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**DETECTING DIAGENESIS: $^{87}\text{Sr}/^{86}\text{Sr}$ ANALYSIS OF ARCHAEOLOGICAL
BIOAPATITES BY LA-MC-ICPMS TO ASSESS DIAGENETIC UPTAKE OF Sr IN
ENAMEL**

J. Lewis¹, C.D. Coath¹ and A.W.G. Pike²

- 1 University of Bristol, School of Earth Sciences, Bristol Isotope Group
Wills Memorial Building, Queens Road, Bristol BS8 1RJ, Great Britain
- 2 University of Southampton, Department of Archaeology
Avenue Campus, Southampton, Great Britain
e-mail: jamie.lewis@bristol.ac.uk

ABSTRACT

Sr isotope analysis is a popular method for characterising mobility and migrations in archaeological populations. The method has its basis in the geological variability in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of Sr in rocks as a function of age and initial Rb/Sr ratio and the observation that as this geological Sr is cycled into the food chain via soils and plants the mass fractionation corrected ratio of ^{87}Sr to ^{86}Sr in the biologically available Sr is preserved. In mammals, Sr is concentrated in bones and teeth where it replaces Ca in the (bio)-apatite lattice and thus calcified tissues preserve a record of where dietary Sr was being sourced during mineralisation. When this analysis is applied to archaeological populations and with suitable characterisation of biologically available $^{87}\text{Sr}/^{86}\text{Sr}$ this allows archaeologists to determine the presence allochthonous individuals in populations and assess mobility and migrations.

The basis of archaeological strontium isotope analysis is that the strontium that is analysed in bones and teeth is of biogenic origin and that this Sr has not been contaminated by exogenous Sr from the burial environment. Bone and tooth dentine have been shown to be problematic for recovering biogenic Sr isotope signals however enamel has been shown to be relatively resistant to diagenesis. Nevertheless, tooth enamel is chemically similar to bone and dentine (both mineralogically approximate carbonated hydroxyapatite) and is in contact with the same burial environment.

When considering the possibility of diagenetic uptake of strontium into archaeological enamel one may consider that diagenetic strontium may not be equally distributed across the whole thickness of an enamel section, with greater amounts of diagenetic strontium at the edges of the enamel compared to the enamel core. Thus, it is desirable to work with a techniques that can detect diagenetic Sr in spatially resolved manner with a spatial resolution in the 100 μm range. Furthermore, detection of diagenetic Sr in enamel is more compelling if one can measure both the Sr concentration and the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of altered enamel relative to pristine enamel. This, in combination with samples where one can make *a priori* assumptions about either the diagenetic or biogenic $^{87}\text{Sr}/^{86}\text{Sr}$ with a high degree of certainty allows for conclusive identification of diagenetic Sr in enamel.

LA-MC-ICPMS would appear to be ideally suited to detecting diagenetic Sr in archaeological enamel and is able to determine Sr concentrations and $^{87}\text{Sr}/^{86}\text{Sr}$ to respectable precisions at spatial resolutions in the $\sim 100 \mu\text{m}$ range. However, making accurate measurements of $^{87}\text{Sr}/^{86}\text{Sr}$ in bio-apatites by LA-MC-ICPMS is an extremely challenging analysis which is beset by a complex series of interferences on the isotopes of interest.

Interference species are numerous but come principally from the gases used to generate the plasma ion source (Kr^+) and the from the sample matrix being ablated. Sample derived interferences range in nature from singly charged isobaric interferences ($^{87}\text{Rb}^+$) and doubly charge rare earth elements (e.g., $^{174}\text{Yb}^{++}$) which are present in the singly charged Sr mass range through to more exotic plasma

species such as Ca and Ar dimers ($^{40}\text{Ca}, ^{40}\text{Ar}-^{44}\text{Ca}^+$). The final problematic interference for $^{87}\text{Sr}/^{86}\text{Sr}$ analyses is $^{40}\text{Ca}(^{40}\text{Ar})^{31}\text{P}^{16}\text{O}^+$ on $^{87}\text{Sr}^+$ which is responsible for small yet consistent offsets in $^{87}\text{Sr}/^{86}\text{Sr}$ on teeth measured by LA-MC-ICPMS relative to the known values.

In this presentation we describe the analytical complications of undertaking $^{87}\text{Sr}/^{86}\text{Sr}$ analysis by laser ablation, how tuning of the plasma conditions and modifications to the ICP interface can improve the accuracy of analysis and the need for well characterised standards with a range of Sr concentrations. We then present the results of $^{87}\text{Sr}/^{86}\text{Sr}$ analysis of a series of Pleistocene age large mammal teeth recovered from the North Sea and use these teeth to assess diagenetic strontium uptake into archaeological enamel.

