



Tin stable isotope analysis of geological materials by double-spike MC-ICPMS



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ABSTRACT

Tin is a volatile as well as chalcophile and siderophile element, and this geochemical behaviour gives rise to a broad range of potential applications for Sn as a stable isotope tracer in geological processes. We present the first high-precision method to analyse the stable isotopic composition of Sn in geological materials using ion-exchange chromatography and double-spike multi-collector inductively-coupled-plasma mass-spectrometry (MC-ICPMS). We apply these methods to analyse the Sn stable isotopic composition of four geological reference materials, including a number of replicate digestions of BHVO-2 and BCR-2 to assess the reproducibility of the technique. Tin was purified prior to analysis using TRU resin to remove matrix and interfering elements. Isotopic ratios were measured using a Thermo-Fischer Neptune Plus MC-ICPMS combined with a ^{117}Sn – ^{122}Sn double-spike to correct for any mass dependent fractionation resulting from instrumental mass bias or incomplete yields from chemical purification. Results are expressed in delta notation as $\delta^{122/118}\text{Sn}$, representing the per mil (‰) difference in the $^{122/118}\text{Sn}$ ratio of the sample relative to our in-house standard Sn_IPGP. Based on replicate analyses of the USGS reference materials BHVO-2 and BCR-2, we estimate the external reproducibility to be ca. $\pm 0.065\%$ (2 sd) on the $\delta^{122/118}\text{Sn}$ ratio, or ca. $\pm 0.016\%$ per amu. Analyses of these plus two additional USGS reference materials, AGV-2 and GSP-2, show a large range ($> 0.2\%$ on $\delta^{122/118}\text{Sn}$) of Sn stable isotopic compositions that are correlated with igneous differentiation indicators (e.g. SiO_2 content), indicating that Sn isotopes are fractionated during igneous processes. These results indicate significant potential for Sn stable isotopes as a tracer of magmatic differentiation and the redox state of the mantle. In addition, Sn stable isotopes may prove useful in tracing diverse geological processes such as volatilisation/condensation and metal–silicate/metal–sulphide differentiation.

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1. Introduction

Tin is a moderately siderophile, chalcophile and volatile element with 10 naturally occurring stable isotopes. It has two main oxidation states (+2, +4), and forms alloys with many metals. Tin exhibits incompatible and lithophile behaviour during igneous processes and, as such, is concentrated in the crust relative to the mantle with basalts typically containing 0.5–5.0 ppm Sn, as compared with 0.12 ppm in primitive mantle (Jochum et al., 1993).

Due to its geochemical behaviour, the abundance of Sn in the silicate Earth is a consequence of both segregation of metals during core formation and volatility related depletion in the precursor materials from which Earth formed. Tin is depleted in the silicate Earth

relative to CI chondrites by a factor of 33 (Jochum et al., 1993). A major unresolved issue in cosmochemistry is the widespread depletion of volatile elements that is observed in the terrestrial planets and in meteorites (e.g., Halliday and Porcelli, 2001; O'Neill and Palme, 2008). At first order, the abundance of moderately volatile elements is correlated with their condensation temperature: the CV chondrites are depleted in volatile elements when compared to the CI chondrites (meteorites that have the same chemical composition as the Sun), the Earth is more depleted in volatile elements, and the Moon even more so. In addition, carbonaceous chondrites exhibit a volatile depletion trend in the order $\text{CI} > \text{CM} > \text{CO} > \text{CV}$. Several scenarios have been proposed to explain this volatile element depletions including incomplete condensation from solar nebula (Wasson and Chou, 1974; Albarède, 2009), or evaporation on the parent body (Tyburczy et al., 1986; Moynier et al., 2006; O'Neill and Palme, 2008; Paniello et al., 2012; Kato et al., 2015). Isotopes are known to fractionate during kinetic processes related

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to volatility, and therefore isotopic variations of moderately volatile elements have the potential to differentiate between these different mechanisms. For instance, Zn isotope ratios have been shown to correlate with Zn concentration in carbonaceous chondrites (Luck et al., 2005), which is opposite to what would be expected from evaporation processes and therefore was interpreted as an evidence for incomplete condensation in the nebula. On the other hand, large Zn isotopic fractionation in lunar samples compared to terrestrial rocks argues for evaporation during global heating of the Moon (Paniello et al., 2012; Kato et al., 2015). Recent work on Se isotopes did not find any isotopic variations amongst carbonaceous chondrites, suggesting a decoupling between Se and Zn (Vollstaedt et al., 2016), which may be related to the difference of volatility (Se is more volatile than Zn) between these elements or their different geochemical behaviour (chalcophile vs lithophile). Tin has a 50% condensation temperature of 704 K (Lodders, 2003), intermediate between Zn (723 K) and Se (697 K), and is strongly chalcophile. It therefore has the potential to investigate the origin of the difference of behaviour between Zn and Se isotopes. In addition, volatility-related stable isotope fractionation of Sn may give insights into the compositions and source regions of accreting bodies and the relative timing of their accretion to Earth and provide a means to trace volatilisation during thermal events such as impacts or planetary magmatism.

Volatility-corrected depletion of Sn in the silicate Earth is comparable to other moderately siderophile elements, such as W, Mo and Pb (Jochum et al., 1993; Palme and O'Neill, 2014). Corresponding depletions between moderately siderophile elements, such as Sn and Pb, are useful for providing constraints on the physical conditions that prevailed during metal–silicate equilibrium (e.g., Vogel et al., 2012). Metal–silicate partitioning of Sn has been studied at a range of temperatures and pressures, and has been shown to vary significantly with changing metal composition and oxygen fugacity (Capobianco et al., 1999; Righter et al., 2010). Stable isotope fractionation may result from segregation of metals during metal–silicate differentiation, and may provide further tools for investigating these processes. Such fractionations have been sought for a number of isotopic systems, with some revealing significant isotopic fractionation (e.g., Burkhardt et al., 2014; Savage et al., 2015; Creech et al., 2017). Stable isotope analysis of Sn in various materials have considerable potential to provide further constraints on metal–silicate/metal–sulphide differentiation in Earth and other terrestrial bodies, especially if combined with physical partitioning experiments.

In this paper, we present the first high-precision method to analyse the stable isotopic composition of Sn in geological materials using ion-exchange chromatography and double-spike MC-ICPMS. We apply these methods to analyse the Sn stable isotopic composition of four geological reference materials, including a number of replicate digestions of BHVO-2 and BCR-2 to determine the reproducibility of the technique. We present data for these and two additional geological reference materials, and explore the possibility for stable isotope fractionation of Sn in nature.

2. Design and preparation of the tin double-spike

The double-spike method is a well established approach for the precise determination of isotope ratios, and has been applied to a broad range of isotope systems using both TIMS and MC-ICPMS analysis (e.g., Pb, Cr, Zn, Fe, Ni, Ti, Mo, Ca, Cd, Pt; Compston and Oversby, 1969; Hamelin et al., 1985; Beard and Johnson, 1999; Anbar et al., 2001; Siebert et al., 2001; Baker et al., 2004; Dideriksen et al., 2006; Gopalan et al., 2006; Schoenberg et al., 2008; Schmitt et al., 2009; Arnold et al., 2010; Gall et al., 2012; Greber et al., 2012; Creech et al., 2014; Millet et al., 2016; Creech et al., 2017). The double-spike approach has a number of advantages over other methods (e.g. sample–standard bracketing), such as the possibility

to determine mass-dependent isotopic fractionation from a single isotope measurement, and correct for any mass-dependent isotope fractionation induced during chemical purification and mass spectrometry. The double-spike method is also less susceptible to potential analytical artefacts induced by trace amounts of sample matrix that may remain and incomplete yields of the analyte following chemical purification (Dideriksen et al., 2006; Schoenberg et al., 2008). In addition, the double-spike also permits for precise and accurate determination of Sn concentrations from the same analysis as the isotope data.

With 10 naturally occurring stable isotopes of Sn, there are numerous possible combinations for the Sn double-spike and for the double-spike inversion. Our choice of Sn double-spike was made on the basis of i) avoiding potential interferences from elements with overlapping masses, and ii) minimum theoretical errors as calculated using the *Double Spike Toolbox* of Rudge et al. (2009). The low mass isotopes of Sn are the least abundant, and suffer from isobaric interferences from abundant isotopes of Cd and In (Fig. 1). Although some isobaric interferences also exist for high mass Sn isotopes, these occur from relatively low abundance isotopes that are either readily separated from Sn and occur in lower abundances in silicate rocks (i.e., Te), or are only present as rare, gas based interferences that are readily corrected, if indeed present, through the subtraction of on-peak zeros (where baseline is monitored on-peak and subtracted from sample measurements; i.e., Xe). We elected to use a ^{117}Sn – ^{122}Sn double-spike, using a ^{117}Sn – ^{118}Sn – ^{122}Sn – ^{124}Sn inversion. In addition to minimising the potential for isobaric interferences, this combination is predicted to have minimal error on double-spike corrected ratios (ca. 29 ppm/amu; Rudge et al., 2009) and to be accurate over a broad range of sample–spike mixing ratios (Fig. 2A), which is advantageous when sample Sn concentrations are not accurately known.

Two Sn isotope spikes (^{117}Sn , ^{122}Sn) were obtained from Isoflex (www.isoflex.com) in the form of metal powders, with certified isotopic compositions as given in Table 1. The spikes were carefully weighed before transferring to Savillex Teflon beakers for dissolution in 6 M HCl. Once the spike material was fully digested, the spike solutions were repeatedly evaporated to dryness, and finally redissolved in 6 M HCl for concentrations of 1000 $\mu\text{g mL}^{-1}$.

The ^{117}Sn – ^{122}Sn double-spike was then prepared by mixing the two spikes in the optimal proportions (54.63% ^{117}Sn , 45.37% ^{122}Sn) as calculated using the *Double Spike Toolbox* of Rudge et al. (2009). The double-spike mixture was then repeatedly evaporated to dryness, before taking up in 6 M HCl for a concentration of 1000 $\mu\text{g mL}^{-1}$. Precise isotopic determination by the double-spike technique requires accurate calibration of the double-spike composition. The method for calibration of the double-spike prepared here and a determination of the accuracy of the calibration are described below.

3. Materials and methods

3.1. Chemicals and standard solutions

All laboratory work was performed in a class-100 clean room environment using class-10 laminar flow hoods at the Institut de Physique du Globe de Paris, France. Pre-cleaned Savillex Teflon PFA beakers were used for all samples and solutions processed in this study. BASF Selectipur® AR grade acids (69% HNO_3 ; 37% HCl) were further purified by sub-boiling distillation using Savillex DST-1000. All dilutions were carried out using ultra-pure (18.2 M Ω cm) Milli-Q water.

Due to the unavailability of any certified isotope reference materials for Sn, we employed a Sn ICP solution standard for this purpose (PlasmaCal 1000 $\mu\text{g mL}^{-1}$ Sn ICP std in 20% HCl, lot #SC9202950), hereafter referred to as Sn_IPGP, and aliquots of this solution will be made available to other laboratories on request.

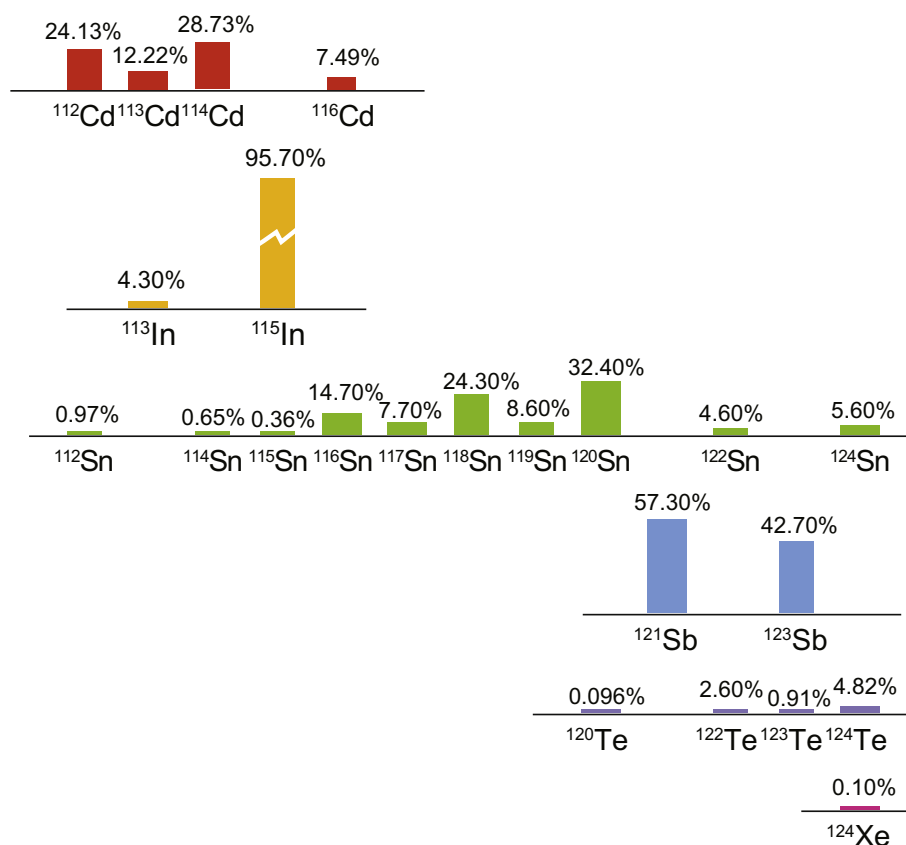


Fig. 1. Relative abundances of isotopes in the mass range of Sn from Meija et al. (2016).

3.2. Sample preparation and dissolution

Four well characterised, internationally available geological reference materials were analysed in this study, all of which are distributed by the USGS. These are: BHVO-2, which is a basalt from Kilauea, Hawaii, USA; BCR-2, which is a basalt from Colombia River, Oregon, USA; AGV-2, an andesite from Guano Valley, Oregon, USA; and GSP-2, a granodiorite from Silver Plume, Colorado, USA.

Digestions of rock powders were carried out using common HF-HNO₃ methods. Samples comprising 250–500 mg of rock powders were digested in a 1:3 mixture of HF:HNO₃ in closed Teflon beakers on a hotplate at 120 °C. Samples were double-spiked prior to digestion by adding the double-spike directly to the sample beaker for proportions of approximately 39.77% Sn from the double-spike and 60.23% from the sample. After dissolution, samples were dried down and the residue taken up in aqua regia and refluxed overnight at 150 °C to destroy any fluoride complexes that may have formed during the digestion. After drying down, the samples were then evaporated to dryness in 10 M HCl before finally bringing into solution in 2 mL of 0.5 M HCl for anion-exchange chemistry.

3.3. Chemical separation of Sn

Chemical separation of Sn was performed using Eichrom TRU resin, and is summarised in Table 2 and Fig. 3. While this resin is typically intended for extraction chromatography of actinides, it shows strong selectivity for other elements. Biorad columns were prepared with 1 mL per column of TRU resin and cleaned prior to sample loading with alternating volumes of acids (0.5 M HCl, 2 × 0.5 M HNO₃) and H₂O. Samples were loaded on the columns in 2 mL of 0.5 M HCl,

and subsequently rinsed with 4 mL of 0.5 M HCl and 7 mL of 0.25 M HCl. Tin cuts were collected in 10 mL of 0.5 M HNO₃. A small volume (0.3 mL) of 10 M HCl was added to the beakers prior to collection of Sn cuts to avoid the production of insoluble compounds arising from the Sn-HNO₃ mixture.

The chemical separation procedure was found to have Sn yields of ca. 70% for solution standards, which was deemed adequate for analysis using the double-spike. However, when applied to geological samples, Sn yields were found to be lower and variable between 13 and 66%. Despite this, replicate analyses of geological reference materials produced reproducible isotopic results, indicating that the double-spike correction is effective even with these variable yields, as discussed in Section 4.3 below.

3.4. Mass spectrometry and data reduction

Tin stable isotope measurements were carried out using a Thermo-Scientific Neptune Plus multi-collector inductively-coupled-plasma mass-spectrometer (MC-ICPMS) at the Institut de Physique du Globe de Paris, France. Operating conditions and measurement parameters are summarised in Table 3. Sample and standard solutions were prepared for isotope measurements with Sn concentrations of 100 ng mL⁻¹ in 0.5 M HCl. Solutions were introduced into the mass spectrometer using an ESI Apex-HF desolvator with a 100 μL min⁻¹ PFA nebuliser. The Neptune was run in low resolution mode, with a mass resolution of ~1860 (Table 3). Ion beams at ^{116}Sn , ^{117}Sn , ^{118}Sn , ^{119}Sn , ^{120}Sn , ^{121}Sb , ^{122}Sn , ^{123}Sb and ^{124}Sn were simultaneously collected in a single cycle using Faraday cups, with all Sn channels connected to amplifiers with 10¹¹ Ω resistors. This configuration resulted in a combined ion beam

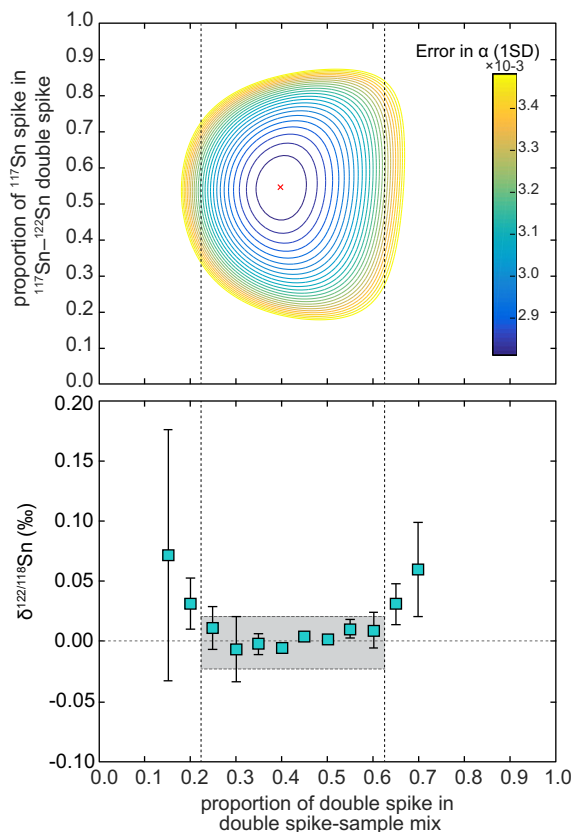


Fig. 2. A) Contour plot of error in α for the ^{117}Sn – ^{122}Sn double-spike with a ^{117}Sn – ^{118}Sn – ^{122}Sn – ^{124}Sn inversion, as a function of double-spike composition and double-spike–sample proportions, calculated using the *Double Spike Toolbox* of Rudge et al. (2009). Contours are at intervals of 1% of the optimal error on α (indicated by red cross), and thresholded to show only show data within 25% of the optimal error. Note that this combination results in a relatively broad region around the optimum where low errors are found. B) Measured $\delta^{122/118}\text{Sn}$ as a function of the proportion of double-spike in the double-spike–sample mixture from 0.15 to 0.70, equivalent to a standard-spike ratio from 5.7 to 0.4, or a factor of 0.4–1.8 times the theoretical optimal spike-sample proportion of 0.3977. The acceptable range of double-spike–sample mixtures is indicated by the shaded box, and the correspondence with the theoretical error in panel A is indicated by the dashed vertical lines.

intensity for all monitored Sn isotopes of ~ 60 V at an uptake rate of $\sim 100 \mu\text{L min}^{-1}$, corresponding to a sensitivity of ~ 600 V ppm^{-1} . Faraday collector gains were calibrated prior to the beginning of each analytical session. Baselines were measured on-peak for a duration of 14 min between every analysis, with the last ca. 120 s being used as the actual baseline and subtracted from the subsequent analysis. Analyses of samples had a duration of 412 s, corresponding to a total of ca. 70 ng of Sn consumed per analysis.

Isotope results are reported in $\delta^{122/118}\text{Sn}$ notation, which reports the per mil (‰) difference in the $^{122}\text{Sn}/^{118}\text{Sn}$ ratio relative to our in-house Sn isotope standard, which is denoted as Sn_IPGP. All data reduction was conducted offline using the freely available double-spike data reduction tool *IsoSpike* (www.isospike.org; Creech and Paul, 2015).

Table 1
Isotopic compositions (certificate values) of single isotope spikes provided by Isoflex, and calibrated composition of ^{117}Sn – ^{122}Sn double-spike.

Spike	Form	Certificate no.	^{112}Sn (%)	^{114}Sn (%)	^{115}Sn (%)	^{116}Sn (%)	^{117}Sn (%)	^{118}Sn (%)	^{119}Sn (%)	^{120}Sn (%)	^{122}Sn (%)	^{124}Sn (%)
Sn-117	Metal ingot	1216	0.08	0.05	0.02	1.7	90.10	5.8	0.86	0.72	0.39	0.28
Sn-122	Metal ingot	1698	0.02	0.01	0.02	0.35	0.26	0.8	0.44	2.96	94.2	0.94
^{117}Sn – ^{122}Sn double-spike			0.023	0.016	0.009	1.399	54.302	5.104	0.699	2.051	35.908	0.489

Table 2
Elution scheme for Sn.

Step	Eluent	Volume (mL)
Clean column	0.5 M HCl	4
Clean column	H ₂ O	4
Clean column	0.5 M HNO ₃	4
Clean column	H ₂ O	4
Clean column	0.5 M HNO ₃	4
Clean column	H ₂ O	4
Conditioning	0.5 M HCl	4
Load sample	0.5 M HCl	2
Rinse	0.5 M HCl	4
Rinse	0.25 M HCl	4
Rinse	0.25 M HCl	3
Collect Sn	0.5 M HNO ₃	4
Collect Sn	0.5 M HNO ₃	3
Collect Sn	0.5 M HNO ₃	3

4. Results and discussion

4.1. Double-spike calibration

For precise determination of isotope ratios by double-spike, it is critical that the isotopic composition of the double-spike be accurately calibrated to the composition of the isotope standard. To correct for instrumental mass bias during the calibration we doped samples with an Sb ICP-standard solution and normalised to $^{123}\text{Sb}/^{121}\text{Sb}$ of 0.74785 based on natural abundances for the Sb isotopes of 57.213% for ^{121}Sb and 42.787% for ^{123}Sb (Meija et al., 2016). Measurements of both the reference standard and the double-spike solution had matched sb:Sn concentrations (1:4) and instrumental mass fractionation was corrected assuming an exponential fractionation law. In this approach with both the standard and double-spike measured in the same session, the calibration of the double-spike is relative to the calibration of the standard, and thus this method gives accurate results, relative to the isotope standard, even if the absolute isotopic composition of the isotope standard is not accurately known. Ten analyses of both solutions were measured in the same session and the averages of these analyses assumed as the isotope ratios of each solution relative to each other.

The double-spike calibration was tested by analysing a series of double-spike–standard mixtures in different mixing proportions, with the proportion of double-spike varying from 0.15 to 0.7 (i.e., standard–spike ratio 5.7–0.4, or a factor of 0.38–1.76 times the theoretical optimal spike–sample proportion of 0.3977). The results of these tests show that the double-spike corrected values yield a delta value $\delta^{122/118}\text{Sn}$ within typical reproducibility (i.e., ± 0.023 ‰; see below) of zero and with minimum internal errors over the range of spike proportions from 0.25 to 0.60 (Fig. 2B). Outside of this range, the standard tends towards inaccurate values.

4.2. Isotopic fractionation associated with matrix effects

Non-spectral matrix effects may arise due to the presence of other elements besides the analyte remaining in the sample solution after chemical purification, which may depress the ionisation and throughput of the analyte in the plasma. In order to test for such effects, solutions of the Sn_IPGP standard were doped with

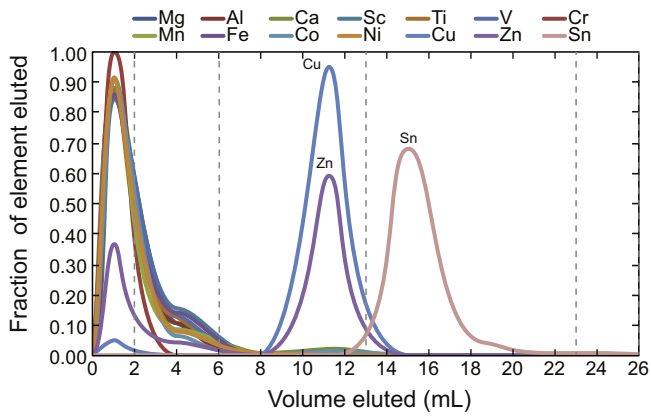


Fig. 3. Elution profile for a synthetic matrix prepared from single element solutions.

different elements (Na, Mg, Ca, Ti, Cr, Fe, Ni, Zn, Cd) in varying concentrations relative to Sn ($[X]/[Sn] = 0.01\text{--}0.50$; Fig. 4). These tests show that, using the double-spike approach, the presence of common rock-forming elements at proportions up to $[X]/[Sn] = 0.5$ do not impact our double-spike corrected results at levels comparable to our analytical reproducibility.

4.3. Accuracy and reproducibility of double spike MC-ICP-MS measurements

4.3.1. Solution standards

Double-spike corrected analyses of the Sn_IPGP standard, under the analytical conditions given in Table 3, yield an internal precision on $\delta^{122/118}\text{Sn}$ of ca. 0.05‰ (2 se, $n = 50$), i.e., ca. 0.013‰ per amu. Within an analytical session, the 2 sd uncertainty of repeat measurements was typically on the order of $\sim 0.01\text{‰}$ for $\delta^{122/118}\text{Sn}$. Small offsets between sessions may arise from small changes in the abundance sensitivity of the MC-ICPMS, drifts in the relative gains of the Faraday collectors, or a variable component of non-exponential mass bias that is not readily corrected for by the double-spike method (e.g., Schoenberg et al., 2008; Moeller et al., 2012; Creech et al., 2014). To account for this, the data from each analytical session were adjusted by normalising the session average $\delta^{122/118}\text{Sn}$ of the Sn_IPGP standard to the nominal $\delta^{122/118}\text{Sn}$ value of zero. After correcting for these small offsets from session to session, the technique has a long-term (over a period of ~ 12 months) reproducibility

Table 3

Instrumental operating conditions and measurement parameter for the Neptune Plus MC-ICPMS.

<i>Instrument operating conditions</i>	
RF power	1300 W
Plasma cool gas flow rate	16 L min ⁻¹
Interface cones	–Sampler Jet cone
	–Skimmer Ni skimmer, H-type
Source slit width	0.25 mm
Acceleration voltage	10 kV
Instrument resolution	~ 1860
Mass analyser pressure	Ca. 8×10^{-9} mbar
Detector	9 Faraday detectors; all Sn channels using $10^{11} \Omega$ preamplifiers
Sample introduction system	ESI Apex HF
Sample uptake rate	Typically 100 $\mu\text{L min}^{-1}$
<i>Measurement parameters</i>	
Solution concentration	100 ng mL ⁻¹
Typical sensitivity	$\sim 600 \text{ V ppm}^{-1}$ total Sn
Sample measurement time	$50 \times 8.4 \text{ s}$ integrations
Washout time	14 min
Background measurement time	$15 \times 8.4 \text{ s}$ integrations, on-peak

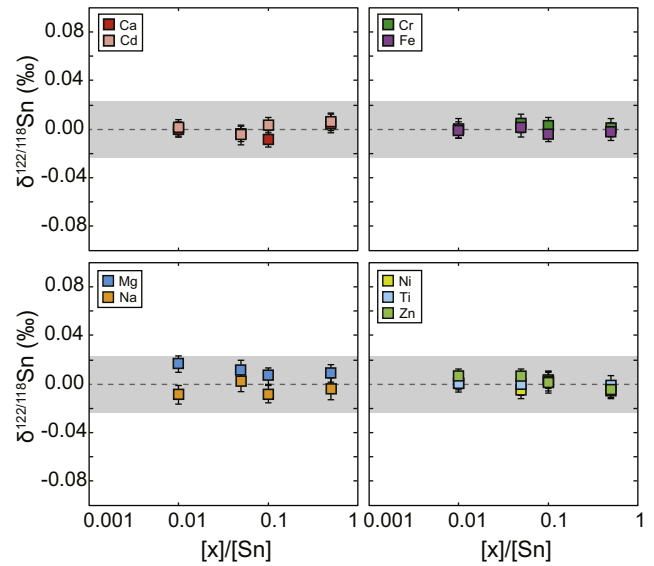


Fig. 4. Results of doping the Sn_IPGP standard at a range concentrations relative to Sn with a number of common rock forming elements. Shaded boxes indicate the long-term reproducibility on undoped measurements of the Sn_IPGP standard.

on measurements of Sn_IPGP of ca. $\pm 0.023\text{‰}$ (2 sd) on $\delta^{122/118}\text{Sn}$ (Table 4).

4.3.2. Natural samples

The reproducibility of our technique for samples with a geological matrix was tested by analysis of replicate digestions of the rock standards BHVO-2 and BCR-2, with each digestion comprising ca. 0.25–0.50 g of rock powder (Table 4). Five replicates of BHVO-2 yield a mean $\delta^{122/118}\text{Sn}$ of $0.452 \pm 0.027\text{‰}$ (2 sd), whereas four replicates of BCR-2 give a mean $\delta^{122/118}\text{Sn}$ of $0.404 \pm 0.065\text{‰}$ (2 sd; Table 4). Tin concentrations calculated from the double-spike equations (2.36 ppm for BCR-2 and 1.903 ppm for BHVO-2) are consistent between replicates, and are in good agreement with published Sn concentrations for those reference materials (2.28 ppm for BCR-2 and 1.776 ppm for BHVO-2; Jochum et al., 2016). While Sn yields from chemical purification were found to vary considerably (ca. 13–66%) for the geological samples (Table 4), the consistency in the double-spike corrected isotope ratios and calculated Sn concentrations indicate that the double-spike was fully equilibrated with the sample during the sample dissolution and that the double-spike accurately corrects for any mass-dependent isotopic fractionation arising from the incomplete yields as well as during isotopic analysis. Thus, we conservatively adopt the 2 sd of replicate analyses of BCR-2 as the external reproducibility of our technique, with a reproducibility on $\delta^{122/118}\text{Sn}$ of $\pm 0.065\text{‰}$, or $\pm 0.016\text{‰}$ per amu.

4.4. Tin stable isotope variations in nature

The geological reference materials analysed in this study represent only a small sample set, yet they span a broad compositional range, from basaltic to granodioritic. Significant variations in Sn isotope composition ($>0.2\text{‰}$ on $\delta^{122/118}\text{Sn}$) are apparent across this compositional range (Table 4). Tin concentrations covary with incompatible lithophile elements, in particular Sm (Jochum et al., 1993), although Sn concentrations do not strongly covary with major lithophile elements. However, we observe strong correlations between $\delta^{122/118}\text{Sn}$ and a number of major and trace lithophile elements, some of which are shown in Fig. 5 (e.g. $\delta^{122/118}\text{Sn}$ is positively correlated with MgO and negatively correlated with SiO_2). This

Table 4

Sn stable isotope and concentration results for terrestrial rock reference materials by double-spike MC-ICPMS.

Sample	Total digested (g)	$\delta^{122/118}\text{Sn}$	\pm	n	Total Sn in sample (μg)	Sn conc. ($\mu\text{g g}^{-1}$)	Ref. conc. ($\mu\text{g g}^{-1}$)	Approx. Sn yield (%)
Sn_IPGP		0.000	0.023	107				
AGV-2	0.0468	0.310	0.120	1	0.10	2.07	1.83	31.9
GSP-2	0.4289	0.180	0.022	1	3.68	8.32	6.4	27.6
BCR-2 #1	0.5171	0.392	0.025	1	1.25	2.34	2.28	13.7
BCR-2 #2	0.3380	0.447	0.029	1	0.83	2.39	2.28	27.3
BCR-2 #3	0.5171	0.408	0.025	1	1.25	2.35	2.28	13.5
BCR-2 #4	0.5058	0.370	0.030	1	1.24	2.37	2.28	38.0
BCR-2 average		0.404	0.065			2.36		
BHVO-2 #1	0.2979	0.465	0.012	1	0.58	1.90	1.776	58.2
BHVO-2 #2	0.4583	0.443	0.021	1	0.91	1.92	1.776	28.2
BHVO-2 #3	0.4167	0.464	0.026	1	0.82	1.91	1.776	59.1
BHVO-2 #4	0.2906	0.445	0.012	1	0.57	1.90	1.776	65.7
BHVO-2 #5	0.5040	0.432	0.013	1	1.00	1.92	1.776	58.2
BHVO-2 #6	0.2719	0.461	0.022	1	0.53	1.87	1.776	66.2
BHVO-2 average		0.452	0.027			1.90		

Uncertainties on single measurements are the 2 se internal error for that analysis; where $n > 1$, data represent the mean and 2 sd of the analyses. Reference Sn concentrations are from Jochum et al. (2016) and Cotta and Enzweiler (2013).

suggests that Sn stable isotopes are fractionated during magmatic differentiation, either during partial melting or during fractional crystallisation. The exact mechanism of this fractionation is not yet clear, but may relate to the difference in compatibility between Sn^{2+} and Sn^{4+} and the bonding environment between mineral phases crystallising from the melt as previously observed for Fe isotopes (Teng et al., 2008). These results indicate significant potential for Sn stable isotopes as a sensitive geochemical tracer, and this technique could be used to study magmatic differentiation and the redox state of the mantle similar to what has been done previously with Fe isotopes (e.g., Williams et al., 2004; Dauphas et al., 2014; Dauphas et al., 2009), in addition to a range of other geological processes such as volatilisation/condensation and metal–silicate/metal–sulphide differentiation.

5. Conclusions

Volatile siderophile element stable isotopes have significant potential to reveal large isotopic fractionations resulting from a range of different geological processes. Our method allows for the precise determination of Sn stable isotope compositions of geological materials, using a simple chemical purification procedure combined with double-spike MC-ICPMS. Our results show that the double-spike method effectively corrects for any mass dependent fractionation that can potentially arise from incomplete yields from chemical purification and mass spectrometry, and yields reproducible Sn isotopic compositions from replicate digestions of two geological reference materials. We found large ($>0.2\%$ on $\delta^{122/118}\text{Sn}$) Sn stable isotope variations amongst igneous terrestrial rocks, which correlate with tracers of magmatic differentiation. These results demonstrate the effectiveness of our technique and the potential for Sn stable isotopes as a geochemical tracer in diverse systems.

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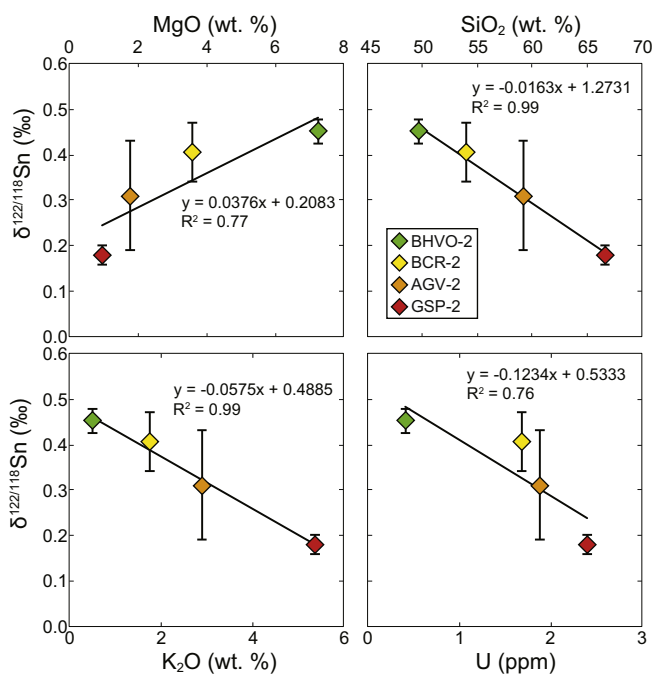


Fig. 5. Sn stable isotope data for USGS geological reference materials BHVO-2, BCR-2, AGV-2 and GSP-2 plotted against GeoReM reference concentration data for a range of lithophile elements.

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