1   Revision 3

Equilibrium Sn isotope fractionation between aqueous Sn and Sn-bearing minerals: Constrained by first-principles calculations

4   7464

5   Mingguang Sun[1,2], Ryan Mathur [3], Caihong Gao[4], Yanjing Chen[2], Shunda Yuan[1, *]

6   [1] China University of Geoscience, Beijing 100083, China

7   [2] MOE Key Laboratory of Orogenic Belts and Crustal Evolution, Peking University,

8   Beijing 100871, PR China

9   [3] Department of Geology, Juniata College, Huntingdon, PA 16652, USA

10   [4] State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese

11   Academy of Sciences, Guiyang 550081, China

12

13   *Corresponding author: Shunda Yuan; Email: shundayuan@cugb.edu.cn

14

Abstract

16   Equilibrium Sn isotope fractionation properties between aqueous Sn (2+, 4+) species

17   and Sn-bearing minerals are the key to using tin isotope to trace the transportation,

18   enrichment and precipitation of tin in various geological processes. However, the

19   application of Sn isotope geochemistry has been impeded by the absence of equilibrium

20   Sn isotopic fractionation factors between Sn-bearing minerals and fluid and between

21   mineral pairs. In this contribution, we conducted first-principles calculations based on the

22   density functional theory to obtain the equilibrium Sn isotopic fractionation factors

23   between aqueous Sn complexes and minerals. For Sn-bearing complexes in solution, the

24   reduced partition function ratios (β) are determined by taking snapshots from the

25   molecular dynamic trajectories and computing the average β of the snapshots based on

26   the lowest energy atomic coordinates. For Sn-bearing minerals, the static first-principles

27   periodic density functional theory methods are performed. The results show that the β

28   factors decrease in the sequence of malayaite$_{(s)}$ (Sn^{4+}) > cassiterite$_{(s)}$ (Sn^{4+}) >

29    $Sn^{4+}Cl_4(H_2O)_{2(aq)}$ > $Sn^{2+}F_3^-{}_{(aq)}$ > $Sn^{2+}(OH)_{2(aq)}$ > $Sn^{2+}CO_{3(aq)}$ > stannite$_{(s)}$ (Sn^{4+}) >

30    $Sn^{2+}Cl_3^-{}_{(aq)}$. The predicted Sn isotope fractionation follows several distinct patterns: (1)

31   for minerals, the Sn isotope fractionations ($1000ln\alpha_{minerals-stannite}$) of cassiterite-stannite

32   and malayaite-stannite minerals pairs are controlled by the coordination elements of tin,

33   and equilibrium Sn isotope fractionations factors between mineral pairs are large enough

34   to make them powerful Sn isotope thermometry; (2) for Sn-bearing aqueous species, the

35   β values of tin (4+) complexes are remarkably larger than those of all aqueous Sn^{2+}

36   species, indicating that higher valence tin preferentially enriched heavy tin isotopes. For

37   aqueous Sn^{2+} species, the aqueous species with shorter bonds are enriched in heavy Sn

38   isotopes than those with longer bonds. When both the valence state and bond length are

39   different, the valence state is the main factor controlling tin isotope fractionation; (3)

40   during precipitation of various Sn^{2+} aqueous complexes into cassiterite or malayaite,

41   heavy Sn isotopes tend to be enriched in minerals, while there are two situations for the

42   precipitation of Sn^{2+} complexes into stannite. When Sn is transported in hydrothermal

43   solution as $Sn^{2+}Cl_3^-$, stannite precipitation leads to the enrichment of light tin isotopes in

44   residual solution and late minerals. On the contrary, other Sn^{2+} species ($Sn^{2+}F_3^-$,

45    $Sn^{2+}(OH)_2$ and $Sn^{2+}CO_3$) precipitate as stannite will result in the enrichment of heavy tin

46   isotopes in the residual solutions . In addition, the direct precipitation of Sn^{4+} complexes

47   into cassiterite, malayaite, or stannite also produces considerable tin isotope fractionation.

48   During precipitation, Sn^{4+} aqueous complexes form cassiterite or malayaite, and heavy Sn

49   isotopes tend to be enriched in minerals; while it is precipitated into stannite, heavy Sn

50   isotopes enrich in residual fluid and late minerals. The calculated results are essential for

51   further understanding the mechanisms of Sn isotopic fractionation in various Sn-involved

52   geological processes.

53   Key words: Equilibrium Sn isotope fractionation; First-principles molecular dynamics;

54   Sn-bearing aqueous species; Sn-bearing minerals

55

56   **1. INTRODUCTION**

57   Tin is an important metal for global high science and the technology industry, and it

58   has been identified as a critical metal for the development of decarbonization technology

59   (Moss et al., 2013). Most of the Sn production (99%) throughout the world originates

60   from hydrothermal tin deposits, and consequently, the ore-forming processes and mineral

61   exploration of tin have attracted closer attention. (Yuan et al., 2019; Lehmann,1990, 2021;

62   Mao et al., 2019, 2021). A great deal of research has shown that Sn (Sn^{2+} and Sn^{4+}) forms

63   various complexes with different ligands in different geological fluids (e.g., Tobias, 1958;

64   Mark, 1977; Pettine et al., 1981; Séby et al., 2001; Müller and Seward, 2001; Uchida et

65   al., 2002; Duc-Tin et al., 2007; Cigala et al., 2012; Schmidt, 2018; Liu et al, 2020; She et

66   al., 2020; Wang et al., 2021). According to the limited experimental studies, the Sn

67   isotope fractionations are obvious among aqueous Sn species and Sn-bearing minerals,

68   indicating that the Sn isotope geochemistry is a robust tool to trace the Sn-involved

69   geological process (Polyakov et al., 2005; Brugger et al., 2016; Mason et al.,2016;

70   Badullovich et al., 2017; Creech et al., 2017; Mathur et al., 2017; Yao et al., 2018; Wang

71   et al., 2019; Liu et al., 2021). The equilibrium Sn isotopic fractionation factors among

72   Sn-bearing substances are prerequisite to use Sn isotope to trace geological processes.

73   However, equilibrium Sn isotopic fractionation factors between mineral and fluid and

74   between mineral pairs are mostly lacking because Sn^{2+} is readily oxidized under

75   environmental conditions (Wang et al., 2019) and dividing Sn^{2+} and Sn^{4+} complexes in

76   solutions is tough (Altunay and Gürkan, 2015), which makes it difficult to further decode

77   the evolution process of Sn in geological systems.

78   Recently, the reduced partition function ratios (β factors) of Sn-Cl species in solution

79   were preliminary calculated by using the cluster method (one configuration) (She et al.,

80   2020; Wang et al., 2021; Sun et al., 2022), and the β values of Sn^{2+}-Cl species and

81   tin-bearing minerals (cassiterite, megawite, and romarchite) were calculated by two

82   different methods: the cluster method and the periodic boundary calculations (Wang et al.,

83   2021), respectively. However, due to the dynamic property of aqueous solutions, previous

84   studies have demonstrated that the configuration disorder of the aqueous solutions can

85   affect the β values (e.g., Li et al., 2009; Li and Liu, 2011; Wang et al., 2019; Gao and Liu,

86   2021). Therefore, different configurations are required to be sampled when calculating

87   the β factors for the complexes in solutions. First principles molecular dynamics (FPMD)

88   simulations based on DFT (Density functional theory) can generate sufficient long and

89   stable trajectories for solutions at constant volume, temperature and pressure, which can

90   provide enough configurations to calculate β values of complexes in solutions. This

91   approach has successfully predicted the equilibrium isotopic fractionation factors among

92   minerals and aqueous species for many isotope systems (e.g., Blanchard et al., 2009,

93   2017; Kowalski and Jahn, 2011; Dupuis et al., 2015; Qin et al., 2016; Wang et al., 2019;

94   Gao and Liu, 2021).

95   In the present work, we apply this method to calculate the β values of aqueous Sn

96   species and tin-bearing minerals. All tin-bearing substances are treated at the same

97   theoretical level. We focused on $[Sn^{2+}(OH)_2]^0_{(aq)}$, $[Sn^{2+}F_3]^-{}_{(aq)}$, $[Sn^{2+}Cl_3]^-{}_{(aq)}$,

98   $[Sn^{2+}CO_3]^0_{(aq)}$ and $[Sn^{4+}Cl_4(H_2O)_2]_{(aq)}$ which have been identified as the predominant

99   stable Sn-bearing species in various geological fluids (e.g., Mark, 1977; Heinrich, 1990;

100 Edwards et al, 1996; Sherman et al., 2000; Cigala et al., 2012; Schmidt, 2018; Liu et al,

101 2020; She et al., 2020; Wang et al., 2021). As for Sn-bearing minerals, we mainly focused

102 on cassiterite$_{(s)}$ ($Sn^{4+}O_2$), malayaite$_{(s)}$ ($CaSn^{4+}SiO_5$) and stannite$_{(s)}$ ($Cu_2FeSn^{4+}S_4$) which

103 are dominant in various types of tin deposits (Hosking, 1988; Eadington, 1983; Eadington

104 and Kinealy, 1983; Peng and Bromley, 1992; Bortnikov, 2006; Aleksandrov and Troneva,

105 2007; Yao et al., 2018). The controlling factors of tin isotope fractionation among these

106 minerals and the aqueous Sn species have been further discussed, and the calculated

107 equilibrium Sn isotope fractionation between aqueous Sn species and minerals are key to

108 the utilization of Sn isotopes in geological processes.

109

110   **2. METHODS**

111 **2.1. Theory**

112   Equilibrium Sn isotopic fractionation is determined by the vibrational frequency of

113 tin atoms in two distinct phases (Bigeleisen and Mayer, 1947; Urey, 1947), and more

114 details information about the terms and equations of the theory can be found in many

115 reviews (Schauble, 2004; Chacko et al., 2001; Liu et al., 2010; Dauphas and Schauble,

116 2016; Blanchard et al., 2017). The isotope exchange reactions of the light tin isotope

117 (^{116}Sn) and the heavy tin isotopes (^{122}Sn or ^{124}Sn) in two tin-bearing substances (SnA and

118 SnB):

119 $$^{116}SnA + {}^{122}SnB \leftrightharpoons {}^{122}SnA + {}^{116}SnB \qquad (1)$$

120 where A and B is a ligand of tin substance. The reduced partition function ratios (β_{SnA}

121 or β_{SnB}) represent the fractionation factors in two phases (Sn phases of interest and its

122 ideal gas atom). The isotope fractionation factor ($\alpha_{SnA\text{-}SnB}$) between the two Sn substances

123 (SnA and SnB) can be described by:

124 $$\alpha_{SnA\text{-}SnB} = \beta_{SnA}/\beta_{SnB} \qquad (2)$$

125 Based on the Bigeleisen-Mayer equation, the β factors is defined as follows

126 (Bigeleisen and Mayer, 1947; Urey, 1947):

127 $$\beta = \prod_{i}^{N} \frac{u_i^* \exp\left(-u_i^*/2\right)[1 - \exp(-u_i)]}{u_i \exp\left(-u_i/2\right)[1 - \exp(-u_i^*)]} \qquad (3)$$

128 and

129 $$u_i = \frac{h v_i}{k_B T} \qquad (4)$$

130 Where N depicts the amount of harmonic vibrational modes. v_i depicts the vibrational

131 frequency of ith mode; h represents Planck constant; k_B depicts Boltzmann constant

132 and T depicts the temperature in Kelvin. The above expressions are applicable to the

133 calculation of isotope fractionation between molecules.

134 For crystals, the β factor are calculated in a similar way which can be represented

135 as following:

136 $$\beta = \left[\prod_{i}^{N} \prod_{q} \frac{u_{q,i}^* \exp\left(-u_i^*/2\right)[1 - \exp(-u_i)]}{u_{q,i} \exp\left(-u_i/2\right)[1 - \exp(-u_i^*)]}\right]^{1/Nq} \qquad (5)$$

6

137

138 where N_q depicts the amounts of $\boldsymbol{q}$-vectors in the Brillouin zone. In this study, the

139 vibrational frequencies of minerals are achieved by computing supercells. The vibrational

140 frequencies of $\boldsymbol{q} = 0$ modes can yield adequately precise β values. Three translational

141 modes with vibrational frequencies verging on zero are neglected.

142

143 **2.2. Computational details**

144 **2.2.1. Sn-bearing Minerals**

145 We carried out calculations on cassiterite$_{(s)}$ ($Sn^{4+}O_2$), malayaite$_{(s)}$ ($CaSn^{4+}SiO_5$) and

146 stannite$_{(s)}$ ($Cu_2FeSn^{4+}S_4$) (Fig.1). Based on the density functional theory (DFT), the first

147 principles periodic method is used to calculate the vibrational frequency which is

148 implemented with Vienna ab initio simulation package (VASP) (Kresse and Furthmüller,

149 1996). The exchange-correlation functional is defined by the Perdew, Burke and

150 Ernzerhof (PBE) (Perdew et al., 1996) of generalized gradient approximation (GGA) and

151 projector augmented wave (PAW) method. The cut-off energy of plane wave is set at 600

152 eV. On the basis of the Monkhorst-Pack scheme (Monkhorst and Pack, 1976), the k-point

153 grids in the Brillouin-zone integration are shown in Table 1. Supercells are used for the

154 structural relaxations (Table 1), and both the cell parameters and atomic positions are

155 optimized. The force convergence criterion is set as 10^{-3} eV/Å. After relaxations, the

156 vibration frequencies are computed by applying the density functional perturbation theory

157 (IBRION=5).

158 In addition, in order to detect the influence of size on Sn isotope fractionation, we

159 compared the calculated β values with different sizes. For instance, we calculated the β

160 factors of stannite with supercells of $1\times1\times1$ and $2\times2\times2$, the calculated β values are

7

161   1.00323 and 1.00326, respectively. The difference is very small, which indicates that

162    $2\times2\times2$ supercells are already large adequately to remove the size effect.

2.2.2 Sn-bearing species in aqueous fluids

164   For aqueous Sn (2+,4+) complexes (Table 1), we carry out the FPMD simulations to

165   provide configurations for calculating the final β factors. This technique has been used to

166   predict the Si, Mg, and Br isotope fractionations among various minerals and aqueous

167   species (Kowalski and Jahn, 2011; Dupuis et al., 2015; Pinilla et al., 2015; Wang et al.,

168   2019; Gao and Liu, 2021). The simulations of all Sn complexes are carried out in the

169   NVT (canonical ensemble) thermodynamic ensemble at a fixed temperature of 300K. The

170   cut-off energy of plane wave is set at 600 eV, and the k-point grids are $1\times1\times1$. For

171    $[Sn^{2+}F_3]^-$ and $[Sn^{2+}Cl_3]^-$ species, the Na atom is added to keep the charge balance. These

172   cell parameters are selected to guarantee that the statistical pressure is verging on zero

173   and the densities are nearly 1 g/cm^3. The time step for all simulations is set to 1 fs. The

174   FPMD simulation are totally performed for 50 ps and the energies converge to a constant

175   value after 30 ps. The Sn-bearing solute molecules and 50 water molecules are embedded

176   in a cubic box (Table 1). Isotope fractionation has previously been shown to be a

177   relatively local effect, and fractionations are closely linked to the local structures of the

178   atoms of interest (e.g., Liu and Tossell, 2005; Li and Liu, 2011; Fujii and Albarede, 2018).

179   It is sufficient to simulate the local structures of Sn (2+, 4+) ions in solutions using a

180   solute molecule surrounded by 50 water molecules (e.g., Gao and liu, 2021; Wang et al.,

181   2019). Because structure after FPMD simulation, with at least 3 layers of water molecules

182   surrounding the Sn-bearing solute, and each water molecule is in a location that allows

183   for the formation of two or more hydrogen bonds. They form many four-, five-, and

184 six-member rings (e.g., Xantheas and Dunning, 1993; Estrin et al., 1996; Ludwig and

185 Weinhold, 1999; Liu and Tossell, 2005).

186 The Sn-bearing species ($Sn^{2+}Cl_3^-(H_2O)_{50}$, $Sn^{2+}CO_3(H_2O)_{50}$, $Sn^{2+}(OH)_2(H_2O)_{50}$,

187 $Sn^{2+}F_3^-(H_2O)_{50}$ and $Sn^{4+}Cl_4(H_2O)_{50}$) solution structures are sustained at 300 K for 50ps

188 and the energies converge to a constant value between 30ps and 50ps. Because of the

189 configuration disorder of the aqueous solution, it is necessary to sample enough

190 configurations to get the converged β value. Here, we take 10 configurations for each

191 aqueous solution (Fig.2). The configurations are extracted from the equilibrated

192 trajectories (> 30 ps) with equal intervals (2 ps). Then the atomic positions of the

193 configurations are optimized with a force convergence criterion of 1e-3 eV/Å. Finally, the

194 vibration frequencies are calculated to predict the β values for each aqueous species.

195

196 **3. RESULTS**

197 **3.1. Structures and β factors of minerals**

198 The relaxed crystal structures of all calculated minerals are shown in Fig.1. The

199 calculated lattice parameters of Sn-bearing minerals, bond lengths and frequencies are

200 listed in Table 1 and Table 2. The β factors of minerals ($^{124/116}Sn$ and $^{122/116}Sn$) are

201 calculated by equation (5). In Table 3, we present the polynomial fit parameters for the

202 minerals β factors calculated. The computed β values for cassiterite, malayaite and

203 stannite are shown in Table S2, and their variation with temperature is shown in Figure 2a.

204 The β factors of cassiterite and malayaite are much larger than that of stannite. The

205 1000ln(β) values of cassiterite ($^{124/116}Sn$) decreased from 11.128 ‰ at 25 °C to 2.666 ‰

206 at 350 °C, and the 1000ln(β) values of malayaite ($^{124/116}Sn$) decreased from 11.434 ‰ at

9

207   25 °C to 2.766 ‰ at 350 °C, and the 1000lnβ values of stannite ($^{124/116}$Sn) decreased from

208   3.225 ‰ at 25 °C to 0.750 ‰ at 350 °C (Table S2). Malayaite has the shortest Sn-O bond

209   length and the largest 1000lnβ value. Though the tin valence states of the three minerals

210   are the same (4+), and the coordination number of Sn in stannite (4) is smaller than those

211   of cassiterite (6) and malayaite (6), the 1000lnβ value of stannite is much lower than that

212   of the other two minerals (Table S2). This is related to the fact that the bonds formed by

213   Sn and S are much weaker than those formed by Sn and O. Light Sn isotopes are

214   therefore enriched in Sn-S bonds.

215

216   **3.2. Structures and β factors of Sn-bearing species in aqueous solutions**

217   In order to evaluate the structural properties of all Sn-bearing aqueous species, we

218   performed calculations on the partial radial distribution functions (RDFs) of the Sn-O

219   pair of atoms. The coordination numbers (CNs) for O around Sn and the RDFs of various

220   Sn aqueous species are shown in Fig.3. Short-range order and long-range disorder are

221   reflected by the initial peaks and the decrease in magnitude of subsequent fluctuations in

222   liquids (e.g., Karki, 2010). For $Sn^{2+}(OH)_{2(aq)}$, $Sn^{2+}Cl_3^-{}_{(aq)}$, $Sn^{2+}CO_{3\,(aq)}$ and $Sn^{4+}Cl_{4(aq)}$ at

223   300 K, the Sn-O RDF peaks occur at ~ 2.15 Å, ~ 2.25 Å, ~ 2.15 Å and ~ 1.95 Å,

224   respective (Fig. 3). The calculated coordination numbers (CNs) are ~ 3.13, ~ 1.55, ~ 3.89

225   and ~ 1.07, respectively (Fig. 3 inset). For SnF_3^-, at 300 K, there is no sharp peak in the

226   Sn-O RDF, indicating that F$^-$ dominates the first shell of SnF_3^-, while water molecules

227   inhabit the second shell.

228   Ten configurations are extracted from the equilibrated trajectories at equal intervals

229   of each Sn-bearing species (Fig.2). The β factors are calculated by averaging the β values

230   of 10 configurations (Table S2; Table S1). The β factors of aqueous Sn species are in

231   order of $Sn^{4+}Cl_4(H_2O)_2 >$ $Sn^{2+}F_3^- >$ $Sn^{2+}(OH)_2 >$ $Sn^{2+}CO_3 >$ $Sn^{2+}Cl_3^-$ (Fig. 4b and Table

232   S2). $Sn^{4+}Cl_4(H_2O)_2$ has the largest β factors ($^{124/116}$Sn: 7.627±0.04 ‰ at 25 °C), and the β

233   factors of $Sn^{2+}Cl_3^-$ is the smallest ($^{124/116}$Sn: 2.639±0.14 ‰ at 25 °C) (Table S2). In Table

234   3, we list the polynomial fit parameters for Sn-bearing aqueous species β factors.

235

236   **4. DISCUSSION**

237   **4.1.   Comparison with previous work**

238   Previous studies have shown that the nuclear volume effects (NVE), which results

239   from the isotopic change in the nuclear size and shape, is larger for heavy elements and it

240   is recognized as the major origin of the mass-independent isotope fractionation

241   (Bigeleisen, 1996; Schauble, 2007; Abe et al., 2008, 2010; Fujii et al., 2009, 2011, 2013).

242   For example, the NVE effect is ~1‰/amu (atomic mass unit) for Hg (Schauble, 2007), Pb

243   (Fujii et al., 2011; Yang and Liu, 2015), TI (Schauble, 2007; Yang and Liu, 2015) and U

244   (Bigeleisen, 1996; Abe et al., 2008, 2010). Here, the method of applying the

245   first-principles calculations obtains the mass-dependent fractionation in Sn-bearing

246   substances resulting from differences in vibrational frequencies, without considering the

247   effect of NVE on Sn isotope fractionation originating from differences in volume and

248   shapes of the atomic nuclear. However, according to previous studies, the influence of

249   NVE on Sn isotope fractionation is usually quite small (0.5‰ in $^{124/116}$Sn for cassiterite

250   and romarchite at 25°C, 0.14‰ at 727°C) (Schauble, 2013), and therefore the

251   mass-dependent fractionation at low and moderate temperatures is the main factor leading

252   to the fractionation of Sn isotopes.

253   Our calculated lattice coefficients of Sn-bearing minerals are well consistent with

254   the previous experimental values (Table 1) (Brockway,1934; Takenouchi, 1971; Bolzan et

255   al., 1997). The calculated Sn-O and Sn-S bond length of cassiterite and stannite are 2.059

256   Å and 2.566 Å, respectively, which are in good agreement with the experimental

257   measured value, 2.058 Å and 2.539 Å. The calculated of bond length of Si-O, Sn-O and

258   Ca-O of malayaite (1.647 Å, 2.064 Å and 2.448 Å) are also well consistent with the

259   experimental measured values (1.641 Å, 2.042 Å and 2.483 Å) (Table 2) (Scott, 1970;

260   Higgins and Ribbe,1977; Zhang et al., 1999; Olekseyuk et al., 2002; Fontané et al, 2012;

261   He et al., 2021). For aqueous Sn species, among different configurations, the variation of

262    $1000ln(\beta)$ values are exceeded 0.1 ‰ (Fig.2), indicating that it is essential to sample

263   different configurations when computing β factors in solution, which is similar to the

264   previous calculation of Br and Mg species in solution (Wang et al., 2019; Gao and Liu,

265   2021). In this study, ten configurations are sampled for each aqueous Sn (2+, 4+) species

266   to calculate the cumulative average values of β, and the values converge to constants

267   (Fig.2 and Table S2). The $1000ln^{122/116}\beta$ values of $Sn^{2+}Cl_3^-·50H_2O$ using the same

268   theoretical level with the minerals and $Sn^{2+}Cl_3^-·18H_2O$ (one configuration) (Wang et al.,

269   2021) calculated at B3LYP/def2-TZVP level were 2.07 ‰ and 2.18 ‰, respectively (Fig.

270   4b and Table S2). For Sn-bearing minerals, the results show that the $1000ln^{122/116}\beta$ values

271   of cassiterite we calculated (PBE) are well consistent with the X-ray scattering (NRIXS)

272   in synchrotron radiation experiments values (Polyakov et al., 2005) (Fig.4a). The

273   consistency of these data indicates that our calculation results are accurate and reliable.

274

275   **4.2. Controlling factors on equilibrium Sn isotope fractionation in solution**

276   Based on the calculation, the β values of $Sn^{4+}Cl_4(H_2O)_2$ are larger than those of Sn^{2+}

277   species, indicating that heavy Sn isotopes are preferentially enriched in higher Sn

278   oxidation states, and the enrichment trend is similar to that of Br, Se, and V species in

279   solution (Li and Liu, 2011; Wu et al., 2015; Gao and Liu, 2021). For the Sn^{2+} aqueous

280   species, the bond lengths of Sn^{2+}-$F_{(aq)}$, Sn^{2+}-$O_{(aq)}$ and Sn^{2+}-$Cl_{(aq)}$ are 2.13 Å, 2.14 Å and

281   2.77 Å, respectively, and the β factors decrease with the increase of bond length (Fig.2b

282   and Table S2), indicating that bond length is the major controlling factor for the Sn

283   isotope fractionation of aqueous Sn^{2+} species. It conforms to the rule that shorter bonds

284   have a higher vibrational frequency, which favors enriching heavier isotopes over longer

285   and weaker bonds (Urey, 1947; Schauble et al., 2004; Young et al., 2009; Huang et al.,

286   2013, 2014). When the valence states and bond lengths of Sn-bearing species are

287   different, the valence state has a stronger effect on Sn isotopic fractionation than that of

288   the bond length among these Sn complexes. For instance, at constant temperature, the

289   bond length of $Sn^{4+}Cl_4(H_2O)_2$ (2.44 Å) is longer than those of $Sn^{2+}F_3^-$ (2.13 Å) and

290    $Sn^{2+}(OH)_2$(2.14 Å), but the β factors of $Sn^{4+}Cl_4(H_2O)_2$ is larger than those of $Sn^{2+}F_3^-$ and

291    $Sn^{2+}(OH)_2$ (Fig.2b and Table S2).

292

293   **4.3. Sn isotope fractionations among minerals**

294   In previous theoretical studies, a strong correlation has been demonstrated between β

295   values and cell parameters of minerals in equilibrium isotope fractionation of other

296   elements, such as the valence state of an element (e.g., Schauble et al., 2001), the

297   coordination number (e.g., Huang et al.,2013; Liu et al., 2018), and the average bond

298   length (e.g., Huang et al.,2019; Liu et al., 2018; Méheut and Schauble, 2014). For

299   cassiterite (malayaite) and stannite with different coordination numbers and coordination

300   elements, heavy tin isotopes are preferentially enriched in cassiterites with high CNs (6),

301   and light tin isotopes are enriched in stannite with low CNs (4), deviating from the

302   general rule that minerals with low CNs are preferentially enriched in heavy isotopes.

303   This is because the coordination element of Sn is S in stannite (Sn-S), while the

304   coordination element of Sn is O in cassiterite and malayaite (Sn-O). The bond strength of

305   Sn-O is stronger than that of Sn-S, which makes the Sn-O bond length of cassiterite (or

306   malayaite) shorter than the Sn-S bond length of stannite, suggesting that the properties of

307   the coordination element have a stronger effect on isotopic fractionation than the

308   coordination number in these three minerals. The general principle of coordination in

309   qualitative fractionation factors is also unsuitable for Cu- and Fe-bearing minerals. For

310   instance, the CNs of Cu in cuprite is two and that of Cu in carbonates and sulfates is four,

311   but cuprite tends to enrich lighter Cu isotopes than that of carbonates and sulfates (Liu et

312   al., 2021); the CNs of Fe in chalcopyrite is four, but it is more enriched in lighter Fe

313   isotope than Fe in hematite and pyrite which CNs is eight (Blanchard et al., 2017).

314   Although stiff bonds tend to enrich heavy isotopes in various isotopic systems, it is

315   unclear which of these crystal chemical parameters is the most important factor in

316   determining the interatomic bonds (Schauble, 2004). This demonstrates the complexity of

317   factors affecting equilibrium stable isotope fractionation (Liu et al., 2021).

318   In addition, temperature is an important factor influencing the formation of ore

319   deposits. As a function of temperature, equilibrium stable isotope fractionation among

320   minerals is a robust tool to reconstruct the thermal evolution process of hydrothermal

321   deposits. The first-principles calculation provides a reliable method to predict equilibrium

322   isotope fractionation factors ($1000\ln\alpha$). Recently, a few mineral pairs isotope

323   geothermometer have been obtained by first-principles calculation, such as Ag

324   (argentite-stephanite), Mg (garnet-pyroxene, garnet-olive) and Ti (ilmenite-clinopyroxene)

325 (Huang et al., 2013, Wang et al., 2020; Wang et al., 2022). Here, we calculated the

326 equilibrium Sn isotope fractionation factors among the three minerals (Fig.5) and found

327 that the Sn isotope fractionation of cassiterite-malayaite varies little ($1000ln\alpha_{cassiterite -}$

328 $_{malayaite} \approx 0$) with temperature (Fig.5), which indicates that it is not suitable for an isotopic

329 geothermometer. Cassiterite–stannite and malayaite–stannite, whose $1000ln\alpha$ values

330 show a strong dependence on temperature and vary widely

331 ($1000ln\alpha^{124/116}$malayaite-stannite = 8.209 ‰ and $1000ln\alpha^{124/116}$cassiterite-stannite =

332 7.903 ‰ at 25 °C) (Fig. 5). Therefore, cassiterite–stannite and malayaite–stannite have

333 potential as Sn isotope geothermometers. The tin isotope fractionation of cassiterite–

334 stannite and malayaite–stannite as functions of temperature is as follows:

335 malayaite-stannite:

336 $^{124/116}Sn\ 1000ln\alpha = (0.57756 \pm 0.00706) \times 10^6/T^2 + (0.67364 \pm 0.03543) \times 10^3/T -$

337 (0.55507 ± 0.04181)

338 $^{122/116}Sn\ 1000ln\alpha = (0.43843 \pm 0.00546) \times 10^6/T^2 + (0.52238 \pm 0.02741) \times 10^3/T -$

339 (0.43413 ± 0.03234)

340 cassiterite-stannite:

341 $^{124/116}Sn\ 1000ln\alpha = (0.58368 \pm 0.00595) \times 10^6/T^2 + (0.52472 \pm 0.02985) \times 10^3/T -$

342 (0.43037 ± 0.03522)

343 $^{122/116}Sn\ 1000ln\alpha = (0.44036 \pm 0.00461) \times 10^6/T^2 + (0.42179 \pm 0.02314) \times 10^3/T - (0.353$

344 $\pm 0.0273)$

345

346 **4.4. Sn isotope fractionation during precipitation processes**

347 The precipitation of various Sn-bearing complexes from hydrothermal solution into

348 tin-bearing minerals is important for better understanding tin mineralization. According to

15

349   the calculated results of this study (Fig. 6), the oxidation of Sn^{2+} complexes in solution

350   into Sn^{4+}-bearing minerals produces significant tin isotopic fractionation (0 ~ 400 °C)

351   (Tables 4 and 5), which indicates that the oxidation state of Sn (Sn^{2+} aqueous species $\rightarrow$

352   Sn^{4+} minerals) (except stannite) is the major controlling factor on Sn isotopic

353   fractionations during precipitation. Therefore, the precipitation of cassiterite or malayaite

354   from aqueous Sn^{2+} complexes (Figs. 6a and 6b) can lead to the enrichment of the lighter

355   Sn isotope in residual hydrothermal fluid and the later-precipitated Sn-bearing minerals.

356   This is well consistent with the Sn isotope fractionation in typical tin deposits

357   investigated by Yao et al. (2018), which show the precipitation of heavy-Sn-enriched

358   isotope cassiterite results in residual dissolved Sn with lighter isotopic composition in

359   different types of tin ores.

360   There are two cases of Sn isotope fractionation in the process of precipitation of

361   these Sn^{2+} complexes into stannite (Fig. 6c). When tin transports dominantly as

362    $[Sn^{2+}(OH)_2]^0$, $[Sn^{2+}F_3]^-$ and $[Sn^{2+}CO_3]^0$, the precipitation of stannite will lead to the

363   enrichment of heavy tin isotopes in the residual hydrothermal and later-deposited

364   minerals. On the contrary, the precipitation of stannite from hydrothermal solution

365   dominated by $[Sn^{2+}Cl_3]^-$ leads to the enrichment of light tin isotopes in the residual

366   hydrothermal solution.

367   In addition, recent studies indicate that Sn can also be transported by Sn^{4+} aqueous

368   species (Wang et al., 2021; Schmidt, 2018). For the precipitation process of Sn^{4+} species,

369   our results show that when Sn^{4+} precipitates as cassiterite (or malayaite), the values of

370    $1000\ln(\alpha)[Sn(IV)Cl_4(H_2O)_2]^0$-$SnO_2$ ($^{124/116}Sn$) ranging from -3.479 to -0.834‰ (from 25

371   to 350 °C) (Tables 4 and 5), which indicate that direct precipitation of Sn^{4+} (Sn^{4+} aqueous

372 species → Sn^{4+} mineral) from solution can also cause significant Sn isotope

373 fractionation. When Sn^{4+} precipitates into stannite, it will lead to the enrichment of heavy

374 tin isotopes in residual hydrothermal and late minerals. The direct precipitation of Sn^{4+}

375 species may also be a fractionation mechanism that cannot be ignored in the process of

376 tin mineralization. $1000\ln(\alpha)$ values between Sn-bearing aqueous species and minerals at

377 different temperatures (Fig.5 and Table S3) provide a guideline to understand Sn isotope

378 fractionations in different geological processes.

379
380

381

382 5. Conclusion and Implication

383 The tin isotope fractionation among Sn aqueous species and minerals are

384 investigated, and according to the calculated β factors, the enrichment trend of heavy tin

385 isotopes is malayaite (Sn^{4+}) > cassiterite$_{(s)}$ (Sn^{4+}) > $Sn^{4+}Cl_{4(aq)}$ > $Sn^{2+}F_3^-$ $_{(aq)}$> Sn^{2+}

386 $(OH)_{2(aq)}$ > $Sn^{2+}CO_{3(aq)}$ > stannite$_{(s)}$ (Sn^{4+}) > $Sn^{2+}Cl_3^-{}_{(aq)}$. The predominant factors causing

387 tin isotope fractionation are as follows: (1) for Sn^{2+} aqueous species, shorter bonds are

388 enriched in heavier Sn isotopes relative to longer and weaker bonds, and for Sn(2+, 4+)

389 aqueous species, the influence of valence state on tin isotope fractionation is stronger

390 than bond length; (2) for minerals, the properties of coordination elements are the

391 important factors controlling tin isotope fractionation in the process of tin mineralization,

392 and malayaite-stannite and cassiterite-stannite, as functions of temperature, have the

393 potential to be used as geothermometers; (3) and the precipitation of cassiterite or

394 malayaite leads to the enrichment of light tin isotopes in residual solution and late

395 minerals, and when stannite precipitates in hydrothermal solution, the fractionation of tin

396 isotopes is controlled by the type of tin complex and valence state, and direct

397 precipitation of Sn^{4+} from hydrothermal solution to Sn^{4+} minerals (Sn^{4+} species $\rightarrow$ Sn^{4+}

398 minerals) also leads to considerable Sn isotope fractionation (0 ~ 400 °C). This study

399 provides reliable equilibrium Sn isotope fractionation factors among Sn-bearing aqueous

400 species and minerals, which are key to the potential applications of Sn isotopes in various

401 geological processes.

ACKNOWLEDGEMENTS AND FUNDING

407

408

409

References Cited

411 Abe, M., Suzuki, T., Fujii, Y., and Hada, M. (2008) An ab initio study based on a finite

412 nucleus model for isotope fractionation in the U (III)–U (IV) exchange reaction

413 system. The Journal of chemical physics, 128(14), 144309.

414 Abe, M., Suzuki, T., Fujii, Y., Hada, M., and Hirao, K. (2010) Ligand effect on uranium

415 isotope fractionations caused by nuclear volume effects: An ab initio relativistic

416 molecular orbital study. The Journal of chemical physics, 133(4), 044309.

417 Aleksandrov, S. M., and Troneva, M. A. (2007) Composition, mineral assemblages, and

418 genesis of titanite and malayaite in skarns. Geochemistry International, 45(10):

419 1012-1024.

420   Altunay, N., and Gürkan, R. (2015) An inexpensive and sensitive method for speciative

421   determination of Sn (IV), Sn (II), and total Sn as Sn (IV) in selected beverages by

422   micellar improved spectrophotometry. Food Analytical Methods, 8(4), 994-1004.

423   Badullovich, N., Moynier, F., Creech, J., Teng, F. Z. and Sossi, P. A. (2017) Tin isotopic

424   fractionation   during   igneous   differentiation   and   Earth's   mantle

425   composition. Geochem. Perspect. Lett, 5, 24-28.

426   Bigeleisen, J. (1996) Nuclear size and shape effects in chemical reactions. Isotope

427   chemistry of the heavy elements. Journal of the American Chemical Society, 118(15),

428   3676-3680.

429   Bigeleisen, J. and Mayer, M. G. (1947) Calculation of equilibrium constants for isotopic

430   exchange reactions. The Journal of Chemical Physics, 15, 261-267.

431   Blanchard, M., Balan, E., and Schauble, E. A. (2017) Equilibrium fractionation of

432   non-traditional isotopes: a molecular modeling perspective. Reviews in Mineralogy

433   and Geochemistry, 82, 27-63.

434   Blanchard, M., Poitrasson, F., Meheut, M., Lazzeri, M., Mauri, F., and Balan, E. (2009)

435   Iron isotope fractionation between pyrite (FeS_2), hematite (Fe_2O_3) and siderite

436   ($FeCO_3$): A first-principles density functional theory study. Geochimica et

437   Cosmochimica Acta, 73, 6565–6578.

438   Bolzan, A. A., Fong, C., Kennedy, B. J., and Howard, C. J. (1997) Structural studies of

439   rutile-type metal dioxides. Acta Crystallographica Section B: Structural Science, 53,

440   373-380.

441 Bortnikov, N. S. (2006) Geochemistry and origin of the ore-forming fluids in
442   hydrothermal-magmatic systems in tectonically active zones. Geology of Ore
443   Deposits, 48, 1-22.

444 Brockway, L. O. (1934) The crystal structure of stannite, Cu_2FeSnS_4. Zeitschrift für
445   Kristallographie-Crystalline Materials, 89, 434-441.

446 Brugger, J., Liu, W., Etschmann, B., Mei, Y., Sherman, D. M. and Testemale, D. (2016) A
447   review of the coordination chemistry of hydrothermal systems, or do coordination
448   changes make ore deposits? Chemical Geology, 447, 219-253.

449 Chacko, T., Cole, D. R., and Horita, J. (2001) Equilibrium oxygen, hydrogen and carbon
450   isotope fractionation factors applicable to geologic systems. Reviews in mineralogy
451   and geochemistry, 43, 1-81.

452 Cigala, R. M., Crea, F., De Stefano, C., Lando, G., Milea, D. and Sammartano, S. (2012)
453   The inorganic speciation of tin (II) in aqueous solution. Geochimica et
454   Cosmochimica Acta, 87, 1-20.

455 Creech, J. B., Moynier, F., and Badullovich, N. (2017) Tin stable isotope analysis of
456   geological materials by double-spike MC-ICPMS. Chemical Geology, 457, 61-67.

457 Dauphas, N., and Schauble, E. A. (2016) Mass fractionation laws, mass-independent
458   effects, and isotopic anomalies. Annual Review of Earth and Planetary Sciences, 44,
459   709-783.

460 Duc-Tin, Q., Audétat, A., and Keppler, H. (2007) Solubility of tin in (Cl, F)-bearing
461   aqueous fluids at 700 °C, 140 MPa: A LA-ICP-MS study on synthetic fluid
462   inclusions. Geochimica et Cosmochimica Acta, 71, 3323-3335.

463   Dupuis, R., Benoit, M., Nardin, E., and Méheut, M. (2015) Fractionation of silicon

464   isotopes in liquids: The importance of configurational disorder. Chemical Geology,

465   396, 239-254.

466   Eadington, P. J. (1983) A fluid inclusion investigation of ore formation in a

467   tin-mineralized granite, New England, New South Wales. Economic Geology, 78,

468   1204-1221.

469   Eadington, P. J., and Kinealy, K. (1983) Some aspects of the hydrothermal reactions of tin

470   during skarn formation. Journal of the Geological Society of Australia 30, 461-471.

471   Edwards, R., Gillard, R. D., and Williams, P. A. (1996) The stabilities of secondary tin

472   minerals. The hydrolysis of tin (II) sulphate and the of

473          $Sn_3O(OH)_2SO_4$. Mineralogical Magazine, 60, 427-432.

474   Estrin, Y. (1996) Dislocation-density-related constitutive modeling. Unified constitutive

475   laws of plastic deformation, 1, 69-106.

476   Eugster, H. P., and Wilson, G. A. (1985) Transport and deposition of ore-forming

477   elements in hydrothermal systems associated with granites. In High heat production

478   (HHP) granites, hydrothermal circulation and ore genesis. Conference (pp. 87-98).

479   Farges, F., Linnen, R. L., and Brown Jr, G. E. (2006) Redox and speciation of tin in

480   hydrous silicate glasses: a comparison with Nb, Ta, Mo and W. The Canadian

481   Mineralogist, 44, 795-810.

482   Fontané, X., Izquierdo-Roca, V., Saucedo, E., Schorr, S., Yukhymchuk, V. O., Valakh, M.

483   Y., and Morante, J. R. (2012) Vibrational properties of stannite and kesterite type

484   compounds: Raman scattering analysis of $Cu_2(Fe, Zn) SnS_4$. Journal of Alloys and

485   Compounds, 539, 190-194.

486   Fujii, T., and Albarede, F. (2018) ^{109}Ag–^{107}Ag fractionation in fluids with applications to

487   ore deposits, archeometry, and cosmochemistry. Geochimica et Cosmochimica Acta,

488   234, 37-49.

489   Fujii, T., Moynier, F., Agranier, A., Ponzevera, E., Abe, M., Uehara, A., and Yamana, H.

490   (2013) Nuclear field shift effect in isotope fractionation of thallium. Journal of

491   Radioanalytical and Nuclear Chemistry, 296(1), 261-265.

492   Fujii, T., Moynier, F., and Albarède, F. (2009) The nuclear field shift effect in chemical

493   exchange reactions. Chemical Geology, 267(3-4), 139-156.

494   Fujii, T., Moynier, F., Dauphas, N., and Abe, M. (2011) Theoretical and experimental

495   investigation of nickel isotopic fractionation in species relevant to modern and

496   ancient oceans. Geochimica et Cosmochimica Acta, 75(2), 469-482.

497   Gao, C., and Liu, Y. (2021) First-principles calculations of equilibrium bromine isotope

498   fractionations. Geochimica et Cosmochimica Acta, 297: 65-81.

499   He, J., Zhang, H., Yue, T., Sun, W., Hu, Y., and Zhang, C. (2021) Effects of Hydration on

500   the Adsorption of Benzohydroxamic Acid on the Lead-Ion-Activated Cassiterite

501   Surface: A DFT Study. Langmuir, 37, 2205-2212.

502   Heinrich, C. A. (1990) The chemistry of hydrothermal tin (-tungsten) ore

503   deposition. Economic Geology, 85, 457-481.

504   Higgins, J. B., and Ribbe, P. H. (1977) The structure of malayaite, CaSnOSiO$_4$, a tin

505   analog of titanite. American Mineralogist, 62, 801-806.

506   Hosking, K. F. G. (1988) The world's major types of tin deposit. In Geology of tin

507   deposits in Asia and the Pacific (pp. 3-49). Springer, Berlin, Heidelberg.

508   Huang, F., Chen, L., Wu, Z., and Wang, W. (2013) First-principles calculations of

509   equilibrium Mg isotope fractionations between garnet, clinopyroxene,

510   orthopyroxene, and olivine: implications for Mg isotope thermometry. Earth and

511   Planetary Science Letters, 367, 61-70.

512   Huang, F., Wu, Z., Huang, S., and Wu, F. (2014) First-principles calculations of

513   equilibrium silicon isotope fractionation among mantle minerals. Geochimica et

514   Cosmochimica Acta, 140, 509-520.

515   Huang, F., Zhou, C., Wang, W., Kang, J., and Wu, Z. (2019) First-principles calculations

516   of equilibrium Ca isotope fractionation: Implications for oldhamite formation and

517   evolution of lunar magma ocean. Earth and Planetary Science Letters, 510, 153-160.

518   Karki, B. B. (2010). First-principles molecular dynamics simulations of silicate melts:

519   structural and dynamical properties. Reviews in Mineralogy and Geochemistry, 71,

520   355-389.

521   Kowalski, P. M., and Jahn S. (2011) Prediction of equilibrium Li isotope equilibrium

522   fractionation between minerals and aqueous solutions at high P and T: an efficient ab

523   initio approach. Geochimica et Cosmochimica Acta, 75, 6112–6123.

524   Kresse, G., and Furthmüller J. (1996) Efficiency of ab-initio total energy calculations for

525   metals and semiconductors using a plane-wave basis set. Computational materials

526   science, 6, 15-50.

527   Lehmann, B. (1987) Tin granites, geochemical heritage, magmatic differentiation.

528   Geologische Rundschau, 76, 177-185.

529   Lehmann, B. (1990) Large-scale tin depletion in the Tanjungpandan tin granite, Belitung

530   Island, Indonesia. Economic Geology, 85, 99-111.

531   Lehmann, B. (2006). Metallogeny of tin (Vol. 32). Springer.

532   Lehmann, B. (2021) Formation of tin ore deposits: A reassessment. Lithos, 402, 105756.

533   Li, X., and Liu, Y. (2011). Equilibrium Se isotope fractionation parameters: a

534   first-principles study. Earth and Planetary Science Letters, 304, 113-120.

535   Li, X., Zhao, H., Tang, M., and Liu, Y. (2009) Theoretical prediction for several important

536   equilibrium Ge isotope fractionation factors and geological implications. Earth and

537   Planetary Science Letters, 287, 1-11.

538   Liu, P., Mao, J., Lehmann, B., Weyer, S., Horn, I., Mathur, R., and Zhou, Z. (2021) Tin

539   isotopes via fs-LA-MC-ICP-MS analysis record complex fluid evolution in single

540   cassiterite crystals. American Mineralogist, 106, 1980-1986.

541   Liu, Q., Tossell, J. A., and Liu, Y. (2010) On the proper use of the Bigeleisen–Mayer

542   equation and corrections to it in the calculation of isotopic fractionation equilibrium

543   constants. Geochimica et Cosmochimica Acta, 74, 6965-6983.

544   Liu, S., Li, Y., Ju, Y., Liu, J., Liu, J., and Shi, Y. (2018) Equilibrium nickel isotope

545   fractionation in nickel sulfide minerals. Geochimica et Cosmochimica Acta, 222,

546   1-16.

547   Liu, S., Li, Y., Liu, J., Yang, Z., Liu, J., and Shi, Y. (2021) Equilibrium Cu isotope

548   fractionation in copper minerals: a first-principles study. Chemical Geology, 564,

549   120060.

550   Liu, Y., and Tossell, J. A. (2005) Ab initio molecular orbital calculations for boron isotope

551   fractionations on boric acids and borates. Geochimica et Cosmochimica Acta, 69,

552   3995-4006.

553   Liu, Y., Li, J., and Chou, I. M. (2020) Cassiterite crystallization experiments in alkali

554   carbonate aqueous solutions using a hydrothermal diamond-anvil cell. American

555   Mineralogist: Journal of Earth and Planetary Materials, 105, 664-673.

556   Ludwig, R., Weinhold, F., and Farrar, T. C. (1999) Quantum cluster equilibrium theory of

557   liquids: molecular clusters and thermodynamics of liquid ethanol. Molecular Physics,

558   97(4), 465-477.

559   Mao, J. W., Yuan, S. D., Xie, G. Q., Song, S. W., Zhou, Q., Gao, Y. B., Liu, X., Fu X. F.,

560   Cao, J., Zeng Z. L., Li T. G. and Fan, X. Y. (2019) New advances on metallogenic

561   studies and exploration on critical minerals of China in 21st century. Mineral

562   Deposits, 38, 935-969.

563   Mao, J., Zheng, W., Xie, G., Lehmann, B., and Goldfarb, R. (2021) Recognition of a

564   Middle–Late Jurassic arc-related porphyry copper belt along the southeast China

565   coast: Geological characteristics and metallogenic implications. Geology, 49,

566   592-596.

567   Mark, W. (1977) Hydrolysis of the Tin (II) ion, Sn^{2+}, in alkaline solution. Acta Chemica

568   Scandmavica A, 31, 157-162.

569   Mason, A. H., Powell, W. G., Bankoff, H. A., Mathur, R., Bulatović, A., Filipović, V. and

570   Ruiz, J. (2016) Tin isotope characterization of bronze artifacts of the central

571   Balkans. Journal of Archaeological Science, 69, 110-117.

572   Mathur, R., Powell, W., Mason, A., Godfrey, L., Yao, J., and Baker, M. E. (2017)

573   Preparation and measurement of cassiterite for Sn isotope analysis. Geostandards

574   and Geoanalytical Research, 41, 701-707.

575   Monkhorst, H. J. and Pack, J. D. (1976) Special points for Brillouin-zone
576   integrations. Physical review B, 13, 5188.

577   Moss, R. L., Tzimas, E., Willis, P., Arendorf, J., Thompson, P., Chapman, A. and Ostertag,
578   K. (2013) Critical Metals in the Path towards the Decarbonisation of the EU Energy
579   Sector. Assessing rare metals as supply-chain bottlenecks in low-carbon energy
580   technologies. JRC Report EUR, 25994.

581   Méheut, M. and Schauble, E. A. (2014) Silicon isotope fractionation in silicate minerals:
582   insights from first-principles models of phyllosilicates, albite and pyrope.
583   Geochimica et Cosmochimica Acta, 134, 137-154.

584   Müller, B., and Seward, T. M. (2001) Spectrophotometric determination of the stability of
585   tin (II) chloride complexes in aqueous solution up to 300℃. Geochimica et
586   Cosmochimica Acta, 65, 4187-4199.

587   Olekseyuk, I. D., Gulay, L. D., Dydchak, I. V., Piskach, L. V., Parasyuk, O. V. and
588   Marchuk, O. V. (2002) Single crystal preparation and crystal structure of the
589   Cu_2Zn/Cd, $Hg/SnSe_4$ compounds. Journal of Alloys and Compounds, 340, 141-145.

590   Peng, Q., and Bromley, A. V. (1992) Fluid inclusion studies of the skarn-type tin
591   mineralization at Red-A-ven, Northwest Dartmoor, England. Chinese journal of
592   geochemistry, 11, 362-369.

593   Perdew, J. P., Burke, K., and Ernzerhof, M. (1996) Generalized gradient approximation
594   made simple. Physical review letters, 77, 3865.

595   Pettine, M., Millero, F. J., and Macchi, G. (1981) Hydrolysis of tin (II) in aqueous
596   solutions. Analytical Chemistry, 53, 1039-1043.

597   Pinilla, C., Blanchard, M., Balan, E., Natarajan, S. K., Vuilleumier, R., and Mauri, F.

598   (2015) Equilibrium magnesium isotope fractionation between aqueous Mg^{2+} and

599   carbonate minerals: Insights from path integral molecular dynamics. Geochimica et

600   Cosmochimica Acta, 163, 126-139.

601   Polyakov, V. B., Mineev, S. D., Clayton, R. N., Hu, G., and Mineev, K. S. (2005)

602   Determination of tin equilibrium isotope fractionation factors from synchrotron

603   radiation experiments. Geochimica et Cosmochimica Acta, 69, 5531-5536.

604   Qin, T., Wu, F., Wu, Z., and Huang, F. (2016) First-principles calculations of equilibrium

605   fractionation of O and Si isotopes in quartz, albite, anorthite, and zircon.

606   Contributions to Mineralogy and Petrology, 171, 1-14.

607   Roskosz, M., Amet, Q., Fitoussi, C., Dauphas, N., Bourdon, B., Tissandier, L. and Alp, E.

608   E. (2020) Redox and structural controls on tin isotopic fractionations among

609   magmas. Geochimica et Cosmochimica Acta, 268, 42-55.

610   Schauble, E. A. (2004) Applying stable isotope fractionation theory to new

611   systems. Reviews in mineralogy and geochemistry, 55, 65-111.

612   Schauble, E. A. (2007) Role of nuclear volume in driving equilibrium stable isotope

613   fractionation of mercury, thallium, and other very heavy elements. Geochimica et

614   Cosmochimica Acta, 71(9), 2170-2189.

615   Schauble, E. A. (2013) Modeling nuclear volume isotope effects in crystals. Proceedings

616   of the National Academy of Sciences, 110(44), 17714-17719.

617   Schauble, E. A., Rossman, G. R., and Taylor Jr, H. P. (2001) Theoretical estimates of

618   equilibrium Fe-isotope fractionations from vibrational spectroscopy. Geochimica et

619   Cosmochimica Acta, 65, 2487-2497.

620   Schmidt, C. (2018) Formation of hydrothermal tin deposits: Raman spectroscopic
621   evidence for an important role of aqueous Sn (IV) species. Geochimica et
622   Cosmochimica Acta, 220, 499-511.

623   Scott J. F. (1970) Raman spectrum of SnO_2. The Journal of Chemical Physics, 53,
624   852-853.

625   She, J. X., Wang, T., Liang, H., Muhtar, M. N., Li, W., and Liu, X. (2020) Sn isotope
626   fractionation during volatilization of Sn (IV) chloride: Laboratory experiments and
627   quantum mechanical calculations. Geochimica et Cosmochimica Acta, 269,
628   184-202.

629   Sherman, D. M., Ragnarsdottir, K. V., Oelkers, E. H. and Collins, C. R. (2000) Speciation
630   of tin (Sn^{2+} and Sn^{4+}) in aqueous Cl solutions from 25 °Cto 350°C: an in-situ
631   EXAFS study. Chemical Geology, 167, 169-176.

632   Sun, M., Mathur, R., Chen, Y., Yuan, S. and Wang, J. First-principles Study on
633   Equilibrium Sn Isotope Fractionations in Hydrothermal Fluids. Acta Geologica
634   Sinica-English Edition.

635   Séby, F., Potin-Gautier, M., Giffaut, E. and Donard, O. F. X. (2001) A critical review of
636   thermodynamic data for inorganic tin species. Geochimica et Cosmochimica
637   Acta, 65, 3041-3053.

638   Takenouchi, S. (1971) Hydrothermal synthesis and consideration of the genesis of
639   malayaite. Mineralium Deposita, 6, 335-347.

640   Tobias, R. S. (1958) Studies on the hydrolysis of metal ions. Acta Chem Scand, 12,
641   198-223.

642   Uchida, E., Sakamori, T., and Matsunaga, J. (2002) Aqueous speciation of lead and tin

643   chlorides in supercritical hydrothermal solutions. Geochemical journal, 36, 61-72.

644   Urey, H. C. (1947) The thermodynamic properties of isotopic substances. Journal of the

645   Chemical Society (Resumed), 562-581.

646   Wang, D., Mathur, R., Powell, W., Godfrey, L., and Zheng, Y. (2019) Experimental

647   evidence for fractionation of tin chlorides by redox and vapor

648   mechanisms. Geochimica et Cosmochimica Acta, 250, 209-218.

649   Wang, J. L., Wei, H. Z., Williams-Jones, A. E., Dong, G., Zhu, Y. F., Jiang, S. Y., and Lu,

650   J. J. (2022) Silver isotope fractionation in ore-forming hydrothermal systems.

651   Geochimica et Cosmochimica Acta, 322, 24-42.

652   Wang, T., She, J. X., Yin, K., Wang, K., Zhang, Y., Lu, X. and Li, W. (2021) Sn (II)

653   chloride speciation and equilibrium Sn isotope fractionation under hydrothermal

654   conditions: A first principles study. Geochimica et Cosmochimica Acta, 300, 25-43.

655   Wang, W., Huang, S., Huang, F., Zhao, X. and Wu, Z. (2020) Equilibrium inter-mineral

656   titanium isotope fractionation: Implication for high-temperature titanium isotope

657   geochemistry. Geochimica et Cosmochimica Acta, 269, 540-553.

658   Wang, W., Zhou, C., Liu, Y., Wu, Z. and Huang, F. (2019) Equilibrium Mg isotope

659   fractionation among aqueous Mg^{2+}, carbonates, brucite and lizardite: Insights from

660   first-principles molecular dynamics simulations. Geochimica et Cosmochimica Acta,

661   250, 117-129.

662   Wu, F., Qin, T., Li, X., Liu, Y., Huang, J. H., Wu, Z., and Huang, F. (2015)

663   First-principles investigation of vanadium isotope fractionation in solution and

664   during adsorption. Earth and Planetary Science Letters, 426, 216-224.

665   Xantheas, S. S., and Dunning Jr, T. H. (1993) Ab initio studies of cyclic water clusters

666    $(H_2O)_n$, n=1–6. I. Optimal structures and vibrational spectra. The Journal of

667   chemical physics, 99(11), 8774-8792.

668   Yang, S., and Liu, Y. (2015) Nuclear volume effects in equilibrium stable isotope

669   fractionations of mercury, thallium and lead. Scientific reports, 5(1), 1-12.

670   Yao, J., Mathur, R., Powell, W., Lehmann, B., Tornos, F., Wilson, M. and Ruiz, J. (2018)

671   Sn-isotope fractionation as a record of hydrothermal redox reactions. American

672   Mineralogist, 103, 1591-1598.

673   Young, E. D., Manning, C. E., Schauble, E. A., Shahar, A., Macris, C. A., Lazar, C., and

674   Jordan, M. (2015) High-temperature equilibrium isotope fractionation of

675   non-traditional stable isotopes: Experiments, theory, and applications. Chemical

676   Geology, 395, 176-195.

677   Young, E. D., Tonui, E., Manning, C. E., Schauble, E., and Macris, C. A. (2009) Spinel–

678   olivine magnesium isotope thermometry in the mantle and implications for the Mg

679   isotopic composition of Earth. Earth and Planetary Science Letters, 288, 524-533.

680   Yuan, S., Williams-Jones, A. E., Romer, R. L., Zhao, P. and Mao, J. (2019)

681   Protolith-related thermal controls on the decoupling of Sn and W in Sn-W

682   metallogenic provinces: Insights from the Nanling region, China. Economic

683   Geology, 114, 1005-1012.

684   Zhang, M., Meyer, H. W., Groat, L. A., Bismayer, U., Salje, E. K. H., and Adiwidjaja, G.

685   (1999) An infrared spectroscopic and single-crystal X-ray study of malayaite,

686    $CaSnSiO_5$. Physics and Chemistry of Minerals, 26, 546-553.

687

688   **Figure and table captions**

689

690   **Figure 1.** Mineral crystal structure calculated in this study: (A) malayaite (supercell

691     $2\times1\times1$), (B) cassiterite (supercell $2\times2\times3$), and (C) stannite (supercell $2\times2\times2$).

692

693   **Figure 2.** The calculated $1000\ln(\beta)$ ($^{124/116}$Sn) values of 10 configurations (Grey points)

694   and their cumulative average values (Colored points) at 25 °C.

695

696   **Figure 3.** Radial distribution functions (RDFs) for Sn-O pairs of $Sn^{2+}(OH)_{2(aq)}$, $Sn^{2+}Cl_3^-$

697     $_{(aq)}$, $Sn^{2+}CO_3\;_{(aq)}$, $Sn^{2+}F_3^-\;_{(aq)}$ and $Sn^{4+}Cl_{4(aq)}$. The insets represent the coordination

698   numbers (CNs) varied with the distance.

699   **Figure 4.** The calculated $1000\ln(\beta)$ (‰) for (a) minerals and (b) Sn-bearing species in

700   solutions (0 – 400 °C). The $^{122/116}$Sn (cassiterite) and $^{122/116}$SnCl$_3^-$ from Polyakov et al.

701   (2005) and Wang et al. (2021) are also shown for comparison.

702   **Figure 5.** Calculated $1000\ln\alpha$ values of malayaite-stannite, cassiterite-stannite and

703   malayaite-cassiterite as a function of temperature.

704

705   **Figure 6.** $1000\ln(\alpha)$ $_{\text{minerals – aqueous species}}$ ($^{124/116}$Sn and $^{122/116}$Sn) (‰). (a) $1000\ln(\alpha)$

706   aqueous species – cassiterite ($^{124/116}$Sn and $^{122/116}$Sn); (b) $1000\ln(\alpha)$ aqueous species –

707   malayaite ($^{124/116}$Sn and $^{122/116}$Sn); $1000\ln(\alpha)$ aqueous species – stannite ($^{124/116}$Sn and

708     $^{122/116}$Sn).

709

710

711   **Table 1.** Calculation parameters of minerals and aqueous complexes

712

713   **Table 2.** Coordination number and calculated bond length of minerals

714

715   **Table 3**. Polynomial fit parameters for the calculation of tin isotope fractionation factors

716   as $1000\ln(\beta) = ax + bx^2 + cx^3$, where $x = 10^6/T^2$ and T is the temperature in Kelvin

717   (273.15 K to 673.15 K)

718

719

720

721

722

723

724

Table 1. Calculation parameters of minerals and aqueous complexes

Model			Lattice parameters					
Minerals	Supercell	k-point grid	a(Å)	b(Å)	c(Å)	α(°)	β(°)	γ(°)
cassiterite	2×2×3	3×3×3	4.736 (4.737)[a]	4.736 (4.737)[a]	3.187 (3.186)[a]	90	90	90
	2×2×2	3×3×4	4.737	4.737	3.186	90	90	90
malayaite	1×1×1	1×1×1	7.152 (7.150)[b]	8.888(8.890)[b]	6.667 (6.660)[b]	90	113.37	90
	2×1×1	1×1×1	7.152	8.888	6.667			
stannite	1×1×1	3×3×3	5.14 (5.46)[c]	5.414 (5.46)[c]	5.414(5.46)[c]	90	90	90
	2×2×2	1×1×1	5.14	5.414	5.414	90	90	90
Complexes in aqueous solution								
$Sn^{2+}Cl_3^- \cdot 50H_2O$		1×1×1	12.3188	12.3188	12.3188	90	90	90
$Sn^{2+}CO_3 \cdot 50H_2O$		1×1×1	12.1474	12.1474	12.1474	90	90	90
$Sn^{2+}(OH)_2 \cdot 50H_2O$		1×1×1	12.0491	12.0491	12.0491	90	90	90
$Sn^{2+}F_3^- \cdot 50H_2O$		1×1×1	12.1361	12.1361	12.1361	90	90	90
$Sn^{4+}Cl_4 \cdot 50H_2O$		1×1×1	12.0491	12.0491	12.0491	90	90	90

Notes: The experimental values which are listed in brackets are compare with the optimized cell parameters.
[a] Bolzan et al.(1997).
[b] Takenouchi, (1971).
[c] Brockway. (1934).

Table 2. Coordination number and calculated bond length of minerals

Model		Bond length(Å)	Coordination number	Frequencies(cm-1)
Cassiterite $(Sn^{4+}O_2)$	Sn-O	$2.059(2.058)^a$	6	$776(773)^d$
Malayaite $(CaSn^{4+}SiO_5)$	Si-O	$1.647(1.641)^b$	6	$951(941)^e$
	Sn-O	$2.064(2.042)^b$		
	Ca-O	$2.448(2.483)^b$		
Stannite $(Cu_2FeSn^{4+}S_4)$	Sn-S	$2.566(2.539)^c$	4	$346(350)^f$

Notes: Comparison between calculated value and the experimental value which show in brackets.
[a] Bolzan et al.(1997)
[b] Higgins and Ribbe,(1977)
[c] Olekseyuk et al (2002)
[d] Scott (1970)
[e] Zhang et al (1999)
[f] Fontané et al (2012)

Table 3. Polynomial fit parameters for the calculation of tin isotope fractionation factors as $1000\ln(\beta) = ax + bx^2 + cx^3$, where $x = 10^6/T^2$ and T is the temperature in Kelvin (273.15 K to 673.15 K).

| Model		a	b	c
Cassiterite	$^{124/116}$Sn	1.0506	−0.00634	7.59E–05
	$^{122/116}$Sn	0.80108	−0.00487	5.68E–06
Malayaite	$^{124/116}$Sn	1.09313	−0.00789	9.40E–05
	$^{122/116}$Sn	0.83357	−0.00614	7.84E–05
Stannite	$^{124/116}$Sn	0.29093	−2.10E-04	−1.58E–05
	$^{122/116}$Sn	0.22286	−4.52E-04	4.40E–06
$Sn^{2+}Cl_3^-{\cdot}50H_2O$	$^{124/116}$Sn	0.25039	−9.80E-04	1.43E–05
	$^{122/116}$Sn	0.19085	−7.48E-04	1.10E–05
$Sn^{2+}CO_3{\cdot}50H_2O$	$^{124/116}$Sn	0.34162	−0.00219	2.78E–05
	$^{122/116}$Sn	0.2607	−0.00182	3.30E–05
$Sn^{2+}(OH)_2{\cdot}50H_2O$	$^{124/116}$Sn	0.40894	−0.00281	4.06E–05
	$^{122/116}$Sn	0.31107	−0.00195	1.91E–05
$Sn^{2+}F_3^-{\cdot}50H_2O$	$^{124/116}$Sn	0.42503	−0.00217	2.25E–05
	$^{122/116}$Sn	0.32389	−0.00166	1.79E–05
$Sn^{4+}Cl_4{\cdot}50H_2O$	$^{124/116}$Sn	0.72425	−0.00458	5.59E–05
	$^{122/116}$Sn	0.5518	−0.00346	4.15E–05

Fig.1
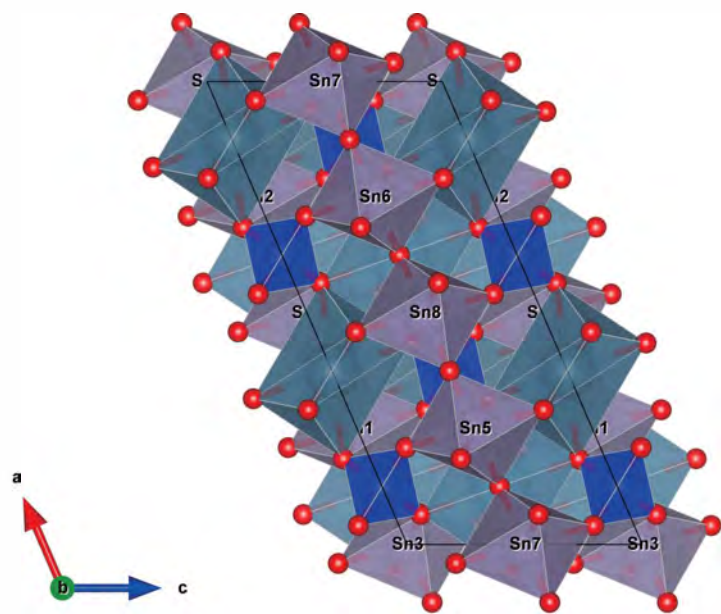
(A) malayaite
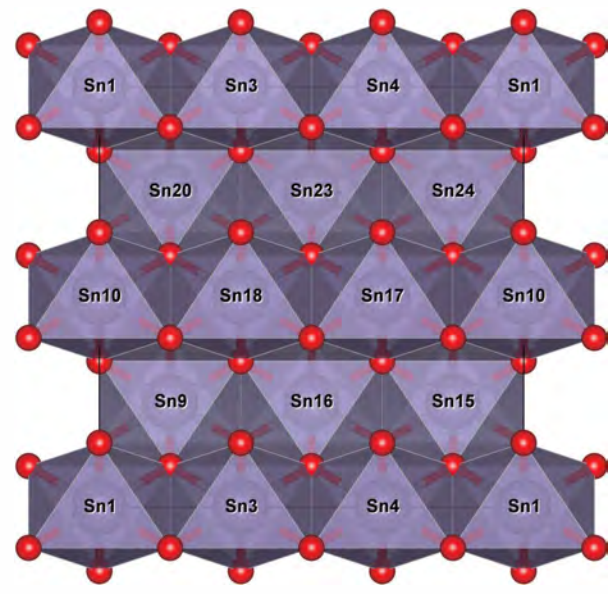
(B) cassiterite
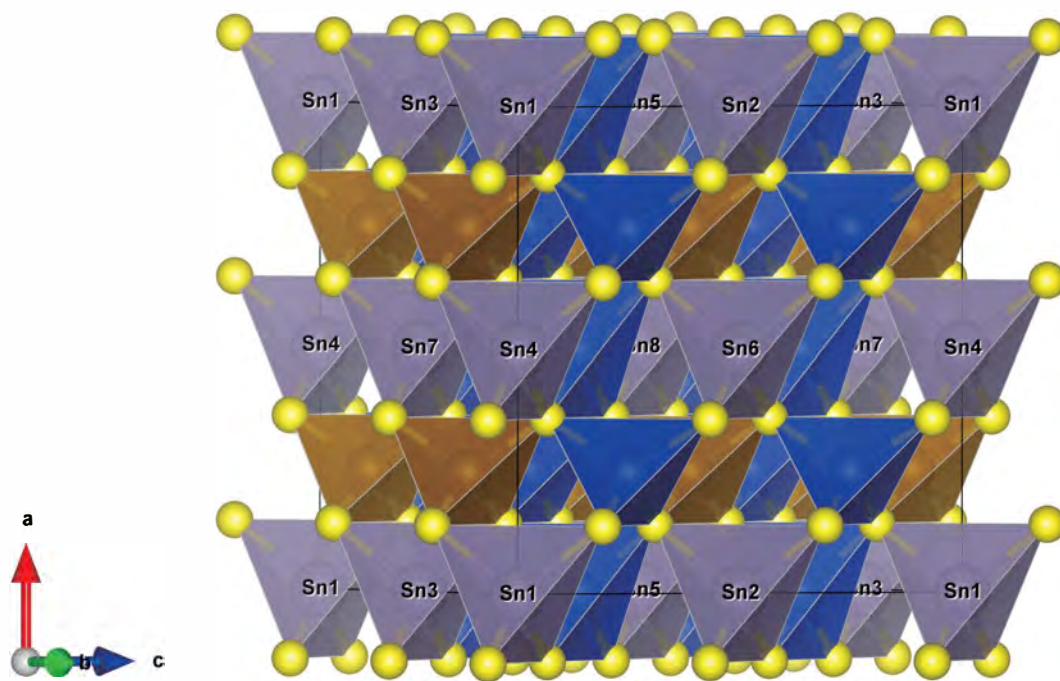
(C) stannite

Fig.2

Fig.3

Fig.4

Fig.5

Fig.6