Sn(II) chloride speciation and equilibrium Sn isotope fractionation under hydrothermal conditions: A first principles study

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Abstract

Knowledge of Sn(II) speciation in aqueous and gaseous phases and the corresponding isotope effects are critical for understanding the transport and deposition of Sn in various geological and cosmochemical processes. In this study, we use first principles method to investigate the speciation of stannous (Sn(II)) chloride in fluids under hydrothermal and supercritical conditions. The results show that SnCl₃(CO), SnCl₂(H₂O) and SnCl(H₂O)₂⁺ are stable in hydrothermal solutions at temperatures of up to 300 °C, with SnCl₃ being the dominant species, whereas SnCl₂ and SnCl₂(H₂O) are the stable species in vapor phases. Notably, SnCl₂ is found to be stable under supercritical conditions. The reduced partition function ratios (β factors) for the stable Sn(II) species and three major Sn minerals (cassiterite, megawite, and romarchite) are also calculated by first principles methods. The calculation results show that under equilibrium, heavy Sn isotopes are preferentially partitioned into stannic (Sn(IV)) species, and gaseous species enrich heavy Sn isotopes relative to aqueous species. Based on the equilibrium Sn isotope fractionation factors derived in this study, we use a transport-precipitation model to evaluate the Sn isotope response to cassiterite precipitation in hydrothermal fluids. The modeling results show that significant Sn isotope variability could be produced during cassiterite precipitation, with temperature and Sn speciation being the primary controlling factors. Furthermore, by comparing the Sn isotope variability in natural cassiterite and those derived from the model, we argue that Sn should occur predominantly as Sn(IV) species in hydrothermal fluids during cassiterite precipitation in tin mineralizing systems.

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Keywords: Tin; Hydrothermal fluids; Speciation; Equilibrium isotope fractionation; First principles molecular dynamics (FPMD); First principles calculation

1. INTRODUCTION

Tin (Sn) is recognized as a strategic critical metal because of its vital roles in many emerging industries such as clean energy and electronics (Hayes and McCullough, 2018; Tarselli, 2017). Tin is a volatile trace element with three oxidation states (i.e., 0, +2 and +4), and thus its geochemical behavior can be strongly influenced by redox con-
ditions (Chen et al., 2000; Teng et al., 2017). For example, tin is an incompatible element during magmatic processes and there may be difference between the incompatibility of Sn\(^{4+}\) and Sn\(^{2+}\) (e.g., Farges et al., 2006; Badullovich et al., 2017). Redox conditions also have strong effect on the solubility of cassiterite in hydrothermal fluids or silicate melts (e.g., Jackson and Helgeson, 1985; Bhalla et al., 2005). Tin has ten stable isotopes (i.e., \(^{112}\)Sn, \(^{114}\)Sn, \(^{115}\)Sn, \(^{116}\)Sn, \(^{117}\)Sn, \(^{118}\)Sn, \(^{119}\)Sn, \(^{120}\)Sn, \(^{122}\)Sn and \(^{124}\)Sn) and its isotope geochemistry has aroused great interest in recent years for its applications in probing planetary processes (Creech and Moynier, 2019; Wang et al., 2019b), magmatic and hydrothermal processes (Badullovich et al., 2017; Wang et al., 2018; Yao et al., 2018; Roskosz et al., 2020), environmental processes (Malinovskiy et al., 2009) and archaeological problems (Balliana et al., 2013; Mason et al., 2016, 2020).

Mineralization of Sn is primarily associated with hydrothermal processes (Heinrich, 1990; Lehmann, 1990; Chen et al., 2000). Therefore, knowledge of speciation of Sn in geological fluids is crucial for understanding its deposition mechanisms. Speciation of Sn in hydrothermal fluids has been studied using various methods but it remained a topic of hot debate. Stability of Sn(IV) species in aqueous solutions has been reported based on data of in situ extended X-ray absorption fine structure (EXAFS) spectroscopy (Sherman et al., 2000), Raman spectroscopy (Schmidt, 2018) and first principles molecular dynamics (FPMD) simulations (She et al., 2020), however, numerous solubility experiments have indicated that Sn(II) chloride is most likely to be responsible for the transport of Sn in hydrothermal fluids (e.g., Pabalan, 1986; Wilson and Eugster, 1990; Taylor and Wall, 1993; Duc-Tin et al., 2007). Furthermore, the exact speciation of Sn(II) chloride remains unclear. Solubility experiments at 200–350 °C by Pabalan (1986) emphasized the dominance of SnCl\(_4^{2-}\) and SnCl\(_3^-\). Similarly, Sherman et al. (2000) suggested that the Sn(II)–Cl coordination numbers increased from 3.4 at 25 °C to about 4.0 at 350 °C, and attributed it to the enhanced stability of SnCl\(_3^-\) at higher temperature. In contrast, in an in situ ultraviolet (UV) spectroscopy study, Müller and Seward (2001) only detected the presence of SnCl\(_3^-\) at T ≤ 150 °C, and proposed that SnCl\(_3^-\) and SnCl\(_2^-\) were the dominant Sn(II) chlorides at higher temperatures up to 300 °C. In a recent in situ Raman spectroscopy study on cassiterite dissolved in HCl solutions, SnCl\(_3^-\) was thought to be the only detectable Sn(II) species (Schmidt, 2018). The FPMD simulations by Sherman (2010) indicated that SnCl\(_3^-\) and SnCl\(_2^-\) coexisted at 25 °C and SnCl\(_3^-\) was dominant at 325 °C, whereas SnCl\(_2^-\) was not stable. However, no detailed structural or thermodynamic information was provided by Sherman (2010). In supercritical aqueous fluids, SnCl\(_3^-\) was proposed as the common dominant species based on solubility experiments from 400 °C to 800 °C (Wilson and Eugster, 1990; Taylor and Wall, 1993; Duc-Tin et al., 2007).

The poor understanding of Sn speciation in various kinds of fluids is also a main obstacle for applying Sn isotopes to many systems. Existing studies demonstrated that Sn isotope fractionation takes place during crystallization fractionation (Badullovich et al., 2017), partial melting (Wang et al., 2018), redox reactions (Yao et al., 2018; Wang et al., 2019a) and liquid–vapor partitioning (Wang et al., 2019a; She et al., 2020). The diversity of the bonding environments of Sn in various geological materials (e.g., Sherman et al., 2000; Polyakov et al., 2005; Roskosz et al., 2020) is likely the main reason for causing Sn isotope fractionation (Badullovich et al., 2017; Yao et al., 2018; Wang et al., 2019b; Qu et al., 2020). However, Sn isotope fractionation factor data are available for only a very limited number of Sn-bearing solids (Polyakov et al., 2005) and molecules (She et al., 2020). No experimental isotope fractionation factor for Sn(II) species has been reported due to the tendency of Sn(II) oxidation at ambient conditions (Wang et al., 2019a). Additional challenges in experimental approaches include the difficulty in separating aqueous Sn(II) and Sn(IV) (Altunay and Gürkan, 2015). Detailed knowledge of Sn speciation in geological fluids and corresponding fractionation factors are necessary for interpreting Sn isotope data from natural samples (Yao et al., 2018; Qu et al., 2020).

First principles molecular dynamics (FPMD) simulation has proven powerful for investigating the coordination chemistry of metal elements in hydrothermal fluids (see the reviews in Brugger et al., 2016; Pokrovski et al., 2013a) and magmas (e.g., Wagner et al., 2017a, b; Wang et al., 2020). First principles modelling has been applied to aqueous chloride species of many metal ions, such as copper (Sherman, 2007, 2010; Mei et al., 2013, 2014), silver (Liu et al., 2012; Pokrovski et al., 2013b), high field strength elements (HFSE) (Jahn et al., 2015) and rare earth elements (REE) (Stefanski and Jahn, 2020; Guan et al., 2020). First principles calculation is also a powerful method to derive equilibrium isotope fractionation factors that are relevant to geological problems (see the reviews in Blanchard et al., 2017; Schauble, 2004), including aqueous/gaseous species (e.g., Liu and Tossell, 2005; Rustad et al., 2008; Hill and Schauble, 2008; Li et al., 2009) and minerals (e.g., Schauble, 2011; Huang et al., 2013; Wu et al., 2015b; Méheut et al., 2021). In our earlier study, by using first principles calculation, we evaluated the stability of possible Sn(IV) chloride species and calculated the equilibrium isotope fractionation factors of the stable Sn(IV) chloride species (She et al., 2020).

In this study, we applied first principles methods to constrain the speciation of Sn(II) chloride in fluids under hydrothermal conditions, and to calculate equilibrium Sn isotope fractionation factors between aqueous, vapor, supercritical fluids, and three major Sn-bearing minerals. The calculation results provide basic constraints for understanding hydrothermal Sn mineralization and interpretation of the rapidly growing Sn isotope data from Sn mineral deposits.

2. METHODOLOGY

The workflow of this study is as follows. We firstly used free energy calculations to constrain the stability of the dominant Sn(II) species under hydrothermal conditions. Based on these results, we calculated the reduced partition
function ratios (β factors) for the stable Sn(II) species based on the vibrational frequencies derived with static first principles calculations. Reduced partition function ratios (β factors) of cassiterite (SnO₂), megawite (CaSnO₃), and romarchite (SnO) were also calculated using static first principles methods. These β factors were used to derive equilibrium Sn isotope fractionation factors between different fluids and minerals, which were then coupled to a transport-precipitation model for discussion of Sn isotope fractionation during the hydrothermal ore-forming processes. The details of the calculation methods in this study are shown as below.

2.1. First principles molecular dynamics (FPMD)

2.1.1. Models

The systems of FPMD simulations are listed in Table 1. The simulation cells were cubic boxes with 3D periodic boundary conditions with a side length of 12.43 Å. The numbers of water molecules were estimated from the equation of state of water for each temperature and the corresponding saturated vapor pressure (P sat) (for aqueous solutions at 330–573 K) or 1.5 kbar (for supercritical aqueous fluids at 773 K and 973 K) (Wagner et al., 2000; Zhang and Duan, 2005). The temperature of 330 K was set for the ambient conditions to avoid the glassy behavior of liquid water at lower temperatures (VandeVondele et al., 2005a).

2.1.2. Method of constraint

To determine the stability of Sn(II)−Cl complexes in aqueous solutions, the free energy changes of the relevant dissociation reactions (i.e., from SnCl₄²⁻/SnCl₃⁻/SnCl₂⁻/SnCl⁺/Sn₂⁺ to SnCl⁻/SnCl₂/SnCl⁺/Sn⁡²⁺) were computed by a series of constrained FPMD simulations. The free energy change (∆F) was obtained by integrating the mean force (f) along a reaction coordinate (Q) (Carter et al., 1989; Sprik and Ciccotti, 1998):

$$\Delta F(Q) = -\int_{Q_0}^{Q} dQ f(Q)$$  \hspace{1cm} (1)

The distance between one Cl⁻ and Sn²⁺ was chosen as the reaction coordinate (Q) in the simulations.

2.1.3. Computational details

FPMD simulations were performed with the CP2K/QUICKSTEP package (Kühne et al., 2020; Hutter et al., 2014; VandeVondele et al., 2005b). In this package, density functional theory (DFT) is implemented with the mixed Gaussian and plane waves (GPW) method (Lippert et al., 1997). PBE (Perdew-Burke-Ernzerhof) exchange–correlation functional (Perdew et al., 1996), D3 dispersion correction (Grimme et al., 2010), double zeta valence polarizable (DZVP) basis sets (VandeVondele and Hutter, 2007) and GTH (Goedecker-Teter-Hutter) pseudopotentials (Goedecker et al., 1996) were employed. The cutoff of the electronic density was set to be 400 Ry. The wave function optimization tolerance was set to be 10⁻⁶. All FPMD simulations were performed in canonical (NVT) ensemble with a time step of 0.5 fs. Except for the simulations of SnCl₄²⁻ (see below), each production simulation was performed for over 30.0 ps, following a prior equilibration for over 5.0 ps. The temperatures were controlled with the Nose–Hoover chain thermostat (Nosé, 1984a,b; Hoover, 1985).

For the equilibration of SnCl₄²⁻, the four Sn—Cl bonds were restrained by using harmonic potentials to avoid the rapid spontaneous dissociation of the complex. The Sn—Cl equilibrium distance was set to 2.47 Å, based on the EXAFS study by Sherman et al. (2000). The restrained simulations were carried out for 10.0 ps. After that the production runs without restraints were performed for at least 60.0 ps at 330 K and 368 K, and for 10.0 ps at 573 K.

2.2. Static first principles calculations

2.2.1. Models

According to the FPMD simulations in this study, SnCl₃⁻ is the dominant Sn(II)—Cl species in aqueous solutions up to 300 °C, and SnCl₂(H₂O) can coexist with it (see Section 3.1). For the static calculations of aqueous species, SnCl₃⁻ and SnCl₂(H₂O) were modeled with 18 or 24 solvent molecules at each temperature. The systems of static calculations are listed in Table 1.

Table 1

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Pressure (bar)</th>
<th>System</th>
</tr>
</thead>
<tbody>
<tr>
<td>330 (aqueous)</td>
<td>0.17 (P sat)</td>
<td>SnCl₂(H₂O) + 61 H₂O</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SnCl₁⁻ + 62 H₂O</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SnCl⁺ + 63 H₂O</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Sn²⁺ + 64 H₂O</td>
</tr>
<tr>
<td>368 (aqueous)</td>
<td>0.84 (P sat)</td>
<td>SnCl₂(H₂O) + 58 H₂O</td>
</tr>
<tr>
<td>573 (aqueous)</td>
<td>85.70 (P sat)</td>
<td>SnCl₂(H₂O) + 44 H₂O</td>
</tr>
<tr>
<td>773 (supercritical)</td>
<td>1500.00</td>
<td>SnCl₂ + 40 H₂O</td>
</tr>
<tr>
<td>973 (supercritical)</td>
<td>1500.00</td>
<td>SnCl₂ + 25 H₂O</td>
</tr>
</tbody>
</table>
water molecules accounting for the solvation effect. The initial structures of the complexes were derived from the FPMD simulations.

Geological vapors usually have very low dielectric constant, favoring neutral species (Pokrowski et al., 2013a). Therefore, six neutral complexes including SnCl₂, SnCl₂(-H₂O), SnCl₃(HCl), SnCl(OH), Sn(OH)₂ and SnO were selected as the possible gaseous Sn(II) species for calculation.

For Sn-bearing minerals, we focused on cassiterite (SnO₂), megawite (CaSnO₃), and romarchite (SnO), to compare with the results from the nuclear resonant inelastic X-ray scattering (NRIXS) study by Polyakov et al. (2005). The models of cassiterite, megawite, and romarchite were supercells consisting of \(2 \times 2 \times 4\) (96 atoms), \(2 \times 2 \times 2\) (160 atoms), and \(5 \times 5 \times 4\) (400 atoms) unit cells respectively. To evaluate the finite size effects, we also built the \(3 \times 3 \times 5\) (270 atoms) for cassiterite and \(3 \times 3 \times 3\) (540 atoms) for megawite, respectively. Their initial structures were constructed based on neutron diffraction data for cassiterite and romarchite (Bolzam et al., 1997; Pannetier and Denes, 1980) and X-ray diffraction data for megawite (Zhao et al., 2004).

2.2.2. Thermodynamic equilibrium isotope fractionation

For the isotope exchange reaction of light Sn isotope \(^{116}\)Sn and heavy Sn isotope \(^{122}\)Sn in two tin isotopomers SnA and SnB:

\[
\text{light } \text{SnA} + \text{heavy } \text{SnB} \leftrightarrow \text{heavy } \text{SnA} + \text{light } \text{SnB}
\]

the thermodynamic equilibrium Sn isotope fractionation factor (\(\alpha_{\text{SnA-SnB}}\)) between SnA and SnB can be expressed as

\[
\alpha_{\text{SnA-SnB}} = \frac{\text{light } \text{SnA}}{\text{light } \text{SnB}} \times \frac{\text{heavy } \text{SnB}}{\text{heavy } \text{SnA}} = \frac{\beta_{\text{SnA}}}{\beta_{\text{SnB}}}
\]

where \(\beta_{\text{SnA}}\) and \(\beta_{\text{SnB}}\) are the reduced partition function ratio (RPFR) of Sn isotopes in SnA and SnB respectively. The difference of Sn isotope compositions between SnA and SnB, \(\Delta\alpha_{\text{SnA-SnB}}\), can be expressed as

\[
\Delta\alpha_{\text{SnA-SnB}} \approx 1000\ln\beta_{\text{SnA}} - 1000\ln\beta_{\text{SnB}}
\]

According to the Urey model or Bigeleisen-Mayer equation (Urey, 1947; Bigeleisen and Mayer, 1947), the beta factor or RPFR can be calculated from the harmonic approximation:

\[
\beta_{\text{SnA}} = \prod_{i=1}^{N} \left(1 + \frac{e^{\frac{\hbar v_i}{k_B T}} - 1}{e^{\frac{\hbar v_i}{k_B T}} + 1}\right)
\]

with

\[
v_i = \frac{\hbar v_i}{k_B T}
\]

where \(N = 3n - 6\) or \(3n - 3\), which denotes the number of harmonic vibrational modes for a non-linear molecule containing \(n\) atoms or the number of phonon modes for a solid system containing \(n\) atoms, respectively. \(h\), \(v_i\), \(k_B\), and \(T\) denote the Planck constant, vibrational (phonon) frequency, the Boltzmann constant, and temperature, respectively. In this study, the equilibrium fractionation factors of \(^{122}\)Sn/\(^{116}\)Sn among the aqueous and gaseous Sn(II) chlorides and Sn-bearing minerals were calculated.

2.2.3. Computational details for aqueous and gaseous species

The static first principles calculations for aqueous and gaseous Sn(II) species were carried out by using the Gaussian 09 package (Frisch et al., 2013). B3LYP hybrid exchange-correlation functional (Becke, 1993; Lee et al., 1988) and def2-TZVP basis sets (Weigend and Ahlrichs, 2005) were employed. Our previous study has shown that with this setting, the calculated bond length of SnCl₂ was in good agreement with experimentally determined results, and the differences between calculated and observed vibrational frequencies were within 5.4% (She et al., 2020). For comparison, the structures and vibrational frequencies of SnCl₄ and SnCl₂ were also calculated with the CCSD(T) method (Raghavachari et al., 1989), which is regarded as the “gold standard” for quantum chemical calculation (Foresman and Frisch, 2015). The aug-cc-pVTZ(-pp)/aug-cc-pVQZ(-pp) basis sets were used for Sn and Cl (Peterson, 2003; Woon and Dunning, 1993). We also compared the calculated bond lengths and vibrational frequencies of Sn(II) species with previous studies (see Table 2 in Section 3.3).

To determine the relative stability of the gaseous species, the Gibbs free energy changes (\(\Delta G\)) of the reactions in Table 3 in Section 3.3 were calculated with:

\[
\Delta G = \sum G_{\text{prod}} - \sum G_{\text{react}}
\]

where \(\sum G_{\text{prod}}\) and \(\sum G_{\text{react}}\) are the total Gibbs free energy values of the product and the reactant states, respectively. These quantities were computed with Gaussian (Foresman and Frisch, 2015) following the methods of McQuarrie and Simon (1999).

To evaluate the computational bias of the transport-precipitation model in Section 4.2, we performed additional calculations for SnCl₄, cis-SnCl₄(H₂O)₂(aq) and SnCl₃(aq) with B3LYP hybrid functional, triple zeta valence polarizable (TZVP) and auxiliary basis sets (VandeVondele and Hutter, 2007; Guidon et al., 2010) and GTH pseudopotentials by using the CP2K/QUICKSTEP package. For cis-SnCl₄(H₂O)₂(aq) and SnCl₃(aq), 18 solvent water molecules were added to the model. These calculations were carried out in cubic boxes with a side length of 25.00 Å by using the BFGS (Broyden-Fletcher-Goldfarb-Shanno) algorithm (Byrd et al., 1995). The Martyna-Tuckerman scheme was used to solve the Poisson equation of non-periodic boundary conditions systems (Martyna and Tuckerman, 1999). The cutoff of the electronic density was set to be 1200 Ry, and the wave function optimization tolerance was set to be \(10^{-8}\).

2.2.4. Computational details for Sn-bearing minerals

For Sn-bearing minerals, cell optimization was performed by using the CP2K/QUICKSTEP package, and the phonon frequencies were calculated by combining QUICKSTEP with the Phonopy package (Togo and Tanaka, 2015). We optimized the structure and calculated the \(1000\ln(\frac{122}{116})\beta\) values of cassiterite at different theoretical levels to investigate the effect of exchange-correlation
functionals and basis sets on the results. In these calculations, LDA (local density approximation) (Goedecker et al., 1996), PBE functional (GGA (generalized gradient approximation) level) and B3LYP hybrid functional were employed, together with DZVP or TZVP basis sets and GTH pseudopotentials. Cell optimization was carried out by using the BFGS algorithm. The cutoff of the electronic density and the wave function optimization tolerance were set to be 1200 Ry and $10^{-8}$, respectively.

The optimized lattice parameters of cassiterite (see Table S1 in the supplementary materials) show that there was no obvious difference between the results of DZVP and TZVP basis sets. The optimized lattice parameters are given in Table S1.

### Table 2

<table>
<thead>
<tr>
<th>Key structural parameters of gaseous SnCl₂ and SnO molecules.</th>
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<td>Bond length (Å)</td>
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<td>SnCl₂</td>
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<tr>
<td>SnO</td>
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^a See Levy et al. (2003) and Lee et al. (2007) for more structure parameters and vibrational frequencies of SnCl₂.

^b At the B3LYP/def2-TZVP level.

^c At the CCSD(T)/aug-cc-pVTZ(-pp) level.

^d At the CCSD(T)/aug-cc-pVQZ(-pp) level.


^f Thanthiriwatte et al. (2015).

^g Ermakov et al. (1991).

^h Fields et al. (1995).

^i de Lima Batista et al. (2012).

^j Wolf et al. (2004). See this article for more structure parameters and vibrational frequencies of SnO.

^k Davico et al. (2000).

### Table 3

<table>
<thead>
<tr>
<th>Gibbs free energy changes ($\Delta G$) of the reactions among possible Sn(II) species in vapor phases calculated at the B3LYP/def2-TZVP level.</th>
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<tbody>
<tr>
<td>Reaction</td>
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<tr>
<td>SnCl₂(H₂O) → SnCl₂ + H₂O</td>
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<td>SnCl₂(HCl) → SnCl₂ + HCl</td>
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<tr>
<td>SnCl(OH) + HCl → SnCl₂ + H₂O</td>
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<tr>
<td>Sn(OH)₂ + 2 HCl → SnCl₂ + 2 H₂O</td>
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<tr>
<td>SnO + 2 HCl → SnCl₂ + H₂O</td>
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and TZVP basis sets. With DZVP basis sets, calculation using LDA led to the best match with the experimental lattice parameters (<0.9%), whereas the relative errors produced by PBE and B3LYP are greater than 2.3% and 1.4%, respectively. The calculated 1000ln122/116Sn values of SnCl2 can be reflected based on Sn−Cl RDF ranging from 2.32 Å to about 3.69 Å, and peaking at 2.62 Å (Fig. 2a). The corresponding CN curve amounts to an average coordination number of 3.2 at 3.0 Å. There is no obvious peak in Sn−O RDF (Fig. 2b), indicating that Sn2+ does not form any stable bond with water molecule.

SnCl3− has a pyramidal geometry in aqueous solutions with an average Sn−Cl bond length of 2.58 Å at 330 K and 2.55 Å at 573 K, respectively (see the RDFs and snapshot in Fig. 2d and 2f). These distances are slightly longer than the previous EXAFS result (2.47 Å) (Sherman et al., 2000). No obvious peaks can be seen in the Sn−O RDFs of SnCl3− (Fig. 2e), indicating no Sn−OH2 coordination.

For SnCl2 at 330 K and 573 K, the Sn−Cl RDF peaks are centered at 2.58 Å and 2.55 Å, respectively (Fig. 2g). The first Sn−O RDF peak occurs at 2.38 Å and 2.42 Å for 330 K and 573 K respectively, and their corresponding CN curves at 3.0 Å amount to about 2.1 and 1.6 at 330 K and 573 K respectively (Fig. 2h). The hydration structure of SnCl2 can be reflected based on Sn−OH2 distance trajectories extracted from FPMD simulations in Fig. 3a. It can be seen that there is one water molecule coordinating with Sn2+ with a bond length of about 2.4 Å, and other water molecules interact with SnCl2 at slightly greater distances. In the snapshot of Fig. 2i, the pyramidal geometry of SnCl2(H2O) and a weakly bonded water molecule is shown. Such geometry of SnCl2(H2O) persists at a higher temperature of 573 K (see the trajectories in Fig. S3a in the supplementary materials). The Sn−OH2 distance trajectories show that the ligand exchange (i.e., between the coordinated and the solvent water molecules) is very frequent, i.e., at a timescale of 10.0 ps, implying that the Sn−OH2 bonding cannot be strong.

Similar to the complexes above, the average Sn−Cl bond length in SnCl3− was not significantly influenced by temperature, i.e., 2.55 Å at 330 K and 2.49 Å at 573 K (Fig. 2j). As shown in the Sn−OH2 distance trajectory plots at 330 K (Fig. 3b), one water ligand (the red line) of SnCl3− did not escape in the simulation period (i.e., 50.0 ps), while the other one (the black line) could exchange with the solvent water (i.e., from 25.0 ps to 30.0 ps in Fig. 3b). At 573 K, the water exchange happened more frequently (see

3. RESULTS

3.1. Sn2+−Cl−/OH2 complexes in aqueous solutions (below the critical point)

3.1.1. Structures

The temporal fluctuations in Sn−Cl distances in the simulations of SnCl3− in aqueous solutions are shown in Fig. 1. The stability of SnCl3− can be reflected from these trajectories. Although SnCl3− did not completely dissociate at 330 K in the simulation period, it could be seen in Fig. 1a there was always one Cl that was weakly attached to Sn with a long bond length (i.e., beyond the range of Sn−Cl distance of 3.0 Å). This implies a low stability of SnCl3− even under ambient conditions. At 368 K, one Cl detached from Sn after 20.0 ps (the red line in Fig. 1b). At 573 K, the dissociation occurred more rapidly, i.e., within 5.0 ps (see Fig. S2 in the supplementary materials). These simulations indicate that SnCl3− should only exist under ambient conditions, but is not stable in hydrothermal fluids.

The radial distribution functions (RDFs) and coordination numbers (CNs) curves for Cl and O around Sn for different aqueous Sn(II)−Cl species are shown in Fig. 2. At 330 K, SnCl3− has a seesaw geometry (Fig. 2c) with Sn−Cl bond length in SnCl2 at 330 K and 573 K respectively (Fig. 2h). The hydration structure of SnCl2 at 330 K and 573 K, the Sn−Cl RDF peaks are centered at 2.58 Å and 2.55 Å, respectively (Fig. 2g). The first Sn−O RDF peak occurs at 2.38 Å and 2.42 Å for 330 K and 573 K respectively, and their corresponding CN curves at 3.0 Å amount to about 2.1 and 1.6 at 330 K and 573 K respectively (Fig. 2h). The hydration structure of SnCl2 can be reflected based on Sn−OH2 distance trajectories extracted from FPMD simulations in Fig. 3a. It can be seen that there is one water molecule coordinating with Sn2+ with a bond length of about 2.4 Å, and other water molecules interact with SnCl2 at slightly greater distances. In the snapshot of Fig. 2i, the pyramidal geometry of SnCl2(H2O) and a weakly bonded water molecule is shown. Such geometry of SnCl2(H2O) persists at a higher temperature of 573 K (see the trajectories in Fig. S3a in the supplementary materials). The Sn−OH2 distance trajectories show that the ligand exchange (i.e., between the coordinated and the solvent water molecules) is very frequent, i.e., at a timescale of 10.0 ps, implying that the Sn−OH2 bonding cannot be strong.

Similar to the complexes above, the average Sn−Cl bond length in SnCl3− was not significantly influenced by temperature, i.e., 2.55 Å at 330 K and 2.49 Å at 573 K (Fig. 2j). As shown in the Sn−OH2 distance trajectory plots at 330 K (Fig. 3b), one water ligand (the red line) of SnCl3− did not escape in the simulation period (i.e., 50.0 ps), while the other one (the black line) could exchange with the solvent water (i.e., from 25.0 ps to 30.0 ps in Fig. 3b). At 573 K, the water exchange happened more frequently (see

![Fig. 1. Trajectories of Sn−Cl distances (annotated by different colors) in the simulations of SnCl3− in aqueous solutions at (a) 330 K and (b) 368 K. Trajectories at 573 K are shown in Fig. S2 in the supplementary materials. At 330 K, there is always one Sn−Cl bond that is longer than the others and can reach up to 6.0 Å, which implies low stability. At higher temperatures (i.e., 368 K and 573 K), one Cl escaped spontaneously.](image-url)
Fig. 2. RDF and CN curves for Cl and O around Sn and corresponding snapshots (at 330 K) in the simulations of (a–c) SnCl\textsubscript{4}\textsuperscript{2−}, (d–f) SnCl\textsubscript{3} \textsuperscript{−}, (g–i) SnCl\textsubscript{2} and (j–l) SnCl\textsuperscript{+} in aqueous solutions. Blue dashed lines denote the weak Sn–OH\textsubscript{2} bonding in aqueous SnCl\textsubscript{2} and SnCl\textsuperscript{+}. Bond lengths (in angstrom) are shown in the snapshots. Most of the solvent water molecules are removed for clarity.
the trajectories at 573 K in Fig. S3b in the supplementary materials). The average Sn–O bond lengths are 2.33 Å at 330 K and 2.40 Å at 573 K (Fig. 2k). According to the Sn–OH2 distances trajectories, there are also some weak Sn–OH2 bonding, which lead to the Sn–O CNs at 3.0 Å amounting to about 3.7 at 330 K and 3.2 at 573 K (Fig. 2k). These simulations show that the aqueous complex should be SnCl(H2O)2+ (see the snapshot in Fig. 2l).

For the hydration structure of Sn2+ at ambient conditions, the RDF curve derived from FPMD simulation shows an average Sn–O bond length of 2.31 Å. The first RDF peak ends at 3.4 Å and the corresponding CN amounts to about 5.4 (see the RDF and CN curves in Fig. 4a). The Sn–OH2 distance trajectories plotted in Fig. S4a in the supplementary materials show a three-fold coordination. This result is consistent with the X-ray absorption spectroscopy (XAS) and X-ray scattering results (Persson et al., 2016; Yamaguchi et al., 1982; Johansson and Ohtaki, 1973). At 573 K, the average Sn–O bond length is also 2.31 Å, and the corresponding CN curve amounts to about 5.3 at 3.3 Å, where the first RDF peak ends. In the Sn–OH2 distance trajectories plotted in Fig. S4b in the supplementary materials, it can be seen that Sn2+ is also three-coordinated at 573 K.

3.1.2. Stability

In this section, we focus on the stability of SnCl42−, SnCl3−, SnCl2 and SnCl+ in aqueous solutions, and the free energy profiles for their dissociation reactions are shown in Fig. 5. Since the Sn–Cl distance trajectories in Fig. 1b has shown that SnCl42− is unstable at elevated temperatures, i.e., 368 K and 573 K, we only calculated the free energy change for its dissociation at ambient conditions. The free energy change of SnCl42− dissociation at ambient conditions is only 0.6 ± 0.5 kcal/mol, which confirms the low stability of SnCl42−. At 4.6 Å, the dissociating Cl− was separated from Sn2+ by a water molecule (Fig. 5a), and thus it was taken as the end of the dissociation process.

The free energy changes from SnCl3− to SnCl2(H2O) are 4.1 ± 0.6 kcal/mol and 7.5 ± 0.8 kcal/mol at 330 K and 573 K, respectively. Here we take the dissociation process at 330 K as an example as that is similar at 573 K. As shown in Fig. 5b, the free energy increased as one Cl− was drawn away from Sn2+. After reaching a maximum at a Sn–Cl distance of 4.0 Å, the free energy curve in Fig. 5b bent downwards slightly, and reached a minimum at 4.6 Å. At this point, Cl− and Sn2+ was separated by water molecules, marking the end of the dissociation process.

The free energy changes for SnCl2(H2O) dissociation are 6.5 ± 0.6 kcal/mol and 7.9 ± 0.7 kcal/mol at 330 K and 573 K, respectively. The structures of aqueous SnCl2(H2O) derived from the FPMD simulations at 330 K and 573 K (as shown in Fig. 2i) were taken as the initial configurations. At 330 K, the free energy firstly increased and reached the maximum value at 4.0 Å. After that a minimum occurred at 5.0 Å. As shown in Fig. 5c, at this point a
water molecule separated the dissociating Cl\(^-\) from Sn\(^{2+}\), pinpointing the end of SnCl\(_2\)(H\(_2\)O) dissociation.

The free energy changes for SnCl\(_2\)(H\(_2\)O\)\(^+\) dissociation are 4.4 ± 0.6 kcal/mol and 10.2 ± 0.6 kcal/mol at 330 K and 573 K, respectively. At ambient conditions, the maximum value of the free energy curves occurred at 4.0 Å and the minimum occurred at 4.6 Å, respectively. Similar to the dissociation processes of SnCl\(_3\)/Cl\(^-\) and SnCl\(_2\)(H\(_2\)O), one solvent water molecules became coordinated with Sn\(^{2+}\) as Cl\(^-\) moved away from Sn\(^{2+}\), forming Sn(H\(_2\)O\)\(_3\)\(^2+\) at last (Fig. 5d).

According to the above results, free energy changes for the dissociation of SnCl\(_4\)\(^2-\), SnCl\(_3\)(H\(_2\)O) and SnCl\(_2\)(H\(_2\)O\)\(^+\) at 573 K are larger than those at ambient conditions. The free energy data indicate that SnCl\(_3\) is the more stable Sn(II)—Cl species in hydrothermal solutions up to 573 K.

### 3.2. Sn\(^{2+}\)—Cl\(^-\) complexes in supercritical aqueous fluids

Supercritical water has low dielectric constant (e.g., 12.06 at 773 K–1.5 kbar and 4.83 at 973 K–1.5 kbar according to Sverjensky et al. (2014)), and therefore neutral species such as SnCl\(_2\) are favored under these conditions. FPMD simulations indicated that SnCl\(_2\) was stable at 773 K–1.5 kbar and 973 K–1.5 kbar, with average Sn—Cl bond lengths of 2.50 Å and 2.45 Å, respectively (Fig. 6a). The average Cl—Sn—Cl angles are 97.3° and 99.6° at 773 K–1.5 kbar and 973 K–1.5 kbar, respectively. The average Sn—Cl bond length is shorter than that in hydrothermal solutions below the critical point (i.e., 2.58 Å at 330 K and 2.55 Å at 573 K), which can be attributed to the very weak Sn—OH\(_2\) bonding under supercritical conditions (i.e., water molecules can coordinate with Sn\(^{2+}\) sporadically; see the
comparison. SnCl₂ has a trigonal geometry with the Sn—Cl bond length and that the Sn—Cl bond lengths in gaseous SnCl₂ and SnCl₂(H₂O) are 2.39 Å and 2.44 Å, respectively. The Cl—Sn—Cl angles in gaseous SnCl₂ and SnCl₂(H₂O) are 99.6° and 99.5° respectively, close to the average Cl—Sn—Cl angle in supercritical aqueous fluids.

3.3. Sn(II) species in vapor phases

SnCl₂ is the dominant Sn(II) species in vapor phases (see below). The calculated Sn—Cl/O bond lengths, Cl—Sn—Cl angle, and vibrational frequencies of gaseous SnCl₂ and SnO molecules are listed in Table 2. Computational and experimental results in previous studies are tabulated for comparison. SnCl₂ has a trigonal geometry with the Sn—Cl bond lengths of 2.39 Å and the Cl—Sn—Cl angle of 99.6° at the B3LYP/def2-TZVP level. At the CCSD(T)/aug-cc-pVQZ(-pp) level, the calculated 1000ln 122/116 values for gaseous SnCl₂ and SnCl₂(H₂O) are 25.3 and 25.4 Å respectively, consistent with the FPMD geometry of SnCl₂(H₂O) having a weakly bonded water molecule in aqueous solutions. These comparisons indicate that the optimized structures of aqueous species can represent the structures derived from FPMD simulations reasonably.

The Gibbs free energy changes (ΔG) of the reactions among possible gaseous Sn(II) species from ambient to elevated conditions were calculated at the B3LYP/def2-TZVP level and listed in Table 3. The ΔG value for the reaction of SnO to SnCl₂ is negative, e.g., −60.44 kcal/mol at ambient conditions and −60.32 kcal/mol at 573 K. The ΔG values for the reaction of SnCl₂(HCl)/SnCl(OH)/Sn(OH)₂ are also negative. These results indicate that SnCl₂ is more stable than SnO/SnCl₂(HCl)/SnCl(OH)/Sn(OH)₂. It should be noted that the ΔG values for the dehydration reaction of SnCl₂(H₂O) are quite small, indicating similar stability of SnCl₂(H₂O) and SnCl₂ in vapors.

3.4. Equilibrium Sn isotope fractionation factors

The calculated 1000ln¹²²/¹¹６β values of Sn(II)—Cl species (at the B3LYP/def2-TZVP level) and Sn-bearing minerals (at the LDA/DZVP level) as a function of temperature are tabulated in Table 4, and shown in Figs. 7 and 8. The computational results of Sn(IV) chloride species by She et al. (2020) and the NRIXS results of Sn-bearing minerals by Polyakov et al. (2005) are also plotted in Figs. 7 and 8 for comparison. Comparison between the optimized lattice parameters and calculated 1000ln¹²²/¹¹６β values of 2 × 2 × 4 and 3 × 3 × 5 cassiterite supercells, as well as 2 × 2 × 2 and 3 × 3 × 3 megawite supercells, is tabulated in Tables S1 and S2 in the supplementary materials. The calculated 1000ln¹²²/¹¹６β values at other levels, i.e., values for SnCl₂ and SnCl₄ at the CCSD(T)/aug-cc-pVTZ(-pp) level and values for SnCl₄, cis-SnCl₄(H₂O)₂(aq), SnCl₂(aq), cassiterite at the B3LYP/TZVP level, together with the relevant vibrational frequencies data, are tabulated in the supplementary materials.

For Sn(II)—Cl species, there is no obvious difference in 1000ln¹²²/¹¹６β values of aqueous species between the 18
Table 4
Calculated $\ln^{122/116}_b$ values for aqueous and gaseous Sn chlorides and Sn-bearing minerals.\textsuperscript{a}

<table>
<thead>
<tr>
<th>System</th>
<th>25 °C</th>
<th>96 °C</th>
<th>300 °C</th>
<th>500 °C</th>
<th>700 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn(II) chlorides</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SnCl(_2)</td>
<td>2.62</td>
<td>1.73</td>
<td>0.73</td>
<td>0.40</td>
<td>0.25</td>
</tr>
<tr>
<td>SnCl(_2)(H(_2)O)</td>
<td>2.77</td>
<td>1.83</td>
<td>0.77</td>
<td>0.43</td>
<td>0.27</td>
</tr>
<tr>
<td>SnCl(_3) + 18 H(_2)O</td>
<td>2.18</td>
<td>1.43</td>
<td>0.60</td>
<td>0.33</td>
<td>0.21</td>
</tr>
<tr>
<td>SnCl(_2)(H(_2)O) + 18 H(_2)O</td>
<td>2.45</td>
<td>1.62</td>
<td>0.68</td>
<td>0.38</td>
<td>0.24</td>
</tr>
<tr>
<td>Sn(IV) chlorides</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SnCl(_4)</td>
<td>6.56</td>
<td>4.35</td>
<td>1.84</td>
<td>1.02</td>
<td>0.64</td>
</tr>
<tr>
<td>SnCl(_6)(^2-) + 18 H(_2)O</td>
<td>4.72</td>
<td>3.11</td>
<td>1.30</td>
<td>0.72</td>
<td>0.45</td>
</tr>
<tr>
<td>cis-SnCl(_4)(H(_2)O)(_2) + 18 H(_2)O</td>
<td>6.03</td>
<td>4.00</td>
<td>1.70</td>
<td>0.94</td>
<td>0.60</td>
</tr>
<tr>
<td>Minerals</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cassiterite (SnO(_2))</td>
<td>7.85</td>
<td>5.21</td>
<td>2.21</td>
<td>1.22</td>
<td>0.77</td>
</tr>
<tr>
<td>Megawite (CaSnO(_3))\textsuperscript{d}</td>
<td>7.71</td>
<td>5.11</td>
<td>2.16</td>
<td>1.19</td>
<td>0.76</td>
</tr>
<tr>
<td>Romarchite (SnO)</td>
<td>3.13</td>
<td>2.05</td>
<td>0.86</td>
<td>0.47</td>
<td>0.30</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Data for aqueous and gaseous species were calculated at the B3LYP/def2-TZVP level. Data for minerals were calculated at the LDA/DZVP level.

\textsuperscript{b} Data from She et al. (2020), calculated at the B3LYP/def2-TZVP level.

\textsuperscript{c} Calculated using the $2 \times 2 \times 4$ supercell.

\textsuperscript{d} Calculated using the $2 \times 2 \times 2$ supercell.

Fig. 7. Calculated $1000\ln^{122/116}_b$ values for Sn chlorides in aqueous solutions and vapor phases (at the B3LYP/def2-TZVP level).

Fig. 8. Calculated $1000\ln^{122/116}_b$ values for Sn-bearing minerals (at the LDA/DZVP level).
and 24 solvent water molecules for Sn(II) chlorides (see Table S4 in the supplementary materials), as has been demonstrated for aqueous Sn(IV) chlorides (She et al., 2020). Therefore, we only show the results of the models with 18 solvent water molecules in Table 4 and Fig. 7. As shown in Fig. 7, the enrichment of $^{125}$Sn decreases in the order SnCl$_4$ (g) > cis-/trans-SnCl$_4$(H$_2$O)$_2$(aq) > SnCl$_6^{2-}$ (aq) > SnCl$_3$ (aq) > SnCl$_2$ (g) > SnCl$_2$(H$_2$O)/(aq) > SnCl$_4$ (aq). No significantSnCl$_3$ (aq) 

The equilibrium Sn isotope fractionations among Sn (II) chlorides are much smaller than the values among Sn (IV) chlorides. From ambient temperature to 1000 °C, the 1000ln$^{125/115}$β values for SnCl$_4$ and SnCl$_2$ calculated from the DFT level applied are slightly (i.e., within –10.5% of relative error) smaller than those calculated from the CCSD(T) level. For instance, at 25 °C, the 1000ln$^{125/115}$β values for SnCl$_4$ and SnCl$_2$ calculated at the CCSD(T)/aug-cc-pVTZ(-pp) level are 7.28 ‰ and 2.91 ‰, respectively, and the corresponding values at the B3LYP/def2-TZVP level are 6.56 ‰ and 2.62 ‰, respectively.

The optimized lattice parameters of the minerals are listed in Table S1 in the supplementary materials. The calculated lattice parameters at the LDA/DZVP level match the experiments within 1.1% except that the c-axis length of romarchite cell is underestimated by 3.0%. This discrepancy is due to the inability of semilocal functionals in accounting for the interlayer van der Waals interactions (Perdew and Ruzsinszky, 2010; Grimme, 2011; Méheut and Schauble, 2014). There is no significant difference between the optimized lattice parameters and calculated 1000ln$^{125/115}$β values of cassiterite and megawite with different size of supercells (see Tables S1 and S2 in the supplementary materials), indicating that a 2 × 2 × 4 supercell for cassiterite and a 2 × 2 × 2 supercell for megawite are sufficient. The calculated 1000ln$^{125/115}$β values for cassiterite calculated with different functionals (i.e., LDA, PBE and B3LYP) and basis sets (i.e., DZVP and TZVP) shown in Fig. S1 in the supplementary materials indicate that the results at the LDA/DZVP level match the NRIXS results in Polyakov et al. (2005) well (with relative errors within ~4.6%). As shown in Table 4 and Fig. 8, the calculated 1000ln$^{125/115}$β values of megawite at the LDA/DZVP level are also very close to the NRIXS results, and there is no significant equilibrium Sn isotope fractionation between cassiterite and megawite. The difference in 1000ln$^{125/115}$β values for romarchite between the results in this study and Polyakov et al. (2005) is slightly greater (i.e., 1.04 ‰ at 25 °C).

4. DISCUSSION

4.1. Sn chloride complexation in hydrothermal fluids

The results show that the stable Sn(II)–Cl species include SnCl$_4^{2-}$, SnCl$_2$(H$_2$O) and SnCl$_2$(H$_2$O)$_2$ in aqueous solutions (below the critical point), SnCl$_2$ and SnCl$_2$(H$_2$O) in vapor, and SnCl$_2$ in supercritical fluids. Free energy calculations indicate that SnCl$_4^{2-}$ is the dominant Sn(II)–Cl complex from ambient conditions to 300 °C in aqueous solutions. SnCl$_2$ can only exist with very low stability at ambient conditions, and is not important at elevated temperatures. These results are consistent with the in situ UV spectroscopy study on hydrothermal Sn(II)–Cl species by Müller and Seward (2001), who suggested that SnCl$_4$ and SnCl$_2$ are the dominant species up to 300 °C and SnCl$_2$ is stable only at low temperatures. In supercritical aqueous fluids, SnCl$_2$ is stable, which is consistent with the previous solubility experiments (Wilson and Eugster, 1990; Taylor and Wall, 1993; Duc-Tin et al., 2007). During evaporation of Sn(IV) chloride solution in air, SnCl$_4$ is the dominant gaseous Sn(IV) species (She et al., 2020). By contrast, calculations in this study show that Sn can be transported in vapor phases in the form of SnCl$_2$ and SnCl$_2$(H$_2$O) under reduced conditions.

Results in this study, together with previous studies of Sn(IV) chloride species (Sherman et al., 2000; Schmidt, 2018; She et al., 2020), place strong constraints on the speciation of Sn(II/IV)–Cl complexes in hydrothermal fluids, and provide a physical basis for understanding the transport and mineralization of Sn. Although the dominance of Sn(IV) chloride species in aqueous solutions remains a controversial topic, e.g., SnCl$_6^{2-}$ in Sherman et al. (2000) vs. SnCl$_4$(H$_2$O)$_2$ (Schmidt, 2018), FPMD simulations have indicated that both of them are stable at ambient conditions and 95 °C (She et al., 2020). Additionally, the detailed geometries of Sn–Cl species derived from the first principles calculations indicate that the Sn–Cl/O bonds in Sn (II) species are longer than that in Sn(IV) species. For example, the average Sn–Cl bond lengths in Sn(II)Cl$_4$, Sn(II)Cl$_3$(H$_2$O), Sn(IV)Cl$_6^{2-}$ and Sn(IV)Cl$_4$(H$_2$O)$_2$ in aqueous solutions at ambient conditions are 2.58 Å, 2.58 Å, 2.48 Å and 2.45 Å, respectively.

Compared with Sn$^{2+}$, Sn$^{4+}$ coordinates with more Cl$^-$ in hydrothermal fluids. The transformation between SnCl$_3$/SnCl$_4$(H$_2$O) and possible Sn(IV)–Cl complexes can be expressed as:

Sn(II)Cl$_5^{2-}$ + 3Cl$^-$ – 2e$^-\rightleftharpoons$ Sn(IV)Cl$_2^{2-}$

Sn(II)Cl$_2$(H$_2$O) + 4Cl$^-$ – 2e$^-\rightleftharpoons$ Sn(IV)Cl$_4^{2-}$ + H$_2$O

or

Sn(II)Cl$_5^{2-}$ + Cl$^-$ + 2H$_2$O – 2e$^-\rightleftharpoons$ Sn(IV)Cl$_4$(H$_2$O)$_2$

Sn(II)Cl$_3$(H$_2$O) + 2Cl$^-$ + H$_2$O – 2e$^-\rightleftharpoons$ Sn(IV)Cl$_4$(H$_2$O)$_2$

and the precipitation of cassiterite from hydrothermal fluids can be expressed as:

Sn(II)Cl$_3^{2-}$ + 2H$_2$O – 2e$^-\rightleftharpoons$ Sn(IV)O$_2$ + 4H$^+$ + 3Cl$^-$

Sn(II)Cl$_2$(H$_2$O) + H$_2$O – 2e$^-\rightleftharpoons$ Sn(IV)O$_2$ + 4H$^+$ + 2Cl$^-$
Eqs. (8)–(11) imply that during the transport of Sn in geological fluids, higher Cl− activity can enhance the conversion to Sn(IV)−Cl complexes, which can facilitate the formation of tin deposits as tin exists as tetravalence in cassiterite. This is supported by fluid inclusions studies on Sn deposits. For example, Müller et al. (2001) reported high salinity (up to 22 wt% NaCl equiv.) in Sn-mineralizing fluids from the Huanuni tin deposit, Bolivia. A statistical study in Naumov et al. (2011) show that more than 25 wt % of fluid inclusions from tin deposits have salinity >20 wt% NaCl equiv. On the other hand, Eqs. (12)–(15) show that cassiterite precipitation reactions are H+-releasing processes, and therefore neutral to alkaline (H+-consuming) environments can promote cassiterite mineralization. This is corroborated by the facts that hydrothermal Sn mineralization is generally associated with the alteration reactions of feldspars (greisenization) or carbonates (skarnization) (Heinrich, 1990; Lehmann, 1990; Chen et al., 2000). Additionally, the electron transfer in the oxidation of Sn(II)−Cl complexes in hydrothermal fluids, i.e., Eqs. (8)–(13), can be caused by the reduction of Fe3+, which can be supported by the coexistence of cassiterite and some Fe3+-bearing minerals such as pyrite or chalcopyrite in some tin deposits (e.g., Heinrich and Eddington, 1986; Schwartz et al., 1995; Pavlova et al., 2015). The dissolved oxygen can also oxidize Sn2+ because of the low redox potential for Sn4+/Sn2+ in aqueous solutions (i.e., ΔE⁰ (Sn⁴⁺/Sn²⁺) = 0.384 ± 0.020 V according to Gajda et al. (2009)).

4.2. Sn isotope fractionation in ore-forming processes

A comparison of the β factors for the aqueous and gaseous Sn(II)−Cl and Sn(IV)−Cl species (Fig. 7) highlights the effects of redox potential and evaporation on the equilibrium Sn isotope fractionation. In geological fluids, heavy isotopes of metals preferentially partition into high valence species. For example, first principles calculations by Li and Liu (2011) and Wu et al. (2015a) indicated that high valence Se and V species enrich heavy isotopes. For both Sn(II)−Cl and Sn(IV)−Cl species, heavy Sn isotopes preferentially partition into the vapor phases relative to aqueous solutions. During hydrothermal mineralization processes, Sn is transported in hydrothermal fluids as vapor or aqueous species, then ultimately precipitated as Sn-bearing minerals. Cassiterite, the most important ore mineral for Sn, can precipitate via hydrolysis of Sn complexes in hydrothermal fluids. Figs. 7 and 8 shows that, regardless of the method to derive equilibrium Sn isotope fractionation data for cassiterite (i.e., the first principles calculation in this study or the NRIXS in Polyakov et al. (2005)), the obtained 1000Δ¹²²/¹¹⁶Sn values of cassiterite are higher than those of all aqueous and gaseous Sn(II)/IV−Cl species. In other words, hydrothermal precipitation of cassiterite would be accompanied with preferential removal of heavy Sn isotopes from fluids under isotopic equilibrium.

Presently, a significant amount of Sn isotope data from natural cassiterite are available in literature (Yao et al., 2018; Wang et al., 2019a; Mason et al., 2020), from which a variability of 1.84% for 1000Δ¹²²/¹¹⁶Sn has been reported (Fig. 9c). Although the Sn isotope data were measured from separate mineral deposits without specific paragenetic and temperature constraints, the statistical properties (i.e., range and distribution pattern) of 1000Δ¹²²/¹¹⁶Sn values for cassiterite still hold invaluable clues for a deeper understanding of Sn mineralization, with the help of a probabilistic model-driven approach that connects Sn isotopic variability of cassiterite to speciation of Sn in hydrothermal fluids. The core idea is to calculate a series of distribution patterns of 1000Δ¹²²/¹¹⁶Sn with the observed pattern of 1000Δ¹²²/¹¹⁶Sn for natural cassiterite, and the best match would be indicative of the most important Sn speciation during cassiterite mineralization.

We firstly model the evolution of Sn isotope composition of hydrothermal fluids in a mineralization system following a transport-precipitation model of Li et al. (2010). In this model, we envision a high-Sn hydrothermal fluid of magmatic origin to exsolve from a fertile source pluton. As the fluid is transported away from the magma, its temperature decreases and cassiterite is precipitated due to the strong temperature dependence of cassiterite solubility in hydrothermal fluids (Audétat et al., 1998). Consequently, cassiterite of different stage would be precipitated along the fluid pathway. Sn in such theoretical scenario follows both elemental and isotopic mass balance:

\[ F(n) = F(n + 1) + C(n + 1) \]

\[ \delta^{122/116}\text{Sn}_{\text{fluid}}(n) \times F(n) = \delta^{122/116}\text{Sn}_{\text{fluid}}(n + 1) \times F(n + 1) + \delta^{122/116}\text{Sn}_{\text{cassiterite}}(n + 1) \times C(n + 1) \]

where \( \delta^{122/116}\text{Sn}_{\text{fluid}} \) denotes \( \delta^{122/116}\text{Sn} \) value of Sn in the hydrothermal fluid that contains a Sn mass of \( F(n) \) at a given stage (n), and temperature drops and this fluid evolved to the next stage (n + 1), cassiterite is separated from the fluid, removing Sn that has a mass of \( C(n + 1) \) and a Sn isotope composition of \( \delta^{122/116}\text{Sn}_{\text{cassiterite}}(n + 1) \), as a consequence, the Sn isotope composition of the fluid evolves to \( \delta^{122/116}\text{Sn}_{\text{fluid}}(n + 1) \), and the mass decreases to \( F(n + 1) \). The Sn isotope fractionation between the hydrothermal fluid and the precipitated cassiterite can be described as:

\[ \Delta^{122/116}\text{Sn}_{\text{cassiterite}} = \delta^{122/116}\text{Sn}_{\text{cassiterite}}(n + 1) - \delta^{122/116}\text{Sn}_{\text{fluid}}(n + 1) \]
(2005), and (2) the $1000 \ln^{122/116} \beta$ values for SnCl$_4$, cis-SnCl$_4$(H$_2$O)$_2$(aq), SnCl$_3$(aq) and cassiterite calculated at the B3LYP/TZVP level. These two models are referred to "Model-II" and "Model-III", respectively. The $1000 \ln^{122/116} \beta$ values employed in these models are tabulated in Table S5 in the supplementary materials.

Because hydrothermal Sn deposit is commonly associated with granite magmatism (Heinrich, 1990; Lehmann, 1990; Chen et al., 2000), the $\delta^{122/116}$Sn of the starting hydrothermal fluid is set to be the same as that of granodiorite GSP-2, which is 0.53‰ relative to NIST 3161a (Creech et al., 2017; She et al., 2020). The transport-precipitation model (i.e., Eqs. (16) and (17)) requires a solubility function of cassiterite. Both theoretical (Jackson and Helgeson, 1985) and experimental (Wilson and Eugster, 1990; Taylor and Wall, 1993; Schmidt, 2018) studies have consistently pointed to a strong positive temperature dependence of Sn solubility in hydrothermal fluids. When the hydrothermal fluid reaches saturation to precipitate cassiterite, the Sn concentration in fluid inclusions can be regarded as its solubility at the specific temperature recorded in the fluid inclusion. For the convenience of the following discussion, we derived a temperature-dependent function of cassiterite solubility by empirical fitting of the systematic in situ LA-ICP-MS data of well-characterized fluid inclusions in Audétat et al. (1998). For modeling of Sn isotope evolution during transport-precipitation, we assume that the starting hydrothermal fluid reaches satura-
tion at 500 °C (Audétat et al., 1998) and has a Sn concentration of 361 ppm. Tin mineralization was found to be mainly associated with hydrothermal fluids of 500 °C and 200 °C (Fig. 9a) (Heinrich, 1990; Naumov et al., 2011; Bodnar et al., 2014). The Sn isotope composition of the precipitated SnO₂ at different temperature intervals (50 °C every step) during cooling is calculated according to the equilibrium fractionation factors between hydrothermal fluids and cassiterite. The cassiterite solubility data employed in the transport-precipitation model are tabulated in Table S6 in the supplementary materials.

The results of Model-I are plotted in Fig. 9b, and the results of Model-II and Model-III are plotted in Figs. S7b and S8b in the supplementary materials. In the model, the most intense Sn precipitation occurs in the temperature bracket of 300–450 °C, and the amount of Sn precipitation decreases rapidly with decreasing temperature, a trend expected from the strong temperature dependence of Sn solubility. Because cassiterite enriches heavy Sn isotopes relative to all aqueous Sn species, the remaining hydrothermal fluid becomes isotopically light as the transport-precipitation process proceeds, and thus the δ²⁰⁹⁸Sn of subsequent cassiterite precipitates also becomes progressively smaller. However, the trend of δ¹²²⁰¹¹Sn evolution in the model is dependent on the Sn isotope fractionation factor between aqueous fluid and cassiterite, which is controlled by the Sn speciation in the model setting. As shown in Fig. 9b, if we assume that the Sn in hydrothermal fluids occurs as Sn(IV) species (i.e., SnCl₄(g), SnCl₄(H₂O)(aq), SnCl₂²⁻(aq), SnCl₂⁺(aq)), the model will predict a moderate decrease in δ¹²²⁰¹¹Sn of cassiterite as the transport-precipitation process goes on. For Model-II and Model-III, we obtain almost the same results (see Figs. S7b and S8b in the supplementary materials). Specifically, in Model-I, cassiterite precipitated at 200 °C would have δ¹²²⁰¹¹Sn of −0.56‰, −0.98‰, and −2.15‰, if Sn occurs as SnCl₄(g), SnCl₂(H₂O)(aq), and SnCl₂⁺(aq), respectively.

However, numerous previous studies did report stability of Sn(II) species under hydrothermal conditions (e.g., Pabanal, 1986; Wilson and Eugster, 1990; Taylor and Wall, 1993; Sherman et al., 2000; Müller and Seward, 2001; Duc-Tin et al., 2007). If Sn(II) species had existed in tin mineralization systems, an increase in redox state of Sn (from Sn²⁺ to Sn⁴⁺) prior to its precipitation needs to be incurred, and such redox change could occur immediately after fluid exsolution from magma, or at the very early stage of fluid transport in the hydrothermal system. Finally, we note that the modeling in Fig. 9 assumes cassiterite precipitation is driven by temperature decrease. If the cassiterite precipitation process is associated with other processes such as boiling, liquid–vapor Sn isotope fractionation will complicate the scenario and allow for the existence of redox reactions during precipitation. Hence, we do not completely rule out the role of Sn(II) for tin mineralization and we do not deny the importance of redox reactions in tin deposits as proposed in Yao et al. (2018). Instead, both Yao et al. (2018) and this study highlighted the usefulness of Sn stable isotopes in deepening our understanding of Sn mineral deposits.

5. CONCLUSIONS

In this study, by using first principles simulations, we investigated the speciation and stability of Sn(II)—Cl spe-
cies in hydrothermal fluids, and calculated the equilibrium Sn isotope fractionation factors of dominant species as well as Sn-bearing minerals (cassiterite, megawite, and romarite). The following Sn(II)—Cl species have been found to be stable: SnCl₂, SnCl₂(H₂O), and SnCl₃(H₂O)₂ in aqueous solutions with SnCl₄²⁻ dominating, SnCl₂ and SnCl₃(H₂O) in vapor phases, and SnCl₂ in supercritical aqueous fluids. SnCl₄²⁻ has low stability even at ambient conditions and it is unstable at elevated temperatures. The calculated equilibrium Sn isotope fractionation factors indicated that heavy Sn isotopes tend to concentrate in high valence species and minerals, and gaseous species enrich heavy Sn isotopes over aqueous species. Based on the calculated equilibrium isotope fractionation factors, we evaluated the isotopic effect of Sn speciation on cassiterite precipitation by a transport-precipitation model coupled with Monte Carlo simulation, and found that only when Sn (IV) species are considered in the model, the modeling results can match Sn isotope data measured from natural cassiterite. Based on these, we reasoned that Sn occurs as Sn(IV) species in hydrothermal mineralization systems for cassiterite. As such, the derived speciation, molecular level structures and equilibrium isotope fractionation factors provide a basis for future studies on the properties and behaviors of Sn in various geochemical processes.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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APPENDIX A. SUPPLEMENTARY MATERIAL

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REFERENCES


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