

# 8<sup>th</sup> Bone Diagenesis Meeting

12-15 September 2017, Oxford



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# Scientific Program

**Keynote:** Antoine Zazzo – Radiocarbon dating of bad bones: problems and prospects

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- S1-2 Beasley et al. – Understanding enamel diagenesis of  $\delta^{18}\text{O}_{\text{en}}$  using high resolution SIMS data and CLFM imaging
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- S1-4 Stein et al. – Preservation and diagenesis of the bones and teeth of *Iguanodon bernissartensis* (Dinosauria: Ornithomimidae) from the Early Cretaceous of Belgium.
- S1-5 Kiseleva et al. – Compositional and Structural Features of Permian Tetrapod Bone Remains (Kotelnich Site, Russia) and Their Alteration during Fossilisation
- S1-6 Anné et al. – De Novo advances in bone preservation: Characterizing extinct vertebrate physiology using synchrotron X-ray analyses
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## Session 2 – Multi-proxy Approaches to Diagenesis

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- S3-5 Kontopoulou et al. – Assessing Petrous Bone Diagenesis: A Multi-Analytical Approach
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- S4-1 Böhm et al. – Diagenetic alteration of dental surface textures by sediment transport: a tumbling experiment
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- S4-5 Harris et al. – A comparison of alkali pretreatments on collagen preservation and the removal of post-depositional humic contaminants
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- P2 Clementz & Laker – Assessing Preservation of Tympanic Bullae of Fossil and Modern Cetacea Using Raman Spectroscopy (1064 nm)
- P3 Czermak et al. – Visualising degraded collagen in tooth dentine
- P4 de Winter et al. – Elemental analyses on bioapatites: Proxy or diagenesis?
- P5 Elster – Easy Access to “Fossil Gelatine”?
- P6 Jacob et al. – Nitrogen content variation in archaeological bone and its implications for radiocarbon dating
- P7 Kiseleva et al. – From Sedentism to Mobility: Tracing Changes in a Way of Life of the Southern Ural Population in the Bronze Age - an Interdisciplinary Approach
- P8 Kontopoulou et al. – Blood and Fire: The Effects of Heating on the Preservation of Archaeological Petrous Bone
- P9 Margariti et al. – Origin of black bones within a waterlogged context: a multidisciplinary approach.
- P10 McMillan et al. – Diagenetic Housekeeping: Applying the Perio-spot Technique for Evaluating Pre-treatment Methods for Old and Cremated Bone
- P11 Niessner & Chatters – Amino acid extraction and radiocarbon analysis of environmentally degraded archaeological bone from Mexico
- P12 Portmann et al. – Bone Afterlife: insights into post-mortem bone biographies by a multi-disciplinary histological approach
- P13 Turner-Walker – An FTIR study of experimentally burned sheep bones
- P14 Turner-Walker – How Reversible are the Consolidants Used on Fragile Archaeological Bones? A Practical Evaluation

|       | 12-SEPT                                              | 13-SEPT            | 14-SEPT                   | 15-SEPT                                         |                 |  |  |
|-------|------------------------------------------------------|--------------------|---------------------------|-------------------------------------------------|-----------------|--|--|
| 9:00  |                                                      | Registration       | Registration              | Registration                                    |                 |  |  |
| 09:10 |                                                      |                    |                           |                                                 |                 |  |  |
| 09:20 |                                                      |                    |                           |                                                 |                 |  |  |
| 09:30 |                                                      | Opening            | Talk S3-1                 | Talk S4-1                                       |                 |  |  |
| 09:40 |                                                      |                    |                           |                                                 |                 |  |  |
| 09:50 |                                                      |                    |                           |                                                 |                 |  |  |
| 10:00 |                                                      | Talk S1-1          | Talk S3-2                 | Talk S4-2                                       |                 |  |  |
| 10:10 |                                                      | Talk S1-2          | Talk S3-3                 | Talk S4-3                                       |                 |  |  |
| 10:20 |                                                      |                    |                           |                                                 |                 |  |  |
| 10:30 |                                                      | Talk S1-3          | Talk S3-4                 | Talk S4-4                                       |                 |  |  |
| 10:40 |                                                      |                    |                           |                                                 |                 |  |  |
| 10:50 |                                                      | Coffee Break       | Coffee Break              | Coffee Break                                    |                 |  |  |
| 11:00 |                                                      |                    |                           |                                                 |                 |  |  |
| 11:10 |                                                      |                    |                           |                                                 |                 |  |  |
| 11:20 |                                                      | Talk S1-4          | Talk S3-5                 | Talk S4-5                                       |                 |  |  |
| 11:30 |                                                      |                    |                           |                                                 |                 |  |  |
| 11:40 |                                                      |                    |                           |                                                 |                 |  |  |
| 11:50 |                                                      | Talk S1-5          | Talk S3-6                 | Talk S4-6                                       |                 |  |  |
| 12:00 |                                                      | Talk S1-6          | Talk S3-7                 | Talk S4-7                                       |                 |  |  |
| 12:10 |                                                      |                    |                           |                                                 |                 |  |  |
| 12:20 |                                                      | Talk S1-7          | General Information       | Talk S4-8                                       |                 |  |  |
| 12:30 |                                                      |                    |                           |                                                 |                 |  |  |
| 12:40 |                                                      | Lunch              | Lunch                     | Lunch                                           |                 |  |  |
| 12:50 |                                                      |                    |                           |                                                 |                 |  |  |
| 14:00 |                                                      | Keynote – A. Zazzo | Talk S3-8                 | General Discussion & Conclusions with A. Sillen |                 |  |  |
| 14:10 |                                                      |                    | Talk S3-9                 |                                                 |                 |  |  |
| 14:20 |                                                      |                    | Poster Session            | Student Awards                                  |                 |  |  |
| 14:30 |                                                      | Talk S2-1          |                           |                                                 | Closing remarks |  |  |
| 14:40 |                                                      | Talk S2-2          |                           |                                                 |                 |  |  |
| 14:50 |                                                      |                    |                           |                                                 |                 |  |  |
| 15:00 |                                                      | Coffee Break       | Coffee Break              | Coffee Break                                    |                 |  |  |
| 15:10 |                                                      |                    |                           |                                                 |                 |  |  |
| 15:20 |                                                      |                    |                           |                                                 |                 |  |  |
| 15:30 | Talk S2-3                                            | Poster Session     | Tour of Oxford & Colleges |                                                 |                 |  |  |
| 15:40 |                                                      |                    |                           |                                                 |                 |  |  |
| 15:50 |                                                      |                    |                           |                                                 |                 |  |  |
| 16:00 | Talk S2-4                                            |                    |                           |                                                 |                 |  |  |
| 16:10 |                                                      |                    |                           |                                                 |                 |  |  |
| 16:20 |                                                      |                    |                           |                                                 |                 |  |  |
| 16:30 | Talk S2-5                                            |                    |                           |                                                 |                 |  |  |
| 16:40 |                                                      |                    |                           |                                                 |                 |  |  |
| 16:50 |                                                      |                    |                           |                                                 |                 |  |  |
| 17:00 |                                                      |                    | Post conference PUB       |                                                 |                 |  |  |
| 17:10 |                                                      |                    |                           |                                                 |                 |  |  |
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| 18:00 |                                                      |                    |                           |                                                 |                 |  |  |
| 18:20 |                                                      |                    |                           |                                                 |                 |  |  |
| 18:40 |                                                      |                    |                           |                                                 |                 |  |  |
| 19:00 | 18.30 - Registration & Welcome Reception (Ashmolean) |                    |                           | 18.30 – Conference Dinner (Trinity College)     |                 |  |  |
| 19:20 |                                                      |                    |                           |                                                 |                 |  |  |
| 19:40 |                                                      |                    |                           |                                                 |                 |  |  |
| 19:50 |                                                      |                    |                           |                                                 |                 |  |  |
| 20:00 |                                                      |                    |                           |                                                 |                 |  |  |



# Keynote

## Radiocarbon dating of bad bones: problems and prospects

Antoine Zazzo – [antoine.zazzo@mnhn.fr](mailto:antoine.zazzo@mnhn.fr)

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Radiocarbon dating is the most widely used scientific method for estimating the age of archaeological bones. Since the early days of radiocarbon dating, bone proved to be a difficult material to deal with. Bone carbon is present in the organic (mostly collagen) and in the inorganic phase (carbonate bound to the apatite crystals). The vast majority of bone radiocarbon dates are obtained from the collagen phase. Collagen is assumed to give more reliable dates because the chemical integrity of this biomolecule can be assessed using simple biochemical criteria such as the collagen yield, %C, %N and C/N ratio. As diagenetic alteration proceeds, the quantity and quality of the collagen decreases and sample size must increase in order to compensate for protein loss. In arid and semi-arid regions, collagen degradation proceeds rapidly and the mineral fraction of skeletal tissues is often the only source of carbon remaining for radiocarbon dating. But bone carbonate is prone to isotopic exchange with dissolved inorganic carbonate which can alter its original  $^{14}\text{C}$  content. Understanding bone diagenesis processes is therefore crucial to propose quality control criteria prior to bone radiocarbon dating.

This presentation will focus on the radiocarbon dating of “bad bones” i.e., bones for which very little or no collagen at all is preserved. Based on case studies taken from my own research and from the literature I will first review recent progress and limits regarding bone and enamel apatite dating. I will then question the criteria commonly accepted by the scientific community to validate a date obtained from bone collagen. Finally, I will present the latest advances of our team regarding the dating of tiny amounts (<60 mg) of bone using compact AMS systems.

# Session 1 – Diagenesis in Deep Time

*Chair – Thomas Tütken*

## **S1-1 Riddled: Patterns of Bioerosion in Ancient Human Bone**

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Bacterial bioerosion is the most common form of diagenesis found in the internal microstructure of archaeological bones. Microscopic studies of bone from forensic, archaeological and palaeontological contexts suggest that it is an early diagenetic process, but there is still a lack of clarity regarding the origins of osteolytic bacteria and the factors affecting their proliferation. Bacterial alteration of bone may be crucial to biomolecular preservation and fossilisation, therefore a better understanding of bacterial bioerosion would contribute to models of fossilisation, biomolecular preservation and early taphonomy.

Here we discuss results from recent large-scale studies of bacterial bioerosion in archaeological human bones. Our studies replicate previous results from mixed human/faunal assemblages in suggesting that bacterial bioerosion is linked to environmental conditions and early post mortem processes which control how far the bone is exposed to soft tissue decomposition. However, we found the biggest factor controlling the appearance of bacterial bioerosion is whether a bone came from a young infant (aged osteologically as <1 month old). The best explanation for this is that bioerosion is primarily caused by endogenous putrefactive bacteria and unbioeroded young infant skeletons represent individuals that had died before their osteolytic microbiome had developed.

## **S1-2 Understanding enamel diagenesis of $\delta^{18}\text{O}_{\text{en}}$ using high resolution SIMS data and CLFM imaging**

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<sup>b</sup> Department of Geoscience, University of Wisconsin, Madison

<sup>c</sup> Department of Anthropology, University of California, San Diego

The aim of this research project is to identify areas of enamel diagenesis in fossil fauna from Allia Bay, Kenya (3.97 MA), an early *Australopithecus anamensis* site. Tooth enamel has long been assumed to be resistant to diagenesis of stable isotope values. Previous research identified chemical changes to the tooth enamel crystal structure using cathodoluminescence (CL). It is unclear whether changes identified by CL correspond to altered stable isotope ratios in enamel. To test if mineral structure change in enamel correlates with altered  $\delta^{18}\text{O}_{\text{en}}$  values, a secondary ion mass spectrometer (SIMS) is used to generate high-resolution serial spot analyses (13  $\mu\text{m}$  spots) of  $\delta^{18}\text{O}_{\text{en}}$  across “alteration boundaries” identified by confocal laser fluorescence microscopy (CLFM). CLFM is a microscopic technique that produces images that can provide highly sensitive evidence of structural changes within hard tissue such as teeth, similar to CL imaging. It was not until technological advancements with instrumentation, such as the SIMS, that the question of diagenesis in enamel could be addressed directly because oxygen isotope values could not be measured at a high enough resolution to test this question.

### **S1-3 From deserts to the tropics: the benefits and pitfalls of Fourier Transform Infrared Spectroscopy (FTIR) as a fossil tooth enamel diagenesis detection tool across diverse environments**

Patrick Roberts<sup>a</sup> - [roberts@shh.mpg.de](mailto:roberts@shh.mpg.de)

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Although fossil mammalian tooth enamel has been shown to provide reliable stable carbon ( $\delta^{13}\text{C}$ ) and oxygen ( $\delta^{18}\text{O}$ ) isotope data across millions of years, protocols to check the structural preservation enamel samples remain important. This is particularly the case in tropical and desertic settings with challenging burial environments. Fourier Transform Infra-red Spectroscopy (FTIR) provides one means of studying the presence and crystallographic context of key structural groups in tooth enamel, yet it remains under-applied in diagenetic studies of Pleistocene assemblages, particularly beyond African and European environmental settings. Here, I present FTIR indices (WAMPI, PCI, API, BPI, and BAI) developed to study the crystal-chemical properties of enamel bioapatite from modern, unburied tooth enamel samples from Sri Lankan tropical forest and the Nefud Desert of Saudi Arabia. I compare these data to those from fossil samples excavated in the same regions and environmental settings, dated to 36-12 ka and 500 ka respectively. The results demonstrate that minor crystallographic changes between burial environments can be observed. However, there is no correlation with time. These subtle indices are not considered to have had major impacts on enamel apatite structure or  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  measurements, though our understanding of the correlation between these parameters remains limited.

**S1-4 Preservation and diagenesis of the bones and teeth of *Iguanodon bernissartensis* (Dinosauria: Ornithopoda) from the Early Cretaceous of Belgium.**

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<sup>c</sup> Royal Belgian Institute of Natural Sciences, Brussels, Belgium

The genus *Iguanodon* comprises some of the earliest discovered dinosaur taxa. It acquired an iconic status when a large number of more or less complete skeletons was exhumed from a coal mine near Bernissart, Belgium. The skeletons represent the largest find of its kind in Europe, and their morphology has been studied extensively. However, these natural treasures are notably threatened by decay of the pyrite which is ubiquitously present in the skeletons, therefore continued action is needed to preserve them. Here we present the first results on the bone histology and preservation of *Iguanodon bernissartensis* from Bernissart (Belgium) and the contemporary bonebed locality of Nehden (Germany), from which hundreds of mostly disarticulated bones of *I. bernissartensis* of similar preservation were uncovered. We sampled cores, and cut small sections of 16 individuals from Bernissart but also made full cross sections of eight specimens from Nehden.

Our analytical approach (polarized light microscopy,  $\mu$ XRF, FTIR spectroscopy, carbon and oxygen stable isotope analysis) demonstrates the morphological preservation of the bony tissues, and presence of metal sulfides and silicates in the medullary cavity. Pyrite has thus not affected the bony tissues themselves, which allowed assessment of the growth of this iconic taxon.

## **S1-5 Compositional and Structural Features of Permian Tetrapod Bone Remains (Kotelnich Site, Russia) and Their Alteration during Fossilisation**

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<sup>c</sup> Kazan Federal University, Kazan, Russia

Kotelnich location of vertebrates (the Vyatka River), one of the richest of the Permian period, is characterised by the excellent preservation of fossil remains due to burial in a silty anaerobic environment similar to modern bogs.

The aim is to carry out a comprehensive study of composition and structure of Permian parareptile *Deltavjatia vjatkensis* bone fragments, as well as its host rocks for further restoration of fossilisation processes, and palaeoecological reconstructions.

The bones and the surrounding strata were investigated using physico-chemical methods - optical microscopy, SEM, EMPA, XRD and ICP-MS.

The data on phase and element composition, degree of crystallinity and crystal lattice parameters of fossil bone are given. The sources of REE in the bone tissue are revealed. (La/Sm)<sub>n</sub> ratios (0.4-0.5), high Y/Ho ratios, high uranium content, and high La/Yb ratios (2-3) in the bones indicate the absence of recrystallisation during the late stages of diagenesis. Positive cerium anomaly detected in the bones indicates the presence of anoxic reducing alkaline environment during the early stages of diagenesis in shallow coastal basins.

Financial support was provided by the Russian Presidential grant № NSh-9723.2016.5.

## **S1-6 De Novo advances in bone preservation: Characterizing extinct vertebrate physiology using synchrotron X-ray analyses**

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Bone physiology, growth and repair are regulated by a series of organometallic compounds that regulate these biosynthetic pathways. Specific elements can be correlated with key biological pathways, making it possible to use trace metals to identify bone physiological processes in the fossil record.

Here we focus on mapping and quantifying trace elements crucial to the maintenance and repair of bone using a combination of multi-scale (micro-decimetre) synchrotron X-ray fluorescence elemental mapping and X-ray Absorption Spectroscopy. This setup allows for simultaneously: 1] rapidly and non-destructively map elements in large specimens under ambient conditions, 2] detect elements present at biological levels (ppm), and 3] determine the atomic configuration of these elements, revealing whether an element is organic or inorganic in nature.

The combination of chemical mapping, quantification and spectroscopy has resulted in the identification of biomarkers, notably Zn and Sr, for ossification, remodelling and cartilage replacement in a variety of fossilised tissues ranging from 40 ka to 145 ma in age. Concentrations and coordination chemistry of the element biomarkers within the fossil sample are comparable to those seen in extant bone suggesting these elements were endogenous to the samples and that the chemistry of bone physiology can be preserved through deep time.

## **S1-7 Fossilization processes in Miocene vertebrate bones from Sahabi, NE Libya**

Eirini Margariti<sup>a</sup> - [eimar@geol.uoa.gr](mailto:eimar@geol.uoa.gr)

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The present work is the first to deal with the geochemical analysis and the study of the fossilization of vertebrate skeletal remains from the Upper Miocene site of Sahabi (NE Libya, Africa).

A multi-disciplinary approach was used in order to investigate the diagenetic alterations of fifteen fossil bones (postcranial mammal bones) in terms of histology, mineralogical and chemical composition, crystallinity, structural parameters and precipitation of secondary mineral phases. The results are presented in correlation to the sedimentological context of the site.

From the observation of bone histology by means of Scanning Electron Microscopy (SEM), a moderate preservation of bone microstructure as well as restricted microbial attack, were inferred. The combination of fluorine wt% concentrations that Electron Probe Microanalysis (EPMA) yielded, the interpretation of carbonate bands from the infrared spectra (FTIR) as well as the structural parameters calculated by XRD and the Rietveld method, indicate the biomineral of bone to be carbonated fluorapatite. In nearly all specimens, quartz and gypsum were identified as the main secondary phases inside bone cavities while the S and Fe enrichment yielded by EPMA analyses and further studied with S K-edge XANES and Mössbauer spectroscopy were attributed to the presence of gypsum and goethite submicroscopic inclusions respectively.

## Session 2 – Multi-proxy Approaches to Diagenesis

*Chair – Anne-France Maurer*

### **S2-1 Experimental thermal change of texture of ostrich eggshell *Struthio camelus***

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Ostrich eggshell fragments are a frequent occurrence on archaeological sites throughout semi-arid and arid Africa. Their stable isotopes analyses can be performed to reconstruct past environments and climate conditions. However, it is necessary to characterise the state of preservation of the eggshell. In several sites, ostrich eggshell fragments seem to have been heated. In order to study the effect of fire on the isotopic composition of the ostrich eggshell, thermal experiments have been performed on modern OES eggshells. We observed a gradual eggshell colour modification throughout the temperature range investigated (20°C to 900°C). XRD, ATR-FTIR and SEM observations allowed us to track textural and mineralogical transformations of calcite to lime after 600°C. These transformations also affect the isotopic composition of the eggshell carbonate with an amplitude of less than 1 per mil in both  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$ .

## **S2-2 Thirty years of bone diagenesis research: What do we know and how do we know it?**

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The 8th Bone Diagenesis Meeting takes place nearly thirty years after the first Workshop held in Oxford in 1988. This interval has seen great advances in our understanding of the chemical, physical and biological processes influencing human and animal bone deposited in a range of terrestrial and marine sites, and how these processes affect subsequent analyses. Nevertheless, many questions remain unanswered. Principal among these is the identity and source of the microorganism(s) responsible for the tunnelling seen in bioeroded bones from terrestrial sites. Do they originate in the gut flora of the organism or do they originate from the soil? What is the role, if any, of fungi in the tunnelling of buried bones? Another thing that is unclear is the exact nature of the ultrastructural modifications that lead to the changes in microporosity and crystallinity seen in excavated bones and how these two parameters may be related. It is also unclear where, and how, biomolecules are preserved within ancient mineralised tissues. This paper summarises what we know to date about bone diagenesis and attempts to answer the question of how much confidence we can place in our understanding.

### **S2-3 Major element, minor diagenesis and vice versa**

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The routine measurement of calcium isotopes using new generation mass spectrometers allows us now to extract, in combination with other techniques, a more complete isotopic suite of information recorded in fossil bone and teeth. We present here the results combining isotopes of the major elements (calcium, carbon, oxygen) with those of trace elements (strontium) in modern and Plio-Pleistocene enamel samples of mammals coming from East Africa. The first results show that diagenetic processes have substantially altered the concentrations of many trace elements with potential for isotopic alteration, while these diagenetic processes left pristine the isotopic ratios of major elements.

## **S2-4 Enamel mineralization and compositional time-resolution in human teeth evaluated via histologically-controlled LA-ICPMS profiles**

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Mammalian dental enamel is of key interest for the reconstruction of past environments. Sequentially mineralizing enamel (e.g. ~15 years in humans) provides a several year-long archive that spatially-resolved sampling can ‘read’ at high-time resolution, yet how much enamel maturation overprints any primary signal remains underexplored. We report results of a systematic investigation of histologically-defined compositional profiles from human enamel obtained by laser-ablation inductively-coupled plasma mass spectrometry (LA-ICPMS). By focusing on two time-equivalent, yet topographically contrasting orientations, along the enamel-dentine junction (EDJ) and enamel prisms, we evaluate the compositional effect of enamel secretion vs. maturation throughout varying enamel thickness. These two time-equivalent profiles are compared with those along nominal isogrowth profiles (all relating to enamel secretion), namely neonatal/ Retzius lines (NNL / R) that connect the other two profiles. We focus on Sr/Ca, Pb/Ca, Zn/Ca and Ba/Ca as commonly-utilized proxies of (palaeo)diet, pollution and/or mineralization in both modern and archaeological individuals. Overall, we demonstrate that the elemental ratios investigated behave strongly differently with respect to maturation overprint and that the highest degree of initial signal variability can be retrieved along and closest to the EDJ. The corresponding data will be presented and discussed in the context of mineralization models and mechanisms.

## S2-5 Spatially-resolved Ca isotope and trace element variations in modern human deciduous teeth – records of diet and physiological changes?

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### ABSTRACT

We present spatially-resolved Ca-isotope and trace element (esp. Sr/Ca & Ba/Ca) data in enamel of three deciduous human canines of early 20<sup>th</sup>-century Italians, firstly to investigate any physiological effects on Ca-isotope variations, and secondly to examine the utilization of Ca-isotopes to study past human weaning practices.

At Royal Holloway University of London, enamel microsamples were laser-cut along the enamel-dentine junction using a 193nm laser-ablation system (RESOLUTION M-50), extracted and analysed for Ca isotopes ( $\delta^{44/40}\text{Ca}$ , relative to NIST 915a) by TIMS (PhoeniX-62) using double-spike technique. Trace element data were obtained on the matching, non-laser cut lingual enamel side using LA-ICPMS.

The Ca-isotope profiles drop to the lowest values ( $\sim$ -2.5 ‰) at birth in all three individuals, indicating a likely link between physiological change and negative Ca-isotope excursions. Two individuals show an increase of 0.5 – 1‰ in enamel  $\delta^{44/40}\text{Ca}$  after birth, but the third one records a drop of 0.5 ‰ post birth. This may suggest different early-life diets between the former (formula-fed?) and the latter (breast-fed?) because human milk has the lowest Ca-isotope composition. Corresponding histologically-controlled Sr/Ca and Ba/Ca profiles will be presented, which help to contextualize the Ca-isotope data across birth and weaning.

## Session 3 – Taphonomy & Preservation

*Chair – Wolfgang Müller*

### **S3-1 What is ancient bone collagen?**

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In this presentation we will attempt to answer a question once posed by the late Geoffrey Eglinton; what actually is archaeological collagen? Collagen is ubiquitous in bone and is the primary protein used in both radiocarbon dating and isotope analysis. Its widespread utility in archaeology stems from its rather unusual properties, a highly repetitive, mineralized fibrous protein. What do we know and still not know about how collagen decays, and does any of this matter? Advances in protein mass spectrometry have opened up a number of new avenues for archaeologists. We will focus primarily on the new insights gained by these new approaches to study and characterise collagen. We will discuss the application of bone collagen to identify bone fragments (ZooMS) and explore what we are beginning to learn about protein decay. We will then consider how these findings may impact upon our decisions to select and prepare collagen for radiocarbon dating and stable isotope analysis.

### S3-2 Atomic scale transformation of bone in natural and controlled experimental environments

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Stable isotope composition of biogenic apatite, particularly the composition ( $\delta^{13}\text{C}$ ,  $\delta^{18}\text{O}$ ) of structural carbonate groups, is an important geochemical marker used to infer past climates, biomineralization processes, dietary preferences and habitat of vertebrates. However an important limit for successful palaeoenvironmental and palaeoclimatic studies based on stable isotope analysis of fossils is the preservation of the isotopic signal in biogenic apatites. Fossil apatites generally exhibit an overall decrease in carbonate content, enrichment in fluorine, incorporation of trace elements and an increase in crystallinity. Detailed understanding of these transformations induced by fossilisation is thus required to improve the interpretation of isotopic records in apatites. In this contribution, we use vibrational (ATR-FTIR, RAMAN) and solid-state NMR spectroscopies to investigate the crystal-chemical transformations, and more specifically the environment of carbonate groups and fluoridation mechanisms, in both fossil bones from the Bolt's Farm fossiliferous area (Cradle of Humankind, South Africa) and modern bio-apatites altered under controlled conditions. Systematic formation of secondary carbonated fluorapatite is observed in all fossil bones. Based on the experimental results, we will discuss the fluoride incorporation mechanisms and their implications for reconstructions based on the isotopic composition of apatite carbonates.

### **S3-3 Microbial degradation of bone – an experimental study of bone taphonomy in the marine environment**

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Bone is used extensively as a source of information in biological and archaeological research as it is usually the only animal or human tissue preserved on an archaeological site. Often on a microstructural level the bone is altered and biomolecular information is lost. This lost information can be of key relevance when designing studies, or making important ethical decisions about what material should be subject to destructive analyses. Although microbes play a major role in the degradation of the bone material, little is known about the structure of their community, and how the local environment around the bone influences their diversity and function throughout the burial period. A series of burial experiments of modern bone fragments at four different sites has been carried out. The environment of the sites has been well documented and samples have been collected every month for a year. Using state-of-the-art DNA sequencing and informatics techniques on both the modern bones and freshly excavated archaeological bones from the same sites a profile of the microbial DNA has been made. The data will be synthesized with histological analysis in order to develop a general tool for assessing the potential of valuable archaeological bone samples for DNA analyses.

### **S3-4 Investigating the preservation state of bone and dentine collagen in faunal and human samples from Chalcolithic and Bronze Age Cyprus: implications for future isotopic studies**

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This study explores issues of collagen preservation in faunal and human remains selected from nine Chalcolithic and Bronze Age sites in Cyprus (ca. 4th-2nd millennia BC) for diet isotope analysis. Collagen extraction for carbon and nitrogen isotopic measurements was undertaken in 96 faunal and human skeletal samples including bones and teeth. Evaluation of collagen yields, atomic C:N ratios, and carbon and nitrogen concentrations in the extracted collagen residues suggest extensive collagen diagenesis, although intra- and inter-site differences in the preservation state of collagen were also noted. These quality indicators are described and discussed in relation to environmental (temperature, hydrology, soil type) as well as archaeological parameters (burial mode, funerary ritual) in the attempt of better understanding the factors influencing the survivability of bone and dentine collagen in Prehistoric Cyprus.

### **S3-5 Assessing Petrous Bone Diagenesis: A Multi-Analytical Approach**

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The discovery of petrous bone as an excellent repository for ancient biomolecules is a turning point in biomolecular archaeology, especially in aDNA research, but excessive and uncontrolled sampling could result in loss of this valuable resource.

This study reports on the histological (optical microscopy) and biochemical (FTIR-ATR, Collagen, CHN, and DNA analysis) preservation of 15 human petrous in order to refine the understanding of their preservation. Samples come from two different environments and chronological periods: nine from the later historical period in Denmark (c. 1650–1850 AD) and six from the Bronze Age period in Kazakhstan (c. 2100–1800 BC).

We present the findings of the combined application of a number of diagenetic parameters (Oxford Histological Index; Birefringence Index; Crystallinity Index; Carbonate/Phosphate ratio; Amide/Phosphate ratio; Col wt. %; % C, % N and C/N of whole bone and collagen; % endogenous DNA) used to assess the preservation of petrous bone. We explore potential ways to enhance screening practices and provide new insights into petrous bone diagenesis through a multidisciplinary approach.

### **S3-6 Investigating the causes of staining of Early Bronze Age human skeletal remains from Charterhouse Warren, UK.**

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Excavations of the Early Bronze Age site at Charterhouse Warren Farm Swallet, Somerset, UK, in the 1970s and 80s identified the scattered remains of at least 20 men, women and children within a 20m deep rubble-filled sinkhole. Cutmarks on the bones indicate dismemberment, as well as perimortem fracturing of long bones and injuries to skulls, suggesting extreme violence and post-mortem processing of human remains at the site on a scale not seen anywhere else in the UK.

Many of the bones are darkly stained and/or possibly charred. Here, we present XRF and FTIR data identifying the cause of any staining (e.g manganese and/or iron-based staining or organics such as humic acids from the depositional environment) or whether the bones had been charred or burned. This is important in terms of understanding the extent and possible reasons behind the modifications to the human remains. Further XRD analysis of burned and/or charred bones was also undertaken to investigate alterations to the bone mineral and potentially inform on burning conditions.

### S3-7 Recovering bone proteins in arid environments using paleoproteomics

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The timing and routes of diffusion of domestic caprines through the African continent are still poorly documented. This is partly due to the highly fragmented nature of the bone remains which often limits their determination on a morphological basis. Bone diagenesis also affects the preservation of biomolecules, especially DNA. Long term survival of proteins has previously been reported in fossil hominid sites from Tanzania highlighting the potential of paleoproteomics to reconstruct the scenario of diffusion of domestic caprines through the continent.

We report the use of ZooMS (Zooarchaeology by Mass Spectrometry) on archaeological bones from the sites of Toteng (Botswana) and Leopard Cave (Namibia). These sites were selected because they are considered as providing the first evidence of caprines in Austral Africa. Teeth and bones of small ungulates identified as caprines (*Ovis aries* and *Capra hircus*) as well as unidentified bone fragments were selected. Preservation of the organic phase was assessed using FT-IR. Different protocols were tested in order to extract structural proteins prior to their characterization. Sequences were identified with an UHPLC-ESI-MS/MS and assigned to the corresponding species thus allowing to ascertain the presence (or absence) of caprines in these sites.

### **S3-8 Lying through your teeth, strontium diagenesis in archaeological enamel**

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Strontium isotopes are an increasingly popular method for studying migration and mobility in archaeological populations. However, the basis of all strontium isotopic analysis is that strontium analysed in archaeological calcified tissues is of biogenic origin and that it has not been contaminated by exogenous strontium from the burial environment. Recovery of biogenic strontium isotope ratios from dentine and bone has been shown to be problematic and, with noteworthy exceptions, these are not considered reliable for preserving biogenic strontium. Relative to bone and dentine, tooth enamel has been shown to be resistant to diagenetic uptake of strontium. Nevertheless, tooth enamel is fundamentally the same mineral as bone (carbonated hydroxyapatite) and is in contact with the same burial environment so why should it be absolutely immune to diagenetic strontium uptake?

We will present the results of a study using laser ablation inductively coupled plasma mass spectrometry to investigate diagenetic strontium uptake in a suite of archaeological teeth. We demonstrate the presence of diagenetic strontium in archaeological enamel and then apply models of trace element uptake in bones and teeth to make quantitative predictions about the survival of biogenic strontium isotopes into deep time.

### **S3-9 Buried Bones: Identifying Post-Depositional Processes through Use-Wear Analysis**

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This experiment identified markers of chemical and mechanical post-depositional processes through the application of FTIR, metallurgic, and Scanning Electron Microscopes. While the post-depositional history of an archaeological site's matrix can never be replicated, diagnostic markers of individual processes are imprinted on bone material as part of its taphonomic history. We artificially exposed bone material to three different processes of degradation which commonly characterize faunal material buried in archeological sediments: heat, moisture, and pressure. We measured preservation before and after burial using FTIR. Using microscopic use-wear analysis, we distinguished textures left by these different processes. By differentiating the distortion of degradation from the uniformity of unaltered bone material, taphonomy recognizes patterns in modified bone, thus drawing proximate and ultimate interpretations about site formation processes and relationships with the surrounding paleoenvironment. However, the complexity of taphonomic processes prevents a complete identification of all agents responsible for post-depositional modification. The continued presence of equifinality within archaeozoology therefore forces researchers to develop new methods in the analysis of bone material. Through the application of cutting-edge use-wear techniques and state-of-the-art technology, we developed a new way to cogently reconstruct a bone's taphonomic history.

# Session 4 – Experimental Developments and Pre-treatments

*Chair – Maura Pellegrini*

## **S4-1 Diagenetic alteration of dental surface textures by sediment transport: a tumbling experiment**

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3D dental surface texture (3DST) is a powerful dietary proxy for mechanical food properties of the last meals, and for tooth function generally. Abrasion and/or attrition cause material loss and wear features at  $\mu\text{m}$ -scales on the enamel surface. The surface wear can be related to feeding traits, enabling us to distinguish soft- from hard-object feeders among herbivores and faunivores.

Fossil teeth encounter various taphonomic processes prior to or during burial. These may alter original diet-related 3DST. Here we systematically investigate the physical effects of fluvial transport on the 3DST by tumbling experiments of teeth from animals of different feeding behaviours. We tumble teeth in sediment-water suspensions with different sediment grain sizes (clay:  $<2\ \mu\text{m}$  to gravel:  $>2\text{mm}$ ) and amounts to determine how diet-related signatures are altered under such conditions. Teeth of different extant mammal taxa (enamel: hydroxyapatite) and sharks (enameloid: fluorapatite) are tumbled for different time intervals (0.5 to 256 hours) and their 3DST are characterized prior and after the tumbling experiments. The 3DST data from the tumbled teeth will be compared to those of fossil teeth from different depositional settings (low to high transport energy) to assess if experimental and natural alteration processes lead to comparable alteration features.

## S4-2 When an old story of diagenesis meets the LA-ICP-MS

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Although LA-ICP-MS is used since around 15 years for applications in archaeology, this technique is still not routinely applied for analysing skeletons, and especially bones. Studies dealing with bone trace elemental (TE) content are still very scarce because, 1) bone isotopic composition is often preferred to TE as bone  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  values yield dietary information whose reliability is assessed by “simple” criteria, while none exist for validating the reliability of bone TE content, and 2) there is no matrix-matched glass standard for analysing bone sections using LA-ICP-MS.

We propose here to test different calibration approaches (CRMs and homemade pellets and glasses) and apply the best method obtained to two Precolumbian skeletons. These individuals show different degrees of preservation (crystallinity, calcite, F and organic matter content) which have been previously explored at the intra-skeletal level.

Data obtained from LA-ICP-MS, compared to those defined as reflecting best the biogenic signal yielded by these two skeletons will help to better interpret the results acquired using LA-ICP-MS and to know whether it is possible to access the last years of an individual’s dietary behaviour with minimal sample preparation, high spatial resolution and fast analysis.

### **S4-3 In vitro alteration of tooth enamel in isotope tracer solutions**

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Stable isotopes and trace elements of fossil bones and teeth are important geochemical proxies for the reconstruction of diet and past food webs in archaeology and palaeontology. However, diagenesis can significantly alter diet-related isotope signatures. Here we experimentally assess how non-traditional dietary isotope proxies are affected by diagenetic alteration.

We perform in vitro alteration experiments of tooth enamel in aqueous solutions under controlled temperature and pH conditions in cold-seal Teflon vessels. Cubes of dental tissue with 3 mm edge length (~1 mm dentine and ~1 mm enamel) of an African elephant tooth are put for one month into aqueous solutions enriched in different isotopes (<sup>18</sup>O, D, <sup>44</sup>Ca, <sup>86</sup>Sr, <sup>26</sup>Mg, <sup>67</sup>Zn, <sup>11</sup>B) as well as a mixture of trace elements (~100 ppm). Experiments will be run at different temperatures (30°C and 90°C). Element distribution profiles across the cubes are measured with LA-ICP-MS and EMPA to quantify the alteration of the dental tissues. Additional complete shark and rodent teeth will be immerse to assess whether fluorapatite (shark enameloid) and hydroxyapatite (rodent enamel) display different resistance against alteration.

Results will be used to determine how well dental tissues retain original isotope compositions when subject to diagenetic alteration.

#### **S4-4 Using Non-Destructive Raman Spectroscopy to Investigate Young Fossil Diagenesis**

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The increased use of geochemical analyses on fossil material necessitates the development of a non-destructive assessment of diagenetic alteration prior to the analysis being conducted. An orbital-scanning surface Raman spectrometer from Metrohm Raman was used to investigate the detection limits of Raman spectroscopy on diagenesis, using two sites (Buldir Island, Alaska; and Last Canyon Cave, Montana) with relatively young fossils (Holocene and Pleistocene aged, respectively).

Preliminary results revealed that heavily burned specimens (those of the Buldir Island midden) easily fluoresced under the laser, suggesting a change in crystal structure. Unfortunately, details of composition are obfuscated by fluorescence, which made it difficult to retrieve additional information. For Last Canyon Cave specimens, Raman spectroscopy yielded a significant decrease in the v1 phosphate peak relative to the carbonate peak, suggesting the dissolution of phosphate and possibly secondary calcite mineralization. Also noted were the combination of the v3 and carbonate peaks, further suggesting phosphate dissolution. Relative to modern bone reference peaks, peaks for fossil bone appear to narrow and have shifted to the left, suggesting incipient recrystallization of bone crystallites and ion substitution within crystal lattices. These findings suggest that the stages of early diagenesis are detectable by Raman spectroscopy.

#### **S4-5 A comparison of alkali pretreatments on collagen preservation and the removal of post-depositional humic contaminants**

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Post-depositional contamination of archaeological bone with humic substances (humic and fulvic acids) is a persistent problem in archaeology and palaeontology. The presence of humic substances in bone collagen can alter stable carbon ( $\delta^{13}\text{C}$ ) and nitrogen ( $\delta^{15}\text{N}$ ) isotope values and produce aberrant radiocarbon ages. Affected bone samples that are targeted for biomolecular analyses are commonly pretreated with an alkali rinse in either sodium- (NaOH) or potassium hydroxide (KOH), followed by gelatinization and filtration. However, alkaline reagents have been shown to damage the collagen molecule, as suggested by reduced collagen yields with potential implications for the accuracy of stable isotope ratios. To assess the effect of alkali pretreatments on the removal of humics and preservation of collagen, we exposed demineralized humic-contaminated faunal bone samples of varying ages to NaOH and KOH, varying the solution concentration and exposure time. The alkali extracted samples were gelatinized, filtered, lyophilised. We examined the efficacy of the pretreatments using Fourier transform infrared spectroscopy in attenuated total reflection mode (FTIR-ATR) before and after gelatinization and filtration. Following the pretreatment procedures, collagen preservation was assessed using common preservation indicators (%C, %N, C:N), bulk  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  values, and amino acid composition as measured by high performance liquid chromatography (HPLC).

## S4-6 Survival and Detection of Dietary Metabolites in Bone from Iron Age Pigs

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Following sporadic reports of molecules with affinity for bone (namely alizarin and tetracycline) detected in ancient bone, we looked for preservation of dietary polyphenols in archaeological and modern bone. That is, with modern acorn-fed pig bone, and with Italian Iron Age pig bones, presumed to have eaten acorns, using other herbivores as controls.

We have identified the polyphenols urolithin A and B in modern bone (at levels of low picogram/g bone) using different extraction protocols with LC-MS/MS detection in bone from pigs fed acorns. Urolithins are known to be produced by gut bacteria from the conversion of ellagic acid, an abundant constituent in acorns.

We report here the detection of these same urolithins in many of the archaeological pig bones recovered from the site of Forcello (N Italy). No urolithin was detected in other herbivore bone apart from a red deer bone (also an acorn consumer).

There is much scope for improving extraction methods, and for investigating other compounds. Also a statistical analysis of the thousands of unidentified LC-MS peaks observed suggests that other interesting but quite different dietary discriminations can be applied rather generally.

#### **S4-7 Evaluating collagen pretreatment with XAD resin**

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The presence of exogenous organic carbon is a major concern when radiocarbon dating bone. In particular, the analysis of bone that has undergone diagenesis can be frustrating because the process of humification may potentially introduce contaminant organic carbon. Diagenesis occurs during burial and results from a combination of two distinct processes: (1) reactions involving indigenous organic carbon, (2) the complexation of collagen with soil humic substances. The radiocarbon measurement of altered bone, then, affects the age of the bone and reflects the presence of the exogenous humic carbon. Because the influence of contamination on radiocarbon measurements is dependent on the age of the sample, removal of humic carbon, particularly for older samples, is a necessity for accurate measurement. Pretreatment methods, such as XAD treatment and single-amino acid radiocarbon dating, have been applied to eliminate contaminant carbon and provide a purified sample for dating. In this study, we assessed the effectiveness of XAD for the removal of humics from collagen samples with disparate consensus ages,  $39,305 \pm 121$  yr BP and  $2,513 \pm 5$  yr BP, which were artificially spiked with a peat fulvic acid standard of known age.

## **S4-8 Developing a protocol to remove carbonate contaminants from tooth enamel for radiocarbon dating**

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In warm environments, such as those common in Australia and SE Asia, the collagen normally targeted for radiocarbon dating rapidly degrades meaning that it is often impossible to directly date skeletal remains. Carbon contained in apatite provides an alternative dating material. Unfortunately, it is difficult to remove carbonate contaminants from enamel: radiocarbon dates on unburnt apatites are typically erroneously young by several 100 <sup>14</sup>C years in the Holocene, and several 1000 <sup>14</sup>C years in the Pleistocene. Little is known about where this contamination is located within the complex enamel structure of apatite crystallites separated by a high magnesium amorphous phosphate phase. This makes development of a protocol to remove contaminants challenging.

This presentation will propose that although some 'recrystallisation' of the mineral phase is likely to have occurred and introduced some contamination, in the majority of teeth erroneous ages are most likely caused by the diffusion of carbonate through the enamel porosity. By designing protocols to remove the crystallite surfaces, radiocarbon dates on tooth enamel can be drastically improved. Although it is not yet possible to accurately date enamel, we will show that with work to examine diagenesis, this may be possible in the future.

## Posters

### P1 Diagenesis as cause for 'modified laminar bone' in sauropod dinosaurs?

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*Ampelosaurus* is a sauropod dinosaur from the Late Cretaceous of Southern France. Its long bone histology was described as 'modified laminar bone', characterized by a high degree of vascularization, but in absence of woven bone. Because it is illogical to have a high apposition rate with dense vascularization but no woven bone, we hypothesized that diagenetic effects may play a role in the formation of 'modified laminar bone'. Using geochemical techniques (XRF, FTIR, stable isotopes), combined with the observation of thin sections by microscopy (especially longitudinal sections), we found that the meaning of the modified laminar bone is rather diagenetic than biological. There is indeed woven bone inside the specimen where the modified laminar bone was described. There are also important iron proportions and some "weathered" figures, resulting in different aspects of the bone cells. These features are also linked with the low cell density. Finally, a stable isotope analysis suggests that  $\delta^{18}\text{O}_p$  is linked to the presence of strontium (similar to  $\delta^{13}\text{C}_{ap}$ ) or with the palaeo-latitudes which suggests that long bones from continental vertebrates may constitute a valuable material to reconstruct palaeo-climates.

This poster presents the initial results of this research, that the modified laminar bone is only a diagenetic artefact, and discusses the wider implication for the study of bone diagenesis.

## **P2 Assessing Preservation of Tympanic Bullae of Fossil and Modern Cetacea Using Raman Spectroscopy (1064 nm)**

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Within vertebrate skeletons, bone is considered more susceptible to alteration than other bioapatites (dentin, enamel) because of its high organic content, small crystallite size, and elevated porosity. However, not all bone types match this description. We examined bone from tympanic bullae of whales and dolphins (Mammalia: Cetacea), which has a density and porosity more akin to enamel than other skeletal bone. Using a nondestructive method of assessment (Raman spectroscopy), we quantified the compositional qualities of tympanic bullae in recent and fossil specimens (late Neogene) to determine how these characters impact preservation.

Thick sections were taken from the medial wall of tympanic bullae from recent and fossil specimens to examine compositional variation within bullae. For recent specimens, position of the primary phosphate band shifted from the interior ( $960\text{-}961\text{ cm}^{-1}$ ) to the exterior surface of bullae ( $963\text{ cm}^{-1}$ ). This shift, along with decreasing intensity of the carbonate band ( $1070\text{ cm}^{-1}$ ), indicated a decrease in carbonate content towards the outer surface of the tympanic. Within fossil specimens, the position of the primary phosphate band and intensity of the carbonate band fell within the observed range for modern specimens and outside of that of other fossil skeletal bone recovered from the same deposits ( $966\text{ cm}^{-1}$ ), suggesting tympanic bullae may be more resistant to compositional alteration than other bone types.

### **P3 Visualising degraded collagen in tooth dentine**

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Isotope analysis of collagen from dentine serial samples has become a popular tool in archaeology providing diachronic insights into individual's diet such as weaning pattern and subsistence, inferring social structures and mobility.

We developed an imaging-assisted microsampling approach to increase temporal resolution enabling to trace alterations in diet within small time-spans. Sample size and accordingly the covered time span depend on the minimum amount of collagen required for isotope analyses. Hence, collagen preservation and local concentration are important determinants for sample size.

Here we present a method utilising high-resolution transmission and fluorescence imaging of tooth root longitudinal thin sections to map collagen preservation. By using auto-fluorescence of intact and degraded collagen at different wavelengths the relative collagen quantity and quality can be detected and correlated with the respective sampling area. This enables to visualize areas with degraded collagen in tooth samples. Even in histologically intact areas decay was visible. Collagen yield was less in degraded areas, whereas isotope analyses confirmed that collagen quality in the unaffected regions was still good. Severely degraded areas, however, vanished after demineralisation.

This imaging approach can serve as quality control ahead of performing collagen isotope analyses and thereby saving resources.

#### **P4 Elemental analyses on bioapatites: Proxy or diagenesis?**

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The study of archaeological and palaeontological bioapatites yields much information about the life history and environment of humans and animals. A successful approach to extract this information is through studies that combine several chemical analyses on the same sample. The advent of high spatial resolution (semi) non-destructive chemical analysis techniques, such as micro-X-Ray Fluorescence ( $\mu$ XRF) and Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) allows such multi-proxy measurements. While the chemical study of bioapatites has focused mostly on isotopic analyses, further studies show that information about diet, environment and preservation state can be gained from trace element analysis.

In this study, LA-ICP-MS and  $\mu$ XRF trace element analyses are combined with stable oxygen, carbon and strontium isotope analyses to study the origin and preservation of trace element signatures in bioapatites. Combined trace element and stable isotope profiles through modern and archaeological teeth shed light on diet, environment and bioapatite preservation. Trace element profiles show seasonal patterns, reveal trace element leaching rates and localize shifts in mobility and diet. This study demonstrates the use of bioapatite trace element records in tracing taphonomical processes, diet and mobility and as proxy records for archaeological and palaeontological reconstructions.

## **P5 Easy Access to “Fossil Gelatine”?**

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Gelatine in fossil bones is the source for Radiocarbon, Stable Isotopes and Racemization studies. Its isolation and cleaning is a time consuming procedure and can introduce errors.

By synthesizing and optimizing a “Molecularly Imprinted Polymer” (MIP) for gelatine this procedure can be faster and more specific.

The application in Racemization studies will be described.

## **P6 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 and diet studies, but it is impossible to tell the state of collagen preservation from visual inspection. At the Oxford Radiocarbon Accelerator Unit (ORAU), a ~5 mg sample of bone powder is measured on a mass spectrometer for its percent nitrogen by weight (wt%N), which is used as a proxy for protein content. Samples with wt%N >0.7 are considered likely to produce sufficient collagen for radiocarbon dating. However, it is unclear what the extent is of intra-bone variation in collagen preservation and the variation between wt%N and collagen yield obtained using the routine chemistry pretreatment.

Here we present data from a series of Palaeolithic archaeological bones that have been sub-sampled in different locations for wt%N. Significant variation in wt%N is found within the same bone and there is not always good correlation between wt%N and collagen yield. These results suggest that for samples from difficult environments or from ancient bones it may be worth sub-sampling for wt%N in different locations of the bone (if possible) and then attempting to extract collagen from marginally preserved bones (wt%N around 0.3-0.7), as they may still yield sufficient collagen for radiocarbon dating.

## **P7 From Sedentism to Mobility: Tracing Changes in a Way of Life of the Southern Ural Population in the Bronze Age - an Interdisciplinary Approach**

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The Southern Urals, due to unique location in the centre of the Eurasian Steppes and the availability of mineral resources, became one of the centres of technological development and active social and cultural process in the 2nd millennium BC. The Sintashta (or Sintashta-Petrovka) archaeological culture provided the material in which local societies had been reflected. The sites are represented by enclosed fortified settlements and burial mounds with a complex structure of funeral rites. The fortified settlements of Kamenny Ambar and Konoplyanka (2100-1700 cal. BC) were studied by international multidisciplinary team.

Aim: to obtain new knowledge about the resource base, technology and life of the Southern Ural population in the Bronze Age.

Methods: the determination of trace elements using ICP-MS and strontium isotope composition using MC-ICP-MS in animal and human teeth and bones.

Results: Here, we present the preliminary results of strontium isotope along with trace element composition of teeth and bones from burials of Kamennyi Ambar and Konoplyanka.

Financial support was provided by RSF, grant №16-18-10332 (archaeological studies, L.N. Koryakova), and Russian Presidential grant № NSh-9723.2016.5.

## **P8 Blood and Fire: The Effects of Heating on the Preservation of Archaeological Petrous Bone**

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The survival of ancient biomolecules in archaeological bone has shaped the way archaeologists and anthropologists interpret the archaeological record over the last few decades. Cremation was a common burial practice throughout antiquity, but it induces many physical and chemical changes to bone. Here, we study the effects of burning on the macrostructure (bone colour), microstructure (optical microscopy) and molecular structure (FTIR-ATR, Collagen, CHN, and DNA analysis) of human skeletal remains (7 burned and 9 unburned) from the Iron Age and later historical period in Denmark. Our comparative data indicate that heating has severe effects on both the macro-, micro- and molecular structure of petrous bone. These results are discussed with reference to the implications for the biomolecular and archaeological study of cremated petrous bone.

## **P9 Origin of black bones within a waterlogged context: a multidisciplinary approach.**

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Identifying burnt skeletal remains in archaeological contexts is important, as it indicates human activities and fire-related episodes. Past zooarchaeological studies were mostly based on features, such as colour and crystallinity. However, the need for analytical techniques has become obvious as black-oxide stained but unburnt bones are frequent, especially within lake environments.

This paper presents an interdisciplinary study on the origin of “black bones” at the Neolithic lakeside settlement of Dispilio, Greece (5500–3500 BC). Animal bones have been recovered from a soil-matrix very rich in charcoal and ash, but at the same time waterlogged and organic, suggesting that the village was destroyed by fire. This study aims to examine this theory through the distinction of burnt vs. unburnt bones, while attempting to develop a more methodological protocol.

A selection of 44 fish and 16 mammal bone samples are examined through Optical Microscopy, Scanning Electron Microscopy (SEM), X-ray Microanalysis (EDXA), X-ray Diffraction (XRD) - Rietveld Analysis, Infrared Spectroscopy (ATR, NIR), chemical analyses (ICP-MS) and chemometric modelling in order to conclude on the origin of their colouration. Alterations of histology, mineralogy, chemistry, crystallinity and structural parameters due to diagenesis and/or possible burning are presented and correlated to the intriguing regional geochemical context.

## **P10 Diagenetic Housekeeping: Applying the Perio-spot Technique for Evaluating Pre-treatment Methods for Old and Cremated Bone**

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Cation replacement in the bioapatite crystal lattice occurs in- and ex-vivo, recording both life and death histories. Early diagenetic degradation of organic material causes the instability of bioapatite post-mortem, which results in elemental and isotopic exchange between a bone and its surrounding environment. Such processes overprint in-vivo chemical and isotopic signatures and simultaneously record a bone's ex-vivo history. Evidence of the diagenetic history of bone is preserved in concentration gradients of ex-vivo trace elements (taphonomic 'fingerprints') that extend inward from a bone's periosteal surface. To avoid accidental sampling of diagenetically altered bone during life history investigations, researchers often chemically clean or remove the contaminated external bone surface prior to analysis. We characterised the effects of chemical pre-treatment on diagenetically altered bone by observing the evolution of trace element concentration profiles before and after cleaning. Trace element concentrations were analysed by laser ablation inductively coupled plasma mass spectrometry on three megafaunal bones of different ages from Scladina Cave (Belgium) and three cremated human bones from Ireland and Belgium using the Perio-spot Technique to 1) characterise diagenetic alteration with high spatial resolution and 2) evaluate the effectiveness of chemical pre-treatment for bones of different ages and with various states of alteration.

## **P11 Amino acid extraction and radiocarbon analysis of environmentally degraded archaeological bone from Mexico**

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Radiocarbon dating of archaeological bone has been a point of consternation for many researchers due to the lack of sophisticated techniques that can be applied to not only thoroughly remove absorbed exogenous environmental contaminants, but also effectively obtain datable material from severely altered bone. Collagen extraction methods that employ additional techniques, like ultrafiltration, endeavor to show contamination removal, but without a supplemental method to characterize the constituents, radiocarbon assays still evoke doubt. However, by isolating total amino acids from bone, chemists can not only approach exclusion of all contaminants, but also employ a less intensive methodology in order to preserve the precious organic matrix. In extraction of total amino acids from archaeological bone from Mexico, where the tropical climate is well known to heterogeneously degrade bone and deplete the organic collagen matrix, we show consistency in the chemically-eluted textures that subsequently produce repeatable radiocarbon assays.

## **P12 Bone Afterlife: insights into post-mortem bone biographies by a multi-disciplinary histological approach**

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Funerary archaeology is rediscovering histological methods regarding their potential for reconstructing post-mortem biographies of bones. We analysed skeletal remains of humans and animals from burials and settlement features at the late Iron Age site of Basel-Gasfabrik (Switzerland) using a combination of anthropological and geoarchaeological histological procedures. Additionally, we performed an assessment of corresponding substrate types and sedimentation processes. Our data revealed no apparent correlation between bioerosive phenomena observed in the bones and the types of sediment these were embedded in. Moreover, the analysis enabled us to trace multi-stage mortuary processes among the complex handling of the dead in the late Iron Age. Our results demonstrate that the two approaches utilised are complementary both in their techniques and topics, so that the interdisciplinary collaboration not only permits new insights into bone taphonomy but also generates methodological benefits.

### P13 An FTIR study of experimentally burned sheep bones

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Mature sheep metapodials were heated overnight in a muffle furnace at 300-600 Celsius at 50° intervals. Weight loss and colour change were recorded. Quantitative evaluations of changes in protein content and crystallinity index were undertaken using the ratios of absorbance values at the amide I (1655 cm<sup>-1</sup>) and phosphate v3 PO<sub>4</sub> (1030 cm<sup>-1</sup>); and by summing the absorbance values of the two v4 phosphate bands and dividing by the depth at c. 590 cm<sup>-1</sup>, respectively. Bone mineral carbonate was also investigated using absorbances at the carbonate v3 CO<sub>3</sub> (1415 cm<sup>-1</sup>) and v2 CO<sub>3</sub> (870 cm<sup>-1</sup>) divided by the main phosphate v3 absorbance. Results show a linear relationship between weight loss and the amide I to phosphate ratio ( $R^2 = 0.980$ ). Weight loss was rapid between 300-400°, levelled off around 450° and climbed sharply after 550°. Comparing amide I to phosphate ratio to ashing temperatures shows that above 350° the loss of protein is approximately linear. Interestingly, both measures of carbonate increased up to 350° with greater changes in the carbonate measured at 1415 cm<sup>-1</sup>. Crystallinity initially declined before rising progressively up to 600°. Crystallinity changes appear closely linked to carbonate content.

## **P14 How Reversible are the Consolidants Used on Fragile Archaeological Bones? A Practical Evaluation**

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Ancient DNA studies are an emerging field in Taiwan. However, Taiwan is warm and humid but the soils are generally dry and porous to air – meaning soil bacteria rapidly destroy bone tissues leaving them fragile and fragmentary. Because of this, skeletons are often lifted in a “block” on site and taken to the laboratory or museum for later excavation. As part of this process the bones may be consolidated to hold the fragmentary bones in place. These consolidants are usually synthetic polymer resins such as Paraloid B-72 which are widely used in the conservation of museum objects and are considered to be “safe” and “reversible”. However, their long-term effects on ancient bones have never been evaluated.

We are investigating how far into the bone structure solutions of B-72 penetrate, their distribution within the pore network and the efficiency of solvent extraction. Density and viscosity of a 10% wt:vol solution of B-72 in acetone were measured by gravimetric and by falling ball measurements, respectively. Pore volumes of bone samples were measured by water absorption. Surprisingly, a 10% solution of B-72 penetrated almost as thoroughly as water and solvent appeared evenly distributed throughout the bone porosity. Extraction efficiency was up to 90%.