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Improvement of laser ablation *in situ* micro-analysis to identify diagenetic alteration and measure strontium isotope ratios in fossil human teeth

M. Willmes [a, *], L. Kinsley [a], M.-H. Moncel [b], R.A. Armstrong [a], M. Aubert [a, 1], S. Eggins [a], R. Grün [a, 2]

[a] Research School of Earth Sciences, The Australian National University, Canberra ACT 2601, Australia
[b] Département de Préhistoire, Muséum National d'Histoire Naturelle, CNRS UMR 7194, 1 Rue René Panhard, France

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ABSTRACT

Strontium isotope ratios measured in fossil human teeth are a powerful tool to investigate past mobility patterns. In order to apply this method, the sample needs to be investigated for possible diagenetic alteration and a least destructive analytical technique needs to be employed for the isotopic analysis. We tested the useability of U, Th, and Zn distribution maps to identify zones of diagenetic overprint in human teeth. Areas with elevated U concentrations in enamel were directly associated with diagenetic alterations in the Sr isotopic composition. Once suitable domains within the tooth are identified, strontium isotope ratios can be determined either with micro-drilling followed by TIMS analysis or *in situ* LA-MC-ICP-MS. Obtaining accurate $^{87}Sr/^{86}Sr$ isotope ratios from LA-MC-ICP-MS is complicated by the potential occurrence of a significant direct interference on mass 87 from a polyatomic compound. We found that this polyatomic compound is present in our analytical setup but is Ar rather than Ca based, as was previously suggested. The effect of this interference can be significantly reduced by tuning the instrument for reduced oxide levels. We applied this improved analytical protocol to a range of human and animal teeth and compared the results with micro-drilling strontium isotopic analysis using TIMS. Tuning for reduced oxide levels allowed the measurement of accurate strontium isotope ratios from human and animal tooth enamel and dentine, even at low Sr concentrations. The average offset between laser ablation and solution analysis using the improved analytical protocol is 38 ± 394 ppm ($n = 21$, 2σ). LA-MC-ICP-MS thus provides a powerful alternative to micro-drilling TIMS for the analysis of fossil human teeth. This method can be used to untangle diagenetic overprint from the intra-tooth isotopic variability, which results from genuine changes in $^{87}Sr/^{86}Sr$ isotope ratios related to changes in food source, and by extension mobility.

1. Introduction

Radiogenic strontium isotope compositions ($^{87}Sr/^{86}Sr$) of human and animal skeletal remains can be used to reconstruct their habitat use and ranging patterns (Bentley, 2006; Price et al., 2002; Slovak and Paytan, 2012). Radiogenic strontium isotope ratios vary between different regions, primarily depending on the age and composition of the underlying geology, augmented by external processes such as precipitation, seaspray, and dust (Bentley, 2006; Capo et al., 1998; Evans et al., 2010; Maurer et al., 2012; Montgomery et al., 2007; Sillen et al., 1998). Strontium enters the body through diet, substitutes for calcium in biological apatite, which is used in the formation of bones and teeth, and serves no metabolic function. Therefore, the $^{87}Sr/^{86}Sr$ isotope ratio measured in skeletal remains will reflect the concentration-weighted average of dietary Sr, that was consumed while the skeletal tissue was formed (Beard and Johnson, 2000; Bentley, 2006). Thus, $^{87}Sr/^{86}Sr$ isotope ratios can be used to reconstruct change in food source and by extension residence area. A common problem when working

* Corresponding author.
E-mail address: malte.willmes@googlemail.com (M. Willmes).
[1] Now at: Research Centre of Human Evolution, Environmental Futures Research Institute, Griffith University, Gold Coast, Queensland 4222, Australia.
[2] Now at: Research Centre of Human Evolution, Environmental Futures Research Institute, Griffith University, 170 Kessels Road, Nathan, Queensland 4111, Australia.

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with fossils remains is that diagenetic processes can change the original isotope compositions, rendering the sample unsuitable for isotopic provenance studies. In addition, isotopic analyses are often destructive, which prohibits their application to valuable fossil remains. Laser ablation multi-collectorinductively coupled plasma mass spectrometry (LA-MC-ICP-MS) is an analytical method that has the potential to overcome both of these limitations, because it allows for rapid *in situ* screening for diagenetic overprints, and least-destructive strontium isotope analysis of the same sample (Benson et al., 2013; Grün et al., 2014). In this paper, we outline a method to investigate diagenetic overprinting in fossil teeth using U, Th, and Zn concentration distribution maps. We then tested our protocol for $^{87}Sr/^{86}Sr$ isotope analysis in teeth in regard to the current limitations in terms of accuracy and precision, which have been observed in a significant number of analytical facilities, and are hypothesised to be mainly caused by a polyatomic interference on mass 87 (Horstwood et al., 2008; Lewis et al., 2014).

1.1. Diagenetic alteration of fossil teeth

The formation of human tooth enamel and dentine of the permanent dentition is a complex process beginning *in utero* (Ash and Nelson, 2003; Nanci, 2012). The mineral component of teeth is bioapatite, which is similar to hydroxyapatite, but affected by numerous substitutions of the Ca, PO_4, and OH groups with secondary groups, such as Sr, Mg, and Ba. These secondary groups are subject to biological selection and vary in concentration with changes in trophic levels, between different species, and with the element abundance in the underlying substrate (Burton and Wright, 1995; Elliott, 2002). Intra-tooth measurements in mammals may be used to connect the intra tooth isotopic variations to mobility (Balasse et al., 2002; Britton et al., 2009). In human teeth, enamel does not remodel after formation and is closed to chemical exchange (Nanci, 2012). Thus, intra-tooth isotopic variations may relate to the sequential mineralisation of the tooth enamel. However, while the timing of tooth development in humans is well constrained, the complex pattern, timing and rates of mineralisation and maturation of tooth enamel are currently not completely resolved (Balasse, 2002; Montgomery et al., 2012; Suga, 1989).

The preservation of skeletal remains depends on their environmental surroundings. Diagenetic alterations are a common problem for many archaeological samples. To ensure that the isotopic ratios measured in a tooth reflect the original isotopic composition, it is important to identify the domains within the tooth that are least affected by diagenetic alteration (Nelson et al., 1986). For the investigation of diagenetic changes in tooth enamel, a variety of methods have been used, including infra-red (IR) spectroscopy (Sponheimer and Lee-Thorp, 1999) and cathodoluminescence (CL) imaging (Schoeninger et al., 2003). Nearly all of these studies have employed bulk analysis with the aim of testing cleaning techniques (Hoppe et al., 2003; Price et al., 1992; Trickett et al., 2003) or coarse sub-sampling using mineralogical information (e.g. by CL) as a guide. While these approaches provide some information as to the mineralogical state of the hydroxyapatite or functional groups within this mineral (such as hydroxyl or phosphate), any conclusions about sample integrity for isotopic analysis are derived from conjecture. Mapping of element distributions has been used to identify the degree of diagenesis in bones (Fernandes et al., 2013; Koenig et al., 2009; Trueman et al., 2008). In addition, a few studies have investigated the mechanisms of diagenetic alteration using high resolution elemental or isotope analysis (Jacques et al., 2008; Kohn et al., 1999; Martin et al., 2008; McCormack et al., 2015).

Systematic mapping of U, Th, and Zn concentrations may help to qualitatively identify domains of diagenetic alteration in skeletal materials. The basic principle is that modern teeth and bones contain only trace amounts of uranium and thorium and thus their presence in archaeological skeletal remains can be used to identify zones of diagenetic overprinting (Boel, 2011; Budd et al., 2000; Eggins et al., 2003; Grün et al., 2008; Hinz and Kohn, 2010; Koenig et al., 2009). Uranium is water soluble and highly mobile in skeletal tissues and consequently its concentration and spatial distribution are highly variable and can change on small scales on the order of tens of μm (Duval et al., 2011; Grün et al., 2008, 2014). Thorium, on the other hand, is water insoluble and represents mechanical overprinting of the sample, for example by clay particles in pores and on the surface. However, there is no linear correlation between uranium and thorium incorporation and the uptake of other elements, such as Sr. This hinders the quantification of possible Sr overprint based on the distributions of U and Th. Nevertheless, zones within a tooth showing high U or Th concentrations can indicate diagenetic overprints, while zones with low U and Th concentrations are more likely to preserve the original Sr isotope ratio. In mammals, low U zones often occur close to the surface of the tooth enamel, within 200–400 μm (Boel, 2011; Budd et al., 2000; Eggins et al., 2003; Grün et al., 2008). The first aim of this research paper is to further test this screening method and to evaluate the usefulness of Zn as an additional tracer to identify zones, which have retained the original strontium isotopic compositions.

1.2. Strontium isotope analysis of fossil teeth

Strontium isotope ratios from fossil teeth can be analysed either using sample dissolution followed by mass spectrometric measurements (thermal ionisation mass spectrometry (TIMS) or multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS)), or *in situ* using laser ablation (LA)-MC-ICP-MS. For solution analyses, a micro-drill can be used to extract a small amount of sample, which is then digested in acid and Sr is separated from the matrix elements using ion exchange chromatography. This technique is accurate and reliable, but also time intensive and potentially more destructive to the sample than *in situ* LA-MC-ICP-MS. The amount of material required varies between a few μg to several tens of mg depending on the Sr concentration, drill setup, and instrument capacity. For samples requiring more than 0.5 mg, drilling causes large destructive marks on the sample, making this technique unsuitable for valuable archaeological materials. Micro-drilling smaller amounts of sample <0.1 mg is much less destructive, but it is also technically challenging and the equipment is not widely available (e.g., Charlier et al., 2006). LA-MC-ICP-MS allows *in situ* analysis of a sample and has shown great potential in analysing skeletal remains because it is fast, requires minimal sample preparation, and provides high spatial resolution (50–200 μm). Additionally, this method allows for large numbers of measurements on the same skeletal fragment to test for compositional variability within the same specimen. Traditionally, samples were cut to create a flat sample surface for laser ablation analysis, which creates significant damage. However, recent studies have shown that accurate data can also be obtained from the outer uncut sample surface (Benson et al., 2013; Copeland et al., 2011; Le Roux et al., 2014).

Problems with laser ablation analysis of the $^{87}Sr/^{86}Sr$ isotope ratios in fossil skeletal material result from molecular interferences from Ca, Kr, Ar, and Rb, that can severely limit the accuracy and precision (Copeland et al., 2008; Horstwood et al., 2008; Paton et al., 2007; Simonetti et al., 2008; Vroon et al., 2008; Woodhead et al., 2005). In particular, the occurrence of a direct interference on mass 87 from a polyatomic compound, possibly $^{40}Ca^{31}P^{16}O$, has been suggested to be the main cause for