Developing reliability criteria for isotope and trace element analysis of ancient bone mineral (Ref IAP_15_108)

Durham University, Department of Archaeology
In partnership with Scottish Universities Environmental Research Centre, University of Glasgow

Supervisory Team
- Dr Andrew Millard, Durham University
  https://www.dur.ac.uk/archaeology/staff/?id=160
- Dr Philippa Ascough, SUERC
  http://www.gla.ac.uk/research/az/suerc/ourstaff/ascoughphilippa/

Key Words
1. Bone diagenesis
2. Carbon and oxygen isotopes
3. Palaeodiet
4. Elemental analysis

Overview

The investigation of the diet and location of origin of past humans and animals via the chemical and isotopic analysis of the mineral portion of their bones has along history in archaeological science. However, opinion in the field is divided between those who think that such analysis are useful and produce easily interpreted results and others who consider the mineral to be so altered and contaminated by post-burial diagenesis as to make such analyses suspect or downright misleading. This project aims to investigate whether it is possible to develop criteria for independent assessment of the reliability of for isotope and trace element analysis of ancient bone mineral.

Analysis of the $\delta^{13}C$ and $\delta^{18}O$ of archaeological bone is increasingly widely used to investigate the diet and origin of past peoples. One reason for this is that some studies have clearly demonstrated a theoretical and empirical basis for obtaining additional dietary information by compression of carbonate $\delta^{13}C$ with collagen $\delta^{13}C$ (Fernandes et al. 2012; Kellner and Schoeninger 2007). Another reason is that the $\delta^{18}O$ of carbonate is easier to measure than the $\delta^{18}O$ of co-existing phosphate and is claimed to correlate well with the phosphate $\delta^{18}O$ in enamel (Chenery et al. 2012) though earlier studies had suggested the same comparison as a measure of bone diagenesis (Iacumin et al. 1996). There are relatively few studies of $\delta^{18}O$ in bone but the use of phosphate $\delta^{18}O$ values is now increasing (Britton et al. 2015).

Trace element analysis of bone mineral to recover biogenic signals has been generally considered unreliable due to diagenesis (e.g., Trickett et al. 2003), but some groups employ this method to obtain results with sensible interpretations in terms of biogenic signals. However other analyses have been shown to produce biologically implausible values (Millard 2006; Pike and Richards 2002).

In many of the apparently successful studies outlined above diagenesis is not considered or is considered only cursorily, despite the fact that it is known to cause extensive changes to bone mineral (Millard 2001). It has been demonstrated that radiocarbon dating of enamel carbonate does not work due to diagenetic contamination (Hedges et al. 1995a), which calls into question the use of the much less stable bone mineral for isotopic analysis of carbonate. Numerous trace elements are well known to be taken up from, or exchanged with, the burial environment by bone, such as uranium (Millard and Hedges 1996), rare earth elements (Trueman et al. 2011), lead (Waldron 1983) and strontium (Budd et al. 2000).

In contrast to the debates and uncertainty in the analysis of bone mineral, researchers using isotopic analysis of bone collagen have long used reliability criteria, based on C:N ratios, and the %C and %N
composition of the extract (DeNiro 1985; Van Klinken 1999) and these are widely adopted within the field. Likewise for radiocarbon dating of shells the calcite/aragonite ratio is used as a measure of diagenesis (Douka et al. 2010). If the field of isotope and trace element analysis of ancient bone mineral is to move forward then it likewise needs clear reliability criteria which are demonstrated to exclude unreliable samples, and which can be widely applied.

In bone mineral a variety of measures have been suggested as criteria for detection of diagenetic change, including FTIR (Weiner et al. 1993), XRD, and histological index (Hedges et al. 1995b) but the application of these methods is usually site or project specific and not placed within a more general framework for the understanding of bone diagenesis.

Methodology

1. **Empirical evaluation of measures of diagenesis and sample preparation protocols**

   The project will focus initially on developing reliability criteria for isotope analysis of bone carbonate in bones where the carbonate isotopic composition is predictable, but with varying burial environments. The methods to be investigated for their correlation with aberrant isotope analyses include FTIR, XRD, FT-Raman, histological index and analysis of elements known to be subject to uptake (U, REEs). These will be compared to the isotopic results produced using different preparation protocols such as acetic acid and HCl pretreatments and will explore the utility of pyrolysis methods (Meredith et al. 2012).

2. **Development of a model of bioapatite stability**

   The second element of the project will be to develop models for the stability of bone mineral and the exchange of carbonate with the burial environment based on the data generated in the first stage.

3. **Extension to trace element analysis**

   Once reliability criteria for carbonate isotopic analysis and an underlying theoretical basis for those criteria have been developed the project will be extended to consider other trace elements such as lead, strontium and fluoride in ancient bioapatites.

### Timeline

<table>
<thead>
<tr>
<th>Year</th>
<th>Month</th>
<th>Activity</th>
</tr>
</thead>
<tbody>
<tr>
<td>2016</td>
<td>Oct-Dec</td>
<td>Induction, initial literature review and introductory laboratory training</td>
</tr>
<tr>
<td>2017</td>
<td>Jan-Apr</td>
<td>Screening of potential samples and initial analysis of diagenesis</td>
</tr>
<tr>
<td></td>
<td>May-Jun</td>
<td>Sample analysis at SUERC</td>
</tr>
<tr>
<td></td>
<td>Jul-Oct</td>
<td>Sample analysis in Durham</td>
</tr>
<tr>
<td></td>
<td>Nov-Jan</td>
<td>Preparation of initial paper on criteria for carbonate isotope analysis</td>
</tr>
<tr>
<td></td>
<td>Dec-Apr</td>
<td>Development of bioapatite stability model</td>
</tr>
<tr>
<td>2018</td>
<td>Feb-Jul</td>
<td>Further sample analysis to underpin the model</td>
</tr>
<tr>
<td></td>
<td>Aug-Oct</td>
<td>Preparation of paper on stability model</td>
</tr>
<tr>
<td></td>
<td>Nov-Jan</td>
<td>Sample analysis in Durham</td>
</tr>
<tr>
<td>2019</td>
<td>Feb-Mar</td>
<td>Sample analysis at SUERC</td>
</tr>
<tr>
<td></td>
<td>Apr-Jun</td>
<td>Preparation of paper on application of stability model to carbonate isotope analysis</td>
</tr>
<tr>
<td></td>
<td>Jun-Aug</td>
<td>Further analyses and processing results</td>
</tr>
<tr>
<td></td>
<td>Oct-Dec</td>
<td>Preparation of paper on criteria for elemental analysis</td>
</tr>
<tr>
<td>2020</td>
<td>Jan-Mar</td>
<td>Final preparation and submission of thesis</td>
</tr>
</tbody>
</table>

### Training & Skills

Through this project the student will receive training and develop skills in:

1. **stable isotope and trace element preparation and analysis methods at two leading laboratories in Durham and SUERC**
2. A wide range of (geo-)chemical methods applicable to the analysis of archaeological bone
3. Geochemical modelling of bone mineral diagenesis
4. A range of scientific skills including research design, data analysis, and report writing.

In addition the student will receive a range of training in generic research skills at Durham such as presentation skills, and paper writing and the broad training in environmental science training provided within the IAPETUS DTP.

### References & Further Reading


Further Information

Dr Andrew Millard
Department of Archaeology, University of Durham
E: a.r.millard@durham.ac.uk  T: 0191 334 1147