar yield information about the age of the main binder calcite component as well as the presence of contaminating components, their abundance, dissolution rate and carbon isotopes. Different <sup>14</sup>C profiles reflecting several types of contaminants will be discussed and theoretical models of how to interpret them are presented. The most common contaminant, underburned limestone is discussed with an example from lime burned in 2016, and a case study showing the effect of sampling depth is presented.



Thursday 21-Jun-18 - 13:40 - 15:20 - Sansiro 1

## Lead white preparation for dating painting

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Lead white is one of the major coloring material since the 7th century BC. It was widely used as a medical treatment (unguents, cosmetics) during the Antiquity and the Modern Time, and as a pigment in European paintings until chemists try to replace it in the 19th century because of its poisonous lead content. [1] This pigment is composed of two lead carbonates, cerussite  $\text{PbCO}_3$  and hydrocerussite  $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$ . [2]

Unlike most ancient pigments, lead white is obtained by a synthetic route. The process of elaboration is described by several authors from different times as, for example, Pline (1st century BC), Theophrastus (300 years BC), Isidore da Sevilla (6th-7th century) or Gabriel Jars (18th century). The method relies on the corrosion of metallic lead in presence of vapor of acetic acid (vinegar) in a fermentation environment, like manure which produces heat and  $\text{CO}_2$ . These conditions allow the formation of lead carbonates. As lead white is formed by trapping  $\text{CO}_2$  from organic origin, the radiocarbon dating of the pigment can be considered. In order to validate this approach, we have tested various protocols of preparation.

First of all, the presentation will deal with the preparation of pure lead white samples - previously characterized by XRD - using two methods: acid hydrolysis of carbonates and thermal decomposition. Then, the preparation of mixtures of lead white with other paint components (oil as binder, calcite as filler) will be discussed. In particular, we will focus on the selective separation of lead and calcium carbonates. Last, historical lead white samples coming from wall paintings were dated using the LMC14-ARTEMIS facility. [3,4]

[1] M. Stols-Witlox, The National Gallery Technical Bulletin 30th Anniversary Conference Postprints, Studying Old Master Paintings - Technology and Practice, 284. Londres, Archetype Editions, 2011

[2] V. Gonzalez et al., Anal. Chem., 2017, DOI: 10.1021/acs.analchem.6b04195

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[4] C. Moreau et al., Radiocarbon 55(2-3), 331, 2013.

Thursday 21-Jun-18 - 13:40 - 15:20 - Sansiro 2

## A calibration curve based on annual samples, applied to radiocarbon dates from the oldest town in Scandinavia

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We are currently performing high-precision radiocarbon dating of annual tree ring samples to construct a new calibration curve for the period AD 650-900. We will present preliminary results from the intervals AD 650-750 and AD 800-900. The period AD 750-800 is covered by the poster by Fogtmann-Schulz et al. (session A6).

The new calibration curve will be used for high-precision dating of the stratigraphy of Ribe, the oldest town in Scandinavia and an important site for the chronology of the Viking age. Many Viking Age artefact types are dated based on their stratigraphical position in the Ribe sequence. The older layers, containing preserved timber, are well-dated by dendrochronology. However, not all of the phases in Ribe have been dated by absolute dating methods yet. The latest dendro-date is AD 741, but activities at the site continue more than 100 years after that date. The calendar ages of some important typological reference points for Viking Age chronology are thus only estimated by relative methods, e.g., the duration of phases derived from the thickness of the layers. Therefore, a precise radiocarbon chronology of the entire occupation history of Ribe has the potential to consolidate or shift the dating of important artefact types. Our measurements could thus have an impact on Viking Age chronology in general. As Ribe was embedded in global networks of transcontinental trade, reflected by finds such as Early Islamic trade commodities, our results have the potential to resonate in the wider research field of urban networks.

We are developing an age model for the Viking Age activities at Ribe based on the ongoing excavations by the Northern Emporium project. We will present the first radiocarbon dates from Ribe and will illustrate the effect of using different calibration curves based on decadal or annual samples.

Thursday 21-Jun-18 - 13:40 - 15:20 - Sansiro 2

## The 1952-1965 rise in atmospheric bomb <sup>14</sup>C in a Trondheim tree

Helene Løvstrand Svarva<sup>1</sup>, John Haarsaker<sup>1</sup>, Sylvie LÉlu<sup>1</sup>, Marie-Josée Nadeau<sup>1</sup>, Martin Seiler<sup>1</sup>, Sølvi Stene<sup>1</sup>, Terje Thun<sup>1</sup>, Einar Værnes<sup>1</sup>, Pieter M. Grootes<sup>1</sup>

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Direct atmospheric measurements of the <sup>14</sup>C concentration of atmospheric CO<sub>2</sub> started on a regular basis in 1959, after the first series of atmospheric nuclear weapons tests had already raised atmospheric <sup>14</sup>C levels significantly. These measurements reveal a clear seasonal cycle in <sup>14</sup>CO<sub>2</sub> concentrations, superimposed on the general rise, with an increase in spring and summer, when stratospheric air mixes with the troposphere at mid latitudes, and a decrease in fall and winter. The mixing period coincides roughly with the growth period of tree rings at mid latitude.

The early part of the atmospheric bomb curve is based largely on single year tree rings as a proxy for atmospheric CO<sub>2</sub>. Cellulose <sup>14</sup>C concentrations of a full ring, however, represent growth-weighted averages for the atmosphere in spring-summer. Detailed sub sampling of single tree rings over the 1963 bomb peak have shown that the <sup>14</sup>C concentration of cellulose within a single ring closely follows atmospheric <sup>14</sup>C concentrations.

We present <sup>14</sup>C measurements for the years 1952-1965, obtained from a Scots pine tree (*Pinus sylvestris* L.) growing near Trondheim in central Norway. The results at biweekly to monthly resolution show the early increase in bomb <sup>14</sup>C in the Trondheim area. Atmospheric measurements from Trondheim and sub-annual tree-ring sampling from the US Pacific Coast are available for the 1960s and will be compared to the later part of the new data.

Thursday 21-Jun-18 - 13:40 - 15:20 - Sansiro 2

## Olive wood research at the D-REAMS Laboratory: verified annual signal, circumference sectors growth, and cross-section complexity

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The olive tree (*Olea europaea*) is known to be in the 'blacklist' of the dendrochronological community. Ring boundary identification is highly problematic due to intra-annual wood density fluctuations, and growth by sectors of the cambium along the circumference can cause differences in the actual number of rings in various radii.

Here we present the use of the 'bomb peak' for a novel integration of  $\delta^{13}\text{C}$  measurements and radiocarbon dating, to identify, for the first time, a proven annual signal in modern olive wood. Comparing these results with a computed tomography (CT) scan of a parallel radial section indicated that CT might not be sufficient for assessing the total number of rings in olive wood. This was tested with fresh and charred samples, in order to be applicable in archaeology. Furthermore, we have quantified (using radiocarbon determinations) the different growth by sectors along the circumference in two olive trees and found it to be up to several decades. Lastly, we demonstrate the difficulties of dating an olive tree by 'coring and extrapolating' using a test case of dating a full section of the trunk.

Our results have implications for former and future chronological questions, being answered using olive wood samples, and open possibilities for future dendrochronological and climatological research using olive wood.

Thursday 21-Jun-18 - 13:40 - 15:20 - Sansiro 2

## Study on radiocarbon Dating of Chinese Ancient Tea Trees

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Deep in the heart of Southern west in Guangxi Zhuang Autonomous Region of China, there exist tea trees unlike any other on Earth. The jungles of Linyun and Longlin Autonomous Prefecture are home to the oldest tea trees in the world. In these regions grow tea trees that range in age from several centuries to over a millennium, and the ages of subtropical tea trees provide critical information for understanding the dynamics of tea tree populations, determining historical patterns of disturbance, developing sustainable forestry practices and calculating carbon cycling rates. Nevertheless, the ecological life history of most wild tea trees is unknown and even the ages of the Ancient tea trees remain to be determined. Tree ages are typically measured by counting annual rings, but for most of tea tree's rings can be non-existent, annual or irregular due to the very low growth rates. In the absence of annual rings, radiocarbon is the only and a powerful tool that can potentially help the determination of ages and growth rates of these plants. In this work, cores were extracted from 12 large, ancient tea trees from a central Longlin rain forest, and were performed with an automated sample preparation system. The <sup>14</sup>C levels in the tree cores were measured using accelerator mass spectrometry (AMS) jointly by Guangxi Normal University and University of Tsukuba, and find that, contrary to conventional views, ages of trees in these forests rang from 500 to more than 1000 years. It was demonstrate that <sup>14</sup>C analyses provide accurate determination of ages and growth rates for subtropical wild tea trees. Furthermore, the application of <sup>14</sup>C analyses in tea trees allows the determination of the camellia sinensis stage, rarely quantified in forest inventories and life-history studies.

Thursday 21-Jun-18 - 13:40 - 15:20 - Sansiro 2

## Main results of thirteen years of radiocarbon investigation of large and old African baobab trees

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In 2005, we started an in-depth research project to elucidate several controversial aspects concerning the architecture, growth and age of the African baobab (*Adansonia digitata*). This research is based on our new approach which enables the investigation of standing live specimens. Our approach consists of AMS radiocarbon dating of small wood samples collected especially from inner cavities, but also from deep incisions/entrances in the stems, fractured/broken stems and from the outer part/exterior of large baobabs.

The obtained results were unexpected and surprising, showing that the African baobab has several unique features. Here we disclose the main findings of our research.

Radiocarbon results demonstrate that big baobabs are always multi-stemmed, having up to 18 stems. This is a consequence of the baobabs' ability to generate new stems periodically, such as other tree species produce branches. Hence, baobabs develop over time architectures of increasing complexity. Therefore, we focused on the investigation of very large and potentially old specimens.

We identified the open and closed ring-shaped structures, which are the most significant architectures that enable African baobabs to reach old ages and large sizes. According to dating results, open and closed ring-shaped structures form progressively and close over time, as they usually consist of 3-8 stems belonging to several generations.

Many old baobabs have large hollow parts in the central area of their trunk/stems. In most cases we found that the age sequence of samples extracted from the cavity shows a continuous increase from the cavity walls up to a certain distance into the wood, after which it decreases toward the outer part. The only reasonable explanation for this age anomaly is that such cavities are in fact false cavities, i.e., natural empty spaces between fused stems disposed in a closed ring-shaped structure. The oldest part of the fused stems is located between the false cavity walls and the outer part/exterior of each stem.

For certain baobabs the outermost rings were found to have ages of several hundreds of years, instead of being very young. Such results show that baobab stems can stop growing due especially to old age or stress factors.

Radiocarbon results indicate that several reported stems, which are triangular in horizontal section, are in fact false stems which act as an anchor. The oldest age can be found toward the upper contact with the larger adjacent stem, while the age decreases toward the opposite sharp extremity.

In several cases, we found an anomalous ring frequency. For these cases, the number of rings between two dated segments of a sample was found to be significantly lower or significantly higher than the calendar age determined by radiocarbon dating. The oldest dated sample had a radiocarbon date of  $2429 \pm 14$  BP. By this value, the African baobab becomes the angiosperm with the longest life span.

The AMS radiocarbon investigations were performed at the NOSAMS Facility of the Woods Hole Oceanographic Institution.

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Friday 22-Jun-18 - 9:20 - 10:20 - Sansiro 1

## The half-life of $^{14}\text{C}$ - why is it so long?

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The half-life of  $^{14}\text{C}$  is  $5700 \pm 30$  years, which makes it particularly useful for dating in archaeology. It is well known that the exact value of the half-life is not important for  $^{14}\text{C}$  dating, because absolute ages are determined with the help of the  $^{14}\text{C}$  calibration curve. However, the order of magnitude value of the half-life of  $^{14}\text{C}$  is of considerable interest from a nuclear physics point of view. The current presentation will discuss the physics behind this unusually hindered  $\beta$ -decay from  $^{14}\text{C}$  to  $^{14}\text{N}$ . With normal transition strength, the half-life would be in the order of days, completely useless for archaeological dating.

The ground state of  $^{14}\text{C}$  has nuclear spin  $0+$ , and the beta decay leads to the ground state of  $^{14}\text{N}$ , which has spin  $1+$ . This is a so called Gamow-Teller transition [1] and the half-life is determined by both the decay energy and the nuclear transition strength. The latter is usually expressed by a quantity called Log ft. A convenient way to relate the decay energy, half-life and Log ft values is given by Moszkowski [2]. A review of beta-decay transitions strengths across all nuclei lists 714 Gamow-Teller transitions [3]. Out of these, the  $^{14}\text{C}$  beta decay is the most hindered transition expressed by the largest Log ft value (9.03). Compared to neighboring nuclei with normal Gamow-Teller strength (Log ft  $\sim 4$ ), this slows down the half-life by 5 orders of magnitude [2]. The reason for the exceptional hindrance of the  $^{14}\text{C}$  decay lies in the detailed structure of the nuclear states connecting  $^{14}\text{C}$  with  $^{14}\text{N}$ . There has been considerable theoretical effort [4-6] to create states which allows one to reproduce the experimental half-life. It appears that this is only possible if so called three-body interactions between the nucleons in the  $^{14}\text{C}$  and  $^{14}\text{N}$  nuclei are taken into account [6]. Once the correct wave functions of the two nuclear states were established, it has been shown [6] that large cancellations in the transition matrix elements lead to the strong hindrance.

An attempt will be made to describe the physics behind this problem, with the intent to make it understandable also to the wider  $^{14}\text{C}$  community. In any case, the long half-life of  $^{14}\text{C}$  is an extraordinary gift of Nature.

[1] G. Gamow, E. Teller, Selection Rules for the  $\beta$ -Disintegration, Phys. Rev. 49, 895 (1936).

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Friday 22-Jun-18 - 9:20 - 10:20 - Sansiro 1

## Annually resolved atmospheric radiocarbon concentrations for the last 1000 years reconstructed from tree-ring records

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The present radiocarbon (<sup>14</sup>C) calibration curve (IntCal13) is primarily based on tree ring data measured by decay counting with a temporal resolution of 10 years over the Holocene. Only during the period from 1510 to 1950 CE are measurements at annual resolution included (Stuiver 1993). Here, we will present a new, annually resolved <sup>14</sup>C record on European oak covering the last 1000 years. The already existing, annually resolved record was re-measured using accelerator mass spectrometry (Wacker 2010) and extended by more than 500 years, with the advantage of using 1000 times less material.

The new record clearly shows more fine structure compared to the present calibration curve and will thus allow for a new more precise IntCal calibration curve with higher temporal resolution over the past 1000 yr. The high frequency fine structure in the new atmospheric <sup>14</sup>C record also allows for high-precision wiggle-matching of undated tree-ring records or precise synchronisation with other archives such as polar ice core records by comparing <sup>14</sup>C with other cosmogenic radioisotopes such as <sup>10</sup>Be (Sigl 2015, Adolphi and Muscheler 2016).

Stuiver, M. & Braziunas, T. F. (1993), *Holocene* 3: 289-305

Wacker L. et al. (2010), *Radiocarbon* 52(2): 252-62.

Sigl, M. et al. (2015) *Nature* 523: 543.

Adolphi, F. and R. Muscheler (2016) *Clim Past*, 12 (1): 15-30

Friday 22-Jun-18 - 10:50 - 12:30 - Sansiro 1

## Selective dating of paint components: <sup>14</sup>C dating of lead white

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Artists' oil paints are rich in carbon-based material, ranging from the support material to the organic binder, pigments and additives. Commonly radiocarbon (<sup>14</sup>C) analyses are restricted to the support material, which in the case of easel paintings is textile fibers from the canvas, where sufficient material can be sampled. However, these <sup>14</sup>C results alone can be misleading, as a support may be older than the actual painting in cases of a reused old canvas by artists themselves or by forgers. Recent technological advances have significantly reduced the minimum sample size requirements, which now opens up the possibility of identifying new candidates datable by <sup>14</sup>C within the artwork.

In the case of natural drying oils, the <sup>14</sup>C clock will initiate with the harvest of the seeds that were used to extract the oil. In a prior study, the dating of the organic binder was targeted, as this one has a high probability of being representative of the time of creation of the paint (Hendriks et al. 2018). Therein sampling locations were defined as paint areas containing no other carbon sources than the natural organic binder, i.e. inorganic pigments are paint samples of choice.

However, exceptions are carbonates, such as lead white, a man-made white pigment in use since the Antiquity. Indeed in the presence of a carbonate pigment, mixed results could arise depending on the relative contributions of the organic binder and the carbon derived from the carbonate anions. The work presented herein introduces the possibility of using <sup>14</sup>C analysis for the dating of the lead white pigment. Due to many different recipes of production, the sources of CO<sub>2</sub> have evolved and the respective <sup>14</sup>C signature can be identified. For this study lead white samples were supplied by the MOLART and HART projects, which provided well dated lead white pigments and paint reconstructions. <sup>14</sup>C ages of lead white pigments produced following the traditional stack process, where the carbonate group results from the incorporation of CO<sub>2</sub> originating from fermentation, matched the production years. <sup>14</sup>C dating of lead white pigments made using other industrial processes indicates that <sup>14</sup>C depleted CO<sub>2</sub> was used in their production and hence this signal can be used as a marker to discriminate lead white produced with alternative industrial methods from the traditional stack process.

The method was applied to two case studies, where lead carbonate samples were dated in two oil paintings, one baroque and one from the 20th century. We hereby show that the lead white pigment can be dated by <sup>14</sup>C and used as a proxy for the time of creation of an artwork. This study thus proposes new strategies for <sup>14</sup>C dating of artworks.

Hendriks et al. 2018 Combined <sup>14</sup>C Analysis of Canvas and Organic Binder for Dating a Painting. Radiocarbon, 60(1), 207-218. doi:10.1017/RDC.2017.107



Friday 22-Jun-18 - 10:50 - 12:30 - Sansiro 1

## Radiocarbon dating of paintings attributed to T'ang Haywen (1927-1991)

Irka Hajdas<sup>1</sup>, Philippe Koutouzis<sup>2</sup>, Laura Hendriks<sup>1</sup>, Mantana Maurer<sup>1</sup>, Maria Bellen Röttig<sup>1</sup>

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Radiocarbon dating is an ideal tool for dating art objects such as paintings, which are typically made of carbon-bearing material. Research is advancing to minimize the sample size as well as extend the application to dating binding media (Hendriks et al., 2016, Hendriks et al., 2017). A very specific application of <sup>14</sup>C dating uses the feature of the 'bomb peak'. This can be applied to detect forgeries created during the last 60 years. Here we present the results of <sup>14</sup>C analysis on authentic and suspected paintings by Chinese painter T'ang Haywen (1927-1991).

The support of the studied paintings is a cotton paper (Arches) that is an ideal material for the <sup>14</sup>C analysis because it is produced from short-lived organic matter. The application of the 'bomb peak' to the paintings of T'ang Haywen requires combining his biographic and art historical information with results of the <sup>14</sup>C analysis. Due to the feature of the 'bomb peak' interpretations of results must be strengthened by the additional information.

We designed the experiment 2 fold: first, we analyzed the authentic works. In the next step, we sampled the suspected works. The signal of <sup>14</sup>C concentration in the Arches paper confirms that the suspected works were produced after the year 2008, i.e. more than 17 years after the death of the artist. In this study, we combine results of the <sup>14</sup>C analysis and the additional information about the art produced (for example the artistic development of the artists, their changes in style and material use), which is of great help in the interpretation of the data. This information combined with the provenances of the objects has a potential of exposing the forgeries.

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Hendriks, L., Hajdas, I., Ferreira, E.S., Scherrer, N.C., Zumbühl, S., Küffner, M., Wacker, L., Synal, H.-A., Günther, D., 2018. Combined <sup>14</sup>C Analysis of Canvas and Organic Binder for Dating a Painting. *Radiocarbon* 60, 207-218.

Friday 22-Jun-18 - 10:50 - 12:30 - Sansiro 1

## Studying human kidney stones using the radiocarbon bomb pulse

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The use of the radiocarbon bomb pulse for biomedical studies of human samples has a long history at ANSTO with samples ranging from DNA in human cortical neurons to lipids in eye lens cell membranes. In 2015 a pilot study of a small human kidney stone was performed which demonstrated the feasibility of the method for such an object (Levchenko and Williams, 2016). About 2% of dead carbon presence was detected in the stone material and had to be corrected for. The most probable source of the dead carbon was from the modern industrialised diet.

Results attracted interest from the medical research community, and later in collaboration with clinical specialists we have applied the method to two stones from patients with different lifestyles. Prior to radiocarbon studies the stones were also characterised by a number of physical methods including X-ray CT scans, PIXE, SEM, etc. Growth histories of two similar sized stones were found to be very different, ranging from 23 to 7 years. Comparison with clinical records provided information to better understand the triggering of the disease. Again presence of dead carbon of about 1.5% has been noted and was corrected for. The project has been expanded to more kidney stone samples, including different stones from the same patient, which after the analysis demonstrated different starting times. In parallel with radiocarbon AMS determinations the stones were again analysed by a number of physical techniques including X-ray micro CT scans, neutron diffraction, etc. Results and future studies are discussed.

### References

Levchenko, V.A., Williams, A.A. (2016) Time History of a Human Kidney Stone Determined by Bomb-Pulse Dating. *Radiocarbon* 58(2):437-441

Friday 22-Jun-18 - 10:50 - 12:30 - Sansiro 1

## Turn over rate in human bone and tissue: a “live” study”

Pieter M. Grootes<sup>1</sup>, Marie-Josée Nadeau<sup>1</sup>, Einar Værnes<sup>1</sup>, Martin Seiler<sup>1</sup>

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Bones and tissue provide information on the animal or person they were once part of. They regenerate, however, at different rates. This makes determining the year of death of an individual who died recently somewhat difficult, considering that bone collagen can have a turnover time of 15-20 years in a human adult. They also reflect dietary habits and contemporaneous environmental conditions in the relative abundance of the stable isotopes of carbon, nitrogen, and oxygen they contain.

We report a study of the <sup>14</sup>C, <sup>13</sup>C, and <sup>15</sup>N concentrations of different bone and tissue fractions obtained in 2017 from a healthy Caucasian male born in 1944. This period includes the rise in atmospheric <sup>14</sup>C, due to atmospheric nuclear weapons tests up to 1963, and its subsequent decrease. The large atmospheric <sup>14</sup>C changes provide a unique opportunity to estimate the turnover rates of the different tissues and their components (e.g collagen, fat, or bio-apatite). The samples studied include healthy and damaged/eroded bone, bone marrow, and periosteum. The different fractions from internal tissues are also compared to the isotopic composition of shorter turnover samples such as nail and hair. We will discuss the implications of the differences in <sup>14</sup>C concentration in tissue and bone fractions for their carbon turnover, dating, and link with dietary intake

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## Identifying fraud in the EU worked-ivory antiques trade

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In the decade to 2015 the population of the African elephant (*Loxodonta africana*) declined by 18% to 415,000 individuals. This decline was primarily due to poaching of elephants for ivory, which is in part driven by demand for worked-ivory objects.

International trade in ivory is governed by the CITES treaty which is implemented by signatories through regional and domestic legislation. The regional legislation controlling intra-EU trade allows for trade in antique worked-ivory objects which were significantly altered from their natural or raw state prior to 3rd March 1947. Currently, post-1947 ivory can be laundered through the EU by being fraudulently sold as antique ivory before re-export to other markets.

The proximity of the 1947 deadline to the radiocarbon bomb spike makes radiocarbon dating a useful technique for identifying post-1947 worked-ivory.

To investigate the extent of fraud within the EU worked-ivory antiques market, here we present radiocarbon ages of 109 worked-ivory objects, obtained from 9 EU countries, which were sold as antiques between October 2017 and March 2018.

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## Calibrating and summarising multiple radiocarbon determinations: A rigorous alternative to summed probability density functions

Tim Heaton<sup>1</sup>

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Suppose that we have a set of radiocarbon determinations from a particular site/sites each with an unknown calendar age. We would like to summarise the calendar age information provided by the set of objects and provide a predictive distribution/density estimate for the calendar age of a future hypothetical object.

If we are willing to assume a simple and specific form for the calendar age density (e.g. uniform, normal, trapezoidal) we can employ standard Bayesian methodology to estimate the few parameters which specify the distribution entirely e.g. the start/end of the uniform distribution. In many cases however, it is not possible/desirable to specify the form of the calendar age density in such a rigid way in advance. Instead we may like to let the data itself inform us as to the shape of the density or the number of distinct periods of activity – to provide a non-parametric density estimate.

The traditional approach to providing such a non-parametric summary is via summed probability distributions (SPDs), a hybrid Bayesian/frequentist technique where each sampled object has its radiocarbon determination individually calibrated and the resulting individual age estimates are summed together. However, SPDs neither provide a statistically valid way to estimate the predictive calendar age density nor likely the most accurate estimate of the age of any of the individual objects sampled.

Firstly, SPDs assume that none of the objects provide information on the age of any other – instead we want to combine information provided by all the objects jointly. It is well known that dates with errors appear more spread than they really are. Rather than calibrating determinations independently better estimation can be achieved by sharing information between objects and “shrinking” the dates towards one another.

Secondly, a proper predictive density estimation needs to consider the observed objects (and their calendar ages) as a small sample drawn randomly from a much wider population of objects (and calendar ages). We then learn, from the observed objects, about the age of a new future object. Instead, by summing the individual densities in SPDs, we are implicitly assuming our sample contains all possible objects we could ever find. All we are estimating is the age if we were to resample an object at random from those we already had i.e. there is no hypothetical future observation.

We present a rigorous method that aims to overcome both these weaknesses: providing both improved dating of the sample objects; and a statistically valid predictive density estimate for a new object. We employ a Bayesian non-parametric approach where the sample objects are assumed to arise from an unknown number of clusters - the number and shape of which we adaptively estimate within the methodology. Calendar ages of the objects are estimated jointly at each step recognising they also arise from the density of interest hence aiming to improving their estimation too. Furthermore, the estimated number of distinct clusters may also provide valuable information on the number of distinct periods of archaeological activity.

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## Exploring the rhythms of occurrences of archaeological events in different geographic areas

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Bayesian models allow to incorporate both relative and absolute chronological information from archaeological or paleoenvironmental projects. The so-called prior distribution of the parameters of interest, that represents expert opinion or prior knowledge, may include, for instance, stratigraphic information, temporal order information. Thus it helps increase the estimation of the parameters. To that aim, several adapted softwares are freely available such as BCal, OxCal or ChronoModel.

In this work we present statistical methods to study the rhythm of occurrences of archaeological events according to measurements. These tools are constructed on the posterior distribution of the dates coming from the Bayesian modelling of a chronology.

The Tempo plot, initially introduced by T. S. Dye (2016) and formalised by Philippe and Vibet (2018a) represents the rate of change in the occurrence of events. It is an estimated counting process in the sense that it estimates the number of events at a fixed date with a credible interval. In complement, we developed the Occurrence Plot that estimates the occurrence of the  $n$ th event with its uncertainty.

We also introduce the Activity Plot as the derivative of the Tempo Plot. It may be used to detect a break or a discontinuity in the rhythm of occurrence of archaeological events. We propose a Bayesian test based on the Activity Plot in order to detect a period of time corresponding to a lack of activity within a sample of dates.

Finally we present a statistical method to compare the rhythms of occurrences of different geographical sites. This tool aims at identifying a potential synchronisation of Tempo Plots modulo a temporal shift.

These tools are developed by Philippe and Vibet and are implemented in the CRAN package 'ArchaeoPhases' (see Philippe and Vibet 2018b). We will illustrate their use with published datasets.

### Reference :

T. S. Dye (2016) Long-term rhythms in the development of Hawaiian social stratification. *Journal of Archaeological Science*, 71, 1-9.

Philippe A. and Vibet M.-A. (2018a ). Analysis of Archaeological Phases using the CRAN Package 'ArchaeoPhases'. HAL .

Philippe A. and Vibet M.-A. (2018b ). ArchaeoPhases: Post-Processing of the Markov Chain Simulated by 'ChronoModel', 'Oxcal' or 'BCal'. R package

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## Signal Processing for the Identification of Miyake Events

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After the potential impact on communication systems of major solar storms was demonstrated by the Carrington Event of 1859 CE, and subsequent solar proton events, it has become important to develop a system that uses the available historical data for the prediction of similar events. Sudden increases (Miyake Events) in the radiocarbon concentration in the atmosphere were identified from single-year measurements on Japanese trees between 774–775 and 993–994 CE. As part of the ECHOES project, we used state-of-the-art signal processing techniques, as well feature extraction from the  $\Delta^{14}\text{C}$  measurements to identify the best method for predicting when such events occurred. More precisely, we tested 5 methods including Dynamic Time Warping, Euclidean Distance and COSFIRE filters and spectral features such as centroid, kurtosis and flatness. We computed our results in terms of true and false positive rates. Here, we compare the performance of the methods applied to this task by measuring the false positive rate at 75% of the true positive rate. The best results are achieved with the COSFIRE filters, but some of the spectral features also perform comparably well. With this work we show that machine learning and computational methods are suitable for the identification of possible Miyake Events in the past radiocarbon concentration of the atmosphere.

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## Wigglematch dating on humans? Dating the Scottish Soldiers in Durham

Andrew Millard<sup>1</sup>

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In November 2013, 28 skeletons in a mass grave were uncovered at the heart of the Durham World Heritage Site, during building works for a cafe at the University's Palace Green Library. The discovery sparked a research project which evaluated whether they were plague victims or Scottish soldiers from the Battle of Dunbar who had been imprisoned in Durham in AD 1650. A combination of evidence from archaeological context, osteology, isotope analysis and radiocarbon dating was considered. Here we report on the dating. Two skeletons showed evidence of habitual pipe-smoking in the form of notches worn between their teeth. This placed the burials after 1612, when cheap tobacco first became available. A building above the burials appeared on a map dated 1754, providing a terminus ante quem. Radiocarbon dating was applied to refine this range, using a novel approach. Following the idea of wigglematching, samples were taken from the first and third molars of two men to obtain samples forming approximately 10 years apart. A Bayesian model incorporating these samples with the known difference in age and the other dating constraints yielded a 95% credible interval of AD 1615–1620 and 1625–1660. Sensitivity analysis was carried out to test the robustness of this result to varying estimates of uncertainty in age-at-death and tooth formation, and the marine reservoir effect. None of these made a material difference to the age estimate. The date obtained is not compatible with known plague outbreaks in Durham but does accord with the date of the Battle of Dunbar, and in combination with other evidence allows us to confidently identify these skeletons as Scottish soldiers.

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## Dating cultural change in the Hallstatt period – a wiggle match of human bone radiocarbon ages

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<sup>3</sup> Centre for Baltic and Scandinavian Archaeology (ZBSA), Schleswig-Holstein State Museums Foundation, Schleswig, Germany.

It is often assumed that <sup>14</sup>C dating is not a viable method of refining archaeological chronologies of the 8th-5th centuries BC, due to the 'Hallstatt plateau' in the calibration curve. Absolute chronologies for this period in Central Europe are based on artefactual cross-dating with Aegean or Italian protohistoric assemblages, occasionally supported by dendrochronology. Here, however, we use <sup>14</sup>C to date the transition between the two main phases of the Hallstatt period, HaC and HaD.

The onset of HaC marks the beginning of the widespread use of iron in southern Germany, while HaD is marked by the appearance of ostentatious burials, the so-called princely graves. Traditionally, the HaC-HaD transition has been dated to c. 620 BC, and certainly not before c. 650 BC (Trachsel 2004), based on dendrochronological evidence from the 'Magdalenenberg' princely burial in Baden-Württemberg, but comparable evidence for Bavaria is lacking.

The site of Dietfurt, in Bavaria, spans the whole Hallstatt period (Röhrig 1994). The graves are richly furnished with ceramics (predominantly HaC) and bronze and iron artefacts (predominantly HaD), which provide secure relative dating. Furthermore, they are tightly interlocked in vertical and horizontal stratigraphies, which render the burial sequence of Dietfurt ideal for Bayesian chronological modelling. We have dated 16 bone samples at Dietfurt, including one cremation, one animal and 14 human bones with minimal collagen turnover time; their <sup>14</sup>C ages span 2410±25 to 2560±25 BP.

Evidence is growing of significant short-term atmospheric <sup>14</sup>C fluctuations during the first half of Hallstatt calibration plateau (760-630 BC). Park et al. (2017) reported a sharp peak in  $\Delta^{14}\text{C}$  around 660 BC, with a rise time of 3-4 years and an amplitude of c.10‰. Because several Dietfurt HaD samples carry the 660 BC event's <sup>14</sup>C signal, the HaC-HaD transition definitely occurred before this date. Solutions from later centuries can be excluded, because after 660 BC we do not observe deviations of the required amplitude in atmospheric <sup>14</sup>C values.

To date the HaC-HaD transition more precisely, we constructed a calibration curve by splicing a smoothed version of Park's single-year data for 670-650 BC into IntCal13, obtaining a transition date of 710-660 cal BC (>95% probability), several decades earlier than anticipated. Our model also indicates an average freshwater reservoir effect in the human bone samples of only 15-20 <sup>14</sup>C years, which suggests that not enough fish was consumed to affect dietary stable isotope results or the estimated HaC-HaD transition date. The outcome of the Dietfurt case-study implies that Hallstatt absolute chronologies can and should be re-assessed, using high-precision <sup>14</sup>C data and Bayesian chronological modelling.

### References

Röhrig, Karl-Heinz. 1994. Das hallstattzeitliche Gräberfeld von Dietfurt a. d. Altmühl. Buch am Erlbach: Leidorf.

Trachsel, Martin. 2004. Untersuchungen zur relativen und absoluten Chronologie der Hallstattzeit. Bonn: R. Habelt.

Park J, Southon J, Fahrni S, Creasman PP, Mewaldt R. 2017. Relationship between solar activity and  $\Delta^{14}\text{C}$  peaks in AD 775, AD 994, and 660 BC. Radiocarbon 59(4):1147-56.

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## Life after SIRI- where next?

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*2 SUERC, University of Glasgow, Glasgow, United Kingdom.*

Radiocarbon dating is very well-established and routinely used, yet occasionally, issues still arise surrounding laboratory offsets, and unexpected and unexplained variability. The degree of sample pre-treatment varies considerably depending on the material, the methods of processing pre-treated material vary across laboratories and the detection of 14-C at low levels remains challenging. Quality assurance and quality control are important in linking to the issue of comparability (and thus bias, accuracy and precision) of measurements from diverse laboratories. The 14-C community and the wider user communities have supported inter-laboratory comparisons as one of several strands to ensure the quality of measurements. The nature of the inter-comparisons has evolved as the laboratory characteristics have changed, with an emphasis on small, individual samples, such as single tree rings. The next inter-comparison is currently being planned to take place in 2019, and to include dendro-dated single rings, annual grain samples and a bulk humic acid sample. The focus of the work is to a) supplement our store of reference materials, b) provide consensus 14-C values and c) to provide estimates of laboratory offsets and error multipliers.



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## The importance of open access to chronological information: the IntChron initiative

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The development of chronologies relies on integrating information from a number of different sources. We have direct dating evidence, such as radiocarbon dates, and we have contextual information which might be an environmental sequence or the contexts in an archaeological site. This information can be combined through Bayesian or other types of age-model. Once the chronology has been developed, we need to use the chronology to estimate, for example, chronological uncertainties, rates of change, or the age of material which has not been directly dated.

Dealing with the information associated with chronology building is complicated and re-evaluation of chronologies often requires structured information which is hard to access. Although there are many databases with primary dating information, these often do not contain all of the information needed for a chronology. The Chronological Query Language (CQL) developed for OxCal was intended to be a convenient way of pulling such information together for Bayesian analysis. However, even this does not include much of the associated information required for reusing data in other analyses.

The IntChron initiative builds on the framework set up for the INTIMATE (Integrating Ice core, Marine and Terrestrial Records) chronological database (Bronk Ramsey et al 2014) and is primarily an information exchange format and data visualisation tool which enables users to pull together the types of information needed for chronological analysis. It is intended for use with multiple dating methodologies and while it will be integrated with OxCal, is intended to be an open format suitable for use with other software tools. The file format is JSON which is easily readable in software such as R, Python and MatLab. IntChron is not primarily intended to be a data depository but rather an index of sites where information in the relevant format is stored. As an initial step, databases of radiocarbon dates from the Oxford Radiocarbon Accelerator Unit (including those for the NERC radiocarbon facility), the RESET tephra database, the INTIMATE chronology database and the database of Egyptian radiocarbon dates are all linked. The intention is that users of OxCal will also be able to make published data accessible to others and to store working data, visible only to the user, to be used with the associated analysis tools. The IntChron site allows data from third party sources to be accessed through a representational state transfer (REST) application programming interface (API) in a number of different formats (JSON, csv, txt, oxcal) and associated bibliographic information in BibTeX format.

The aim of the IntChron initiative is to make it easy for users to provide data (in the single JSON format with limited minimum requirements) as well as to access data and tools, while promoting robust chronologies including realistic estimates of uncertainties. It is hoped that this will help to bring the chronological research communities to a point where data access is as easy as it is in some other fields. This is particularly important for Early Career Researchers and for those seeking to use large datasets in novel ways.

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## Radiocarbon analysis and the protection of cultural heritage—our concerns, problems and proposed solutions

Irka Hajdas<sup>1</sup>, Eric Huysecom<sup>2</sup>, Anne Mayor<sup>2</sup>, Marc-André Renold<sup>3</sup>, Hans-Arno Synal<sup>1</sup>, Timothy Jull<sup>4</sup>, Christine Hatté<sup>5</sup>, David Chivall<sup>6</sup>, Elisabetta Boaretto<sup>7</sup>, Lucile Beck<sup>8</sup>, Lucia Liccoli<sup>9</sup>, Mariaelena Fedì<sup>9</sup>, Ronny Friedrich<sup>10</sup>, Francesco Maspero<sup>11</sup>, Tiberiu Sava<sup>12</sup>, Wan Hong<sup>13</sup>

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*3 Art-Law Centre, University of Geneva, Geneva, Switzerland.*

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*5 L.S.C.E / CEA-CNRS-UVSQ, Gif-sur-Yvette, France.*

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*7 Weizmann Institute of Science D-REAMS, Rehovot, Israel.*

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*9 INFN Sezione di Firenze, Florence, Italy.*

*10 Curt-Engelhorn-Zentrum Archäometrie, Mannheim, Germany.*

*11 Centro Universitario di Datazione e Archeometria, Milano, Italy.*

*12 Horia Hulubei - National Institute for Physics and Nuclear Engineering (IFIN-HH), Bucharest, Romania.*

*13 Korea Institute of Geoscience and Mineral Resources(KIGAM), Daejeon, Republic of Korea.*

Thanks to technical developments, which allow AMS <sup>14</sup>C analysis on very small amounts of material, recent years have seen a dramatic rise in requests from antiquity dealers or private collectors for radiocarbon dating of textiles, manuscripts, wooden and ivory made statues. On the one hand, this is driven by the increasing demand for these luxury objects, but on the other hand by the numerous cases of reported counterfeiting, which has increased awareness of the potential customers, as well as of auction houses.

However, yet another factor must be recognized here. The recent growth in illicit antiquities trade and an organized looting in conflict zones such as Iraq, Syria, Libya or Mali carries a potential for misuse of radiocarbon dating. As observed by archeologists working in conflict regions, the illegal removal of archeological and ethnic pieces of art is usually part of well organized criminal activities. Looted objects can be mixed with recent products, certified as tourist gifts, and cross the borders unnoticed. In such cases, radiocarbon age might be used (or misused) to validate these objects as antiquities. In consequence, the objects become very valuable, which in turn drives further illicit trade and looting. Moreover, illicit antiquities trade is not limited to the conflict zones countries only or it might involve objects removed from the original countries decades ago and remained hidden in the private collections.

Huysecom et al., 2017 proposed a unified approach for all radiocarbon laboratories for the analysis of objects, which are of value to cultural heritage. The first steps and discussions took place at the meeting 'Radiocarbon and the protection of cultural heritage', on 16-17 November 2017 in Zurich. In this paper, we would like to summarize the outcome of that meeting and discuss the future steps.

Huysecom E, Hajdas I, Renold M-A, Synal H-A, and Mayor A. 2017. The "Enhancement" of Cultural Heritage by AMS Dating: Ethical Questions and Practical Proposals. *Radiocarbon* 59: 559-563.

# Poster Presentations

## Poster Session 1

Poster session 1 (Monday, Tuesday)														
1A	Row1	1B	2A	Row2	2B	3A	Row3	3B	4A	Row4	4B	5A	Row5	5B
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M. Nadeau	2	278 B. Longworth	206 K. Sasa	2	21 K. Dong	286 C. Telloli	2	336 M. Diaz Castro	163 G. De Mulder	2	13 P. Richardin	64 I. Chanca	2	189 N. Toshio
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S. Zhu	4	254 L. Calcagnile	289 S. Chopra	4	326 M. Seiler	23 J. Lefevre	4	15 P. Fago	132 S. Hirabayashi	4	262 D. Michalska	126 B. Philippssen	4	84 M. Huelis
M. Roberts	5	94 J. Melchert	74 T. Gentz	5	294 S. Freeman	105 L. Reynolds	5	192 T. Nakanishi	269 J. Olsen	5	204 A. Sironić	133 B. Philippssen	5	100 M. Yokoyama
R. Taylor	6	325 A. Stolz	50 S. Lee	6	285 C. Telloli	273 M. Kurz	6	6 Q. Hua	159 K. Kubota	6	112 K. Haase	47 P. Jacobsson	6	39 H. Oda
Y. Fu	7	107 J. Nordby	51 H. Li	7	333 B. Culleton	62 N. Haghipour	7	316 K. Macario	210 T. Aramaki	7	111 J. Kaizer	179 D. Kunikita	7	118 F. Peng
K. Dong	8	49 Q. Hua	52 Q. Liu	8	93 F. Bertuch	263 Z. Cheng	8	208 T. Nakanishi	185 Y. Yokoyama	8	173 G. De Mulder	148 M. Krapiec	8	181 N. Kessler
W. Zhou	9		321 T. Campos	9	351 J. Olsen	38 H. Grotheer	9	308 M. Oliveira	354 C. Connolly	9	139 J. Frolik	348 J. Olsen	9	108 M. Martinez Carrillo
Y. Guan	10	86 Y. Pang	337 K. Mizohata	10	235 N. Piotrowska	251 M. Uchida	10	7 K. Allen	252 M. Uchida	10	350 J. Olsen	44 P. Jacobsson	10	143 C. Solis
	11	335 E. Vaernes	247 T. Knowles	11		297 K. Loftis	11	29 Ž. Ežerinskis	77 R. Maring	11	213 C. Lubritto	117 G. Hodgins	11	274 M. Rodriguez-Ceja
	12	309 K. Fifield		12		305 K. Yagasaki	12	200 M. Oinonen	283 M. Fedi	12	225 R. Fernandes	339 A. Salavert	12	342 B. Pereira
	13			13		205 A. Servettaz	13	178 J. Walker	136 L. Calcagnile	13	68 E. Wild	229 B. Philippssen	13	264 R. Rodrigues Ramos

## 1A-01 Humic substances- their history in the radiocarbon inter-comparisons studies.

Philip Naysmith<sup>1</sup>, Elaine Dunbar<sup>1</sup>, Gordon Cook<sup>1</sup>, Marian Scott<sup>2</sup>

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Over the past 30 years, the format of the radiocarbon inter-comparison studies, organised by the Glasgow University group, has changed to complement the advances in technology made in the measurement of radiocarbon. However, the selection of sample types used in these studies has remained constant – namely, using natural and routinely dated materials which could subsequently be used as reference materials. One such sample was peat. A decision was made in the late 1980's to collect a peat sample from Central Scotland and extract humic acid from it which could be used first in the ICS study, with the excess material being stored for future use. The main advantage of choosing a peat sample was that the humic acid would be extracted in solution and then precipitated (the solution phase providing the homogenisation). This peat sample has now been used in 3 inter-comparison studies over a 30-year period, and in this paper, we will revisit the consensus value data and give a brief history of the results.

In addition, for the last 8 years, this humic sample has also been used in the SUERC radiocarbon laboratory as an in-house standard. In every routine AMS wheel there are 13 humic acid targets, used to calculate our minimum error associated with the wheel, which is then applied to all the measured unknowns. We also use this humic acid sample as a quality control tool to identify any small problems in the sample preparation. We have made several thousand measurements and will compare these results to the consensus values.

## 1A-02 A database at the heart of a radiocarbon measurement facility.

Marie-Josée Nadeau<sup>1</sup>

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With radiocarbon laboratories processing large numbers of samples, the flow of information in the laboratory becomes very important. In addition, dating of radiocarbon samples usually involves different processes performed sequentially, which are often also carried out by different people. Therefore, an efficient information distribution system is required to allow everyone involved to trace the samples and add process information. Relational databases provide a very powerful tool to collect information generated by different processes. Data distributed over different tables linked to each other allow information to be collected and retrieved in many ways. If the database structure is well planned, adapted to the information it stores, and flexible, this is a valuable tool to store and retrieve information.

We present here a relational database model constructed for the operation of a radiocarbon laboratory. The database structure reflects the processes to which a sample is subjected. It also includes administrative issues such as billing and reporting of results. The database is divided in two layers. A table platform which can be hosted by a database server or a simple Microsoft Access file. It can be accessed via ODBC or other communication protocols by automated processes (e.g. graphitization) from which data is added automatically and external programs that will use the data independently. User interfaces constitute the second layer of the structure. These are linked to the underlying table-layer but remain independent. Depending on the needs, user interfaces can be designed for a single process (e.g. chemical pre-treatment) or as overviews to track samples through the laboratory. This two layer approach brings another level of flexibility in which a "mobile" user can copy the table layers and use the user interfaces without a network link to the primary source of information. The database structure presented here has been used successfully for 23 years in different laboratories for the measurements of more than 50 000 samples and 100 000 results. It is flexible enough that it can be adapted for new laboratory protocols and equipment.

## 1A-03 Recent advancements in quality and information management in Laboratory of Chronology

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Laboratory of Chronology of University of Helsinki, Finnish Museum of Natural History has recently acquired a Laboratory Information Management System (LIMS). LIMS helps laboratory to keep all information regarding customers, invoices, samples, sample data and quality management issues in the same place. With good information management comes cost savings with decreasing work load and reducing the need to find information from different sources. LIMS is currently being finalized and configured and part of the laboratory's analyses has been imported and in addition to test samples, first real sample data has been stored into it. The quality and information management advances will be presented.

## 1A-04 Homogenization of Chinese sugar carbon standard for AMS <sup>14</sup>C measurement

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Chinese Sugar Carbon (CSC), one of Chinese national radiocarbon standard, was produced from sugar beets harvested in 1977 with the exaction and carbonization process. CSC was considered as a pure, stable and homogenous material and widely used as an important standard in many conventional and a few Accelerator Mass Spectrometry (AMS) <sup>14</sup>C laboratories in China. However, the recent study indicated  $\delta^{13}\text{C}$  value of CSC was highly variable in < 5 mg grain aliquots, which was ranging from -15.9 to -22.2‰ and of  $-18.9 \pm 1.3\text{‰}$  on average. Similar variations were observed within one bottle and among different bottles. Though Fm value of CSC was well constrained to 2.4‰ after the fractionation correction to -25‰ with online  $\delta^{13}\text{C}$  measurement, CSC was not an ideal standard in an AMS laboratory without online  $\delta^{13}\text{C}$  measurement. The homogenization process of CSC was necessary to make it widely applicable. Here we reported the preliminary results of CSC homogenization process. 10 bottles of CSC were carefully grounded to 200 meshes. The  $\delta^{13}\text{C}$  variation (1 $\sigma$  stand deviation) of CSC in a single bottle ranged from 0.07‰ to 0.36‰, while the  $\delta^{13}\text{C}$  values of different bottles ranged from -17.92‰ to -20.01‰, with a much larger variation. The mixture process is in progress to further reduce the  $\delta^{13}\text{C}$  variation of CSC. Our aim is to homogenize around 900 bottles of CSC and reduce the  $\delta^{13}\text{C}$  variation to less than 0.2 ‰, making it an available standard for all AMS <sup>14</sup>C laboratories.

## 1A-05 Determination of the <sup>14</sup>C Blank at the National Ocean Sciences AMS Laboratory, WHOI

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Radiocarbon measurements were made on control samples with consensus values ranging from Fm = 1.5 to Fm = 0, and spanning the mass range from 6  $\mu\text{g}$  to  $\sim 2$  mg carbon. These measurements form the basis for determining both the mass and radiocarbon content of the contaminant carbon introduced during sample processing and measurement in our laboratory. This data is used to model the contribution of contaminant over a range of sample masses and subsequently 'blank correct' measured unknowns. Data, formulae, and an assessment of the accuracy of the blank correction are presented.

## 1A-06 Issues in the use of synthetic diamonds for routine radiocarbon analysis

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A previous study (Taylor and Southon 2007) demonstrated the feasibility of employing natural diamonds to monitor "machine" based <sup>14</sup>C backgrounds in an AMS instrument. The expectation was that a natural diamond would exhibit a "cleaner" sputtering surface thereby reducing the effects of crosstalk in the ion source as a source of microcontamination. Measurements on the UCI Keck-CCAMS instrument demonstrated that natural diamonds can exhibit lower background than other natural materials (e.g., geological graphite) which can be used for this purpose. In the UCI Keck-CCAMS instrument, a natural diamond sample exhibited a background of  $0.00005 \pm 0.00001$  F<sup>14</sup>C for an equivalent of an inferred <sup>14</sup>C age value of about 80,000 BP. This value is assumed to have been the "machine" background of the UCI AMS instrument at the time the experiment was conducted. The natural diamonds examined also exhibited beam currents that exceeded that typically measured in geological graphite in the UCI instrument. These observations are only of limited relevance if the goal is to take advantage of a lower background for routine AMS-<sup>14</sup>C measurements of unknown age samples. The reason is that implementation of the use of a synthesized diamond carbon for <sup>14</sup>C analysis of samples requires that CO<sub>2</sub> from samples, backgrounds, and OXI or another contemporary standard would need to be converted to a useful diamond carbon deposited on an appropriate substrate on a routine basis without the addition of significant amounts of contamination. There has been recent developments in chemical vapor deposition (CVD) crystal formation techniques at pressures under 27kPa to produce synthetic diamonds of sufficient size to facilitate mounting in an ion source. The poster will report on the nature of the problems that will need to be addressed if an implementation of this technology to yield sufficient synthesized CVD diamonds exhibiting only trace <sup>14</sup>C contamination has a reasonable chance of being routinely feasible.

Reference cited: Taylor RE, Southon JR. 2007. Use of natural diamonds to monitor <sup>14</sup>C AMS instrument backgrounds. Nuclear Instruments and Methods in Physics Research 259(1):282-287.

## 1A-07 Study of <sup>10</sup>Be/<sup>7</sup>Be in rainwater from Xi'an by Accelerator

### Mass Spectrometry

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The <sup>10</sup>Be/<sup>7</sup>Be ratio is a sensitive tracer for the study of atmospheric transport, particularly with regard to stratosphere-troposphere exchange. Measurements with high accuracy and efficiency are crucial to <sup>7</sup>Be and <sup>10</sup>Be tracer studies. This article describes sample preparation procedures and analytical benchmarks for <sup>7</sup>Be and <sup>10</sup>Be measurements at the Xi'an Accelerator Mass Spectrometry (Xi'an-AMS) laboratory for the study of rainwater samples. We describe a sample preparation procedure to fabricate beryllium oxide (BeO) AMS targets that includes co-precipitation, anion exchange column separation and purification. We then provide details for the AMS measurement of <sup>7</sup>Be and <sup>10</sup>Be following the sequence BeO→Be<sup>2+</sup>→Be<sup>4+</sup> and BeO→Be<sup>2+</sup>→Be<sup>3+</sup> in the 3MV Xi'an-AMS. The <sup>10</sup>Be/<sup>7</sup>Be ratios of rainwater collected in Xi'an were shown. The virtue of the method described here is that both <sup>7</sup>Be and <sup>10</sup>Be are measured in the same sample, and it is suitable for routine analysis of large numbers of rainwater samples by AMS. The preliminary <sup>10</sup>Be/<sup>7</sup>Be time series was established at Xi'an. Next, there are a great number of sites in China that could be studied with this technique.

## 1A-08 The application exploration for AMS measurement of Al-26 and Be-10 in deep-sea ferromanganese crusts

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The dating techniques of  $^{10}\text{Be}/^9\text{Be}$  and  $^{26}\text{Al}/^{10}\text{Be}$  have widely been used in study on the chronology of marine sediments with the development of accelerator mass spectrometry (AMS). However, some controversial topics were still remained due to the influence of isotope fractionation, palaeomagnetic intensity variations and measurement sensitivity etc. The deep-sea ferromanganese crust (DSFC) is a natural archive for recording of the history of the earth evolution, as one of the most common authigenic assemblages in marine sediments. An application exploration for AMS measurement of  $^{26}\text{Al}$  and  $^{10}\text{Be}$  in DSFCs was proposed based on the XCAMS system at Tianjin University. The experimental protocol will focus on previous research and the corresponding relationship of isotopic ratios of Al and Be, discuss and explore a new profile dating method of  $^{26}\text{Al}/^{27}\text{Al}$  based on DSFC samples analysis and linear contrast with  $^{10}\text{Be}/^9\text{Be}$ . The expected results of this project not only provide a new analytical method for the deep-sea sediment chronology, but also provide meaningful reference information for the history of earth evolution, especially the Quaternary. The experimental strategy, program and aim will be detailed in this contribution.

## 1A-09 Paleoprecipitation reconstruction on the Chinese Loess Plateau using $^{10}\text{Be}$

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The Chinese Loess Plateau is located along a semiarid to semi humid zonal boundary under the influence of the Asian Monsoon, and is a very important agricultural region in central China [Liu, 1985]. The Monsoon associated precipitation in the region is important to the maintenance of living environments and socially sustainable development [An, 2000]. To better understand the present process and future trend of Monsoon precipitation changes in this area, it is essential to quantitatively reconstruct the paleoprecipitation variation in the Chinese loess plateau since the last 130 ka. Cosmogenic  $^{10}\text{Be}$  is a promising precipitation index, because its fallout flux in sediments is mainly controlled by wet precipitation after its production in the atmosphere. Here we report on a new study for reconstructing precipitation during the last 130 ka using  $^{10}\text{Be}$  measurements from Chinese loess, with multivariable linear regression to remove the geomagnetic field modulation and dust flux dilution effects from the loess  $^{10}\text{Be}$  record. The broad similarity between our result and speleothem  $\delta^{18}\text{O}$  indicates that the new precipitation record is robust. It also records an interesting increase in precipitation that occurred during Marine Isotope Stage 3 (MIS 3), exhibiting a similar rainfall amount with that of MIS 5, suggesting that MIS 3 is a special period with strengthened summer Monsoon intensity. By comparison with a stacked marine isotope record and a summer insolation record, our precipitation data clearly show a close correspondence with Northern Hemisphere summer (June, July, and August) solar insolation changes on orbital timescales. During MIS 3, our record follows the insolation differential between 30° N and 30° S, suggesting that rising rainfall changes during MIS 3 are a response to the interhemispheric summer insolation differential forcing.



## 1A-10 Accelerator mass spectrometry analysis of <sup>237</sup>Np in environment samples

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In order to determination the values of Np-237 in surface soil samples which were collected from uncontaminated region and measured by AMS at CIRCE, Italy. Pu-242 as a tracer was added to each sample, standard samples with different mass ratio of Np-237 and Pu-242 were analyzed. The results indicated that the concentration of Np-237 are in the range of 0-75.6 pg/kg, and the most probable value of is approximately 20 pg/kg. The concentration of Np-237 is three to five order of magnitude lower than the published values from the contaminated region. The detection limit, transmission efficiency, and ionization efficiency in the source were presented as well.

## 1B-01 Improving the Cs sputtering efficiency by changing cathode geometry of the ion source

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The Cs sputtering efficiency is one of several factors that can evaluate the performance of an ion source. If this efficiency is improved by a few percent, the amount of ion beam currents would increase and the count rate of <sup>14</sup>C also increase, accordingly better statistics can be obtained. Especially, the improved statistics would cause a high accuracy of radiocarbon ratio for micro size samples. Among various efficiency improvement methods, the ion beam current will be raised by optimizing the geometry of the cathode. In this work, the positions of graphite were changed by 0.5 mm from the surface of targets to improve sputtering yield in the ion source.

The samples were prepared by 5 different graphite depths - 0.064(original method), 0.5, 1.0, 1.5 and 2.0 mm – with 1.3 mm diameter. Two samples were made at each depth and ten samples were measured. To investigate sputtering efficiency the <sup>12</sup>C<sup>2+</sup> ion beam currents of the targets were measured at the faraday cup after acceleration in every minute until exhaustion of graphite. The carbon ion beam current recorded the highest value with the graphite position of 0.5 mm and decreased in the order of 0.065, 1.0, 1.5 and 2.0 mm. The ion beam current of the target with the 0.5 mm depth samples were measured from 18 to 21 μA for 90 minutes and then the beam current began to decrease. The ion beam current of the target with the 0.064 mm depth sample were measured 14 to 17 μA for 140 minutes. The targets with the depth 0.5 mm showed beam current increased by 26% compared with the conventional targets. However, the targets with the depth 1.0, 1.5 and 2.0 mm showed the beam currents down by 20%, 53% and 71%, respectively, compared with the targets made with conventional methods.



## 1B-02 Development of a Hybrid Gas Ion Source and Gas Inlet Systems at NOSAMS

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Here we present progress on development of gas inlet systems for a hybrid sputter gas ion source (HGIS). Our HGIS is a lightly modified gas-capable 134-sample MCSNICS source from NEC. The ion optics and cesium delivery have been upgraded following Roberts et al. [1]. Gas delivery to the source is via a short glass capillary which crosses the source high voltage potential.

We are developing two inlet technologies, (1) delivering gas to the source at low pressure using modified gas handling hardware from a VG stable isotope ratio mass spectrometer (SIRMS), and (2) sampling gas at atmospheric pressure using an open split. The gas handling system designed for use with SIRMS is nearly ideal for our purposes, providing low volume, low pressure delivery of gas, and control of mixing ratios and delivery pressure using variable volumes. We will initially use the open split for larger carbonate samples (>2mgC), which will be hydrolysed and delivered using the gas preparation system developed as an interface for our microwave plasma gas ion source [2].

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[2] M.L. Roberts, S.R. Beaupré, J.R. Burton, A high throughput, low-cost method for analysis of carbonate samples for <sup>14</sup>C, *Radiocarbon*. 55 (2013) 585–592.

## 1B-03 Mathematical model for CO<sub>2</sub> mass flow during pulse gas continuous-flow injection using a low-budget interface that couples an elemental analyzer with a MICADAS AMS.

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Direct CO<sub>2</sub> analysis with gas-accepting ion sources has been extensively used for fast radiocarbon analysis with accelerator mass spectrometers (AMS). This allows to process a large number of small samples (tens of µg) and facilitates the coupling of CO<sub>2</sub>-producing analytical devices with AMS. The process of handling and effectively injecting the gas is fairly complicated with CO<sub>2</sub>-trapping interfaces which need multiple parts and thus become expensive. A second disadvantage is that the absorbing material adds constant and cross contamination. In addition, the trapping step prevents real-time <sup>14</sup>C analysis. On the other hand, continuous-flow (CF) interfaces bypass the trapping step, injecting the CO<sub>2</sub> by controlling the carrier flow and the dead volume of the tubing.

It is important to understand the effects of the CO<sub>2</sub> flow over the ionization efficiency for CF interfaces. It is easy to determine the carbon mass flow (mf) as  $mf = C \times F$ , if the carrier flow (F) is known and the CO<sub>2</sub> concentration (C) is constant and uniform. However, many CF applications inject the CO<sub>2</sub> in the form of a pulse and its spatial concentration approximates to a Gaussian distribution. Here, we are showing a low-budget CF interface and developing a mathematical model to predict its carbon mass flow during pulse injection.

A 1/8" Swagelok Tee was set at the entrance of the interface to split the flow towards a home-made mass flow controller (MFC) and a dead-volume system. The dead-volume consisted of a 25 cm-long tube (16 mm i.d.) with NW16 KF flanges and Swagelok adaptors at the entrance and exit. A pressure gauge was set at the entrance of the dead-volume by means of a 1/8" Swagelok Tee. The dead-volume exit was connected to a commercial MFC that was connected to a 1/16" purge valve which was connected to the ion source with a 1-m long PEEK capillary (0.13 mm i.d.). The EA released the CO<sub>2</sub> at 127 °C in the form of a narrow peak which was transported at 75 sccm. At this moment, the valve before the home-made MFC was closed, so the flow was directed towards the dead-volume and vented to air at the purge valve. When the CO<sub>2</sub> peak was about to exit the dead-volume, the valve before the home-made MFC was opened and the purge valve was closed. The flow of the home-made MFC was set to a value that kept the pressure at the dead-volume constant and allowed the commercial MFC to keep a constant low flow towards the ion source.

We were able to model the instantaneous CO<sub>2</sub> mf during injection and compare it with the measured <sup>12</sup>C beam current. The <sup>12</sup>C signal was linear with the carbon amount when the instantaneous CO<sub>2</sub> mf was kept lower than 3 µg C/min. For the range of 3-5 µg C/min, the signal was no longer linear; and for higher mf, a strong suppression was observed. The interface allowed for real-time radiocarbon measurement with some peak broadening from the original peak.

## 1B-04 Improved performances and routine applications of the gas-accepting ion source at CEDAD

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The experimental capabilities of the AMS system installed at CEDAD have been enhanced in the last years with the design and installation of a new gas-accepting ion source.

An elemental analyzer (EA) is used to combust the samples, measure the C and N content and deliver the gas to an IRMS system for the measurement of stable carbon and nitrogen isotopic ratios. An aliquot of the gas is also sent, through a gas handling interface, to a gas accepting ion source connected to the low injector of the AMS system.

The characteristics of the system, the design choices and the obtained performances are reviewed showing how the optimization of the different parameters resulted in the possibility to obtain C,N,  $\delta^{13}\text{C}$ ,  $\delta^{15}\text{N}$  and  $^{14}\text{C}$  determination in a single measurement run on samples with masses as low as 10  $\mu\text{gC}$ .

The system is now used on a routine basis in the lab for applications spanning from cultural heritage diagnostics, archaeological and environmental sciences.

In this paper we present the first applications in environmental sciences where the possibility to analyze samples with masses of a few microgram is mandatory for instance in the determination of the proportion between fossil and biogenic carbon in biomonitors and airborne particulate matter.

## 1B-05 Exploring sample size limits of AMS gas ion source $^{14}\text{CO}_2$ analysis

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The Centre of Accelerator Mass Spectrometry at the University of Cologne (CologneAMS) recently installed a second ion source from High Voltage Engineering Europa B.V. (HVE) at the HVE 6 MV Tandetron AMS facility. The ion source was coupled with the gas injection system (GIS) manufactured by Ionplus (Switzerland). The GIS introduces  $\text{CO}_2$  provided in glass ampoules, mixed with He, into the ion source. With this approach, small sample sizes can be measured, which is particularly useful for applications such as compound-specific radiocarbon analysis, often limited by the amount of C available (Stolz et al., 2017). First tests of this system showed that smallest  $\text{CO}_2$  samples ( $\sim 5 \mu\text{g C}$ , taken from a bottle) can be processed directly without the need for graphitisation and resulted in blank values ( $^{14}\text{C}$ -free standards) around 0.005  $F^{14}\text{C}$ .

We now performed a more detailed investigation to quantify contributions by exogenous C, both fossil and modern, introduced during pretreatment and gas purification. Multiple series of  $^{14}\text{C}$ -free and modern standards ranging from 2.5 - 50  $\mu\text{g C}$  were treated and analysed. We also compared the processing and measurement of small versus large (1 mg C) samples; i.e. producing gas aliquots after combustion, rather than weighing in the desired amount of C directly. Gas aliquots were taken in sizes respective to prior standard series sizes.  $\text{CO}_2$  filled ampoules were then injected into the GIS. The data show that the relative importance of exogenous C contribution increases with decreasing sample size. Furthermore, we estimated the amount of contamination introduced using the model of constant contamination (Ruff et al., 2010), which yields the best fit for an averaged 0.3  $\mu\text{g}$  of atmospheric C contamination (1.021  $F^{14}\text{C}$ ; Hammer et al., 2017), for each sample. The injection of standards, produced from  $^{14}\text{C}$ -free  $\text{CO}_2$  bottled gas, into the ion source resulted in almost one order of magnitude lower concentrations (at sample sizes smaller than 15  $\mu\text{g C}$ ), reflecting that part of the contamination is introduced during sample processing. The results for the  $\text{CO}_2$  splits taken from the large 1 mg C samples, plot in the range of bottled gas measurements, indicating that a significant amount of contamination is introduced during weighing and treatment of the sample prior to combustion.

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## 1B-06 Improvements in the measurement of small $^{14}\text{CO}_2$ samples at CologneAMS

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A second SO-110 B ion source from High Voltage Engineering Europe (HVE) has been installed at the 6 MV TANDETRON accelerator at the University of Cologne, especially for the measurement of gaseous  $\text{CO}_2$  samples. A gas interface (GIS) from Ionplus AG is used for mixing the  $\text{CO}_2$  sample with He and to transfer the sample gas into the ion source. Additionally, a EuroVector EA3000 elemental analyzer was coupled to the GIS. Dedicated software was developed to control both the GIS and the accelerator in order to allow batch measurements with ampulle and EA samples without the need of any user interaction. The acquired isotope ratios are automatically analyzed.

Special effort was devoted to determine optimized operation parameters for the ion source, aiming for a maximum negative ion yield. Based on SIMION calculations, a modified immersion lens was designed. In addition, the target position was changed with respect to the position used for solid targets. Also the target geometry was slightly modified to optimize the coverage of the sputter area by the caesium beam. Another focus was put on measuring ultra-small samples ( $< 5 \mu\text{g}$ ) while maintaining a low  $^{14}\text{C}/^{12}\text{C}$  blank level of about  $3 \cdot 10^{-15}$ .

We present the results of the first measurements from which specific quantities were determined, e.g. reproducibility of measured standards, yield efficiencies and the precision of isotopic ratios for different sample sizes.

The project is partly funded by the University of Cologne in the frame of the DFG excellence initiative.

## 1B-07 The Effect of Sample Mass and Iron-to-Carbon Ratio on Radiocarbon Measurements at the University of Arizona AMS Facility

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Sample mass is an important factor that can determine what is and what is not a datable sample. As sample mass decreases, different factors influence the radiocarbon measurements. We examined how fraction modern measurement changes as a function of decreasing sample mass, using two different sample types: a modern-aged sample, Oxalic acid II (N.I.S.T SRM 4990 C); and, a  $^{14}\text{C}$ -free material, Brown Coal, a sub-fossil wood estimated to be 65-10 million years old. Samples of each type, with extracted carbon masses ranging from 2.00 mg down to 0.02 mg, were measured for radiocarbon content. The observed change in the measured fraction modern of both sample types were used to construct sample-size dependent correction algorithms. In a second study, we examined how an increasing iron-to-carbon ratio (which can occur as extracted carbon mass decreases) affected the measured fraction modern of a fixed mass OXII in the context of the Fe/Zn graphite reduction system used in our lab.

## 1B-08 Direct AMS <sup>14</sup>C Analysis of Carbonate

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We have investigated the possibility of direct AMS <sup>14</sup>C measurement of carbonate samples at ANSTO using the STAR 2 MV tandem accelerator from High Voltage Engineering and its 846 Cs sputtering ion source. The method is based on previous research of Longworth et al. (2013) and Bush et al. (2013). Each carbonate sample was powdered and mixed with metal powder, before being pressed into an aluminium cathode for direct Ca<sup>14</sup>CO<sub>3</sub> measurement by AMS. Beam currents for carbonate targets containing 0.7-2.5 mg (or 0.08-0.3 mg C) were ca. 10% of those obtained from graphite targets of standard size (>0.5 mg C), with carbonate targets readily providing good output for more than an hour in the ion source. Of the three high-purity metal powders (Ag, Fe and Nb) used in our investigation, Nb was found to be the best metal, which delivered higher beam currents and lower background. Typical measured blank for Carrara marble (IAEA-C1) of >40 ka was obtained. The accuracy of the method was determined by (i) measurement of reference carbonate material IAEA-C2 (41.14 pMC), and (ii) comparison the results of this method with those obtained from high-precision analysis of graphite targets derived from shell and coral samples having an age range of 0.7-6 ka (~47-92 pMC). Typical precision of this method was 1.5-2% for samples <8 ka and ca. 1% for modern samples. Applications of the method of direct carbonate measurement by AMS at ANSTO will be discussed.

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## 1B-10 Development of <sup>14</sup>C measurement with home-made AMS system at CIAE

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A home made AMS system dedicate to <sup>14</sup>C measurement was built at China Institute of Atomic Energy(CIAE). The system is a kind of single stage AMS system with a working voltage of 200KV. After the system was installed, systematic experiments have been carried out to optimize the performance of the system for <sup>14</sup>C measurement. After the systematic experiments test, the <sup>14</sup>C measurement with precision of 0.5% and the background level of 0.5 pMC were achieved. Details for the system description and the experimental performance are given

## 1B-11 Comparison of $\delta^{13}\text{C}$ measurements from IR-MS and AMS

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Physical and biochemical processes discriminate/fractionate between carbon isotopes. Therefore, radiocarbon ages are corrected for isotopic fractions to a common  $\delta^{13}\text{C}$  value (-25‰ VPDB). The correction is such that a 1.0‰ variation in  $\delta^{13}\text{C}$  correspond to a change of about 16.5 radiocarbon years, independent of the sample age.

Many AMS radiocarbon measurements are fractionation corrected using the  $\delta^{13}\text{C}$  from the AMS system itself. To determine the precision of the  $\delta^{13}\text{C}$  measurements from the AMS system, we measured graphite samples prepared for AMS by IRMS using a Delta V Advantage coupled to a FLASH 2000 EA. In addition, we measured the  $\delta^{13}\text{C}$  in the AE/IRMS directly from the sample material to detect fractionation introduced during the combustion/graphitization processes.

## 1B-12 A Compact Ionization Chamber for the detection of 300 keV $^{14}\text{C}$ ions from a single-stage accelerator mass spectrometer (SSAMS)

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A compact ionization chamber, closely modelled on that developed at ETH Zürich [1], is being designed and constructed at the Australian National University. It will be mounted on the SSAMS in the Research School of Earth Sciences for the detection of 300 keV  $^{14}\text{C}$  ions. The design of the new detector, and the results of initial tests, will be described and discussed.

[1] Müller et al., NIM B287 (2012) 94-102

## 2A-01 LASIS enhancements of C- currents from CO<sub>2</sub> samples

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Ion-pair production from colliding neutral atoms is proposed as the dominant mechanism for creating negative ions in the cesium sputter ion source. The process depends on the electron donor atom having an ionization potential slightly greater than the electron affinity of the negative ion. That is the only requirement: ionization is possible between any two atoms if one has a positive electron affinity. The mechanism is better known in molecular chemistry than in elemental physics. Aside from the halogens, pair production has been quantified for only calcium (Ca) and rubidium (Rb) atoms, the first in collisions with excited neon and the second with excited Rb. Competition between sputtered products for specific excited Cs states as well as increased C- upon laser excitation of Cs(7p) are known. A model of the Ca-Ne\* collision has been generalized to predict the excited state energy for creating any elemental anion. This model explains the competition between sputtered O atoms and C atoms for the Cs(5d) state for CO<sub>2</sub> samples and allows speculative solutions for the low C- output. The most obvious solution from the model is to use Rb as the primary ion beam with 421 nm laser excitation of secondary Rb<sup>0</sup> to the Rb(6p) state. Poster discussions may reveal other solutions.

## 2A-02 Performance of the New Tsukuba 6 MV AMS Facility for Radiocarbon Dating

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A new 6 MV AMS facility has been operated at the University of Tsukuba since 2016 after 2 years of construction and preparation. The Tsukuba 6 MV AMS facility was designed and constructed for high-sensitivity detections of <sup>10</sup>Be, <sup>14</sup>C, <sup>26</sup>Al, <sup>36</sup>Cl, <sup>41</sup>Ca and <sup>129</sup>I [1]. A five-electrode gas  $\Delta E$ -E ionization detector is installed on the end station at the rare-particle detection system. The high terminal voltage has advantages in <sup>14</sup>C AMS for the detection limit. The background of the system is reached to <sup>14</sup>C/<sup>12</sup>C  $\sim 2.4 \times 10^{-16}$  ( $0.04 \pm 0.01$  pMC) using the 4+ charge state with the terminal voltage of 5 MV. The standard reference materials of IAEA C1-C8 were measured for <sup>14</sup>C preliminary tests. The typical beam currents are 30 to 60  $\mu$ A for <sup>12</sup>C- from graphite samples. The beam transmission is about 40% to the detector. The measuring precision is better than 0.2% for <sup>14</sup>C/<sup>12</sup>C  $\sim 10^{-12}$ . The CO<sub>2</sub> gas introduction system can be used for the gas/solid hybrid type MC-SNICS in the Tsukuba 6 MV AMS facility. The CO<sub>2</sub> gas feed into a cathode that has the same conical rear face for standard type. There is a Ti insert in the center inside of the cathode for CO<sub>2</sub> gas passageway. It is possible to extract <sup>12</sup>C- beam up to 12  $\mu$ A and typically 5  $\mu$ A about one hour in duration from 1 mg CO<sub>2</sub> gas sample with the proper gas flow rate of 1.6  $\mu$ l min<sup>-1</sup>. The background is <sup>14</sup>C/<sup>12</sup>C  $\sim 5.0 \times 10^{-15}$  ( $0.48 \pm 0.05$  pMC) for a CO<sub>2</sub> gas sample of IAEA C1. The precision of measured <sup>14</sup>C/<sup>12</sup>C is better than 0.6% for NIST-HNOxII. In this report, we will present the performance of radiocarbon dating at the new Tsukuba 6 MV AMS facility.

[1] K. Sasa et al., Nucl. Instrum. Methods Phys. Res. B 361 (2015) 124–128.

## 2A-03 The all-new radiocarbon measurement facility at the Center for Isotope Research, University of Groningen.

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The radiocarbon measurement facility at the Center for Isotope Research, University of Groningen, which previously housed a 2.5MeV AMS (High Voltage), has now been upgraded with a newly acquired Ionplus-MICADAS, since June 2017. The MICADAS is equipped with the Gas Interface System (GIS, Ionplus) which allows the measurements of samples in the form of pure CO<sub>2</sub> obtained either from an Elemental Analyzer (Elementar vario MICRO cube) or from the Carbonate Handling System (CHS, Ionplus). The MICADAS have been fully operational since September 2017. The radiocarbon facility is also equipped with a unique capability that will allow us to measure all the stable isotopes of pure CO<sub>2</sub> (<sup>16</sup>O<sup>13</sup>C<sup>16</sup>O, <sup>18</sup>O<sup>12</sup>C<sup>16</sup>O and <sup>17</sup>O<sup>12</sup>C<sup>16</sup>O) samples with a Tunable Infrared Laser Differential Absorption Spectrometer (TILDAS, Aerodyne Research Inc.) along with the radiocarbon measurements. This will be achieved by directing a small portion of any sample in the form of pure CO<sub>2</sub> in to the TILDAS through the GIS while the remaining sample is used for radiocarbon measurements on the MICADAS. We are currently in the process of testing this coupled system. Here, we will show the status and the performance of our new radiocarbon measurement facility.



## 2A-04 A new accelerator mass spectrometry facility for $^{14}\text{C}$ , $^{10}\text{Be}$ and $^{26}\text{Al}$ dating at Inter University Accelerator Centre (IUAC), New Delhi, India

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A new accelerator mass spectrometry (AMS) facility for the dating of  $^{14}\text{C}$ ,  $^{10}\text{Be}$  and  $^{26}\text{Al}$  radioisotopes has been setup and is operational at IUAC, New Delhi, India. The AMS facility is equipped with a 500kV Pelletron tandem ion accelerator and three automatic graphitization equipment (AGE). The facility is established with an objective to perform measurements of quality isotopic data for geochronological analysis including relevant characterizations. The AMS facility is part of upcoming Geochronology facility at IUAC where other equipment such as HR-ICPMS with femto second laser ablation, Q-ICPMS, FESEM with CL, XRD, XRF etc. are also installed. A precision of better than 1‰ in the ratio of  $^{14}\text{C}/^{12}\text{C}$  for the modern carbon sample has been achieved and the background level from dead carbon sample is  $\sim 4 \times 10^{-16}$ . The 500kV accelerator facility also has the capabilities to perform  $^{10}\text{Be}$  and  $^{26}\text{Al}$  measurements. A precision of 1% was achieved in  $^{10}\text{Be}$  measurements performed with SRM 4325. The background value with the blank sample SRM 3105a was  $\sim 8.5 \times 10^{-14}$ . A precision of about 2% has been achieved in  $^{26}\text{Al}$  measurements performed with standard sample having a known ratio of ( $^{26}\text{Al}/^{27}\text{Al}$ )  $4.694 \times 10^{-12}$ . A large number of samples have been measured by researchers from various inter disciplinary fields of research. A detailed description of AMS facility and results of measured samples as well as standards for  $^{14}\text{C}$ ,  $^{10}\text{Be}$  and  $^{26}\text{Al}$  will be presented.

## 2A-05 First year of routine measurements at the AWI MICADAS <sup>14</sup>C dating facility.

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In November 2016, the first Mini-Carbon-Dating-System (MICADAS) manufactured by Ionplus AG was delivered and installed at the Alfred-Wegener-Institute Helmholtz Centre for Polar and Marine Research (AWI), Germany. After one year of establishing the instrument and preparation methods, we started routine operation for scientific purposes in January 2018. The new facility includes a graphitization unit (AGE3) connected to an elemental analyser (EA) or a carbonate handling system (CHS), and a gas inlet system (GIS).

The facility at AWI focuses on analysing carbonaceous materials from samples of marine sediments, sea-ice, and water to investigate various aspects of the global carbon cycle. A particular emphasis will be on sediments from high-latitude oceans, in which radiocarbon-based age models are often difficult to obtain due to the scarcity of carbonate microfossils (e.g., foraminifera). One advantage of the MICADAS is the potential to analyse samples as CO<sub>2</sub> gas, which allows radiocarbon measurements on samples containing as little as 10 µgC. For example, it is possible to determine <sup>14</sup>C ages of foraminifera from carbonate-lean sediments allowing paleoclimate reconstructions in key locations for the Earth's climate system, such as the Southern Ocean. Likewise, compound-specific <sup>14</sup>C analyses receive growing attention in carbon cycle studies and require handling of small samples of typically <100 µgC.

The wide range of applications including gas analyses (e.g., foraminifera and isolated compounds), and graphite targets require establishing routine protocols for various methods including sample preparation and precise blank assessment. We report on our standard procedures for dating organic matter from sediments or water including carbonate removal, combustion and graphitization using the AGE3 coupled to the EA, as well as on the methodology applied for carbonate samples using the CHS system and the GIS.

We have investigated different sample preparation protocols and present the results using international standard reference materials (e.g., IAEA-C2  $F^{14}C = 0.4132 + 0.0052$  ( $n = 14$ );  $Ref = 0.4114 + 0.0003$ ). Additionally, we present the first results of process blanks for sediments (Eocene Messel shale  $F^{14}C = 0.0007$ ; equivalent to a conventional <sup>14</sup>C age of > 52000yr ( $n=29$ )), as well as Eemian foraminifera ( $F^{14}C = 0.005$ ; equivalent to a conventional <sup>14</sup>C age of >42700yr ( $n=98$ )). We are also presenting results of samples processed and analysed as graphite and directly as gas showing a good reproducibility irrespective of the method used.

## 2A-06 New Installation of AMS at Dongguk University

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A compact AMS system which is dedicated to measuring <sup>14</sup>C is installed in Dongguk University in Korea. The acceptance test was conducted with Oxalic acid 1, Oxalic acid 2, IAEA C7, and IAEA C8. The result of the acceptance test demonstrates the capability to radiocarbon dating with regard to <sup>12</sup>C/<sup>14</sup>C precision and background level. After the installation, the analyses performed with other types materials about dendrochronology, are presented in this paper.

## 2A-07 Introduction of the NTUAMS Lab and its performance

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The NTUAMS Lab at the National Taiwan University was established in 2013, equipped with a HVE 1.0MV Tandatron Model 4110 BO-AMS (installed in September 2012) and three graphitization lines. In October 2013, the lab had passed the quality control for sample measurement by checking international standards, backgrounds, inter-comparison samples (IRIs), known age samples, and intra-lab comparisons. In order to avoid 2Li+ interference completely, the AMS measures <sup>14</sup>C3+ mode. The graphitization systems now use TiH<sub>2</sub>+Zn+Fe method. The mean values of the measured <sup>14</sup>C/<sup>12</sup>C ratios of the AMS machine background, standard (OXII), organic carbon background (BKG - anthracite) and inorganic carbon background (NTUB - an upper Devonian limestone) in the lab during the past four years are 1.5xe-15, ~1.12xe-12, ~5xe-15 and ~5xe-15, respectively. For every batch of samples, three OXII, three BKG, NTUB and two IRIs run with samples. Up-to-date, the Lab has measured 4500 targets, including standards, backgrounds, inter-comparison samples and dating samples. A total of 160 measurements on the 19 inter-comparison samples from Glasgow University demonstrate that our dating quality is reliable. The dating samples at NTUAMS Lab include speleothems, tree-rings and various deposits (charcoals, plant remains, peats, bulk organics, shells, foraminifera shells, bones) from archaeological sites, lakes, peatlands and oceans. The main research projects in the NTUAMS Lab contain geological dating, carbon cycle in caves, karst basins and peatlands, as well as paleoclimate and paleo-vegetation reconstructions. This presentation will show the results of all inter-comparison sample runs, dating examples of stalagmites, tree rings, and peat cores carried out in the NTUAMS Lab.

## 2A-08 A new AMS laboratory at Beijing Normal University in China

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The Interdisciplinary Research Center of Earth Science Frontier (IRCESF) has been established in 2015 at Beijing Normal University (BNU), in co-operation with the Institute of Earth Environment, Chinese Academy of Science (IEECAS). A new AMS laboratory was proposed among the multiple facilities under consideration. The purchase contract of a 1MV multi-element AMS has been signed in November 2016 with HVEE, and the system will have the analytical capacities for  $^3\text{H}$ ,  $^{10}\text{Be}$ ,  $^{14}\text{C}$ ,  $^{26}\text{Al}$ ,  $^{41}\text{Ca}$ ,  $^{129}\text{I}$ ,  $^{236}\text{U}$ ,  $^{239/240}\text{Pu}$  and other actinides. The latest version of the SO-110 ion source with a 200 sample position will be equipped, from which the beam current of  $^{12}\text{C}$  has been tested to exceed 400  $\mu\text{A}$ . Both the injection system and the high energy system will provide sufficient mass-energy resolutions and bending powers for the full range of nuclide masses. Three particular features will be: (1) Double gas choices and double circulation turbo pumps at the tandem terminal. (2) The high energy spectrometer and the detection system are separated into two beam lines after the first pair of large magnetic and electrostatic analyzers: one with another identically large magnet for heavy elements, and the other with a small but large-gap magnet for measuring  $^{10}\text{Be}$  ions after the degrader foil with high ( $\geq 85\%$ ) transport efficiency. (3) For actinides, the high energy magnet and electrostatic analyzers are all capable of fast bouncing to maximize the duty cycles for their selection and detection. This custommade AMS system will be installed in early 2019 in Xi'an, at the new site of IEECAS, together with the AMS facilities of Xi'an AMS Center, and the scientific programs will be devoted to geology, environmental and earth sciences.

## 2A-09 New graphitization facility at CENA-USP

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After the installation of the first  $^{14}\text{C}$  accelerator mass spectrometry (AMS) laboratory in Latin

America at the Physics Institute of the Universidade Federal Fluminense (LAC-UFF), Brazil, collaborative research has been developed (Macario et al. 2013) with Center for Nuclear Energy in Agriculture (CENA) a low-level liquid scintillation counting  $^{14}\text{C}$  laboratory of the São Paulo University (USP). A joint effort to establish a sample preparation laboratory for AMS at CENA was performed and we now present the results of our first intercomparison. Reference material from the International Atomic Energy Agency and other secondary standards were prepared and graphitized at CENA-USP and sent to the University of Georgia (UGAMS), Georgia, USA. All the results obtained from distinct inorganic and organic samples were in very good agreement.

### References

Macario, Kita D., et al. "The Brazilian AMS Radiocarbon Laboratory (LAC-UFF) and the intercomparison of results with CENA and UGAMS." *Radiocarbon* 55.2 (2013): 325-330.

## 2A-10 Development of the gas injection system of Helsinki AMS

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The graphitization of the samples for AMS is time consuming, which limits sample throughput. Also interest in <sup>14</sup>C measurements of small samples, containing few tens of ug carbon has increased. Such small samples are very difficult to prepare using conventional graphitization facilities. Direct measurement of carbon dioxide gas bypasses the graphitization phase. The ion sources of Helsinki AMS are hybrid Cs sputter ion sources, which allow measurement of both, graphite targets and gaseous CO<sub>2</sub> samples.

In this work, we introduce our newly installed gas injection system and the automated radiocarbon measurement system of gaseous samples for high sample throughput. The sample gas handling line is designed to store and handle 12 samples and a pneumatically controlled syringe is used to inject CO<sub>2</sub> into the ion source. The first measurements of standard samples are presented and discussed.

## 2A-11 Development and validation of sample preparation methods at the Bristol Radiocarbon AMS Facility

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In January 2016, the Bristol Radiocarbon AMS (BRAMS) facility was established at the University of Bristol, with the installation and commissioning of a MICADAS AMS (developed and built by the Laboratory of Ion Beam Physics at ETH, Zurich, Switzerland). BRAMS is equipped with an AGE3 graphitization system, a gas interface system interfaced to the MICADAS' gas-capable ion source, two elemental analysers and a carbonate handling system, enabling the analysis of both organic samples and carbonates as both graphite targets and gas samples. After two years of routine operation, we report on our standard pretreatment methods for a wide range of sample types, and their validation using a range of blanks, reference materials and interlaboratory comparison samples. We also briefly report on several novel sample preparation and introduction techniques and data from the development and validation of these methods. Longer-term and repeated analyses of a range of samples reveal the reliability and repeatability of sample pretreatment, CO<sub>2</sub> generation, graphitization and analysis.

## 2B-01 ARTEMIS, the <sup>14</sup>C AMS Facility of the LMC14 national laboratory – Status report

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The LMC14 National Laboratory is holding the <sup>14</sup>C ARTEMIS AMS facility and the associated benches for <sup>14</sup>C sample preparation. ARTEMIS is dedicated to high precision <sup>14</sup>C measurements. It routinely measures over 4500 samples a year for the French research institutions. ARTEMIS is a 3MV NEC 9SDH-2 Pelletron. It was installed in 2002 in Saclay and gave its first date in April 2003. Since 15 years of C14 dating, the quality control of the measurement is a daily concern.

Quality control procedures are applied in each step of the sample route, from the preparation to the data analysis. Routine procedures are applied to the sample preparation according to the type and size of each sample. An accurate AMS facility tuning procedure is implemented in order to control the carbon beam evolution through the optical elements of the beam line. Each unknown sample is measured with accompanying samples, international standards, blanks and intercomparison samples, which give a powerful set of data to control the quality of each measurement. These quality control samples are consistently chosen according to the type, the species, the size and the period of production of the unknown sample. An homemade database has been created to store the sample information and the evolution of the control samples. This database is the main tool to control the quality of the <sup>14</sup>C AMS measurement in the LMC14 National Laboratory.

In addition to quality control procedures and tools, the LMC14 laboratory participated to the sixth International Radiocarbon Intercomparison, named SIRI. This radiocarbon laboratory quality assurance programme gives the possibility of comparing every SIRI radiocarbon date coming from ARTEMIS to the SIRI consensus values calculated on all the dates coming from the laboratories involved in the SIRI programme. Statistical tests are then used to appreciate the quality of the preparations and measurements made by the LMC14 national laboratory.

## 2B-02 Progress in XCAMS at Tianjin University

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A new eXtension of the Compact Accelerator Mass Spectrometer (XCAMS) for <sup>14</sup>C, <sup>10</sup>Be and <sup>26</sup>Al manufactured by the National Electrostatics Corp. (NEC) has been installed successfully at Tianjin University in October 2017. As an initial testing result, a sensitivity of 4.4E-16 for <sup>14</sup>C/<sup>12</sup>C, 6.9E-15 for <sup>26</sup>Al/<sup>27</sup>Al and 3.8E-15 for <sup>10</sup>Be/<sup>9</sup>Be was respectively achieved. Hundreds of real samples have already been measured by the XCAMS system based on the sensitivities. The results show that the condition of this machine is very optimistic for the nuclides AMS measurement of <sup>14</sup>C, <sup>10</sup>Be and <sup>26</sup>Al, but some further improvements seem still possible. In this paper, the performance of the three AMS modes and measurement results are discussed, and the possible meaningful improvements and future perspectives will be presented.

## 2B-03 Progress report and methodical improvements in the radiocarbon analysis at the CologneAMS facility

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The radiocarbon laboratory of the CologneAMS facility at the University of Cologne was established in 2010 and is since then run as a collaborative initiative of geologists and nuclear physicists. The laboratory performs own research and methodical developments focusing on the analysis of small samples including compound-specific <sup>14</sup>C analysis of lipid biomarkers and CO<sub>2</sub> samples. It also provides dating service for researchers from various fields including environmental sciences, quaternary geology, soil science, and archaeology, as well as for customers from the industry and the public domain.

Five years after reporting our pre-treatment procedures and first results for reference and standard materials (Rethemeyer et al., 2013), we now summarize our analytical activities. Our progress report includes the on-going, long-term monitoring of blanks and summarizes efforts for the reduction of sample contamination during the various stages of sample preparation of different sample types (e.g. organic samples, carbonates, bone collagen). Different tin boats/capsules were used for the combustion of C-rich, C-poor, and liquid samples in the elemental analyzer. We report blanks for normal sample sizes in the range of 150 to 1000 µg C that are prepared with the automated graphitization equipment (AGE; Ionplus, Switzerland). Since the installation of a gas injection system (GIS; Ionplus, Switzerland) small samples (<150 µg C) are measured directly as CO<sub>2</sub> at our HVE 6 MV Tandetron AMS (for more details see presentation by Melchert et al.).

In addition to such routine techniques, we perform compound-specific <sup>14</sup>C analysis on individual organic compounds isolated via gas chromatography. Blank levels of this complex isolation procedure have been continuously monitored with standards of modern and (close to) fossil <sup>14</sup>C concentration since 2011. The isolated compounds are dissolved in an organic solvent and their removal is a critical step in the purification procedure. We tested different evaporation techniques with regard to effectiveness and possible addition of extraneous carbon. A further development of the last five years is a stainless steel cartridge filled with a molecular sieve (zeolite; Wotte et al., 2017a, b) which allows for in situ sampling and subsequent <sup>14</sup>C analysis of CO<sub>2</sub> samples. We present process blanks obtained in laboratory tests as well as in field studies.

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## 2B-04 Status report of the Trondheim radiocarbon laboratory

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The 1 MV AMS system at the National Laboratory for Age Determination at NTNU was installed in 2009 (Nadeau et al. 2015). While the AMS system has not been changed after installation, related processes in the sample treatment were improved and adapted to optimize the workflow in the laboratory.

We will present the current cleaning protocols for the most common samples types in our laboratory, such as charcoals and bones. We will also discuss our newly acquired automated combustion/reduction system which increased our sample preparation capacity significantly. The elemental analyzer for sample combustion provides carbon and nitrogen contents of our radiocarbon samples. The system also interacts with our database system, which allows us to easily keep track of the samples throughout the different processes from entering the laboratory to the completion of results. Data reduction will also be discussed.

The commissioning of a Thermo isotope ratio mass spectrometer (Delta V Advantage) equipped with Elemental analyzer and gas multiport system extends our measurements capabilities with stable isotope measurements (<sup>13</sup>C, <sup>15</sup>N and <sup>18</sup>O).

Nadeau et al., Nucl. Instr. Meth. B, 361 (2015) 149-155

## 2B-05 On the quality of SUERC radiocarbon measurement

Stewart Freeman<sup>1</sup>, Sheng Xu<sup>1</sup>, Richard Shanks<sup>1</sup>, Pauline Gulliver<sup>1</sup>, Cameron McIntyre<sup>1</sup>, Derek Fabel<sup>1</sup>, Brian Tripney<sup>1</sup>, Elaine Dunbar<sup>1</sup>, Philip Naysmith<sup>1</sup>, Gordon Cook<sup>1</sup>

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The SUERC Radiocarbon Laboratory prepares samples for mass spectrometry in the SUERC AMS Laboratory, which is equipped with three <sup>14</sup>C spectrometers.

Measurements on the established NEC 250 kV single-stage and NEC 5 MV tandem accelerator mass spectrometers are subject to negligible external uncertainty beyond Poisson statistics, permitting radiocarbon dating with appropriate precision by the acquisition of sufficient <sup>14</sup>C counts: 3‰ measurement is expeditious and typical, but higher-precision analyses are also undertaken. The inter-groups quality assurance programme includes VIRI T & SIRI N humic acid secondary standard samples (these are the same reference material) processed and analysed as a proxy for organic material analysis. Secondary standard results bracketing the last thousand AMS measurements are normally distributed with 2.8‰ average uncertainty and 2.9‰ relative standard deviation, i.e. of the age-converted 23.7 years average uncertainty, all but 1 year is counting-statistics derived. This demonstrates near-perfect analysis, in that it is not possible to improve upon Poisson statistics, and confirms the validity of our use of off-line  $\delta^{13}\text{C}$  measurement for age correction.

The third spectrometer is the recently installed NEC PIMS instrument, that is the first of its type. This permits comparison of conventional AMS with the new radiocarbon mass spectrometry.



## 2B-06 ENEA <sup>14</sup>C laboratory update

Chiara Telloli<sup>1</sup>, Antonietta Rizzo<sup>1</sup>, Paolo Bartolomei<sup>1</sup>

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We report on the status and capabilities of the ENEA <sup>14</sup>C Laboratory. After a technical evaluation, ENEA decided to move the entire laboratory - including equipment and personnel - in a new location at the main headquarters in Bologna (Italy). The laboratory was definitely closed in November 2014 and all experimental activities have been stopped. The construction works for the new location, after the acceptance of the engineering and architectural plan, has been initiated in January 2015. In April 2015 the new facility in Bologna was ready and we were authorized to start the packing of the equipment and of the materials of the <sup>14</sup>C laboratory. Up to now the re-location has been completed and since the beginning of September 2015 we will start to install all the equipment of the lab, including the prototype of the newly designed combustion system (Reiller et al., 2014).

The double chamber combustion cell will be directly set up within the pipeline of the existing combustion system so the possibility to have pyrolysis and/or oxidation will be completely embedded in the original design of the ENEA combustion system.

During the re-location period the opportunity for improving the instrumentation of the laboratory has been taken by procuring a new equipment for the combustion of organic based samples to add some functionality for the recovery of the C content (CO<sub>2</sub>).

The new configuration allowed to analyze samples from biobased field to nuclear technology applications.

Reiller, P.E., Bucur, C., Comte, J., Heisbourg, G., Lebeau, D., Rizzato, C., Rizzo, A., Vecernik, P. 2014. Annual progress report on WP4 – 2014 – (D4.2). Carbon-14 Source Term (CAST) Project, N° 604779, CAST - D4.2.

## 2B-07 The Penn State University AMS <sup>14</sup>C Facility: Initial Operation and Performance

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The Penn State AMS <sup>14</sup>C Facility (PSUAMS) provides radiocarbon measurements on carbon-bearing materials spanning the last 45,000 years running a National Electrostatics Corporation 500kV 1.5SDH-1 Compact Accelerator Mass Spectrometer. The PSUAMS facility is supported by a preparation lab capable of processing wood, charcoal, pollen, marine and terrestrial shell, speleothems, hair, teeth, and bone collagen. Our research emphasizes human-earth interactions with special focus on integrating human and environmental histories through the development of high-resolution chronologies. We aim to foster the development of inter-disciplinary archaeological research and greater articulation with the earth and environmental sciences. The NEC 1.5 SDH-1 Pelletron Accelerator runs on a 40-sample MC-SNICS ion source with modified with a spherical ionizer operating at high cathode voltage (7.4 V) and injector modifications include the addition of a 2nd einzel lens, an increased ion source voltage to 53.5 kV combined with a redesigned large gap injector magnet. These alterations allow for analytical error in the 2–3‰ range for near-modern samples under currents of 120-150 μA of <sup>12</sup>C-. Here we report progress during the first two years of operation in: sample processing and throughput; process backgrounds for organics, bone and carbonates; and, replicability of secondary standards.

## 2B-08 ANSTO Radiocarbon Laboratory: A status report

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Dedicated radiocarbon sample processing and AMS target preparation laboratories were established at ANSTO in the early 1990s at the time of commissioning the ANTARES accelerator (Tuniz et al 1995). They have now evolved into a suite of specialised areas that include facilities for physical preparation, chemical pre-treatment, combustion or hydrolysis, CO<sub>2</sub> characterisation (including IRMS determinations) and a clean area for graphitisation and cathode pressing. A separate area is dedicated to the processing of samples older than 30 ka by stepped combustion. The laboratory utilises various physical and chemical methods for sample pre-treatment (Hua et al., 2001). We present an update of our procedures for processing samples including bones, wood, charcoal, groundwater, carbonate samples for radiocarbon analysis. A new semi-automated acid-alkali-acid pre-treatment system for routine charcoal samples preparation has also been developed in-house.

Reducing the required radiocarbon sample size continues to be a development priority –currently we are able to handle and reliably measure samples containing as little as 5 µg of carbon. A set of specialised miniaturised conventional and laser-driven graphitisation furnaces, together with special handling hardware is now in use, and are outlined in this presentation.

All four AMS machines (ANTARES – 10 MV FN, STAR – 2 MV HVEE Tandetron, VEGA – 1 MV NEC Pelletron and SIRIUS – 6 MV NEC Pelletron) in ANSTO's Centre for Accelerator Science (CAS) are capable of high-precision radiocarbon analysis (~0.3%). Of these, STAR and VEGA are used for routine sample measurements, whereas ANTARES is dedicated to ultra-small carbon samples, typically less than 50 µg C. In this paper, we present a status report of our equipment, systems reproducibility tests, as well as routine laboratory quality controls, including blanks determinations for various chemical procedures and blank correction procedure.

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## 2B-09 Status report of the Aarhus 1MV HVEE Tandetron

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Here a status report of the 1MV multi-element AMS system installed at the Aarhus AMS Centre, Department of Physics and Astronomy. Long-term trends and performance of known age samples are presented. Recently a new immersion lens (design from University of Ottawa) has been installed. Initial test have shown very stable conditions for high precision <sup>14</sup>C measurements and removal of previously reported <sup>13</sup>C/<sup>12</sup>C current dependencies.

## 2B-10 50 years of the Gliwice Radiocarbon Laboratory (AD 1967-2017)

Natalia Piotrowska<sup>1</sup>, Danuta J. Michczyńska<sup>1</sup>, Adam Michczyński<sup>1</sup>, Fatima Pawełczyk<sup>1</sup>, Sławomira Pawełczyk<sup>1</sup>, Jacek Pawlyta<sup>1</sup>, Anna Pazdur<sup>1</sup>, Barbara Sensuła<sup>1</sup>, Andrzej Z. Rakowski<sup>1</sup>, Konrad Tudyka<sup>1</sup>, Alicja Ustrzycka<sup>1</sup>

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The Gliwice Radiocarbon Laboratory was established by Prof. Włodzimierz Mościcki, a pioneer in the <sup>14</sup>C measurements with gas proportional counters, and subsequently headed by Prof. Mieczysław Pazdur (in years 1977-1995) and Prof. Anna Pazdur (1995-2016).

The <sup>14</sup>C method was the foundation of today's Department of Radioisotopes. As more scientific challenges appeared, the development of other dating methods: luminescence (TL and OSL), <sup>210</sup>Pb, <sup>137</sup>Cs was undertaken, as well as stable isotope research of hydrogen, carbon, nitrogen and oxygen. Within 5th Framework Programme of the European Commission the Department gained a Centre of Excellence status: Gliwice Absolute DAting Methods (GADAM) in 2003.

Since AD 2000 four EU projects have been realised:

1. CONTINENT: High-resolution continental palaeoclimatic record in the Lake Baikal (2001-2004)
2. GADAM Centre: Centre of Excellence Gliwice Absolute DAting Methods Centre (2003-2006)
3. ISONET: 400 years of annual reconstruction of European climate variability using high resolution isotopic network (2003-2006)
4. ATIS: Absolute Time scales and Isotope Studies for investigating events in Earth and human history (2006-2010)

Other significant international projects:

1. CLIMPOL: Climate of northern Poland during the last 1000 years: Constraining the future with the past (Polish-Swiss Research Programme, 2011-2015)
2. PARAD: PeAt bog Records of Atmospheric Dust fluxes – Holocene palaeoenvironmental and paleoclimatic implications for Southern South America (ANR, France, 2011-2015)
3. Bilateral cooperation with University of Liege on reconstruction of air pollution in Europe recorded in sedimentary and biological archives (Polish-Walloon Cooperation, since 2006)
4. INTIMATE: INTegrating Ice core, MARine and TERrestrial records - 60,000 to 8000 years ago (COST Action, 2011-2014)
5. Tree-ring climate reconstruction (FWF Austrian Science Fund, 2013-2015)

Fifteen projects funded at the national level have been coordinated in the Laboratory, and the staff actively participated in dozens of such projects. Scientific cooperation resulted in more than two hundred of publications, at average 11 per year in the last decade, most of them in indexed international journals.

The current equipment of Gliwice Radiocarbon Laboratory include:

1. AMS Laboratory (responsible: Natalia Piotrowska):
  - a. Automated graphitisation equipment AGE-3 (IonPlus AG)
  - b. Vacuum line for carbonate decomposition and CO<sub>2</sub> purification
  - c. Oxygen-flow line with infra-red oven for stepped-combustion
2. LSC Laboratory (responsible: Adam Michczyński):
  - a. Two Quantulus 1220 spectrometers
  - b. Two ICELS spectrometers
  - c. Prototype multi-chamber scintillation spectrometer for rapid measurements of low radioactivities
  - d. Three vacuum lines for sample combustion and conversion to benzene
3. Mass Spectrometry Laboratory:
  - a. Continuous-flow IRMS IsoPrime
  - b. Elemental analyser for analysis of organic samples
  - c. MultiFlow device for preparation of water and carbonate samples

At present state the Gliwice Radiocarbon Laboratory carries out yearly ca. 450 AMS dates, 150 LSC measurements and a few hundred of stable isotope determinations.

The GADAM Centre is managing editorial work for the “Geochronometria”, an open-access multi-disciplinary journal on methods and applications of absolute chronology. Since 2005 “Geochronometria” has been indexed in Web of Science (IF(2016)=1.426).

The GADAM Centre has been organising a number of conferences, workshops and training schools. The next 13th international „Methods of Absolute Chronology” conference will take place in 2019.

## 3A-01 Determination of biogenic fraction in Polyethylene plastic bags: monitoring the production process

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For environmental reasons, the production of renewable plastics is an important issue worldwide. Brazil is the greatest producer of sugar cane in the world with an annual production of 739,300 thousand metric tons. Sugar cane based products, including bioplastics such as polyethylene (PE), constitute an important slice of the country economy but the final producers are often small home-based industries. In Brazil, there is not yet a national regulation for monitoring the industrial process or for verifying the biogenic fraction of what is already on the market. The ASTM 2016 is applied, stating the only technique capable of distinguishing identical chemical compounds of biogenic or fossil origin is the measurement of radiocarbon concentration in the samples. Despite the installation of the first <sup>14</sup>C-AMS facility in Latin America, the Radiocarbon Laboratory of the Fluminense Federal University (LAC-UFF) in 2009 (Macario et al. 2013), what have greatly contributed to increasing the number and quality of research developed in Brazil, the technique is still unaffordable for most small industries. In the specific case of PE made from sugar cane based ethanol, carbon stable isotopes ratios can serve the purpose. In this work, we compare conventional mass spectrometry for measurement of stable isotopes ratio and Accelerator Mass Spectrometry for radiocarbon measurement, as tools for monitoring and fiscalization of the green PE production in Brazil.

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## 3A-02 Evolution of IERs

Chiara Telloli<sup>1</sup>, Antonietta Rizzo<sup>1</sup>, Stefania Bruni<sup>1</sup>, Alessandro Gessi<sup>1</sup>, Giuseppe Marghella<sup>1</sup>, Lorenzo Moretti<sup>1</sup>, Paolo Bartolomei<sup>1</sup>, Alfredo Luce<sup>1</sup>

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**Introduction:** Ion exchange resins (IERs) are commonly used in PWR nuclear reactors as filters for <sup>14</sup>C impurities. Their efficiency, both as filters and as waste containers, is strictly connected with their morphology. The preservation of the spherical shape of both cationic and anionic resins in time, in use or just stocked, is one of the key parameters for their quality assessment and for the evaluation of the potential release of radioisotopes during the storage condition. In the present work, we investigated the change in the morphology of the IERs during storage periods and the content of <sup>14</sup>C in their volatile and non-volatile components upon natural ageing and artificial degradation.

**Methods:** The IERs three-dimensional and symmetric shape has been studied by means of SEM microscopy, on new and aged specimens, in order to assess the quality of the resins after 10 years of disposal and contribute to the understanding of the mechanism of radiocarbon release. The <sup>14</sup>C content has been measured by the means of a tailored system, designed and implemented at the ENEA laboratory.

### 3A-03 Synthesis of Poly(arylene ether)s from Biomass-derived Isosorbide and Characterization of Biomass-content using Accelerator Mass Spectrometry (AMS)

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Generally, petro-based plastics have been produced and consumed over the past decades and can be found everywhere because of their benefits. However, these petro-based plastics have common disadvantages that using bisphenol-A (BPA): an endocrine disruptor.

Recently, interests in bioplastic as an alternative to BPA-based plastics have been increased by using biomass resources. The renewable monomer isosorbide (ISB) is one of candidates replacing BPA-based synthetic polymers produced from fossil resources. Also, this bio-based monomer has thermal-stability as well as high molecular rigidity and good mechanical properties which cannot be found in conventional synthetic biopolymers.

Herein, we introduced and investigated ISB-based poly(arylene ether)s via solution polymerization for high performance and sustainable super engineering bioplastics which derived from biomass resources. Also, we confirmed quantitative contents of biomass in polymers with <sup>1</sup>H Nuclear Magnetic Resonance (NMR) and Accelerator Mass Spectrometry (AMS).

### 3A-04 Use of the radiocarbon activity deficit in vegetation as a sensor of CO<sub>2</sub> soil degassing: example from la solfatara (naples, southern italy)

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Soil CO<sub>2</sub> flux measurement is a key method that can be used to monitor the hazards in an active volcanic area. In order to determine accurately the variations of the CO<sub>2</sub> soil emission we propose an approach based on the radiocarbon (<sup>14</sup>C) deficiency recorded in the plants grown in and around the Solfatara (Naples, Italy). For almost two years, twice a year, we sampled selected poaceae plants in 17 defined sites around the Solfatara volcano. <sup>14</sup>C measurements by liquid scintillation counting (LSC) were achieved on the grass samples. The <sup>14</sup>C deficiency determined in the sampled plants, compared to the atmosphere <sup>14</sup>C activity, ranged from 5.0 to 50.3%. We then compared the proportion of magmatic CO<sub>2</sub> inferred to the instantaneous measurements of CO<sub>2</sub> fluxes from soil performed by the accumulation chamber CO<sub>2</sub> degassing measurement at the moment of the sampling at each site. The determination of the plants <sup>14</sup>C deficiency provides an estimate of the CO<sub>2</sub> rate within a few square meters, integrating CO<sub>2</sub> soil degassing variations and meteorological incidences over a few months. It can therefore become an efficient bio-sensor and can be used as a proxy to cartography CO<sub>2</sub> soil degassing and to determine its variations through time.

## 3A-05 Sampling $^{14}\text{CO}_2$ as a tracer for hydrocarbon biodegradation: Making AMS target material in the field

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The accidental release of hydrocarbons into the environment is a common source of contamination around the world. In certain locations such contamination is best mitigated by natural source zone depletion (NSZD), or in situ biodegradation. NSZD is an appealing option rather than potentially intrusive remediation methods such as removal or pump and treat. This is particularly relevant for remote locations, sites with minimal risk of human interaction, or ecologically sensitive environments. In the community of Old Crow in Northern Yukon, diesel contamination has been documented in the ground sediments at the Old Crow Health Centre. NSZD is being investigated for its viability at this site and is considered to be the best option due to the remote nature of this community and the presence of permafrost approximately 2 metres below the ground surface.

To determine the viability of this process rather than other remediation efforts in Old Crow, the attenuation rate of these contaminants must be quantified by analysis of the radiocarbon content of  $\text{CO}_2$  emissions from the soil. Radiocarbon is present in all living biomass, but due to its relatively short half life of 5730 years it is absent in hydrocarbons of geologic age. The use of radiocarbon provides a two end-member system for the apportionment of soil  $\text{CO}_2$  emissions at contaminated sites.  $\text{CO}_2$  samples traditionally have been brought to the laboratory as soil gas in 250 mL glass septum bottles where  $\text{CO}_2$  is cryogenically isolated before the carbon is graphitized. Sample transport in this state, combined with considerable laboratory preparation before analysis, have proven to be costly for shipping and analysis, and a constraint to such field programs. Here we present results of field tests at a contaminated site at Old Crow, Yukon following the successful deployment of a new in-field method for rapid  $\text{CO}_2$  extraction from soil gas and precipitation as  $\text{BaCO}_3$  by injection directly into 4.5 mL vials containing barium hydroxide solution. In this study approximately 65 samples were collected on site in under one week. The resulting stable  $\text{BaCO}_3$  samples were easily transported to the laboratory and were effectively ready for direct analysis by accelerator mass spectrometry (AMS) in the Lalonde AMS Laboratory. Final radiocarbon results were obtained from this study within one week of returning from the field.

## 3A-06 <sup>14</sup>C and Deep Sea Volcanic Processes: the Mid Atlantic Ridge at 14° North

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We present new <sup>14</sup>C measurements related to the emplacement of unique CO<sub>2</sub> rich submarine lava flows found at 14° North on the Mid-Atlantic Ridge, called “popping rocks” because the vesicles pop when brought to the surface from the seafloor. They are the most CO<sub>2</sub> rich Mid Ocean Ridge basalts (MORB), with implications for mantle volatile abundances and the terrestrial carbon budget. Popping rocks were recovered in situ using the submersible Alvin on R/V Atlantis in 2016. Preliminary measurements by crushing in vacuo, to release gases from the vesicles, show <sup>14</sup>C/<sup>12</sup>C values below blank level (> 50 Ka age equivalent), demonstrating that there is undetectable influence of modern seawater or atmosphere. This is consistent with mantle δ<sup>13</sup>C values in the CO<sub>2</sub>, and places new constraints on the processes by which atmospheric noble gases are introduced into MORB. Atmospheric noble gas isotopic signals in MORB have been enigmatic for decades, and could be explained by introduction of air during sample handling, seawater interaction, or by melting of hydrothermally altered ocean crust.

New <sup>14</sup>C measurements on planktonic foraminifera from sediment cores that directly overlay lava flows, near the popping rock area (using Alvin push cores), provide new constraints on emplacement ages and will be presented. Despite collection depths below the carbonate compensation depth, both planktonic and benthic foraminifera are extremely well preserved. Preliminary analysis of planktonic foraminifera assemblages from sediments which overlay adjacent lava flows indicate that these flows are great than 9,000 years BP in age. These data demonstrate that <sup>14</sup>C can provide unique tracer and geochronological information on seafloor volcanic processes.



## 3A-07 Online compound specific Radiocarbon analysis (CSRA): Analytical challenges

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With the new developments in accelerator mass spectrometry (AMS) and online <sup>14</sup>C measurements, it is now possible to measure samples as small as 5 µgC. However, it is very important to test the reproducibility of data at small sample size and do proper blank assessments for contamination correction. Low abundance and multiple-step during purification and isolation procedures are the most demanding analytical challenges for compound specific Radiocarbon analysis (CSRA).

Most of the compound specific samples have been measured using vacuum lines with samples either in ampoule cracker systems or as graphite targets. The vacuum line technique is time and money consuming. The direct coupling of Elemental Analyzer (EA) to the gas ion source reduces both time and money investment and, in addition, handling steps, which results with smaller carbon blank and better recovery.

Several studies have shown the feasibility of online measurements on small (<100 µgC) and ultra-small (< 10 µgC) samples in environmental and carbon cycle applications. Our main motivation was to test the <sup>14</sup>C limits of the instrumental and methodological capabilities for dating small compounds (10-50 µgC) in paleoclimate and paleoceanography applications for which high precision measurements are required. In order to test the precision, accuracy and reproducibility of processed compounds we show results of reference materials and of three classes of compounds extracted from sediment cores. We present long-term (3 years) measurements of method blanks and standards for different preparation methods using the EA-AMS setup at ETH-Zurich to document the reproducibility of different preparation procedures for some compounds.

Results from online measurements show that values from processed and non-processed blanks are very similar to the values obtained from offline measurements. This outcome shows that online measurements using EA-AMS is as promising as offline measurements for CSRA. However, the user of CSRA should consider and be aware of the magnitude of uncertainty to provide meaningful information and avoid misinterpretation of data in research applications. Regardless of the application, duplicate measurements are important in the case of small compounds with low concentration, as the magnitude of the uncertainty can be very high after error propagation. To present the corrected data, we developed a Matlab code using the model of constant contamination. Our results show that the conservative value to produce relatively high precision <sup>14</sup>C data in low concentration samples (with age >20 ka) with acceptable errors (<10%) and high reproducibility starts with the mass of 50 µg C for the methods presented in this work.



### 3A-08 Compound specific radiocarbon analysis (CSRA) of fatty acids and n-alkanes in a city aerosol sample

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Compound specific radiocarbon analysis of individual fatty acids and n-alkanes were conducted for a city aerosol sample using preparative capillary gas chromatography (PCGC) and accelerator mass spectrometry (AMS). Sample size for radiocarbon determination ranged from 50–300 µg C. Blank carbon introduced to samples during PCGC isolation was evaluated. Radiocarbon analysis of C16-C25 fatty acids showed modern Delta<sup>14</sup>C values, suggesting that the acids were from living higher plants or possibly from marine organisms. Lower Delta<sup>14</sup>C values were obtained for n-alkanes, which might reflect sources of fossil fuel.

### 3A-09 Compound specific radiocarbon analysis at the AWI-MICADAS facility

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Compound specific radiocarbon analysis (CSRA) of n-alkanes, n-alkanoic acids or other biomarkers is a powerful, yet challenging tool to determine the cycling and fate of organic carbon in environmental settings. For example, the radiocarbon ages of long chain n-alkanoic acids of terrestrial origin extracted from high latitude marine sediments aid to decipher the impact of climate change on the carbon cycle, and vice versa.

The quality of Interpretations made from radiocarbon analysis highly depend on the precise determination of and the correction for external carbon contamination incorporated during sample preparation and measurement. Since recent advances in accelerator mass spectrometry (AMS) and direct gas measurements made it possible to analyze samples as small as 5 µgC, even smallest non-confined and corrected contaminations could impair <sup>14</sup>C results and associated interpretations significantly. CSRA requires laborious and demanding wet chemical extraction and purification steps followed by preparative gas chromatography for the isolation of individual compounds and is thus prone to incorporation of external carbon. Traditionally, isolated compounds were combusted in evacuated quartz tubes and produced CO<sub>2</sub> was purified on vacuum lines for subsequent <sup>14</sup>C analysis. A recent study calculated the amount of carbon contamination for n-alkanoic acids prepared for <sup>14</sup>C analysis to be 5.0 ± 0.15 µgC (Sun et al. in prep) highlighting the necessity for blank carbon corrections and a modified preparation protocol to reduce the contamination for very small CSRA samples.

Here we report on a modified analytical procedure replacing the time-consuming vacuum line preparation by direct combustion of analytes using an elemental analyzer (EA). The EA is directly connected to the AMS (Mini Carbon Dating System, MICADAS, Ionplus) via a gas interface system (GIS) enabling the direct and fast (~4 samples per hour) <sup>14</sup>C analysis of purified CO<sub>2</sub> generated from the analytes. Immediately prior to the EA combustion isolated compounds were transferred in solution (1 µgC/µl DCM) into 50 µl liquid tin capsules, the solvent was carefully evaporated at 35 °C on a hot plate and tin capsules were tightly packed and added to the EA sequence. Initial results of n-alkanoic acids extracted and processed as fatty acid methyl esters (FAMES) from a fossil sediment (Messel Shale) and modern apple peel (collected in 2013) show a significant blank reduction to 1.7 ± 0.2 µgC. The data show that the blank reduction is directly associated to the change from vacuum line preparation to EA combustion. The blank contributions for other compound classes (e.g., n-alkanes) are currently being evaluated alongside the validation of this method by processing mixtures of model compounds of different classes with known and varying <sup>14</sup>C concentration.

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### 3A-10 Evidence for microbial assimilation of ancient organic carbon during moraine-debris weathering in Glacier foreland, Ny-Ålesund: Implications from radiocarbon analysis of phospholipid fatty acids (PLFAs)

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The total global inventory of organic carbon (OC) contained in sedimentary rocks is estimated at roughly 10<sup>9</sup>Gt C, more than is present in other surface reservoirs, such as oceans, soils, and biomass (Hedges and Oades, 1997). Glacier retreat in high latitude regions is one of typical environmental changes under warming Arctic climate and OC in sedimentary rock derived debris was strongly oxidized and decomposed by microbe during weathering, this novel carbon cycle of refractory OC reservoir emerged after Glacier retreat should be investigated. Here moraine-debris consisting immature soil samples until soil depth of 100cm were collected in a successional glacier foreland in Ny-Ålesund, Spitsbergen island, Norway. We measured <sup>14</sup>C contents and δ<sup>13</sup>C values of soil respired CO<sub>2</sub>, soot-black carbon, bulk OC and microbial phospholipids fatty acids (PLFAs) in moraine-debris consisting immature soil after Glacier retreat to investigate recently microbial decomposed carbon sources. The PLFAs were extracted from soils and then purified using preparative capillary gas chromatograph (PCGC) for compound-specific radiocarbon analysis. From isotopic mass balance approach, PLFA-<sup>14</sup>C data were used for estimation of source-apportionment for two carbon sources from modern plant derived OC and ancient preaged OC, which probably derived from <sup>14</sup>C dead OC accumulated in the geological time scale. Our results showed microbial PLFA-<sup>14</sup>C data provide strong tracer of novel organic carbon dynamics after on-going glacier retreat under warming Arctic climate.

### 3A-11 Purification of conchiolin for radiocarbon and stable isotope analysis

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Information obtained from oyster shell analyses, and in particular radiocarbon and stable isotope analysis, has been influential in understanding past events, including sea-level changes, land-use, and coastal ecosystem evolution. Frequently, radiocarbon and stable isotope studies of oyster shell rely on the inorganic, carbonate fraction of the shell, while the mineral-bound organic matrix, conchiolin, is less widely targeted. Conchiolin, which is composed predominately of polysaccharides and proteins, retains information on mollusk dietary sources and potentially on the local environment; the latter possibly resulting from the adsorption of organic molecules during the formation of the mineral-organic shell matrix. Because conchiolin facilitates mineral precipitation and is integral to the mineral-organic composite matrix of mollusk shells, the organic molecules are incorporated into the mineral structure, relatively isolated from degradative forces, in a process that aides the preservation of biogeochemical signals. In this study, we compare 4 different methods for the isolation of conchiolin from eastern oysters (*Crassostrea virginica*) for radiocarbon and stable-carbon isotope analysis: (1) low-temperature combustion, (2) wet oxidation, (3) acid dissolution, (4) and acid dissolution aided by dialysis. Stable carbon and radiocarbon isotope analyses were performed on the isolated conchiolin and on the soft tissue. We demonstrate that the isolation method affected the stable carbon and radiocarbon signals of the isolated material. The products of all methods were enriched in  $^{13}\text{C}$  relative to the soft tissue, and with the exception of the low temperature combustion method, all methods produced material that was depleted in  $^{14}\text{C}$  relative to the soft tissue. While low-temperature combustion produced material with a  $\Delta^{14}\text{C}$  signal comparable to that of the soft tissue (-11.90‰ and -10.10‰, respectively), the  $\delta^{13}\text{C}$  signal of the combustion product was enriched in  $^{13}\text{C}$  by roughly 20‰ relative to the tissue. This method produced the highest  $\delta^{13}\text{C}$  and  $\Delta^{14}\text{C}$  signals out of the methods studied. On the other hand, the acid-dissolution method produced conchiolin with the lowest  $\delta^{13}\text{C}$  and  $\Delta^{14}\text{C}$  signals. The  $\delta^{13}\text{C}$  of conchiolin produced by acid dissolution was most similar to the  $\delta^{13}\text{C}$  of the soft tissue (-23.63‰ and -25.42‰, respectively), however this method produced conchiolin that was significantly depleted ( $\sim 45\%$ ) in  $^{14}\text{C}$  relative to the soft tissue. The  $\Delta^{14}\text{C}$  signals of conchiolin isolated by wet oxidation and dialysis-aided acid dissolution methods were statistically indistinguishable but were depleted in  $^{14}\text{C}$  relative to the tissue by 15 – 21‰. On the other hand, the wet oxidation and dialysis-aided acid dissolution methods produced conchiolin that was enriched in  $\delta^{13}\text{C}$  relative to the tissue by 5.1 – 7.6‰. The four methods also produced variable carbon yields relative to the starting shell mass. The highest carbon yield was observed for the low-temperature combustion, 0.2%, while the acid dissolution method produced material with the lowest carbon content 0.05%. The carbon yields from the wet oxidation and dialysis-aided acid dissolution methods were comparable at 0.1% and 0.07-0.09% respectively. The observed differences in isotopic signals are likely linked to differences in the composition of the material being analyzed, as a function of the isolation method.

## 3A-12 Correction model for complex deep marine environments at cold seep vents off Tokai, Japan: Seawater DIC acquisition by *Calypptogena* sp. bivalves

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Shells and corals are often used as proxies for sea surface temperature reconstructions in paleoclimatology. These species utilise the dissolved inorganic carbon (DIC) in seawater making it suitable for analysing ocean circulation through the measurement of radiocarbon <sup>14</sup>C. It is also possible to estimate the age of the shell through analysing the growth increments within the shells and radiocarbon <sup>14</sup>C dating. Yet correction models in deeper marine environment remains complicated due to the multiple variables that must be considered, which include problems such as carbon sinks, ocean current flux and dead carbon effect from seafloor vents.

This study proposes a correction model at a depth of 600m at the Daini Tenryu Knoll off Tokai, Japan, which is a renowned region for recurrent M8 class earthquakes that occur very 100-150 years. Due to the regular tectonic activity and the presence for rich methane hydrate layers below the seafloor (Ashi et al., 2002, Otsuka et al., 2015), the fault regions are common with cold seep vents, which accommodate various sized colonies of *Calypptogena* sp. bivalves. We propose a method for developing such a correction model in this complex environment and to determine if the *Calypptogena* sp. is affected by the methane from beneath the seafloor or from biogenic origins. Radiocarbon age of seawater DIC depth profiles and bivalve shell measurements conducted using a Single-Stage Accelerated Mass Spectrometer (AMS) at the AORI, The University of Tokyo (Yokoyama et al., 2007).

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### 3A-13 Origin of water masses in the western Coral Sea based on radiocarbon

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The South Pacific Ocean contributes to the global carbon cycle by storing CO<sub>2</sub> in Antarctic Intermediate Waters (AAIW). The path of the AAIW following its circulation in the South Pacific gyre has been inferred from salinity and oxygen measurements, but few other geochemical tracers have been measured. Here, we use <sup>14</sup>C to identify the origin of water masses in the western Coral Sea, off Queensland, North-East Australia, and compare our measurements with data acquired during the World Ocean Circulation Experiment (WOCE). Subsurface and intermediate waters circulate from the South Pacific to the Coral Sea via the South Equatorial Current (SEC), with outflows to the Tasman Sea to the south and the Solomon Sea to the north. Surface and subsurface waters in the Coral Sea cannot be attributed to a single source based on their  $\Delta^{14}\text{C}$  signatures, and we observe a penetration of bomb-produced <sup>14</sup>C. AAIW in the western Coral Sea shows  $\Delta^{14}\text{C}$  values comparable with those in the South Pacific gyre, consistent with circulation of AAIW in the SEC. The deepest waters at our sites however, at ~2200 m, have significantly higher <sup>14</sup>C than the South Pacific at the same isopycnal, which marks the northward circulation of Circumpolar Deep Waters from the Tasman Sea.

### 3B-01 The Northern Pacific $\Delta R$ estimates: new data and synthesis

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Numerous estimates of  $\Delta R$  value for the Northern Pacific region have already been provided either via radiocarbon dating of sea shells with known collection dates (summarized by McNeely and coauthors in 2006) or via dating of coeval marine and terrestrial materials from archaeological sites (Khasanov et al., 2015; Fitzhugh and Brown, 2017; Khasanov et al., 2018, in press). These studies provide  $\Delta R$  assessments for North American coast from British Columbia to Bering Strait, Central and Eastern Aleutian Islands and Kuril Islands. The western coast of the Bering Sea remains unexplored in this relation. We present new data on  $\Delta R$  estimates conducted for Chukotka and Commander Islands. Paired radiocarbon dates of coeval marine and terrestrial materials from archaeological site Kaniskak (17 pairs) were obtained in Chukotka. Three samples of sea otter bones with known collection dates were used for  $\Delta R$  assessment in Commander Islands. Along with the analysis of previously published data, the new results showed that mean  $\Delta R$  value calculated across the Northern Pacific amounted to  $528 \pm 50$  years. Yet numerous measurements, which were either higher or lower than this value, were observed as well. We propose that observed deviations in  $\Delta R$  value could be influenced by local conditions and/or peculiarities of dated animals diet.

## 3B-02 Radiocarbon marine reservoir effect on the North-Eastern and southern coasts of Cuba

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The Radiocarbon Marine Reservoir effect has a local component DR, a regional offset from the global marine calibration curve. This offset was studied for three locations of northeastern and seven at south of Cuba. More than twenty pre-bomb known-age marine shells specimens were dated by AMS. Sample preparation and grafitization were performed at Radiocarbon Laboratory of the Universidade Federal Fluminense (LAC-UFF Macario et al 2015; 2017), Brasil and radiocarbon measurement was carry-out at Max-Planck Institute for Biogeochemestric of Jena, Germany. In this work we analyze these results and make a comparison with the previous values from the northwestern Cuban coast (Diaz et al. 2016) considering the differences between ocean dynamics in the areas.

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### 3B-03 Marine reservoir effects in eastern oyster (*Crassostrea virginica*) from southwestern Florida, USA

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Eastern oyster (*Crassostrea virginica*) is a ubiquitous estuarine shellfish taxon in eastern North America and one of the most abundant materials available to coastal archaeologists for radiocarbon dating. The natural hydrology of the coastal strand was disrupted in the late 19th century due to efforts to drain and develop the Florida Everglades for agriculture. Here we examine carbon reservoir effects in both pre-bomb and prehistoric archaeological eastern oysters from southwestern Florida, USA. We present 14 <sup>14</sup>C ages for 5 known-age, pre-bomb oyster shells collected between AD 1932–1948, from the Gulf of Mexico, southwestern Florida. In addition, we present 6 <sup>14</sup>C ages for archaeological oyster/charcoal pairs from the Turner River Mound Complex, Everglades National Park (ca. AD 650).

Oyster shells were sampled at multiple points along the exterior left valve to provide a time-series record of <sup>14</sup>C variation during the life of the mollusc. <sup>14</sup>C ages within shells varied as much as 210 <sup>14</sup>C yr, indicating large fluctuations in reservoir offsets over short (sub-decadal) time scales. Average <sup>14</sup>C ages of pre-bomb shells ranged from 515 ± 15 yr BP to 926 ± 15 yr BP, corresponding to reservoir offsets (ΔR) ranging from approximately 60 to 460 <sup>14</sup>C yr. The greatest offset was observed in a specimen that was collected from the mote surrounding Fort Jefferson, a 19th-century coastal fortification, and likely reflects carbon input from <sup>14</sup>C-depleted limestone and coral rubble that was used in the fort's construction. Because the conditions of the fort mote are unique and not characteristic of the region as a whole, the ΔR values estimated for the mote oyster are excluded from the regional average. Excluding this anomalous specimen, reservoir offsets for the early 20th century range from 60 to 190 <sup>14</sup>C yr, with a weighted average of 99 ± 53 <sup>14</sup>C yr for the greater southwestern Florida region. Archaeological oysters from the Turner River site indicate local reservoir offsets ranging from -80 to 80 <sup>14</sup>C yr, with a weighted average ΔR of -16 ± 69 <sup>14</sup>C yr. As with the pre-bomb specimens, within-shell variability in <sup>14</sup>C was large, in excess of 100 yr.

Positive ΔR values may be associated with the upwelling or geological sources of dissolved inorganic carbon, whereas negative values can represent freshwater influence. The variability observed within specimens, both archaeological and modern, suggests that short-term and localized variability in the carbon reservoir inherently limits the precision possible for calibrated radiocarbon ages for this taxon. Until further studies assessing spatial and temporal variability in reservoir offsets are available, we recommend a weighted average regional ΔR value of 96 ± 74 yr for southwestern Florida.

## 3B-04 Estimation of the reservoir age in the Mar Piccolo basin in Taranto (Southern Italy) by AMS <sup>14</sup>C dating on *Cerastoderma glaucum* (Poiret, 1789)

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The stratigraphic succession of the "Mar Piccolo" basin (Taranto, Southern Italy) is well known in the scientific literature dealing with the last interglacial and its morphological evolution is influenced by sea level changes during Late Pleistocene-Holocene.

In order to reconstruct the evolutionary model of the Mar Piccolo, as connected to the sea level rise, an Accelerator Mass Spectrometry (AMS) <sup>14</sup>C dating campaign was carried out on *Cerastoderma glaucum* (Poiret, 1789).

*C. glaucum* is a benthic filter feeder mollusk that lives in waters characterized by different salinity values at various depths. In particular in the Mediterranean basin, *C. glaucum*, is associated with lagoons/inner basins environments. This means that it can be considered a sea level marker with max 2 meters of approximation.

In literature, AMS <sup>14</sup>C dating on *C. glaucum* are widely used in paleoenvironmental reconstructions though in lagoonal/basin systems large age offsets have been reported in different areas. These offsets can be explained as due to the combination of the marine reservoir effect (MRE) and hardwater effect (HWE) associated, in the study area, with freshwater flows coming from karst aquifer through submarine springs.

In this study, 27 AMS <sup>14</sup>C dating analysis carried out on *C. glaucum* sampled from different sediment cores up to a maximum of 30 meters from seafloor are presented. Only samples in physiological position with coupled valves were selected and analyzed.

The interpretation of the data was performed after the estimation of the local reservoir age calculated by analyzing live samples collected in 2017 and specimens sampled in the 1960's and preserved at the Museum of the Department of Biology (University of Bari).

The results show that for both the class of samples (2017 and 1960's) an age offset ranging from 400 to 600 years can be estimated. The obtained results allowed to correct and refine the chronological model of the sedimentary sequences.

This study was conducted within the framework of the Collaboration Agreement (ex article 15 of law 241/90) "Activities of common interest preparatories for the remediation, environmentalization and redevelopment of the Mar Piccolo of Taranto" between the Extraordinary Commissioner for Urgent Interventions of Remediation, Environmental and Regeneration of Taranto, University of Bari and the National Research Council.



## 3B-05 Radiocarbon age offsets of plant and shell in the Holocene sediments from the Sukumo plain, southwest coast of Shikoku, Japan

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To identify the chronological and spatial changes of the marine reservoir effect in western Japan, the radiocarbon ages of 10 pairs of marine shells and terrestrial plants were measured from same horizons of one core of Holocene sediments. This core of 38.5 meters length was obtained from the northern part of the Sukumo plain in southwestern Shikoku Island, which faces on the Kuroshio warm current. This drilling site locates in a subsidence area associated by the subduction of the Philippine Sea Plate. Based on analyses of lithology, molluscan and ostracod assemblages, and radiocarbon dating, we interpreted eight units in order of decreasing age: the basement rock, braided channel, estuary, transgressive bay floor, the Kikai-Akahoya volcanic ash (K-Ah: ca. 7,300 cal BP; Machida and Arai, 2003), deltaic bay floor, tidal flat, and artificial soil (Tsuji et al., 2018; Yamaguchi et al., 2018). These paleoenvironmental changes had been mainly associated by the sea-level rise during the last deglacial period. The reservoir ages of 8 pairs were obtained from the estuary to tidal flat sediments during 4,000-9,000 cal BP. The average was  $330 \pm 70$  within  $260 \pm 70$  to  $430 \pm 70$  years. The chronological change in the reservoir effect allows us to correlate the Sukumo core sediments with from the Holocene sediments around other southwestern Japan (Nakanishi et al., 2017ab) and Korean Peninsula (Nakanishi et al., 2013, 2015, 2017c). This study was partially funded by the Japan Society for the Promotion of Science Kakenhi grant number 18H01310.

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## 3B-06 Marine radiocarbon reservoir correction for the Southern Marshall Islands for the past 2500 years

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A robust marine radiocarbon reservoir correction ( $\Delta R$ ) is essential for calibrating  $^{14}\text{C}$  dates of marine mollusks and fish bones routinely found in archaeological sites as discarded food remains and bones of terrestrial animals (including humans) with an appreciable marine diet. Here we report new  $\Delta R$  values for the atoll archipelago of the Marshall Islands, eastern Micronesia. Atolls consist of biogenetic material - mostly coral and foraminifera - that can be directly dated for establishing sequences of atoll emergence and islet development. After sectioning and examination using scanning electron microscopy (SEM) to check for sample diagenesis, 6 pristine branch coral samples were selected from the modern oceanside beach, archaeological sites and islet developmental facies from Ebon Atoll. Each sample was analysed by U-series and accelerator mass spectrometry (AMS)  $^{14}\text{C}$  showing no substantial temporal  $\Delta R$  variations and yielding a weighted mean  $\Delta R$  of  $41 \pm 42$   $^{14}\text{C}$  yr. The  $\Delta R$  spans  $\sim 500$  years before earliest human colonization (the period when islets first became habitable) through the entire 2000-year occupation sequence. Reliable published  $\Delta R$  values for Micronesia and  $\Delta^{14}\text{C}$  data for Palmyra Island, together with our results for Ebon Atoll, indicate that the Pacific North Equatorial Counter Current is almost stable for the past 2500 years.

## 3B-07 Temporal Variation of the Marine Reservoir Effect on the Coast of Rio de Janeiro

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At present time, coastal upwelling near Cabo Frio, on the coast of Rio de Janeiro, SE Brazil is responsible for increasing biological productivity. Previous works based on different proxies, such as sedimentological and foraminifera analyses, have presented evidence of upwelling already thousands of years ago (Albuquerque et al. 2016; Lessa et al. 2016). Changes in coastal dynamics influence the local radiocarbon marine reservoir effect (MRE) and the calibration of marine radiocarbon ages (Alves et al. 2018). Comparing radiocarbon ages of archaeological materials from terrestrial and marine origins found on coastal sites, freshwater and upwelling influences can be distinguished (Macario et al. 2018).

We present our study on the local MRE along the Rio de Janeiro coast from a temporal perspective. Two shellmounds, located at islands on the southwest and northeast of the coast were dated and the respective  $\Delta R$  values were calculated for different time ranges. We discuss sea-level changes, upwelling, biological productivity and their impact on human occupation of the Rio de Janeiro Coast during Late Holocene.

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## 3B-08 Radiocarbon age offsets of plant and bioclast in the Holocene sediments from the Miyazaki plain, southeast coast of Kyushu, Japan

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In order to investigate the relationship between paleoenvironmental changes and marine reservoir effects, the radiocarbon ages of marine bioclasts (shells and crustaceans) and terrestrial plants were measured from same horizons of one core of the Holocene sediments. This core with length of 9 meters was obtained from the southern part of the Miyazaki plain in southeastern Kyusyu Island, which faces on the Kuroshio warm current. This drilling site locates in an uplift area associated by the subduction of the Philippine Sea Plate (Nagaoka, 1986; Hasegawa et al., 2018). Based on analyses of lithology, molluscan and foraminifera assemblages, and radiocarbon dating, we interpreted seven sedimentary units in order of older age: tidal flat, estuary, prodelta, delta front, Kikai-Akahoya volcanic ash (K-Ah: ca. 7,300 cal BP; Machida and Arai, 2003), delta plain, and artificial soil. These paleoenvironmental changes had been mainly associated by the sea-level rise during the deglacial period. Reservoir ages of 8 pairs from the tidal flat to delta front facies were found to be time span from 7,300 to 8,300 cal BP in detail. The average was  $520 \pm 50$  years within  $440 \pm 70$  to  $610 \pm 70$ . Using the chronological change in the reservoir effect, the Miyazaki plain sediments will be correlated with the Holocene sediments from the other coastal area around southwestern Japan (Nakanishi et al., 2017ab, 2018). This core was obtained by the Grants-in-Aid for Scientific Research (Kakenhi 16K03159; Organizer: Mitsuhiro Kuwahata) funded by the Japan Society for the Promotion of Science (JSPS). This study was also partially funded by the JSPS Kakenhi grant number 18H01310.

## 3B-09 Coral Based Marine Reservoir Corrections for the Brazilian Northern Coast.

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Research on the Marine Reservoir effect (MRE) on the coast of Brazil has increased over the last few years (Alves et al. 2015a; 2015b; Carvalho et al. 2015; Macario et al. 2015; 2016; 2018). Due to its extensive area and varied geomorphological features, the available estimates for  $\Delta R$  offsets between local and global oceans are far from ideal for Brazilian coast. Several archaeological and environmental researches are based on marine materials and the reliability of such chronological records are completely dependent of the understanding of local reservoir effect (Alves et al. 2018). The Abrolhos bank, in southern Bahia State, is the largest corals reef system in the Southwestern Atlantic. It is highly influenced by the Brazil Current since it is located in the continental shelf. In contrast, Todos os Santos Bay, in Salvador, capital of Bahia State has an important coral biodiversity located in a bay inlet with restrict water circulation. Coral cores were collected in those both sites and were previously analyzed for density band counting and by Th/U dating technique to estimate growth rates and chronology. In this work, we present  $^{14}\text{C}$  ages of some of these bands in order to evaluate the MRE to which the colonies were subjected during growth. It is the first study making use of coral skeleton samples to allow the MRE determination on the Brazilian coast. For the Abrolhos region, fairly constant negative values (mean  $\Delta R = -151 \pm 23$   $^{14}\text{C}$  yr) were found in the period from 1884 to 1937 AD, indicating no variation in ocean dynamics and favoring the presence of  $^{14}\text{C}$  for air/sea gas exchange and freshwater influence. For Todos os Santos Bay, the result for the year of 1934 was  $\Delta R = -107 \pm 51$   $^{14}\text{C}$  yr, in contrast to a previous work based on a pre-bomb sample collected in 1948 (Alves et al. 2015b). In this case, the beginning of oil exploitation in the area after 1940 may have impacted the radiocarbon concentration.

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## 3B-10 An investigation into <sup>14</sup>C offsets in modern mollusc shell and flesh from Irish coasts

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Our ability to reliably use radiocarbon dates of mollusc shells to estimate calendar ages depends on the feeding preference and habitat of the particular species and the geology of the region (Mangerud, 1972). Gastropods which feed by scraping are particularly prone to incorporation of carbon from the substrate into their shells as evidenced by studies comparing the radiocarbon dates of shells and flesh from different species from the same location and the same species on different substrates (Dye, 1994; Hogg et al., 1998). Limpet shells (*Patella* sp.) are commonly found in prehistoric midden deposits in the British Isles and were presumably part of the palaeodiet, however these shells have been avoided for use in radiocarbon dating in regions of limestone outcrops. Preliminary results from limpets (*Patella vulgata*) collected alive on limestone and granite substrates on the west coast of Ireland indicate that the shells were formed in equilibrium with the seawater, with no significant <sup>14</sup>C offsets. Limpets collected from the east coast of Northern Ireland have elevated <sup>14</sup>C due to the output of Sellafield nuclear fuel reprocessing plant. In all locations, the flesh was depleted in <sup>14</sup>C compared to the shells. Mussels (*Mytilus edulis*), which are suspension feeders, were also collected alive from the same locations and these yielded statistically indistinguishable results to the limpets suggesting that there are no offsets specific to the feeding ecology of these two species. The results will have an important consequence for radiocarbon dating of midden deposits as well as the bones of humans and animals who fed on the limpets.

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### 3B-11 Tracing $^{14}\text{C}$ variation in the lake sediments caused by environmental factors

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As an object of our research was selected a common lake of Lithuania- a dimictic lake Tapeliai. It has bottom feeding sources. Its basin is of the glacier origin (tunnel valley lake, groove type) [1]. A ditch connecting Lake Tapeliai with its important water source- strongly eutrophicated Red-Lake was blocked and Tapeliai became the first water body of the lake chain connected by brook/channel in 1960s. Appeared water level changes caused rise of colored water inflow from a swamp.

In the literature we can find that the sediments have been dated using either bulk sediments or individual humic fraction as fulvic acid, humic acid, and humin. Interrelationships between individual humic fractions are still unclear [2]. Together with the radiocarbon the  $\delta^{13}\text{C}$  were also measured in the lake sediments core of Tapeliai in order to trace rate of eutrophication processes. Two fractions of humin and humic acid were used in the present study for  $^{14}\text{C}$  and  $\delta^{13}\text{C}$  analysis. It was assumed that radiocarbon dating of bottom sediments would not give us reliable radiocarbon age as there are too many processes that influences organic and inorganic carbon origin and cycling pathways. However the obtained data of  $^{14}\text{C}$  revealed an interesting results which were useful in understanding of the hydrological events of the lake history. The main purpose of this study was to show an influence on  $^{14}\text{C}$  content in lake sediments caused by hydrological changes in lake system. According to the  $^{14}\text{C}$  records of the sediments core it is clear that at the beginning of the XX century a huge impact of old dissolved organic carbon was delivered to the lake. In consequence of this event the “reservoir effect” had changed drastically – it dropped from 1330BP to 2360BP and lasted for 50 years. Another braking point in the radiocarbon records was observed in 26 cm depth of the column. According to the sedimentation rate (estimated from  $^{210}\text{Pb}$  measurements) that depth corresponds to the date of 1950. At this point  $^{14}\text{C}$  content in the sediments sharply elevated from 75pMC to 87pMC. Several major events occurred at this time: a) from the measured  $^{137}\text{Cs}$  profile we can suggest that at this time the nuclear weapon test in atmosphere happened; b) historical records and changes in sedimentation rates at this point allows us to make an assumption that the ditch which was connecting the Tapeliai lake with a Red-lake was blocked and no old DOC was delivered to the lake basin. It is not clear which of these two events was the most dominant however from the reviled data it is obvious that during the 20 years  $^{14}\text{C}$  content in the lake sediments reached and exceeded previous value (85pMC in 1900y) and the last decade it shows stable trend with minor changes.

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## 3B-12 Freshwater reservoir effect within Eastern Fennoscandia

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Understanding of freshwater reservoir effect (FRE) has been considered to be fairly small within the Eastern Fennoscandian lakes since the bedrock is limestone-free and the lakes are shallow and therefore easily in equilibrium with the atmospheric CO<sub>2</sub>. Nevertheless, the long Holocene history of organic matter coupled with increased land use during the industrial era act as potential drivers for supplying old carbon into aquatic ecosystems. During the recent years a considerable attention has been paid into studying ancient human DNA within the area. Consequently, an interest has been reborn to assess the FRE more thoroughly in contributing the human timeline. In this work, we gather together estimates of FRE from several Iron Age contexts within Eastern Fennoscandia based on <sup>14</sup>C measurements of modern fish samples. Particularly, we present results of Levänluhta / Kyrönjoki river in Southern Ostrobothnia, Rapola / Vanajavesi in Tavastia and Luistari / Pyhäjärvi in Satakunta. Implications on the observed FRE on human and animal bone and food crust <sup>14</sup>C measurements is discussed.

## 3B-13 Using natural and engineered recharge end members to examine how water source impacts carbon cycling in groundwater in the Los Angeles coastal basin

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The cycling of dissolved inorganic carbon (DIC) and dissolved organic carbon (DOC) within an aquifer is controlled by many biogeochemical processes, such as carbonate dissolution and heterotrophic microbial respiration. However, the impact of recharge source waters on groundwater DIC and DOC biogeochemistry could be significant and often is not fully understood [1,2]. This study compares two monitoring sites near the Montebello Forebay region of the Los Angeles Basin coastal aquifer. Each site comprises several wells installed within a single borehole at various depths, but isolated by grout seals. The well depths span three aquifer systems [3]. Within the two uppermost aquifer systems, recharge is driven by percolation of natural water sources (precipitation and local rivers) and anthropogenic sources (recycled water mixed with local water sources in engineered spreading grounds)[4]. The deepest aquifer system is isolated from the above layers, and isn't influenced by engineered recharge. Recharge at this depth is believed to have occurred up to 20,000 years before present [3]. Here we present groundwater  $\delta^{18}\text{O}$  and  $\delta\text{D}$  data to determine water source end members at all well depths. We will also use DIC and DOC  $\delta^{13}\text{C}$  and <sup>14</sup>C values to assess atmospheric CO<sub>2</sub> input, carbonate dissolution and the heterotrophic microbial respiration of DOC within these groundwater aquifer systems.

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## 4A-01 The 'Old Wood' effect: Questions about the accuracy of radio-carbon dating at the Chudov Monastery, within the grounds of the Moscow Kremlin

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Over 2016-2017 the Institute of Archaeology of the Russian Academy of Sciences carried out archaeological investigations at the eastern side of the grounds of the Moscow Kremlin, at the site of a demolished administrative building that had been built there during the Soviet era.

Archaeologists were given a unique opportunity to investigate an area of the cemetery of the Chudov Monastery – one of the most venerated monasteries in Russia during the period of the 15th-17th centuries. The monastery had been founded in 1365, and continued to function until the 1920s-1930s, after which time it was demolished.

A total of 115 burials were identified during research conducted in the north-western area of the cemetery. Despite the identification of the cemetery's internal structure, it proved difficult to put an accurate date on these burials, for several reasons. The first was that not only the had the gravestone markers been destroyed, but also the upper tier of burials too. The second reason - almost no artifacts whatsoever were found among the burials which were excavated.

The possibility of dating the graves arises from the chance of dating the partially-preserved wood of the coffins. This was achieved by using radiocarbon dating of the examples. By tradition, burials were made using coffins carved from whole trunk-sections of aged trees. The practice was to hollow-out the core of the trunk for the chamber of the coffin – and the remaining section served as the walls of the coffin. The samples of wood analyses in our study were taken from either wall-sections or end-sections of the coffins. Examples of bones from each coffin were similarly carbon-dated. Comparing the AMS carbon-dating of pairings of the bones and the coffin which contained them – is shown below, for sample from six different burials.

The AMS dating was undertaken at the laboratories of the Center for Applied Isotope Studies, of the University of Georgia, USA, under the supervision of Dr A.E. Cherkinsky.

Calibration of these dates shows that the bone samples of those buried are from the 15th century. However, the dating of the timber of the coffins of the same pairings gives date results which are significantly earlier – the 13th or 14th century:

Burial 5[UGAMS-28882;29143 (CalAD1300-1406;1412-1444)],

Burial 19[UGAMS-28880;29141 (CalAD1287-139;1421-1453)]

Burial 31[UGAMS-28885;29143 (CalAD1304-1409;1438-1611)]

Burial 41[UGAMS-28881;29142 (CalAD1220-1275;1416-1446)]

Burial 93[UGAMS-28883;29144 (CalAD1268-1380;1416-1446)]

Burial 103[UGAMS-28884;29145 (CalAD1218-1271;1428-1468)].

The cemetery have been laid out from the second half of the 14th century. The reason for the dating discrepancy between bone material and coffin material arises from funeral rites. The width of the coffins examined in the study varies between 85cm and 120cm. This would have required the use of large aged tree trunks, whose age would have been up to 200 years at the date of felling. Thus, we can see what can be termed 'the Old Wood effect'. Dating the burials in this case would be appropriate only according to the data compiled from the bones themselves. Radiocarbon dating work on layers and artifacts from these excavations in the Moscow Kremlin is ongoing.

## 4A-02 <sup>14</sup>C-dating of wooden buildings in Belgium. A problem of reliability?

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From the prehistory until the 19th-early 20th century wood was the most important construction material for buildings in Belgium and in the adjoining regions. With the exception of some waterlogged areas, such as the so-called Dutch river area for example in the center of the Netherlands, the wooden posts of the structures are not preserved anymore. The only remains are a discoloration in the soil where once the wooden posts have been erected. Because of this, these buildings are difficult to date. Material finds in postholes, which can help to date the structure, are mostly limited to only a few sherds, remnants of human garbage on the site. Although in some periods, as for example the Roman era, the chance of ceramic finds in postholes is higher than in the pre- and protohistory.

Charcoal or charred grains preserved in these postholes are a dating option, although the origin of these materials is not clear. They can have been deposited in the postholes in different ways and in different periods during the lifespan of the building. So, archaeologists are confronted by a question of the reliability of the charcoal to be dated, which is an important matter. However, in many cases this is the only material to get an absolute date for the studied structures.

To tackle this problem of reliability, a strategy is to date several samples from the postholes of the same structure. A pattern of contemporaneous <sup>14</sup>C-data will give us insight in the age of these structures and outliers can be eliminated. To verify the results of the <sup>14</sup>C-dating a comparison is made with the fragments of material culture, mostly ceramics that were recorded in the infill of the postholes to control if they can be dated in the same time span. If possible, the dated structure is also compared with typologically related buildings to establish a chronological framework. This method has resulted in the recognition and dating of buildings types during protohistory and in the Roman period in Belgium and the adjoining regions.

## 4A-03 Radiocarbon distribution in the North Atlantic from GEOVIDE cruise in May-June 2014 and its comparison with historic data sets.

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Atlantic Meridional Overturning Circulation (AMOC) plays an important role in the Earth's climate system with its impact on sea surface temperature, sea-ice, marine ecosystems, the ocean carbon budget and global sea levels. The ongoing GEOVIDE project, an international collaborative program, aims to better understand and quantify AMOC and disentangle the uncertainties on water masses, heat fluxes and Trace Element and Isotope (TEI) cycles in the North Atlantic and Labrador Sea. To achieve these objectives, an oceanographic mission (GEOVIDE cruise) was carried out in the subpolar North Atlantic along the OVIDE section and across the Labrador Sea on board RV "Pourquoi Pas?" in May-June 2014. Physical, chemical and biological variables were measured on the two sections to produce a synoptic of the distribution of relevant physical and biogeochemical properties.

We report here radiocarbon measurements of dissolved inorganic carbon (DIC) in seawater samples collected from nine stations (seven stations along the OVIDE section and two stations in the Labrador Sea). The comparison of the radiocarbon distribution obtained during this campaign and previous data (GEOSECS, WOCE) allows to investigate spatio-temporal variability of radiocarbon ( $\Delta^{14}\text{C}$  and <sup>14</sup>C age) over the last fifty years in the North Atlantic. We discuss in detail the causes of this <sup>14</sup>C variability in response to the uptake of bomb <sup>14</sup>C and changes in water masses circulation.

## 4A-04 Seasonal bomb-<sup>14</sup>C variability recorded in the coral from the northwest part of the Luzon Island, Philippines

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Coral skeletons record the radiocarbon (<sup>14</sup>C) content in the surface ocean when they incorporate dissolved inorganic carbon from ambient seawater. After the atmospheric nuclear bomb testing in the 1950s,  $\Delta^{14}\text{C}$  records in coral skeletons can be used as a sensitive water mass tracer and contribute to our understanding of ocean circulation because of the excess bomb-<sup>14</sup>C. Previous studies revealed that the three early  $\Delta^{14}\text{C}$  spikes related to close-in fallout of the atmospheric nuclear bomb tests in the US Proving Grounds at Bikini and Enewetak atoll conducted in 1954, 1956, and 1958 were detected from the Ishigaki coral (Hirabayashi et al., 2017a) and the Guam coral (Andrews et al., 2016), which will contribute to the oceanographic models of North Equatorial Current and Kuroshio. However, the oceanography of the upper stream of Kuroshio, especially the area of Kuroshio intrusion into the South China Sea (SCS), is still unclear. Therefore, long-term, high vertical-resolution observations are needed to improve our understanding of the SCS current system.

Here we report seasonal  $\Delta^{14}\text{C}$  changes in the coral from Currimao, Luzon Island, Philippines. Our data indicated a significant increase in  $\Delta^{14}\text{C}$  from 1945 to 1995 related to atmospheric nuclear bomb testing. A clear early  $\Delta^{14}\text{C}$  spike in Currimao is observed only once in 1955, whose amplitude was 47 ‰. The amplitude of <sup>14</sup>C variability after the first  $\Delta^{14}\text{C}$  spike in late 1950s and early 1960s are almost constant at ~20 ‰, which suggested that the <sup>14</sup>C variability after first  $\Delta^{14}\text{C}$  spikes indicated usual seasonal variability such as seasonal local upwelling at Currimao. Because the seasonal  $\Delta^{14}\text{C}$  difference in the late 1950s and early 1960s increased in Currimao, the second and third  $\Delta^{14}\text{C}$  spike could not be recognized clearly. Compared with other coral records reported from the area of Northwest Pacific and SCS in the post-bomb period, the data suggest that the area of the Kuroshio loop current through the Luzon Strait decreased from the 1970s to 1980s, as a result of the change in Kuroshio transport and the migration of the North Equatorial Current bifurcation latitude after a regime shift in 1976 (Hirabayashi et al., 2017b).

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## 4A-05 North Atlantic Ocean <sup>14</sup>C bomb-pulse data from cod otoliths

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We use the radiocarbon activity in cod otoliths from Faroese cods to trace the atmospheric <sup>14</sup>C bomb-curve signal into the North Atlantic Ocean. Our record covers the period from 1950 AD to 2000 AD and have been retrieved from the archive at the Faroe Marine Research Institute. A 1.5D diffusion box model is used to fit the <sup>14</sup>C otolith data and is able to explain the diffusion

of atmospheric <sup>14</sup>C into the North Atlantic Ocean from 1950 AD to about 1975 AD. From 1975 AD onwards there appears to be a misfit between the 1.5D diffusion box model and the <sup>14</sup>C otolith data.

## 4A-06 North Pacific bomb-<sup>14</sup>C record reconstructed from long-lived bivalve shells and its application

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Nuclear bomb testing conducted actively in 1950s and 1960s increased radiocarbon concentration in the surface ocean (bomb-<sup>14</sup>C), which became an important tracer to study ocean physics and biogeochemical cycles. To reconstruct the time-series of radiocarbon concentration in the seawater, hard-parts of marine organisms such as coral skeleton are useful. Of these, shells of long-living bivalve are one of the most important archives, especially in the high latitude area, because of absence of reef-building corals. We report bomb-<sup>14</sup>C record in the high latitude northwest Pacific reconstructed from shells of cold-water bivalve *Mercenaria stimpsoni* (Stimpson's hard clam) living in North East Japan (39.4°N, 142°E). The record showed a strong influence of Kuroshio warm current, though the study area is located in a relatively high latitude. We also show tsunami-related death of this animal revealed by radiocarbon dating and schlerochronology (annual ring counting) of dead shells collected from the seafloor of the study area.

## 4A-07 Variations of surface radiocarbon of the North Pacific in summer season during the past decade

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In the Center for Global Environmental Research of the National Institute for Environmental Studies, Japan (CGER/NIES), the oceanic net CO<sub>2</sub> flux observations in the North Pacific have been conducted since 1995 with the help of commercial shipping companies. A suite of analytical equipment was installed on board a cargo ship, and the ship traveled between Japan and United States or Canada on approximately the same route at least six times a year performing underway sampling and measurements for the study of seasonal and interannual variability of the air-sea CO<sub>2</sub> flux in the North Pacific. The surface water for radiocarbon measurement has been collected since summer 2003 by this volunteer observation ship. The surface water drawn into the ship's water intake at about 7 m depth was used for the pCO<sub>2</sub> measurements and also radiocarbon samples of ca. 250 ml were taken every 12 hours during the cruise. By the sampling interval, we can get a sample from every 5 ° along longitude direction. In this presentation, we report the temporal and spatial variation of surface radiocarbon ( $\Delta^{14}\text{C}$ ) of the North Pacific in summer season during 2004-2016.

Because of the volunteer observation ship's lane: Japan to U.S. West Coast or U.S. East Coast, we could get wide range (20-50 °N) of surface  $\Delta^{14}\text{C}$  data in the North Pacific and their values ranged from -55‰ to 108‰ during 2004-2016. The surface  $\Delta^{14}\text{C}$  in high latitude, north of 40°N are significantly lower than either of latitudes. This reflects the strong vertical mixing in that region and the trend is similarly to previous worldwide observations such as GEOSECS and WOCE. The  $\Delta^{14}\text{C}$  of subtropical region (the Kuroshio/ Kuroshio Extension, North Pacific and California Current area) was decreasing by 3.3-4.5‰ per year, and the long-term  $\Delta^{14}\text{C}$  decreasing trend after 1970's in this region have continued. On the other hand, the  $\Delta^{14}\text{C}$  of subarctic regions (the Subarctic and Alaska Current area) may shift to increasing trend since 2009. This may be attributed to mix the surface water having low  $\Delta^{14}\text{C}$  with sub-surface water accumulated bomb-produced <sup>14</sup>C by the strong vertical mixing in winter.

## 4A-08 North Pacific surface water radiocarbon recorded in abalone obtained from Otsuchi bay, Japan

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Changes in ocean circulations are related to nutrient supplies to the surface water that is closely related to regional environmental conditions including ecosystems. It is known that the variations have been occurred with large-scale climate changes such as ENSO (El Niño Southern Oscillations) and PDO (Pacific Decadal Oscillations). Thus reconstruction of seawater conditions in the past in the coastal regions is needed to better understand the relationship between oceanographic changes and coastal ecosystems. Seawater radiocarbon is a unique proxy to understand the properties of water masses. Reef-building corals have been employed to conduct this type of research widely and successfully reconstructed past ocean circulation histories. However their distribution is limited to the low latitude and hence alternative archives are required. Here we used abalone samples obtained from Otsuchi bay located at Tohoku region in the Pacific coast of Northern Japan. Abalone has been used as a food in Japan during the historical past and their stiff shell structure is persistent to diagenesis thus suited for radiocarbon analyses. Two years long river water as well as seawater radiocarbon of dissolved inorganic carbon have been measured and compared with the data analyzed for abalone samples. The record indicates that the abalone can be used to reconstruct past seawater record in northern Japan where coral skeletons cannot be applied for ocean mixing using radiocarbon.

## 4A-09 Tracing terrestrial sources of dissolved organic carbon in an Arctic lagoon ecosystem using Ramped PyrOx

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Strong seasonal inputs of terrestrial dissolved organic carbon (DOC) are tightly coupled to lagoon biogeochemical cycling along the Eastern Alaskan Beaufort Sea coast. Riverine inputs are already recognized as important sources of DOC to estuarine ecosystems in the Arctic. Terrestrial groundwater inputs, on the other hand, may be a far more important source of DOC to these systems than currently recognized, especially along stretches of shoreline without major rivers and during the late summer when the active layer depth is at a maximum and river flow is typically at a minimum. This is of particular interest from a climate feedback perspective because anticipated increases in groundwater flow as permafrost thaws may be transporting large amounts of liberated organic matter directly into coastal environments. However, dynamic mixtures of DOC are inherent to estuarine environments, making it challenging to elucidate diverse sources of OC even among terrestrial inputs. This information is needed to better understand how the strength of these two organic matter delivery pathways will change as permafrost thaws in the future. Here we use a serial thermal oxidation technique (Ramped PyrOx) coupled with radiocarbon and stable carbon isotope composition analysis (<sup>14</sup>C and <sup>13</sup>C) to elucidate the sources of DOC in a lagoon ecosystem along the Eastern Alaskan Beaufort Sea coast. Ramped PyrOx provides information related to the distribution of isotopic composition within a single sample that is not apparent when considering only bulk averages. Groundwater, river water, and lagoon water DOC were collected near Kaktovik, Alaska in August 2017. DOC was extracted using solid-phase extraction (SPE) with PPL cartridges and subsequently analyzed for <sup>14</sup>C and <sup>13</sup>C composition at the Woods Hole Oceanographic Institution, National Ocean Sciences Accelerator Mass Spectrometry (NOSAMS) facility. An inverse model was employed to further relate DOC thermal reactivity and isotopic composition measurements. Together this study presents the application of a novel approach to trace terrestrial sources of DOC in estuarine environments in the Arctic.

## 4A-10 The trans-Arctic water sections radiocarbon inventory for reconstruction of surface-mid-deepwater ventilation ages

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We present  $\Delta^{14}\text{C}$  data collected in the Arctic Ocean during four cruises that took place in the summers of 1999(MR99-K04), 2002(MR02-05), and 2008(MR08-04, NABOS2008). The cruises tracks of these four expeditions cover all the major basins of the Nansen, Amundsen, Makarov and Canada. The section is based on 20 stations covering the entire water column (about 250 data points). We use the  $\Delta^{14}\text{C}$  section, together with previously published  $\Delta^{14}\text{C}$  data from single stations located in several basins of the Arctic Ocean, to derive mean movement age (isolation times) of intermediate water via Fram Strait from the Atlantic Ocean. We estimated these mean movement age to be ca. 30 years in the western Canada Basin. Such first movement of Atlantic intermediate water may provide a sensitive sign to detect variation of North Atlantic deep water formation under changing climate in the future.

## 4A-11 Recalibration of Human Individuals from the Danish Mesolithic-Neolithic Transition

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In the early 1980s when Henrik Tauber published a novel and comprehensive carbon isotope study of prehistoric humans from Denmark (Tauber 1981), an unmistakable transformation was observed in the diet coinciding with the transition between the Mesolithic and the Neolithic in c. 4000 cal BC. The transformation was characterised by a shift from a diet consisting mostly of marine products to a sustenance apparently based exclusively on terrestrial food resources. The significant marine food intake has become the symbolic of the Late Mesolithic Ertebølle culture, yet the substantial intake of marine foods complicates the use of <sup>14</sup>C-dating for individuals from this particular time period.

Traditionally, radiocarbon dates are not corrected for the reservoir effect, unless a minimum intake of 10 % marine food is observed. Thus, a  $\delta^{13}\text{C}$  value of -21 ‰ or lower will result in no correction, while a  $\delta^{13}\text{C}$  value of -10 ‰ or more, implying 100% marine diet, involves a correction of minus 400 years. The reservoir age of 400 years is the average in the open Danish waters (Heier-Nielsen et al. 1995). Recently advanced methods for calculating the marine intake more precisely have evolved; FRUITS (Food Reconstruction Using Isotopic Transferred Signals) is based on a Bayesian mixing model and allows calculations of food group probability in the overall diet (Fernandes et al. 2014).

This paper compares the traditional proportional calculation methods with the FRUITS-models and evaluates their implications for reservoir corrections. The paper focuses particularly on a case from a Ertebølle culture shell midden at Rødhals, Sejro, where a  $\delta^{13}\text{C}$  value of -11.7 ‰ measured on a human bone indicates fully marine diet (Fischer et al. 2005). The above-mentioned idea of a dietary shift at the Mesolithic-Neolithic transition therefore places this individual in the Ertebølle culture. Yet, it is <sup>14</sup>C-dated to the Early Neolithic Funnel Beaker culture (3955-3705 cal BC). The male skeleton from Sejro is the only analysed individual from the Funnel Beaker culture with  $\delta^{13}\text{C}$  values above -18 ‰, which would otherwise be indicative of the Late Mesolithic period. These circumstances raise doubts to the robustness and reliability of prevailing methods and calls for a re-assessment or revision of the basis for marine intake calculations. We will scrutinize all available radiocarbon dates and isotope values ( $\delta^{13}\text{C}$ ,  $\delta^{15}\text{N}$ ) of human bones from the Late Mesolithic Ertebølle and Early Neolithic Funnel Beaker cultures and re-calibrate them both with the traditional and with the FRUITS approach.

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## 4A-12 Combined radiocarbon and anthropological studies on prehistoric human remains from the “Tecchia di Equi” cave in Northern Tuscany

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Caves probably represent one of the best natural archives to study past climate and populations. In particular, some caves throughout Europe have allowed us to reconstruct human development and habits since Palaeolithic. “Tecchia di Equi” on the Apuan Alps (Fivizzano, Northern Tuscany) is an example of a cave that bears evidence of human occupation from Middle Paleolithic to Medieval times, in a stratigraphic context that often shows some degree of admixture among the different levels. The archaeological excavations performed more than one century ago brought to light many human remains that now belong to the prehistoric anthropological collections curated by the Natural History Museum of the University of Florence. These remains constitute a large assemblage deriving from a secondary deposition context, where bones from single individuals have been extensively mixed. The bones have been considered in the past as coming from an Eneolithic context. After a comprehensive anthropological revision, radiocarbon was applied to especially exclude a more recent origin.

The anthropological analysis has indicated the presence at the site of a MNI (Minimum Number of Individuals) of 12. Among them, 4 subadults of different ages were identified and later excluded from radiocarbon dating, since preservation of collagen is not typically favoured in such young individuals. For <sup>14</sup>C measurements, eight samples from the different adults, i.e. navicular bones of the tarsus, were thus collected. In this presentation, we will discuss the data obtained from radiocarbon measurements and anthropological observations: data point to the use and occupation of the cave during the first half of the 3rd millennium BC.



## 4A-13 New radiocarbon dating results from the Upper Paleolithic levels in Grotta Romanelli-Italy

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"Grotta Romanelli" is a natural cave located along the Adriatic coast of the Salento Peninsula in Southern-East Italy in the territory of Castro (Lecce). The cave can be regarded as one of the key Paleolithic sites in Italy. It was discovered in 1871, but it was only thanks to the systematic excavations carried out at the beginning of 1900 that its great archaeological importance was assessed and the presence of fossil vertebrate assemblages recognized. Since then, the stratigraphy of the cave is recognized as a reference for the definition of the Late Pleistocene and Paleolithic chronology in Italy. The deposit infilling the cave was divided in two main complexes: "terre rosse" (red soils – levels K-I-H and G) with large mammals and limestone artefacts referring to the Middle Paleolithic and "terre brune" (brown soil – levels E-D-C-B-A) characterised by upper Paleolithic artefacts and by a diversified fossil vertebrates assemblage including mammals and more than 100 species of birds. A sub-horizontal stalagmitic layer (level F) separates the two complexes. The lower complex lays on a marine terrace cut into Cretaceous limestone (Level L) and referred to the MIS5.

With the aim of obtaining a closer and more detailed definition of the site stratigraphy, a systematic excavation campaign was initiated in 2015. Aim of the study was also to define an absolute chronology of the different levels which was so far based on nine <sup>14</sup>C dates measurement performed in the 1960's on humic acid and charcoal samples from the uppermost layers (A, B, C, D) and on two U/Th ages obtained from level F and level H.

In this paper, we present the results of the AMS (Accelerator Mass Spectrometry) radiocarbon dating campaign performed on samples selected from the different levels referring to the upper level "terre brune" section of the stratigraphy.

## 4B-01 Radiocarbon dating of St. George's Rotunda in Nitrianska Blatnica, Slovakia: Consortium results

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Radiocarbon dating of St. George's Rotunda in Nitrianska Blatnica (Slovakia) was carried out with the aim to solve discrepancies about its origin preliminary estimated to be between the 10th and 14th century. The Rotunda represents a small object build from stony walls about 80 cm thick, which passed several reconstructions which changed its shape. It has been believed that only walls could represent a building material which was originally used for construction, and which has not been replaced during past reconstructions. An international consortium consisting of radiocarbon laboratories from Debrecen, Prague, Tucson, Vienna, Zurich, and Bratislava has been organized to so solve the age problem and to provide internationally acceptable age of the Rotunda. Samples of charcoal, thin twigs and mortar found inside the walls, as well as internal coatings were used for radiocarbon analyses. The radiocarbon data obtained by consortium laboratories have been in good agreement resulting in radiocarbon calibrated age of 790-870 AD. The wide age interval has not been influenced only by uncertainties of partial radiocarbon measurements, but mainly by the specific character of the calibration curve (plateau) during this time interval. The obtained radiocarbon age makes the Rotunda probably the oldest existing Christian object in the Central Europe, built (with 95% probability) before arrive of Cyril and Methodius to Great Moravia (863 AD).

## 4B-02 Radiocarbon dating of Relics and Reliquaries -The case of the ecclesiastical treasure from Chapter St. Aldegonde of Maubeuge (France)

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The church of Saint-Pierre-Saint-Paul, built from 1955 as a part of the reconstruction of the city of Maubeuge, preserves the treasure called "of St. Aldegonde of Maubeuge" (° around 630, † 684). It is composed of many items including a relic of the veil, a cross stick, a set of items consisting of a chasuble, a veil, a stole and a modern reliquary containing some bones of the St. A research project on the analysis of relics and reliquaries of this chapter was undertaken after the discovery of inventories of this treasure. This project aims at conducting a comprehensive study of a treasure - direct and indirect relics of a saint and his family.

Among the analyzes carried out, radiocarbon dating have been performed on the chasuble and the cross stick. In the same way, we had access to the relics of the parents of Saint Aldegonde, Saint Walbert of Hainaut and Saint Bertille of Thuringe. These relics are mentioned from 1453, the year of their transfer from the old to the new church of Cousolre. Because they are precious treasure and valuable relics, only very small samples can be taken. Thus, less than 5 mg of silk for the chasuble and fifteen milligrams of wood from the cross stick were taken. We were able to obtain a half-vertebra from each body for the bones of Saint Walbert and Saint Bertille. In addition, we received some pieces of blue silk that surrounded the bones in the reliquary.

The date obtained for the chasuble is  $720 \pm 30$  years BP (cal AD 1230 – 1300). The assumption that the fabric used would be a diplomatic gift from a Mongolian emperor to St. Louis could be confirmed. The radiocarbon age of the stick is  $818 \pm 22$  years BP, which corresponds to a calibrated date between 1180 and 1265 AD. This date is older than the one historians estimated. The cross was supposed to be made between the middle of the 13th century and the first decades of the 14th century.

The bones of Saint Walbert and Saint Bertille could be compatible with those of Saint Aldegonde's parents. The radiocarbon age of St. Walbert is  $1515 \pm 30$  years BP (cal AD 525 – 615 at 68.5%) and St. Bertille is  $1470 \pm 30$  years BP (cal AD 545 - 645). The blue silk contained in the reliquary seems contemporary to the transfer of the relics in the new church of Cousolre ( $420 \pm 30$  years BP, which corresponds to cal AD 1425 - 1515).

## 4B-03 Embroidered epitrachelion from St. Elisabeth's Cathedral in Košice (Slovakia) dates to 15th century

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For almost 100 years a richly embroidered epitrachelion is known to have been a part of the treasure of St. Elisabeth's Cathedral in Košice. The epitrachelion is a band embroidered with metal thread and coloured silks in surface couching. Embroidery techniques used are underside couching, laid work, satin stitch, and couched work. Nowadays, the epitrachelion is used as orphrey (a decorated band applied to liturgical vestments) on a chasuble of Roman cut.

According to art historical analysis, the epitrachelion has close analogues to the Late and Post Byzantine embroidered liturgical vestments (e.g. Mt. Athos) but it also has formal affinities to the 19th century embroideries. Neither research in the Košice Archdiocesan Archives could until now give conclusive information on the artefact's dating. This typical work of the Eastern Orthodoxy may have been brought into Catholic area of the former Kingdom of Hungary by pilgrims in the 16th century or acquired by Košice Bishop Bubics as a part of his art collections around 1900.

In order to chronologically characterise the artefact we have employed radiocarbon dating (AMS) of textile fibres. Since we suspected that this outstandingly preserved artefact could be one of the earliest pieces of historical textiles in Slovakian collections, we collected samples from a very limited and visually not exposed area. From the spot with no signs of reparations and material replacements we sampled three independent elements of the artefact mediating three independent events: basal thread (sample 1), basal canvas (sample 2), and embroidery base (sample 3), first two being the plant fibres, the third one silk. The samples were treated by soxhlet extraction (hexane-acetone-ethanol) and by acid-base-acid washes at 60 °C. The weight of carbon to be analysed was 0.99 a 1 mg from plant fibres in sample 1 and 2 and 0.23 mg for the silk, which was well distinguishable also by the C/N ratio.

The radiocarbon dating has shown that basal thread and basal canvas are coeval and originate from the 1st half of the 15th century. As for the silk embroidery base, it gave two unimodal intervals. While the low probability density of the earlier interval of HPD region for basal canvas (sample 2) is clearly an artefact of the calibration curve, the earlier interval of the silk HPD region has higher values (sample 3).

Ultimately, we interpret our results as all being coeval and date the production of the epitrachelion from St. Elisabeth's Cathedral treasure to the first half of the 15th century. Whether the silk base may present an earlier material in the artefact is a matter of our future investigation.

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## 4B-04 Royal castle from Poznań- Comparison of mortar and bricks dating

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The Royal Castle in Poznań (Góra Przemysła), was built on a hill, at the confluence of Warta and Bogdanka river valleys (Poland). On the basis of historical data and relative chronology, it is estimated that the buildings and walls of the castle were raised at the end of 13th cent. AD. The first significant damage of the castle was brought by the Brandenburg occupation (1657) and Swedish wars. At the turn of the 17th and 18th century AD the role of the castle as a residence ended.

According to the archaeological research, the most probable is that the castle was raised in the times of Duke Przemysław II (1273-1296), along with the city walls raised between 1275-1285 (Karolczak 2008). The castle served as a residence of Przemysław II since the early eighties of the 13th century, firstly as the center of Duke's, and later King's power until his death in 1296. However, there is an ongoing dispute regarding the beginnings of the castle as the Duke residence (Linette, 1981; Karolczak 2008). As a consequence, the timing of the oldest construction phase of the castle remains unknown. To verify the age of the first phase of castle erection, the sample of mortars were collected for radiocarbon dating (Ringbom et al., 2014). To compare the results with another chronometer also the bricks from the chronologically oldest part were taken for TL analyses (Murray and Wintle, 2000). Both types of dating analysis were preceded by detailed material characterization. Compilation of the results of dating different materials (mortars and bricks) by two different methods (<sup>14</sup>C and TL) allows determining the first phases of the castle complex construction.

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## 4B-05 Radiocarbon dating of mortar: Case study of the Aqueduct in Skopje

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Dating of mortar has been a challenge since the early days of the radiocarbon dating method. The idea is to date only the carbon fixed in mortar at the time of binding (i.e., the binder). However, results of <sup>14</sup>C mortar dating are often compromised with dead carbon contamination originating from unreacted limestone during preparation of quick lime. Also, non-binder carbon can be incorporated into mortar sample (1) due to precipitation of secondary carbonates from environment, (2) in case of fire accidents, it is replaced with the carbon from the atmosphere at the time of accident, or (3) if the mortar is too alkaline, it still incorporates carbon from the atmosphere. Therefore, an effort is placed into developing of a method that can isolate strictly the binder carbon, with the help of the accelerator mass spectrometry (AMS) measurement technique enabling analyses of various phases of mortar. However, no reliable procedure has yet been established for each mortar type (Hajdas et al., 2017).

The Zagreb Radiocarbon Laboratory was approached with a request to determinate time of the Aqueduct in Skopje (FYR Macedonia) construction through <sup>14</sup>C dating of mortar samples. The Aqueduct is one of the landmarks of Skopje, a monumental building more than 385 m long. It was a part of a water-supply system with a total length of about 10 km. The age of the Aqueduct is not known – several hypotheses place it to periods between 6th and 16th century. Six mortar samples from different positions of the eastern façade and the upper parts with remains of tubes were collected in July 2017, paying attention that samples were not deteriorated and were situated at higher levels with less possibility of containing the secondary carbon. In the Laboratory, the maximum 5 cm of the mortar from the surface was subsampled, than broken by alternately changing temperatures from -198 °C to 80 °C. In order to extract only the carbon from the binder three strategies for separation of binder carbon were used: 1) mechanical separation of calcite inclusions formed during mortar hardening (not possible for all mortars), 2) selection on the basis of particle size and the ability to suspend in water induced by ultrasonic shock, and 3) collection of at least two fractions of CO<sub>2</sub> produced by reaction of calcite with acid.

With the premise that all mortars originated from the same era, the results of <sup>14</sup>C dating of each fraction were combined to yield a plausible date of the Aqueduct building. Some results were eliminated due to very low δ<sup>13</sup>C values combined with modern <sup>14</sup>C dates and some implied dead carbon contamination. The most reliable results were obtained from two inclusions and one suspended fraction placing the time of the Aqueduct construction in 15-16 century AD.

The analyses will be presented and possibility of using the method for future mortar dating will be discussed.

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## 4B-06 Modelling time -

### Applying Bayesian statistics to the chronology of a medieval urban site in Denmark

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Radiocarbon dating is rarely used in Danish medieval urban archaeology when trying to date events and create an absolute site chronology. Dendrochronology, coins finds and ceramics chronologies are considered to be more effective and precise tools. However, this can turn out to be problematic due to re-deposition of artefacts and reuse of timber. Therefore site chronologies often end up being relative and events being very broadly dated.

By applying Bayesian statistics on all available information from an excavation of a medieval urban site in Odense, Denmark, it has been possible to establish a more precise and detailed chronology of the overall settlement. It has also been possible to determine duration and pace of selected features and events.

Combined with a careful evaluation of the quality and statement value of the radiocarbon samples the case shows the potential of building a detailed site chronology by combining stratigraphy, dendrochronology, datable artefacts and radiocarbon dating. The case also shows how the modelling process is a valuable tool in validating and reassessing the stratigraphic interpretations and selecting new samples for additional radiocarbon dating.

The case is an example of how radiocarbon dating and Bayesian statistics is a valuable but, so far, underused tool in relation to complex urban stratigraphy in Danish medieval archaeology.

## 4B-07 Update on the absolute chronology of the migration period in central Europe (375-568 AD): new data from Maria Ponsee, lower Austria

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During the Migration Period in the middle of the first millennium AD, various ethnic groups wandered through the continental Europe, either to conquer new territories or to retreat from other invading tribes. The Danube region in the western part of the Pannonian Basin in Central Europe was one of the areas where several groups appeared before moving further or being defeated. Among them were the Lombards, who took control over the area surrounding Mautern and in 505 AD they crossed the river to also settle in the “Tullnerfeld” (Klement 2014). About fifty Lombard burial grounds were discovered in Austria, among them the well documented site of Oberbierbaum/Maria Ponsee, located south of the Danube and approximately 40 km west of Vienna. Here, a graveyard with 95 graves (and the skeletal remains of 100 individuals) was excavated between 1965 and 1972. Following the archaeologists’ suggestion, which is based on the grave arrangements (three separated grave groups) and different grave goods, the cemetery of Maria Ponsee seems to be used by three groups of migrants (Friesinger und Adler 1979). From historical evidence about the temporal and spatial migration of the Lombards it was concluded that the graveyard in Maria Ponsee was in use between 505 and 568 AD. To verify the assumptions about the chronology of the graveyard the already existing <sup>14</sup>C data set (see Stadler et al, 2008) was enlarged by new AMS <sup>14</sup>C data from 20 human and 3 horse bones, recovered from this site. The determined radiocarbon dates fit well to the expected time-interval, but a chronological discrimination between the three different grave groups could not be obtained.

Nevertheless, the obtained dates were added to the chronological sequence, recording the Migration Period in Central Europe (Stadler et al, 2008). The sequence, based on a Bayesian model (Bronk Ramsey 2009), lead to a reasonable agreement (A(model) = 77.3%), meaning a good correlation of the modelled and historical data. The results show clear time differentiations of the respective tribes (Goths, Huns, East Germanics) in the pre-lombardic period, however, transitions between the Lombard phases (North Danubian and North Pannonian) were rather ambiguous, indicating that Lombards set up new settlements before abandoning the already inhabited ones, as they were moving to Italy.

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## 4B-08 CRUMBEL: Cremations, Urns and Mobility – Ancient population dynamics in Belgium

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Cremation was one of the main funerary practices if not the major one in Belgium during the Late Neolithic through to the Roman Period. It remained also important during the following ‘Early-Medieval Period’ (up to 700 AD). Still, Belgian cremated bone collections have only been studied in a limited number of cases. However, almost twenty years ago, it has been shown that radiocarbon dates could be obtained from cremated bone. Several Belgian collections have since been dated providing much more in-depth information about the chronology, development, and disappearance of cremation as funerary practice in Belgium. Furthermore, thanks to the recent demonstration that calcined bone provides a reliable substrate for strontium isotopes, it is now possible to study population dynamics.

The CRUMBEL project takes advantage of these new developments and will apply them to Belgian cremated bone fragments from the Late Neolithic to the Early Medieval Period improving our current understanding of how people lived in Belgium between 3000 BC to 800 AD. Until now, the dominance of cremation as funeral practice from that period in Northwestern Europe led to limited information on migrations and living conditions.

As for most large scale archaeological research project, radiocarbon dating plays a central role in replacing the osteoarchaeological and isotope results in a chronological context. As such, more than 600 cremated bone fragments will be radiocarbon dated. Together with the radiocarbon dates already available for Belgian cremated bone fragments (ca. 400), it will represent one of the largest set of radiocarbon dates of cremated bone. Combining these results with information gathered on funerary rituals, particular attention will be given to the “old wood” effect as the importance of its impact on the dates is still often under evaluated.

## 4B-09 Early Mediaeval Ducal Graves K1 and K2 at Prague Castle (Czech Republic)

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The graves K1 and K2 were found in 1911 in the nave of the St. Guy rotunda situated in front of the grave of St. Wenceslas. The graves are according building development of the rotunda dated to the period between 938 and 1039 AD. The grave K1 was found complete. Iron knife was only found equipment. The grave K2 was disturbed and only fragment of lower limb survived. The individual in grave K1 was determined to be a male and was identified as Prince Bořivoj (†c.888/889) or Prince Boleslav I (†972) or Prince Boleslav II (†999). The K2 was not interpreted or supposed to be a wife of the man from grave K1.

All available data (archaeology, anthropology, stable isotopes, DNA) were revised or newly analysed. It can be assumed that the individual in grave K1 died at the age of 30-40 years (age category of adultus II). Individual in grave K2 lived longer than 30 years. Dietary habit raises the hypothesis that the individuals were probably members of the earliest generations of ruling Přemyslid dynasty. Their diet reveals the surprisingly 'non-elite' character. The DNA results show that the individual in grave K2 was female. A rib fragment was collected from the individual K1 for <sup>14</sup>C dating (sample CRL 17\_197). The result of the dating is the compact interval between the years 774 and 894 (95% absolute probability). However, if the result of the <sup>14</sup>C analysis is interpreted for a probability level of 99.7%, the dating result gives two intervals: the main interval is between 770 and 903 (with an absolute probability of 95.3%), the secondary interval between 919 and 962 (with an absolute probability of 4.4%). The obtained data do enable a simple interpretation. Radiocarbon dating and age determination apparently correspond best to Bořivoj I, archaeological conclusions rule out this possibility. In the case of Boleslav I and Boleslav II, the anthropological determination of age collides with the historical notes from which their age is deduced. However, the result of the radiocarbon dating is inconsistent, as the end year of the 95% interval of probability is exceeded by more than 100 years (894x999 – for Boleslav II). It is also chronologically removed from the latest specified interval (916-962) with a probability of roughly 96% (for Boleslav I and Boleslav II).

The existence of male non-ruling Přemyslids was taken into consideration. The one of the sons of Boleslav I is documented in 950, when he defended the 'Urbs nova' hillfort against the army of Emperor Ota I. This son died before the death of his father is most probably the person in the grave K1. The individuals were a married couple, as indicated DNA analysis identifying the person in grave K2 as female.

## 4B-10 The chronology of two medieval cemeteries in central Copenhagen –Bayesian modelling and archaeological relative age information

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Historical sources reveals that Copenhagen was founded in the late 12th century AD by Bishop Absalon. However, during the excavation for the new metro in central Copenhagen a previously unknown early medieval cemetery was discovered and excavated at the Town Hall Square. Radiocarbon analysis was conducted on the 9 individuals found in situ, together with 11 individuals from the other early medieval cemetery in Copenhagen, belonging to the St Clemens church. The radiocarbon analysis place the onset of the cemeteries to the early 11th century AD and therefore questions the age of Copenhagen and hence the archaeological and historical perception of the Danish historical record (Dahlström et al., 2017). Here a detailed account of the radiocarbon based Bayesian model is presented

## 4B-11 Chronological reconstruction and dietary habit of the copper archaeological site of Selvicciola (Viterbo, Italy)

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The Copper Age cemetery at La Selvicciola (Ischia di Castro, Viterbo) was discovered in the 1987, very close to the confluence of the Fosso Strozzevolpe and the Fiora River. In spite of the post-depositional disturbance, mainly due to Roman structures, the prehistoric graves are rather well preserved. The 31 Copper Age graves were excavated into the travertine bedrock and are usually constituted by a small access pit and a funerary chamber, containing a variable number of individuals, from a single primary deposition up to 14 commingled and disarticulated individuals. The archaeological excavations and the post-excavation studies have been carried out by a team of specialists, including physical anthropologists, in order to reconstruct the taphonomic processes affecting bones and document the complexity of mortuary rituals (Conti et al. 1997; Conti et al. 2006).

At the present day, 120 individuals have been identified, spanning over almost two millennia, approximately from the half of the fourth millennium BC to the end of the third. The good preservation of the context, the demographic sample and the richness of grave goods above all highlight the extreme relevance of La Selvicciola for the understanding of Rinaldone Culture.

One of the most “provocative” characteristics of the cemetery is the topographic distribution of the graves into two clearly separated areas, namely “settore Est” (eastern area) and “Settore Nord” (northern area). The human bone and grave good distributions suggest that the funerary space might be assigned to two segment of the community, e.g. two distinct kinships or lineages. Concerning metals, for example, we see the presence of silver and antimony objects in the eastern area, whilst implements and copper weapons have been found exclusively in the northern area (Petitti et al. 2012). Moreover, a wide set of radiocarbon dates seems to reveal some chronological asymmetries in the use of the two burial groups.

In this paper, we present the results of the interdisciplinary study, focussing on stable and radioactive isotope analysis addressed to the reconstruction of chronology and dietary habits of the La Selvicciola population, also in the perspective of the intra-population variability expressed by the above-mentioned topographic partition of the cemetery.

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## 4B-12 Radiocarbon dating in Protohistorical and Classical archaeology: the Monte Bernorio case study

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Essential to historical research is the availability of reliable and precise chronologies. This is often achievable within Classical Archaeology given the abundance of written sources and well-datable artefacts. However, chronological uncertainties may persist when contexts are poor in datable remains, the stratigraphy is unclear or has been disturbed, or when organic artefacts (e.g. bone) are decontextualized. In these cases, radiocarbon dating of organic materials, a chronological tool typically underused within Classical Archaeology, can make valuable contributions. Furthermore, the employment of a Bayesian modelling approach in which multiple sources of chronological data are combined with radiocarbon dating results can allow for great improvements in the precision of chronological determinations.

Such an approach was applied in the study of the site of Monte Bernorio, a large fortified settlement (oppidum) from the first millennium BCE, located in the Province of Palencia in Northern Spain. During the Iron Age, Monte Bernorio was one of the main centres of the Cantabri until its conquest by the Roman army of Emperor Augustus during the Cantabrian Wars (29-19 BC).

Bayesian modelling relied on a combination of older and newer radiocarbon measurements, stratigraphic information, and approximate typological dating of artefacts. Model outputs offered significant insights into the chronology of burial practices at Monte Bernorio and practices of artefact exchange with the Roman world.

## 4B-13 <sup>14</sup>C-Dating of the Late Bronze Age city Hala Sultan Tekke, Cyprus

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Hala Sultan Tekke is a large Bronze Age city which flourished roughly at 1600–1100 BCE. In archaeological circles this ancient city has been known since the 19th century when unprofessional excavations began. The city is located on the southeastern littoral of Cyprus along today's isolated Larnaca Salt Lake which earlier was connected to the Mediterranean Sea. Owing to the best protected harbour on the island the city became one of the most important and wealthiest trading centres at that time.

From the 1970s on the exploration of the city developed into a Swedish project which since 2010 is directed by Peter M. Fischer. Most recent excavations have exposed three new city quarters with three occupational phases (Strata 3–1) the dating of which is of highest importance. The recently excavated material demonstrates imports from a vast area. This includes most of the Mediterranean comprising Italy, the Aegean, Anatolia, the Levant and even southern Scandinavia. In 2014, 600 m to the east of these city quarters, one of the richest cemeteries on the island was discovered and explored by the Swedish mission (Fischer and Bürge 2017).

So far, the material from the city dates – according to the archaeological evidence and partly supported by radiocarbon dates – to the 13th and 12th centuries BCE. However, many of the rich tomb gifts from the cemetery are considerably older: in archaeological terms they date to the 16th century (confirmed by radiocarbon dates). This raises the question where the oldest city quarters are situated.

In the 2016 the Swedish Research Council provided an advanced grant (no. 2015-01192, Principal Investigator Peter M. Fischer) for the project “The Collapse of Bronze Age Societies in the Eastern Mediterranean: Sea Peoples in Cyprus?”. Consequently, the original objectives of the initial project which include the investigation of the total extent of the city and the location of the oldest city quarters has been supplemented by studies of the reasons for the sudden abandonment of this flourishing city around 1150 BCE. This event falls into the much-discussed period of the appearance of the mysterious “Sea Peoples”.

Radiocarbon dating is essential to this interdisciplinary project. We strive to provide numerous <sup>14</sup>C age determinations of preferentially short-lived samples. To date, a number of <sup>14</sup>C results from different parts of the excavated area have already been obtained and will be presented in our contribution.

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Fischer, P.M. and T. Bürge (a), Tombs and Offering Pits at the Late Bronze Age Metropolis of Hala Sultan Tekke, Cyprus. *BASOR* 377, 2017: 161–218.

## 5A-01 To Date or Not to Date? Do Radiocarbon Dates on Charred Food Crust Reflect time of Food Preparation?

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Carbon sources for animals and plants selected as food are varied and can include at least carbon dioxide from the atmosphere, dissolved inorganic carbon (DIC), and ancient organic carbon. People harvested plants, hunted animals, and/or fished, creating a mixed bag of carbon for their food pots and their bodies.

In most areas of North America dates on charred wood are recognized as having the potential to be older than their context due to tree lifespans and patterns of burning wood, which consumes the outer portions of the logs, often leaving the inner rings for recovery in thermal features. Bones are considered to be more closely associated with contexts due to relatively short lifespans of most hunted game animals. Annuals (nutshells and seeds) should provide accurate dates for contexts. Charred food crust was originally thought to be as accurate as bones and perhaps nearly as accurate as annuals for radiocarbon dating. Unfortunately, bones and charred food crust from some areas both show potential to date “too old”. Lab methods using XAD resin to remove post-depositional contamination from bone gel do not compensate for the diet of the animals.

Dating charred food crust presents unique challenges, in part due to the fact that cooked food is rarely one single ingredient; it combines plant and animal organic compounds, each of which has different properties that require evaluation. The carbon content in charred food crust (residue) can be a combination of carbohydrates from land plants and proteins and fats/lipids from either land or aquatic animals. Wild rice and other aquatic plants also contribute carbohydrates to the food pot. Pyrolysis, which does not occur in the presence of water, is the process of forming a golden-brown (or darker) crust in carbohydrates or protein when cooked (pyrolysis of fats/lipids occurs at much higher temperatures). The portion of food that rises above the water level to the neck or rim of the ceramic vessel is the most likely to char. Observing boiling pasta, we expect carbohydrate-rich debris on the rim and both outside and inside the neck of vessels, whereas soot from fires is expected on the lower to middle portion of the vessel exterior. This observation guides our sampling protocol. This apparent separation of food compounds during cooking offers a unique opportunity to apply chemical methods to separate the more completely charred carbohydrates from the less charred proteins and uncharred fats/lipids.

Use of a chemical pre-treatment protocol in the laboratory prior to radiocarbon dating charred food crust has met with considerable success. Adding a mixture of polar and non-polar solvent to the existing acid-base-acid protocol removes the uncharred animal fats/lipids that contain more ancient carbon. The original target for removal using this protocol was fats/lipids. The objective was to reduce the material being dated to only or primarily the carbohydrate constituent. Dates on treated charred food crust and associated annuals are presented, while dates on reference animals are presented elsewhere.

## 5A-02 Discussing the dietary patterns of indigenous groups in Cerritos through the stable isotope analysis

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Cerritos are archaeological sites described as earthen mounds, present along the lowlands of the Pampas biome and La Plata Basin, among Brazil, Uruguay and Argentina. The earthen mounds located at the Patos Lagoon (an estuarine system), southern Brazil, were built for different functions over time including temporary camps and residential household, refuse disposal areas, ritual places and, perhaps agriculture.

The radiocarbon dating performed on hearths found on the base of the mounds suggests the beginning of occupation around 2200 cal BP, when the Pontal da Barra swamp was occupied as transient fish camps. After that, there is a clear process of architectural complexity between 1800 and 1200 cal BP. The later period of occupation, according to the radiocarbon dates, was approximately 800 cal BP. The reason for the abandonment of the region was not clearly known.

Through the stable isotope analysis it is possible to reconstruct dietary patterns of past populations based on their bone remains. Aligned to the radiocarbon dating, such analyses become a powerful tool that may allow us to identify behaviour patterns of occupation. In this study we used such analyses to try to understand what have motivated the abandonment of the settlement after centuries of systematic occupation and additionally to better describe the habits of this indigenous group.

Through the statistical analyses based on the  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  values on the collagen and apatite fractions of the human and animal bones found in these sites we observed a distinguished marine signal on the diet of some individuals likely due to the Patos Lagoon resources exploitation. Therefore, it must be applied a MRE correction to the  $^{14}\text{C}$  ages proportional to the marine protein intake. Such correction was estimated by us in a previous work. It showed, however, a strong continental influence in the isotopic signal of the Patos Lagoon and, consequently, in the isotopic signal of the aquatic samples in the Cerritos' sites.

The results obtained in this work are inedit for the Brazilian Cerritos and have contributed to the clarification of key questions about their function and the behaviour and economy of the Cerritos' groups.

## 5A-03 Less is more – Reducing artefact damage through integrating ZooMS into the radiocarbon dating process

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ZooArchaeology by Mass Spectrometry (ZooMS) is a powerful technique for species identification of collagen based materials. It is especially effective in combination with direct radiocarbon dating of archaeological artefacts and human fossils, which can lay the chronological basis for investigating raw material use and biocultural expressions. However, the combined application of radiocarbon dating and ZooMS is often complicated by the fact that many osseous artefacts and potentially human fossils are small, precious, and – especially in the Palaeolithic – show low collagen yields. As a result, reducing sampling damage is crucial to maximising analysis potential, and preserving the artefact/fossil. We present the results of integrating ZooMS analysis into the radiocarbon dating process at the Oxford Radiocarbon Accelerator Unit (ORAU) by recycling waste products from the radiocarbon pre-treatment, resulting in a reduction in required sample mass by up to 25%. Application of this integrated methodology is illustrated through a case study on precious Aurignacian osseous spear points.

ZooMS uses restrictive enzymes (e.g. trypsin) to cut the sample's proteins at specific sites, resulting in consistent and predictable peptide fragments. Matrix-assisted laser desorption/ionisation (MALDI) is used to analyse the peptide structures and compare the result to a reference database for genus and species identification. Therefore, the most frequent target material for ZooMS samples is bone collagen. Radiocarbon dating of bone also targets the collagen – or its components – for many standard (modified Longin, ultrafiltration) and non-routine protocols (single amino acid dating). While radiocarbon dating discards the HCl solution used to demineralise the bone powder, ZooMS can use the collagen dissolved in the HCl solution for analysis. In principle, this allows ZooMS to use a waste product from the radiocarbon dating pre-treatment, thereby eliminating the need for a separate bone powder sample and reducing the required overall sample size.

The effectiveness of our technique was tested on 12 Palaeolithic faunal fragments, which cover an age range from 26k BP to radiocarbon background and a collagen yield from very poor (0.07 wt.%) to very good (8.61 wt.%). Following the standard ORAU bone protocol (Brock et al. 2010), we extracted HCl solution for ZooMS after each radiocarbon demineralisation step, leading to three individual and one combined fraction per sample. The spectra were compared to ZooMS results obtained from bone powder using standard ZooMS protocols for soluble and insoluble collagen.

After having demonstrated its potential, we apply the new integrated radiocarbon/ZooMS methodology to analyse osseous spear points from the Aurignacian in Hungary and Slovakia. These are artefacts for which sample material is very limited, and stratigraphic information is often insufficient to address questions of spatio-temporal variability in manufacturing technique and raw material use.

This research demonstrates the effectiveness of obtaining ZooMS species identifications from radiocarbon pre-treatment waste. The new integrated methodology leads to a reduction in required sample size (and preparation time), thus increasing the analysis potential of precious archaeological artefacts. This novel technique can offer an important analysis strategy for investigating the spatio-temporal variability of osseous tools, weapons and figurative art.



## 5A-04 Approaches to determine reservoir effects in elk/moose

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The elk/moose (*Alces alces*) was an important resource for prehistoric societies. In prehistoric art, it is often depicted in connection with water. Also, biologists find that elk spend a lot of time in water and consume considerable amounts of aquatic plants. As freshwater plants can have reservoir ages of hundreds or even thousands of years, there is a risk of a significant reservoir effect in elk bones and antler, and artefacts made of these materials. This study followed several approaches to investigate the possibility of a freshwater reservoir effect in elk. We analysed modern, historical and archaeological bones and antler from several sites across Eurasia. Skull bone and antler of the same individual were radiocarbon dated, as antler is formed in summer, when the proportion of aquatic diet is supposed to be highest.

The maximum reservoir effect measured in this study was about 500 years, and only found in one individual. A difference between bone and antler could not be determined. The reservoir effect appears to be smaller than estimated from accounts of elk diet, even in regions where a substantial freshwater reservoir effect is expected. Therefore, the hypothesis of a large proportion of aquatic diet can be rejected for several of the individuals studied here.

This study was supported by the IFA Ideas prize 2014.

## 5A-05 $\delta^{13}\text{C}$ values of wood and charcoal reveal broad isotopic ranges at the base of the food web

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This study presents over 400 radiocarbon and  $\delta^{13}\text{C}$  analyses of wood and charcoal samples from a large excavation project in Denmark. Prior to the construction of a tunnel through the Femern belt, between the Danish island of Lolland and the German island of Fehmarn, an area of about 300 ha is under archaeological investigation. The excavations uncover about 10,000 years of human activities in a changing coastal landscape. The former sea floor offers excellent conditions for the preservation of wood, while charcoal is found in great quantities on dryland sites. All dated wood and charcoal samples are identified to species, if possible, and their  $\delta^{13}\text{C}$  values measured by offline isotope ratio mass spectrometry (IRMS).

Our results span a range of over 11 ‰. A time dependence of the  $\delta^{13}\text{C}$  values could not be observed. However, different species seem to comprise different  $\delta^{13}\text{C}$  ranges, although there are large overlaps between species.

When stable isotope measurements are used for studies of subsistence and diet, great emphasis is placed on a thorough analysis of the isotopic baseline, i.e., the isotope ratios of potential food items. Traditionally, animal bones of as many species as possible are used for this purpose, with several measurements on different individuals of the same species in order to assess the possible isotopic ranges. Plant food, however, is often underrepresented, as it only is present in the archaeological record when charred grains, hazelnut shells or fruit seeds are preserved. The  $\delta^{13}\text{C}$  values of wood and charcoal (and a few hazelnut shells) presented here cannot serve as a proxy for plant food in general, but can illustrate the degree of variability that has to be expected at the base of the food web.

## 5A-06 Chronological challenges to understanding the earliest farming communities in SW Asia

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Agriculture in south-west Asia emerged within a context of specific cultural and historical developments. Hence, to understand the transition from cultivating wild plants and animals in the final Pleistocene, to the emergence of morphological domesticates in the earlier Holocene, we need to have a good understanding of the communities behind this process. Such an understanding requires a strong empirical basis that has to include real-time chronology of cultural change on all scales, from that of the whole of south-west Asia, to that of specific settlements.

However, the specific challenges posed by both the nature of the sites in question, and the diagenetic processes of arid environments, mean that the scope of reliable data is limited and so is our understanding of the communities that developed agriculture. The paper explores how the taphonomic and diagenetic processes limit the range of archaeological contexts that can be radiocarbon-dated, and how the nature of the sites themselves limits the range of inferences that can be drawn from these contexts. This highlights the importance of the ongoing technical developments in microarchaeological sampling, dating bone with little or no preserved collagen, and the nuance of interpreting chronological models.

## 5A-07 Dating charred remains on pottery and analyzing food habits in the Paleometal period in Lower Amur Basin, Russia

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In recent years, carbon and nitrogen isotope ratios of charred residues on pottery unearthed from archaeological sites have provided information about prehistoric diets. The authors have engaged in such studies in Northeast Asia (cf. references). At the Ustinovka 8 site in Russian Far East, we demonstrated that this analysis can be used for dietary reconstruction, and described the possibilities that millet were used by the Lidovka culture of the Bronze period.

This study reconstructs food habits through carbon and nitrogen isotope analysis, and C/N analysis of charred residues inside pottery from Amur River sites (Petropavlovka 5, Malmyzh 1, Zhertyj Yar) in Russia. The transformation process of the Neolithic and Paleometal subsistence in Lower Amur Basin has been examined through the fieldwork and analysis of related materials. The aims of the research project are establishing the Neolithic to Paleometal chronology and investigation of food habits in this period. Identifying the age and subsistence activities of regional cultural groups is important for discussing the process of cultural formation. One of the major subject is acceptance of cultivated cereals and spread.

We obtained dates 2330-2260BP for Petropavlovka 5, 2310-1815BP for Malmyzh 1, 1835-1685BP for Zhertyj Yar site in the Paleometal period. The charred samples from the Zhertyj Yar and Petropavlovka 5 site tended to have a higher carbon isotope ratio and lower nitrogen distribution, suggesting that the people utilized C4 plants such as millet. In particular, the result of the Zhertyj Yar site indicated distribution of the region covering C4 plants ( $\delta^{13}\text{C}$   $-10.5\%$  and  $\delta^{15}\text{N}$   $6.1\%$ ). On the other hand, we identified millet (*Setaria italic*, *Panicum miliaceum*) using the archaeobotanical analysis of cultivated cereals identified from seed impressions on potsherds. The food boiled in the pots indicated a high dependence on millet during the the Paleometal period in Lower Amur Basin.

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## 5A-08 The nature of Hallstatt-period cultural transformation in the north of Central Europe in light of radiocarbon dating of the Late Bronze Age stronghold at Łubowice near Racibórz, SW Poland

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At the close of the Bronze Age, in the stylistic phase HaB (1050/1020-810/800 BC), a tendency became evident in Central Europe for settlement concentration and rise of territorial communities of the “little homelands” type. This specific, “barbarian” form of synoecism (Greek: *synoikismós*) manifested itself through the fortification of settlements and the establishment, in places marked by the regionally highest concentrations of environmental and cultural resources, of centres (strongholds) serving special economic and social functions. One of the largest sites of that type, nearly 25 ha in area, is the stronghold at Łubowice near Racibórz, situated to the north of the Moravian Gate, a nodal place for communication routes linking the north and south of Central Europe. Archaeological evidence suggests that the stronghold was founded and developed during the stylistic phase HaB, and later met a violent end (being burned down) in the Hallstatt period (810/800-520 BC), in a time by which Hallstatt cultural patterns (including a distinct style of pottery manufacture) had already become predominant. In the absence of other clues, this fact was associated with the catastrophic impact of what is known as the Scythian invasions, a wave of nomadic military raids which affected some parts of Central Europe between the last quarter of the 7th century BC (e.g. the destruction of the Smolenice stronghold in SW Slovakia) and 570-550 BC (e.g. the destruction of the Wicina stronghold in Lower Lusatia, in the west of Poland). Since the stronghold in Łubowice lay near the Moravian Gate, which means on a route used by nomads originating from steppe areas of the Great Hungarian Plain, its destruction was believed to have been chronologically connected with one of these raids. However, radiocarbon analyses of charcoal samples from the burnt fortifications have shown that, while the monumental timber and earth fortifications protecting Łubowice were indeed constructed within the stylistic phase HaB (975-850 cal BC), their destruction should be dated much earlier than previously thought (830-800 cal BC). Thus, the fortifications were burnt down at the transition from HaB to HaC or in the very beginnings of HaC (HaC1 = 810/800-720 BC). The spreading of a new, Hallstatt cultural model probably involved a deep transformation of social structures, with the rise of politically strong elites as one of the main features. These processes could have locally brought about much political turmoil, which could have resulted, among other things, in the destruction of some earlier settlement centres, such as the Łubowice stronghold.

## 5A-09 Bronze Age human activity inferred from ‘cocking stone’ pits, southern Jutland, Denmark

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Archaeological investigation conducted by Haderslev Museum have revealed that during the Bronze Age in southern Jutland that ‘cocking stone’ pits functioned as gathering points for social activities. These gathering points are likely to have gathered people from within a 30 km radius. The gathering points are concurrent with <sup>14</sup>C dated finds of house structures in the region. However many of ‘cocking stone’ pits are found to be unrelated to permanent structures such as houses or other settlement activities. Here we present 126 <sup>14</sup>C dated ‘cocking stone’ pits. The calibrated ages range more than a 1000 years and cannot be related to settlement activities or put into a stratigraphically context. Hence, Bayesian analysis appears out of reach in order to improve the accuracy of the calibrated age ranges. Still the 126 <sup>14</sup>C dated are believed to hold information on the human activity of using the ‘cocking stone’ pits as gathering points. Using the ‘cocking stone’ pits as a proxy for human activity we present a new method for estimating activities from cumulative calibrated age probability distributions.

## 5A-10 Seeing through the Hallstatt plateau at Loch Tay Scotland.

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There are at least 18 recognized lake dwellings (crannogs) within Loch Tay, Scotland. Previous sampling and radiocarbon dating campaigns identified that the earliest stages of this phenomenon date to the Hallstatt plateau (750—400 cal BC). This means that, currently, we have a very limited understanding of the motivations behind, and the nature of, the beginning of lake dwelling in Loch Tay, as the chronology of these sites is limited to by a 350-year window imposed by the calibration plateau.

The Living on Water Project seeks to change this through a combination of radiocarbon wiggle-match dating and relative dendrochronology. These two techniques can relate preserved structural features of the lake dwellings both within and between sites, and date them with sub-centennial precision. Hence, evidence of structural practices, provided by three-dimensional recording of the exposed areas, and of environmental change provided by samples of organic material collected from features associated with the sampled structures, is placed in time. These results can also be related to the surrounding land-form and extant terrestrial settlement, thus providing a nuanced understanding of the communities living on the water in Loch Tay in the mid-first millennium BC. To date three of the 18 sites were re-visited and re-sampled, with the new data confirming Hallstatt plateau attribution of the sites and identifying potential refurbishment or maintenance events. Further three sites will be explored in 2018.

## 5A-11 Radiocarbon measurements on a charred olive tree from Therasia, Greece.

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We report new radiocarbon dates on a charred olive shrub recovered from a clifftop archaeological site on the Island of Therasia, Greece. The site was abandoned before the Late Minoan eruption of the Thera volcano, at the end of the Middle Bronze Age. The olive sprouted on the surface of the abandonment layer of the site, by an ellipsoid structure, and was found below the layer of pumice of the Minoan eruption which buried the shrub and carbonized the wood. Three roughly cylindrical, small diameter twigs were removed from the trunk. They were selected based upon the presence of bark, and visible, semi-concentric rings which cannot be interpreted as annual growth. Pith, outer wood, and bark sections were dissected and radiocarbon dated. The mean radiocarbon content of the outer wood from the three twigs is statistically identical to radiocarbon dates from the outer '13-ring' section of the Santorini olive branch reported by Friedrich et al. 2006. It is also identical to radiocarbon measurements both on a subset of Akrotiri seeds and the outer three rings of a Tamarisk buried at Akrotiri under Thera ash, and reported by Manning et al. 2006. The Therasia site completes a geographic triangle surrounding the Santorini caldera with Akrotiri and the Santorini olive tree comprising the other two points. The congruence of the new Arizona measurements with past measurements from multiple laboratories has particular relevance in light of new studies by Pearson et al. (in review). These studies demonstrate that the radiocarbon content of dendrochronologically dated, annually resolved tree rings from American Bristlecone Pine and Irish Oak spanning the 17th to mid-15th Centuries BC do not sit on the IntCal calibration curve. The determination of a true calendar date range for the Therasia olive twigs is therefore, for the moment, controversial. Calibration using this new annually resolved calibration dataset pushes the Therasia olive wood dates into the early 16th Century BC, and has similar implications for dates from other sites around the caldera, and hence the timing of the Late Minoan eruption of the Thera volcano.

## 5A-12 Chronology of the origin and early dispersal of opium poppy in Europe.

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Opium poppy (*Papaver somniferum* L.) has been of economic, therapeutic and symbolic importance for thousands of years. Seeds are regularly discovered on archaeological sites. The earliest are dated between 5300 and 2000 BC in Western Europe. In the absence of textual sources, these remains correspond to the most direct and reliable evidences of the presence, the use and the cultivation of opium poppy in the past (Bakels 1996, Salavert 2011, Antolín et al. 2015, Martin 2015). The opium poppy does not seem to have followed the same trajectories than cereals (wheat, barley) and legumes (pea, lentil) which have accompanied the first farming communities from the Near-East to Western Europe, from the beginning of the seventh millennium BC (Salavert 2017). One of the hypothesis concerning its origin is that the plant was initially cultivated in the Western Mediterranean basin from the middle of the sixth millennium BC, where its putative wild ancestor – *Papaver somniferum* subsp. *setigerum* (DC.) Arcang – developed. However, to date, the most numerous discoveries of *Papaver somniferum* beyond the Mediterranean region are located in Linear Pottery Culture sites (5300-4900 BC) thus following a dispersal dynamic from south to north. One of the main obstacles currently preventing us from going further in the study of the opium poppy is an imprecise chronological framework, which covers the origin and distribution of the poppy, based on absolute and relative dates of low resolution. The purpose of this one-year project funded by the Fondation Fyssen is to identify the initial centre of cultivation of the plant and to establish a chronological setting of its cultivation and dispersal during the Early Neolithic in Western Europe. This work is based on a solid dataset of archaeological sites where seeds are identified as well as an ambitious program of radiocarbon dating. We will directly date poppy seeds which is a real challenge due to the size of the samples (typically 10-30 micrograms per seed). The use of the “Mini Radiocarbon Dating System” installed at Gif-sur-Yvette in France (ECHO-MICADAS) will allow measuring the <sup>14</sup>C activity of these very small samples. The results will then be analysed using a geographic information system (open-source software, QGIS©). This tool will help us to identify the potential cradle(s), rhythms and diffusion processes of opium poppy in Neolithic Western Europe.

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## 5A-13 Radiocarbon dating and Bayesian modelling in Jerash/Gerasa, Jordan

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This paper presents radiocarbon dates obtained within the Danish-German Jerash Northwest Quarter project. Since 2011, the largely unexplored Northwest Quarter of the Decapolis town of Gerasa, today's Jerash, has been under investigation by Aarhus University and Ruhr-Universität Bochum. The project studies the settlement history of this city from Hellenistic/Roman times into the Medieval period. The extensive excavation campaigns of the Northwest quarter of Jerash resulted in more than 80 radiocarbon samples on a number of different materials. Whereas most of these results are presented here for the first time, the radiocarbon dates of mortar samples from trench Q have previously been reported (Lichtenberger et al. 2015). Our overall aim here is to present the radiocarbon results for each trench and not least to discuss their implications on the overall chronology of the Northwest Quarter. In order to do so we will employ Bayesian statistics to constrain calibrated age ranges. The prior information for these Bayesian models is based on archaeological field observations and stratigraphy.

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## 5B-01 A refined chronology for caves 268, 272 and 275 in the Dunhuang Mogao grottoes utilising a Bayesian statistical framework

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The Dunhuang Mogao Grottoes complex is widely known as one of the largest and best-preserved ancient Buddhist sites in the world. These caves, dating from various dynasties, were built in the Mingsha mountains, approximately 25 km northeast of the modern Dunhuang city, Gansu province, northwestern China. Today, the Dunhuang complex comprises a total of 715 caves, 2145 statues, and approximately 45,000 m<sup>2</sup> of wall paintings, and was designated a UNESCO World Heritage Site in 1987.

However, the chronology relating to the Grottoes' construction – in particular to three of the earliest grottoes (Caves 268, 272 and 275) – has been the subject of ongoing debate for over half a century. The establishment of the Grottoes is of critical importance to the spread of Buddhism within the Gansu corridor and its relationship with the development of Buddhism in the Central Plains. Here, we utilise Bayesian statistical modelling to combine archaeological information with new and previously published radiocarbon data to provide a refined chronology for these caves. Thus, we determine that all three of these caves were constructed around AD 410–440, a period in which Dunhuang was controlled by the Western Liang and the later Northern Liang dynasties. Our data suggest coeval rather than sequential construction. And, moreover, that none of these three caves can be the earliest cave constructed at Dunhuang Mogao (in AD 366) indicated by an inscription from the Tang dynasty.



## 5B-02 Radiocarbon dating of the medieval silk costumes from Ryukyu Islands, Japan

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The cultural heritages have been preserved to some extent in Ryukyu Islands after heavy destructions of not only military facilities but also privately owned property during the Second World War. In the research on historical clothing and accessories, some Ryukyuan traditional costumes have been preserved privately and can be investigated directly. Nowadays, analysis on producing processes of the ancient silk costumes is going on based on the studies of techniques for dyeing and weaving as well as sewing and embroidering by hand. In addition, it is important to know whether the ancient silk costumes were produced domestically or imported from Japan and/or China. For such systematic studies, it is important to know the age when the costumes were produced.

We collected a part of cloth or cloth-fragments of unknown positions, from the costume for radiocarbon dating. The cloth sample was treated with acetone to get rid of lipid contamination on sample surface, and rinsed with diluted acid-alkali-acid solutions (0.2-0.3M), without damaging the silk and cotton threads. The pre-treated samples were combusted to CO<sub>2</sub> and the produced CO<sub>2</sub> was changed to graphite in a routine method. The carbon isotope analyses were performed with a 3.0 MV Tandetron AMS system (Model 4130-AMS, HVE, the Netherlands) at Nagoya University.

The oldest among thirteen costumes dates back to mid-fifteenth century, but some younger ones are in the ambiguous calibrated-age range (AD 1650- 1940). Among the costumes, one with gorgeous and colorful embroidery has an evident historical record. The costume was a holy dress special for local woman priest and has been preserved by the Naka family in Izena Island. Legend says that the costume was a present from Shoen, the king of Ryukyu Islands (he ruled the islands from AD1470 to 1476) to his elder sister who lived in Izena Island. It was dated to be AD1426 – 1474 by radiocarbon analysis, and the date is quite consistent with the historical record.

The present experiment suggests that acetone and AAA treatments are adequate for radiocarbon dating of silk and cotton samples that were produced in the final of medieval and after. To answer the question whether the silk costumes existing in the Ryukyu Islands were produced domestically or transported from Japan and/or China after mid-fifteenth century, we need to date more silk costumes in collaboration with researchers on historical clothing and accessories.

## 5B-03 AMS Dating of wooden sculptures from a Shinto shrine in Akita, Japan

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Determining the timing of the formation of historical objects is a key to understanding the cultural development of societies. One such object that we investigate in this study is a pair of guardian dog statues, called KOMAINU. These statues are often installed at Shinto shrines in Japan and are ordinarily made of stone due to better preservation. However, here we analyzed rare wooden KOMAINU found at Akagami Shrine in Akita prefecture, Japan. The age determination exercises have been conducted measuring <sup>14</sup>C-wiggle matching techniques. The calendar ages obtained from the body of the KOMAINU shows the statue was formed in the Heian era at around 1200 cal yr BP. This is consistent with the age of the shrine establishment written in historical documents, though a calibrated age obtained from another body shows it is more than 100 years older. Moreover, a calibrated age obtained from one of the KOMAINU legs shows more than 100 years younger than that of the shrine age. This suggests that KOMAINU could be repaired ~100 years after they were originally carved. Thus, the multiple <sup>14</sup>C-wiggle matching method can determine precise calendar ages of historical artifacts, as well as the history of said artifact after the its original formation.

## 5B-04 Absolut dating of early iron objects from the ancient Orient: Radiocarbon dating of Luristan Iron Mask Swords

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Iron Mask Swords are somewhat mysterious iron objects. Recovered mostly from illegal diggings in the 1920ies, the about 90 known objects are distributed in private and museum collection. Just recently one sword was recovered during a rescue excavation in Nurabad, Luristan, Iran (Hasanpur et al. 2015). The swords are characterized by a rounded pommel on the top of the handle with two mounted bearded heads on two sides, a rectangular shaped handle with 2 clamps and two kneeling animal figures on the lower part. The blade is turned 90° with respect to the handle. The overall size of these objects are about 30 -60 cm.

Lacking contextual finds, a first assessment of the age of these objects came from two radiocarbon measurements on two Luristan swords from 1) Royal Ontario Museum and 2) the Massachusetts Institute of Technology collection (2880 ± 60 BP and 2940 ± 60 BP, resp.; Chresswell 1992).

Here we present the results of 1. metallurgical analysis and 2. radiocarbon measurements for 4 newly acquired Luristan swords, which were donated to the Royal Museums of Art & History, Brussels.

Metallurgical analysis (microstructure analysis, SEM/EDX) indicate an iron production via the bloomery furnace technique. Analyzed samples show large slag inclusions (Fayalith, wustite, glass) within mostly ferritic and perlitic iron. Carbon contents varied between <0,1 wt% to 0.8 wt%.

Radiocarbon measurements on thermally extracted carbon (e.g. Hüls et al. 2011; single and duplicate measurements) gave radiocarbon ages between 2800 BP - 3360 BP (calibrated ~1745BCE - 900 BCE). The reliability of the radiocarbon measurements are discussed with respect to external (contamination during handling) and intrinsic contamination (e.g. fossil carbon sources during manufacture).

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## 5B-05 Radiocarbon dating of ancient textiles owned by the Kyoto University Museum.

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The Egyptian antiquities collection of Kyoto University Museum were mostly donated by EEF through Professor Kosaku Hamada who had been studied at Professor Flinders Petrie's laboratory in London University.

In our previous study, the Coptic textiles of the museum collections were examined by radiocarbon dating and natural dye analysis for understanding Professor Hamada's idea, that is, the reason why he had selected and collected these Coptic textiles for starting his archaeology studies in Kyoto University, Japan. Professor Hamada has collected and used these Coptic textiles as educational tools for students and researchers to understand Egyptian studies.

Although the collection of Coptic textiles are small (less than 30 items), our previous studies could say that Professor Hamada had collected these items varied with age, site and techniques.

Additional radiocarbon dating on the Egyptian antiquities collection, a fragment of mummy cloth and an excavated sandal, was carried out to investigate archaeological information of the collection.

## 5B-06 Dating the ages of ancient calligraphy fragments attributed to important persons in Japanese history: Nakatomi no Kamatari, Ono no Tōfū, Saigyō, and Retired Emperor Gotoba

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Ancient Japanese books, manuscripts, and scrolls that are older than the 14th century tend to be rare because their pages were often cut and separated for display as hanging scrolls to be appreciated in tea houses. From the 17th century onwards, collecting the pages became popular among warriors and the nobility and dismantling of ancient books was accelerated. Existing pages from lost books, manuscripts, and scrolls are referred to as kohitsugire and are often characterized by beautiful and elegant calligraphy. Although kohitsugire comprise just single calligraphy fragments, their value as historical artifacts are nevertheless extremely high because they are small parts of ancient books, sutras, or manuscripts that have been lost. Kohitsugire fragments are highly prized historical artifacts. However, many copies were written later using ancient examples as models, and because a large number were used as material for hanging scrolls and collections, numerous counterfeits are in circulation. In this study, we focused on kohitsugire attributed to famous persons in Japanese history: Nakatomi no Kamatari, Ono no Tōfū, Saigyō, and Retired Emperor Gotoba. Their names appear in the textbooks of Japanese history of high school. The radiocarbon age of the kohitsugire fragments were determined using accelerator mass spectrometry (AMS). To do this, Japanese paper samples were cut from the kohitsugire fragments; however, as these document pieces are commonly mounted onto other sheets that comprise a lining pasted after the calligraphy was written and therefore younger in age, such mounting elements must first be removed from the surface. The kohitsugire samples were soaked in distilled water on a plastic plate to separate the mounting pieces. The surface sheet samples were washed in distilled water with an ultrasonic cleaner, treated with 1.2 M HCl solution, and with 1.2 M NaOH solution. Subsequent to retreatment with 1.2 M HCl solution and rinsing with distilled water, the samples were combusted using CuO at 850°C to form CO<sub>2</sub>. This gas was then purified and reduced to graphite by H<sub>2</sub> in the presence of Fe powder catalyst at 650°C and radiocarbon ages were measured by AMS using CAMS-500 (NEC, USA) at Paleo Labo Co., Ltd., Japan. The calibrated radiocarbon ages of all samples were younger than the time when each persons was alive. However, they were older than the 14th century when ancient manuscripts were cut for hanging scrolls and the 17th century when collecting the kohitsugire fragments became popular. Therefore, the samples dated in this study are not counterfeits for hanging scrolls or collection, but is considered as copies written later using ancient examples as models or calligraphy in which incorrect judgment was made later. Ancient calligraphies written by famous persons in history will be important materials for history, classical literature, paleography, and bibliography. However, there are numerous counterfeits among kohitsugire fragments attributed to such famous persons. Radiocarbon dating of these kohitsugire means determining their academic value as historical material.

## 5B-07 Dating the Chinese Late Paleolithic at Shuidonggou Locality 2

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Located at the edge of the Ordos Desert, the site of Shuidonggou Locality 2 (SDG2) being one of the earliest Late Paleolithic sites in North China (Li et al. 2013) features prominently in discussion of modern human dispersal in East Asia (Gao et al. 2017). The site contains stone artefacts exhibiting a blade technology associated with the so-called Initial Upper Paleolithic (IUP) in Siberia and Mongolia, whose occurrence 40–30 ka ago has been linked to the arrival of modern humans (Morgan et al. 2014). However, the timing for the IUP at SDG2 is debated (Li et al. 2013; Keates and Kuzmin 2015). Based on a series of data, Li and colleagues (2013) placed the IUP of SDG2 at 38–34 ka. This chronology is on par with the timing of IUP farther north, and implies a rapid spread of the IUP cultural phenomenon across Central Asia during Marine Isotope Stage 3 (MIS3). Yet, the validity of this chronology is controversial. For instance, the used ages do not always correlate with the stratigraphic sequence, and show notable discrepancies within single stratigraphic units. In addition, the existing ages were derived from different techniques [radiocarbon vs. optically stimulated luminescence (OSL)] by different laboratories. There are also notable disparities between and among the C14 and OSL ages that are difficult to reconcile, especially for the lower half of the stratigraphic sequence with the IUP artefacts. To clarify the SDG2 chronology, we conducted systematic radiocarbon dating on charcoal and ostrich egg shell fragments recovered during a renewed excavation of the site in 2014–2016. Our results are in general agreement with the earlier determinations, especially with the OSL ages. Because of more rigorous and aggressive pretreatment practices (prolonged AAA and ABOx when possible), our results have on average smaller errors and correlate well with the stratigraphic sequence. Using Bayesian age-depth modelling, we demonstrate that the timeframe of IUP at SDG2 is similar to that proposed by Li et al. (2013). However, the new ages suggest a shorter overall chronology for the site, terminating at ~32 ka BP rather than 20 ka published previously. This implies rapid sedimentation rate. The ‘cultural layers’ (vertically constrained artefact concentrations) along the sequence may thus reflect relatively short periods of human presence in between major sedimentation events during MIS3.

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## 5B-08 A Radiocarbon Dating Study of Montezuma Castle

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Montezuma Castle Cliff Dwelling, AZ O:05:14 (ASM) is an iconic multi-story structure within the National Park Service's Montezuma Castle National Monument. In spite of its importance to interpretations of regional prehistory, its occupation span and construction sequence remain approximate. The structure consists of mortared rock walls with mud plastered surfaces, and ceilings/floors constructed from wooden beams and latilla capped by grasses, reeds and dried mud. Previous architectural studies hypothesized a sequence of room construction events beginning in the 13th Century AD (Wells and Anderson 1988, see also Nordby 2015). Although the structure contains more than 160 timbers, the vast majority are from local trees that are too complacent and short-lived to date by dendrochronology. A previous radiocarbon dating study that focused on dating short-lived materials from different rooms produced confusing and in some cases implausible results. In a pilot study, we investigated wiggle-match dating on timbers from complacent tree species with ring counts between 50 and 7 rings. Wiggle matches even on short-lived timbers linked by architectural association significantly improved the precision of calendar date ranges compared to previous results. The approach has great potential for dating structures throughout the Southwest United States that previously were undateable by dendrochronology.

## 5B-09 <sup>14</sup>C AMS Dating of first settlements in northern desert of Mexico: The Cave of the Antlers, Cuatro Ciénegas, Coahuila, Mexico

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On the eastern Chihuahuan desert, in the Sierra Madre Oriental it is located one of the most remarkable places on Earth: the Cuatro Ciénegas valley. Part of the state of Coahuila, this valley is flanked by tall mountains and karstic soils, forming ample plains. This landscape has a network of surface and underground water channels that fed springs on the central part of the valley. These springs form a myriad of pools, streams and wetlands with varying sizes and depths. The geologic and hydrologic characteristics of this valley have sustained for millennia diverse but highly endemic groups of animals and plants. Several hunter-gatherer groups inhabited this ecosystem thousands of years ago, finding shelter on the surrounding caves, formed by meteoric or hydrogeologic processes.

Due to the fact that the springwater is phosphate-poor, and that only a handful of gypsophilic plants grow on the gypsum-rich soil, it is probable that human groups settled intermittently in the Cuatro Ciénegas valley. It is important to note that the dates and durations of the different human settlements remain unknown, with only some punctual studies reporting objects dating back 10000 years ago. Nevertheless, a systematic study analyzing objects from a same context is still lacking, precluding a reliable correlation between the objects found on the caves inside and outside the valley. This information is important to map the extension of the territories of the distinct groups that settled in this region.

Beside the timing of the valley's occupations, it is important to locate in time the development of the techniques and tools that allowed the settlers to exploit the resources available in this region. This is a crucial point as the survival in this ecosystem depended in a very delicate equilibrium, easily affected by environmental factors such as droughts or climate change.

This work represents the start of a dating program using radiocarbon and accelerator mass spectrometry (AMS) focused on diverse objects obtained from the Cueva de las Cornamentas (Cave of the Antlers) and other regions of the Cuatro Ciénegas Valley. Our objective is to create a database with dated points in and out of the Valley, which will help establish the timing and extension of the different settlements on the region, with a special focus on the first establishments.

Our dates obtained from extremely well-preserved objects, show that the Cave of the Antlers was inhabited 8.5 Kyr. This date is 6 Kyr after the first settlements in the American continent and provide compelling evidence of early occupations on northern Mexico, in an isolated and harsh environment. The prevailing theory for the migration of the first inhabitants of America points to a movement through the coastline, with a slower expansion to the west due to the physical barriers imposed by mountains and the desert. Locating a site that helped this migration and establishing the dates of these movements will provide valuable information on the establishment of humans on the American continent.

## 5B-10 AMS <sup>14</sup>C dating of the first occupations of the Ciudadela, Teotihuacan, Mexico.

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Teotihuacan, is undoubtedly the best known pre-Columbian site in Mexico. It became the largest city in Mesoamerica, with near to 20km<sup>2</sup> in its heyday. During nine centuries of occupation there were continual changes in the appearance of the city, through renovation of its buildings, demolitions, and new constructions. At the time of the conquest the site had already been abandoned and there were only myths of ideology, religion, technology and splendor of this city. For long time it was thought that the North part of Teotihuacan with the Pyramids of the Moon and of the Sun was the oldest part of the City, and that the Ciudadela complex (Citadel, name given by the Spanish) with the Temple of the Feathered Serpent, at the South of the city, had been conceived until later. New excavations conducted by J. Gazzola and S. Gómez at the Ciudadela complex, have shown that in this space there was a first sanctuary. This complex, called Pre-Ciudadela, had mural paintings, temples, altars, courtyards and rooms with several constructive stages. A peculiar feature is that these structures present a range of orientations, that differ from the present one. All these buildings were partially demolished and covered by the new Ciudadela, a majestic complex that remained in its final appearance until the collapse of Teotihuacan, by the seventh century.

To establish a chronology of the first occupations of the Pre-Ciudadela, organic materials recovered from the different layers were dated by <sup>14</sup>C at LEMA, the AMS facility at the National Autonomous University of México. Bones from individuals offered in funeral rites of sacrifice, found in a drain associated with the constructions, were recovered, screened for their preservation state by FT-IR and dated. These results together with the ceramic chronology, were used to establish the temporal chronology of constructive phases exposed during the excavation of the Pre-Ciudadela. Our results show that the first sanctuary from the Pre-Ciudadela may have been built since the first century of our era and functioned for more than 100 years, before being turndown to give place to the majestic Complex of the Ciudadela as it is known today.

### Acknowledgements

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## 5B-11 Radiocarbon Dating of human remains from El Gigante Cave in Chihuahua Mexico

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Between 2010 and 2011, archaeologists of the Mexican National Institute of Anthropology and History (INAH) found 23 partially mummified human bodies and skeletons inside the El Gigante Cave, in the Sierra Tarahumara, Chihuahua State, north of Mexico.

The region has been occupied since pre-Columbian times by different ethnic groups. One of the most important is the raramuri, who live in this area until present days, occupying caves for different purposes.

In the El Gigante cave, individuals were deposited on the floor, with offers of different materials around. Some of the mummies correspond to infants, and others to young people and adults. Most of the bodies were found in fetal position, and there is evidence that they were deposited in the cave in the form of bulk, wrapped with blankets and cotton fibers plant, and tied with ropes.

The entrance of the cave was covered with a wall. The human remains were buried by dust and leaf litter. The dry condition and the stable climate helped the remains to be preserved, favoring a natural mummification.

According to archaeological criteria, the age of the individuals was estimated between 1000 and 1200 years, and the site would correspond to a pre-Columbian cemetery.

With the aim to determine when the bodies were deposited, and how long the cave was used for burial purposes, AMS radiocarbon dating studies of the remains (hair, skin and bones) of some of these individuals, as well as some textiles and fibers, were carried out at LEMA, the AMS laboratory at the Institute of Physics, National Autonomous University of Mexico.

Results show that the individuals were buried between 1000 and 400 BP (1000- 1600 AD) indicating that the rock shelter was used as a cemetery during several centuries.

## 5B-12 The use of anthracology and Bayesian models of radiocarbon dated charcoal to establish the occupation chronology of two archaeological shellmounds on the Guanabara Bay, Rio de Janeiro, Brazil

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This work aims to associate the techniques of radiocarbon dating and anthracological analysis in charcoal samples collected from two archaeological sites in the Guanabara Bay, state of Rio de Janeiro, Southeastern Brazil. Sernambetiba and Amourins shellmounds present a very well-defined stratigraphy and abundance of potential dating materials (Gaspar et al., 2013a, Heredia et al., 1982). This feature enables the construction of sequential depositional models through OxCal software (Bronk Ramsey, 1995). Previous dating for the Amourins was  $3800 \pm 40$  BP to  $3530 \pm 60$  BP and for the Sernambetiba  $2510 \pm 60$  BP to  $1960 \pm 70$  BP (Gaspar et al. 2013). Other sites studied in the region are typically dated between 5 and 1 ky BP. The use of terrestrial material in this context has the advantage of not depending upon the knowledge of local marine reservoir effect, which is not yet well established for the Guanabara bay. On the other hand, the potential drawback of inbuilt age of charcoal is overcome by the association of anthracological analysis, allowing to choose very short-lived materials such as nuts and barks. For this research, 9 samples of palm nuts (probably *Syagrus* sp) from each site were selected and 6 charcoals were also dated for comparison.

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## 5B-13 Rock art in ancient Puerto Rico: A chronological assessment

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Puerto Rico contains the highest concentration of rock art images in the insular Caribbean. Despite this, little effort has been placed on establishing absolute chronologies for this cultural manifestation, as most previous studies conducted thus far have relied on a diverse array of typological approaches aimed at providing relative temporalities for the existing repertoire of rupestrian images in the islands. Here, we present the results of the most extensive chronological study conducted thus far in Caribbean rock art, based on the radiocarbon dating of 32 black pictographs from six caves located in Puerto Rico. The images were not only traced with charcoal fragments, but were also produced with a newfound technique in the Antilles which consisted of the execution of drawings with the soot derived from torches made with resins from local trees, hereby labeled pyroglyphs. Since most of petroglyphs were made by using charcoal, small charcoal samples were collected from each of them. Based on the sample size, these were separated into five group for analyses: the samples larger than 300 µg; the samples in the range of 180-270 µg; the samples in the range of 108-165 µg; the sample in the range of 50-92 µg; and the samples in the range of 19-38 µg. Each group was measured with the backgrounds, primary and secondary standards with the same size range, correspondently, using Pelletron tandem AMS system NEC 1.5SDH-1. The generated assays provide the first robust evidence for Archaic rock art in Puerto Rico, examples of which are recorded since the third millennium BCE. The early pictograph assemblage not only include figurative elements (a boat, an anthropomorphic face and grapheme-like images), but also geometric designs. After a temporal hiatus between 400 BC and AD 600, there is a resurgence of pictograph-making going back to what is commonly known as the Ostionoid series in Puerto Rico. These painted images initially depicted human faces followed by the incorporation of zoomorphic designs, which continue to be produced throughout the precolonial history of the island. Interestingly, some of images with indigenous renderings continued to be made at least two centuries after the Spanish colonization of Puerto Rico, indicating the survival of at least some indigenous populations for far more time than commonly assumed. This study was also able to provide the earliest direct date of an European vessel in the Americas, going back to the XVIth Century.

## Poster Session 2

Poster session 2 (Thursday, Friday)														
1A	Row1	1B	2A	Row2	2B	3A	Row3	3B	4A	Row4	4B	5A	Row5	5B
147	1	338	70	1	76	276	1		304	1	237	233	1	168
T. Jull		I. Major	A. Rakowski	E. Keaveney	E. Keaveney	B. Hmiel			J. Rethemeyer		I. Kontul'	M. Capano		T. Moriya
106	2	26	161	2	341	180	2	215	196	2	30	153	2	144
S. Murseli		E. Jacob	L. Cisneros-Dozal	S. Cersoy	S. Cersoy	V. Petrenko		E. Zazovskaya	M. Molnar		A. Pabedinskas	A. Rakowski		A. Scifo
175	3	211	142	3	183	256	3	103	194	3	315		3	54
B. Walker		M. Minami	K. Elder	R. Bao	R. Bao	P. Neff		P. Wischhöfer	T. Kertész		T. Matsunaka			A. Fogtman-Schulz
327	4	221	334	4	8	267	4	203	60	4	232	57	4	134
D. Bragança		Y. Naito	I. Kontul'	P. Cheng	P. Cheng	M. Dyonisius		Y. Miyairi	I. Chanca		I. Svetlik	J. Park		A. Neocleous
287	5	90	281	5	319	116	5	150	271	5	43	195	5	349
A. Gagnon		H. Fewlass	Y. Saito-Kokubu	B. Netto	B. Netto	C. Welte		A. Alexandrovskiy	K. Finstad		Y. Pang	F. Terrasi		J. Olsen
197	6	241	239	6	313	158	6	318	346	6	20	279	6	367
H. Takahashi		H. Rose	E. Zazovskaya	S. Barone	S. Barone	Y. Yokoyama		I. Hammerschlag	E. Prastowo		Z. Niu	J. Southon		R. Kearney
353	7	104	162	7	290	366	7	288		7	113	359	7	258
R. Jou		M. Boudin	D. Paul	S. Moreton	S. Moreton	F. Kumon		M. Okuno			T. Varga	H. Svarva		S. Therre
347	8	177	299	8	322	125	8		53	8	190	152	8	240
R. Jou		E. Mintz	R. Varney	V. Moreira	V. Moreira	A. Jaeschke			N. Ishizawa		I. Faurescu	A. Patrut		M. Krapiec
167	9	83	231	9	218		9	186	317	9	24	79	9	199
K. Pugsley		M. Huelis	M. F. Schou	M. Yamane	M. Yamane			B. Buró	K. Macario		S. Palstra	A. Rakowski		M. Sakamoto
28	10	245	42	10		33	10	5	236	10		155	10	98
M. Garnett		M. Llewellyn	Y. Pang			R. Wood		R. Fancy	A. Agatova			T. Sava		M. Scott
191	11	260	115	11	363	171	11	331	198	11		291	11	138
I. Vagner		D. Michalska	C. Welte	E. Wild	E. Wild	C. Salfs		A. Cherkinsky	H. Matsuzaki			L. Wacker		I. Svetlik
46	12	25		12	95	227	12			12		69	12	
M. Garnett		G. Barrett		G. Quarta	G. Quarta	R. Fernandes						J. Pawlyta		
	13	214		13	323	209	13			13		332	13	
		P. Ricci		E. Dunbar	E. Dunbar	M. Durier						C. Crann		

## 1A-01 Improvements to dissolved organic carbon extraction methods using chemical and UV oxidation and long-term measurements of DIC/DOC in an ephemeral fresh-water stream in southern Arizona

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We report on a long-term study of dissolved inorganic and organic carbon (DIC and DOC) from Sabino Creek, located in Pima County, Arizona, close to Tucson. This stream flows for much of the year, except during very dry periods (predominantly May-June is the driest time). Flow can be rapid during heavy rainfall periods, such as the southwest summer “monsoon” period. Catastrophic debris-flow events have also occurred, most recently in 2006 (Webb et al. 2007). The purpose of this study was to monitor changes in dissolved <sup>14</sup>C with time and to understand the processes contributing to these variations. From 2009, we have been collecting water samples at varying times to understand the differences in the source of the DIC and DOC. Samples were collected in 0.5 to 1.5 litre containers and then processed at the University of Arizona AMS Laboratory. DIC samples were extracted by acid hydrolysis and DOC samples were generally extracted by oxidation with KMnO<sub>4</sub>, as reported by Leonard et al. (2013). Results showed some interesting trends of the dependence of the <sup>13</sup>C and <sup>14</sup>C on the flow rate of the stream.

UV Methods: Recently, we also have been experimenting with UV-photolysis methods (Williams & Druffel, 1987; Beaupré et al. (2007) originally developed for sea-water samples. We have considered several different approaches. At Arizona, we have designed a system based on the approach of Xue et al. (2015) using a commercially-available high-power UV device. We house the system in a custom-built UV-opaque housing. Our design includes UV irradiation of the sample in multiple quartz tubes to oxidize the DOC to DIC and offline extraction of the CO<sub>2</sub> for AMS and stable-isotopic analysis. We are currently assessing optimal conditions for conversion of DOC to DIC and CO<sub>2</sub> extraction. We report on these improvements as well as interpretations of the DIC/DOC data from Sabino Creek.

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## 1A-02 The Preparation of Water (DIC, DOC) and Gas (CO<sub>2</sub>, CH<sub>4</sub>) Samples for Radiocarbon Analysis at AEL-AMS, Ottawa, Canada

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The A. E. Lalonde AMS Laboratory (AEL-AMS) has been in operation since 2014, offering routine radiocarbon analysis for a wide range of organic and inorganic carbon-bearing materials (Crann et al. 2017). The radiocarbon content of dissolved inorganic carbon (DIC), dissolved organic carbon (DOC) in freshwater systems, and CO<sub>2</sub> and CH<sub>4</sub> in gas mixtures, provides insights on carbon cycling dynamics and source apportionment. To meet increasing demand, a method development program has been undertaken to improve sample preparation techniques for precision and to accelerate processing of waters and gases at AEL-AMS. Sample preparation techniques for the analysis of DIC and DOC in freshwater, including CO<sub>2</sub> and CH<sub>4</sub> in gas mixtures are presented. Focused efforts have been on developing a robust and low-background wet oxidation extraction method for DOC in freshwater following routine methods developed for stable carbon isotope analysis (Lang et al. 2012; Zhou et al. 2015) and adapted for radiocarbon analysis by AMS (Leonard et al. 2013; Lang et al. 2016). DIC (by acidification) and DOC (by wet oxidation) are converted to CO<sub>2</sub> in pre-baked septum-fitted borosilicate bottles, where CO<sub>2</sub> is extracted from the headspace on a low-flow He-carrier extraction line interfaced to a vacuum extraction line. A peripheral CH<sub>4</sub> extraction line interfaces to the flow line to separate CH<sub>4</sub> from environmental samples following the methods of Pack et al. 2015. Up to 5-8 samples can be prepared and extracted in one day. DIC and DOC blanks are now consistently <1.0 pMC, whereas CO<sub>2</sub> and CH<sub>4</sub> blanks are <0.2 pMC. Work is underway to interface a CTC robotic auto-sampler with a semi-automated gas cleanup line (St. Jean et al. 2017) for rapid analysis of carbonates, gas mixtures and waters.

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## 1A-03 Halide-induced carbon isotopic fractionation during UV oxidation of dissolved organic carbon in saline solutions

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UV photo-oxidation (UVox) is often used for determining the concentration and carbon isotopic ( $\Delta^{14}\text{C}$ ,  $\delta^{13}\text{C}$ ) composition of dissolved organic carbon (DOC) in aquatic environments. During this process, hydroxyl radicals ( $\text{OH}\bullet$ ) are generated when high intensity UV light interacts with water. These  $\text{OH}\bullet$  are a primary reactant in the photochemical oxidation of DOC to  $\text{CO}_2$  gas. In saline solutions (i.e. seawater and brines), abundant chloride anions ( $\text{Cl}^-$ ) can quench the photochemical oxidation of DOC through scavenging of  $\text{OH}\bullet$ , and thus act to diminish the UVox of DOC. We hypothesize that this process may lead to preferential oxidation of photochemically reactive C-C bonds, potentially inducing carbon isotopic fractionation. Here we present a series of DOC UVox experiments examining the recovery and carbon isotopic values of i) a simple, non-volatile organic compound (Norleucine) and ii) a complex riverine organic matter (Suwannee River OM) mixture at varying  $[\text{NaCl}]$  concentrations from fresh ( $<0.01$  Molar) to brine (10 Molar). The isotopic ( $\delta^{13}\text{C}$ ) fractionation of DOC compounds with varying NaCl concentration was observed in all of our experiments. Norleucine had a higher  $\delta^{13}\text{C}$  fractionation, while Suwannee River OM showed a lower degree of  $\delta^{13}\text{C}$  fractionation. Suwannee River brine also showed a significant shift in  $\Delta^{14}\text{C}$  value, suggesting incomplete oxidation of complex natural organic mixtures can result in bias towards high  $\Delta^{14}\text{C}$  DOC moieties. These results suggest that the presence of  $\text{Cl}^-$  can affect % recovery,  $\delta^{13}\text{C}$  values, and to a lesser extent  $\Delta^{14}\text{C}$  values of DOC as determined by UVox.

## 1A-04 Establishing water samples protocols at LAC-UFF, Brazil

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In Brazil, the demand for radiocarbon measurements of water samples, both scientifically and economically, comprises oceanic, surface freshwater and groundwater. On the one hand, one fifth of the world's freshwater reserve is within Brazilian lands (ANA, 2005) with ca. 111 trillion of cubic meters in groundwater (Rebouças, 1999, Hirata and Conicelli 2012). On the other hand, the linear extension of the Brazilian coast has over 8000 km, with 3.6 million km<sup>2</sup> of oceanic waters (Marinha do Brasil, accessed in October 2017) and very distinctive oceanographic conditions. <sup>14</sup>C has been used to determine sources, groundwater recharge, ages and pathways (Mook and Koene 1975; Broecker and Peng 1982). Radiocarbon measurements of Dissolved Inorganic Carbon (DIC) performed directly in a Brazilian laboratory can simplify sample submission, decrease the costs of analysis and contribute to increasing the number of scientific studies performed in Brazil in this area.

Since the establishment of the first Radiocarbon Accelerator Mass Spectrometry facility in Latin America in 2009, the Radiocarbon Laboratory of Universidade Federal Fluminense (LAC-UFF), we have been improving sample preparation protocols and increasing the range of sample matrices to be analyzed (Macario et al. 2015). We now present the preliminary results for DIC sample preparation protocols and the dedicated vacuum system designed for water samples at LAC-UFF. The first validation tests include background evaluation and optimization of hydrolysis, extraction of dissolved CO<sub>2</sub> and transfer conditions of samples to vacuum line prior to graphitization.

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## 1A-05 Comparison of Techniques and Reproducibility on Canada Basin DIC <sup>14</sup>C Sea Water Stored at NOSAMS for 26 Years

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Canada Basin seawater depth profiles were collected in 1992 and 1993 as part of Coast Guard Icebreaker Polar Star research cruises, and a couple cases of over sampled locations have been in storage at the National Ocean Sciences AMS (NOSAMS) facility for the past 26 years. Here we present recently measured  $\Delta^{14}\text{C}$ ,  $\delta^{13}\text{C}$ , and  $\Sigma\text{CO}_2$  results on these long-term stored samples and compare the data with radiocarbon profiles published from similar locations in the basin (Jones et.al. [1] 1994 and Griffith, et.al. [2] 2012). Aliquots from each sample were measured using both NOSAMS' standard dissolved inorganic carbon (DIC) extraction method and our new REDICS (rapid extraction of DIC system) [3]. We will compare the results from both methods and provide a comparison to the previously measured samples.

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## 1A-06 Suitable procedure in preparing water samples for radiocarbon inter-comparison

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The radiocarbon inter-comparison had been traditionally arranged several times as <sup>14</sup>C community projects (e.g., SIRI, VIRI...). They were involved only solid samples, but not on water samples. We investigated a suitable protocol to achieve a comparison objective using water samples, targeting on dissolved inorganic carbon (DIC). Water sample for inter-laboratory comparison (here after "comparison water") must have inalterable <sup>14</sup>C concentration during the comparison campaign and inter-batches homogeneity. Prior to this study, the <sup>14</sup>C inalterability had been investigated using natural waters, i.e., seawater, hot-spring water and groundwater, and artificial water, NaHCO<sub>3</sub> solution (Takahashi et al, submitted). The large <sup>14</sup>C changes of unsterilized natural waters within the several days were reported, but artificial waters and sterilized natural water showed constant <sup>14</sup>C concentration over a preservation period of years. We employed that comparison waters were artificially made by mixing chemical reagents, because the sterilizer, HgCl<sub>2</sub>, will be unable to be used in near future. In this study, the procedure in preparing the comparison water was discussed.

We prepared six comparison waters having different sets of <sup>14</sup>C concentration and chemical composition in this program. The approximate <sup>14</sup>C concentrations were measured to be 1, 14, 37, 56, 72 and 100 pMC, respectively. They were controlled by the mixing of NaHCO<sub>3</sub> solution (dead), CO<sub>2</sub> of gas cylinder (dead), and CO<sub>2</sub> reacted from shell powder (modern). The CO<sub>2</sub> gas was dissolved to hydroxide solutions by bubbling for 3-5 hours until pH was decreased to be ~7.6. The hydroxide solutions of 1M NaOH or 0.01M Ca(OH)<sub>2</sub> were used as a source of supplier of cation species as chemical compositions of the comparison waters were similar to the natural water. Other chemical reagents were dissolved to purified water and homogenized with DIC solutions using a magnetic stirrer. Each water sample was prepared to be ~20 L volume and was divided to batches of the γ-ray sterilized PAN bottles (250 mL).

The stable carbon isotopic values and chemical compositions of some batches were measured to examine the inter-batches homogeneity. The fluctuations of both were enough low, and this suggested the <sup>14</sup>C discrepancies among the batches were negligible for the inter-laboratory comparison. The comparison water prepared in this study can be concluded to satisfy the requirements for <sup>14</sup>C inter-comparison. Accordingly, we will be able to initiate the <sup>14</sup>C inter-comparison for water sample near future.

The trial inter-comparison campaign by six laboratories in Japan was carried out using the comparison waters prepared in this study. Most of <sup>14</sup>C results of CO<sub>2</sub> extracted by each laboratory showed good agreements each other. However, variation of the <sup>14</sup>C results became larger in the case of the waters with low DIC concentration rather than those with low <sup>14</sup>C concentration. It can be considered the water with low DIC concentration were susceptible to the carbon contamination and/or isotopic fractionation during the CO<sub>2</sub> extraction and graphitization in each laboratory.

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## 1A-07 Testing methodologies for Radiocarbon AMS dating of soil samples from Brazil at LAC-UFF

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Many of the radiocarbon dating applications are based on soil samples, in paleoenvironmental reconstruction, linked to phytolith analyses, stable isotopes, palinological studies, all depend upon soil dating. However, soils are complex mixtures which comprise organic matter from several time scales. Assuming that the biologically inert fractions of the soil have a closed system behavior, appropriate chemical treatments could be developed in order to extract only the fraction of interest that represents the actual age of the deposition. However, different soil types may have different responses to <sup>14</sup>C dating (Campbell et al., 1967; Pessenda et al., 1996b; 2001) and specially tropical soils may behave differently from temperate ones.

Usually the humin is the organic fraction considered more stable of the soil and therefore, the one that better represent the ground age (Campbell et al., 1967; Balesdent et al., 1987; Becker-Heidmann et al., 1988). In this work, we have selected a few methodologies from the literature for radiocarbon soil dating and compared with charcoal fragments found at the same depth. Firstly, we have compared SOM to the humin fraction of the soil, following Pessenda et al (1996a, 1996b). Secondly, we used a varied number of acid treatments aiming to separate the non-hydrolyzable soil (Paul et al., 2001). At last, we used physical separation with different sieves to compare the cost benefit ratio of chemical separation. In this study we used latosol samples, collected from Campos Amazônicos National Park, covering municipalities in the states of Rondônia, Mato Grosso and Amazonas in Brazil.

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## 1A-08 Comparison of soil preparation methods for radiocarbon AMS dating

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The radiocarbon dating technique can have many applications when it comes to soil samples. Several methodologies were studied in order to obtain a more accurate dating according to the types of applications. Some chemical treatments were developed in order to extract only the fraction of interest that represents the actual age of the event, since the soil is a very complex system that has many variables that influence the dynamics of the carbon, there is no standard protocol for the chemical treatment of soils.

Methods to evaluate <sup>14</sup>C data from soil organic matter (SOM) were developed, one option was to define the inert fraction of humus, where its age would be as close as possible to true age. Humins and humic acids are older than the total organic matter, except in the deepest horizon (Becker-Heidmann et al. 1987). The humina is the organic fraction considered more stable of the soil and also the one that has better representativeness of the ground age (Balesdent et al. 1987). The humin dating was verified by comparison with the age of charcoal fragments collected at similar depths in different regions of Brazil (Pessenda et al., 1996, 2001, and Gouveia et al. 2002).

We selected methodologies for radiocarbon soil dating and compared with carbon fragments found at the same depth. Methodologies for obtaining humina fraction of the soil, considered the most stable (Pessenda et al 1996b), methodology uses acid hydrolyzate to date the non-hydrolyzable soil (Paul et al., 2001) and methodology to separate the different soil fractions (Trumbore et al. 1996). In this study we used latosol samples, located in Campos Amazônicos National Park, covering municipalities in the states of Rondônia, Mato Grosso and Amazonas in Brazil.

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## 1A-09 Novel method of extraction for atmospheric $^{14}\text{CO}_2$ samples for determination of $\text{CO}_2$ emissions from fossil fuel

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The radiocarbon ( $^{14}\text{C}$ ) content of atmospheric carbon dioxide ( $\text{CO}_2$ ) has interested atmospheric researchers; most notably in the last 50 years, as a method to quantify recent  $\text{CO}_2$  emissions from fossil fuels in the atmosphere. Now that decades have passed since the Partial Nuclear Test Ban Treaty and the peak in  $\Delta^{14}\text{CO}_2$ , fossil fuels are the main influence on the long-term trend of  $\Delta^{14}\text{CO}_2$ .

The effect on  $\Delta^{14}\text{CO}_2$  to local additions of fossil fuel-derived  $\text{CO}_2$  depends on the concentration of the atmospheric  $\text{CO}_2$  and fossil carbon (-1,000 ‰). Not considering other effects from the carbon cycle, the influence of  $\Delta^{14}\text{CO}_2$  to fossil fuel-derived  $\text{CO}_2$  is approximated by  $(-1,000 \text{ ‰} - \Delta^{14}\text{CO}_2)/\text{CO}_2$ . This is presently - 2.6 ‰ ppm<sup>-1</sup> but with predictions from climate models, this is likely to drop to - 1.6 ‰ ppm<sup>-1</sup> by 2050, - 0.8 ‰ ppm<sup>-1</sup> by 2100 (Graven, 2015). This suggests that measurement precision, currently  $\sim 2 \text{ ‰}$ , will have to increase by a factor of 2 in the next decade.

To improve the precision of the measurement a novel extraction method, with a reduction in the number of steps, has been established. Following the development of the of the Automated Graphitisation Equipment (AGE III) (Wacker et al., 2010), we have developed an attachment system for whole air glass flasks. This is currently a manual extraction system. The system directly traps  $\text{CO}_2$  from a whole air glass flask sample onto a molecular sieve (zeolite, 13X) trap, part of the AGEIII system, before automated graphitisation. Tests have been conducted to find the optimum trapping time. This system has been used to test both in-house standards and inter-laboratory comparisons, we will present the results from this. In the future, we aim to automate and integrate an extraction system into the software that controls the graphitisation system to decrease the human interaction required with the extraction to improve the precision.

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## 1A-10 Advances in the radiocarbon analysis of carbon dioxide at the NERC Radiocarbon Facility (East Kilbride) using molecular sieve traps

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Radiocarbon analysis of carbon dioxide (CO<sub>2</sub>) provides unique information on the age, turnover and source of this important greenhouse gas, raising the prospect of novel scientific investigations into a range of natural and anthropogenic processes. To achieve these measurements, cartridges containing zeolite molecular sieve are a reliable and convenient method for collecting CO<sub>2</sub> samples, and are especially useful when the CO<sub>2</sub> exists at low concentrations. At the NERC Radiocarbon Facility (East Kilbride, UK) we have been developing and refining our molecular sieve methods for over twenty-five years to achieve high-quality, reproducible and precise measurements. At the same time, we have been developing novel field sampling methods to expand the possibilities in collecting gas from the atmosphere, soil respiration and aquatic environments. Here, we provide an update on our latest improvements to cartridge design and procedures. We present the results of tests used to verify the reliability of the method using known age standards, and report the results of quality assurance standards processed over the last two years. We also describe our latest automated procedures for the preparation of cartridges prior to use.

## 1A-11 Reproducibility of CO<sub>2</sub> absorption method for measurement of radiocarbon using a Parr bomb and LSC

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### Introduction

The CO<sub>2</sub> absorption method and liquid scintillation counting are methods used in radioactivity monitoring programs of nuclear facilities for C-14 measurements due to high number of samples and relatively high expected level of C-14 concentration, more than 226 Bq/kg C (IRSN, 2012). The paper describes the chemical sample preparation applied to a reference material (IAEA-C3), in order to evaluate the correction factors of CO<sub>2</sub> absorption method established previously (Vagner et al., 2017).

### Methods

The preparation steps involved: combustion of the reference material in a Parr bomb type 1121, bubbling of the combustion gasses directly through the scintillation cocktail for CO<sub>2</sub> absorption, and bubbling of the combustion gases through a sodium hydroxide aqueous solution followed by solution acidification and CO<sub>2</sub> capture in the scintillation cocktail. In the experiment we used two home-made scintillation cocktails, containing two amines (L'Annunziata, 2003), which detained CO<sub>2</sub> forming carbamates: methoxypropylamine (MPA) and methoxyethylamine (MEA).

### Results and discussions

Radiocarbon measurements using liquid scintillation counting were performed with a Quantulus 1220 (Wallac). The counting efficiency was 57.77 % for samples prepared with MPA and 59,39 % for samples prepared with MEA. Also the masses of CO<sub>2</sub> detained in the scintillation cocktails were lower for bubbling of the combustion mixture (around 1.5g for MPA and 1.8 g for MEA) comparing with the CO<sub>2</sub> detained after acidification (around 2,2 g for MPA and 2.5g for MEA). The reproducibility of the applied preparation method, involved the comparison of the obtained results from both combustion gasses mixture bubbling and pure CO<sub>2</sub> bubbling obtained from acidification), and for both scintillation cocktails used, with the certified value.

Due to the fact that the reference material used in the experiments described is cellulose (contained in the most of the vegetable materials) and it had an C-14 activity of  $129.41 \pm 0.06$  pMC (close the environment), the method can be considered as appropriate for C-14 determination from environmental samples.

### Acknowledgments

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## 1A-12 Radiocarbon analysis of methane at the NERC Radiocarbon Facility (East Kilbride)

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Methane is the second most important anthropogenically produced greenhouse gas. Radiocarbon analysis of methane can be extremely valuable for identifying its age and source. At the NERC Radiocarbon Facility (East Kilbride, UK) we have developed expertise and methodological approaches to field sampling and analysis of methane radiocarbon concentration over the past twenty years. This has opened a wide range of applications, which have mainly focussed on: i) the age and source of methane emitted by peatlands and organic soils (e.g. to identify the release of ancient carbon), ii) the source of aquatic emissions of methane, and iii) the age of methane generated in land fill. Many of these scientifically important applications involve challenging sampling and measurement considerations, which our development has continually aimed to overcome. Here, we describe our current methods, and recent improvements for the field collection, and laboratory processing of methane samples for radiocarbon analysis. We present the results of tests used to verify the advances we describe in sample collection and storage methods, and the results of <sup>14</sup>C standards used to test the laboratory procedures.

## 1B-01 Evaluation of AMS radiocarbon dating of bones using blank and known-age samples at HEKAL

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Bone is one of the most complex sample materials used in radiocarbon dating. After burial, many environmental processes can modify its physical state and chemical composition therefore pretreatment of bones for radiocarbon dating is of great importance. The installation of the EnvironMICADAS AMS in 2011 required the adaptation of new sample preparation techniques at the Hertelendi Laboratory of Environmental Studies of the Institute of Nuclear Research, dedicated to bones with small amounts. With a purpose of quality management, inner laboratory blank and known-age bones have also been prepared and AMS measured along with unknown samples thereby the reproducibility and viability of the sample preparation can be monitored and evaluated. In addition, blank correction of the samples can also be made. Our inner laboratory blank samples prepared using our protocol has been continuously above 40 kyr (i.e. below ~0.7 pMC) due to the efficient bone pretreatment and precise measurements. Good preparation was also confirmed by the results of the inner laboratory known-age bones where the standard deviation of the samples is better than 0.3 pMC. In addition, the reproducibility of samples with an age very close to the blank was also investigated and good results were obtained. We are planning to include and try other bone pretreatment methods such as ultrafiltration in the future to optimize further our protocol and obtain more accurate results.



## 1B-02 Nitrogen content variation in archaeological bone and its implications for radiocarbon dating

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The collagen component of ancient bones is routinely isolated for radiocarbon dating. However, it is impossible to tell the state of collagen preservation from visual inspection of bones. At the Oxford Radiocarbon Accelerator Unit (ORAU), the percent nitrogen by weight (%N) of a ~5 mg sample of bone powder is measured on a mass spectrometer and used as a proxy for protein content. A previous study showed that samples with %N >0.76 are considered likely to produce sufficient collagen for radiocarbon dating (Brock et al., 2010). However, the extent of variation between bone %N and collagen yield is unclear, as is the intra-bone variation in %N. Here, we report tests performed on Palaeolithic bones known to have variable collagen preservation. This new study shows significant variation in %N within the same bone and that there is sometimes a lack of correlation between %N and collagen yield. These results suggest that for bones from difficult environments or from Pleistocene contexts, it may be worth sub-sampling for %N in different locations of the bone and then attempting to extract collagen from marginally preserved bones (%N around 0.2-0.7%), as they may still yield sufficient collagen for radiocarbon dating.

### Reference:

Brock, F., Higham, T., Ramsey, C.B., 2010. Pre-screening techniques for identification of samples suitable for radiocarbon dating of poorly preserved bones. *Journal of Archaeological Science* 37, 855–865.

## 1B-03 Radiocarbon dating of carbonate hydroxyapatite in bones burned at low temperatures

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Bone collagen is commonly used for <sup>14</sup>C dating because it is less susceptible to chemical weathering, but it is often the case that little organic carbon remains due to degradation or cremation. Carbonate hydroxyapatite (CHa), an inorganic mineral bone component, contains ~1% of bone carbon by weight, as a carbonate incorporated in the crystalline structure during bone formation, and it could be used for <sup>14</sup>C dating. The cremated bone exposed to temperatures above 600°C is reported to contain highly crystalline apatite, which is not easily affected by exogenous contaminants, and can provide accurate <sup>14</sup>C dates. The purpose of this study is to investigate the possibility of <sup>14</sup>C dating of CHa in bones burned at lower temperatures (<600°C). The samples examined are some burned bones with gray to black colors of known-age collected from the Göytepe and Damjili cave archeological sites in Azerbaijan. The X-ray diffractometry patterns of the bones showed low crystallinity of apatite, suggesting that they had not been exposed to the temperature of >600°C. The <sup>14</sup>C dates were 5980–6250 BP for the Göytepe bones, and 5400–6370 BP for the Damjili cave bones, which are ~400 and ~1400 years younger than the dates obtained by charred materials excavated from the same layer as the burned bones, respectively. The degree of contamination by foreign carbon depended on individual burial environment of the archeological sites. The results indicate that CHa in bones burned at the low temperature is heavily contaminated through diagenetic alteration during burial because of low crystallinity of apatite, and so it is important to check crystallinity of apatite and the burial environment to perform reliable <sup>14</sup>C dating.

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We thank Prof. Y. Nishiaki of The University of Tokyo for providing us the bone samples. This study was supported by the Japan Society for the Promotion of Science, Grant-in-Aid for Challenging Exploratory Research (No. 26560144).

## 1B-04 A pre-screening protocol for radiocarbon dating of ancient bone collagen using FTIR

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Radiocarbon analysis of collagen extracted from ancient bones is one of the most common approaches to date archaeological deposits in late Pleistocene or Holocene. However, bone collagen suffers from contamination and alteration, depending on their conservation state and previous restoration and consolidation processes. We have designed a pre-screening protocol based on Attenuated total reflection (ATR)-Fourier transform infrared (FTIR) spectroscopy analysis to assess the conservation and quality of collagen in a variety of ancient bones of different origin and age. <sup>14</sup>C dating of collagen extracted using an ultrafiltration method with cutoff molecular sizes of 10 kDa and 30kDa was measured after the ATR-FTIR analysis of chemically untreated bone sample to evaluate the changes or variations in the chemical composition and mineralogy. In this presentation, we introduce some evaluation criteria of the screening protocol of ancient bone samples.

## 1B-05 Size matters: new frontiers in dating archaeological bone

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For Palaeolithic bone samples, starting weights of around 500 mg bone material are necessary to produce enough high-quality collagen for AMS dating with graphite targets. However some rare archaeological samples are much too precious for the destruction of so much material, and are therefore unavailable for direct dating using standard methods. The improved gas ion source of the MICADAS (MIni CARbon DAting System) [1] now offers a way to measure gaseous samples of < 100 µg carbon. The direct coupling of an elemental analyser to the gas-interface system of the MICADAS cuts out the graphitisation step, reducing the risk of contamination and speeding up the dating procedure [2]. We present the results of the first comparison between 'routine' graphite dates (2 mg bone collagen) and dates of gaseous samples of < 100 µg carbon (<0.3 mg bone collagen), undertaken with the highest possible precision in mind [3]. The experiment demonstrates the performance of the AixMICADAS [4] in achieving reliable radiocarbon measurements from gaseous collagen samples back to 35,000 BP. The technique has great implications for resolving chronological questions relating to precious archaeological artefacts and fossils.

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## 1B-06 Radiocarbon dating cremated bone and comparing pretreatment methods

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Radiocarbon dating cremated bone has become a standard procedure in archaeology, and results are frequently published in high-ranking journals. Yet there are still unknowns in the carbon pathways during cremation and burial and how to most efficiently tackle this when pretreating the material.

As part of her doctoral research on the Bronze-Iron Age transition in Southern Denmark, the first author has sampled over 50 cremations from Aarupgaard, a large urnfield cemetery spanning several phases of the Pre-Roman Iron Age, c.500–150 BC. Samples were sent for <sup>14</sup>C dating to the Leibniz Labor in Kiel (DE), Centre for Isotope Research (CIO) in Groningen (NL) and the Laboratory for Radiocarbon Dating (KIK-IRPA) in Brussels (BE). All three laboratories have a long history of dating cremated bones, and took part in the cremated bone dating intercomparison study (Naysmith et al. 2007). Duplicate measurements between the laboratories were carried out and a large proportion of samples were pretreated in one laboratory and dated in another.

The three radiocarbon laboratories each have their own pretreatment protocols. They all use acetic acid to dissolve calcite, but two of them also use hydrochloric acid to etch 30–50% of the apatite, on the basis that any diagenetic carbon substitution must be greater near the surface of a bone (Van Strydonck et al. 2005). Van Strydonck et al. (2009) raised the issue of exogenous carbon contamination of cremated bone, and showed it to be most pronounced, but not exclusive, for material from carbonate-rich burial environments. They suggest removing the surface of bone using acetic acid to remove secondary carbonate. Snoeck et al. (2016) however suggest acetic acid pretreatment to be superfluous, as organic compounds derived from the burial environment should not directly affect <sup>14</sup>C ages.

We present new radiocarbon dates of cremated bone, comparing different pretreatment methods and testing whether they have any measurable influence on the obtained results.

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Snoeck C, Staff RA, Brock F. 2016. A Reassessment of the Routine Pretreatment Protocol for Radiocarbon Dating Cremated Bones. *Radiocarbon* 58(1):1-8.

Van Strydonck M, Boudin M, Hoefkens M, De Mulder G. 2005. <sup>14</sup>C-dating of cremated bones, why does it work? *Lunula. Archaeologia protohistorica* XIII:3-10.

van Strydonck M, Boudin M, De Mulder G. 2009. <sup>14</sup>C Dating of Cremated Bones: The Issue of Sample Contamination. *Radiocarbon* 51(2):553-68.

## 1B-07 Radiocarbon dating of Chinese lacquer: a preliminary study

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The term lacquer is used for a number of hard and potentially shiny finishes applied to materials such as wood. Chinese lacquerware (till the early 18th century AD are mostly made from the urushiol-based exudate of *Toxicodendron verniciflua* trees that grow throughout specific regions of China, Japan and Korea. These lacquers produce very hard, durable finishes that are very resistant to damage by water, acid, alkali or solvents. The active ingredient is urushiol, a mixture of various phenols. Other products such as oils, carbohydrates, proteins were used to prepare the lacquer but do not modify the <sup>14</sup>C age because of their natural provenance.

Two Chinese objects from the 16th century AD (known age based on stylistically dating and historic documents) were treated with different solvents and radiocarbon dated. Sample size decreased with 10% after pre-treatment and lacquer contains circa 40-50% of carbon. Consequently, only 3 mg of lacquer is necessary to obtain 1 mg of graphite. This makes lacquer a perfect and suitable material for <sup>14</sup>C dating. The <sup>14</sup>C ages of these two objects were in perfect agreement with the expected age.

## 1B-08 What is hidden under the glitter of museum exhibits?

### Characterization and treatment of unique contaminants

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Museum artifacts are often samples for radiocarbon dating laboratories. In the process of conservation, restoration, and preparation of the items to be exhibited, various organic substances are used, containing variable radiocarbon levels. In order to correctly date such samples, one should overcome two problems: a) the identification of all the additives introduced to the items; b) finding the most effective treatment to remove those contaminants.

It is not always possible to ask the curator of the items which substances were used in the process of conservation-restoration. Furthermore, even when the material is known by name, manufacturers might not provide complete information on its chemical composition, as many of these materials are subject to patents (1). Moreover, in many cases, standard procedures are adapted to the specific item due to its state of preservation and details of the exact amount of preservatives added is not known.

Here we present several case studies of objects treated by both commonly used and more unique preservatives and the tailor-made pretreatment procedures used. We demonstrate the effectiveness of FTIR spectroscopy in the identification and characterization of the additives, followed by the selection of the most effective solvents, and a purity control of the cleaned material.

#### Reference:

Analytical characterization of polymers used in conservation and restoration by ATR-FTIR spectroscopy  
Ruth Chércoles Asensio, Margarita San Andrés Moya, José Manuel de la Roja & Marisa Gómez  
Anal Bioanal Chem (2009) 395:2081–2096  
DOI 10.1007/s00216-009-3201-2

## 1B-09 Interpreting <sup>14</sup>C measurements on 4th century AD iron artefacts from Nydam, Denmark

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The Nydam peat bog in South Jutland, Denmark, became internationally famous in the mid-19th century when two 20-25m long wooden boats were discovered, equipped with hoards of iron weapons attributed to the late Roman period. One of the boats, which is still preserved, has been dated dendrochronologically to the early 4th century AD, but detailed archaeological analysis of the weapon hoards indicates that sacrificial deposits of weapons were made at Nydam in several distinct phases, between AD 250 and AD 475 (Rau 2008). The dendro-dated oak boat was itself already old when it was abandoned, as the iron rivets holding the planks in place are clearly replacements.

Here we report on the radiocarbon dating of two swords, one axe, and several rivets from the oak boat. All iron objects had been treated with a waxy conservation agent, and the unique depositional environment at Nydam led to the formation of a siderite corrosion layer on the iron artefacts (Matthiesen et al 2003).

Before thermal (~1000°C) oxidation to extract carbon for radiocarbon measurement (Hüls et al 2011), therefore, samples were treated with a combination of solvent extraction, acid leaching and low-temperature combustion to remove natural and anthropogenic contamination. Resulting radiocarbon ages were evaluated with respect to the removal of contamination, <sup>14</sup>C-age offsets due to the intrinsic age of wood/charcoal, and possible reservoir effects introduced by carbon dissolution in iron during production.

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## 1B-10 Cooking with contaminants: things to consider when dating ceramics

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Contamination is a significant issue in all areas of archaeological science and can severely affect the chance of clear and precise results. Contamination can occur already before deposition, during deposition, during excavation and post-excavation during handling and storage. Contamination can range from biological material to the sunscreen on excavators hands to the phthalates in plastic storage bags. All of these can significantly hinder the analysis of amorphous food residues; a material that is being increasingly selected for dating for sites where other material may not be available. It seems that the longer the time between deposition, excavation and analysis the higher the chance of contamination. Whilst working on ceramic material from multiple Northern Eurasian sites from the Stone Age, larger amounts of contamination were present in material excavated in the 1950s and 1960s in comparison to material excavated more recently. This not only affected the interpretation of GC-MS results but also the yield of lipids which reduces the possibility of dating. This poster will be presented as a cautionary tale of foodcrust analysis and highlight issues that need to be considered before radiocarbon dating can be carried out, and issues that must be accounted for when interpreting any results from radiocarbon dating.

## 1B-11 Effect of recrystallization of mortars—can sequence dissolution of suspension provide accurate <sup>14</sup>C ages?

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One of the most important steps in radiocarbon dating of carbonaceous mortars is the applications of appropriate pretreatment, which is always dependent on the composition of the sample (Michalska et al., 2017 and references therein).

Here we present the carbonaceous mortars from Royal Castle in Poznan, Poland. Those samples are rich in clay minerals in the binder, mainly with quartz and smaller group of limestones as aggregate. The carbonates content in the binder varies between 60- 69%, to compare, the fraction 100-1000µm has the significantly smaller CaCO<sub>3</sub> content (20%).

Beside the limestone aggregate, the big influence on dating results had the recrystallization within pores.

Accepted for the majority of mortars is an assumption that usually closest to the real age, are the <sup>14</sup>C ages obtained on CO<sub>2</sub> collected in the shortest possible time of leaching reaction. However, as presented here this assumption does not apply to clay-rich mortars with secondary calcite presence.

The CO<sub>2</sub> portions from the first seconds of leaching reaction are rather small, because of clay minerals going to suspension in the first place, in comparison to other components. In that case, the seemingly large enough sample has a low carbon content. In those first portions, the gas from secondary calcite is present. On the other hand, too long reaction time allows for a release of dead carbon from limestone aggregate fragments. This influence of all components results in a large scatter of ages obtained on fractions from different dissolution time and grain size portions of suspension.

Based on the observation made by (Michalska et al., 2017), CO<sub>2</sub> collected in different time intervals and different fractions of suspension might provide a solution to exclude both potential contamination effects observed in the <sup>14</sup>C dating of mortar. One is the rejuvenation effect due to secondary calcite and the second one is the dead carbon from hard, solid limestone fragments. We propose sequential dissolution of carbonate in 4 portions each 3 sec. The dating of carbon from the second/third CO<sub>2</sub> dissolution portion (4-6; 6-9 sec) has a potential to provide most accurate ages of the mortar.

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## 1B-12 Mortar Dating: A Comparison of Approaches and the use of Characterization Methods, FTIR and TGMS, in Sample Selection and Confidence Estimation

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Dating of mortars is of great value to archaeology on account of the secure contexts in which it is often preserved. However, there is no consensus regarding the most suitable mortar dating method. A range of approaches exist, including: the dating of pure lime lumps (e.g. Pesce and Ball 2012); the isolation of a fine lime binder suspension following cryogenic breaking and ultrasonification, Cryo2Sonic (e.g. Carmine et al. 2015); the sequential dissolution of a sieved fine fraction (Lindroos et al. 2007; Heinemeier et al. 2010); and nano fraction isolation (Ortega et al. 2012). Often, these methods are applied in isolation of each other and reliant on prior chronological information to provide confidence in the interpreted results. Work elsewhere suggests that methods such as infrared spectroscopy (Chu et al. 2008) and thermal analysis (Fabbri et al. 2014) could potentially provide a more objective means of assessing the reliability of samples based on their binder to limestone content.

In this work, several prominent mortar dating methods (lime lumps, Cryo2Sonic, sequential dissolution) are applied, in parallel, to date material from historical buildings. Additionally, dating of organics/charcoal in the mortar is conducted to compare with lime binder derived dates. Characterization of the samples, following application of each treatment method, is carried out using infrared spectroscopy (FTIR) and thermogravimetric mass spectrometry (TGMS). A comparison between both the dating and characterization results from these methods is presented, along with an assessment of the reliability of each method; this assessment is based on intra-comparison of dates, historical information and characterization results. The feasibility of using FTIR and TGMS as a means of screening and evaluating the reliability of samples is discussed.

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## 1B-13 Mortar Radiocarbon Dating: advancing in the methods of preparation and characterization of materials

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Absolute chronology of archaeological contexts is mostly based on the radiocarbon dating of organic materials. Such analytical approach often provides misleading results when the goal is to find striking relationship between the organic matter and the archaeological structures. Therefore discover new methodologies and protocols of radiocarbon dating of mortars, represents one of the main “open issues” involving the whole radiocarbon community.

Mortars are heterogeneous building materials composed of a mixture of inorganic and/or organic binders and sandy-sized aggregate. Actually, the lime binder of the mortar can be used for dating the archaeological structures since carbon dioxide absorbed during the setting of the mortar likely reflects the content of <sup>14</sup>C existing in the atmosphere at that time.

The main sources of carbon dioxide that potentially contribute to a biasing in the final measurement are primary carbonates residues (calcinations relics) originating from the incomplete burning of the limestone during the quicklime production process; carbonate-bearing aggregates used as inert materials during the mortar production phases; newly-formed carbonates precipitated after the interaction of current water or rain.

Therefore, the samples preparation has to eliminate contamination (aggregate, calcination relics or crystallization of new calcite) that must be separated from the carbon belonging to the original binder. The methods, nowadays, most commonly used for mortar samples preparation consist of a mechanical pre-treatment or a chemical treatment.

In this paper the “mechanical” preparation method named Cryo2SoniC is presented and some of improvement of it, made in the phases of preparation and characterization of mortar, are analysed.

In the Cryo2Sonic method, the mechanical separation is based to the fact, that the limestone of aggregate is stronger and more resistant than the more porous mortar binder carbonate. The procedure aiming to eliminate contamination that may occur in a mortar, with cryobreaking, a double step of ultrasonication with different time-evolved suspensions, centrifugation and sieving procedures. Nevertheless, an appropriate mineralogical and textural characterisation of the mortars has been lately invoked to optimize the representativeness of the sampling strategy. With this aim we use a multi-analytical approach based on mineralogical, textural and spectroscopic techniques in order to correctly discriminate the different carbon dioxide sources.

The first step is to investigate textural and mineralogical features by using thin section (MO) and detect the crystalline phases that result from carbonation and hardening with x-ray diffraction (XRD). Moreover the main key-parameters necessary for dating mortars, from the bulk samples to suspensions, has to be evaluated, such as the calcite content (by thermogravimetry - TG) and the v<sub>2</sub>/v<sub>4</sub> ratio (by FT-IR). This basic information can be useful to figure out a significant sampling strategy by using on-site FT-IR measurements in order to select the most suitable samples to be investigated and to reduce time consuming and high cost radiocarbon dating.

An improvement to the Cryo2SoniC method is proposed, mainly based on differentiating both ultrasonic time and sieving size. Results coming from these experiments confirms the validity of Cryo2Sonic method for particular typologies of mortar and lime lump.

## 2A-01 Status of graphitization line in Dendrochronological laboratory at AGH-UST Krakow

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Accelerator mass spectrometry (AMS) technique is the most common technique used in radiocarbon dating. The procedure of age determination with this technique is divided into two parts, sample preparation and measurement. Sample preparation includes mechanical and chemical processes of cleaning, combustion, graphitization and pressing into sample holder.

A new system for preparation of graphite targets for AMS measurements of radiocarbon concentration has been built in the Dendrochronological Laboratory at AGH-UST Kraków. This system consists of equipment for mechanical and chemical sample pre-treatment, vacuum line for sample sealing and purification of CO<sub>2</sub>, and graphitization line, where occurs reduction of CO<sub>2</sub> on iron powder. Performance of the system was tested with samples of NIST Ox-II, IAEA standards (IAEA C3, C5, C6, and C8), and blank samples. The test confirms good reproducibility of results obtained for the samples prepared using this system.

## 2A-02 Testing the application of the sealed tube zinc method of graphitization to sample sizes down to ~100 µgC in the NERC Radiocarbon Facility, East Kilbride

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The sealed tube zinc method of graphitization has been successfully developed by Xu et al., (2007), Khosh et al., (2010) and Walker and Xu, (2018) for a wide range of sample sizes (1000 µgC to 2 µgC). We have tested this method for the bulk of sample sizes processed at the NERC Radiocarbon Facility, which range from ~1000 µgC to ~100 µgC. Initial tests using the reagents and methodology as in Xu et al., (2007) for 100-600 µgC showed elevated modern-carbon (MC) background levels, which was size-dependent and as much as ~2% MC for 100 µgC. We tested our glass tubes showing no apparent effect on the MC background levels while testing our reagents against the reagents used by Xu et al., (2007) and Khosh et al., (2010) showed MC background values higher by  $\sim 0.12 \pm 0.02$  and  $\sim 0.23 \pm 0.02$  %MC for 1000 µgC and 350 µgC, respectively, highlighting the importance of pre-cleaning reagents and/or testing different batches and suppliers. Graphitization of bulk-combusted NIST Oxalic acid II (~60-750 µgC) and Belfast Cellulose (~100-400 µgC) showed acceptable results, within 1% error of consensus values. Subsequent tests showed that, relative to our routine zinc reduction method (after Slota et al., 1987), we are able to obtain comparable background levels using the sealed tube method on samples sizes down to ~200 µgC. However, we observed a size-dependent increase in background levels when increasing the amount of iron used (e.g. from ~5mg to 6-7 mg). Lastly, we explored the effect of reducing the volume of the reactor tube, and thus the glass surface area, by reducing the length of the sealed tube by as much as 6cm and by reducing the diameter and length of the inner tube. Altogether these tests indicate two important aspects of minimizing MC background levels using this method: 1) careful selection and pre-cleaning of reagents and 2) reducing the overall glass surface area in the reactor tube. Controlling both of these aspects can result in the successful application of the sealed tube method of graphitization to samples sizes ranging from 1000 µgC to 100 µgC, which spans the demand of most radiocarbon applications.

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## 2A-03 Single Step Production of Graphite from Organic Samples

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We present a low-cost, high-throughput method for converting many types of organic samples into graphite. The method combines sample combustion and reduction into a single process. Using a modified sealed reduction method (1, 2), solid samples are placed directly into a Pyrex tube containing zinc, titanium hydride and iron catalyst. The tube is evacuated, flamed sealed, and placed in a muffle furnace for 7 hours. This method has successfully produced graphite from a variety of organic samples including several pure compounds, wood, peat, collagen and humic acid. The simplified method significantly reduces the time required to produce a radiocarbon sample with analytical precision and accuracy approaching that of traditional hydrogen reduction methods for certain sample types. Accuracy, background and limitations of the method are presented.

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## 2A-04 Comparison of hydrogen and zinc graphitization methods used in sample preparation for accelerator mass spectrometry

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The majority of accelerator mass spectrometry (AMS) systems used for radiocarbon analysis works with solid samples in the form of graphite targets. The reduction of sample CO<sub>2</sub> from combustion or hydrolysis to graphite form is therefore a very important part of the sample preparation process. Two graphitization methods using iron powder catalyst were studied - one uses hydrogen gas and the other one zinc granules as the reducing agent. The aim of this study was a comparison of these two methods in regard to reaction kinetics. Closed reactor volumes monitored by a pressure transducer were used for the studied graphitization reactions. The changing pressure inside the reactor was used to evaluate the reaction yields and the time required for complete graphitization. The presented results show that the reaction kinetics is heavily influenced by changes in reactor geometry and the two compared methods exhibit different sensitivity to these changes. These findings could be important for the design of new reactors adapted to the intended graphitization method.

## 2A-05 Coral <sup>14</sup>C measurements using the automated graphitization equipment AGE3 to estimate marine reservoir correction in the Ogasawara Islands, western subtropical Pacific

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We performed <sup>14</sup>C measurements of two fossil and one modern corals using a combined system of an elemental analyzer and an automated graphitization equipment AGE3 (EA-AGE3 system) and a tandem Pelletron AMS system at Tono Geoscience Center, Japan Atomic Energy Agency (JAEA-AMS-TONO). The fossil corals were collected by drilling into mid-Holocene emerged coral reefs in the southern coast of Okinawa Island (26°07'N, 127°45'E) in the Ryukyu Islands located between the Pacific Ocean and the East China Sea. The modern coral was collected by drilling into a massive coral colony living close to Chichi-jima Island (27°04'N, 142°13'E) in the Ogasawara Islands, western subtropical Pacific, to extract a 153 cm-long core. X-ray radiography of the modern coral core revealed annual growth bands from ~1900 to 1998 AD, which cover pre- and post-nuclear-bomb periods. The <sup>14</sup>C concentrations (pMC values) of the mid-Holocene corals obtained by our EA-AGE3 system appear to be slightly higher than those obtained by the conventional graphitization method using phosphoric acid. The pMC increase in our EA-AGE3 system may result in significant underestimation of <sup>14</sup>C age especially for older samples (e.g., 10,000 BP); however, the pMC increase is negligible in <sup>14</sup>C measurements of modern or recent samples. We applied the EA-AGE3 method to the pre- and post-bomb annual-band samples from the modern Ogasawara coral for <sup>14</sup>C measurements. On the basis of the pre-bomb coral <sup>14</sup>C data, we estimated marine reservoir correction (deltaR) around the Ogasawara Islands and its stability between ~1900 and 1950 AD.

## 2A-06 Experiences in the use of AGE 3 for graphite preparation at the Radiocarbon Dating Laboratory (IGAN), Russia

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The Radiocarbon Dating Laboratory (Lab code IGAN) was founded at the Institute of Geography of the Russian Academy of Sciences in the 1970s and has since continuously dated different carbon-containing materials using the liquid scintillation counting method. In 2015, our Laboratory has acquired the Ionplus automated graphitization system – AGE 3, together with a Vario Isotope Cube CHNS elemental analyzer. In early 2018 (with the help of Ionplus specialists), an isotope ratio mass spectrometer was coupled to the AGE 3 and our Laboratory staff members attended a brief training course at Ionplus. Since that time, our laboratory has obtained about 2000 separate graphite samples. Graphite <sup>14</sup>C/<sup>13</sup>C ratios were measured using the CAIS 0.5 MeV Accelerator Mass Spectrometer at the Center for Applied Isotope Studies (CAIS), University of Georgia. As background standards in graphitization process, anthracite and phthalic anhydride were used, with their ages being consistently determined at 44000-49000 BP and 46000-49000 BP, respectively. The OXII and OXI oxalic acids were used as modern standards in graphitization. An inter-laboratory comparison between IGAN and CAIS was conducted in respect to graphitization and dating of materials of known ages, with the results obtained being highly comparable. Since purchasing the AGE 3 system, the IGAN Lab has prepared graphite samples from the different kind of organic materials: charcoal, wood (cellulose), animal and human bones, soils, sediments of different genesis, peats, varnish from ceramic surfaces, fabrics (linen and silk). Samples for graphitization were prepared by use of standard techniques. Dating of soil organic matter also involved the use of techniques modified by the IGAN Laboratory. We also conducted an experiment on the graphitization of carbonate-containing materials Using AGE 3 system. The materials of known ages selected for the experiment were as follows: SIRI K (feldspar), VIRI R (mollusk shell) and soil carbonates. The samples underwent 30% H<sub>2</sub>O<sub>2</sub> treatment to remove organic carbon and direct carbonate decomposition in the CHNS-analyzer at 920°C with following graphitization. This experiment was conducted at both IGAN and CAIS laboratories to allow for inter-laboratory comparisons. The graphite samples obtained from K, R and soil carbonates had ages of 47400-48620 BP, 2450-2490 BP and around 500 BP, respectively. This experiment has demonstrated that graphite samples from carbonate-containing materials can be reliably prepared by direct decomposition of carbonate in EA combustion tube at 920°C.

## 2A-07 Using the Ionplus-Carbonate Handling System (CHS) as a Gas Handling System with an integrated flame-sealed glass ampule cracker.

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The newly installed Ionplus-MICADAS with its accompanying accessories at the Center for Isotope Research (CIO), University of Groningen has made routine measurements of samples both in the form of elemental carbon and in the form of pure CO<sub>2</sub> possible (gas measurements were not possible with the previous 2.5 MeV HV-AMS). Pure CO<sub>2</sub> samples are delivered to the MICADAS through the Ionplus-GIS (Gas Interface System)[1] either by an EA (Elemental Analyzer, Elementar) or by the Ionplus-CHS (Carbonate Handling System)[2]. Although the Ionplus-CHS is a sampling system especially designed for handling carbonate and liquid combustion samples[3], its design versatility allows it to be also used as a Gas Handling System (GHS), e.g., CO<sub>2</sub> obtained from various extraction systems and CO<sub>2</sub> samples in flame-sealed glass ampules. At the AMS facility of CIO, we have been using the Ionplus-CHS as a system dedicated for handling pure CO<sub>2</sub> samples mostly obtained from customers in flame-sealed glass ampules. We have developed a miniature flame-sealed glass ampule cracker which is placed within the CHS, and thus allows us to measure the CO<sub>2</sub> samples obtained in such glass ampules (with outer diameter 6-9 mm) directly using the CHS. The AMS facility at CIO is equipped with a unique ability of radiocarbon measurements in pure CO<sub>2</sub> samples combined with the possibility of the measurements of all stable isotopes of CO<sub>2</sub> (16O<sup>13</sup>C16O, 18O<sup>12</sup>C16O and 17O<sup>12</sup>C16O) using a Tunable Infrared Laser Differential Absorption Spectrometer (TILDAS, Aerodyne Research Inc.). It can thus be foreseen that such a system combination will be very useful in various fields of research. Hence, in our case, using the CHS more efficiently would allow us to measure both carbonate samples and pure CO<sub>2</sub> samples, obtained from customers in glass ampules, with the setup in its current form. In this work, we will present the details and the performance of this setup.

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## 2A-08 A Wood Charcoal Mass Loss Study: How much survives chemistry

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Charcoal identification prior to radiocarbon analysis assists selecting charcoal from short-lived species for dating and allows tracking the mass lost during standard chemical pre-treatment and wet oxidation. A robust database of thirteen years of accumulated data weighing taxon-specific wood charcoal, charred seeds, and other plant materials prior to and after chemical pre-treatment provides the basis for this preliminary study. Additionally, comparison of results from standard chemical pre-treatment (ABA) and ABA plus wet oxidation allows us to make recommendations important when selecting appropriate sample size prior to chemistry. Condition of the charcoal, as well as taxon represented, contribute to percentage of mass lost during pre-treatment. Charcoal that can be identified to genus and/or species generally loses less mass than charcoal identified to family or a higher taxonomic group. This is due to the fact that most charcoal identification relies on good preservation to observe the morphological traits. In the absence of good preservation, charcoal is relegated to a less distinct category. Standards (Tiri-B, Tiri-J, EUA wood, Two Creeks, Rio Frio charcoal, Gray site wood, Fugla ness pine, Lake Gribben wood, and Kauri wood) were included in the database.

Trends observed are discussed by taxonomic category. Most charred conifers lost between approximately 20% and 80% of their mass. Although it appears to be contradictory, charred conifers that received wet oxidation (ABAN) after ABA did not always lose more mass than those that received only ABA. This pattern holds true for other taxa and is attributed to the fact that only the more well preserved and thoroughly charred specimens received wet oxidation (ABAN). Most hardwoods (oak, hickory, buckthorn family, ash, rose family, legumes) and some softwoods (birch, poplar, and willow) generally lost between approximately 20% and 60% of their mass, with the exception being acorn shell, which lost more. Some plants from arid areas (members of the sunflower family including sagebrush, Atriplex and other plants in that family, and creosote bush, agave, yucca, and cacti) exhibit a high rate of loss, while others react more similarly to hardwoods. We have noted a tendency for plants containing resin to lose more mass than other plants. Poaceae, including maize cobs, generally experience a high rate of mass loss.

Guided by this information, smaller samples may be processed if the charcoal identified to genus or species level belongs to the hardwood group. Vitrification is less important with regard to mass lost when the charcoal is well preserved and readily identified than when it is poorly preserved and not identifiable. Therefore, identification of charcoal prior to radiocarbon analysis functions not only to know the lifespan of the plant and select the shortest-lived specimen to date, it also is a good predictor of behavior of the charcoal during chemical pre-treatment.



## 2A-09 A fully automated ABA preparation system for radiocarbon samples

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ABA (acid-base-acid) sample pretreatment is among the most frequent used preparation methods for radiocarbon samples of plant, wood and charcoal. Though simple, the method is labor intensive and requires constant attention by a laboratory technician. Here we present a fully automated ABA preparation system capable of running 3x 10 samples per day.

Samples are loaded into glass tubes sealed by a filter disk in either end. Sample tubes can be loaded before hand and are fitted to the system using Luer Lock fittings. Five different solvents can be connected to the automated system, which is chemically resistant to the most common chemicals (HCl and NaOH). Further, the temperature of each sample holder can be adjusted between room temperature and 80°C. The sequence for loading chemicals, duration, rinsing and temperature can be fully controlled in the software.

The samples' chemical purity and degree of purification are evaluated by comparing FTIR (Fourier-transform infrared spectroscopy) before and after the ABA pretreatment and for samples pretreated manually and by the automated system.

Using the software we have optimized the efficiency and duration of the pretreatment sequence by testing known-age samples and backgrounds. Finally, using known-age samples and backgrounds, we have tested the automated ABA preparation system for memory effects.

## 2A-10 Progress on <sup>14</sup>C AMS sample preparation laboratory at CIAE

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In order to satisfy <sup>14</sup>C measurement with the new developed 200kV single stage electrostatic accelerator mass spectrometer, the sample preparation processes for <sup>14</sup>C were investigated. The experimental conditions for <sup>14</sup>C sample preparation were optimized on self-designed <sup>14</sup>C sample preparation system. Moreover, in order to obtain the contribution of radiocarbon for OC and EC in the atmospheric particles by the accelerator mass spectrometry, we have developed a new method for the separation of OC and EC. The result indicates that the background of <sup>14</sup>C/<sup>12</sup>C ratio of 6×10<sup>-15</sup> can be obtained. The beam current of <sup>12</sup>C- for all prepared samples can reach 15-40μA. The yield of graphitization can reach more than 95% for the carbon content of 100μg—5mg. The feasibility of the method for the separation of OC and EC has been verified.

## 2A-11 Towards the limits: analysis of microscale radiocarbon samples using EA-AMS

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The demand for radiocarbon (<sup>14</sup>C) analysis of small (< 100 µg C) and ultra-small samples (< 25 µg C) in various fields has increased substantially in the last few years. Applications range from archeological studies in the context of Paleolithic bones dating, compound specific <sup>14</sup>C analysis and dating of sediments using macrofossils. With the installation of the gas interface at the MICADAS AMS (Accelerator Mass Spectrometry) system at ETH Zurich, Switzerland, the <sup>14</sup>C analyses of small samples are performed on a routine basis. In the case of combustible organic samples an elemental analyzer (EA) is used for sample introduction, which is a comparably simple and cheap method. Small and ultra-small samples are extremely sensitive to extraneous C, which is inevitably introduced through the vessels used for sample delivery and during sample preparation. All of these contaminations will bias the results; hence a minimum number of effective pretreatment steps and a suitable data correction strategy are necessary. Complementary sets of processing standards are required to precisely determine the mass and <sup>14</sup>C content of the contaminants. Optimized <sup>14</sup>C gas measurement procedures for EA-AMS analyses and the corresponding limit of detection will be presented. Corrections applied during data reduction will be discussed [1] and the results for ultra-small samples of certified reference materials will be presented.

[1] Hanke, U.M. et al. (2017), Radiocarbon 59, 1103.

## 2B-01 Characterisation of bulk sediment using Ramped Pyrolysis and thermogravimetric analysis

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Bulk soil/sediment is comprised of multiple carbon components, integrating labile (readily degraded) and recalcitrant carbon, yet is difficult to characterise as geochemical extraction of compounds (e.g. humic/humin) does not effectively isolate the various organic carbon fractions. Ramped Pyrolysis, or Ramped Pyrooxidation (RP) is a valuable tool that uses the thermal stability of organic carbon (OC) to isolate components from a bulk sample [1-3]. RP incrementally heats bulk samples in the absence of oxygen to precipitate the breakdown of OC fractions according to their degradation temperature. This produces a CO<sub>2</sub> spectra (after oxidation at 850°C). The CO<sub>2</sub> can be collected over selected temperature steps for radiocarbon and stable isotopic analysis. Lake sediment can comprise labile OC produced by algal production (autochthonous carbon), which will degrade at low temperatures, and terrestrial OC with a range of diagenetic properties. Soil and peat also contain multiple carbon pools that can be identified by RP. In this study we analysed bulk sediment from a short core collected in a eutrophic alkaline lake, dominated by autochthonous carbon yet subject to inputs from development in the surrounding catchment over time. We also analysed bulk peat samples from a blanket bog undergoing restoration. We examined the CO<sub>2</sub> spectra of bulk samples using a CA10-CO<sub>2</sub> analyser, and compared them to results of thermogravimetric-mass spectrometry. Thus we can characterise compositional diagenetic characteristics of organic matter in sediment

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## 2B-02 Using Py-GC×GC/MS as a new tool to assess the purity of ancient collagen prior to <sup>14</sup>C dating

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Exogenous carbonaceous contaminants coming from sediments significantly bias the radiocarbon date of collagen samples extracted from archaeological bone and teeth. We propose a new approach combining pyrolysis, comprehensive gas chromatography and mass spectrometry (Py-GC×GC/MS) to ensure their removal during the demineralization and collagen extraction. This method permitted to identify hydrocarbon contaminants for archaeological samples from the Neolithic period, in 30-40 µg of collagen. The use of GC×GC improved importantly the separation, selectivity and resolution compared to 1D GC thus permitting to detect organic contaminants within the complex chromatograms issued from collagen pyrolysis. Moreover, efficiency of the extraction steps in collagen sample preparation for radiocarbon dating (acid and alkali treatments, filtration steps) could be evaluated for four different protocols on the basis of organic contaminant removal. The extracted collagen of four of the tested protocols were radiocarbon dated on EchoMICADAS after graphitization with AGE 3 system. The significant shift obtained for one of protocol including a soft solubilization step and ultrafiltration, and corresponding to the lower level of detected contaminants in the chromatograms, corroborated the results of the Py GC×GC/MS data. These results open new perspectives for the use of comprehensive gas chromatography in the domain of archaeological sciences.

## 2B-03 Influence of different acid treatments on the radiocarbon content spectrum of sedimentary organic matter determined by Ramped PyrOx / Accelerator Mass Spectrometry

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Quantifying the radiocarbon (<sup>14</sup>C) content of organic matter (OM) in sediments has become a common tool to facilitate our understanding of the sources and fate of organic carbon (OC) in aquatic systems. In practice, obtaining the <sup>14</sup>C composition of bulk OM in sediments requires first removing inorganic carbon by acid treatment. Two common treatments are acid rinsing and fumigation. Resulting carbon isotopic compositions obtained by different methods can differ significantly, but underlying causes of these differences remain elusive. Recently, a new approach involving ramped pyrolysis/oxidation (RPO) followed by <sup>14</sup>C and <sup>13</sup>C isotopic analyses of the evolved CO<sub>2</sub> allows for separation of OC based on the thermochemical stability of OM. To assess the influence of different acid treatments on <sup>14</sup>C content of sedimentary OM, we examine the variability in <sup>14</sup>C content for a range of marine and river sediments subjected to RPO. By comparing results for unacidified and acidified sediments [1.0 N HCl rinsing (RinseHCl) and 37 % HCl fumigation (FumeHCl)], we demonstrate that each acid treatment can differentially affect OC <sup>14</sup>C content. Experiments conducted on sediments with high (>30 %) and low (<1.5 %) carbonate contents suggest that RinseHCl may remove young organic components from thermally recalcitrant OM in high-carbonate samples compared with FumeHCl, while the opposite may occur in low-carbonate samples. Additionally, changes in <sup>14</sup>C content between the two acid treatments depend on OM thermal lability and the depositional environment of the samples. This study highlights the value of RPO for systematically comparing the effects of acid treatments on the reliability of OM <sup>14</sup>C measurements and emphasizes the sensitivity of complex natural OM to methodological differences.

## 2B-04 Stepped-combustion <sup>14</sup>C dating in loess-paleosol sediments

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In this study, organic carbon samples were dated after extraction from two loess and paleosol profiles using low temperature (400°C LT) and high temperature (900°C HT) combustion. Comparison of results shows that <sup>14</sup>C ages of samples with actual ages below 30 ka can be accurately acquired from the HT fraction. After ruling out long-term storage, sample contamination during pretreatment, and other possible contributing factors, it is thought that the relatively young <sup>14</sup>C ages obtained may be caused by constant exposure of the loess and paleosol to contamination by materials leached from overlying layers after deposition. The acid-base-acid (ABA) process, a traditional pretreatment method, is incapable of completely removing young carbon from samples from relatively young upper horizons. The HT fraction could hardly give correct <sup>14</sup>C ages of the samples from older horizons, possibly due to the inherent nature of loess and paleosol. In addition to affecting the <sup>14</sup>C dating results, contamination by materials leached from overlying layers also affect the δ<sup>13</sup>C signals. After the LT fraction (young carbon) is separated, δ<sup>13</sup>C better reflects regional climate change.

## 2B-05 Determination of <sup>14</sup>C concentration in diferente foraminifera species and size limitation tests at LAC-UFF

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Many ocean dynamics studies are based on sediment core analysis, with several indicators used to reconstruct the palaeoenvironment. As chronological records, carbonate microfossils, such as foraminifera of planktonic or benthonic life habits, are usually radiocarbon dated. Since assemblages of foraminifera can be easily collected at various points on the ocean floor, they have become great tools for obtaining information on paleotemperature, paleosalinity, paleoproductivity and sedimentation rate (Petró et al., 2016). A drawback is their very small size, each individual weighing ca. micrograms. In addition, accurate dating requires separation of planktonic and benthonic species, or single species separation if possible, since several anomalies have been reported in foraminifera radiocarbon dates (Broecker et al., 2006).

We compare <sup>14</sup>C incorporation in samples of *Globigerinoides ruber*, *Globorotalia menardii* and bulk of foraminifera, all of planktonic habit, from a core collected from the Campos Basin (Brazil). We also evaluate the amount and age of contamination in background and modern carbonate samples (Mueller and Muzikar, 2002) at LAC-UFF with the aim of lowering the laboratory background and establishing size limitations for our carbonate protocols (Khosh et al., 2010).

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## 2B-06 Carbonate samples combustion by elemental analyser for radiocarbon dating

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In this work, we explored the possibility of collecting carbon dioxide from carbonate samples by burning them using an elemental analyser, as an alternative approach with respect to acid digestion: indeed, orthophosphoric acid is typically used to collect the CO<sub>2</sub> evolved from carbonates as shells or mortars.

Marine shells and IAEA C2 (travertine powder) were employed to check the CO<sub>2</sub> extraction yield, the combustion reproducibility and the overall measurement accuracy too. For the shell samples, a pre-treatment was applied: they were washed with deionized water in an ultrasonic bath, then they underwent a gentle acid attack using H<sub>2</sub>O<sub>2</sub> to remove the outer layers. After cleaning, they were carefully crushed to obtain as much homogenised as possible samples, since it is expected that the combustion and the CO<sub>2</sub> yield depend on the sizes of the burnt samples. A fraction of each crushed sample was collected for X-ray diffraction analysis, so that the mineral composition of the burnt material was characterized as well.

The configuration of the elemental analyser was adapted: different reagents to fill the combustion column were exploited; a quartz inset was added at the top of the combustion column in order to collect ashes, which can be very abundant in the combustion of carbonates, and easily remove them from the column.

We investigated the relation between the CO<sub>2</sub> yield and the burnt masses, verifying its linearity by burning different portions of the same sample. Fractions of other shells samples and IAEA C2 were burnt, verifying the reproducibility of the process. These data have been useful to estimate the mass to be burnt to produce CO<sub>2</sub> samples from carbonates with a mass similar to our "standard" samples. The accuracy of <sup>14</sup>C measurements of IAEA C2 samples was also verified as satisfactory.

The good reproducibility of the combustion process can be also used as an indicator to verify the "purity" after pre-treatment of more complex carbonate samples, like mortar: in this case, for example, the CO<sub>2</sub> yield can suggest us whether all the aggregates have been fully separated from the binder.

## 2B-07 Radiocarbon background measurements on marine shells.

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In order to properly report radiocarbon measurements on samples it is necessary to have an appropriate background measurement of material analogous to the samples material under investigation. We made repeat measurements on six samples of marine shells recovered from in situ continental shelf marine sediments and from terrestrial exposures of marine sediments from the UK which were known to be in excess of 80,000 years in age. Additionally we measured three samples of foraminiferal carbonate from in situ continental shelf marine sediments also thought to be in excess of 80,000 years in age. We compare those sample-specific background measurements with a similar number of measurements of Iceland Spar Calcite and compared them with the NERC Radiocarbon Facility (East Kilbride) long-term average value for Iceland Spar Calcite.

All shell and Iceland Spar Calcite samples were etched with dilute HCl to remove the outer 20%, rinsed in deionised water, dried and homogenised. The forams were not etched. Samples were hydrolysed to CO<sub>2</sub> using 85% orthophosphoric acid at room temperature. The CO<sub>2</sub> was converted to graphite by Fe/Zn reduction. Graphite targets were analysed at the SUERC AMS Laboratory, East Kilbride.

The measured per cent modern carbon of the background marine shell samples ( $0.30 \pm 0.09$ , n=21) and forams ( $0.30 \pm 0.06$ , n=3) was higher than both the mean of the project specific Iceland Spar Calcite measurements ( $0.13 \pm 0.06$ , n=25) and the NERC Radiocarbon Facility’s long term average value for Iceland Spar Calcite ( $0.17 \pm 0.08$ , n=192).

These results indicate that organically precipitated carbonates have a naturally higher background than inorganic crystalline calcite. Consequently these results highlight the importance of obtaining sample-specific background material whenever possible.

## 2B-08 Separation of the aragonite fraction of Vermetid shells prior to radiocarbon dating

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In order to study and understand the coastal dynamics in Brazil several research efforts have been made to reconstruct paleo-sea levels during the Late Quaternary, to comprehend changes and their causes, and by correlating these to the present-day situation, to predict and prevent near-future disasters (Angulo et al. 2006; Jesus et al. 2017). In such studies, several bioindicators are used, among them the fossil shells of vermetids (Pirazzoli 2005). Techniques are combined to obtain space-time information, such as relative height measurement by GPS and direct AMS <sup>14</sup>C dating of such samples.

The vermetid shell has a structure originally formed by aragonite, a calcium carbonate with orthorhombic crystalline system. However, these shells are susceptible to diagenetic processes, during which the aragonite dissolves and recrystallizes in the form of low-Mg calcite, a more stable polymorph of calcium carbonate, with a rhombohedral crystalline system. Identifying and tackling recrystallization is a critical factor in the reliable radiocarbon dating of shell, since during this process, exogenous carbon can be incorporated and thus mask the original radiocarbon concentration, and as result the age, of the dated sample.

Here we apply a previously tested protocol (CarDS: Carbonate Density Separation) that uses a heavy liquid of known density to separate physically original aragonitic structures from secondary calcitic ones of the same shell, prior to AMS dating (Douka et al. 2010). We successfully separated samples using the density protocol, verified each separation by X-ray diffraction analysis, and subsequently measured the <sup>14</sup>C concentration of both aragonite and calcite fractions. In addition, raw (untreated) fractions and fractions treated with our routine protocol were also measured. The preliminary results show that the aragonite fraction is on average 800 <sup>14</sup>C y older than the raw sample, thus confirming the efficacy of CarDS and the importance of density separation to vermetids prior to AMS dating. We discuss the impact of the observed discrepancies to the construction of sea-level curves.

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## 2B-09 A promised method of diatom frustule separation from sediments for radiocarbon dating

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Radiocarbon-based chronology is usually applied in the fields of paleoclimatology and paleoceanography for the last 50,000 years. The applicability is limited by the existence of appropriate materials for radiocarbon dating such as foraminifera. Diatom includes a trace amount of organic matter in frustules (“diatom-bound organic matter” hereafter). It is dealt with that the diatom-bound organic matter is a potential target for radiocarbon dating of sediments. Previous studies have suggested that the purity of diatom frustule separated from sediments is crucial to promise radiocarbon-based chronology. In this study we have assessed some available methods of diatom frustule separation from sediments. The radiocarbon age of diatom-bound organic matter is compared with that of foraminifera separated from same layers of marine sediment cores to evaluate the effectiveness of separation methods.

## 2B-11 <sup>14</sup>C bomb peak analysis of African elephant tusks and its relation to CITES

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CITES (the Convention on International Trade in Endangered Species of Wild Fauna and Flora) is an international agreement between governments, which was established 1973 in Washington DC [1]. Its aim is to ensure that international trade in specimens of wild animals and plants does not threaten their survival. Austria joined CITES in 1982 [2]. In 1989, the African elephant was put by CITES into Appendix I, which lists species with the highest degree of protection [3]. Unfortunately, this did not prevent the recent killing of African elephants, which was confirmed by <sup>14</sup>C measurements in seized ivory from illegal trade [4].

An important point in this context is the proof that material from African elephants originates indeed from times before the corresponding CITES regulation entered into force.

We were recently contacted by the owner of three pairs of elephant tusks, which are part of the heritage of a professional hunter with a so called “White Hunter Licence”, who lived and worked in Tanzania and Kenya from 1961/62 till 1979. The elephant tusks originate from elephants most likely shot during this time. Interestingly each of the tusks was marked with an individual signature and it was suspected that part of the numbers indicated the year, when the animal was shot. Modern ivory is a material that is well suited for <sup>14</sup>C dating, particularly when the time of interest falls into the so-called <sup>14</sup>C bomb peak era. Thus we performed AMS <sup>14</sup>C-determinations of samples from each tusk. Usually at least two samples with an age difference of some years should be available for <sup>14</sup>C dating with the bomb peak to decide if the ascending or the descending part of the bomb peak curve is relevant for the age determination [4, 5]. For an elephant tusk this is no major problem since the tusks are continuously growing, with the recently formed part next to the skull and the oldest part at the tip. We decided to take two consecutive samples from only one tusk, because the elephants were most likely hunted in the period between 1961/62 and 1973, when the professional hunter worked in Tanzania and it should only be clarified whether the tusks originate from pre-CITES times. For an initial investigation we therefore took only one sample from the youngest part of the other tusks. Sample preparation and <sup>14</sup>C measurements were performed at the VERA laboratory. The result of our investigation indicates a pre-CITES origin for all tusks.



## 2B-12 Radiocarbon dating of ivory: potentialities and limitations in forensics

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Ivory illegal trade is still a relevant problem and it has triggered the decline of Elephant populations due to poaching in different areas of the globe. Indeed, African and Asian Elephants are both included with the highest level of protection in the Appendix 1 of CITES, the Convention on International Trade in Endangered Species of Wild Fauna and Flora, entered into force in 1975. As a consequence of this a total ban of ivory trade has been enforced with effective year changing from country to country depending on the year of ratification of the convention.

In the forensics practice it is then important to establish whether an ivory sample, object or artefact is dated before or after the trade ban. Radiocarbon dating is then often required to supply the conclusive answer through the detection of the excess of <sup>14</sup>C due to nuclear detonation tests in the samples and the following dating by calibration against the "bomb peak" curve. Indeed, the application of the methodology is often limited by different aspects such as the multiple intercepts with the bomb curve, its dependence on latitude and the issues related to the carbon turnover in the analysed sample. All these aspects have to be properly taken into account in order to supply results with a confidence level consistent with the impact they usually have.

Aspects related to the definition of properly sampling strategies, data analysis and interpretation are presented and discussed referring to real cases and applying Bayesian modelling techniques for combining a priori known information with those resulting from <sup>14</sup>C analyses.

## 2B-13 Reconstructing the F<sup>14</sup>C bomb peak using known age whisky to assist in the identification of fraudulent products

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With over 100 active distilleries across Scotland, the Scotch whisky industry contributes around 4 billion GB Pounds per annum to the UK balance of trade. In particular, malt whisky is a high-priced commodity, particularly old or rare malt whiskies and there are ever increasing attempts to counterfeit these products. The efforts of the whisky industry have focused on expanding the range of analytical techniques available to support brand protection and, as part of this work, distillers can use chemical fingerprinting techniques to determine whether a given sample is the product of their distillery. However, they still have difficulty in verifying the year of production using traditional methods and this is where <sup>14</sup>C analysis can be helpful. The annual F<sup>14</sup>C data for the last 60+ years derived from atmospheric and tree ring measurements has proven to be a useful tool in both environmental processes and forensic science. At SUERC this 'bomb curve' data is frequently used in the identification of modern human remains, however, for each F<sup>14</sup>C value >1 there are two potential 'years' based either on the up slope or down slope of the curve. With modern forensic samples this is resolved by the additional analysis of another sample with a different carbon turnover rate which can further define the sample year. Current research at SUERC is; i) reconstructing the atmospheric bomb peak using <sup>14</sup>C measurements made on known age 'new make spirit' and single year malt whiskies and ii) developing a reliable technique to differentiate between samples on the up slope and down slope of the curve. It is anticipated that this will provide an accurate calibration for whisky samples to aid in the identification of potentially fraudulent products.

## 3A-01 Constraining the Evolution of the Fossil Component of the Global Methane Budget Since the Pre-Industrial Using $^{14}\text{C}$ Measurements in Firn Air and Ice Cores

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Radiocarbon of atmospheric methane ( $^{14}\text{CH}_4$ ) is much less studied than radiocarbon of atmospheric carbon dioxide ( $^{14}\text{CO}_2$ ), yet has potential to serve as an unambiguous indicator of the balance between fossil and contemporaneous sources of this important greenhouse gas. Few measurements of atmospheric  $^{14}\text{CH}_4$  exist before the late 20th century. We present measurements of past atmospheric  $^{14}\text{CH}_4$  in firn air and ice at Summit, Greenland. These data provide a record of atmospheric  $^{14}\text{CH}_4$  from 2013 back to ~1780 CE. Results have been corrected for cosmogenic in-situ production of  $^{14}\text{CH}_4$  within the ice crystal lattice. A firn gas transport model was used to simulate the transport of gases through the firn column and into fully closed ice, and an inverse model reconstructed the firn air and ice  $^{14}\text{CH}_4$  data into an atmospheric history. Our results from the mid-late 20th century agree with the only published measurements of  $^{14}\text{CH}_4$  from firn air at Law Dome, Antarctica. Pre-industrial samples show a  $^{14}\text{CH}_4$  activity of ~97 pMC, indicating that natural geologic methane emissions are very low and have been commonly overestimated in the global methane budget. Between 1920 and 1940 CE the  $^{14}\text{CH}_4$  activity decreased to 85-88 pMC due to the rise of anthropogenic emissions from fossil fuel use. The  $^{14}\text{CH}_4$  activity began increasing mid-century due to atmospheric nuclear bomb testing and emissions from nuclear power plants.

## 3A-02 Using atmospheric $^{14}\text{CO}$ to constrain OH variability: first results from a new approach and potential for future measurements

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The primary source of  $^{14}\text{C}$ -containing carbon monoxide ( $^{14}\text{CO}$ ) in the atmosphere is via  $^{14}\text{C}$  production from  $^{14}\text{N}$  by secondary cosmic rays, and the primary sink is removal by OH. Variations in the global abundance of  $^{14}\text{CO}$  that are not explained by variations in  $^{14}\text{C}$  production are mainly driven by variations in the global abundance of OH. Monitoring OH variability via methyl chloroform is becoming increasingly difficult as methyl chloroform abundance is continuing to decline. Measurements of atmospheric  $^{14}\text{CO}$  have previously been successfully used to infer OH variability. However, these measurements are currently only continuing at one location (Baring Head, New Zealand), which is insufficient to infer global trends. We propose to restart global  $^{14}\text{CO}$  monitoring with the aim of providing another constraint on OH variability. A new analytical system for  $^{14}\text{CO}$  sampling and measurements has been developed, allowing for a ten-fold reduction in the required sample air volumes and simplified field logistics. The first  $^{14}\text{CO}$  measurements from Mauna Loa Observatory utilizing this system will be presented. Preliminary work with a state-of-the-art chemical transport model is exploring sensitivity of  $^{14}\text{CO}$  at potential sampling locations to changes in production rates and OH.

## 3A-03 $^{14}\text{C}$ in Antarctic Glacial Ice as a Tracer of Atmospheric OH Abundance from 1880 AD to Present

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Hydroxyl, OH, is the main tropospheric oxidant and determines the lifetime of methane and most other trace gases in the atmosphere, thereby controlling the amount of greenhouse warming that these gases can produce. Changes in OH concentration ([OH]) in response to large changes in reactive trace gas emissions (which may occur in the future) are uncertain. Measurements of  $^{14}\text{C}$ -containing carbon monoxide ( $^{14}\text{CO}$ ) and other tracers such as methyl chloroform over the last  $\approx 25$  years have been successfully used to monitor changes in average [OH], but there are no observational constraints on [OH] further back in time. Reconstructions of  $^{14}\text{CO}$  from ice cores could in principle provide such constraints but are complicated by in-situ production of  $^{14}\text{CO}$  by cosmic rays directly in the ice. Recent work in Antarctica and Greenland shows that this in-situ component would be relatively small and can be accurately corrected for at sites with very high snow accumulation rates. We propose to sample firn-air and shallow ice to  $\approx 230$  m depth at Law Dome, Antarctica (site DE08, 1.2 m a<sup>-1</sup> ice-equivalent snow accumulation), extracting trapped air from the ice cores on-site using a new large-volume ice melting system.  $^{14}\text{CO}$  will be analyzed in firn and ice core air samples, and accurate corrections made for the in-situ cosmogenic  $^{14}\text{CO}$  component in the ice—allowing for the atmospheric  $^{14}\text{CO}$  history to be reconstructed. Interpreted with the aid of chemistry-transport modeling (GEOS-Chem and the Australian Community Climate and Earth System Simulator), the  $^{14}\text{CO}$  history will be used to place the first observational constraints on the variability of Southern Hemisphere [OH] since  $\approx 1880$  AD.

## 3A-04 Old carbon reservoirs were not significant in the deglacial methane budget

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Atmospheric methane concentration [CH<sub>4</sub>] has more than doubled since the preindustrial era due to human activity (MacFarling Meure et al. 2006), contributing to approximately 20% of the total anthropogenic radiative forcing (Myhre et al. 2013). Paleoatmospheric [CH<sub>4</sub>] from ice cores provides unique historical perspective on how natural CH<sub>4</sub> emissions changes with climate (e.g. Chappellaz et al. 1997; Rhodes et al. 2015). Measurements of CH<sub>4</sub> stable isotopes ( $\delta^{13}\text{CH}_4$ ,  $\delta\text{D-CH}_4$ ) from ice cores have been used as top-down constraints to distinguish the specific contributions from various CH<sub>4</sub> sources (e.g. Fischer et al. 2008; Bock et al. 2017), however stable isotopes of CH<sub>4</sub> do not provide a definitive constraint on total fossil CH<sub>4</sub> emission (Petrenko et al. 2017). In this study we provide measurements of <sup>14</sup>CH<sub>4</sub> through most of the Last Deglaciation ( $\approx 15$ -8ka). Our new <sup>14</sup>CH<sub>4</sub> data show that <sup>14</sup>C depleted CH<sub>4</sub> sources (marine hydrates, geologic seeps and old permafrost) were not significant contributors to the observed rapid CH<sub>4</sub> rise during the Oldest Dryas-Bølling (OD-Bø) period ( $\sim 14.6$ ka) and that there is no evidence of delayed significant fossil CH<sub>4</sub> releases after the onset of Northern Hemisphere (NH) warming both during the Bølling-Allerod interstadial and the early Holocene warm period. Combined with the earlier result from Petrenko et al. (2017) this strongly implies that fossil CH<sub>4</sub> emission was not an important component in the overall glacial-interglacial CH<sub>4</sub> budget.

## 3A-05 Radiocarbon and stable carbon isotope systematics in a high alpine cave system

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Speleothems are valuable archives of the past climate, because they can be precisely dated using the U/Th method and at the same time offer several high-resolution proxies. These cave carbonates form by precipitation of Ca-carbonate derived from the dissolution of the host rock. In most karst systems dissolution is driven by soil-derived carbonic acid. However, there are examples where oxidation of sulfide minerals in the host rock contributes considerably to the dissolution of karst host rock [1,2]. As a consequence, the stable C isotope signal of speleothems such as stalagmites lack the signature of depleted soil and consequently the ratio of radiocarbon (<sup>14</sup>C) compared to <sup>12</sup>C is low.

SPA-127 is a stalagmite from Spannagel cave (W Austrian Alps) that grew between 8500 and 2500 a BP at an average rate of 25 µm/a [3]. The δ<sup>13</sup>C record of this stalagmite exhibits large and fast changes between -8 and +1 ‰. These variations are possibly a consequence of rapid switches between the more common process of carbonate dissolution due to carbonic acid and sulfide oxidation. <sup>14</sup>C provides important insights to better understand these water-rock interactions in the karst rock. To this end, a continuous, highly resolved <sup>14</sup>C record of this stalagmite will be presented, which was obtained using laser ablation accelerator mass spectrometry [4]. The spatial resolution of 400 to 800 µm allows to examine the nature of the high-amplitude high-frequency δ<sup>13</sup>C changes.

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## 3A-06 Indian Ocean late Holocene oceanography reconstructed from fossil corals from Malé Island, Maldives

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The Indian monsoon (IM) is an important part of the global atmospheric circulation system. Summer monsoon transports significant quantities of water into inland Asia. Paleoceanographic information from western as well as eastern Indian Ocean Holocene records have been reported using fossil corals with geochemical proxies and sediments cores, yet little is studied in central ocean basin. Here we study fossil corals obtained from Malé Island, Maldives. Radiocarbon bomb peak is clearly recorded in the coral grew during 20 centuries and the signatures are similar to the ones previously reported. The calibration curve of sea surface temperature (SST) for Sr/Ca is constructed using this coral and late Holocene palaeo-SST is established employing this equation. Combined  $\delta^{18}\text{O}$  measurement of these corals revealed past variations of sea surface salinity (SSS) as is attributed as changes in IM intensity. In this presentations, we will report geochemical signatures recorded in fossil corals from Maldives to understand IM variations during the late Holocene.

## 3A-07 Millennial scale variability in the East Asian monsoon: a common signal amongst lakes Suigetsu, Nojiri and Biwa, Japan

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*9 [www.suigetsu.org](http://www.suigetsu.org).*

The nature and timing of millennial scale variability across the East Asian Monsoon (EAM) during the last glacial cycle remains a point of debate. Here we present a new record of hydroclimatic variability based upon the common signal amongst three Japanese lake records (Suigetsu, Nojiri and Biwa), tied to the precise varve and radiocarbon chronology of Lake Suigetsu, Japan. The total organic carbon concentration (TOC) in the three lakes, including new data from Lake Suigetsu, correlate to a high degree, revealing coherent regional scale environmental change on a centennial-millennial timescale between circa 50,000 and 10,000 cal BP. Collectively, these records are interpreted as reflecting regional scale hydroclimatic change, which is linked to variability in the EAM. The Japanese lake TOC records exhibit marked similarities with speleothem, loess, marine and ice core records from across Asia, lending strength to the hypothesis of a linked winter and summer monsoonal cycle.

## 3A-08 Reconstructing past fog events in the hyperarid Atacama desert: Evidence from radiocarbon and stable nitrogen and hydrogen isotopes

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The Atacama is a cold, hyperarid desert, where the availability of water plays a crucial role in determining the presence of plants. Rainfall is basically non-existent (<2mm/year) but brief intense rainfall events occasionally occur during El Niño years. On the other hand, fog is frequently occurring year-round along the coastal mountain range in northern Chile fueling a distinct "lomas" vegetation (Pinto et al., 2006). Here, isolated patches of mainly *Tillandsia landbeckii* plants typically grow in the fog zone at altitudes between 800 and 1300 m. The formation of *Tillandsia* is largely controlled by the availability of fog moisture and the spatial distribution has been related to major fog corridors reaching up to 50 km inland (Cereceda et al., 2002). Little is however known about the controls on fog intensities and frequencies over longer timescales due to the general lack of suitable climate archives.

In this study, we use a stable isotope and lipid biomarker approach together with radiocarbon dating to track present and past variations in available fog moisture. We collected different *Tillandsia* populations (active and dead specimen) along the coastal area between Arica and the Rio Loa Canyon (ca 18.5-21.5°S) in March 2017. We analyzed foliar  $\delta^{15}\text{N}$  and compound-specific n-alkane D/H values, both used as proxies for moisture availability (Latorre et al., 2011; Sachse et al., 2012). In addition, we excavated a series of fossil dunes that revealed multiple relict but well preserved *Tillandsia* layers. We  $^{14}\text{C}$ -dated a total of 27 buried *Tillandsia* layers to develop a chronology of past growth events possibly linked to climate variations and thus moisture supply in the past.  $^{14}\text{C}$  ages of basal layers range between 990 and 2500 years BP. Our first results indicate that *Tillandsia* growth occurred in continuous intervals over the past 2500 years in the North while it ceased at ca 1000 years BP in the South, in agreement with persistent dry conditions during the Medieval Climate Anomaly (Rein et al., 2004). This is also indicated by a shift towards more enriched foliar  $\delta^{15}\text{N}$  values and n-alkane D/H values during the same time interval. Our findings indicate the potential of fossil *Tillandsia* dunes as a valuable paleoclimate archive for past fog events that may be largely controlled by ENSO-related climate anomalies.

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## 3A-10 Turnover of the petrous part of the temporal (the inner ear) bone in humans

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The exceptionally dense otic capsule of the petrous (ear) bone is thought form during the first two years of life, and not remodel during later life. The bone could therefore be used (1) for assessment of date of birth in forensic studies and (2) as an alternative record to tooth enamel for isotopic analysis, for example for Sr isotope analysis of childhood location in archaeological cremations. To confirm whether remodelling occurs after childhood, three bones from recently deceased cadavers born in the 1940s were dated. Samples were taken from the dense bone of the otic capsule of the superior semi-circular canal, the dense bone surrounding the internal acoustic meatus, and spongy bone surrounding the otic capsule. The results demonstrate that turnover does occur in the otic capsule after the age of 10, but it is limited. As expected, the spongy bone turns over during later life.



## 3A-11 Radiocarbon-AMS analysis in tooth for age estimation as part of forensic science task in Mexico

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Identification of unknown human remains is necessary not only for ethical reasons, but also because it carries legal consequences. The estimation of age, sex determination, geographical origin and biological affinity are important factors for identification. Forensic investigations of unknown human remains that have not experienced major alterations use morphological or metric identification methodologies. However, identification of victims of natural disasters, accidents or crimes is a more complex task. These bodies are usually mutilated, charred, exposed to chemicals, skeletonized or mixed in clandestine tombs with high decomposition. Furthermore, it is not uncommon for there to be only a simple tooth available for identification. Teeth are the hardest and more resistant part of the human body; able to endure environment exposition and extremal conditions as premeditated fires or chemical attack. In these cases <sup>14</sup>C- accelerator mass spectrometry (AMS) analysis has a direct application in Forensic Sciences.

We are interested in generating knowledge to improve our forensic practices. The National Autonomous University of Mexico has the first Accelerator Mass Spectrometry Laboratory in Mexico, at the Physics Institute. Our research group has been working to determine the age in human teeth remains and contemporary samples by <sup>14</sup>C dating. Dating modern organic samples uses the <sup>14</sup>C incorporated by the <sup>14</sup>C bomb peak. The amount of sample used is very small, from 50 µg to 1 mg, depending on the preservation state of the tissue. One of our main goals is to design and develop a methodology that allows us to know the date of birth by means of the concentration of <sup>14</sup>C in the teeth, comparing the yield between <sup>14</sup>C analysis from carbonate in enamel, to collagen of dentin.

The forensic analysis of teeth begins with the sample selection, which can be organic material or in the mineral part. Carbon is extracted, converted to graphite, and pressed into a cathode. The sample is taken to the accelerator, where carbon isotopes are separated, counted and the <sup>14</sup>C/<sup>12</sup>C and <sup>13</sup>C/<sup>12</sup>C ratios determined. With this new facility in Mexico, we are trying to set-up the best conditions for forensic studies in Mexican samples as well as the analysis of relevant biological factors, which can modify the results, for example: the differences between the mineralized tissues that conform the teeth (enamel and dentin), the genesis for specific tooth, the formation time of the crown and root, and the location or place of birth. Also we studied the effect of temperature on the integrity of the enamel of the teeth, analyzing the changes induced by exposure to temperatures in an inert N<sub>2</sub> atmosphere by Raman spectroscopy and X-ray diffraction. Our <sup>14</sup>C results are in good agreement with the expected values for samples of teeth which age is known.

## 3A-12 Investigating potential dietary effects on the radiocarbon dating of modern human hair

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The determination of an individual's time of death from the analysis of human remains represents an essential component of forensic investigations. Multiple methods are employed for this purpose including radiocarbon dating which is able to provide a dating precision of a few years for modern individuals alive during the so-called "bomb-spike" event (from the 1950's until recently). However, no previous research has addressed the influence of diet on radiocarbon measurements of human remains. The relevance of this is shown through archaeological studies in which human radiocarbon dates were significantly older than independently and securely known time of death as a result of the consumption of aquatic foods. The same may be expected for modern individuals that include in their diets fish, molluscs, seaweeds, or other aquatic foods.

To test the above we subjected to radiocarbon and stable isotope analyses (C,N,S) hair samples from living individuals having diverse dietary preferences (e.g. vegans, vegetarians, heavy meat or fish consumers). The results showed, with one exception, that radiocarbon dating reliably provided hair collection date demonstrating its usefulness for forensic research.

### 3A-13 Radiocarbon dating application to modern musical instruments: an interdisciplinary study

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Thanks to technical developments that allow <sup>14</sup>C analysis of an increasingly small amount of carbon, radiocarbon dating is becoming a powerful tool to overcome scientific obstacles for musical instruments examination. Besides a variety of classical analysis methods used in cultural heritage institutions, radiocarbon is also essential for deepening the scientific knowledge on the “restoration history” of instruments and for understanding their use since they emerged from the instrument factories.

Although these radiocarbon analyses were used for archeological instruments, there have been a few studies on instruments manufactured during the Modern period between the 16th to the 19th century (only one publication to our knowledge, [1]). Indeed, there are three challenges to meet: i- the sample size, which will not extend a few hundred micrograms, ii- the composite constitutions of the instrument (varnishes, glues, restored parts), which requires specific and complex chemical protocols to extract the carbon to be dated and iii- the historical period not favorable to radiocarbon dating due to complex calibration curves [2].

Our research program gathered the recent technological advances in radiocarbon dating, the expertise of the museum conservators at the Musée de la Musique and material characterization techniques as XRF, FTIR, UV, Optical Microscopy or dendrochronology. Our team focus on four identified corpus: 1- violin bows of the 17th century and their successive musical practices, 2- harpsichords and their elements that have been renovated over time (wrestplank, jacks, string, tail, bentside), 3- emblematic lutes of the 16th and the 17th centuries and their braces to authenticate, 4- Indian rudra-veenas of an unknown age.

Here, we present the first results and the added value of the interdisciplinary framework of this study. As an example, two samples were collected from an Indian rudra-veena belonging to the Musée de la Musique collection (E.997.24.1); they were suspected to be manufactured at the end of the 17th century. The radiocarbon dating performed on each sample perfectly match, however they output four equiprobable calibrated date ranges. Thus, the comparison with a Govardhan’s pictorial representation of a similar rudra-veena allows to determine the most likely date range: [AD 1650-1683].

The meeting between the mentioned fields is a scarce opportunity. All the results obtained convey an improved understanding of the use and restoration of instruments for museums and private instrument makers (Cels, Vatelot-Rampal) beyond the current scientific boundaries.

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## 3B-02 The stabilization of organic matter in soils within oases of East Antarctica based on radiocarbon dating research

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A temporally stable pool of organic matter (OM) is likely to exist under the extreme conditions of Antarctica, where sources of OM are represented by cryptogamic organisms and microbial photoautotrophs, but not vascular plants. Our previous research (Zazovskaya et al., 2017) has shown that the radiocarbon age (mean residence time) of OM does not exceed 450-500 BP in most soils and soil-like systems within oases of East Antarctica. However, we have recently obtained a series of radiocarbon dates of more than 1000 BP in samples from some soils and soil-like systems with very low OM concentrations (less than 1%). To address the questions of, what are the mechanisms of OM stabilization within Antarctic oases and which OM pools are most stable over time, we conducted radiocarbon dating of particle density/size fractions separated from soils under moss-algal communities, which are the most developed soils within the Antarctic oases. The use of densitometric analysis allowed for soil sample separation, without the use of chemical treatment, into particle-density fractions containing OM of different nature and genesis. The particle-density fractions selected for radiocarbon dating were as follows: (a) free particulate organic matter (FPOM) – most short-lived fraction of soil OM, (b) occluded particulate organic matter (OPOM), (c) a pool of occluded matter of a higher density than that of the OPOM, dominated by organo-mineral complexes and (d) heavy fraction (HF). These particle-density fractions allowed for the differentiation of OM according to its stability and age. The particle-size fractions of OM included the following: (a) 250-100  $\mu\text{m}$ , (b) 100-50  $\mu\text{m}$ , (c) 50-20  $\mu\text{m}$ , (d) less than 20  $\mu\text{m}$  and (e) elementary soil particles with magnetic properties. All the specified fractions were subjected to radiocarbon dating with the use of accelerated mass spectrometry (AMS). In addition, isotope data and nuclear magnetic resonance (NMR) spectroscopy were used as sources of information on the composition and properties of the OM of the studied soils. The results of this research will be presented at the conference meeting.

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### 3B-03 Tracing the degradation of ancient organic carbon in permafrost-affected soils via <sup>14</sup>C analysis of microbial, in-situ respired CO<sub>2</sub>

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Microbial degradation of organic carbon (OC) stored in permafrost-affected soils may act as an important positive feedback upon global warming. However, the decomposability of the OC and therefore the dimension of the so-called permafrost carbon feedback are not well understood. For a better understanding, it is necessary to identify the OC sources prone to microbial breakdown that upon permafrost thaw may become part of the active carbon cycle. <sup>14</sup>C analysis is a valuable tool to estimate the contribution of young and old OC sources in microbial respired CO<sub>2</sub> (e.g. Hicks Pries et al., 2016). So far, it has been mainly used in studies investigating OC degradability in permafrost soils in laboratory incubation experiments, though, where field conditions are simplified.

Here, we present an in-situ approach to differentiate OC sources of respired CO<sub>2</sub> emitted from the thawing part of permafrost soils, the active layer, in the Lena River Delta, NE Siberia. We collected CO<sub>2</sub> from the rims and centers of two low-centered ice wedge polygons using dynamic closed respiration chambers and diffusive depth samplers equipped with molecular sieve cartridges (Wotte et al., 2017). The depth samplers collected CO<sub>2</sub> from the bottom of the active layer (30.5–42.5 cm at the time of insertion). The respiration chambers were used to collect CO<sub>2</sub> emitted from the whole depth of the active layer. Respiration chambers were placed on vegetated and bare surfaces to further distinguish ecosystem and heterotrophic respiration. Additionally, atmospheric CO<sub>2</sub> was sampled.

The <sup>14</sup>C concentration of all samples collected on vegetated surfaces (n=10) equals in 1-σ the <sup>14</sup>C concentration of the atmosphere (1.027 ± 0.077 F<sup>14</sup>C) indicating that mainly fresh OC sources are respired. The samples collected on bare surfaces (n=8) and thus presumably representing heterotrophic respiration mostly equal the atmospheric <sup>14</sup>C concentration, too. The CO<sub>2</sub> respired at the bottom of the active layer, above the permafrost table, is enriched in <sup>14</sup>C compared to the atmosphere in the polygon centers (1.050 and 1.093 F<sup>14</sup>C), while it is equal to atmosphere or depleted in the polygon rims (0.954–0.978 F<sup>14</sup>C). This depletion may derive from the bulk OC being overall more depleted in <sup>14</sup>C in the polygon rims (0.684 F<sup>14</sup>C at 30 cm of depth) compared to OC in the polygon centers (0.972 F<sup>14</sup>C at 27 cm of depth; Höfle et al., 2013). The results prove a dominant turnover of relatively fresh OC, although there is evidence of degradation of older OC at the bottom of the active layer.

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## 3B-04 Sequential radiocarbon measurement on peaty sediments to reconstruct high precision age model of marsh deposits

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Radiocarbon dating on sediment cores relies on the abundant of macrofossils such as plant remains. In their absence bulk sediment radiocarbon dates have been used to construct age models of sediment cores recovered from terrestrial environments. Here we employ sequential radiocarbon measurements to make better resolution and precision age model of cores retrieved from the Sarutake river marshland in Hokkaido, northern Japan. High organic carbon content easily of the sediment allowed us to conduct bulk radiocarbon measurements relatively readily. However the sediment is still mixed with other materials thus the radiocarbon results are for both in-situ and ex-situ carbon. Therefore we also measured the age of aquatic plant remains to correct the bulk dates. We employed sequential radiocarbon measurements (eg., Ishizawa et al., 2017;2018) to overcome this difficulties together with evaluations of reservoir effects using diatom based paleo salinity estimates (Sagayama et al., 2018).

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## 3B-05 Chronology of sediments and soils of the Old Ladoga: from Neolithic to early Middle Ages

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The oldest Russian city Staraya Ladoga is located 100 km west of St. Petersburg on the left bank of the river Volkhov at the confluence with the river Ladoga. The Old Ladoga fortress, the Zemlyanoye hillfort and the adjoining medieval settlement are located on a low river terrace six meter in height.

A cultural layer with thickness up to 4 m was discovered during the excavation at the Zemlyanoye hillfort. According to the dendrochronology data, its accumulation began in the middle of the 8th century AD. Buried Soil 1 with arable horizon lies under the cultural layer, coal from this horizon was dated 6-9th centuries AD (date series  $1480 \pm 40$  -  $1260 \pm 60$  BP). The humus date for Soil 1 was older than the coal date ( $1600 \pm 80$  BP), since the accumulation of humus in the terrace, soil began much earlier, possibly around 2500 BP. A thin (20-30 cm) layer of sediments of the Ladoga transgression (sapropel) lies under the Soil 1. The buried Soil 2 lies under sapropel, humus from it was dated 2456-2208 cal BC. Soil 2 was possibly rejuvenated, because due to the small depth of the burial, it was affected by the processes associated with the formation of Soil 1. To the north, in the mouth of the Ladozhka River, the thickness of the sapropel increases to 90 cm. The integrity of humus is higher there, so the humus date of the Soil 2 is older - 3488-3105 cal BC. The Neolithic culture layer in the Soil 2 was found there. Based on our results and the literature data (Shitov et al., 2005), the following stages of sediments and soils formation of Old Ladoga can be identified.

1. Accumulation of glacial and lacustrine-alluvial deposits, late Glacial - Middle Holocene.
2. Formation of the lower buried Soil 2, Middle Holocene (Neolithic, > 5000 cal BP).
3. Ladoga transgression. Accumulation of sapropels (maximum of transgression 4000 cal BP).
4. Debacle of the Neva River, drainage of the terrace, 3100 cal BP.
5. Formation of the upper buried Soil 1 of meadow-forest genesis, the soil-forming material was sapropel, late Holocene (2200-1200 BP).
6. Plowing. Presumably 6-8th centuries AD.
7. The beginning of the cultural layer formation and burial of the Soil 1, 8-9th centuries AD.

### 3B-06 A very well-behaved Cedrela fissilis from central Brazil

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Given the difficulty in obtaining robust chronologies from tree rings in tropical regions, the search for adequate species is very important. Both dendrochronology and radiocarbon measurements are required to validate the use of any specific tree. Some species have proved to be reliable for representing atmospheric radiocarbon concentration over time, such as *Cedrela fissilis* (Baker et al 2017) and *Araucaria angustifolia* (Santos et al 2015). However, different climatic conditions may result in different growth patterns. In this work, we study the annual growth rings of one individual of *Cedrelafissilis* from seasonally dry tropical forest fragment located in the municipality of Montalvânia (MG), in central Brazil. The samples were prepared following standard dendrochronological procedures and crossdating was identified using the skeleton plot technique (Stokes and Smiley 1968). Radiocarbon Accelerator Mass Spectrometry (AMS) was used to compare the isotopic ratios of tree rings with the <sup>14</sup>C concentration in the atmosphere during the nuclear tests based on *cuveSHCal 1-2* (Hua et al 2013). Results show a very good agreement within the period from 1958 and 1980AD.

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### 3B-07 AMS radiocarbon dates and tephra layers of cored sediments from peat land along Iliuliuk River, southeast of Dutch Harbor, Unalaska Island, Alaska

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Unalaska in the Fox Islands group of the Aleutian Islands, Alaska, includes active Makushin volcano (2036 m asl) and two Early Anangula phase archaeological sites (ca. 9 cal ka BP) in the Unalaska Bay. To determine tephra deposition on eastern part of Unalaska, we conducted coring sediments using a peat sampler from the Iliuliuk River, 30 km east of the volcano (53° 51' 2.8" N, 166° 28' 51.0" W, ca. 540 m asl).

We recognized at least fifteen coarse sand to silt-size ash layers in the cored sediments (composite depth = 190 cm). Seven AMS radiocarbon dates were obtained from peat samples and are almost consistent with the stratigraphy. Based on thickness and grain size, most ash layers likely originate from Makushin volcano (Begét et al. 2000) with a few exceptions (fine-grained ashes). The uppermost ash corresponds to historical eruption (VEI = 3) that occurred in the 19th century. Similar eruptions have occurred since ca. 7 cal ka BP. Basal date of peaty deposit (190 cm in depth), 9190 ± 30 BP, almost agrees with the Early Anangula phase of archaeological chronology. The caldera-forming eruptions occurred about 8.1 to 8 ka BP (Begét et al. 2000). No pyroclastic-flow deposit in the cored samples indicates that the 8 ka pyroclastic flow could not reach this valley. A few fine-grained ashes lower than 7 ka BP horizon are candidates to correlate with the pyroclastic flow as co-ignimbrite ash-falls.

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## 3B-09 Quaternary soil development and sand movement periods on the Nyírség alluvial fan, Hungary

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The Nyírség is the second largest sand dune area (ca. 4,600 km<sup>2</sup>) in the northeastern part of the Carpathian Basin. The Nyírség have been studied for over 100 years but geological and geomorphological research can still contribute to a better understanding of the surface development processes of the area.

The Nyírség had been formed on the alluvial deposits of the Tisza River and its tributaries. At around 25 ka, fluvial processes terminated on the territory; and during the rest of the Pleistocene, aeolian processes prevailed. The strong north-westerly, northerly, north-north-easterly winds formed mostly blowouts, oval shaped sand hummocks and residual ridges. Parabolic sand dunes also evolved on a larger scale in the Nyírség.

The first significant sand movement period at the Nyírség happened in the Upper Pleniglacial and the Late Glacial. The main landforms of the Nyírség had been developed at this time. The aeolian transformation of the land had not finished by the end of the Pleistocene. In the Holocene the sand moved within a small area mainly due to anthropogenic impacts.

Our aim was to clarify the periods of wind-blown sand movement periods by different absolute dating methods (Radiocarbon, OSL). Furthermore, we intended to reveal the usefulness of fossil soils ages in this sample area. We compared the charcoal and fossil soil ages collected at the same sampling sites.

In the meantime it was also possible to attest OSL and radiocarbon dating and to provide data not only for aeolian activity, but also for paleo-soil formation.

We had collected sediment (Gyüre, Vásárosnamény, Kótaj, Gégény, Kántorjánosi), charcoal samples (Gégény, Kántorjánosi, Nyíradony, Nagyvarsány, Máriapócs, Petneháza, Gyüre and Lövőpetri) from several sand quarries that contain fossil soil layers and bones from archeological excavation (Nyíregyháza-Oros) suitable for radiocarbon dating. Samples collected from Baktalórántháza, Gégény and Kántorjánosi sand quarries were used for the OSL measurements.

Different age determination methods supported each other well. The age data contributes to the results of previous researches. In the Nyírség the first major sand movements happened in the cold and drier period of the Upper Pleniglacial and Late Glacial (Baktalórántháza, Máriapócs, Lövőpetri, Nagyvarsány-Szabadságtanya, Gyüre, Petneháza). At the end of the Pleistocene the sand movements had not finished in the Nyírség (Gégény, Kántorjánosi).

Sand movement in the first half of the Holocene, in the Preboreal and in the Atlantic Phase took place due to climatic and also anthropogenic effects (Gégény, Kántorjánosi, Kótaj).

In the Subatlantic phase, there were many minor sand movement periods, mainly caused by anthropogenic impacts (Nyíradony, Nyíregyháza-Oros).

Radiocarbon ages derived from the charcoal and fossil soils collected at the same sampling sites showed u, that the soil ages are in a good correlation with the charcoal ages. These soil age dates can be applied well in this research.

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## 3B-10 Concentrations and <sup>14</sup>C content of total and dissolved organic carbon under contrasting land uses in northern NSW, Australia

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We investigated the quantity and distribution of total organic carbon (TOC) and dissolved organic carbon (DOC) under three contrasting land uses (woodland, improved pasture and cultivated) in northern NSW, Australia. For each land use, we determined the concentration of TOC and DOC down the soil profile to a depth of 100 cm using six soil depth increments. We also measured the <sup>14</sup>C content of the TOC and DOC samples to explore the mechanisms of transporting carbon into the deeper soil profile. We found that TOC concentrations in woodland soils were generally higher than those in agricultural soils, with highest values near the soil surface and decreasing values with depth. Substantially larger DOC concentrations in woodland soils at all depths were also observed. Similarly, for most of the depths TOC of woodland soils had higher <sup>14</sup>C content (or contained younger carbon) than TOC of agricultural soils. In addition, DOC was found to be consistently and substantially younger than the associated TOC. These results indicate that changes in land use might lead to large losses of young carbon down the entire soil profile, supporting the concept that organic carbon storage in soils is input driven (Hobley et al., 2017). The results also provide new insights into the mechanisms and importance of DOC to soil carbon dynamics.

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### 3B-11 <sup>14</sup>C distribution in soils with different history of land use, Calhoun CZO, USA.

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The soil organic matter (SOM) is the major carbon reservoir in terrestrial ecosystems. The understanding of potential impact of soil and anthropogenic processes on biogeochemical cycling remains one of the great uncertainties. Radiocarbon measurements of SOM provide powerful constraints for determining carbon dynamics and the magnitude and rates SOM response to the environmental changes. The performed experimental tests were aimed to find out the distribution of <sup>14</sup>C in Ultisols with different history of land use located in the Sumter National Forest. We analyzed: a) reference hardwood stands, mainly of oak and hickory that are taken to be never cultivated; b) pine stands, which had been used for growing cotton from beginning of the 19th century and then was abandoned in the beginning of 20 century and naturally reforested; c) currently cultivated plots, which were also used growing cotton prior to the 1950's but for the last 50-60 years for growing corn, wheat, legume, sorghum, and sunflowers. There were analyzed 3 profiles for each - reference hardwood and pine reforested sites and 2 profiles for cultivated sites. There were obtained 53 radiocarbon AMS dates.

The top AO and A horizons in all soils have very close <sup>14</sup>C concentration between 25-65‰, which mostly controls by quality (e.g. pine needle vs wheat) and quantity of the carbon input. However starting from AB horizon we have observed the huge differences even inside the sites with similar land use history. The AB, Bt, Bt2, and BC horizons have got <sup>14</sup>C concentrations under hardwood in the ranges -32- -140‰

-270- -480‰, -400- -530‰, and -320- -610‰, correspondently. Soil under reforested sites also has wide ranges of variations with the slightly lower <sup>14</sup>C concentrations as a result of previous erosion of the top horizons during their cultivation with lowest concentration in Bt2 horizon about -700‰. The cultivated sites have got the lower concentration compare to the undisturbed hardwood soil starting from Bt2 horizon.

It varies from -460 to- 670‰ and depends from the geomorphological position. As the rule the profiles in the low part of the slope have lower <sup>14</sup>C concentration in under surface horizons for any type of land use so the soil hydrology and input of carbon with the vertical and lateral transport could also affect <sup>14</sup>C concentration. As a result we can observe some inversion of <sup>14</sup>C concentration in BT and BC horizons when the ground water gives some input of modern carbon in the underlying horizons.

The <sup>14</sup>C distribution in the top 60-80 cm of the cultivated soils clears sings of the erosion when underlying horizons with lower <sup>14</sup>C concentration appear closer to the surface. In the case of the reforested sites we also can observe the similar phenomena, however this process is smoothed out by higher biological productivity of the pine forest compare to the cultivated sites.

## 4A-01 Are root zones hot spots of organic carbon in subsoils?

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About 50% of the global terrestrial organic carbon pool (OC) is stored in subsoil, i.e. below the uppermost soil horizon (A), but its distribution and turnover is not well understood because most research focuses on surface soils. It still remains unclear, which OC sources and what kind of transformation and stabilization processes control the strong increase in the apparent <sup>14</sup>C age with depth observed in most soils. The high <sup>14</sup>C ages were assumed to reflect very low OC accumulation rates in over long time scales. Thus, the organic matter in deep parts of the soil appears to be very stable, i.e. composed of relatively degradation resistant compounds. Consequently, subsoil OC was considered as not relevant in the global C cycle due to its low carbon sequestration potential and a low risk for destabilization.

New evidence suggests, however, that in subsoils OC is concentrated along roots, which are considered as one of the main or even the most important OC source at greater soil depth. Growing roots and their rhizosphere alter the physical structure of bulk soils and thus the habitats within. Changes associated with an increased input of organic matter near roots are accompanied by a higher microbiological activity, changing physical properties, and the protection of the organic matter in aggregated soil structures. The complex interplay of these different soil properties and its influence on OC storage in subsoils is not well understood.

We thus investigate how growing roots alter organic matter composition and OC turnover by comparing the elemental and lipid biomarker composition as well as the <sup>14</sup>C content of rhizosphere soil and the surrounding bulk soil. We evaluate results for the surface soil (A horizon) and subsoil (B horizon) in three soil profiles at two forest sites with different parent materials including Triassic sandstone and Loess. Our results generally reflect a strong spatial heterogeneity at each study site. At the loess site, the rhizosphere soil is much younger particularly in the B horizon suggesting large inputs of root-derived OC resulting also in higher OC contents than the surrounding soil. In contrast, the influence of roots in the soil developed in Triassic sandstone is less pronounced and does not increase <sup>14</sup>C contents in the rhizosphere soil. Compositional differences between rhizosphere and bulk soil at the different sites will be revealed by on-going lipid biomarker analyses.

## 4A-02 Soil organic matter C-14 dating – comparison of charred and non-charred carbon fractions of paleosoils under kurgans from the Hungarian Great Plain

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Mounds in Hungary have been protected since 1996 due to their special landscape, botanic and cultural historical values. Since only a fraction of the almost two thousand mounds currently existing in Hungary has been exposed so far the available information is relatively little. The complete archaeological excavation of the mounds are not only expensive and time consuming but frequently result in irreversible consequences: the shape and appearance of the mounds in the landscape could be damaged and it is possible that the valuable loess grassland vegetation on top of the mounds is completely destroyed.

In our study several archaeologically unexplored mounds were investigated in the area of the central Great Hungarian Plain. The age and methods of the construction of the mounds were cleared on the basis of shallow boreholes, geo-electric analyses and radiocarbon age determination of buried soil layers. Dating of the soil organic matter (SOM) seems attractive, since many anthropogenic constructions contain buried soil surfaces or sods with moderate or high carbon content. Radiocarbon ages of the organic carbon extracted by combustion from the soils at temperatures 400 °C and 800 °C degree were compared in each soil samples.

The age of the buried soils was corrected with the reservoir age of the recent soils found in the surroundings of the mounds. A living top soil has a steady-state “apparent” radiocarbon age which is resulted by the accumulation of biological carbon over hundreds or thousands of years (reservoir-effect) in equilibrium with the radiocarbon decay of <sup>14</sup>C. The steady-state apparent <sup>14</sup>C age (reservoir-age) of living soils can be very different (from hundreds to thousands of <sup>14</sup>C years BP) according the geological location depending on the climate, parent material, precipitation, chemical environment, flora and many other parameters. To have an estimate about the original apparent <sup>14</sup>C age of the palaeosoil layer under the kurgans we measured the apparent age of recent top soil at the top of the kurgans and also of some undisturbed recent top soils from the vicinity of each studied kurgans.

## 4A-03 Biospheroid C-14 dating– tests on recent top soils

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Age determination of paleosoils is useful for the studies of archeology, soil development, climate change, paleoenvironment and landscape evolution research. C-14 dating of paleosoils is a challenging task as ordinary soil organic matter (SOM) does not give a realistic C-14 age of a soil layer as SOM is normally accumulated over hundreds or even thousands of years. If one could not find some macrofossil remains in the discovered soil horizon then the age determination is always a matter of debate. On the other hand secondary carbonates in soil could provide detailed information about the paleoenvironment and climate conditions in the past.

In this study we have investigated the earthworms produced biospheroids as a possible material for soil C-14 dating. Recent studies suggested that earthworms consume preferably fresh organic matter during their life in the soil, which means the products of their digestion would contain rather recent organic carbon instead of the aged carbon from the SOM fraction.

Although biospheroids are rather small (diameter < 2 mm and mass < 5 mg) pure calcite granules, accelerator mass spectrometry (AMS) technique gives the possibility of their radiocarbon dating at the AMS Laboratory of the Institute of Nuclear Research of HAS (Atomki).

We have investigated 8 different recent topsoil samples collected at 5 different localities in the Hajduság area (Hungary). Biospheroids were carefully collected from each soil samples and 2-3 granules were used for C-14 dating of the individual soil samples. Results confirmed that biospheroids mostly contain young (max age 30 years) organic carbon, which gives realistic (zero) C-14 age for the top soils.

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## 4A-04 Estimating ages and transit times of carbon in tropical forests using radiocarbon

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Tropical forests are an important component of the global carbon cycle. It is estimated that they account for ca. 50% of Earth's total plant biomass. Therefore, they play a fundamental role in regulating important processes in the Earth system.

In this contribution we will present a method to estimate the age structure of carbon in a tropical rain forest using radiocarbon.

In this sense, radiocarbon is a powerful tool, tracking interactions between different reservoirs and providing information about carbon inputs and losses from and within compartments. On the one hand, the <sup>14</sup>C value of organic matter stored in the forest provides information about the system age, i.e. the time passed since carbon has entered the system through the process of photosynthesis until the time of observation. On the other hand, the <sup>14</sup>C value of the respired CO<sub>2</sub> gives an indication of the transit time, i.e. the time elapsed between the entry and exit of carbon. Such quantities are important system diagnostics and help to define the time scales at which carbon cycles in a tropical forest.

We calculated ages and transit times based on observations of carbon stocks and fluxes from a set of sites in the Peruvian Amazon. Our method provided estimates of the mean age of carbon in each of the forest compartments, namely foliage, wood, roots, and soil, and provided estimates of the expected radiocarbon values that can be observed in these tropical ecosystems.

In addition, we are currently developing an extensive radiocarbon budget at the Amazon Tall Tower Observatory (ATTO) to test our model predictions. With these measurements we expect to obtain estimates of the time that carbon requires to travel across the network of ecosystem compartments in Amazon rain forests.

## 4A-05 Impact of land use change on soil carbon and radiocarbon profiles in tropical forests

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Tropical forests account for 29% of global soil carbon and over 50% of the global terrestrial carbon sink. However, land use changes threaten the stability of this carbon pool. It is estimated that deforestation in the tropics accounts for 12 to 15% of the total global carbon dioxide emissions. A more detailed understanding of how land use changes impact carbon storage and turnover in soil, including the effects of subsequent reforestation, is required to develop more robust carbon accounting and implementation of effective management practices. We quantified stocks and measured  $^{14}\text{C}$  of soil organic carbon profiles in primary forests, pastures, oil palm plantations, and secondary forests at four sites in a lowland tropical forest of Peru, as well as primary forests and oil palm plantations in Indonesia and Cameroon. Soil samples were collected down to 200 cm. Our data show significant losses in carbon stocks in the upper 50 cm from all land use types. Most of the pastures and oil palm plantations show losses throughout the entire profile, while carbon stocks increase in the secondary forests at depths greater than 50 cm. There are decreases in  $\Delta^{14}\text{C}$  throughout the entire profile of most pastures and secondary forests, while the oil palm plantations often only decrease in  $\Delta^{14}\text{C}$  in the upper 50 cm. In all land use types, the largest decrease in  $\Delta^{14}\text{C}$  occurs between 0 – 50 cm in the profiles. Our data suggest that conversion of primary forests to pastures and oil palm plantations in the tropics can result in soil organic carbon losses as high as 50%, with the most profound impacts in the upper 50 cm, due to the rapid decomposition of younger, more labile carbon. In some cases, the establishment of secondary forests can increase carbon stocks at depths > 50 cm offsetting losses in the upper layers, suggesting that soil systems may be able to recover lost soil carbon if converted back to forests.

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## 4A-06 Field variability controls soil depth-distribution of radiocarbon in a tropical environment

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Soil processes vary in any landscape to form a high variety of soil profiles depending on specific local conditions. Together with organic matter, derived from above-ground litter, they give rise to both spatial and temporal differences of organic carbon in the soil columns. To study the extent of soil processes in relation to the depth-dynamics of organic carbon, <sup>14</sup>C-AMS results from both humin and humic samples collected from acid-alkali-acid (AAA) treatments were used as a tracer of soil carbon cycling. This was combined with data on grain size, elemental composition, and <sup>13</sup>C-NMR spectra for the tropical soil profiles of Andosol in Perbawati (PBW), Alisol in Jasinga (JSG), and Vertisol in Ploso lor (PL). These areas studied in Java, Indonesia, allow a comparison of the effects of crop management - rice and non-rice with varying seasonal crop rotations - and topographic positions, i.e. upper-, middle-, and lower slopes, respectively, which explain the origin of soil materials.

Principal component analysis of the variability in elemental composition shows the components PC1 and PC2 cover 75 % of the variation; PC1 with high K, Ca, Mg, Na, Si, and pH values in the Vertisol and PC2 with high P, total organic carbon (TOC) and nitrogen (TON) (soil organic matter) in the Andosol-PBW. The Vertisol exhibits more aromaticity of soil organic matter, with a high proportion of aryl-C, ca. 35% of total humic components, and the other sites show a high proportion of O-alkyl-C. The high aromaticity of organic carbon fractions in the Vertisol may be attributable to the anthropogenic input of charred materials.

The difference in the depth-gradients of carbon ages among soil types, exposes the importance of soil processes. The low lying Vertisol-PL shows a more limited depth-gradient of <sup>14</sup>C-humic/humin, from ca. 100 pMC near the surface to 75 pMC at 100 cm depth, than the other soils that drop from ca. 100 to 50 pMC at 100 cm depth. Some factors related to this regularity may be the active pedoturbation, shallow watertable, and groundwater irrigation for top agricultural practices. Going to the middle slope, Alisol-JSG defines a highly stable environment, as its parent material is homogeneous, in which <sup>14</sup>C-humic/humin may demonstrate a typical depth-distribution. On the upper slope, the Andosol-PBW exhibits a strong irregularity of the <sup>14</sup>C-humic/humin distributions associated with a different origin of the soil material. The highest <sup>14</sup>C concentration occurred at ca. 30 cm depth in the rice plot. With  $111 \pm 0.36$  pMC it was higher than the atmospheric <sup>14</sup>C level in 2012 of ca. 103 pMC.

The effect of crop management variability, rice versus non-rice, on the <sup>14</sup>C-humic/humin concentrations is not clear since no single plot has permanent crop since the first cultivation.

## 4A-08 Large dead carbon fraction detected from stalagmites obtained from the Kyusendo cave in Japan

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East Asian regions are under the influence of millennial scale changes in the Asian summer monsoon, as previously reported by speleothems from Chinese caves (e.g. Wang et al., 2001). Records of oxygen and stable carbon isotopes can be respectively used as proxies for precipitation amount and types of vegetation above the cave, during the past. Radiocarbon dating cannot be applied to obtain dates of samples because carbon recorded in speleothems are derived via drip waters in caves, and have often been aged due to dissolution of host rocks and soils. Departures of radiocarbon dates from corresponding U-Th dating results is called dead carbon fraction (DCF), which reflects the fraction of <sup>14</sup>C-depleted carbon not from the ambient atmosphere (Genty and Massault, 1999). However, the factors contributing to a change in DCF remain poorly understood.

To clarify the factors of DCF variations, we analyzed three stalagmites, KST4, 5 and 6, taken from the Kyusendo cave located in the southeast part of Japan, which is affected by East Asian summer monsoon. Obtained U-Th dates of our speleothems ranged from 9 ka to 45 ka. The DCF in the Kyusendo cave is larger compared to other caves in the world. The DCF of the modern drip waters were 30–50 %, and similar to the range recorded by speleothems. Values during the last ice age were larger than the present day values, which may reflect the precipitation changes due to a reduction in the summer monsoon intensity. Our results suggest that the variation in DCF could be used as a proxy of precipitation or groundwater residence times. Oxygen isotopes and trace element measurements are underway, which will better constrain the mechanism for past DCF variability.

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## 4A-09 Assessing the Dead Carbon Proportion and Bomb Carbon contribution for the isotopic composition of a speleothem from central Brazil

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The study of the isotopic composition of speleothems contributes to palaeoclimate reconstruction and allows for a better understanding of environmental changes. In tropical regions, where trees with regular growth rings are scarce and the lack of well distinguished seasons often forbid a robust chronology to be established, speleothems can offer reliable records of atmospheric radiocarbon concentrations over time. In this context, we present carbon isotope measurements for a one-century old stalagmite from central Brazil, dated by Th-U from 1915 to 1992 AD. By comparing the <sup>14</sup>C concentration of the 5cm laminated calcite with the correspondent atmospheric concentrations, it was possible to see a good match with the Southern Hemisphere zone1-2 bomb peak curve (Hua et al. 2013) provided dead carbon proportion (DCP) can be estimated (Genty et al. 1999; 2001). DCF ranges from 5 to 20% between 1966 and 1992 AD while δ<sup>13</sup>C varies between -12.5 and -11.0 ‰. We evaluate the correlation between DCP and δ<sup>13</sup>C in this stalagmite with the aim of correcting DCP in other metric sized speleothems, which can be a resourceful proxy for improving SH calibration curves in the future.

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## 4A-10 Problems of developing the Pleistocene radiocarbon chronology within high mountainous terranes, case study from intermountain depressions of Russian Altai

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Understanding the Late Pleistocene evolution of intermountain depressions within mountains of Southern Siberia is not possible without numerical dating of deposits of various genesis. By now there is a wide arsenal of different techniques to date Late Quaternary sediments. The application, precision, and accuracy of each of them vary considerably. Nevertheless, today radiocarbon analysis is the most exploitable and widely applicable one. Generally, its application is limited by ~50 ka but some problems occurred while using old dates (more than ~30 ka BP) for any geochronological reconstructions.

In the framework of studying the Late Quaternary of Russian Altai, we came across a case of obtaining a set of the Late Pleistocene radiocarbon ages for tertiary bog-lacustrine deposits, which were brought to the surface as a result of tectonic movements in the Dzhazator valley, and later were affected by landsliding, meltwater runoff from the Pleistocene glaciers, and lacustrine washout. Multidisciplinary investigations included spore-pollen and ostracods analysis, determination of biological composition of deposits, analysis of micromorphological structure, X-ray diffractometry and IR-spectroscopy of the enclosing clay sediments. Since initially the Holocene age of sedimentary records was assumed, geochronological reconstructions were based on radiocarbon analyses, including those applying AMS technique.

Generally, three sections in different geomorphological positions were studied, and eleven radiocarbon ages of redeposited organic material as well as lithified peat – brown coal layers with unbroken structure were obtained. All calculated radiocarbon dates fell within the time interval of about 14-45 ka BP, i.e. the Late Pleistocene. Additionally, to confirm the Neogene age of sediments in the Dzhazator valley, two finite counting radiocarbon ages (50 and 35 ka BP) were obtained for samples from brown coal deposit of the Neogene age in Chuya basin and undivided Paleogene-Neogene deposits in Kurai basin, affected by the Pleistocene Lakes.

Disagreement of numerical dating data with obtained paleontological characteristics, results of geochemical analysis, as well as with the position of studied sections within the geomorphological system was revealed. This fact indicates the presence of young carbon in the ancient peat deposits, which could be transported as a result of complex of post-sedimentary tectonic and exogenous processes (such as influence of meltwater runoff from glaciers, washout lacustrine activity, solifluction, cryoturbation, pedogenetic processes, etc.).

The complex paleogeographical history of regional sedimentation patterns (which is quite common for tectonically active high mountainous provinces) suggests that younger carbon in dated organic material is presented in a form that is not (or just poorly) removed by standard techniques (for example, ABA method). Generally, the problem of rejuvenation of radiocarbon ages of ancient deposits is not new. The similar problem was reported earlier for the Pleistocene chronology of Northern Siberia and Russian plane.

Single ancient (>30 ka BP) radiocarbon dates could hardly serve as reliable age markers, and should cautiously be used only if they are in a regular position in a section and/or have independent control by other proxy data.

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## 4A-11 Radiocarbon profile in soil: its implication for carbon dynamics, land use history, and relation with other anthropogenic radionuclides deposition

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In general,  $^{14}\text{C}/^{12}\text{C}$  ratio in soil, as well as carbon content, has decreasing trend from the surface to the deeper layer. The decreasing trend of the carbon concentration indicate that the organic matter had been provided from the upper region during the soil formation. The  $^{14}\text{C}/^{12}\text{C}$  trend might also supports this rough carbon migration process, i.e., it shows "modern" near the surface and older age in deeper layer. In this way,  $^{14}\text{C}/^{12}\text{C}$  depth profile will give us an information about the carbon dynamics in soil. Recent soil shows higher  $^{14}\text{C}/^{12}\text{C}$  value than "modern" near the surface due to the remnant of the atmospheric nuclear weapons testing. From the detailed depth profile near the surface and the time course  $^{14}\text{C}/^{12}\text{C}$  variation in the atmosphere we can evaluate the downward moving rate of carbon in the soil at least near the surface. The general decreasing depth profile would be used for the land use history. If the depth profile of an unknown soil shows the general decreasing trend, it should be a natural soil. It should not be disturbed for the reasonably long time. On the other hand, if it shows a flat depth profile or inverse trend (increasing with depth), it should be a cultivated field or man-made land. This consideration will apply the origin-estimation of other anthropogenic radio nuclide. For example,  $^{129}\text{I}$  derived from a nuclear accident could be distinguished from the one from the global fallout. If the profile of  $^{129}\text{I}$  shows steep decreasing trend with depth nevertheless  $^{14}\text{C}/^{12}\text{C}$  shows flat profile,  $^{129}\text{I}$  should have deposited recently, i.e., it clearly originates from the recent accident. We will discuss above mentioned issues based on several original data.

## 4B-01 Radiocarbon in the atmosphere and biosphere of Slovakia: Impact of nuclear power plants

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Radiocarbon as one of the most important radionuclides for delivering of long-term radiation doses to the public has been regularly monitored around nuclear power plants (NPP) as well as in Bratislava. Two nuclear power plants (NPP) have been in operation in Slovakia - in Jaslovské Bohunice (4x440 MWe) and in Mochovce (2x440 MWe). Both sites have been using light water nuclear reactors. In the vicinity of both NPP atmospheric carbon dioxide has been sampled on a monthly basis and its radiocarbon activity has been measured by gas proportional counters. The atmospheric  $^{14}\text{CO}_2$  data from these two sampling stations will be presented and compared with results from other sampling sites from both urban and rural parts of Slovakia. Biota samples provide information about  $^{14}\text{C}$  activity accumulated during given plants' growth. Annual tree rings have been used therefore as archives of past radiocarbon levels in the biosphere as well. Atmosphere and tree ring samples from the Jaslovské Bohunice area covering a period of 20 years, measured by gas counters and accelerator mass spectrometry, were compared with similar measurements at Bratislava Vysoká pri Morave background stations.

## 4B-02 Assessment of anthropogenic contamination by $^{14}\text{C}$ in the vicinity of Ignalina nuclear power plant

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$^{14}\text{C}$  found in the atmosphere is produced by natural process and by anthropogenic human activities as well [1]. Anthropogenic radiocarbon appears in a significant amounts in the nuclear power plant (NPP) vessel components, cleaning systems and structural components.  $^{14}\text{C}$  in the nuclear reactor is generated by neutron radiation interaction with  $^{17}\text{O}$ ,  $^{14}\text{N}$  and  $^{13}\text{C}$ . Over decades  $^{14}\text{CO}_2$  gas releases from NPP accumulates in local biosphere by photosynthesis, while increasing overall radiation background.

In order to evaluate Ignalina NPP (Lithuania) exportation impact on environment, there were extracted 8 tree cores around the NPP which were separated to 285 tree rings samples (time span 1980-2016) to determine the overall increase of radiocarbon concentration in NPP surroundings as compare to 3 tree core from clean background area at Vaikšteniai. Samples were physically and chemically (BABAB) prepared [2], graphitized with AGE-3 (IonPlus AG) coupled with elemental analyzer (Vario Isotope Select, Elementar, GmbH) [3] and measured at Vilnius Radiocarbon SSAMS (NEC, USA) facility [4].

Performed radiocarbon analysis provided critical data about radiocarbon releases and atmospheric transport from the NPP and gives us opportunity to estimate environment impact and it's model.

To fit the  $^{14}\text{C}$  measurement data modelling of the routine radiocarbon releases transport from the NPP was performed by using Gaussian model and historical local meteorological data.

The results showed pronounced increase of  $^{14}\text{C}$  up to about 15 pMC in the tree rings during INPP exploitation (Unit 1 - 1983-2004; Unit 2 - 1987-2009) as well during decommission periods. As expected, effect of contamination reduction with distance was observed- in average by 6 pMC by increasing distance from 2 to 8 km from the INPP. Directional and year by year variation was also noticed.

Application of the high sensitive  $^{14}\text{C}$  measurement technique and environmental modelling can be used as a powerful tool for the NPP anthropogenic impact assessment.

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## 4B-03 Pre- and post-accident C-14 levels in tree rings within 25 km of the Fukushima Dai-ichi Nuclear Power Plant

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About 2.81 PBq of anthropogenic <sup>14</sup>C has been released from nuclear facilities after the 1950s [1], which were originated mainly from the neutron activation of <sup>14</sup>N (n, p) <sup>14</sup>C, <sup>17</sup>O (n, α) <sup>14</sup>C, and <sup>13</sup>C (n, γ) <sup>14</sup>C. Although there are 60 nuclear reactors in Japan, studies on the environmental effects of <sup>14</sup>C emitted by the reactors has been limited to the Fukushima Dai-ichi Nuclear Power Plant (FDNPP) with six boiling water reactors [2]. Xu et al. (2016) [2] estimated that total ~53 TBq of <sup>14</sup>C was released from the FDNPP during their normal operation period of 1971–2010. Little is known about the environmental behavior of <sup>14</sup>C discharged from the FDNPP. The main objectives of this study are to estimate the influence area of <sup>14</sup>C discharged from the normal operation of the FDNPP and to detect the accidental <sup>14</sup>C release from the FDNPP occurred in March 2011. For this purpose, we investigated the activity of <sup>14</sup>C preserved in tree rings that grew over the period 2008–2014 including before and after the accident and were collected from a Japanese Cypress and Cedar tree growing at sites 9 km and 24 km northwest of the plant. The <sup>14</sup>C levels in the prepared graphite samples from early and late rings during 2008–2014 were measured using AMS system at the University of Tokyo [3]. The <sup>14</sup>C activities ranged from 231 to 257 Bq kg<sup>-1</sup> C in the tree rings formed during the period 2008–2014 at two sites. The activities in the period 2012–2014 represent the background levels, and the activities recorded between 2008 and 2010 are significantly elevated compared with these background levels, indicating uptake by the tree of <sup>14</sup>C discharged from the normal operation of the FDNPP. The mean excess <sup>14</sup>C activity for the period 2008–2010 before the accident at site 9 km northwest from the plant was 20.0 Bq kg<sup>-1</sup> C, which increased by two times in comparison to that at 24 km northwest site. This distance-dependent distribution revealed that the influence area of <sup>14</sup>C from the normal operation of the FDNPP were at least 24 km northwest from the plants. While, the mean excess <sup>14</sup>C activity in 2011 were 8.6 Bq kg<sup>-1</sup> C for the 9 km northwest site and 4.4 Bq kg<sup>-1</sup> C for the 24 km northwest site. There is a possibility that the tree rings grew at the two sites within 25 km of the FDNPP recorded the accidental <sup>14</sup>C release in 2011. Further investigation are needed to clarify the possibility.

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## 4B-04 <sup>14</sup>C activity in the atmosphere and biosphere around Nuclear Power Plants in the Central Europe

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Radiocarbon is responsible for dominant contribution to the collective effective dose from airborne releases of radionuclides from nuclear power plants (NPP) with light-water pressurized reactors (LWPR) during normal operation. Analyses of tree rings enables retrospective monitoring of this radionuclide in the surrounding of NPPs. Despite to limitation of records only during vegetation periods, it can provide relatively precise time series of <sup>14</sup>C activities. Likewise, seasonal period of annual wood ingrowth corresponds approximately with the period of growth of agricultural products, which are a dominant way human intake of <sup>14</sup>C. Hence, ingestion doses corresponding to <sup>14</sup>C effluents can be calculated/estimated using tree rings data. To calculate <sup>14</sup>C surplus around NPPs, there is necessary estimation/correction of local Suess effect caused by industrial and traffic emissions of fossil CO<sub>2</sub>. In our contribution, <sup>14</sup>C data from vicinity of Czech and Slovak NPPs will be compared and the methods of Suess effect correction will be discussed also. Likewise, a list of surrounding trees and other biomaterials most proper for sampling will be compiled.

## 4B-05 Characterization of PM2.5 in Beijing, China: A case study during the APEC period, 2014

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In order to meet the <sup>14</sup>C application requirement in the field of environment such as PM2.5 monitoring, a 200kV single stage electrostatic accelerator mass spectrometer has been completed at CIAE. Based on this device, we have analyzed the characteristics of radiocarbon in organic carbon and elemental carbon of atmosphere during the APEC period in Beijing, 2014. The results show that before, during and after meetings, the average value of fossil carbon fraction of OC is 0.64, 0.61 and 0.44, respectively, and EC is 0.44, 0.50 and 0.30. It can be seen that vehicle and industry activity contributes about 15.3%-20.2% to the fossil carbon fraction of PM2.5 after the APEC, 2014, in Beijing.



## 4B-06 Atmospheric Fossil Fuel CO<sub>2</sub> Traced by $\Delta^{14}\text{CO}_2$ and Air Quality Index Pollutant in Beijing and Xiamen

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**Abstract:** One year of atmospheric  $\Delta^{14}\text{CO}_2$  were observed in 2014 in the inland city of Beijing and coastal city of Xiamen, China, to trace temporal CO<sub>2</sub>ff variations and to determine the factors influencing them. Additionally, diurnal CO<sub>2</sub>ff variations were indirectly traced by Air Quality Index (AQI) pollutants (AQI, PM<sub>2.5</sub>, PM<sub>10</sub>, and CO), and then these indirectly traced CO<sub>2</sub>ff (CO<sub>2</sub>ff-in) concentrations were validated by simultaneous CO<sub>2</sub>ff-<sup>14</sup>C concentrations traced by  $\Delta^{14}\text{CO}_2$  observations. The average CO<sub>2</sub>ff-<sup>14</sup>C concentrations at the sampling sites in Beijing and Xiamen were 39.7±36.1 ppm and 13.6±12.3 ppm, respectively. These contributed 75.2±14.6% and 59.1±26.8% to their respective annual  $\Delta\text{CO}_2$  offsets over background CO<sub>2</sub> concentrations. Significantly ( $p < 0.05$ ) high CO<sub>2</sub>ff-<sup>14</sup>C values were observed in winter in Beijing. Diurnal CO<sub>2</sub>ff-<sup>14</sup>C variations were plainly evident, with high values between midnight and 4:00, and during morning and afternoon rush hours. The sampling site in the inland city of Beijing displayed much higher CO<sub>2</sub>ff-<sup>14</sup>C inputs and overall temporal variations than the site in the coastal city of Xiamen. The variations in CO<sub>2</sub>ff-<sup>14</sup>C at both sites were controlled by a combination of emission sources, topography, and atmospheric dispersion. In particular, diurnal observations at the urban site in Beijing showed that CO<sub>2</sub>ff-<sup>14</sup>C was easily accumulated under the southeast wind conditions. Diurnal variations in CO<sub>2</sub>ff-in generally showed similar trends to those of CO<sub>2</sub>ff-<sup>14</sup>C, with high agreement in Beijing and relatively poor agreement in Xiamen. AQI pollutant tracers showed high normalized root-mean-square (NRMS) errors for the summer diurnal samples due to low CO<sub>2</sub>ff-<sup>14</sup>C concentrations. After the removal of these summer samples, the NRMS errors for AQI pollutant tracers were in the range of 31.6%–64.2%. CO generally showed a high agreement and low NRMS errors among these indirect tracers.

## 4B-07 Fossil carbon load in urban vegetation at Debrecen city, Hungary

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Leaf samples of deciduous tree and grass are applicable to detect fossil carbon dioxide emission in the air during the vegetation period thanks to the plants collect the CO<sub>2</sub> from the air by the photosynthesis (Baydoun et al. 2015, Alessio et al. 2017, Park et al. 2013). In our study, 92 samples were collected at 39 sampling points in the downtown of the second largest city of Hungary, Debrecen. Grass samples were collected from the ground level and tree leaf samples from head height throughout the downtown. For the determination of fossil carbon ratio background samples were collected from the Great Forest, Debrecen, 4 km far from the downtown and 2 km far from the border of the city. The background environmental samples were also compared with atmospheric CO<sub>2</sub> measurements from a Hungarian regional background site, Hegyhátsál (Haszpra et al. 2005). According to the accelerator mass spectrometry measurements, there was detectable fossil CO<sub>2</sub> emission at almost every sampling site both in the grass and leaf samples. The average fossil carbon content in the tree leaf samples was approximately 1 %, but in the grass samples the mean fossil carbon ratio was a bit higher, more than 2 %. Close to busy crossroads the fossil carbon ratio can be more than 4 %. Our future plan is to compare the results of radiocarbon measurements with traffic related heavy metal contents in plant samples. Recent study shows that the traffic has a non-negligible contribution to the local CO<sub>2</sub> level and fossil ratio.

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## 4B-08 Radiocarbon level in the atmosphere of Ramnicu Valcea, Romania

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The paper presents C-14 variation in the atmosphere of Ramnicu-Valcea Romania. The samples were collected in the vicinity of the Experimental Pilot Plant for Tritium and Deuterium Separation (PESTD) from the Institute of the Cryogenics and Isotopic Technologies (ICSI) placed about 10 km south from the Ramnicu Valcea city (Romania), in the Govora industrial area. This facility is an experimental project in the national nuclear energy research program, which has the aim of developing technologies for tritium and deuterium separation. Until now, PESTD normal operation was with heavy water and tritiated water below exemption level approved by Romanian legislation. Foreseen experiments will be done with tritiated heavy water moderator [1] from Cernavoda NPP (two CANDU-6 reactors), known to contain about half of the C-14 production of a Heavy Water Reactor. Considering the fact that one of the important releases of PESTD is gaseous radioactive effluents, the baseline of atmospheric C-14 was a must for environmental program. It should be noted that in the Govora industrial area operates a 315 MW Coal-Fired Thermoelectric Power Plant and two chemical plants.

In order to determine radiocarbon activity in the atmosphere, samples were collected monthly by absorption of CO<sub>2</sub> into sodium hydroxide (NaOH) at Ramnicu Valcea. In addition, control materials (tree leaves and wild vegetation), known activity standards, and process blanks (marble) were analyzed. Radiocarbon measurements were performed using the direct absorption method. This consists in measuring <sup>14</sup>C contained in a known quantity of carbon, as carbon dioxide, obtained from a sample, standard and background material, counted in an ultra-low level liquid scintillation counter Quantulus 1220. <sup>14</sup>C results were normalized for deviation of the measured  $\delta^{13}\text{C}$ . The <sup>13</sup>C/<sup>12</sup>C ratio was measured by isotope ratio mass spectrometry on a Delta V IRMS on small aliquots of sodium carbonate resulted from absorption of CO<sub>2</sub> into sodium hydroxide.  $\delta^{13}\text{C}$ -corrected  $\Delta^{14}\text{C}$  data are given relative to NBS oxalic acid activity, corrected for decay [2].

The measured  $\Delta^{14}\text{C}$  levels varied between -129.36‰ and 173.33‰. The results have a clear decreasing trend, but due to local influence caused by continuously production of fossil CO<sub>2</sub> we cannot observe  $\Delta^{14}\text{C}$  seasonal variations.

### Acknowledgments

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## 4B-09 Atmospheric <sup>14</sup>CO<sub>2</sub> data sets from Dutch monitoring stations Smilde (1995 – 2003) and Lutjewad (2002 – present)

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Since 1974 the Centre for Isotope Research (CIO) of the University of Groningen measures atmospheric <sup>14</sup>CO<sub>2</sub> in the relatively remote areas in the northern part of the Netherlands. Between 1974 and 2003 CO<sub>2</sub> was extracted from a continuous flow of air from 80 meters above ground at broadcasting tower Smilde. The extracted CO<sub>2</sub> was collected and analyzed monthly. In 2001, measurements started at CIO monitoring station Lutjewad, where air is sampled from a meteorological tower at 60 meters above ground. At this location CO<sub>2</sub> extracted from air is sampled and analyzed monthly, both from a continuous air flow and an air flow that is switched on and off wind-direction specific to discriminate between air from more urban and remote areas (south-west direction – land and northern direction – coast/sea).

The first and main aim of this research is to monitor atmospheric <sup>14</sup>CO<sub>2</sub> over time and use these data for different atmospheric research topics. The data is, combined with datasets of other atmospheric tracers measured at Lutjewad, and datasets from other European monitoring stations, used to investigate seasonal <sup>14</sup>CO<sub>2</sub> differences (Meijer et al., 1995) and regionally added fossil CO<sub>2</sub> fractions in the atmosphere (Palstra et al., 2008; van der Laan et al. 2010). Over the last fifteen years, the atmospheric <sup>14</sup>CO<sub>2</sub> data sets of Smilde and Lutjewad have also been used for biogenic/fossil carbon determination in bio-based products (Palstra and Meijer, 2014) and for forensic research. The data series therefore demonstrate their value for different research topics and are of interest for a broad scientific user group.

Almost 25 years have passed since the last publication of <sup>14</sup>CO<sub>2</sub> data from Smilde (1974 – 1994; Meijer et al., 1995). At the conference, the Smilde (1995 -2003) and Lutjewad (2002-present, ongoing) datasets will be presented and temporal variability will be discussed.

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## 5A-01 Annual <sup>14</sup>C dating of floating dendrochronological sequences.

### Implication for the interhemispheric offset during the Younger Dryas event

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Tree rings are an important archive for the calibration of radiocarbon data. The younger part of the IntCal curve is based essentially on tree-ring chronologies, absolutely dated by dendrochronological analysis. For the Northern Hemisphere (NH), the absolute curve is starting at 12324 cal BP. During the Younger Dryas period, only a few floating dendrochronological sequences exist, essentially from Switzerland (Kaiser et al. 2012, *Quat. Sci. Rev.*; Reinig et al. 2018, *Quat. Sci. Rev.*) and France (Miramont et al. 2011, *Quaternaire*).

We present here <sup>14</sup>C results from French subfossil trees (*Pinus sylvestris* L.) dated to the Younger Dryas. A floating dendrochronological sequence was built from nine trees from Barbiers River site. Results from two dendro-matched trees (Barb12-17) were already reported in Capano et al. (2018, *Radiocarbon*). Here we analyze new <sup>14</sup>C data from two other dendro-matched trees (Barb13-14), extending the Barbiers record over the 312-year period of the chronology. Moreover, we analyzed the <sup>14</sup>C content of tree Barb15, which is not yet synchronized with the Barbiers dendrochronological sequence.

All trees were sampled at annual resolution. So far, every third ring was pretreated for <sup>14</sup>C analysis by using an ABA-B method before combustion and graphitization with the AGE system and measurement with AixMICADAS (Capano et al. 2018, *Radiocarbon*). In order to date our sequence against the Kauri record from New Zealand (Hogg et al. 2016, *Radiocarbon*), the Barbiers data were averaged at the same decadal resolution as the Kauri record. All averaging options were statistically compared with the Kauri sequence, leading to date Barbiers sequence between a start at 12902±10 and an end at 12594±10 cal BP. Assuming the existence of a solar event (producing a rise of 17‰ Δ<sup>14</sup>C in 12 years with a very rapid decrease) around 12680 cal BP, we tentatively refine the dating of the Barbiers sequence between ca. 12911 and 12603 cal BP.

The <sup>14</sup>C sequence of Barb15 tree was compared with Barbiers sequences. The annual <sup>14</sup>C measurements allowed its precise dating and it helped in finding the dendrochronological synchronization with other trees.

Our new record allows estimating the Inter-Hemispheric <sup>14</sup>C gradient (IHG) over the overlapping period with the southern hemisphere Kauri sequence (Hogg et al. 2016, *Radiocarbon*). Depending on the dating option, the mean IHG varies (from ~26 to ~55 years), while a collapse is identified around 12850±10 - 12840±10 cal BP, which corresponds approximately to the beginning of the Younger Dryas event.

## 5A-02 Abrupt increase of radiocarbon concentration around 660 BC in tree rings from Grabie near Cracow (SE Poland)

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Radiocarbon production events are attracting attention, because not only the underlying production mechanism is not fully understood yet and we might gain additional insight on how the earth and solar system changed in the past, but also because they can be used as high-precision anchor-points for chronologies.

Production events were reported by Miyake et al. (2012, 2013 and 2014), after detecting a sudden increase-almost within a single year-of about 11‰-12‰ in radiocarbon (<sup>14</sup>C) concentration in annual tree rings of Japanese cedar (*Cryptomeria japonica*) and Hinoki cypress (*Chamaecyparis obtusa*) between AD 774 and 775 and between AD 993 and 994. A similar increase was recently observed in whole wood of single year samples from German oak from 670 to 650 BC, with a peak height of about 10‰ (Park et al. 2017) and a rise time of 3-4 years.

In this paper, we report <sup>14</sup>C contents of  $\alpha$ -cellulose extracted from single-year samples of dendro-chronologically dated tree rings of deciduous oak (*Quercus robur*) from Grabie, a village near Krakow (SE Poland), spanning the years 670 to 650 BC. The results clearly show a rapid increase of more than 12‰ (94% probability) in the <sup>14</sup>C concentration in tree rings between 665 and 660 BC even more pronounced than observed by Park et al (2017). The difference between the two records is likely caused by the use of  $\alpha$ -cellulose versus ABA treated wood.

## 5A-04 $\Delta^{14}\text{C}$ peak in early and late tree-wood of AD 775 from Zelkova in Korea

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The AD 775  $\Delta^{14}\text{C}$  peak (henceforth M12) has been measured and confirmed globally since Miyake et al.[1] first measured annually, but data of M12 measured in early and late wood are very rare and the locations which data are obtained from are limited. If M12's data measured in early and late wood are enough globally, it would help to understand M12's timing and cause. For example if M12's cause is Solar Particle Event (SPE), the lower sampling latitude is, the later appearing time of M12 is. Here we present  $\Delta^{14}\text{C}$  values in early and late wood from AD764 and AD784 tree-rings of Zelkova (*Zelkova* spp.) samples from Bangu-dong Ulsan, Korea (N35° 33' E129° 20'). Measured samples are treated by alpha cellulose extraction method, then burned by elemental analyzer (EA), then reduced and measured in KIGAM, Korea. These data once again confirm that  $\Delta^{14}\text{C}$  rose in AD 775 and show the detail time variation of  $\Delta^{14}\text{C}$ .

[1] Miyake F, Nagaya K, Masuda K, Nakamura T. 2012. A signature of cosmic-ray increase in AD 774–775 from tree rings in Japan. *Nature* 486:240-242.

## 5A-05 <sup>14</sup>C in high-latitude tree rings around 1054 AD

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In recent years several annual-resolution <sup>14</sup>C measurement series have highlighted short term variations in the atmospheric <sup>14</sup>C content due to sudden changes in its production rate. These events have been ascribed to Solar Proton Events, even if other extra-terrestrial effects, such as Gamma-ray Bursts or Supernova explosions, cannot at present be ruled out. In the investigation of the actual origin of these events, an important piece of information may be derived from the eventual dependence of the position, size and shape of the calibration curve perturbation upon the latitude of the sampled tree.

In the present contribution we present measurements performed on rings from pinewood preserved as subfossil tree trunk in the sediment of Lake Kompsiojärvi and unearthed during the fieldwork by sub-aqua diving. This subarctic site is located in north-eastern Finnish Lapland (68.51°N and 28.15 °E) at the altitude of 191 m above sea level. The tree trunk was pulled to the shore, the sample disk was sawn and the trunk was returned to the lake. Tree-ring widths were measured in the laboratory to the nearest 0.01 mm and the resulting series was cross-dated statistically and visually against the existing master chronology. The rings of this sample represent the AD 996 - 1236 period, covering the timing of the Crab nebula supernova exploded in AD 1054 at about 2 kpc from the earth.

The boundaries of cross-dated rings provided the framework for wooden samples to be extracted with their exact calendar year positions. The particular sampling of the rings AD 1031 through 1080 was done using surgical blades under the light microscope. In tree-ring laboratory, all the work to extract the isotope samples was done on cleaned sample surfaces only to minimize any potential external contamination. Over this interval, the ring widths were on average 0.37 mm, with maximum and minimum widths of 0.71 and 0.10 mm, respectively. The wood slivers were processed to  $\alpha$ -cellulose using the batch-approach described by Wieloch et al. (2011) . The resulting  $\alpha$ -cellulose was then homogenized using an ultrasonic probe and freeze-dried.

$\Delta^{14}\text{C}$  and  $\delta^{13}\text{C}$  measurement results will be presented and compared with the values previously measured for the same time interval on a larch sample from northern Italy.

## 5A-06 The 1859 Carrington Event: is there a radiocarbon signature in South American trees?

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The Carrington Event of 1859 was a major solar disturbance that involved a very large solar flare and at least one (probably two) Coronal Mass Ejection events. This solar disturbance induced dramatic auroral phenomena and geomagnetic effects in both hemispheres on Earth. Energetic solar protons from similar but larger solar events are now thought to be the most likely cause of very sharp (1-2) year increases in  $\Delta^{14}\text{C}$  in tree ring archives. These were first noted by Miyake et al. (2012) in Japanese cedar from 774-775 AD and have since been confirmed from numerous other Northern Hemisphere locations, as well as in New Zealand (Guttler et al., 2015). Miyake et al. (2013) showed that no such increase was present in published single-year Northern Hemisphere tree ring  $\Delta^{14}\text{C}$  from 1859, indicating that the flux of solar protons from that event was significantly weaker and/or softer (lower energy) than that associated with the 774-775 AD spike, but no equivalent single-year Southern Hemisphere records have as yet been examined. Here we present single-ring radiocarbon data for the 1850's and 1860's from locations in Chile ranging from 20 to 53° S, using four tree species whose bomb radiocarbon profiles (de Pol-Holz et al., 2017) show that the dendrochronologically cross-dated rings are annually produced.

Guttler et al., 2015. Rapid increase in cosmogenic  $^{14}\text{C}$  in AD 775 measured in New Zealand kauri trees indicates short-lived increase in  $^{14}\text{C}$  production spanning both hemispheres. *Earth and Planetary Science Letters* 411:290–297

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De Pol-Holz et al. 2017 Tree-ring radiocarbon data from Chile. ICT Workshop - IntCal and Dendrochronology Workshop in the 14th International Conference on Accelerator Mass Spectrometry meeting, Ottawa, Canada, August 14-18 (Abstract ID : 351 – Oral).

## 5A-07 Radiocarbon calibration around 1900 AD and a Scots pine tree (*Pinus Sylvestris* L.) from Northern Norway

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The IntCal calibration curve (Reimer et al. 2013) provides a synthesis of atmospheric  $^{14}\text{C}$  concentrations, which in the Northern Hemisphere is derived from several trees from the US Pacific coast and from Europe. A generally close agreement exists between the different data sets, mostly from trees at mid-latitudes. Yet, around 1870 to 1900 AD there are some differences, which could increase the uncertainty in the calibration curve and influence estimates of local marine reservoir age ( $\Delta R$ ) based on marine samples collected during this period.

Here, we present  $^{14}\text{C}$  measurements on selected tree-rings of a Scots pine tree (*Pinus sylvestris* L.) from Saltdal, northern Norway, for the period AD 1864-1937. This tree grew in a remote location near the Norwegian Sea, with presumably very little influence from local fossil fuel effects. The results, compared to those of wood from the British Isles and from the Pacific Coast of Washington and Alaska, show an agreement with the results from North America.



## 5A-08 AMS radiocarbon dating of very large African baobab trees from Savé Valley, Zimbabwe

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The Savé Valley Conservancy is a large wildlife area (3442 km<sup>2</sup>), located in the semi-arid South East Lowveld of Zimbabwe. The Conservancy hosts thousands of African baobabs, out of which 4 specimens all located to the north of Turgwe river, have very large dimensions (circumference over 23 m) and ages older than 1000 years.

Several tiny wood samples were collected from the inner cavities and/or from different areas of the trunk of the 4 baobabs. The samples were investigated by AMS radiocarbon dating for determining the architecture and the age of the oldest part of the baobab specimens.

Somewhat surprisingly, the two oldest baobabs are basically unknown in the literature and are not included in the registers of the Tree Society of Zimbabwe.

In 2011, a very old baobab was discovered in the Bedford Block of the Humani Ranch. The Humani Bedford baobab (circumference 23.65 m; wood volume 240 m<sup>3</sup>) has a closed ring-shaped structure, which consists of three fused stems that close partially a false cavity. A fourth stem toppled more than one century ago, thus opening the false cavity. The oldest dated sample has a radiocarbon date of 1655 ± 14 BP, which corresponds to a calibrated age of 1575 ± 30 yr. According to this value, the Humani Bedford baobab is around 1800 years old and becomes the oldest living African baobab and angiosperm.

The second oldest baobab of Savé Valley is located in the Matendere Ranch. The Matendere Big baobab (26.30 m; 300 m<sup>3</sup>) has a closed ring-shaped structure, with 5 stems that incorporate a false cavity. The false cavity has only a very tall opening, at a height over 6 m. The oldest sample has a radiocarbon date of 1529 ± 14 BP, which corresponds to a calibrated age of 1430 ± 45 yr. This value suggests an age of 1600 years for the Matendere baobab.

The two biggest and best known baobabs of Savé Valley are located in the Mokore and Chishakwe Ranches. According to our investigation, the Mokore Giant baobab (28.11 m; 320 m<sup>3</sup>) possesses 7 stems of different sizes and ages and a large false stem which acts as a structural support/anchor. It has a closed ring-shaped structure, with a ring composed of 4 stems that close a false cavity. The cavity has an opening at the height of 5 m.

The Chishakwe baobab (26.56 m; 375 m<sup>3</sup>) consists of 7 fused stems. It has a closed ring-shaped structure, with a ring composed of 5 or 6 stems that close completely a false cavity inside. The cavity has only a tall opening at the height of 7-8 m.

The two biggest baobabs of Savé Valley are younger, having ages of only 1100–1200 years. These values confirm that the largest baobabs are not necessarily the oldest.

The AMS radiocarbon investigations were performed at the NOSAMS Facility of the Woods Hole Oceanographic Institution.

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## 5A-09 Absolute dendrochronological scale for pine tree from Ujście (north-west Poland) based on radiocarbon dating to a single year using rapid atmospheric <sup>14</sup>C changes

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Miyake et al. (2012, 2013 and 2014) described a sudden increase of radiocarbon (<sup>14</sup>C) concentration in annual tree rings of Japanese cedar (*Cryptomeria japonica*) and Hinoki cypress (*Chamaecyparis obtusa*) between AD 774 and 775 and between AD 993 and 994. In both analysed periods, the sudden increase was observed almost in a single year. The increase in the <sup>14</sup>C content was about 12‰ in the period AD 774-775 (Miyake et al. 2012) and about 11.3‰ in the period AD 993-994 (Miyake et al. 2013, 2014). Jull et al. (2014) confirmed the occurrence of the Miyake's effect in two series of timber samples from USA and Russia. Samples of long-lived pine (*Pinus longaeva*) from west coast of the USA along with Siberian larch (*Larix siberica*) have been dendrochronological dated and then radiocarbon concentration in  $\alpha$ -cellulose extracted from each annual ring was determinate using AMS system.

Due to the characteristic of the sharp increase in radiocarbon concentration that occurs in this phenomenon, and due to the global character of this effect, it is possible to use it for accurate dating of annual tree rings, using radiocarbon method. In practice, linking the relative dendrochronological dating and radiocarbon analysis of annual growth rings is possible to use "Wiggle matching" technique to precise determination of the calendar age of samples of pine, from the floating pine chronology (2U\_02A) for central Poland. Absolute dating chronology 2U\_02A covering 227 year, determined on the basis of 50 individual sequences is of great importance for archaeology of the early Middle Ages. This is particularly important for polish history, as during the period covered by this chronology, evolutionary changes occurred, such us the transition from tribal organization to the state organization and the emergence of a series of fortified towns, which dendrochronology dating without pine standard is difficult. So far, summarized standard curves for pine in Poland date back from the present to 1106 AD for Gdańsk Pomerania (Zielski 1997) and 1091 AD for Lesser Poland (Szychowska-Krąpiec 2010) and does not include the Xth century AD.

## 5A-10 Radiocarbon dating of single year tree-rings dendrochronologically ordered within an 800 years sequence

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At RoAMS laboratory in Bucharest we put face-to-face the dating results obtained by two different methods on the same set of samples of single tree-rings in a cross-dating exercise. The radiocarbon ages correlated by wiggle matching technique were compared with dendrochronology ages and the observed mismatches were interpreted. The analysed samples were stemming from several wood cores of "pinus cembra" collected from the area of Northern Romania in Moldova region. Following the alfa-cellulose extraction via BABAB (base-acid-base-acid-bleaching) method, the graphitized samples were measured on our 1 MV Tandetron AMS system. The cross dating showed a good agreement on 3 out of 5 wood logs. Whilst one of wood cores (#2) came from the dendrochronology laboratory with a label of time frame uncertainty, the wood core #57 came with a solid time frame. In the end both were corrected, the wood core #2 with more than 600 yr., and for the wood core #57 the consensus dendrochronology ages were established with an offset of - 48 yr. The correlation with the IntCal13 is very good on most of the measured sections, even though, the peaks of the calibration curve (<sup>14</sup>C concentration decrease) might be of a higher amplitude for the regions 1380 AD and 1600 AD.

## 5A-11 First Radiocarbon Intercomparison on Annual Tree-ring samples

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It is today possible to re-measure the radiocarbon calibration curve (IntCal) in higher temporal resolution with accelerator mass spectrometry. Annual tree-ring samples covering several hundred years have already been measured in high precision by multiple laboratories, but are yet waiting to be integrated into the calibration curve. However, a thorough test on how well the individual laboratories compare is still missing. As many of the dated trees were growing in different parts of the world, regional offsets are often suggested where different datasets disagree. However, in most cases it cannot be ruled out that the observed offsets are actually caused by the sample preparation, by the measurement technique applied, or by methods of data reduction.

The first test presented here aims to shed some light on how well high precision radiocarbon analyses on annual tree-rings from different laboratories compare. In this exercise, so far limited to 15 laboratories, 3 sets of 21 consecutive tree-ring samples from different periods of time (c. 180 BP, c. 1700 BP and c. 7600 BP) were analysed, resulting in about 1000 individual radiocarbon measurements. We will present a statistical evaluation of how well the laboratories compare, and how precisely and accurately they can perform high precision radiocarbon measurements using AMS.

## 5A-12 Search for the potential <sup>14</sup>C excursions in the available radiocarbon calibration curve data

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It has been supported by numerous works following Miyake discovery, that there were some rapid changes in <sup>14</sup>C concentration in the atmospheric carbon dioxide. Although the origins of these changes are not well recognized, they are of the radiocarbon community attention because of the potential use in precise radiocarbon dating. Previously published results of researches suggest that the changes have been observed for periods no longer than couples of years with the amplitude of several per mils and rise time of a year or less. We made a survey of available data used to build IntCal'13 radiocarbon calibration curve. Datasets which are potentially suitable for the investigations of rapid <sup>14</sup>C were selected. For some periods of time we tried searching for potential atmospheric <sup>14</sup>C concentration excursions. We will present the results of our investigations.

## 5A-13 Comparison of maple leaf and tree ring radiocarbon signatures near Ottawa, Canada

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Here we compare the  $\Delta^{14}\text{C}$  of leaves and tree rings from maple trees collected in Gatineau Park (Quebec, Canada) for the purpose of better understanding how the atmospheric radiocarbon signature is recorded in these natural archives. The motivations for this project are twofold: (1) to determine if tree rings will record short term (annual) fluctuations in atmospheric  $\Delta^{14}\text{C}$  content such as may be produced near a nuclear generating station; and (2) to better understand why the maple leaves in Gatineau Park record a 10-40‰ enrichment in  $\Delta^{14}\text{C}$  compared to global archives of Hua et al. (2013). The  $\Delta^{14}\text{C}$  of maple leaves from the years 1999-2005 (collected by the Geological Survey of Canada) was analyzed along with the  $\Delta^{14}\text{C}$  of -cellulose extracted from annual (whole) tree rings from a maple tree at a nearby location within the park. This time period was chosen to determine if a  $\Delta^{14}\text{C}$  spike of nearly 50‰ in the maple leaf record in 2002 could also be resolved in the tree ring record. Preliminary results show that, although the maple leaf record is much more sensitive to the 2002 “event” (unknown source), the tree ring  $\Delta^{14}\text{C}$  for the years 2002 and 2003 is stagnant instead of decreasing with the trend for that time period.

## 5B-01 Variation of the 11-year solar cycle before the onset of the Spoerer minimum

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Prolonged solar activity minima are known to occur every a few hundred years. During the past 1000 years, several grand minima have occurred such as the Dalton minimum (AD 1790-1830), the Maunder minimum (AD 1645-1715), the Spoerer minimum (AD 1416-1534), and the Wolff minimum (AD 1280-1350). Such a decrease in solar activity is one of the most important issues in solar physics, and the mechanisms have been studied both observationally and theoretically. In the previous study, it was shown that the length of the 11-year solar cycles during the Maunder minimum was about 14 years; a few years longer than 11 years. This variation of the solar activity cycle might be related to a decrease in solar activity level. Similar tendency was found also for the Spoerer minimum. It was also suggested that solar cycle had started to be lengthened one or two cycles before the onset of the Maunder minimum and the Spoerer minimum. In this study, we conduct high-precision measurement of carbon 14 ( $^{14}\text{C}$ ) content in annual tree-rings around the onset of the Spoerer minimum and discuss the variation of the solar cycle lengths in detail.

$^{14}\text{C}$  is produced by galactic cosmic rays (GCRs) in the atmosphere, which are modulated by interplanetary magnetic fields that varies with solar activity. The variation of the flux of GCRs is about 20 to 30% at the decadal time scale. The variation of  $^{14}\text{C}$  produced by GCRs is strongly attenuated in the carbon cycle and becomes only 2 to 3 ‰. Thus, it is required to measure  $^{14}\text{C}$  with uncertainties less than 2‰ to reconstruct the 11-year cycles.

We used the compact AMS system installed at Yamagata University (YU) to achieve the high-precision measurements. The compact AMS system was installed at the Kaminoyama Research Institute of Yamagata University in 2009. The system (1.5 SDH-1) is based on a 0.5 MV Pelletron accelerator developed by National Electrostatics Corporation (NEC). Using an asunaro tree (*Thujaopsis dolabrata*), we have measured  $^{14}\text{C}$  content for the period AD 1359-1421. In this paper, we will report the results on the variation of 11-year solar cycle before the onset of the Spoerer minimum.

## 5B-02 Radiocarbon Signal from Past Radiation Events with Respect to the Schwabe Cycle

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This study investigates the timing of the Carrington Event (solar storm of 1859CE), and other past radiation events of probable solar origin, with respect to the Schwabe cycle. On the ECHOES project, we performed very high-precision measurements over series of annual tree-rings spanning the years of these events, using an AMS-MICADAS. If all such events occurred around the solar maximum, it would be a strong indication that they were all triggered by solar activity. As radiocarbon is produced in the Earth's atmosphere by means of nuclear reactions during the cosmic ray cascade; its production is directly proportional to the incoming cosmic ray flux, which is modulated by the interplanetary magnetic field according to the Schwabe (11-year) cycle. Indeed, the Schwabe cycle and radiocarbon production on Earth are inversely related, because when the sun increases its activity, the modulation of cosmic rays by the solar plasma in the interplanetary magnetic field is enhanced and therefore a decrease in radiocarbon production on Earth occurs. Evidence of the 11-year solar cycle is observable when performing high precision AMS measurements over the radiocarbon content in tree-rings. The well-known solar storm of September 1859CE (Carrington Event) took place in proximity to the maximum activity of Solar Cycle no. 10 (March 1860CE), according to the record of Smoothed Sunspot Number. Here, we investigate whether modulation due to the Schwabe cycle is detectable in the radiocarbon content of the samples. Secondly, we examine how the data relate to the solar cycle, as expressed by the sunspot number record, which also allows us to make an estimate of the residence time of radiocarbon in the atmosphere. Finally, we are also performing the same study over the 775CE and the 994CE (Miyake) events, in order to establish if they both also took place at approximately the same point on the solar cycle. In fact, if they did occur near the time of maximum activity, it would bolster the hypothesis that both events were of solar origin.

## 5B-03 A better understanding of solar magnetic activity through annual radiocarbon measurements in tree rings

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Changes in radiocarbon in terrestrial archives partly reflect changes in the solar magnetic activity, as variations in the Sun's magnetic field modulate the shielding of Earth from cosmic rays. By analyzing annual radiocarbon measurements in tree rings from three pieces of oak from Jutland, Denmark, covering the Spörer Grand Solar Minimum from 1450 to 1550 AD we aim to unravel rapid changes in solar activity across this time period. We compare the new high-resolution <sup>14</sup>C record with existing <sup>14</sup>C records, including the IntCal13 data, and we identify cyclicities associated with changes in solar activity. We demonstrate how the nature of the short ~11-year solar cycle, known as the Schwabe cycle, changed during the Spörer Minimum, i.e. a long-term period of reduced solar magnetic activity.

Annual radiocarbon measurements furthermore allow the identification and study of cosmic-ray events, so-called Miyake Events, which are thought to have a solar origin. These events are characterized by rapid increases in radiocarbon over 1-2 years. We have measured the radiocarbon fraction annually and for some years sub-annually, in two pieces of Danish oak covering the two Miyake Events in 775 AD and 994 AD, and here we show our results and compare them to the other published records.

## 5B-04 Identification of Possible Miyake Events using COSFIRE Filters

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Several sudden rises in  $\Delta^{14}\text{C}$  have been identified by single-year measurements on known-age tree-rings. These include rises in the years 774–775 CE; 993–994 CE; and 3372–3371 BCE as well as a slightly slower uplift around 660 BCE. On the ECHOES project, we are using COSFIRE filters for the specific task of identifying similar events in the past. We first took the single-year radiocarbon measurements that are publicly available around the first Miyake Event (774–775 CE) and used them as a training signal. Then, we tested our method by finding (validating) the 993–994 CE event. We used as ground-truth the second Miyake Event (993–994 CE) as well as the other two events (3372–3371 and 660 BCE) to compute the results across the whole of the IntCal13 dendrochronological record. We measured the false positive rate at the identification of every event, and we cross-validated our results by using different events for training and validation. Several specific years have been tentatively proposed for other Miyake Events, including 10720, 5480, 1835, 1750, 1588, 1220 and 400 BCE. We examined whether these years were also favoured by our method. Our findings so far suggest that computational methods, and specifically COSFIRE filters, are suitable for the identification and prediction of signals similar to Miyake Events.

## 5B-05 Cumulative probability distributions – what can they tell us?

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Radiocarbon dating is among one the most used methods for absolute chronologies in archaeological sciences. The quantity of radiocarbon dates from archaeological contexts is enormous and as a result it may seem as an obvious opportunity to use cumulative probability density functions (cPDF) as a measure of archaeological activity. However, the interpretations of cPDF are not straightforward and consequently may provide misleading interpretations. Here artificial datasets are generated and evaluated using cPDF's with aim of generating significant activity PDF's. The overall aim is to investigate human activities of Bronze Age houses.

## 5B-06 Comparing records to understand past rapid climate change: An intimate database update and its application to the preboreal oscillation(s)

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Among the most pressing questions in palaeo-environmental research today is the reliable identification of synchronies or asynchronies of past climatic and environmental changes across the globe. A fundamental problem in identifying such temporal relationships in palaeo-records, however, is our current inability to reliably compare inter-regional records beyond the limits of chronological uncertainty.

This issue lies at the heart of the research being undertaken by the INTIMATE network ('INTEgrating Ice-core, MARine and TERrestrial records, 60-8 ka'; <http://intimate.nbi.ku.dk>). Here, we present the current status of the INTIMATE (working group 1) database (<https://c14.arch.ox.ac.uk/intimate/db.php>), demonstrating its utility through application to the early Holocene Preboreal Oscillation(s) across a northwestern to southeastern European transect.



## 5B-07 Atmospheric radiocarbon reconstruction on speleothems from Northern Turkey and Puerto Rico

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Since the first comprehensive radiocarbon data set of U-series dated stalagmites were included to IntCal13 [1], speleothems have been moved into the spotlight of efforts to expand the atmospheric radiocarbon calibration curve. Stalagmites are favourable for these efforts due to the undisturbed conditions during their deposition in caves: shielded from erosion, weathering or direct organic influences. Understanding radiocarbon in speleothems requires profound knowledge of the variability of the reservoir effect mainly derived from very old host rock carbonates. For speleothems, this reservoir effect is often expressed as dead carbon fraction (dcf), which can vary from a few to more than 50 percent. Assessing the reservoir effect of a stalagmite is achieved by coupled U-series and radiocarbon dating in the speleothem growth period corresponding to the tree ring based part of the calibration curve. Subsequently, to infer atmospheric radiocarbon from speleothems beyond that time span a constant reservoir age is commonly presumed and extrapolated to the older parts of the respective stalagmite.

This study presents two high-precision U-series dated speleothem records with novel AMS radiocarbon data from Sofular Cave (Turkey) and Larga Cave (Puerto Rico) revealing stalagmite growth from 50 to 15 kyr BP (Larga) and 50 to 0 kyr BP (Sofular). For stalagmite So-1 (Sofular) the reservoir effect in the tree ring based part of IntCal13 varies between 1000 and 1900yr (12 to 21 percent dcf) with significant dependence on the preliminary age model resolution. In older parts, we observe distinct increases in reservoir age closely linked to significant peaks in precipitation proxies (Mg/Ca, Sr/Ca). This connection potentially allows for corrections of reservoir effect variations in older time periods of stalagmite records enabling new possibilities for radiocarbon calibration efforts.

In PR-LA1 (Larga), first measurements have revealed a relatively constant reservoir effect between 17 and 22 percent dcf in the time period from 25 to 17 kyr BP.

We will present the state of the art of high-precision U-series and radiocarbon measurements on two stalagmites potentially able to contribute to future atmospheric radiocarbon calibration data sets.

[1] P. J. Reimer et al., "IntCal13 and Marine13 Radiocarbon Age Calibration Curves 0–50,000 Years cal BP," *Radiocarbon*, vol. 55, no. 4, pp. 1869–1887, 2013.



## 5B-08 Late Glacial atmospheric radiocarbon variations recorded in scots pine (*Pinus Sylvestris* L.) wood from Kwiatków, Central Poland

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Our project aimed to construct Scots Pine (*Pinus sylvestris* L.) chronology for the part of the Late Glacial and reconstruct changes in the <sup>14</sup>C concentrations during this period. Kwiatków (Kolska Basin, Central Poland) proved to be very prospective site, in which wood from the end of Allerød was recognized. A level of organic deposits with so-called 'fossil forest' was encountered within the late-Vistulian terrace of the low valley of the Warta river.

Dendrochronological analysis allowed to construct the average curve, produced from the 46 tree-ring sequences best correlating mutually, which spanned 265 years.

Two trunks which did not contain extremely narrow annual increments, were selected for the radiocarbon analysis. 52 samples (5 consecutive rings each) were subjected to alpha-cellulose extraction. The chemical tests included 3 methods of  $\alpha$ -cellulose preparation, 2 methods of holo-cellulose preparation, FTIR spectroscopy,  $\delta^{13}\text{C}$  measurements and inter-laboratory comparisons.

The alpha-cellulose extraction was preceded by the mercerization step and the standard ABA treatment. Then, in the bleaching process (with  $\text{NaClO}_2 + \text{HCl}$ ), the production of holo-cellulose followed. Finally, strong sodium bases (10% and 17%) and weak (1%) hydrochloric acid were used.

In order to avoid the influence of possible inter-laboratory shifts, the chemical preparation and graphitization of samples was carried out in one laboratory, the Gliwice Radiocarbon Laboratory. AMS measurements were performed in AMS Laboratory in Poznań, which is equipped with two 1.5 SDH-Pelletron Model "Compact Carbon AMS".

96 results and the wiggle-matching technique anchors the chronology to the period 13821-13561 ( $\pm 8$ ) cal BP (Acomb = 141.6%) according to D\_Sequence procedure and IntCal13 calibration curve.

Independently, the Kwiatków floating chronology was anchored to the raw data (the Heidelberg tree-ring sequence) using the classical wiggle-matching method based on the chi-square test. This approach resulted in anchoring the sequence to years 13800-13540 cal BP. Although the chi-square function has a minimum for 13540 cal BP, the similar test values occur for a range of about 20 years. In fact, there are two minima—one global, anchoring the Kwiatków sequence about 20 years younger than according to D\_Sequence (13540 cal BP), and the other local one giving anchorage closer to D\_Sequence (13554 cal BP).

The length of the plateau in the minimum (20 years) can be a measure of the uncertainty of the anchorage. The values of the test function in the minimum (370.7 and 376.2) indicate that both sequences are not fully compatible with each other. The expected value in the case of full compliance is 257, and the critical value at the confidence level of 5% is 295. Differences between the sequences Kwiatków and Heidelberg are revealed for two periods - about 13580-13600 cal BP and 13680-13700 cal BP. Small wiggles of both sequences are very similar for the rest part of the time period.

## 5B-09 Radiocarbon measurement of remained wood members of Byodo-in Temple: from 10c to 12c CE.

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Radiocarbon measurement of Japanese tree-ring is ongoing to evaluate the possibility of regional effects in atmospheric <sup>14</sup>C concentration around the Japanese archipelago as well as its fine structures such as <sup>14</sup>C spike of 775 CE. Two remained wood members were provided at Byodo-in Temple Amida-do, one of the sites on the UNESCO World Heritage (Historic Monuments of Ancient Kyoto). One was a Japanese cypress and its tree-ring age was determined by dendrochronology, while the other was a Japanese umbrella pine and oxygen-isotope dendrochronology was applied. Bleached butt end was cut into 5-year each, and graphitization and AMS-<sup>14</sup>C measurement were conducted by Institute of Accelerator Analysis, Japan. Some of the samples were also measured by Paleo Labo Inc., Japan for comparison. Although small offset can be found in the latter half of 10c, the significant offset did not appear in 11c and 12c CE. In this presentation, our previous results will be also shown for comparison.

## 5B-10 Learning from the dendro-dated wood samples in TIRI, FIRI, VIRI and SIRI.

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Each of the laboratory inter-comparisons (from TIRI onwards) has included dendro –dated wood samples, highlighted in the table below. In the early years, as a result of the majority of laboratories being radiometric, these samples were typically blocks of 20 rings, but more recently (SIRI), they have been single ring samples. The sample ages have varied from 300 BC through to 3200 BC and beyond. A few samples that have been previously measured have also been included, in addition to some background or close to background wood samples. In some inter-comparisons, we have examined different pre-treatment effects on the results. In the reporting of the results, however, the focus has always been on the 14-C age, not on the calibrated age. With up to 60 laboratories having measured each samples, in this paper, we examine the variability in the calibrated results and the expression of the consensus calibrated age for the dendro-dated samples. Further, we explore deviations from the dendro age and examine evidence for laboratory offsets. In this way, we explore how the results gathered over these extensive inter-comparisons can contribute to the global IntCal effort.

Study Code Type Pre-treatment Consensus age (BP)

TIRI	Sample B	Belfast pine	None	4503 ± 6
	Sample J	Buiston Crannog wood	None	1605 ± 8
FIRI	Sample D	Belfast wood	None	4508 ± 3
	Sample F	Belfast wood	None	4508 ± 3
	Sample H	German wood	None	2232 ± 5
	Sample I	Belfast cellulose	Cellulose	4485 ± 5
VIRI	Sample L	Wood	None	2234 ± 17
	Sample M	Wood	None	2430±16
	Sample N	Wood	None	2437±17
	Sample O	Cellulose	Cellulose	125±16
SIRI	Sample E	Wood	None	10843 ± 6
	Sample F	Wood (Belfast)	None	363 ± 3
	Sample G	Wood (Belfast)	None	377 ± 5
	Sample H	Wood (Belfast)	None	386 ± 3
	Sample I	Wood (Arizona)	None	9995 ± 5

## 5B-11 The best available time resolution of the radiocarbon dating method: verification of the steep parts of a calibration curve

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With high-precision AMS measurements, we can nowadays determine <sup>14</sup>C activity with uncertainties about 15 years of conventional radiocarbon age in samples several thousand year old. Unfortunately, due to fluctuations in the radiocarbon calibration curve, the resulting time intervals vary from decades up to centuries of calibrated age.

In the point of view of the time scale of several decades, parts of the radiocarbon calibration curve (reported in the years of conventional radiocarbon age) can be differentiated into four main types: i) relatively monotonous parts of the curve, with resulting one main time interval; ii) fluctuating parts of the curve, with several resulting time intervals (which can be quite distant) with similar probabilities, e.g. 1640 – 1950 AD, which is rather difficult for radiocarbon dating; iii) plateaus in the curve where refining of a radiocarbon measurement uncertainty is not reflected in a narrower time interval, thus, corresponding approximately to a width of the plateau; iv) relatively steep parts of the curve which enable us to get firm and very narrow time intervals. These steep parts are often seen close to the edges of a plateau. Thus, under favourable circumstances for radiocarbon dating, it is possible to reach the time interval even about 20 years of calibrated age (corresponding to the 2 sigma range of analyse uncertainty). The steep parts of the curve could then be possibly used as a “time magnifier” or an exact “time marker”.

Nevertheless, time periods which correspond to the steep parts of the curve have relatively short duration. Hence, the frequency/number of findings which would correspond to these time periods on the steep parts of the curve can be also low. Likewise, dating using steep parts of the calibration curve could be connected with some discrepancies implying from small (but significant) differences in <sup>14</sup>C activity in the calibration curve and in real samples. This could be caused by slight geographical differences of <sup>14</sup>C activity course, or by different periods of a wood mass growth caused by small microclimatic differences in examined sites or by a type of the tree with a different period of wood growth (we can assume that annual seasonal changes of <sup>14</sup>C activity occurred also in a distant past).

Following above mentioned aspects, together with the dendrochronologists we (at first) evaluated the <sup>14</sup>C activity in tree-rings corresponding to the steep parts of the actual calibration curve IntCal13. After obtaining the results, we will further discuss the possibilities of combination of a present calibration curve and local calibration curves which correspond to the time periods examined. Finally, we would like to also discuss possible application of the results in archaeology and other disciplines.

## Author Index

Due to some programming problems, a new version with author index will be released soon.