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# Tin isotopic fractionation during igneous differentiation and Earth's mantle composition

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#### Abstract





Tin exists both under the 2+ and 4+ oxidation states in igneous systems, and thus its geochemical behaviour changes as a function of oxygen fugacity. To characterise the redox state of Sn during magmatic differentiation and how this affects its isotope composition, we have measured Sn isotopic and elemental abundances in a suite of samples from the Kilauea Iki lava lake. Sn behaves as a highly incompatible element during fractional crystallisation. Lattice strain modelling shows that Sn<sup>2+</sup> has mineral-melt partition coefficients (D<sup>min/melt</sup>)  $\approx$  1 in plagioclase and clinopyroxene, whereas it is highly incompatible in all phases save for ilmenite, attesting to the sole presence of Sn<sup>4+</sup> in basaltic liquid at the Fayalite-Magnetite-Quartz (FMQ) buffer. Furthermore, Sn isotopes are unfractionated during crystallisation of silicates, but decrease to lighter values upon ilmenite precipitation. Isotopic fractionation is onset by the coordination change between Sn<sup>4+</sup> in the melt (6- to 8-fold) and ilmenite (6-fold). The Sn isotope composition of komatiites, which are high degree, high temperature partial melts are used to estimate the

Sn isotope composition of the bulk silicate Earth (BSE). Komatiites have  $\delta^{122}$ Sn within the range of the basalts (before ilmenite precipitation) and together provide the best estimate of the BSE of 0.49 ± 0.11 ‰ (2 s.d., n = 9).

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### Letter

Moderately volatile elements (MVEs) and their isotopes are important tracers for planetary and nebular processes such as evaporation and condensation (*e.g.*, O'Neill and Palme, 2008; Paniello *et al.*, 2012). A condition that must be met before MVEs can be used to answer these questions is knowledge of the isotopic composition of the bulk silicate Earth (BSE) and hence how their isotopes fractionate during igneous processes.

Tin has three oxidation states (Sn<sup>0</sup>, Sn<sup>2+</sup>, Sn<sup>4+</sup>) that confer differing properties as a function of oxygen fugacity ( $fO_2$ ). As such, Sn may behave as a siderophile, chalcophile and lithophile element at high temperatures (*e.g.*, Heinrich, 1990; Witt-Eickschen *et al.*, 2009). Although the dependence of Sn<sup>2+</sup>/Sn<sup>4+</sup> on melt composition, and the  $fO_2$  at which this transition occurs in basaltic melts are poorly known (Farges *et al.*, 2006), the behaviour of Sn in igneous systems may be gleaned by comparison with elements of similar incompatibility. Observations of oceanic basalts show that Sn/Sm, Sn/ Zr and Sn/Hf ratios are nearly uniform across MORB and OIB (Jochum *et al.*, 1993; Jenner and O'Neill, 2012). Correlations with tetravalent, incompatible elements suggest Sn may be lithophile and occurs as Sn<sup>4+</sup> during igneous processes near FMQ. At equilibrium, all else being equal, isotopic fractionation is controlled by differences in bond stiffness between two phases (*e.g.*, Schauble, 2004). The diversity in Sn bonding environments (Sn-O, Sn-S and Sn<sup>0</sup>) combined with differing oxidation states offer scope for significant isotope fractionation. Indeed, Creech *et al.* (2017) analysed four genetically unrelated igneous rocks and identified that the <sup>122</sup>Sn/<sup>118</sup>Sn ratio increases with increasing MgO content, suggesting that Sn isotopic fractionation occurs during igneous differentiation. However, the mechanisms driving this fractionation remain unknown.

In order to determine the behaviour of Sn isotopes in igneous systems and establish the composition of the BSE, it is necessary to investigate natural terrestrial samples from a common source. Kilauea Iki (KI) lava lake is well-suited to test the effects of fractional crystallisation (*e.g.*, Tomascak *et al.*, 1999; Teng *et al.*, 2008; Chen *et al.* 2013; Kato *et al.*, 2017). The cooling lava differentiated in a closed system to form olivine-rich cumulates to andesitic lavas with some rare silicic veins. Extrapolation to the composition of the BSE using a single magmatic suite is tenuous, given the diversity of mantle sources in the present day mantle and the possibility of secular changes in mantle composition (*e.g.*, Maier *et al.*, 2008). In order to assess mantle heterogeneity over space and time, komatities, ranging in age from 3.5 to 2.7 Ga and from 3 cratoms

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(Yilgarn, Kaapvaal, Superior), were analysed for their Sn isotope composition. As komatiites are produced by 25–40 % partial melting (*e.g.*, Herzberg, 1992), and Sn is incompatible during mantle melting (being predominantly hosted in clinopyroxene; Witt-Eickschen *et al.*, 2009), melting quantitatively extracts Sn from their mantle sources. Komatiite sources, especially for older 3.5 Ga examples, have primitive mantle-like compositions (Sossi *et al.*, 2016), and thus permit assessment of the temporal and chemical heterogeneity in Earth's mantle.

Here, we have analysed the isotopic composition of a series of samples from KI lava lake and komatiites utilising the <sup>117</sup>Sn-<sup>122</sup>Sn double spike MC-ICPMS method described by Creech *et al.* (2017) (see Supplementary Information). The differentiation sequence samples form a sub-alkali series with MgO content ranging from 25.83–2.37 wt. % (Helz *et al.*, 1994) (see Supplementary Information). The four spinifex-textured komatiites have 23.54 < MgO (wt. %) < 28.71, and thus chemical compositions close to their respective parental magma (Sossi *et al.*, 2016).

The data are reported in Table 1, with  $\delta^{122} \text{Sn}$  being the ‰ deviation of the <sup>122</sup>Sn/<sup>118</sup>Sn ratio relative to the Sn IPGP standard. In the KI samples,  $\delta^{122}$ Sn ranges from 0.24 ± 0.07 to  $0.46 \pm 0.07$  ‰, which represents a variation (~0.05 ‰/amu) similar to Zn (~0.05 %/amu; Chen et al., 2013). The samples with less than 5 wt. % MgO show a progressive depletion in the heavier isotopes of Sn as MgO decreases (Fig. 1b). In addition, Sn concentration inversely correlates with the MgO content of the samples, defining a parabolic curve typical of highly incompatible elements (Fig. 1a). The Sn/E ratios (E = Sm, Hf or Zr; data from Helz, 2012) in samples across the differentiation sequence are similar to OIBs and MORBs reported in Jochum et al. (1993) and Jenner and O'Neill (2012) (see Supplementary Information). The four komatiites have different Sn contents between 0.15 and 0.36 ppm (BSE = 0.14 ppm), however, their  $\delta^{122}$ Sn fall between 0.48 ± 0.065 ‰ and 0.58 ± 0.065 ‰, and show no systematic differences.

To understand the Sn isotopic variations, it is necessary first to estimate the partition coefficients of  $Sn^{2+}$  and  $Sn^{4+}$  between major minerals and melt. Given the limited experimental data currently available (Adam and Green, 2006; Klemme *et al.*, 2006; Michely *et al.*, 2017), we address this question using lattice strain theory and then model the Sn abundance and speciation during the differentiation of the KI lava lake.

Calculating elemental partitioning of Sn. Partition coefficients for Sn2+ and Sn4+ between crystals and melt were calculated for olivine, clinopyroxene, orthopyroxene, plagioclase and ilmenite using the lattice strain model (Blundy and Wood, 1994; Supplementary Information). The calculated values were then compared to experimentally derived partition coefficients (Michely et al., 2017; Adam and Green, 2006; Klemme et al. 2006; Table 2). Stannous  $\text{Sn}^{2+}$  ( $r_{VI} = 0.96$  Å) substitutes poorly into the M1 sites of Fe-Mg silicates ( $D^{min/melt} \approx 0.1$ ), but has  $D^{min/melt}$  of unity in the larger, Ca-bearing VIII-fold sites of clinopyroxene and plagioclase ( $r_{VIII} \approx 1.15$  Å). Divalent tin is more compatible in all minerals except ilmenite compared to  $Sn^{4+}$  (r = 0.69 Å) due to its substitution for <sup>VI</sup>Ti<sup>4+</sup> (r = 0.605 Å). The experiments of Michely et al. (2017), performed in air, contain exclusively Sn<sup>4+</sup>, whereas those of Adam and Green (2006) may contain both Sn<sup>2+</sup> and Sn<sup>4+</sup> because Sn falls between calculated lattice strain curves for a given redox state and site property. The graphite capsules used imposed fO2 conditions near FMQ-2 (Médard et al., 2008), at least 2 orders of magnitude lower than in the KI lava lake, thereby increasing the stability of divalent Sn, according to:

$$SnO + \frac{1}{2}O_2 = SnO_2$$
 Eq. 1



**Figure 1** (a) Model showing Sn concentration for KI samples in the melt against MgO content. Red circles = KI samples. Thick lines represent modelled evolution with differing  $Sn^{4+}/\sum Sn$ , listed in black boxes from 1 (green line), 0.5 (dashed grey line) and 0 (dashed black line). Thin grey line represents the fraction of melt remaining (F), listed in grey circles, with the grey star representing the parental melt composition. (b)  $\delta^{122}Sn$  and Sn against MgO (wt. %) for the KI lava lake samples. The solid lines represent the modelled  $\delta^{122}Sn$  for  $\Delta^{122}Sn_{mineral-melt} = 0.5$  (grey line), 0.7 (black line) and 0.9 (grey line). Geostandard values are taken from Creech *et al.* (2017). In both cases, the crystallising assemblage is listed at the top of the figure (OI = olivine, Cpx = clinopyroxene, PIg = plagioclase, IIm = ilmenite).

 Table 1
 Tin isotopic composition of the samples analysed in this study.

Sample ID	Rock type	Weight (g)	MgO (wt. %)	Sn conc. (µg/g)	δ <sup>122</sup> Sn (‰)	2 s.d. <sup>b</sup>	n
KI67-3-6.8	picro-Basalt	0.3546	25.83ª	1.0	0.44	0.07	1
KI79-3-150.4	Basalt	0.2506	13.51ª	1.4	0.43	0.07	2
KI67-3-58.0	Basalt	0.2664	8.91ª	1.4	0.46	0.07	2
KI75-1-121.5	Basalt	0.2483	7.77 <sup>a</sup>	2.1	0.40	0.07	2
KI75-1-75.2	Basalt	0.2460	5.77ª	2.5	0.42	0.07	2
KI79-1R1-170.9	Basaltic-andesite	0.2410	3.48 <sup>a</sup>	4.6	0.35	0.08	2
KI67-2-85.7	Basaltic-andesite	0.2475	2.60 <sup>a</sup>	6.6	0.24	0.07	2
KI81-2-88.6	Andesite	0.2512	2.37 <sup>a</sup>	6.2	0.27	0.07	2
331/783	Komatiite (Barberton, 3.48 Ga)	1.5415	26.27 <sup>c</sup>	0.36	0.58	0.07	2
331/948	Komatiite (Yilgarn, 2.7 Ga)	1.1810	23.54 <sup>c</sup>	0.25	0.54	0.07	2
SD6/400	Komatiite (Yilgarn, 2.7 Ga)	1.2648	27.99 <sup>c</sup>	0.25	0.48	0.07	2
422/96	Komatiite (Munro, 2.7 Ga)	1.1968	28.71 <sup>c</sup>	0.15	0.53	0.10	2

<sup>a</sup>SiO<sub>2</sub>/MgO values for Kilauea Iki lava lake taken from Helz *et al.* (1994). <sup>b</sup>Maximum of either 2 times the standard deviation on the sample measurement or BCR-2 external reproducibility. <sup>c</sup> MgO value for komatiites taken from Sossi *et al.* (2016).

Based on the relative compatibility of Sn<sup>2+</sup>, Sn<sup>4+</sup> would accumulate in the melt as fractional crystallisation progresses, such

that 
$$\frac{Sn^4}{\Sigma Sn} \rightarrow 1$$
 as the fraction of melt remaining,  $F \rightarrow 0$ .

Sn speciation during fractional crystallisation. The relative proportions of MgO and  $FeO^{(T)}$  in the KI samples were modelled assuming fractional crystallisation (Fig. 2). The mineral/melt partition coefficients calculated for Sn (Table 2) were used to model the evolution of Sn in the melt.



**Figure 2** Variation of  $\delta^{122}$ Sn with TiO<sub>2</sub> content, MgO (wt. %) shown next to the data point. Sn isotope fractionation occurs only after Fe-Ti oxide (ilmenite) saturation at Kilauea Iki. Symbols as per Figure 1.

The crystallising phase proportions of olivine, augite, plagioclase and Fe-Ti oxides were adjusted such that the modelled evolution of MgO and FeO contents closely follow the natural data, assuming  $K_D^{Fe-Mg}_{ol,aug-melt} = 0.3$  (Fig. 2). Olivine is the dominant crystallising phase until the MgO content falls to ~7.4 wt. % in the melt, as noted in Helz *et al.* (1994), at which point the liquid reaches the cpx + plg + ol cotectic, as shown by

a change in slope of REE abundances against MgO (O'Neill, 2016; see Supplementary Information). Ilmenite then crystallises at the expense of olivine below  $\approx$ 5 wt. % MgO (Fig. 2).

To evaluate the proportion of Sn<sup>2+</sup> and Sn<sup>4+</sup> in the melt, three distinct scenarios were considered: a) 100 % Sn<sup>2+</sup>, b) Sn<sup>2+</sup>/Sn<sup>4+</sup> = 1 and c) 100 % Sn<sup>4+</sup> (see Fig. 1a). The first two cases produce a) no increase in Sn concentration with MgO or b) a rise that is insufficient to describe the observed increase with MgO. Only scenario c), in which Sn is entirely stannic and thus strongly incompatible ( $0.01 < \Sigma D^{min/melt} < 0.21$ ) reproduces the Sn evolution of the melt. Therefore, the Sn<sup>2+</sup> species is likely very minor and the majority of Sn occurs as Sn<sup>4+</sup>.

No experimental constraints exist for the equilibrium constant of Eq. 1 in basaltic liquids. However, a first order  $Sn^{4+}$ 

estimate of  $\frac{\delta n}{\Sigma Sn}$  expected in magmatic systems comes from

the experimentally derived relative reduction potential for the redox couple Sn<sup>4+</sup> and Sn<sup>2+</sup>; -4.4 V in Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub> melt (Schreiber, 1987). Using this value enables calculation of Sn<sup>4+</sup>/ $\Sigma$ Sn at the *f*O<sub>2</sub> (FMQ) and temperature (≈1200 °C) of the parental liquid, yielding a value of ≈0.9 (10 % Sn<sup>2+</sup>). A caveat to this approach is that this result may not be applicable to basaltic melts. However, it also independently suggests that Sn<sup>4+</sup> should predominate in terrestrial magmatic environments.

Isotopic behaviour of Sn during magmatic processes. Since Sn is likely tetravalent and coordinated by oxygen in the KI lava lake, the ~0.2 ‰ isotopic fractionation must reflect the difference in coordination number of Sn between the melt and the mineral assemblage. Sample KI79-3-150.4, with ~14 wt. % MgO ( $\delta^{122}$ Sn = 0.46 ± 0.07 ‰), is close to the parental magma composition (Helz et al., 1994). As olivine crystallises and accumulates at the bottom of the sequence,  $\delta^{122}$ Sn is unchanged, because  $D_{Fe,Zn}^{0lmelt} \approx 0$  (Fig. 1b). This behaviour contrasts with both Fe and Zn, whose isotopic fractionation is indeed controlled by olivine due to their relative compatibility in this phase, where  $D_{Fe,Zn}^{ol/melt} = 1$ , driving both  $\delta^{57}$ Fe and  $\delta^{66}$ Zn to heavier compositions to lower MgO (Teng et al., 2008; Chen et al., 2013). Only in samples with <5 wt. % MgO does  $\delta^{122}$ Sn begin to decrease. Tin is weakly chalcophile, and its  $D_{sn}^{sulph/melt} = 5.3 \pm 3.6$  in KI samples (Greaney *et al.*, 2017). Sulphides are present in evolved basalts as isocubanite and bornite (having exsolved from high temperature intermediate solid solution), however their low modal abundance (<0.01 %; Stone and Fleet, 1991) means they have a negligible effect on the Sn budget of the magma. Furthermore, by analogy with Fe isotopes (Wawryk and Foden, 2017), Cu-bearing sulphides



Table 2 Calculated partition coefficients for Sn<sup>2+</sup> and Sn<sup>4+</sup> using lattice strain theory

	Coordination	Olivine	Orthopyroxene	Clinopyroxene	Plagioclase	Ilmenite
2+	Lattice Strain					
	VI	0.12 - 0.20	0.09 - 0.14	0.04 - 0.07	-	-
	VIII	-	-	1.0 - 1.2	0.94 - 1.27	-
	Bulk Sn <sup>2+</sup>	0.12 - 0.20	0.09 - 0.14	1.04 - 1.27	0.94 - 1.27	-
4+	IV	1x10 <sup>-5</sup>	1x10 <sup>-5</sup>	1x10 <sup>-5</sup>	1x10 <sup>-5</sup>	-
	VI	0.005 - 0.01	0.01 - 0.07	0.05 - 0.39	-	4.5 - 6.8
	Bulk Sn <sup>4+</sup>	0.005 - 0.01	0.01 - 0.07	0.05 - 0.39	-	-
Experimental						
Adam and Green (2006)		0.002 - 0.014	0.015	0.024 - 1	-	-
Klemme <i>et al.</i> (2006)		-	-	-	-	5.1
Michely <i>et al.</i> (2017)				0.19 - 0.46*		

\*Only partition coefficients for the natural, komatiitic 'W' composition are reported here.

should harbour light Sn isotopes (contrary to observations), as also suggested by the long Sn-S bond length of 2.56 Å in SnS<sub>2</sub> (Hazen and Finger, 1979). Rather, comparison with TiO<sub>2</sub> shows that the decrease in  $\delta^{122}$ Sn coincides with crystallisation of Fe-Ti oxides, predominantly ilmenite, in which Sn<sup>4+</sup> is highly compatible (Klemme *et al.*, 2006; Table 2), further attesting to the predominance of Sn<sup>4+</sup> in the melt. The TiO<sub>2</sub> content reaches a maximum of 4.12 wt. % at 5.77 wt. % MgO before dropping to 2.59 wt. % at 2.37 wt. % MgO (Fig. 2). Although the measured  $D_{Sn}^{ilminmelt} = 0.63$  (Greaney *et al.*, 2017) is less than that determined experimentally (5.1), ilmenite nevertheless hosts 50 % of the Sn in solid phases. Coupled with its low modal abundance ( $\approx 5$  %),  $\Sigma D_{Sn}^{min/melt}$  remains below unity (0.2), and Sn continues to increase.

In order to replicate the change in Sn content and isotopic fractionation in the KI samples, a fractionation factor  $^{122}Sn$  $\Delta_{\min eral - melt}^{-Sn}$  of 0.7 ± 0.2 ‰ is required (see Supplementary Information), equivalent to 0.175 ± 0.050 ‰/amu. Sossi and O'Neill (2017) explored the effect of changing coordination environment on iron isotope fractionation, and found that the difference between IV-fold Fe2+ in chromite and VI-fold Fe2+ in ilmenite is only 0.05 %/amu at 1073 K, significantly smaller than that calculated for Sn. Nonetheless, the degree of enrichment of the light Sn isotopes in the more evolved samples is consistent with the observation of Creech et al. (2017) (Fig. 1b). This vector of fractionation to lighter Sn isotopes in the melt precludes the presence of Sn<sup>2+</sup>, which, as it is concentrated in all crystallising phases relative to Sn<sup>4+</sup>, and as a more reduced species, should result in heavy isotope enrichment in the melt. Rather, this argues for the lower coordination of Sn<sup>4+</sup> in minerals relative to the melt. While the lattice strain model predicts that Sn<sup>4+</sup> coordination (N) in minerals is 6-fold (Table 2), its coordination in the melt is poorly known. In melts with higher NBO/T (number of non-bridging oxygens per tetrahedral cation) than the hydrous granitic melts studied by Farges et al. (2006), Sn<sup>4+</sup> may exist in 6 to 8-fold coordination by analogy with Sn<sup>2+</sup>, which is in 8-fold coordination. While further XANES studies will help elucidate this issue, empirically, the shift to lighter Sn isotope compositions

requires  $\frac{C_N^{melt}}{C_N^{mineral}} > 1.$ 

The komatiites plot within uncertainty of the  $\delta^{122}$ Sn plateau defined by KI lava lake samples with MgO > 5 wt. % (Fig. 1b). The komatiites analysed display spinifex textures, indicative of their formation from quenched liquids, representative of the parental magma. This consideration is not crucial for Sn, however, as olivine is the only mineral on the komatiite

liquidus and its removal does not cause resolvable Sn isotope fractionation (Fig.1b), that is,  $\delta^{122}$ Sn should remain constant irrespective of its position on an olivine control line.

Tin contents of the four komatiites positively correlate with La/Sm<sub>N</sub> ratios (Fig. 3). The high degree of melting (25-40 %) undergone during komatiite formation results in quantitative extraction of incompatible elements, including Sn. Therefore, Sn depletion reflects that of its mantle source, where younger (2.7 Ga) komatiites experienced greater (up to 5 %) source depletion than the primitive mantle-derived 3.48 Ga komatiites (see Sossi et al., 2016). Despite this variation in Sn contents (Fig. 3), the absence of isotopic fractionation between komatiite groups indicates that prior melt extraction  $(\leq 5 \%)$  leaves the Sn isotopic composition of their mantle sources unchanged. Hawaiian basalts ( $0.44 \pm 0.03$ , 2 s.d.) are isotopically indistinguishable (0.53  $\pm$  0.08, 2 s.d.), and these asthenosphere-derived igneous rocks yield an average  $\delta^{122}$ Sn = 0.49 ± 0.11 (2 s.d., n = 7). Owing to the constancy of Sn isotope composition in high MgO igneous rocks, and across several spatial and temporal domains, this value is taken to estimate the Sn isotope composition of the bulk silicate Earth.



**Figure 3** Depletion of komatiite source regions, quantified by La/Sm<sub>N</sub>, as a function of Sn concentration (green circles) and  $\delta^{122}$ Sn (blue squares). Tin contents are positively correlated with La/Sm<sub>N</sub>, whereas  $\delta^{122}$ Sn remains constant within uncertainty.

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