Mass fractionation of Rb and Sr isotopes during laser ablation-multicollector-ICPMS: in situ observation and correction

Sung-Gyun Yim[1,2], Min-Ji Jung[1,2], Youn-Joong Jeong[2], Yeongmin Kim[2] and Albert Chang-sik Cheong[1,2*]

Abstract

Background: One of the most critical issues concerning in situ mass spectrometry lies in accounting for elements and molecules that overlap target isotopes of analytical interest in a sample. This study traced the instrumental mass fractionation of Rb and Sr isotopes during laser ablation-multicollector-inductively coupled plasma mass spectrometry (LA-MC-ICPMS) to obtain reliable $^{87}Sr/^{86}Sr$ ratios for high-Rb/Sr samples.

Findings: In the LA-MC-ICPMS analysis, Kr interferences were corrected using Ar and He gas blanks measured without ablating material. Contributions from doubly charged Er and Yb ions were corrected using the intensities of half masses and isotopic compositions reported in the literature. After Kr correction, the calculated $^{166}Er^{2+}$ intensity of NIST SRM 610 approached the measured intensity at mass 83, and the $^{173}Yb^{2+}/^{171}Yb^{2+}$ ratio agreed with the recommended value within error ranges. Kr- and REE^{2+}-stripped peak intensities were further corrected for Rb interference. Use of the Sr mass bias factor for the calculation of measured $^{87}Rb/^{85}Rb$ yielded $^{87}Sr/^{86}Sr$ ratios consistent with the recommended and expected values for low-Rb/Sr materials, such as NIST SRM 616, modern shark teeth, and plagioclase collected from Jeju Island, but failed to account for the ^{87}Rb interference from high-Rb/Sr materials including NIST SRM 610 and SRM 612. We calculated in situ mass bias factor of Rb from the known $^{87}Sr/^{86}Sr$ ratios of the standards and observed a correlation between Rb and Sr mass fractionation, which allowed inference of the Rb bias from the standard run. Reliable $^{87}Sr/^{86}Sr$ and $^{85}Rb/^{86}Sr$ ratios were obtained for SRM 610 and SRM 612 using the inferred mass bias factor of Rb calculated by the standard bracketing method.

Conclusions: This study revealed that Rb and Sr isotopes behave differently during LA-MC-ICPMS and suggests the potential usefulness of the standard bracketing method for measuring the Rb–Sr isotopic compositions of high-Rb/Sr materials.

Keywords: Laser ablation, Multicollector-ICPMS, Rb isotope, Sr isotope, Isobaric interference, Instrumental mass fractionation, Standard bracketing method

Introduction

The natural radioactivity of rubidium was demonstrated in 1906 by Campbell and Wood and came into use in the field of isotope geology when mass spectrometry analysis became available in the 1950s. Rubidium-87, which presently makes up 27.83% of Rb, decays to stable ^{87}Sr by emitting a negative beta particle with a decay constant of 1.42×10^{-11} year^{-1} (Steiger and Jäger 1977) that corresponds to a half-life of 48.8×10^9 years. Strontium consists of four naturally occurring stable isotopes (^{84}Sr, ^{86}Sr, ^{87}Sr, and ^{88}Sr). Its isotopic composition, generally represented by the $^{87}Sr/^{86}Sr$ ratio, varies widely in the geosphere and hydrosphere resulting from contrasting geochemical behavior of Rb and Sr. The Sr isotope signatures of local ecosystems transferred through the

* Correspondence: ccs@kbsi.re.kr
[1]Graduate School of Analytical Science and Technology, Chungnam National University, Daejeon 34134, Republic of Korea
[2]Korea Basic Science Institute Ochang Center, Cheongju 28119, Republic of Korea

food chain have been used extensively to address archeological and forensic questions since the 1980s (Ericson 1985; Aggarwal et al. 2008).

The Rb–Sr isotope data have long been obtained using isotope dilution thermal ionization mass spectrometry (TIMS) or multicollector-inductively coupled plasma mass spectrometry (MC-ICPMS) combined with the separation of Rb and Sr by cation exchange chromatography. Despite the constraint of time-consuming sample preparation, these wet techniques for bulk samples continue to be used widely, particularly when a high level of precision and accuracy is demanded. However, microsampling or in situ analysis is inevitably required to extract the time-series information stored in biogenic materials or to retrieve petrogenetic information from a mineral composed of geochemically heterogeneous micro-domains.

The potential of laser ablation (LA)-MC-ICPMS for in situ Sr isotope analysis was realized in the 1990s (Christensen et al. 1995). Although this technique has become a standard methodology for measuring the Sr isotopic composition of Sr-rich minerals (e.g., feldspar, apatite, and clinopyroxene), carbonate and phosphate rocks, and biogenic materials (e.g., teeth and otoliths), considerable debate remains over isobaric interferences and instrumental mass fractionation (IMF) of Rb and Sr isotopes (Ramos et al. 2004; Vroon et al. 2008; Müller and Anczkiewicz 2016; Willmes et al. 2016).

This study traced the IMF of Rb and Sr isotopes during laser ablation-multicollector-inductively coupled plasma mass spectrometry (LA-MC-ICPMS) and proposed an adequate procedure for correcting Rb interference on ^{87}Sr using synthesized standards and natural samples. The in situ data obtained in this study indicate the feasibility of the LA-MC-ICPMS technique for measuring the Rb–Sr isotopic composition of high-Rb/Sr materials.

Materials
This study used glass standard reference materials (SRMs) provided by the National Institute of Standards and Technology of the USA (NIST), modern shark teeth, and plagioclase crystals separated from a Quaternary basalt on Jeju Island, Korea.

NIST SRMs 610, 612, and 616 were selected for Rb–Sr isotopic analyses in this study. Their base glass was fused from a mixture of quartz sand, alumina, soda ash, and calcium carbonate (72 wt% SiO_2, 2 wt% Al_2O_3, 14 wt% Na_2O, and 12 wt% CaO) (Kane 1998). These SRMs contain many trace elements with concentrations that are relatively uniform and sufficiently high for chemical and isotopic calibration (ca. 400 μg/g for SRM 610, ca. 40 μg/g for SRM 612, ≤ 40 μg/g for SRM 616). Their chemical and Sr-Nd-Pb isotopic compositions have been

measured in many laboratories to evaluate micro-homogeneity in glass samples and constrain best reference values (e.g., Pearce et al. 1997; Rocholl et al. 1997; Woodhead and Hergt 2001; Jochum et al. 2011). Overall means of Sr concentrations are 515.5 μg/g, 78.4 μg/g, and 41.72 μg/g for SRM 610, SRM 612, and SRM 616, respectively (Jochum et al. 2011).

The teeth of two shark species, the bull shark (*Carcharhinus leucas*) and spot-tail shark (*Carcharhinus sorrah*), were purchased during the Denver Gem and Mineral Show in 2018. The enameloid (external tooth layer) of the shark teeth consists typically of fluoroapatite ($Ca_5(PO_4)_3F$) (Kemp and Park 1974) with stoichiometric concentrations of ca. 40 wt% Ca and ca. 18 wt% P. Such teeth are expected to have the Sr isotopic composition of modern seawater (^{87}Sr/^{86}Sr = 0.70918 ± 0.00001; Faure and Mensing 2005).

Plagioclase crystals were extracted from a Quaternary basalt outcrop on Hwasun Beach, Jeju Island, Korea (33° 14′ 10.21″ N, 126° 20′ 18.10″ E). The length of the plagioclase phenocrysts was approximately 1 cm.

Methods
Solution and laser ablation-assisted Rb–Sr isotopic analyses, including sample preparation and mass spectrometry, were performed at the Korea Basic Science Institute Ochang Center. The instrument operating parameters of (LA)-MC-ICPMS are summarized in Table 1.

Solution ICPMS
Solution ICPMS was carried out for the shark teeth and Jeju plagioclase. Fragments (~ 40 mg) of tooth enameloid were digested overnight in 8 mL of 8 M HNO_3 at 160 °C, then dried and stored in 10 mL of 2 M HNO_3. The sample solutions were diluted 20,000 times with 2% HNO_3. The concentrations of Rb and Sr in the teeth were measured using an X-series quadrupole ICPMS (Thermo Fisher Scientific). Plagioclase crystals (~ 10 mg) were digested overnight in 3 mL of mixed acid (HF:HNO_3: $HClO_4$ = 10:3:1) at 160 °C and then dried and redissolved in 2.5 N HCl. Chemical separation of Sr was performed twice using ion-exchange chromatography with Eichrom Sr-spec resin (100–150 μm) for the shark teeth and Bio-Rad AG50W-X8 resin (200–400 mesh) for the Jeju plagioclase. Sample digestion and Sr separation were conducted in a clean room equipped with laminar flow benches. The total Sr in the procedural blank was less than 200 pg.

Strontium isotopic compositions of the shark teeth and Jeju plagioclase were measured with a Neptune MC-ICPMS and a Nu Plasma II MC-ICPMS instrument, respectively. Strontium isotope data were acquired in static mode (n = 20). The IMF was exponentially normalized to ^{86}Sr/^{88}Sr = 0.1194. Isobaric interferences from Kr and

Table 1 (LA)-MC-ICPMS instrument operating parameters

MC-ICPMS	Nu plasma II					Neptune
Faraday detector	9 Faraday cups					7 Faraday cups
	H7 (88) H6 (87) H5 (86.5) H4 (86) H3 (85.5) H2 (85) Ax (84) L1 (83.5) L2 (83)					H2 (88) H1 (87) C (86) L1 (85) L2 (84) L3 (83) L4 (82)
RF power	1300 W					1200 W
Reflected power	< 1 W					< 2 W
Auxiliary gas flow rate (Ar)	0.9 L/min					0.9 L/min
Sweep gas flow rate (Ar)	4~5 L/min					-
Integration time	0.2 s					4.2 s
Sampler & Skimmer cone	Nickel					
	Session 1	Session 2	Session 3	Session 4	Session 5	
ThO^+/Th^+ (248/232)	0.77%	0.21%	0.16%	0.34%	0.68%	-
Laser (ESI machines NWR 193-nm ArF excimer laser)						
Spot size	150 μm	100 μm	150 μm	150 μm	150 μm	
88 peak intensity (NIST SRM 610)	4.5 V	1.0 V	1.7 V	1.7 V	5.0 V	
Ablation mode	Single hole drilling					
Cell	Two volume 2 cell (10 × 10 cm)					
Pulse energy density	8 J/cm^2					
Pulse repetition rate	20 Hz					
Ablation duration	30 s					
Carrier gas flow rate (He)	0.65 L/min					

Rb were negligible. Replicate analyses of NBS 987 with the Neptune and Nu Plasma II MC-ICPMS instruments yielded average $^{87}Sr/^{86}Sr$ ratios of 0.710283 ± 0.000007 [2 standard errors (SE), *n* = 6] and 0.710259 ± 0.000012 (2 SE, *n* = 18), respectively. Errors of isotopic ratios in this study denote 2 SE unless otherwise stated. $^{87}Sr/^{86}Sr$ data were corrected for interlaboratory bias by adjusting them to the recommended NBS987 value (0.710248; Thirlwall 1991).

Laser ablation MC-ICPMS

Fragments of the shark teeth were sonicated in distilled water for 15 min and then dried in an oven at 60 °C. The NIST SRMs were washed with ethanol. The dried teeth and SRMs were mounted in epoxy and ground to expose the sample surface. Plagioclase phenocrysts in polished thin sections (0.1 mm thickness) were used for LA-MC-ICPMS analysis.

The Rb–Sr isotopic measurements were performed with a Nu Plasma II MC-ICPMS connected to an NWR193-nm ArF excimer laser ablation system. The LA-MC-ICPMS measurements consisted of five analytical sessions. SRM 610 was analyzed in all sessions but SRM 612 and SRM 616 were analyzed in session 1 only. The shark teeth were analyzed in sessions 1–4, and the Jeju plagioclase was measured in session 4. The ThO^+/Th^+ (248/232) ratio was measured using path ablation mode before the beginning of each analytical session.

Three Faraday detectors (L1, H3, and H5) were placed at half mass positions to correct the isobaric interferences from doubly charged rare earth elements (REEs). The laser beam was focused to a spot diameter of ~ 150 μm (sessions 1, 3, 4, 5) or ~ 100 μm (session 2), and the intensities of mass 88 for SRM 610 ranged from ca. 5 to 1 V. Raw data (ca. 80–40% in the middle of the total 150 cycles) were processed using an Excel spreadsheet or Iolite 2.5 within Igor Pro 6.3.5.5 software (Paton et al. 2011).

Results and discussion

Solution ICPMS

The Sr concentrations of the shark teeth were ~ 1600 μg/g, whereas the Rb concentrations were beneath the detection limit (0.1 μg/g). The enameloid of bull shark and spot-tail shark teeth yielded $^{87}Sr/^{86}Sr$ ratios of 0.709205 ± 0.000035 and 0.709170 ± 0.000025, respectively. These results were highly consistent with the value of modern seawater ($^{87}Sr/^{86}Sr$ = 0.70918 ± 0.00001; Faure and Mensing 2005). Triplicate analyses for the Jeju plagioclase yielded average $^{87}Sr/^{86}Sr$ ratios of 0.704151 ± 0.000026, 0.704139 ± 0.000024, and 0.704187 ± 0.000024.

Laser ablation MC-ICPMS

Isobaric interferences on Sr isotopes may arise from Ca dimers and Ca argides, Fe dioxides, Ga and Zn oxides,

doubly charged REEs and Hf, and singly charged Kr and Rb (Ramos et al. 2004; Vroon et al. 2008). Among them, critical interferences from Kr, doubly charged Er and Yb ions, and Rb are discussed below. The other molecular species have only a limited impact on Sr isotope ratios (Ramos et al. 2004).

Gas blank and REE^{2+} interference

Kr is usually included in Ar and He gas. The signals of Kr isotopes were monitored for 300 s without ablating material before the beginning of each analytical session. The observed ^{84}Kr intensities were 0.26 mV (session 1), 1.60 mV (session 2), 0.08 mV (session 3), 0.004 mV (session 4), and 5.4 mV (session 5). The fluctuation of Kr signal might be related to the change of ArF and liquid Ar gas. Kr blanks were subtracted from peak intensities at masses 83, 84, and 86.

Doubly charged Er (^{168}Er^{2+} and ^{170}Er^{2+}) and Yb (^{168}Yb^{2+}, ^{170}Yb^{2+}, ^{172}Yb^{2+}, ^{174}Yb^{2+}, and ^{176}Yb^{2+}) ions overlap at masses 84, 85, 86, 87, and 88. Peak intensities at masses 83, 85.5, and 86.5 measured for SRM 610 were in the range of 10–3 mV when the 88 peak intensity was around 5 V (i.e., session 5). We confirmed that the Kr-stripped ^{166}Er^{2+} intensity at mass 83 corresponded to the value calculated from the intensity at mass 83.5 (^{167}Er^{2+}) and the Er isotopic composition reported in the literature (^{166}Er, 33.5027%; ^{167}Er, 22.8691%; Chang et al. 1998). We also confirmed that the ^{173}Yb$^{2+}/^{171}$Yb^{2+} ratio measured at masses 86.5 and 85.5 in each analytical session agreed with the recommended value in the literature (1.132338 ± 0.000050; Vervoort et al. 2004) within errors (for example, session 1 ^{173}Yb$^{2+}/^{171}$Yb^{2+} = 1.13 ± 0.02). These correspondences indicate that the Kr and REE^{2+} intensities were measured correctly.

The contributions of Er and Yb to Rb and Sr isotopes were calculated from the measured intensities at masses 83.5 (^{167}Er^{2+}) and 86.5 (^{173}Yb^{2+}) (Eq. (1), "*I*" denotes a peak intensity) and the isotopic compositions and ratios of Er and Yb (see Table 2). The IMF was not considered in this calculation but was certainly insignificant at the level of REE^{2+} in the samples and standards analyzed in this study.

$$^{84}\text{Sr} = {}^{84}\text{total-}I_{83.5} \times \frac{0.269784}{0.228691} \left({}^{168}\text{Er}^{2+}\right) - I_{86.5} \times \frac{0.008876}{1.132338} \left({}^{168}\text{Yb}^{2+}\right)$$

$$^{85}\text{Rb} = {}^{85}\text{total-}I_{83.5} \times \frac{0.149102}{0.228691} \left({}^{170}\text{Er}^{2+}\right) - I_{86.5} \times \frac{0.212562}{1.132338} \left({}^{170}\text{Yb}^{2+}\right)$$

$$^{86}\text{Sr} = {}^{86}\text{total-}I_{86.5} \times \frac{1.531736}{1.132338} \left({}^{172}\text{Yb}^{2+}\right)$$

$$^{87}(\text{Rb} + \text{Sr}) = {}^{87}\text{total-}I_{86.5} \times \frac{1.531736}{1.132338 \times 0.68321} \left({}^{174}\text{Yb}^{2+}\right)$$

$$^{88}\text{Sr} = {}^{88}\text{total-}I_{86.5} \times 0.796310 \left({}^{176}\text{Yb}^{2+}\right)$$

$$(1)$$

Rb interference

Rubidium limits the types of samples that can be analyzed for Sr isotopic composition without chemical purification. Rb can be removed by "on-filament chemistry" in TIMS, which is not available in ICPMS. The mass resolution required for the separation of ^{87}Rb and ^{87}Sr masses (M/ΔM = ca. 296,000) cannot be achieved by a normal TIMS or ICPMS (M/ΔM = ca. 500).

The main problem of Rb interference correction arises from the IMF; the lighter and heavier isotopes of an element behave differently during the course of mass spectrometric measurement. Each element has its own mass bias factor. For Sr, the assumed ratio of ^{86}Sr/^{88}Sr (= 0.1194) is used for the correction of the IMF, but this internal normalization cannot be applied for Rb because this element consists of only two isotopes.

During ICPMS measurement, isotopic fractionation of two elements of similar mass should be similar, albeit not identical (White et al. 2000). Therefore, for measurement of the ^{87}Sr/^{86}Sr ratio for low-Rb/Sr materials such as biogenic apatite and plagioclase, it has been assumed that Rb and Sr isotopes behave in the same way during LA-ICPMS analysis (Ramos et al. 2004; Vroon et al. 2008; Willmes et al. 2016). After Kr and REE^{2+} interference correction, the measured ^{87}Rb/^{85}Rb ratios of NIST SRM 616, Jeju plagioclase, and shark teeth were calculated using the IUPAC ^{87}Rb/^{85}Rb ratio (= 0.3856; Meija et al. 2016) and mass bias factor (*β*) of Sr calculated exponentially from measured ^{86}Sr/^{88}Sr and 0.1194. Then, the ^{87}Sr peak

Table 2 Er and Yb isotopic compositions and ratios reported in the literature

Amount fraction (Chang et al. 1998)						
	^{162}Er	^{164}Er	^{166}Er	^{167}Er	^{168}Er	^{170}Er
Mean	0.001387	0.016009	0.335027	0.228691	0.269784	0.149102
Error	0.000014	0.000010	0.000104	0.000026	0.000051	0.000103
Isotopic ratio (Vervoort et al. 2004, normalized using ^{172}Yb/^{174}Yb = 0.68321)						
	^{168}Yb/^{171}Yb	^{170}Yb/^{171}Yb	^{172}Yb/^{171}Yb	^{173}Yb/^{171}Yb	^{176}Yb/^{171}Yb	^{176}Yb/^{173}Yb
Mean	0.008876	0.212562	1.531736	1.132338	0.901691	0.796310
Error	0.000008	0.000009	0.000046	0.000050	0.000075	0.000034

intensity was calculated by subtracting the ^{87}Rb contribution from the intensity of mass 87. As shown in Fig. 1, the average ^{87}Sr/^{86}Sr (0.7083 ± 0.0003, n = 14) of SRM 616 closely matched that of the certificate (0.7080 ± 0.0002; Wise and Watters 2012), despite its relatively low Sr concentration (41.72 μg/g). The ^{87}Sr/^{86}Sr ratio (average = 0.70419 ± 0.00003, n = 32) of Jeju plagioclase was consistent with the solution MC-ICPMS result (0.704187–0.704139). These results

indicate that β (Sr) can be used for Rb correction for low-Rb/Sr materials.

Polyatomic molecules (^{40}Ar^{31}P^{16}O or ^{40}Ca^{31}P^{16}O) may exert isobaric interference on mass 87 during the ICPMS analysis of phosphate material (Horstwood et al. 2008; Lewis et al. 2014; Müller and Anczkiewicz 2016; Willmes et al. 2016). The ThO$^+$/Th$^+$ ratio is typically used as an indicator of oxide formation, because ThO$^+$ is the strongest oxide product within the plasma (Kent and Ungerer 2005).
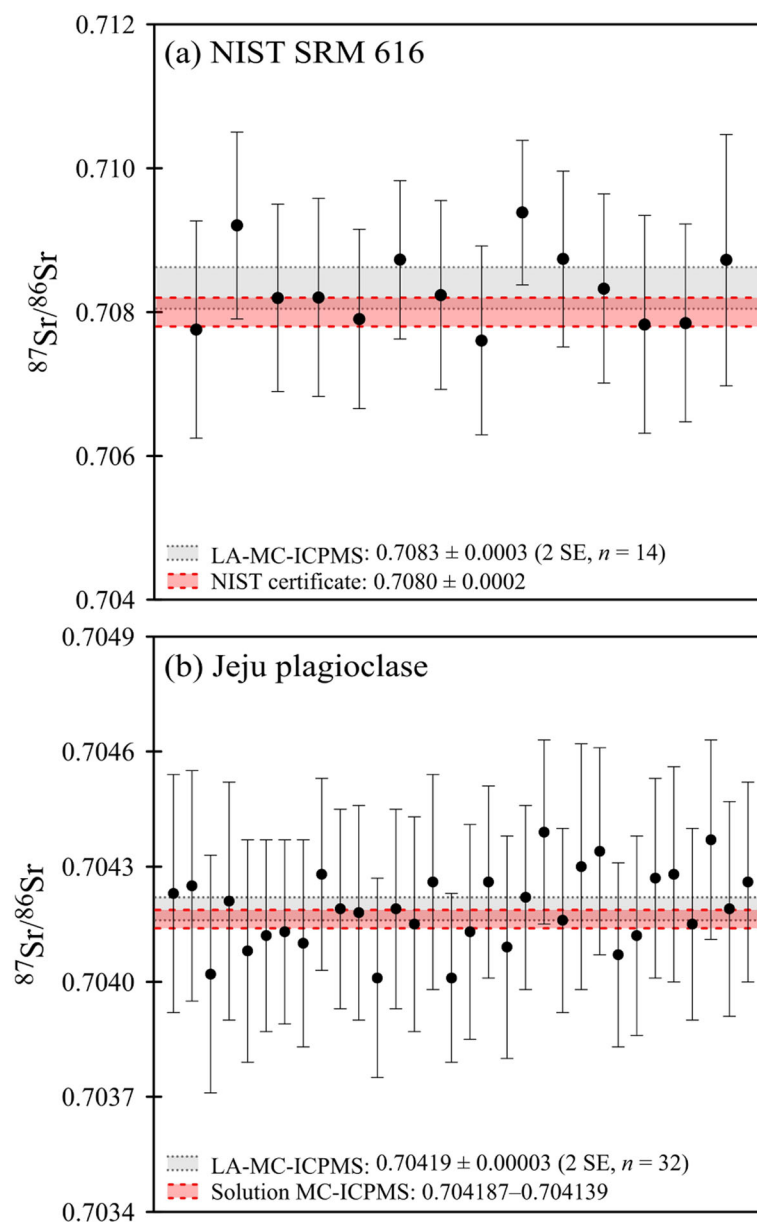
Fig. 1 ^{87}Sr/^{86}Sr ratios obtained via LA-MC-ICPMS for NIST SRM 616 (**a**) and Jeju plagioclase (**b**) assuming equal mass bias factors for Rb and Sr. Vertical error bars denote 2 standard errors. Gray dotted lines represent average LA-MC-ICPMS results. Red dashed lines represent the certified value (**a**, 0.7080 ± 0.0002; Wise and Watters 2012) and the solution MC-ICPMS result (**b**, 0.704187–0.704139)

The ThO$^+$/Th$^+$ ratio measured in each session varied from 0.77 to 0.16%. The enameloid of the shark teeth yielded average ^{87}Sr/^{86}Sr ratios of 0.70929 ± 0.00001 (session 1, n = 11), 0.70922 ± 0.00002 (session 2, n = 19), 0.70921 ± 0.00002 (session 3, n = 16), and 0.70922 ± 0.00002 (session 4, n = 21) (Fig. 2). These ratios approached the modern seawater value (0.70918; Faure and Mensing 2005) and solution MC-ICPMS results (0.709205 ± 0.000035, bull shark; 0.709170 ± 0.000025, spot-tail shark). It is noted that the LA-MC-ICPMS ^{87}Sr/^{86}Sr ratio was highest in session 1, in which ThO$^+$/Th$^+$ was also highest (0.77%). However, small ^{87}Sr/^{86}Sr differences require additional studies to verify the reproducibility of this effect. In fact, it has been reported that polyatomic interference is negligible for samples with Sr contents higher than 1900 μg/g (Simonetti et al. 2008). The shark teeth analyzed in this study are sufficiently high in Sr (∼ 1600 μg/g).

The ^{85}Rb/^{86}Sr ratios of glass SRMs measured during laser ablation varied inconsistently (Fig. 3), manifesting that the IMF of Rb and Sr isotopes occurred differently. The employment of β (Sr) as β (Rb) yielded widely variable ^{87}Sr/^{86}Sr ratios for SRM 610 and 612. The averages for SRM 610 (0.7138 ± 0.0011, n = 81) and SRM 612 (0.7116 ± 0.0004, n = 15) deviated substantially from the recommended values.

We calculated β (Rb) using known ^{87}Sr/^{86}Sr ratios of standard materials as described in Eq. (2), where "m" and "c" denote the measured and corrected values, respectively, and "M" indicates atomic weight. The ^{87}Rb/^{85}Rb ratio of 0.3856 was taken from Meija et al. (2016).

$$\left(\frac{^{87}Sr}{^{86}Sr}\right)_m = \left(\frac{^{87}Sr}{^{86}Sr}\right)_c \times \left(\frac{M_{86\,strontium}}{M_{87\,strontium}}\right)^\beta$$

$$^{87}Rb_m = \text{Intensity}_{87} - \left(\frac{^{87}Sr}{^{86}Sr}\right)_m \times {}^{86}Sr_m$$

$$\beta(Rb) = \frac{\ln\left[\dfrac{0.3856}{\left(\dfrac{^{87}Rb}{^{85}Rb}\right)_m}\right]}{\ln\left(\dfrac{M_{87\,rubidium}}{M_{85\,rubidium}}\right)} \tag{2}$$

The calculated β (Rb) and β (Sr) for SRM 610 and SRM 612 in session 1 are plotted in Fig. 4. As shown here, there were weak to moderate correlations between β (Rb) and β (Sr). The correlation coefficient (R^2) and the difference between β (Sr) and β (Rb) calculated for each analytical session are summarized graphically in Fig. 5. Spot-by-spot data and regression parameters are listed in Table S1. The R^2 values of NIST SRM 610 varied significantly from 0.74 to 0.26 (session 1, n = 14), 0.57 to 0.04 (session 2, n = 23), 0.58 to 0.11 (session 3, n = 17), 0.71 to 0.17 (session 4, n = 17), and 0.61 to 0.29 (session 5, n = 10). This was also true for SRM 612 (R^2 = 0.36–0.02, n = 15). As displayed in Fig. 5, β (Sr) was consistently higher than β (Rb), except for data obtained in session 2.

In summary, Rb and Sr isotopes behaved differently during LA-MC-ICPMS but there was a correlation (albeit not strong) between the mass bias factors of these elements.
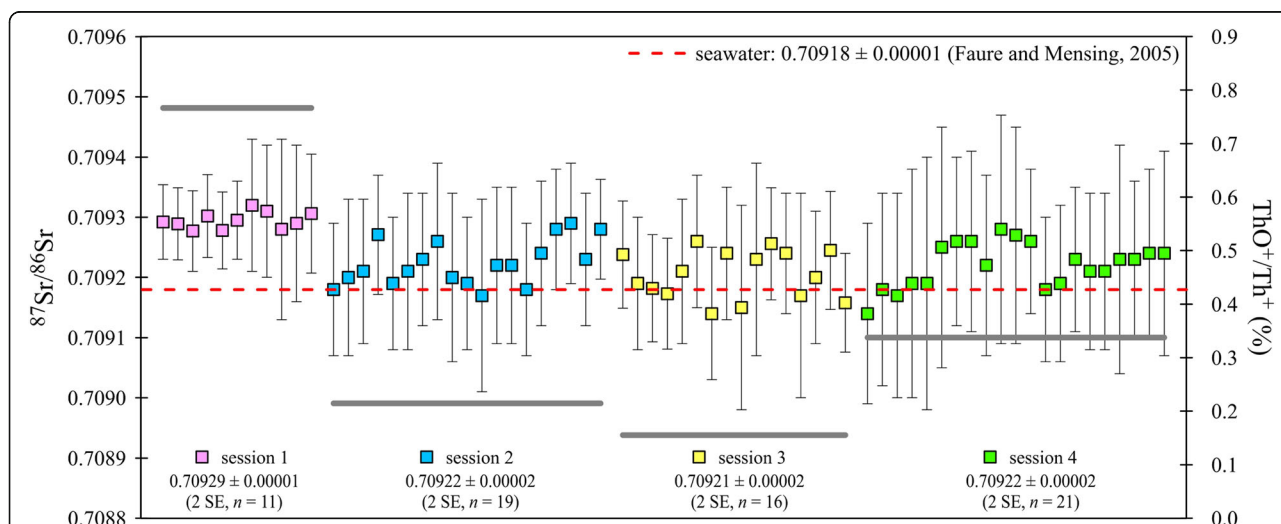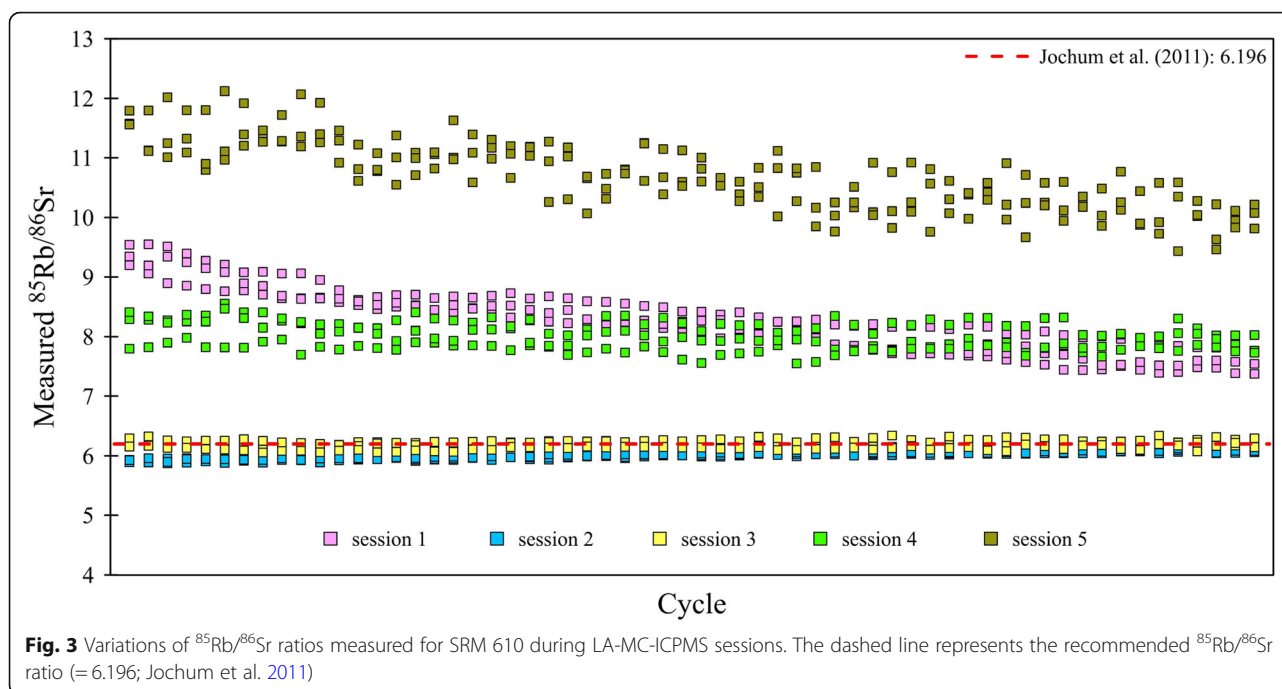
Fig. 2 ^{87}Sr/^{86}Sr ratios obtained via LA-MC-ICPMS for the shark teeth assuming equal mass bias factors for Rb and Sr. Vertical error bars denote 2 standard errors. The dashed line represents the modern seawater value (^{87}Sr/^{86}Sr = 0.70918; Faure and Mensing 2005). The ThO$^+$/Th$^+$ ratios measured before the beginning of each analytical session are marked as thick gray lines

Fig. 3 Variations of $^{85}Rb/^{86}Sr$ ratios measured for SRM 610 during LA-MC-ICPMS sessions. The dashed line represents the recommended $^{85}Rb/^{86}Sr$ ratio (= 6.196; Jochum et al. 2011)

Bracketing calibration

The correlation between the mass bias factors of Rb and Sr led us to apply the standard bracketing method (Albarède and Beard 2004) to measure $^{87}Sr/^{86}Sr$ and $^{85}Rb/^{86}Sr$ ratios. First, β (Rb) was interpolated from the β (Rb)$-\beta$ (Sr) correlation observed before and after each measurement. Then, measured $^{87}Rb/^{85}Rb$ was exponentially derived from the interpolated β (Rb) and IUPAC $^{87}Rb/^{85}Rb$ (= 0.3856, Meija et al. 2016), and the ^{87}Rb contribution was subtracted from the intensity of mass 87. Finally, the $^{87}Sr/^{86}Sr$ ratio was calculated from the Rb-corrected $^{87}Sr/^{86}Sr$ and β (Sr). The corrected $^{87}Sr/^{86}Sr$ ratios of the NIST SRMs are shown in Fig. 6. The mean of all $^{87}Sr/^{86}Sr$ ratios for SRM 610 (0.70986 ± 0.00017, n = 71) was consistent with the recommended value (0.709699 ± 0.000018; Woodhead and Hergt 2001) within an acceptable error range. The $^{85}Rb/^{86}Sr$ ratios calculated using this bracketing protocol ranged from 6.479 to 5.739, with an average of 6.186 ± 0.027 (n = 71), which coincides with the recommended value (6.196; Jochum et al. 2011). Average values of SRM 612 were 0.70899 ± 0.00038 for $^{87}Sr/^{86}Sr$ and 3.001 ± 0.035 for $^{85}Rb/^{86}Sr$ (n = 13), which also agree with the recommended values ($^{87}Sr/^{86}Sr$ = 0.709063 ± 0.000020, Woodhead and Hergt 2001; $^{85}Rb/^{86}Sr$ = 3.005, Jochum et al. 2011). These results suggest the possibility that LA-MC-ICPMS can yield reliable Rb–Sr isotope results for high-Rb/Sr materials using the correlation between β (Rb) and β (Sr). It is noted that the analytical strategy proposed in this study is different from the bracketing method described in previous Sr isotopic works (McCulloch et al. 2005; Jackson and Hart 2006), where the measured $^{85}Rb/^{87}Rb$ of bracketing standard was externally used to correct the mass bias of Rb in samples.

Conclusions

(1) After the Kr and REE^{2+} correction, the $^{87}Sr/^{86}Sr$ ratios of low-Rb/Sr materials (NIST SRM 616, Jeju plagioclase, and shark teeth) were measured accurately by assuming that Rb and Sr isotopes behave in the same way during LA-MC-ICPMS. During measurements of the shark teeth, polyatomic isobaric interference on mass 87 was seemingly insignificant.

(2) Use of the Sr mass bias factor for the correction of Rb interference yielded highly variable and inaccurate $^{87}Sr/^{86}Sr$ ratios for high-Rb/Sr materials such as NIST SRM 610 and SRM 612. The mass bias factor of Rb was calculated from the recommended $^{87}Sr/^{86}Sr$ ratios of these SRMs. There were weak to moderate correlations between the mass bias factors of Rb and Sr. Reliable $^{87}Sr/^{86}Sr$ and $^{85}Rb/^{86}Sr$ results were obtained using the interpolated mass bias factor of Rb calculated by the standard bracketing method.

(3) This study showed that the Rb–Sr isotopic composition of high-Rb/Sr materials can be measured accurately using LA-MC-ICPMS by monitoring the IMF of Rb and Sr isotopes and applying the standard bracketing method.
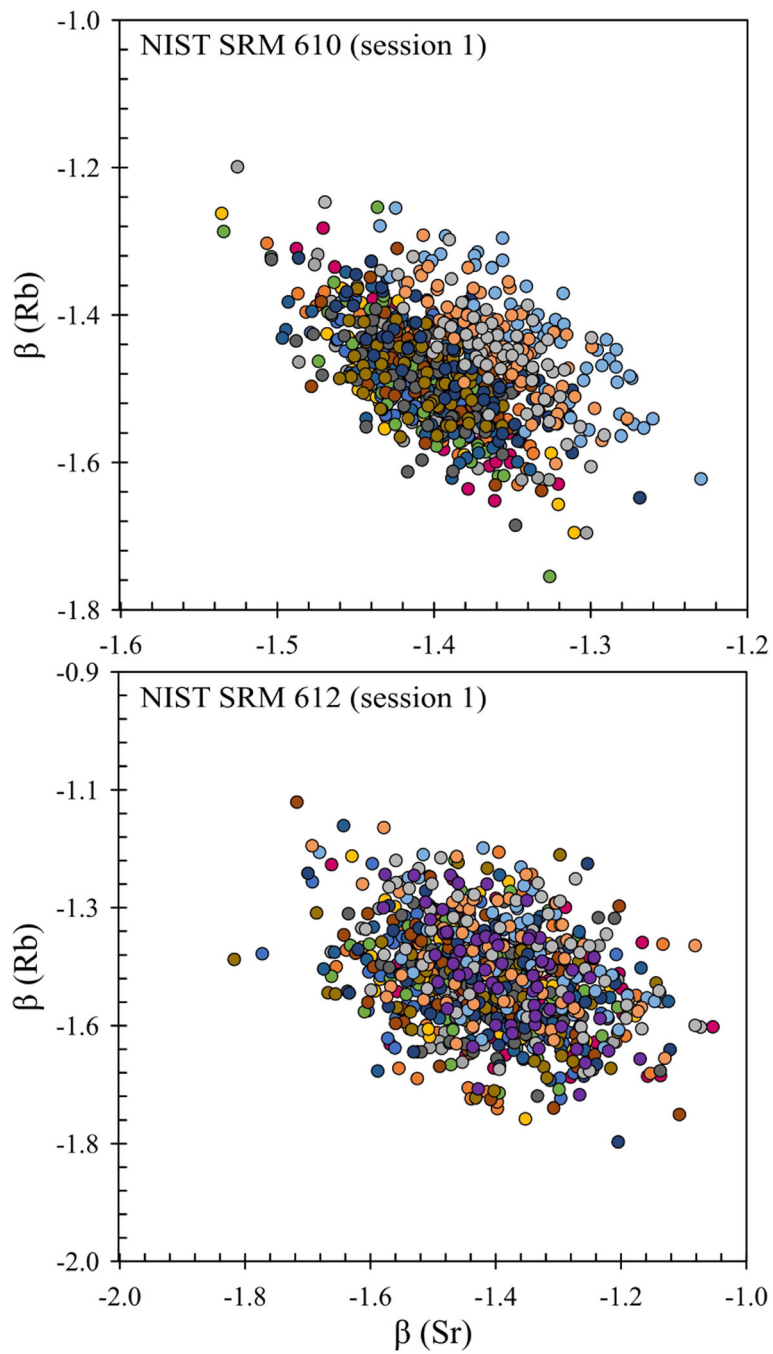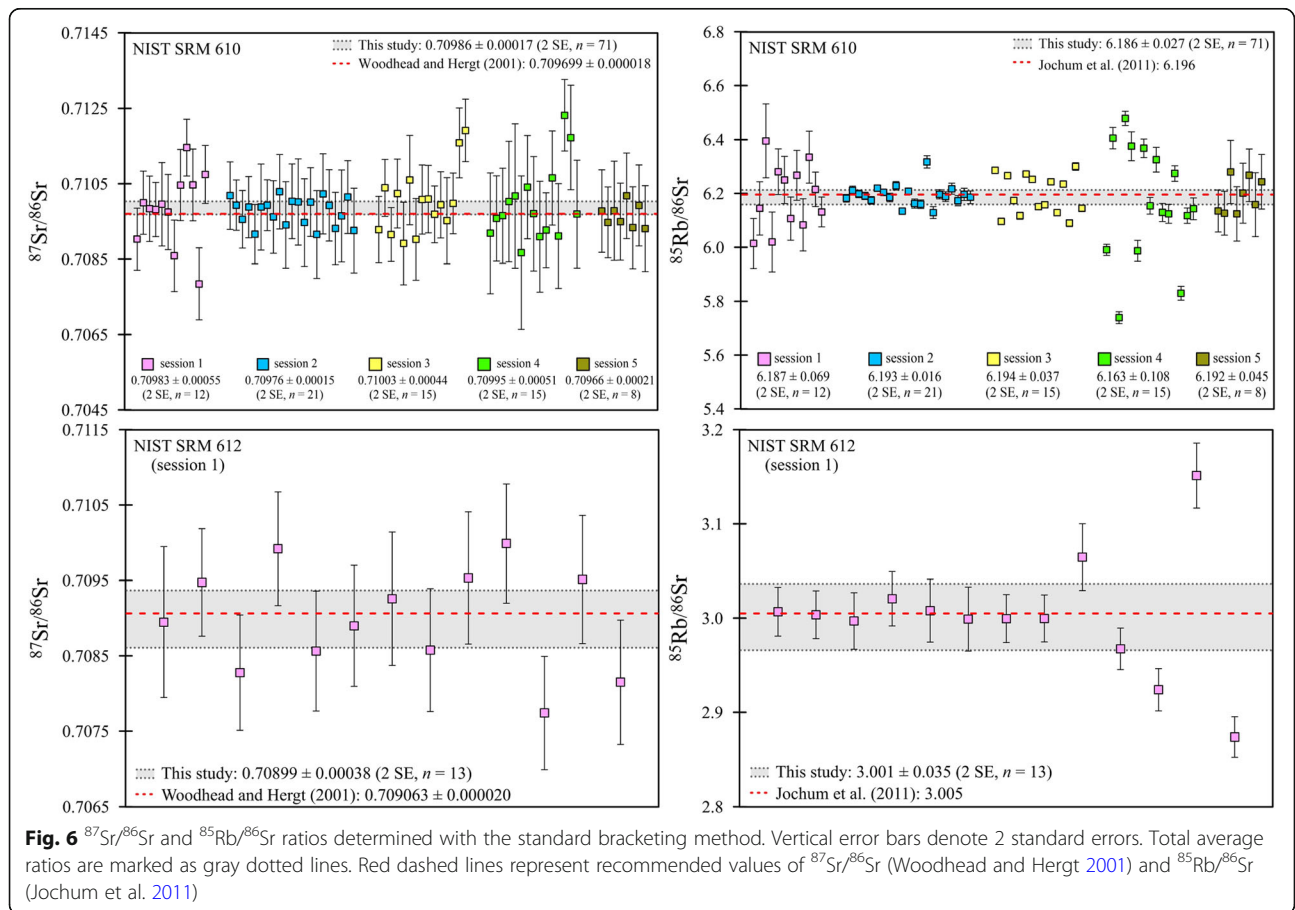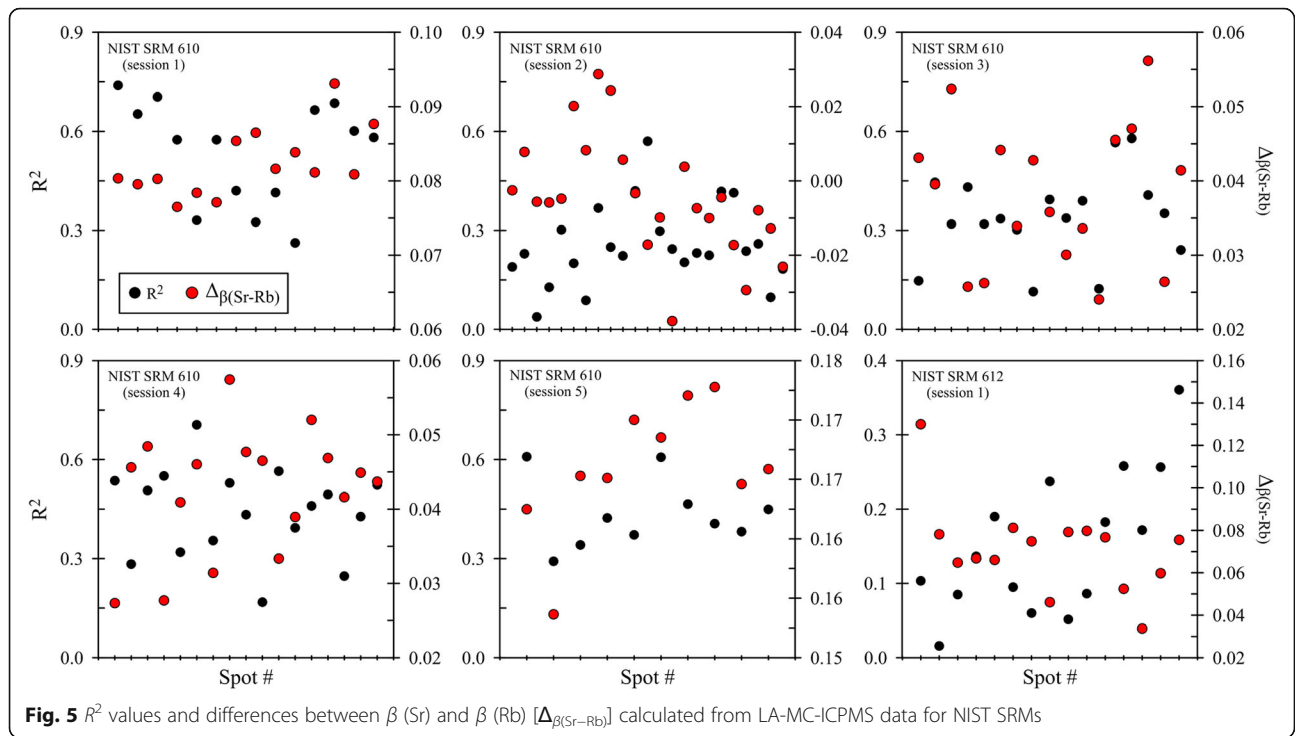
Fig. 4 Plots of β (Rb) versus β (Sr) calculated from NIST SRM data for analytical session 1 of LA-MC-ICPMS. Data for each analyzed spot are shown in different colors

Fig. 5 R^2 values and differences between β (Sr) and β (Rb) [$\Delta_{\beta(Sr-Rb)}$] calculated from LA-MC-ICPMS data for NIST SRMs

Fig. 6 ^{87}Sr/^{86}Sr and ^{85}Rb/^{86}Sr ratios determined with the standard bracketing method. Vertical error bars denote 2 standard errors. Total average ratios are marked as gray dotted lines. Red dashed lines represent recommended values of ^{87}Sr/^{86}Sr (Woodhead and Hergt 2001) and ^{85}Rb/^{86}Sr (Jochum et al. 2011)

Supplementary Information

Additional file 1 : Table S1. Summary of in situ mass bias factors and correlation parameters calculated from LA-MC-ICPMS data for NIST SRMs.

Abbreviations

LA-MC-ICPMS: Laser ablation-multicollector-inductively coupled plasma mass spectrometry; NIST: National Institute of Standards and Technology of the USA; SRM: Standard reference material; REE: Rare earth element; IMF: Instrumental mass fractionation; TIMS: Thermal ionization mass spectrometry; SE: Standard error; IUPAC: International Union of Pure and Applied Chemistry; β: Mass bias factor

Authors' contributions

ACSC designed the research. SGY, MJJ, and YMK prepared the samples and standards. SGY, YJJ, MJJ, and YMK carried out isotope measurements. SGY drafted an early version of the manuscript. All authors polished it and approved the final manuscript.

Availability of data and materials

The datasets analyzed during the current study are available from the corresponding author on reasonable request.

Competing interests

The authors declare no competing interests.

References

Aggarwal J, Habicht-Mauche J, Juarez C. Application of heavy stable isotopes in forensic isotope geochemistry: a review. Appl Geochem. 2008;23:2658–66. https://doi.org/10.1016/j.apgeochem.2008.05.016.

Albarède F, Beard B. Analytical methods for non-traditional isotopes. Rev Mineral Geochem. 2004;55:113–52. https://doi.org/10.2138/gsrmg.55.1.113.

Campbell NR, Wood A. The radioactivity of the alkali metal. Math Proc Camb Philos Soc. 1906;145:15–21.

Chang T-L, Zhao M-T, Li W-J, Wang J, Qian Q-Y. Absolute isotopic composition and atomic weight of erbium. Int J Mass Spectrom. 1998;177:131–6. https://doi.org/10.1016/S1387-3806(98)14057-5.

Christensen JN, Halliday AN, Lee D-C, Hall CM. In situ Sr isotopic analysis by laser ablation. Earth Planet Sci Lett. 1995;136:79–85. https://doi.org/10.1016/0012-821X(95)00181-6.

Ericson JE. Strontium isotope characterization in the study of prehistoric human ecology. J Hum Evol. 1985;14:503–14. https://doi.org/10.1016/S0047-2484(85)80029-4.

Faure G, Mensing TM. Isotopes: principles and applications. 3rd ed. Hoboken: Wiley; 2005.

Horstwood MSA, Evans JA, Montgomery J. Determination of Sr isotopes in calcium phosphates using laser ablation inductively coupled plasma mass spectrometry and their application to archaeological tooth enamel. Geochim Cosmochim Acta. 2008;72:5659–74. https://doi.org/10.1016/j.gca.2008.08.016.

Jackson MG, Hart SR. Strontium isotopes in melt inclusions from Samoan basalts: implications for heterogeneity in the Samoan plume. Earth Planet Sci Lett. 2006;245:260–77. https://doi.org/10.1016/j.epsl.2006.02.040.

Jochum KP, Weis U, Stoll B, Kuzmin D, Yang Q, Raczek I, Jacob DE, Stracke A, Birbaum K, Frick DA, Günther D, Enzweiler J. Determination of reference values for NIST SRM 610-617 glasses following ISO guidelines. Geostand Geoanal Res. 2011;35:397–429. https://doi.org/10.1111/j.1751-908X.2011.00120.x.

Kane JS. A history of the development and certification of NIST glass SRMs 610-617. Geostand Newsl. 1998;22:7–13. https://doi.org/10.1111/j.1751-908X.1998.tb00541.x.

Kemp NE, Park JH. Ultrastructure of the enamel layer in developing teeth of the shark *Carcharhinus menisorrah*. Arch Oral Biol. 1974;19:633–40. https://doi.org/10.1016/0003-9969(74)90131-9.

Kent AJR, Ungerer CA. Production of barium and light rare earth element oxides during LA-ICP-MS microanalysis. J Anal Atom Spectrom. 2005;20:1256–62. https://doi.org/10.1039/B505734E.

Lewis J, Coath CD, Pike AWG. An improved protocol for ^{87}Sr/^{86}Sr by laser ablation multi-collector inductively coupled plasma mass spectrometry using oxide reduction and a customised plasma interface. Chem Geol. 2014;390: 173–81. https://doi.org/10.1016/j.chemgeo.2014.10.021.

McCulloch M, Cappo M, Aumend J, Müller W. Tracing the life history of individual barramundi using laser ablation MC-ICP-MS Sr-isotopic and Sr/Ba ratios in otoliths. Mar Freshw Res. 2005;56:637–44. https://doi.org/10.1071/MF04184.

Meija J, Coplen TB, Berglund M, Brand WA, De Bièvre P, Gröning M, Holden NE, Irrgeher J, Loss RD, Walczyk T, Prohaska T. Isotopic compositions of the elements 2013 (IUPAC Technical Report). Pure Appl Chem. 2016;88:293–306. https://doi.org/10.1515/pac-2015-0503.

Müller W, Anczkiewicz R. Accuracy of laser-ablation (LA)-MC-ICPMS Sr isotope analysis of (bio)apatite – a problem reassessed. J Anal At Spectrom. 2016;31: 259–69. https://doi.org/10.1039/C5JA00311C.

Paton C, Hellstrom J, Paul B, Woodhead J, Hergt J. Iolite: freeware for the visualization and processing of mass spectrometric data. J Anal At Spectrom. 2011;26:2508–18. https://doi.org/10.1039/C1JA10172B.

Pearce NJG, Perkins WT, Westgate JA, Gorton MP, Jackson SE, Neal CR, Chenery SP. A compilation of new and published major and trace element data for NIST SRM 610 and NIST SRM 612 glass reference materials. Geostand Newsl. 1997;21:115–44. https://doi.org/10.1111/j.1751-908X.1997.tb00538.x.

Ramos FC, Wolff JA, Tollstrup DL. Measuring ^{87}Sr/^{86}Sr variations in minerals and groundmass from basalts using LA-MC-ICPMS. Chem Geol. 2004;211:135–58. https://doi.org/10.1016/j.chemgeo.2004.06.025.

Rocholl ABE, Simon K, Jochum KP, Bruhn F, Gehann R, Kramar U, Luecke W, Molzahn M, Pernicka E, Seufert M, Spettel B, Stummeier J. Chemical characterisation of NIST silicate glass certified reference material SRM 610 by ICP-MS, TIMS, LIMS, SSMS, INAA, AAS and PIXE. Geostand Newsl. 1997;21:101–14. https://doi.org/10.1111/j.1751-908X.1997.tb00537.x.

Simonetti A, Buzon MR, Creaser RA. In-situ elemental and Sr isotope investigation of human tooth enamel by laser ablation-(MC)-ICP-MS: successes and pitfalls. Archaeometry. 2008;50:371–85. https://doi.org/10.1111/j.1475-4754.2007.00351.x.

Steiger RH, Jäger E. Subcommission on geochronology: convention on the use of decay constants in geo- and cosmochronology. Earth Planet Sci Lett. 1977; 36:359–62. https://doi.org/10.1016/0012-821X(77)90060-7.

Thirlwall MF. Long-term reproducibility of multicollector Sr and Nd isotope ratio analysis. Chem Geol. 1991;94:85–104. https://doi.org/10.1016/0168-9622(91)90002-E.

Vervoort JD, Patchett PJ, Söderlund U, Baker M. Isotopic composition of Yb and the determination of Lu concentrations and Lu/Hf ratios by isotope dilution using MC-ICPMS. Geochem Geophys Geosyst. 2004;5. https://doi.org/10.1029/2004GC000721.

Vroon PZ, Wagt B, Koornneef JM. Problems in obtaining precise and accurate Sr isotope analysis from geological materials using laser ablation MC-ICPMS. Anal Bioanal Chem. 2008;390:465–76. https://doi.org/10.1007/s00216-007-1742-9.

White WM, Albarède F, Télouk P. High-precision analysis of Pb isotope ratios by multi-collector ICP-MS. Chem Geol. 2000;167:257–70. https://doi.org/10.1016/S0009-2541(99)00182-5.

Willmes M, Kinsley L, Moncel M-H, Armstrong RA, Aubert M, Eggins S, Grün R. Improvement of laser ablation in situ micro-analysis to identify diagenetic alteration and measure strontium isotope ratios in fossil human teeth. J Archaeol Sci. 2016;70:102–16. https://doi.org/10.1016/j.jas.2016.04.017.

Wise SA, Watters RL. Certificate of analysis standard reference material 616. National Institute of Standards and Technology. Gaithersburg; 2012.

Woodhead JD, Hergt JM. Strontium, neodymium and lead isotope analyses of NIST glass certified reference materials: SRM 610, 612, 614. Geostand Newsl. 2001;25:261–6. https://doi.org/10.1111/j.1751-908X.2001.tb00601.x.

Publisher's Note

Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.