Redox and structural controls on tin isotopic fractionations among magmas


Abstract

Recent analytical developments have made possible the determination of the isotopic composition of tin in igneous rocks. In order to establish a framework to interpret the mass-dependent tin isotopic signatures of planetary materials, seven geologically-relevant silicate glasses (basalt, rhyolite, enstatite and anorthite glasses) were synthesized with moderate amounts of $^{119}$Sn (on the order of a weight percent). Redox conditions were controlled during sample synthesis to set the redox ratio ($\text{Sn}^{2+}/\text{Sn}_{\text{tot}}$) from stannous ($\text{Sn}^{2+}$) to stannic ($\text{Sn}^{4+}$) glasses. The mean force constants of tin bonds in these glasses were determined by synchrotron nuclear resonant inelastic X-ray scattering (NRIXS) in order to determine the reduced isotopic partition function ratios ($\beta$-factors) of these glasses. Clues on the coordination chemistry and the valence state of tin in these glasses were also derived from synchrotron Mossbauer spectroscopy (SMS). The force constants of tin drastically increase from $\text{Sn}^{2+}$-bearing to $\text{Sn}^{4+}$-bearing glasses and vary significantly with the glass composition at a given redox state. The average coordination number of tin likely controls these variations with glass composition as suggested by SMS results. The coordination chemistry of tin in silicates strongly affects its isotope partitioning behavior. Our experimental data are finally used to interpret available Sn isotope data collected in terrestrial rocks. The incompatible behavior of $\text{Sn}^{4+}$ in mantle minerals leads to an enrichment in heavy isotopes in mantle melts and to the depletion in heavy isotopes in solid residues of melting with a magnitude consistent with the isotope fractionation between $\text{Sn}^{2+}$ and $\text{Sn}^{4+}$ predicted by NRIXS data. Finally, we show that during fractional crystallization of basalt and considering the effect of tin coordination number in minerals and melts, the partitioning of $\text{Sn}^{4+}$ into ilmenite leads to an enrichment in light isotopes in the residual melt.

Keywords: Tin isotopes; Silicate melts; Magma differentiation; Mantle melting

1. INTRODUCTION

Terrestrial planets are differentiated into metallic cores, and silicate mantles and crusts. The conditions that
prevailed during planetary differentiation are difficult to establish because core formation is a protracted phenomenon that occurs concurrently with planetary growth such that core formation must take place over a range of conditions. Furthermore, only the very top layers of terrestrial planets are available for sampling, which have been tampered by several billions of years of geochemical evolution. Therefore, understanding the conditions (P, T, IO₂) that prevailed during planetary differentiation remains a major question in Earth sciences and planetology. An additional complication is that some siderophile elements are also volatile and have been partially lost during planetary accretion.

The behaviors of some moderately siderophile elements are influenced by the redox state of the source region during partial melting. For such elements, it is difficult to tell whether their low abundance in samples of planetary mantles reflects the fact that they have been scavenged into the core (e.g. Righter, 2011), redistributed by mantle processes (e.g. McDonough, 2003; Palme and O’Neill, 2003), or lost by vaporization or incomplete condensation, either during planetary collisions (Hin et al., 2017; Norris and Wood, 2017; Young et al., 2019) or solar nebula condensation (Cassen, 1996).

In the past decade, new insights into core formation conditions have been gained from the study of non-traditional isotope fractionation among samples from Earth’s mantle (see Bourdon et al., 2018 for a review on this topic). Specifically, the isotopic compositions of Si, Cu and Fe of mantle-derived rocks have been interpreted to reflect the imprint of core formation (Fitoussi et al., 2009; Shahar et al., 2011; Hin et al., 2014; Savage et al., 2015; Polyakov, 2009). Alternative interpretations invoking volatility-controlled processes were also put forward, for instance in the case of Fe, Si and Mg (Poitrasson et al., 2004; Dauphas et al., 2015; Hin et al., 2017). The effect of partial melting, magma differentiation and redox state of the source region have also been pointed out in the case of Fe (Dauphas et al., 2009). To interpret natural isotopic variations in a quantitative framework, it is important to develop an accurate description of equilibrium isotopic fractionation between coexisting phases (namely, iron-based metal alloys, silicates, sulfides and gaseous species in particular). In this context, we have initiated a comprehensive experimental study of the isotope partitioning of tin, a versatile element that is either siderophile, chalcophile, lithophile, volatile, or lost during planetary collisions (Hu et al., 2003, 2013). This technique has already proven to be useful to address several first-order problems in iron isotopes (Dauphas et al., 2014; Roskosz et al., 2015; Shahar et al., 2016; Liu et al., 2017). The determination of these factors is achieved by measuring the phonon excitations using inelastic x-ray scattering (NRXs). The use of the pDOS to derive isotope fractionation factors was initially proposed by Polyakov using available data on 119Sn nuclear resonances (Polyakov et al., 2005; also see Dauphas et al., 2018 for a reevaluation of those results) before it became more extensively used with 57Fe. A major result of this pioneering study was to show that the redox state of tin (Sn⁰, Sn²⁺, Sn⁴⁺) and the changes in coordination chemistry induced by a valence change strongly affect the partitioning of the Sn isotopes. This conclusion was reached based on the behavior of pure compounds yet (metal and oxides, namely pure Sn, SnO and SnO₂). In this study we extend the range of Sn-bearing materials to more geologically-relevant silicate glasses synthesized with moderate amounts of tin (on the order of a weight percent). Redox conditions were controlled during sample syn-

Wood, 2017). Tin has three oxidation states (Sn⁰, Sn²⁺, Sn⁴⁺) so its geochemical behavior is strongly influenced by oxygen fugacity. Since isotopic fractionation is controlled by differences in bond stiffness between two phases (e.g., Schauble, 2004; Dauphas et al., 2012), the diversity in Sn bonding environments could induce significant isotopic fractionation. In order to establish a framework to interpret the tin isotopic signatures of planetary materials, the effects of major igneous processes have first to be quantified.

The manner in which isotopes are fractionated between coexisting phases at equilibrium (β-factor or reduced partition function ratio) can in principle be determined experimentally (Bourdon et al., 2018) but it requires achieving equilibrium and measuring the isotopic compositions of coexisting phases with high precision, which is challenging at the high pressures and temperatures relevant to planetary differentiation (again see Bourdon et al., 2018 for a critical analysis of experimental results collected so far). Further complications arise, in the case of tin because of its high volatility that prevent experiments to be performed in a truly closed system, which can produce large isotopic fractionation that is difficult to control or account for (Bourdon et al., 2018). In the case of iron and tin, however, experimental difficulties can be overcome if the fractionation factors are measured using a synchrotron-based inelastic spectroscopy (Polyakov et al., 2005; Dauphas et al., 2012, 2018). Over the past several years, this technique has seen considerable development (Dauphas et al., 2012, 2014; Blanchard et al., 2015; Dauphas et al., 2018) and it has already proven to be useful to address several first-order problems in iron isotope geochemistry (Dauphas et al., 2014; Roskosz et al., 2015; Shahar et al., 2016; Liu et al., 2017).
thesis to set the redox ratio (Sn^{2+}/Sn_{tot}) from stannous (Sn^{2+}) to stannic (Sn^{4+}) glasses. We also improved the data collection and processing using the recent developments on $^{57}$Fe NRIXS. We show that large isotope fractionation has to be expected between materials containing Sn^{2+} and Sn^{4+}. We also demonstrate that at a given redox state, the coordination chemistry of tin in silicates must strongly affect its partitioning behavior. Our experimental data are finally used to interpret available Sn isotope data collected on mantle-derived rocks.

### 2. EXPERIMENTAL METHODS

#### 2.1. Sample synthesis and characterization

The starting glasses were the same as those studied by Dauphas et al. (2014). They were synthesized from mixtures of reagent grade SiO$_2$, Al$_2$O$_3$, CaCO$_3$, MgO, Na$_2$CO$_3$, K$_2$CO$_3$, TiO$_2$, and Fe$_2$O$_3$ that had been first fired in air from 300 to 1000 °C for several days. The starting material was melted in air at 1550 °C for 1 hour in a thin-walled Pt crucible, quenched on a copper plate, and then finely crushed. Approximately 2 wt% of pure $^{119}$SnO$_2$ (Cyclotron Instruments) was then added to the starting glass powders and crushed in ethanol for several minutes. The reason for that is $^{119}$Sn is the only Mossbauer isotope of Sn and working on enriched samples cuts on acquisition time. Two methodologies were used to prepare the samples depending on the oxygen fugacity that we wanted to achieve.

1. Oxidized samples (labeled AIR) were prepared in a furnace in air. Glass droplets of approximately 25 mg were mounted on platinum wire loops. Glass powders were attached to wire loops using polyvinyl alcohol as a binder and were melted in air at 1550 °C for 10 min. A longer duration was found to induce a complete volatilization of tin. After 10 min, enough tin was preserved in glasses for NRIXS analysis (Table 1). Note that NRIXS is a method that probes the strength of the Sn bonds, so the fact that Sn isotopes could have been fractionated during sample preparation is inconsequential.

2. Reduced glasses (labeled CCO) were prepared at the LMV (Clermont-Ferrand, France) in a non-endloaded piston-cylinder apparatus. Double capsules (platinum and graphite) were used to ensure buffered conditions slightly lower than the C/CO redox equilibrium (Médard et al., 2008) and to avoid any significant loss of tin during experiments. About 80 mg of the SnO$_2$-bearing glass powder was packed in a graphite capsule, which was then placed in a larger welded platinum capsule. A salt/pyrex/MgO assembly as described in Médard et al. (2006) was used to perform these syntheses. The reduced basalt and rhyolite were prepared at 1 GPa and 1550 °C for 46 and 55 min respectively.

The chemical compositions of glasses were determined with an electron microprobe ( Cameca SX 100 at the UM ET
The reduced Planck constant and the Boltzmann constant. The SEM observations of the silicate samples did not reveal any crystallization or heterogeneity.

2.2. NRIXS data collection and processing

The NRIXS measurements were performed on Sector 30-ID-B at the Advanced Photon Source (APS) at Argonne National Laboratory (USA). Details on the NRIXS technique are available in Seto et al. (1995), Sturhahn et al. (1995), Chumakov and Sturhahn (1999), and Dauphas et al. (2012, 2018). The storage ring was in the standard 24 bunch top-up mode of APS. The phonon excitation spectrum is recorded by scanning the incident x-ray energy (from $-100$ to $+120$ meV with 0.25 meV steps) with the high-resolution six-crystal, cryogenically cooled monochromator (Toellner et al., 2011). The flux after the high-resolution monochromator is measured to be 4 GHz/1 meV. Nuclear scattering was measured on small glass chips using two Avalanche Photon Diode (APD) detectors positioned face to face and perpendicular to the incident X-ray beam in order to optimize the signal collection. The lifetime of the first excited state is 18.3 ns and is long enough to be measured.

The equilibrium isotope fractionation coefficient $\alpha_{A-B}$ between two phases $A$ and $B$ can then be calculated as the ratio of their $\beta$ factors:

$$1000 \times \ln \alpha_{A-B} = 1000 \times \ln \beta_A^I - 1000 \times \ln \beta_B^I$$

2.3. SMS data collection and processing

Due to the relatively long lifetime of radioactive parent $^{119m}$Sn (245 days) single line source embedded in CaSnO$_3$ or SnO$_2$, $^{119}$Sn Mossbauer spectroscopy is widely used and is the second most popular spectroscopy after $^{57}$Fe. The lifetime of the first excited state is 18.3 ns and is long enough to be measured. The force constant can in turn either be deduced from $g(E)$ or from $S(E)$ because it is proportional to the third central moment of $S(E)$:

$$\langle F \rangle = \frac{M}{h} \int_0^{+\infty} \frac{E^2 g(E) dE}{(E - E_R)^3 S(E) dE}$$

where $E_R$ is the free recoil energy and $M$ the mass of $^{119}$Sn. The equilibrium isotope fractionation coefficient $\alpha_{A-B}$ can then be calculated as the ratio of their $\beta$ factors:

$$1000 \times \ln \alpha_{A-B} = 1000 \times \ln \beta_A^I - 1000 \times \ln \beta_B^I$$

Fig. 1. Partial projected density of states of Sn in the studied samples. Spectra of SnO and SnO$_2$ are from Dauphas et al. (2018).
enough to be also observed upon excitation by a synchrotron pulse (Alp et al., 1993). The resonance energy is 23.880 keV, and the transition is between ground state of spin 1/2 to excited state of spin 3/2. Despite the high transition energy compared to iron, the recoil free fraction to observe the Mössbauer effect is relatively large.

In order to determine the approximate valence state of Sn in different glasses, we used time-domain Synchrotron Mössbauer Spectroscopy (SMS) at beamline sector 30 (APS, USA). We measured two data sets: a first with glass samples of interest only, and a second set where different reference samples were placed together with the silicate glasses of interest. This procedure allows us to determine the relative isomer shift of the sample against the known value of the reference sample (Alp et al., 1995). Typical SMS measurements take from half an hour to a few hours of collection time. The main difficulty is to find the right thickness of the reference material so that the sample and the reference material have the same effective thickness defined as:

\[ t_{\text{eff}} = f_{\text{LM}} \eta \sigma_0 d \]

where \( f_{\text{LM}} \) is the recoil-free fraction of the Lamb-Mössbauer factor, \( \eta \) is the number of Mössbauer nuclei per unit volume, \( \sigma_0 \) is nuclear resonant cross-section (1.4 x 10^{-18} cm² for 119Sn) and \( d \) is physical thickness of the absorber. The data analysis was performed using the CONUSS software (Sturhahn, 2000).

3. RESULTS

3.1. Partial phonon density of states

The partial phonon density of states \( g(E) \) were derived from the phonon excitation probability density function \( S(E) \) measured by NRIXS, (Fig. 1). The \( S(E) \) previously collected on SnO₂ by Hu et al., (1999) and on SnO by Giefers et al., (2006) were recently processed with Sciphon, published elsewhere (see Dauphas et al., 2018 for an extensive discussion) and are reproduced here. Systematic changes as a function of the valence state for a given glass composition are expected. Reduced glasses exhibit a sharp and intense phonon peak at about 10 meV followed by a featureless tail extending to 80 meV (Fig. 1). Oxidized glasses show a broader first phonon peak at slightly higher energy (around 15 meV) associated with a second peak at 70 meV. In addition, the composition of the glass significantly affects \( g(E) \). This is particularly true in oxidized samples where the first phonon peak is found at lower energy for rhyolite than for basalt (Fig. 1). As discussed below, this feature has a significant effect on the Sn isotope fractionation factors. Another important observation is that the shape of \( g(E) \) in glasses is relatively smooth compared to pure SnO and SnO₂ spectra (Fig. 1a). This is a clear indication that tin is readily accommodated in the glass structure and does not form small crystallites of pure tin oxide or metal nuggets.

3.2. Tin valence state in silicate glasses

The isomer shift (IS) of tin dissolved in silicate glasses were extracted from the fit to the Synchrotron Mössbauer spectra (SMS, Fig. 2). From these IS (Table 2), the valence state of the glass samples was estimated by comparison with existing data also compiled in Table 2. We note here that the SMS is less accurate and straightforward than conventional Sn Mössbauer in determining the redox ratio of tin-bearing silicates. Nonetheless, it appears that the glasses prepared in air have IS indistinguishable from the SnO₂ reference material. It is thus reasonable to assume that these glasses only contain tetravalent tin (stannous tin, Sn⁴⁺). This result is consistent with the conventional Mössbauer study by Sitek et al. (1981), which revealed the presence of only small amounts, restricted to less than 5%, of stannous tin in granitic liquids prepared in air at 1600 °C. This is also consistent with the fact that no stannous tin was detected in granitic melts prepared at the magnetite/hematite fugacity buffer (Durasova et al., 1997) and with the fact that such granitic glasses were systematically found to contain more stannous tin than basaltic glasses at a given oxygen fugacity (Durasova et al., 1984). The coordination chemistry of tin in these samples may be different though as suggested by the slightly different values of IS. Turning to reduced samples, the IS of the rhyolite is very similar to the IS of pure SnO₂, which strongly suggests that this sample contains only divalent tin (stannous tin). Finally,
the IS of the reduced basalt is intermediate between the IS of SnO and SnO$_2$. This might be an indication that some Sn$^{4+}$ is present in this glass. However, this glass, just as the reduced rhyolite, was prepared at high pressure and temperature in a graphite capsule. In these conditions, it is unlikely that significant amount of Sn$^{4+}$ could be stabilized. Based on Ellingham diagrams (Lehmann, 2006), the Sn$^{4+}$/Sn$^{2+}$ equilibrium (defined from data on sodium silicate glasses studied by Johnston, 1965) and the SnO/SnO$_2$ equilibrium at 1550 °C are found at oxygen fugacities several orders of magnitudes higher than the CCO buffer. Therefore, just as these glasses prepared in graphite capsules, do not contain measurable amounts of ferric iron (Roskosz et al., 2018), we can reasonably assume that the reduced basalt cannot contain measurable amount of stannic tin. This view is supported by previous conventional Mössbauer data suggesting that at oxygen fugacities lower than the Ni-NiO buffer no more than 5% of Sn$^{4+}$ were found in granitic and basaltic glasses (Durasova et al., 1984, 1986, 1997). Consequently, the slightly different IS measured for basalt may suggest that Sn$^{2+}$ dissolved in the basalt has a different coordination chemistry compared with tin present in the rhyolite. More experiments, involving tin conventional Mössbauer spectroscopy should be carried out in the future to confirm this interpretation.

### 3.3. Tin force constants in silicate glasses

Table 2 compiles the valence state determined by SMS and the mean force constant \( \langle F \rangle \) measured by NRIXS. A more extensive compilation of physical properties calculated from the NRIXS spectra is also provided in Table 3. It includes estimates of the Lamb-Mössbauer factor, kinetic energy per atom, force constant, mean force constant at \( T = 0 \) K, kinetic energy at \( T = 0 \) K, vibrational specific heat, vibrational entropy, and critical temperature. Because the present paper is concerned with high temperature isotopic fractionation where 1000 ln \( b \) is typically 200–250 N/m, it is unlikely that significant amount of Sn$^{4+}$ could be stabilized. Based on Ellingham diagrams (Lehmann, 2006), the Sn$^{4+}$/Sn$^{2+}$ equilibrium (defined from data on sodium silicate glasses studied by Johnston, 1965) and the SnO/SnO$_2$ equilibrium at 1550 °C are found at oxygen fugacities several orders of magnitudes higher than the CCO buffer. Therefore, just as these glasses prepared in graphite capsules, do not contain measurable amounts of ferric iron (Roskosz et al., 2018), we can reasonably assume that the reduced basalt cannot contain measurable amount of stannic tin. This view is supported by previous conventional Mössbauer data suggesting that at oxygen fugacities lower than the Ni-NiO buffer no more than 5% of Sn$^{4+}$ were found in granitic and basaltic glasses (Durasova et al., 1984, 1986, 1997). Consequently, the slightly different IS measured for basalt may suggest that Sn$^{2+}$ dissolved in the basalt has a different coordination chemistry compared with tin present in the rhyolite. More experiments, involving tin conventional Mössbauer spectroscopy should be carried out in the future to confirm this interpretation.

### 3.4. DISCUSSION

#### 4.1. Redox- and structural dependence of \( \beta \)-factors of Sn-bearing phases

For all studied samples, 1000 ln \( \beta_{122,11660} \) was calculated using the formalism detailed in Dauphas et al. (2012, 2018) with coefficients extracted from NRIXS data by the Sciphon software. Additional data collected on the same beamline for Sn, SnO and SnO$_2$ were included. These data represent an updated version of those used in the earlier work of Polyakov et al. (2005). For SnO and SnO$_2$, small differences (Table 2) are found as compared to the initial evaluation of Polyakov et al. (2009 and 413 N/m for SnO and SnO$_2$, respectively) and the reprocessing performed by Dauphas et al. (2018) and given in Table 2. As emphasized by Dauphas et al. (2014) and Blanchard et al. (2015), great care must be exercised in handling the low and high-energy tails of NRIXS spectra for application to isotope geochemistry. Furthermore, Roskosz et al., (2015) demonstrated that such differences do not affect the equilibrium fractionation factors provided that self-consistent datasets are used to calculate them. In this sense, the present dataset should supersede original estimates of Polyakov et al. (2005) at least for applications to mantle and volcanic contexts.
<table>
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<th>Basalt_air</th>
<th>Basalt_CCO</th>
<th>Rhyolite_air</th>
<th>Rhyolite_CCO</th>
<th>Anorthite_Air</th>
<th>Anorthite_CCO</th>
<th>Enstatite_Air</th>
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<td></td>
<td>-119.22 to 148.833</td>
<td>-119.192 to 147.916</td>
<td>-119.419 to 148.957</td>
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<td>-116.142 to 149.579</td>
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<td>21.2 ± 4.8E03</td>
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<td>a=</td>
<td>5.30E-03 ± 1.62E-03</td>
<td>5.86E-03 ± 1.14E-03</td>
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<td>1.15E+00 ± 1.30E-01</td>
<td>7.20E-03 ± 1.30E-01</td>
<td>6.75E-03 ± 1.30E-01</td>
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<td>b=</td>
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<td>1.15E+00 ± 1.30E-01</td>
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<tr>
<td>Temperature from detailed balance (K):</td>
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<td>303</td>
<td>312</td>
<td>308</td>
<td>299</td>
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<td>From S</td>
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<td></td>
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<td>0.238 ± 0.0021</td>
<td>0.474 ± 0.0037</td>
<td>0.3059 ± 0.0029</td>
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<td>254 ± 16</td>
<td>412 ± 21</td>
<td>250 ± 14</td>
<td>536 ± 20</td>
<td>204 ± 13</td>
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<td>From g</td>
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<tr>
<td>A2</td>
<td>-8.25E+09 ± 9.74E+08</td>
<td>-3.31E+09 ± 6.99E+08</td>
<td>-5.45E+09 ± 7.63E+08</td>
<td>-2.93E+09 ± 4.7E+08</td>
<td>-1.08E+09 ± 1.78E+08</td>
<td>-2.07E+09 ± 3.40E+08</td>
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<tr>
<td>A3</td>
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<td>6.85E+13 ± 2.86E+13</td>
<td>8.32E+13 ± 2.62E+13</td>
<td>5.16E+14 ± 1.56E+13</td>
<td>2.81E+14 ± 6.83E+13</td>
<td>3.23E+13 ± 8.32E+13</td>
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<tr>
<td>1000 ln beta [22Sh/116Sn = B1/F2/B2²/F²/T² (T in K)]</td>
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<td>B1</td>
<td>2492</td>
<td>1929</td>
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<td>Beta-value coefficients from g</td>
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<tr>
<td>1000 ln beta [22Sh/116Sn = A1/T² + A2/T⁴ + A3/T⁶ (T in K)]</td>
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<tr>
<td>A1</td>
<td>983.125</td>
<td>491.262</td>
<td>796.442</td>
<td>483.783</td>
<td>1.036.617</td>
<td>395.538</td>
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<tr>
<td>A2</td>
<td>-8.277E</td>
<td>-3.31E+09</td>
<td>-5.47E</td>
<td>-2.94E</td>
<td>-1.09E</td>
<td>-2.10E</td>
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Table 3
Compilation of parameters derived from NRIXS spectra.
because our samples are geochemically more relevant in these cases (see Fig. 4).

The bond stiffness controls the isotope fractionation between coexisting silicate and oxide phases and it is well accepted that the higher the valence state, the stiffer the bonds. However, the trend of \( \langle F \rangle \) as a function of the valence state is not linear. While \( \langle F \rangle \) is very close for Sn\(^0\) and Sn\(^2+\), it is much higher for Sn\(^4+\). The change in the valence state from metallic to ionic bonds does not necessarily involve significant changes in bond stiffness. This feature has already been observed for other isotopic systems. While the difference in \( \langle F \rangle \) between Fe\(^0\) and Fe\(^2+\) is small, the contrast in \( \langle F \rangle \) is higher between ferrous and ferric iron. This result implies that no significant Fe isotopes fractionation is expected at magmatic temperatures between metal and silicates (Poitrasson et al., 2009, Hin et al., 2012, Dauphas et al., 2014, Liu et al., 2017). A similar result was also found experimentally on Ni, for which no significant Ni isotope fractionation could be experimentally observed during metal-silicate and sulfide-silicate equilibriations at magmatic conditions (Lazar et al., 2012; Guignard et al., 2019). The increase of \( \langle F \rangle \) with the valence state at constant chemical composition also appears larger from Sn\(^2+\) to Sn\(^4+\)-bearing glasses than those documented between Fe\(^2+\) and Fe\(^3+\)-bearing glasses (Dauphas et al., 2014). However, the force constants seem to exhibit the same trend as a function of the oxidation state of the cation of interest. From a purely Fe\(^3+\)-bearing basalt to a purely Fe\(^2+\)-bearing basalt, \( \langle F \rangle \) increases from 200 N/m to 350 N/m. From Sn\(^2+\)-bearing basalt to Sn\(^4+\)-bearing basalt, \( \langle F \rangle \) increases from 250 N/m to 530 N/m. But this increase is comparable (\~140–150 N/m) if it is expressed per valence unit (i.e. from (II) to (III) for Fe and from (II) to (IV) for tin). Therefore, the higher \( \beta \)-factors for tin isotopes as compared to Fe isotopes for a given glass composition reflects primarily the larger relative mass difference between the tin and iron isotopes respectively involved (Am/m = 0.05 for \(^{122}\text{Sn}/^{116}\text{Sn} \) against 0.036 for \(^{56}\text{Fe}/^{54}\text{Fe} \)).

In addition to the effect of the valence state, the coordination chemistry of cations in melts and minerals also plays an important control on the bond stiffness. At constant valence state, our data indicates that Sn\(^4+\)-bearing basalt should be significantly enriched in heavy tin isotopes as compared to rhyolitic melts (by up to 0.2 \( \varepsilon \) at 1000 K). By comparison, such a contrast was not observed for iron isotopes between ferric basalts and rhyolites, but a significant fractionation was resolved between ferrous rhyolites and basalts –rhyolites being enriched in heavy iron isotopes—(Dauphas et al., 2014). Similarly, the reduced anorthite glass shows a significantly lower \( \langle F \rangle \) than other reduced glasses. This points to the entangled effects of the valence state and coordination chemistry. The coordination chemistry of stannous and stannic tin has been documented on pure minerals and glasses (e.g. Kossiakoff and Leavens, 1976; Seki et al., 1984; Giefers et al., 2006; Farges et al., 2006). It was found that Sn\(^4+\)-bearing glasses have a typical EXFAS/XANES spectra very close to the aekerite (Ca\(_2\)-SnAl\(_4\)Si\(_3\)O\(_{16}\)(OH)\(_2\).2H\(_2\)O), where tin is in octahedral position, while the environment of Sn\(^2+\) is closer to the romarchite (SnO), where tin is eight-fold coordinated. In details, the bond length Sn\(\sim\)O in oxidized glasses studied by Farges et al., (2006) was found to be slightly shorter than in crystalline cassiterite (though in both cases Sn is six-fold coordinated), which is consistent with the slightly higher \( \langle F \rangle \) of most oxidized glasses studied here as compared to pure SnO\(_2\) and with the fact that the higher the IS of the oxidized glass, the higher \( \langle F \rangle \) (Table 2). Along the same line, ‘Rhyolite Air’ exhibits a mean force constant that is signifi-
icantly lower than other samples and SnO₂. This must therefore point out either to a higher coordination number of Sn in this glass or to a longer Sn–O bond. Similarly, the isomer shift measured by Mössbauer spectroscopy is also lower for rhyolitic glass than it is for basaltic glass and casseriterite (Table 2). These observations could again reflect a change in coordination of Sn⁴⁺, as argued by Johnson et al. (2005) whereby a higher coordination for Sn⁴⁺ in rhyolite would correspond to the lower isomer shift (−0.29 mm/s). The difference with the observations of Farges et al. (2006) who inferred a constant six-coordination of Sn(IV) may stem from the difference in melt composition. Turning to reduced glasses, no significant differences was found between rhyolitic and basaltic glasses. They both have force constants significantly higher than pure SnO, pointing out to a shorter Sn–O bond in glasses. Farges et al. (2006) demonstrated that Sn⁴⁺ coordination strongly depends on the aluminous content in hapolgranitic melts. It was found that in peralkaline domain, the mean coordination number was higher than in metaluminous and peraluminous domains. In this context the lower force constant of anorthite could be explained by its metaluminous nature, whereas the peraluminite nature of other melts tends to lower the average Sn–O bond length in other glasses.

As a final remark, we note that no large (yet resolved) difference is found between the β-factors of pure α-Sn and SnO-bearing silicates (Fig. 3). In other words, our results would suggest at first sight that no measurable tin isotopes fractionation during core-mantle differentiation should be analytically resolved (ΔS₅₆₋₅₁ ≈ −0.03‰). A detailed study of tin-bearing, geochemically relevant metal alloys at high pressure must however be carried out to confirm this preliminary conclusion.

4.2. Tin isotope fractionation during mantle melting

In the upper mantle, tin should exist both as Sn²⁺ and Sn⁴⁺ (Durasova et al., 1986). As discussed before, owing to their different ionic radius and charge, Sn²⁺ and Sn⁴⁺ behave very distinctly during magmatic processes. During partial melting, as Sn⁴⁺ is more incompatible than Sn²⁺, Sn⁴⁺ is enriched in the melt relative to the residual solid. The measurements of Sn force constant in the ‘basalt Air’ and ‘basalt CCO’ samples show that heavy isotopes will preferentially be associated with the high oxidation state (i.e. Sn⁴⁺), which is consistent with isotope fractionation theory (Schauble, 2004). Hence, heavy Sn isotopes will preferentially be released in the melt during partial melting of a peridotite. Wang et al. (2018) measured the Sn isotopic composition of basalts and peridotites and found that peridotites show an enrichment in light Sn isotopes relative to basalts. This observation is best explained by the higher incompatibility of Sn⁴⁺ relative to Sn²⁺ during partial melting which produces an enrichment of Sn⁴⁺ in the liquid. Because Sn⁴⁺ is associated with a high force constant, high δ¹²⁴Sn values (the ‰ deviation of the ¹²⁴Sn/¹¹⁶Sn relative to the NIST SRM 3161a standard) are observed in the liquid and the solid residue is enriched in light isotopes. Wang et al. (2018) also showed that the Sn isotope composition of peridotites becomes isotopically lighter as the degree of melting increases. Furthermore, they modeled the effect of partial melting using non-modal batch melting to interpret the Sn isotope measurements and found that the isotopic composition of peridotites could be explained by partial melting at ~3 GPa and an isotope fractionation factor Δ¹²⁴Sn between Sn⁴⁺ and Sn²⁺ equal to 1.2‰ at 1200 °C, where this latter value was fit to match the observations.

Here we have reexamined this data set in light of the NRIXS measurements of glasses. The Sn isotope fractionation factor between Sn⁴⁺ and Sn²⁺ determined with the NRIXS data is equal to 0.27‰ for a temperature of 1250 °C. Using the model derived in Wang et al. (2018) the calculated δ¹²⁴Sn of residual peridotites reaches a minimum value of −0.21‰, which is significantly higher than what is observed for an Sn depletion of 70% relative to the primitive mantle (Sn = 180 ppb). This means that in light of the new NRIXS data, the non-modal batch-melting model presented in Wang et al. (2018) is not consistent with the Sn isotope data. For this purpose, based on the new value of Δ¹²⁴Sn between Sn⁴⁺ and Sn²⁺, we have developed a more sophisticated model based on fractional melting that is consistent with the new Sn isotope fractionation factors. We have modified the fractional melting model of Dauphas et al. (2009) for predicting the Fe isotope fractionation during partial melting (this model assumes that the Sn⁴⁺/Sn²⁺ ratio in each phase has a fixed value set by the redox state of Fe). This isotope system is similar to tin as there is an equilibrium isotopic fractionation between Fe³⁺ (incompatible) and Fe²⁺ (compatible). The new equations for Sn²⁺ and Sn⁴⁺ can be written:

\[
\delta_{i} = \delta_{0} + \ln(1 - f) \frac{(Sn(IV)/Sn(II))_{f}}{(1 + (Sn(IV)/Sn(II))_{f})} (K_{Sn(IV) - Sn(II)})_{\Delta_{Sn(IV)}}
\]

(7)

Fig. 5. δ¹²⁴Sn in the solid residue as a function of the degree of partial melting of a peridotite (data for peridotites from Wang et al. (2018) and were measured as ¹²⁴Sn/¹¹⁶Sn relative to the NIST SRM 3161a standard). As Sn⁴⁺ is preferentially associated with heavy Sn isotopes, δ¹²⁴Sn decreases as partial melting proceeds due to the release of more incompatible Sn⁴⁺ to the liquid. At high pressure (3 GPa), Sn⁴⁺ is more incompatible than at low pressure (1.4 GPa) which enhances the isotope fractionation in the solid residue. cxp: clinopyroxene. The curves at 3 GPa were drawn for various temperatures as shown by the color code.
while $Sn^{2+}$ becomes more compatible (sensu, $Sn^{4+}$ becomes more incompatible (sensu) during partial melting. Indeed, at higher pressures was shown to have a major influence on the Sn isotope fractionation but mostly affects the value of partition coefficients for peridotites is best explained by a fractional melting at 3GPa around 1350–1450 °C which is consistent with melting conditions under such pressure (Dasgupta et al., 2007, Mallman and O’Neill, 2009). We considered the partial melting of a peridotite in the garnet stability field would produce little to no Sn isotope fractionation between the liquid and the solid since both Sn(II) and Sn(IV) are compatible in the garnet (Wang et al., 2018). Therefore, the presence of garnet in the source would be inconsistent with data from Wang et al. (2018). Fig. 6 shows that the liquid is enriched in heavy isotopes due to a higher Sn$_{4+}$ abundance in the melt. The Sn$_{4+}$ dilution during partial melting induces a decrease of $\delta^{124}$Sn. Similarly to Fig. 5, a decrease in temperature leads to a higher isotopic fractionation relative to the Bulk Silicate Earth (BSE). Conversely, an increase of pressure does not significantly influence the magnitude of the isotopic fractionation but mostly affects the value of partition coefficients. As shown in Wang et al. (2018), at higher pressures, Sn$_{4+}$ which is located in the M1 site becomes more incompatible in clinoxyroxene, thereby modifying the overall compatibility of Sn during melting. As the majority of Sn is in the form of Sn$_{4+}$ in the upper mantle, most of the tin budget will be in the melt (Sn$_{4+}$/Sn$_{2+}$ = 7.3), leading to a less marked tin enrichment in heavy isotopes (<0.2‰).

4.3. Tin isotope fractionation during fractional crystallization

Badullovich et al. (2017) have shown that fractional crystallization of basalts leads to a large enrichment in tin in the residual melt as tin is incompatible in the crystallizing mineral assemblage. Interestingly, there is enrichment in light Sn isotopes in melts with an MgO below 8 wt%. The calculated bulk tin mineral/melt partition coefficient indicates that the oxidation state of tin must be predominantly Sn$_{4+}$ during magma differentiation, as Sn$_{2+}$ would be far more compatible and Sn concentrations would not fit the trend in Badullovich et al. (2017). Altogether, these observations were suggested to result from the incorporation of isotopically heavy Sn in ilmenite. The Sn isotope fractionation was interpreted in terms of a difference in coordination of Sn$_{4+}$ between the melt (where tin would be eightfold-coordinated) and the ilmenite where it is sixfold-coordinated (Badullovich et al., 2017). However, as discussed above, Sn$_{4+}$ was reported to be six-fold coordinated both in silicate melts (Farges et al., 2006) and in ilmenite (Klemme et al., 2006). Most of our spectroscopic results are consistent with the conclusions of Farges et al. (2006). Nonetheless, the dependence of (F) against the glass composition determined in our study may help to better evaluate the hypothesis of Badullovich et al. (2017) regarding the effect of structural properties of tin in minerals on Sn isotope fractionation.
In order to re-examine this data set, we have attempted to model the Sn isotope composition of the Kilauea Iki lava lake using the force constants determined in the NRIXS data. In this context, we modeled the effect of successive steps of ilmenite fractional crystallization in a magma chamber. The $\delta^{124}_{124}$Sn value in the melt at step $n$, $\delta^n_{02}$ was calculated from the $\delta^{124}_{124}$Sn value at step $n-1$, $\delta_{n-1}$:

$$\delta^n_{02} = \delta^{n-1}_{02} - \phi^n_{10} \Delta Sn_{O2}^{Rhyolite}$$

where $\phi^n_{10} = \frac{f_{1}[Sn]_{l}}{f_{1}[Sn]_{l} + f_{1}[Sn]_{l'}}$, $[Sn]_{l} = \frac{[Sn]^{n-1}_{l} - f_{1}[Sn]_{l}}{f_{1}}$.

$$\delta^n_{02} = \Delta Sn_{O2}^{Rhyolite} + \delta^n_{02}$$

with the following initial conditions:

$$\delta^0_{02} = 0.6\%e, [Sn]_{l} = 7.6ppm, [Sn]_{l}^0 = 1ppm$$

and considering $\Delta Sn_{O2}^{Rhyolite} = 0.09\%e$ at 1100 °C. The rationale here is that the force constant of SnO2 is a proxy for that of ilmenite since Sn$^{4+}$ is likely to substitute to Ti$^{4+}$, where Fe$^{2+}$—O, Ti$^{4+}$—O becomes Fe$^{2+}$—O, Sn$^{4+}$—O. As shown before, SnO3 has a higher force constant than rhyolite glass (unlike basalt and other synthetic glasses studied here), thereby suggesting that the Sn isotope composition of ilmenite could be heavier than the residual liquid, which is qualitatively consistent with the observations of Badullovich et al. (2017). Because samples from Badullovich et al. (2017) are characterized by an intermediate composition between a basalt and rhyolite, both composition could a priori be considered for the residual liquid composition. In this model, at each step, ilmenite enriched in heavy tin isotopes crystallizes and is removed from the system thereby inducing an enrichment of light isotopes in the residual liquid (Fig. 7). Fig. 7 shows that the lowest $\delta^{124}_{124}$Sn observed in Badullovich et al. (2017) (i.e. the most fractionated sample) could be explained by a crystallization of 10.4 ± 0.07 wt% of ilmenite in the magma chamber. This number is roughly consistent with observed modal abundances of ilmenite in Hawaiian basalts (Peck et al., 1966). In order to further verify this hypothesis, we modeled the expected Ti and Sn abundances during fractional crystallization. We observed that crystallization of 10% ilmenite should decrease the TiO$_2$ abundance in the melt to 1.3%. However, the basaltic andesite analyzed by Badullovich et al. (2017) show a TiO$_2$ of 2.59 %wt which reflect that the proportion of crystallized ilmenite is ~1.5% which is far less than the 10% required to explain the Sn isotope composition. Thus, although the idea of ilmenite crystallization is in qualitative agreement with the observations, the observed fractionation would require a much higher Sn isotope fractionation factor between ilmenite and melt than what we considered in this model. We note here that the Sn isotope observations for Kilauea Iki cannot be rationalized in terms of kinetic isotope fractionation with incorporation of light Sn isotopes in the minerals because this would leave a melt with enrichment in heavy Sn isotopes, which is the opposite of what is observed (Badullovich et al., 2017).

5. CONCLUSIONS

Seven geologically-relevant silicate glasses were synthesized with moderate amounts of $^{119}$Sn. Redox conditions were controlled during sample synthesis to set the redox ratio ($^{124}$Sn$^{2+}$/Sn$_{tot}$) from stannous (Sn$^{2+}$) to stannic (Sn$^{4+}$) glasses. The mean force constants of tin bonds in these glasses were determined by synchrotron nuclear resonant inelastic X-ray scattering (NRIXS) in order to determine the reduced isotopic partition function ratios ($\beta$-factors) of these glasses. The coordination chemistry and the valence state of tin in these glasses were also derived from synchrotron Mossbauer spectroscopy (SMS). For all studied samples, $1000 \times \ln \beta_{122}/1660$ was calculated.

Reduced glasses exhibit a sharp and intense phonon peak at about 10 meV followed by a featureless tail extending to 80 meV. Oxidized glasses show a broader first phonon peak at slightly higher energy associated with a second peak at 70 meV. The force constant of tin is a strong function of the valence state and of composition of the silicate melts. The values are also significantly different from those collected for pure crystalline compounds. Whereas reduced basalts and rhyolites have similar force constants, the force constant of the reduced anorthite is significantly lower. Concerning oxidized samples, most glasses have force constants close to pure SnO2 though slightly higher. The force constant of rhyolitic glass is however significantly lower by almost 100 N/m than that of pure SnO2. At constant valence state, our data indicates that Sn$^{4+}$-bearing basalt should be significantly enriched in heavy tin isotopes as compared to rhyolitic melts (by up to 0.2 %e at 1000 K). The effect of Al and possibly K likely explains the $\beta$-factors of outliers (reduced anorthite and oxidized rhyolite) as compared to other samples because these cations affect either Sn=O bond length and/or the coordination number of tin in the melts.

From our dataset it is concluded that the incompatible behavior of Sn$^{4+}$ in mantle minerals leads to an enrichment
in heavy isotopes in mantle melts and to the depletion in heavy isotopes in solid residues of melting with a magnitude consistent with the isotope fractionation between Sn\(^{2+}\) and Sn\(^{4+}\) predicted here. During fractional crystallization of basalt and considering the effect of tin coordination number in minerals and melts, the partitioning of Sn\(^{4+}\) into ilmenite would lead to an enrichment in light isotopes in the residual melt. As a final remark, we note that no large difference is found between the \(\alpha\)-factors of pure Sn (measured elsewhere) and SnO-bearing silicates. Our results would suggest, at first sight that no measurable tin isotopes fractionation during core-mantle differentiation should be analytically resolved in natural samples. A detailed study of tin-bearing, geochemically relevant metal alloys at high pressure must however be carried out to confirm this preliminary conclusion.

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APPENDIX A. SUPPLEMENTARY MATERIAL

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