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Ca isotopic analysis of laser-cut microsamples of (bio)apatite without chemical purification

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ABSTRACT

We report methodological innovations and an initial application to retrieve Ca isotopic ($\delta^{44/40}$Ca) compositions of (bio)apatite at high spatial resolution. We utilize laser-microsampling via laser-cut polygons followed by extraction of μg-sized bioapatite fragments; and apply a 10^{10} Ω resistor for ^{40}Ca and parafilm-dam loading to minimize in-run Ca isotope fractionation for TIMS analysis. We obtain identical internally-normalized TIMS Ca isotopic ratios for natural calcite, apatite and bone meal SRM1486 without chemical separation, suggesting no need of chemical purification of these materials for such analysis. Our ^{42}Ca–^{48}Ca double spike (DS) corrected $\delta^{44/40}$Ca values of standard solutions HPS_{new}, Fisher07 and bone meal SRM1486 are 0.70 ± 0.18‰, 1.03 ± 0.20‰, and −1.03 ± 0.19‰ (2SD), relative to SRM915a, all well in line with published data. Solutions prepared from both laser-cut and non-laser cut Durango apatite have similar $\delta^{44/40}$Ca values (0.70 ± 0.17‰, 2SD), suggesting no resolvable Ca isotope fractionation effect induced from laser-cutting.

A $\delta^{44/40}$Ca profile of a third molar from a modern human female, laser-sampled in the growth direction of the enamel apatite, reveals a 0.5‰ increase from age ~11 to ~11.5, followed by a 0.7‰ drop at age ~12 and a final return to enriched Ca-isotope compositions until age ~14. We surmise that the initial increase is related to her known phase-out of dairy products, whereas the drop may coincide with hormonal changes at the onset of her menstruation. The latter hints at a relationship between physiological change and $\delta^{44/40}$Ca variation, and raises the need for proper evaluation of physiological effects on Ca isotopes before reliable environmental signals can be extracted from the large Ca-isotope variability previously observed in skeletal tissues.

We also investigated the potential for Ca isotopic analysis using an IsoProbe MC-ICPMS in both solution and laser ablation (LA) modes. While the use of a collision cell almost completely removes $^{40}Ar^{+}$ interference on $^{40}Ca^{+}$, partially-resolved hydrocarbon interferences result in only ~30% useable peak flats, that potentially cause problems with peak jumping needed for analysis of ^{46}Ca and ^{48}Ca. Furthermore, it is difficult to correct for Ti isobaric interferences so that analysis without chemical separation is challenging. In-situ Ca isotope analysis of natural calcite (SRM915b), aragonite and apatite by LA-MC-ICPMS shows substantial matrix sensitivity, and therefore requires close matrix matching.

1. Introduction

Precise Ca isotopic analysis was established using modern mass spectrometers and the double spike mass fractionation correction technique by Russell et al. (1978). Since then a large amount of Ca-isotope work has been focused on the global Ca cycle (e.g. Zhu and Macdougall, 1998; Schmitt et al., 2003; Tipper et al., 2006); and palaeoceanographic reconstruction using marine skeletal carbonates (e.g. Nägler et al., 2000; Gussone et al., 2004; Heuser et al., 2005; Hippler et al., 2006; Farkas et al., 2007; Brazier et al., 2015). Ca isotopic variations in biological samples hold vital clues of Ca pathways during bio-mineralisation and metabolism. Some marine bone apatite and calcium carbonate suggest a Ca trophic level effect, namely a lowering in $\delta^{44/40}$Ca of ~1‰ per trophic level in marine environment (Skulan et al., 1997; Clementz et al., 2003; DePaolo, 2004), but such effect is not convincing between herbivores and carnivores, and at the higher end of the food chain in terrestrial environment (Chu et al., 2006; Reynard et al., 2010; Heuser et al., 2011). The larger Ca-isotope variability but lower delta values in human bones relative to fauna at some archaeological sites may result from more complicated processes (e.g. Ca metabolism) than trophic level effects (Skulan and DePaolo, 1999; Reynard et al., 2010). A comprehensive understanding of physiological and environmental controls on Ca isotope fractionation in different skeletal tissues will allow us to reliably extract the environmental signals potentially carried by Ca-isotopes. Improvements in Ca-isotope methodology will help to reveal further details of natural Ca isotopic variabilities and hence are critical to assess fully the potential of using Ca isotopes as a geochemical proxy.

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Ca isotopic ratios have conventionally been measured by TIMS due to its high sensitivity and an external precision of ~0.15–0.30‰ (2SD) in $\delta^{44/40}$Ca has been achieved using the double spike (commonly ^{42}Ca–^{48}Ca or ^{43}Ca–^{48}Ca) technique (e.g. Russell et al., 1978; Skulan et al., 1997; Heuser et al., 2002; Huang et al., 2012; Lehn and Jacobson, 2015), though recent Ca isotope analyses ($\delta^{44/40}$Ca) using an optimized ^{42}Ca–^{43}Ca DS showed an external 2SD of 0.04‰ (Lehn et al., 2013). Such TIMS analyses are accurate and precise, but have required prolonged sample preparation and analysis time. An alternative, more rapid approach using MC-ICPMS was developed with Ca isotopic data corrected for mass bias using the standard-sample bracketing technique (Halicz et al., 1999; Wieser et al., 2004; Chu et al., 2006; Hirata et al., 2008; Reynard et al., 2010). However, compared with TIMS, Ca work by MC-ICPMS faces a big challenge: interference of Ar-species ions from the plasma on Ca isotopes (e.g. $^{40}Ar^+$ on $^{40}Ca^+$). Most hydrocarbon interferences, even those on minor Ca isotopes are resolvable at medium to high resolution on MC-ICPMS, though.

Earlier Ca-work by MC-ICPMS avoided this issue by not measuring ^{40}Ca, so reporting data as $\delta^{44/42}$Ca with 0.1–0.2‰ (2SD) using sample-standard bracketing (Halicz et al., 1999; Wieser et al., 2004). This is equivalent to 0.2–0.4‰ (2SD) on $\delta^{44/40}$Ca. Due to $^{88}Sr^{2+}$ interference on ^{44}Ca, the removal of Sr is very important for MC-ICPMS analysis of Ca isotopes. Introducing samples as dry aerosols to the plasma and chemical purification prior to measurement, have been found to contribute to minimizing isobaric interferences and systematic drift due to matrix differences (Halicz et al., 1999; Wieser et al., 2004; Chu et al., 2006; Reynard et al., 2010, 2011). In practice, the one-step chemical separation of Ca from Sr and the rest of the matrix (Wieser et al., 2004) requires columns with extreme length/diameter ratio (≥50), making both separation and column cleaning very slow and difficult. Although some argue that the use of Sr-specific resin only to remove the Sr ions from carbonate solutions is sufficient to avoid interference and matrix effects (Brazier et al., 2015), the difficulty of the chemical purification for MC-ICPMS depends on the complexity of samples (Tipper et al., 2008). The two column procedure (e.g. Chu et al., 2006; Hirata et al., 2008; Reynard et al., 2010), or the three-step separation (Tipper et al., 2008; Tacail et al., 2014), or even the four-step purification scheme (Schiller et al., 2012), which involve the step separation of Ca from Sr and the rest of the matrix, is costly and time-consuming. More importantly, Ca isotope fractionation can occur during column chemistry if Ca recovery is not nearly 100% (Russell et al., 1978). It is therefore desirable to minimize chemical purification to avoid biasing Ca isotopic measurements.

Another strategy is to make direct $\delta^{44/40}$Ca measurements by MC-ICPMS using the cold plasma technique (Fietzke et al., 2004) or using reaction/collision cells to eliminate ^{40}Ar ions (Palacz, 2004). However, the cold plasma (500 W) technique does not completely eliminate $^{40}Ar^+$ and requires careful sample matrix matching to minimize the changes in sensitivity and mass bias due to matrix changes (Fietzke et al., 2004). On the other hand, a MC-ICPMS, such as the GV Instrument IsoProbe, can theoretically facilitate precise measurements of ^{40}Ca because it has a collision cell where a small flow of H_2 is introduced to neutralize $^{40}Ar^+$ via charge transfer (Palacz, 2004). However, such mass spectrometers are discontinued, so not widely available any more.

Calcium isotope data by MC-ICPMS are often corrected for mass bias using a standard-sample bracketing technique that works on the assumption that sample and bracketing standards experience the same mass bias and that mass fractionation during an analysis is fairly constant. However, this assumption may not always hold true because subtle variations in the matrix between samples and standards can cause change in the instrumental sensitivity and mass bias.

As an alternative to the standard-sample bracketing technique, the standard addition method has recently been used to correct MC-ICPMS Ca isotopic data (Tipper et al., 2008). This method is designed to analyse solutions with significantly different matrix to the standard matrix. Despite the advantage in getting high precision and accuracy (e.g. seawater $\delta^{44/42}$Ca of 0.93 ± 0.05‰, 2SD, n = 7, by Tipper et al., 2008), the success of this technique requires careful and correct performance in each analytical step. This complicated and time-consuming technique limits its wide applicability in MC-ICPMS analysis for stable isotopes.

Others proposed to take advantage of both TIMS and high resolution (HR)-MC-ICPMS to obtain precise and accurate data on a complete range of Ca isotopes for a single sample, with ^{42}Ca to ^{48}Ca measured on HR-MC-ICPMS and ^{40}Ca to ^{44}Ca on TIMS (Schiller et al., 2012). This technique is particularly useful for determining mass-independent effects on small Ca isotopes (e.g. ^{46}Ca) because HR-MC-ICPMS (such as Neptune Plus) can produce long-lasting stable ion beams for even minor Ca isotopes.

While significant efforts have been made in order to improve the precision and accuracy of Ca isotopic data by MC-ICPMS, less has been done to improve the efficiency of TIMS Ca isotopic analysis, in part because DS-TIMS analysis is a well-established method. In this study, we report Ca isotopic measurements (^{40}Ca, ^{42}Ca, ^{43}Ca, ^{44}Ca and ^{48}Ca) of five different Ca isotopic standards and tooth enamel (bio-apatite), using both TIMS and (LA)-MC-ICP-MS with the following improved techniques: 1) laser-cutting for high-precision microsampling; 2) simplified sample preparation with no ion exchange chromatography; 3) parafilm-dam loading technique that profoundly reduces the in-run fractionation and prevents mixing/unmixing between different Ca reservoirs on a Re-filament; 4) 10^{10} Ω resistor on the collector that measures ^{40}Ca, allowing good signals on small Ca isotopes ($^{42}Ca = 1.5 \times 10^{-3}$ nA and $^{48}Ca = 0.5 \times 10^{-3}$ nA); 5) ^{42}Ca–^{48}Ca double spike and a Matlab model for mass fractionation correction. We also present the first microsampled Ca isotope profile in modern human tooth enamel to evaluate the physiological controls on Ca isotopes. Data from our study should help to interpret the large Ca-isotope variability indicated in bones at some archaeological sites (Reynard et al., 2010).

2. Materials and method development

2.1. Tooth enamel sample and standards

A third molar (named CLW2) of a Chinese female that mineralized during her adolescent life (approximately 11–14 years) was donated and made into a thick section with a thickness of 80 μm. The thick section was made using Crystalbond Adhesive (509 Clear) with a low melting point (121 °C) and soluble in acetone, allowing the extraction of laser-cut enamel microsamples via gentle heating.

Five Ca isotopic standards were analysed in this study, including one primary standard NIST SRM915b, and four secondary standards: (1) HPS_{new} (high purity Ca solution, lot no. 1213234) from Greyhound Chromatography Ltd.; (2) Fisher07 (code J/8010/08) from Fisher Scientific Ltd.; (3) NIST SRM1486 (bone meal) and (4) Durango apatite, a fission track age standard from Durango City, Durango, Mexico (Young et al., 1969; McDowell et al., 2005). HPS_{new} and Fisher07 were purchased as calcite solutions (Ca concentration: 1000 mg/l). Weighed NIST SRM915b (powder) and Durango apatite (fragments) were dissolved in concentrated HNO_3 and evaporated, followed with dissolution in 18.2 MΩ cm H_2O. NIST SRM1486 (bone meal) was first treated with concentrated HNO_3 and H_2O_2 to remove collagen, and then evaporated and made into Ca solution with 18.2 MΩ cm H_2O. All the standard solutions have a Ca concentration of 1000 ± 3 mg/l and were analysed for Ca isotopes by TIMS without chemical purification.

2.2. Laser micro-sampling of (bio)apatite

A RESOlution M-50 193 nm laser-ablation system (Australian Scientific Instruments, formerly Resonetics LLC, Müller et al., 2009) at Royal Holloway University of London (RHUL) was used to cut enamel microsamples along the enamel–dentine junction (EDJ) of the wisdom tooth section CLW2. The laser operating conditions for cutting were