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3	Boron coordination and B/Si ordering controls on equilibrium boron
4	isotope fractionation among minerals, melts, and fluids
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32 ABSTRACT

The high mobility of boron during fluid-rock interaction has made it an effective tracer for the 33 34 sources of magmatic and metamorphic fluids, as recorded in minerals such as tourmaline and muscovite. Although advances have been made in quantifying the fractionation of boron isotopes 35 36 among different phases, boron isotope fractionation in complex silicate melts remains poorly 37 understood. Here, we propose appropriate models for the BO₃ and BO₄ units in silicate melts covering 38 a wide range of chemical compositions and boron coordination structures in silicate magmas, and report the results of a theoretical investigation of boron isotope fractionation among silicate melt, 39 40 minerals and fluids using a first principles theoretical approach. A comparison of measured and 41 calculated α factors in mineral-melt and fluid-melt systems shows good agreement, suggesting the 42 applicability of a simplified treatment of boron coordination structures in silicate melt. The results of 43 this study show that the proportion of trigonal/tetrahedral coordinated boron and the B/Si ordering in silicate tetrahedral layers control the boron isotope fractionation among different phases and that the 44 effect of chemical composition is minor (less than 2‰ at 600 K). The temperature-dependent boron 45 46 isotope fractionation is described as $1000 \ln \alpha_{\text{mica-basic fluid}} = 0.8-2.4 \times (1000/\text{T}) - 0.8 \times (1000/\text{T})^2$, $1000 \ln \alpha_{\text{mica-acidic fluid}} = 7.0-14.0 \times (1000/T) - 1.2 \times (1000/T)^2$ and $1000 \ln \alpha_{\text{mica-tur}} = 1.9-5.4 \times (1000/T) - 1.2 \times (1000/T)^2$ 47 $3.4 \times (1000/T)^2$ (T is temperature in Kelvins). At magmatic temperatures, $\Delta^{11}B$ values between 48 49 mineral/fluid and melt also vary with the proportion of the BO₄ unit in the melt. This study 50 demonstrates the applicability of the white mica-tourmaline geothermometer and boron isotopes for fluid source identification, and offers an explanation of boron isotope fractionation in systems that 51 52 contain complex silicate melts.

Keywords: Boron isotope fractionation; Silicate melt; Boron-bearing minerals; Aqueous liquid; Boron
 isotope-geothermometer

55 **1. INTRODUCTION**

Boron has two stable isotopes, ¹⁰B and ¹¹B, and their abundance ratio (expressed as δ^{11} B) varies 56 by over 100% in nature. Consequently, boron isotopes have been widely used to interpret geochemical 57 58 cycles and interactions among magmas, minerals and aqueous fluids (e.g., Williams et al., 2001). The 59 high mobility of boron in aqueous fluids enables boron isotopes to provide important insights into a variety of igneous and metamorphic processes in which such fluids participate. Because of the high 60 sensitivity of δ^{11} B to changes in the fluid source, pressure-temperature (P-T) conditions of 61 crystallization, and phase transitions such as boiling, great attention has been paid to tourmaline group 62 minerals to track the sources of magmatic and hydrothermal fluids (e.g., Palmer and Slack, 1989; 63 Palmer and Swihart 1996; Jiang et al., 2000; Zheng et al., 2016), and to unravel complex petrologic 64 65 histories of deeply subducted material (Bebout and Nakamura, 2003). White mica is also an important 66 boron reservoir in subduction zone rocks at depths of between 15 and 45 km with concentrations of up to ~5500 ppm B (Domanik et al., 1993; Bebout et al., 2007; Menold et al., 2016; Sievers et al., 2016), 67 68 which dominates the boron budget within the slab even in the presence of tourmaline (Leeman and Sisson, 1996; Klemme et al., 2011). In island arc environments, ¹¹B is preferentially enriched in 69 70 aqueous fluids over melts and minerals, hence such magmas are progressively depleted in the heavy 71 ¹¹B with distance from the subduction front (Ishikawa and Nakamura, 1994). Thus, boron concentrations and δ^{11} B in subduction settings can provide insights into the slab transfer mechanisms 72 of dehydration reactions and/or partial melting reactions (e.g., Peacock and Hervig, 1999; Benton et 73 74 al., 2001; Scambelluri and Tonarini, 2012; Harvey et al., 2014; Konrad-Schmolke and Halama, 2014;

Palmer, 2017; De Hoog and Savov, 2018). Boron also can reach concentrations of several weight
percent B₂O₃ in S-type granites that produce hydrothermal ore deposits (Pichavant et al., 1988;
Kowalski and Wunder, 2018; London, 1997; Thomas et al., 2003). Hence, knowledge of boron
partitioning and isotope fractionation during magma-hydrothermal evolution can aid in understanding
granite petrogenesis.

80 In igneous and hydrothermal systems, boron occurs almost exclusively in either trigonal or tetrahedral coordination with oxygen. In terms of isotope partitioning, ¹¹B favors trigonal coordination 81 and ¹⁰B tetrahedral coordination (Kakihana et al., 1977), because of the preferential partitioning of 82 83 light isotopes into phases with higher coordination and longer B-O bonds (Hawthorne et al., 1996; 84 Wunder et al., 2005). Thus, knowledge of the coordination of boron in interacting phases (i.e., fluids, 85 minerals, and melts) is essential for a first-order quantification of boron isotope fractionation among 86 these phases. At P-T conditions corresponding to those near the Earth's surface, the nature of the 87 dominant boron species in hydrous fluids is strongly dependent on pH (Palmer and Swihart, 1996), 88 with $B(OH)_4^-$ dominating at high pH and $B(OH)_3$ dominating in neutral and acidic hydrous fluids. 89 Experiments have shown that this pH dependence also holds true for high pressure and temperature (Schmidt et al., 2005). 90

The boron isotope fractionation factors between tourmaline and white mica measured in natural samples (Klemme et al., 2011) are larger than those estimated from the in-situ experimental data of Meyer et al. (2008) and Wunder et al. (2005). In a theoretical study, Kowalski et al. (2013) interpreted the discrepancy to be due most likely to the presence of $B(OH)_{4^-}$ species in the neutral solutions employed in these experiments, something that also has been observed in the experiments of Schmidt et al. (2005). Hervig et al. (2002) determined the boron isotope fractionation between silicate melts

97 and aqueous fluids experimentally. They attributed the observed large boron isotope fractionation (e.g., 98 -7.1‰ at 750°C) to the dominance of BO₄ in the melt (Hervig et al., 2002). However, a later 99 spectroscopic study suggests that boron is present predominantly as BO₃ in rhyolite melts (Tonarini et 100 al., 2003). 101 Silicate melts are structurally more complex than crystals, because of their more disordered nature 102 and variable chemical composition. The proportions of 3- and 4-fold coordinated boron in silicate 103 melts and glasses are controlled by a combination of chemical composition, temperature and pressure 104 (Kowalski and Wunder, 2018). For example, the average boron coordination number in boron-silicate 105 melts depends on the SiO₂/B₂O₃ ratio and the alkali oxide/B₂O₃ ratio (Dell et al., 1983; Geisinger et 106 al., 1988; Dingwell et al., 1996; Manara et al., 2009). In alkali borate melts, the proportion of 107 tetrahedrally coordinated boron (BO₄) reaches a maximum at an alkali oxide concentration of ~ 35 108 mol%. The addition of SiO₂ increases the proportion of BO₄ in alkali boron-silicate melts, whereas the 109 presence of aluminum destabilizes boron in tetrahedral coordination. Interaction between water and 110 melt also affects the structure of aluminosilicate melts (Mysen, 2010) and stabilizes BO₄ in albite glass 111 (Schmidt et al., 2004), because an increase in the fraction of water dissolved as hydroxl groups leads 112 to the formation of B-OH complexes in the melt (Dingwell et al., 1996). In addition to the chemical 113 composition, the effects of temperature (e.g., Smirnov et al., 2005; Manara et al., 2009; Wu and 114 Stebbins, 2010, 2013) and pressure (e.g., Schmidt et al., 2004; Edwards et al., 2014) on boron 115 coordinated structures are considerable. The forward reaction [BO₄] \Leftrightarrow [BO₃] + NBO (NBO represents 116 the non-bridging oxygen) is favored by increasing temperature and decreasing pressure (Wu and 117 Stebbins, 2010, 2013). For alkali borosilicate melts (e.g., 10B₂O₃·30Na₂O·60SiO₂ and 118 10B₂O₃·15Na₂O·15CaO·60SiO₂), the fraction of tetrahedral boron drops from 0.7 in the glass to 0.3

119 in the melt (Michel et al., 2013). With increasing pressure, the conversion of trigonal BO₃ to tetrahedral 120 BO₄ likely proceeds via a trigonal pyramid precursor phase (Edwards et al., 2014). Generally, 121 conditions of higher pressure and lower temperature help stabilize BO₄ units in melts and glass. In 122 addition, the BO₄ proportion in the melt can be affected by the cooling rate, the field strength of 123 metallic elements (Wu and Stebbins, 2010; 2013), and carbonate assimilation by the magma (Deegan 124 et al., 2016). All these observations demonstrate that understanding the behavior of boron-coordinated 125 structures in natural melt systems is challenging, particularly if coupled with the variable partitioning 126 of boron between aqueous and melt phases. For example, whereas the aqueous fluid/melt partition 127 coefficient ranges from 0.33-0.54 for basaltic melts and is ~1.2 for rhyolite melt (Hervig et al., 2002; 128 Schatz et al., 2004), it reaches 4.6 between aqueous vapor and melt (Schatz et al., 2004). 129 Recently, considerable progress has been made in modeling the equilibrium fractionations of stable 130 isotopes among different phases (Schauble, 2004; Schauble et al., 2009; Blanchard et al., 2017). 131 Examples include, hydrogen isotope fractionation between hydrous minerals and water (Méheut et al., 132 2010), oxygen and silicon isotope fractionation among silicate minerals (Méheut et al., 2007, 2009, 133 2014; Huang et al., 2014), oxygen isotope fractionation among hydroxyl-bearing silicates, anhydrous 134 silicate minerals, magnetite, apatite, carbonate and sulfate minerals and between hydroxide minerals 135 and water (Zheng, 1993ab, 1995, 1996, 1998, 1999; Zheng et al., 1998), chlorine isotope fractionation 136 in Cl-bearing molecules and metal chlorides (Schauble et al., 2003; Balan et al., 2019), sulfur isotope 137 fractionation among sulfide and sulfate minerals, carbon isotope fractionation between carbonate 138 magmas and minerals, boron, zinc and iron isotope fractionation between minerals and aqueous 139 solutions (Schauble et al., 2001, 2004; Hill and Schauble, 2008; Blanchard et al., 2009; Kowalski et 140 al., 2013; Ducher et al., 2016, 2018; Balan et al., 2018; Li et al., 2020), as well as barium, magnesium

141 and calcium isotope fractionation among silicate, oxide and carbonate minerals (Schauble, 2011,

142 Pinilla et al., 2014; Huang et al., 2013, 2019; Antonelli et al., 2019; Mavromatis et al., 2020).

143 Theoretical studies using density functional theory (DFT) and *ab initio* molecular dynamics 144 simulation (AIMD) satisfactorily explain dynamic effects on isotope fractionation in fluids (Rustad 145 and Bylaska, 2007; Kowalski and Jahn, 2011; Kowalski et al., 2013; and Wunder, 2018; Li et al., 146 2020). Modeling the behavior of molten silicates is crucial for our understanding of processes ranging 147 from the cooling and crystallization of Earth's early magma ocean, to the generation and transport 148 mechanisms of magma on modern day Earth (Solomatov, 2007). Diffusivity and viscosity control the 149 mobility and rate of chemical reaction of silicate melts with their surroundings. Therefore, the 150 theoretical simulation of the behavior of silicate melts using first-principle molecular dynamics 151 (FPMD) within the framework of density functional theory provides an essential tool with which to 152 evaluate the physical properties of melts. This includes the development of equations of state to predict 153 thermodynamic properties, atomic and electronic structures, self-diffusion and viscosity etc. (Karki, 154 2010). Because natural silicate melts and silicate glasses are composed of networks of SiO_4 polyhedra, 155 and secondary elements (such as Mg, Ca and Fe) are believed to diffuse through interstitial sites 156 (Vashishta et al., 1990), the diffusion-induced isotope effect (DIE) in silicate melts has been 157 investigated extensively through molecular dynamics (MD) simulations. For example, the thermal 158 (Soret) effect and isotopic fractionation of Mg, Ca and Fe in high-temperature silicate melts are well 159 understood using the quantum-mechanical zero-point energy of diffusing species (Dominguez et al., 160 2011).

161 Owing to the cooperative motions of the many atoms involved in diffusion, significant diffusive 162 fractionation of Si and Mg isotopes has been predicted to occur during magma mixing (e.g., the inter-

163 diffusion between basaltic and rhyolitic magma is capable of producing isotope fractionation of tens 164 of per mil in Si and tens of per mil in Mg) and during crystallization (such as the growth of olivine 165 phenocrysts), if the growth rate is fast (Goel et al., 2012). A comparison of the diffusion coefficients 166 of Mg isotopes in MgSiO₃ and Mg₂SiO₄ melts estimated from FPMD to the experimentally determined 167 values in basalt-rhyolite melts suggests a dependence on the chemical composition of the melts (Liu 168 et al., 2018; Richter et al., 2008). Thus, the DIE of Fe, Mg, Si and Li in immiscible, ascending, silicate 169 melts have been quantitatively predicted (Zhu et al., 2015). In addition to the dynamic properties, MD 170 studies of structural properties of melts have focused mainly on the two most important components 171 (MgO and SiO₂) in silicate melts (Trave et al., 2002; Winkler et al., 2004; Pohlmann et al., 2004; Karki 172 et al., 2006ab, 2007, 2009, 2010; De Koker et al., 2008; Martin et al., 2009; Vuilleumier et al., 2009). 173 In contrast, it is assumed that the kinetic DIE of boron in silicate melts is insignificant at the 174 temperature of melt-crystallization (Kowalski and Wunder, 2018), because of the low diffusivity of 175 boron in haplogranite melts (Chakroborty et al., 1993). Whereas the major element concentrations of 176 SiO₂, Al₂O₃, MgO, CaO, Na₂O and K₂O are at a mol% level, the content of boron is at the ppm level 177 in natural silicate melts. Considering the relatively low abundance of boron and the high variability of 178 the BO₃/BO₄ ratio in silicate melts due to factors that include thermodynamic conditions (T-P), 179 chemical composition, the field strength of metallic elements, the cooling rate, as well as chemical 180 reactions (carbonate assimilation, fluid exsolution etc.), the equilibrium isotope fractionation of the 181 trace boron in melts may be better represented by the energetic differences in the respective bonding 182 environments. This approach involves developing an appropriate model to represent boron structural 183 units in a silicate melt network, and to acquire all the vibrational frequencies for boron species in the 184 melt, especially at high P-T conditions.

185 In general, a simplified treatment can be adopted based on the observation that vibrational 186 frequencies in many strongly-bonded molecule-like species are not sensitive to the environment of the 187 phase in which they occur (Schauble, 2004). For example, Kakihana et al. (1977) proposed a simplified 188 approach for a first approximation of the reduced partition function ratios (RPFRs) of polynuclear 189 borate anions containing BO₃ and BO₄ units, in which the boron sites within the polynuclear species 190 are considered to be present as the isolated monomeric units, $B(OH)_3$ and $B(OH)_4$. Oi et al. (1989) 191 then calculated the RPFRs of polyborate anions in boron-bearing minerals with an extension of the 192 rule of the geometric average of the RPFRs of aqueous $B(OH)_3$ and $B(OH)_4$. This formulation was 193 used to predict the difference in boron isotope composition between different borate minerals forming 194 from similar fluids (Palmer and Helvaci, 1997). However, an inconsistency between the theoretical 195 predictions and experimental data from natural silicate melt and minerals has been observed by 196 Tonarini et al. (2003) using the same approach. These authors concluded that the reduced partition 197 function ratios (RPFRs) assigned for B(OH)₃ and B(OH)₄⁻ species in aqueous solutions by Kakihana 198 et al. (1977) may not be appropriate for BO₃ and BO₄ units in silicate melt/glass structures (Tonarini 199 et al., 2003). The inconsistency likely reflects the complex structures of aluminous-silicate melts, in 200 which the BO₃ and BO₄ units exist in a number of different site arrangements, forming complex 201 structural units with the silicon and aluminum polyhedra in the melt network.

Granitic melts are the most common natural silicate melts in the continental crust and typically contain > 65wt% SiO₂ and ~15wt% Al₂O₃. Previous computational modeling of natural rhyolite melts (84 mol% SiO₂ and 8 mol% Al₂O₃) shows that $[SiO_4]^{4-}$ (^[4]Si) and $[AlO_4]^{5-}$ (^[4]Al) are the most common coordination structures (Vuilleumier et al., 2009). Theoretical calculation for liquid SiO₂ also show that ^[4]Si is generally the dominant structure and that $[SiO_5]^{6-}$ (^[5]Si) and $[SiO_6]^{8-}$ (^[6]Si) only become

207 important at higher pressure (e.g., 7 and 20 GPa) (Rustad et al., 1990; Vuilleumier et al., 2009). In borosilicate melts and glasses, the BO₃ and BO₄ units (quasi-planar [BO₃]³⁻ triangles and [BO₄]⁵⁻ 208 tetrahedra) can form numerous combinations with network-forming components of [SiO4]⁴⁻ and 209 210 [AlO₄]⁵⁻ (Kowalski and Wunder, 2018). Similarly, [BO₄]⁵⁻ in white mica and [BO₃]³⁻ in tourmaline form networks with [SiO₄]⁴⁻ and [AlO₆]⁹⁻. Because the B-O bond is stronger than Si-O and Al-O bonds 211 212 (Navrotsky, 1996), and B-O interactions may overwhelm the effect of next-nearest neighbors, changes 213 in bulk chemistry have a relatively minor impact on boron isotope fractionation (Hervig et al., 2002). Hence, a local structure containing next-nearest neighbor atoms is sufficient to include all the 214 215 significant effects of networks on boron isotope fractionation (Liu et al., 2005; Li et al., 2020).

To the best of our knowledge, there is still no consensus on the precise coordination structures of 216 boron in silicate melts, which limits the interpretation of boron isotope fractionation during the 217 218 evolution of magmatic-hydrothermal fluids. In this study, the BO₃ unit and the BO₄ unit of silicate 219 melts are represented using cluster models with variable chemical compositions. The aim of this 220 approach is to calculate equilibrium boron isotope factors for fractionation among boron-rich silicate minerals, melts and fluids. As an example, this model will be used to examine the boron isotopic 221 222 composition of magmas prior to phase separation and assess the applicability of white mica-tourmaline 223 geothermometers in magmatic-hydrothermal ore-forming systems.

224

225 2. CALCULATION METHODS

226 2.1. Models for white mica minerals

The representative models for tourmaline and aqueous fluids were described in detail in our previous study (Li et al., 2020). Periodic boundary cell (PBC) models for seven white micas were

229	constructed based on the boromuscovite structure (Liang et al., 1995). These models with different
230	variables (polytype, lattice parameters, chemical composition, and B/Si ordering) were considered in
231	order to understand the effect of these different variables on boron isotopes fractionation (Table 1,
232	Figure 1). The PBC models of boromuscovite and phengite were constructed in the Material Studio
233	Materials Visualizer module (Accelrys, Inc., version 7.0) and he original cell volume was maintained
234	with slight changes in the original cell parameters after atomic substitution in crystal lattices,. All white
235	mica models were optimized for fixed cell parameters.

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Table 1. The lattice parameters and calculation sets for the white mica models

	Boromuscovite	Boromuscovite	Boromuscovite	Boromuscovite	Boromuscovite	Phengite-A-	Phengite-B-
	-A-1M	-A-2M1	-B-1M	-B-2M1	-C-2M1	2M1	2M1
F 1	KAl ₂ (BSi ₃ O ₁₀)	KAl4(BSi7O ₂₀)	K2Al4(BAlSi6				
Formula	(OH) ₂	(OH) ₄	O ₂₀)(OH) ₄				
Supercell	$1 \times 1 \times 1$	$1 \times 1 \times 2$	$1 \times 2 \times 1$	$1 \times 1 \times 1$	$1 \times 1 \times 1$	$1 \times 1 \times 1$	1×1×1
<i>a</i> (Å)	10.162	5.093	10.162	5.093	10.185	10.185	10.185
b (Å)	5.081	8.818	10.162	5.093	5.093	5.093	5.093
<i>c</i> (Å)	10.076	19.819	10.076	20.939	19.819	19.819	19.819
α (°)	95.611	94.864	95.611	99.66	92.805	92.805	92.805
β (°)	95.611	87.195	95.611	99.66	92.805	92.805	92.805
γ (°)	119.724	89.967	119.724	120.033	120.033	120.033	120.033
Volume (Å ³)	443.12	885.67	886.24	442.835	885.67	885.67	885.67
Natoms	42	84	84	42	84	82	84
K-points	2×2×2	3×2×1	2×2×1	3×3×1	2×3×1	2×3×1	2×3×1
Cut-off	800	800	800	800	750	750	750
energy (eV)	800	800	800	800	750	750	750
q-points	22	12	8	42	20	20	20
Quality	Fine	Fine	Fine	Fine	Fine	Fine	Fine

239 Note: 'Quality' is a data quality control tab used to limit parameter sets, such as K-points, Cut-off energy, and q-points. Generally,

240 'Medium' gives sufficient precision. 'Fine' means more accurate results at the expense of a longer calculation time.

K-points: used for Brillouin zone sampling; the magnitude of the error in the total energy can be reduced by using a denser set of k-points.

243 Cut-off energy: the periodic system (mineral model) is calculated with plane wave basis sets; a higher cut-off energy corresponds to the

244 use of more plane waves to describe the system.

q-points: used in the real space dynamic matrix calculations to obtain a set of frequencies at each point.



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Figure 1. A series of periodic boundary cell (PBC) models for white mica (left) and the arrangement of boron atoms in tetrahedral silica layers (right). The letters A, B, and C represent possible distributions of boron and silicon in the inter-layers of white mica structures along the *c*-axis.

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251 2.2. Cluster models for silicate melts

252	The BO3 and BO4 units of silicate melts are represented using cluster models with variable
253	chemical compositions (Figure 2). The clusters for the BO_3 unit were constructed with reference to the
254	tourmaline structure, using different major elements (e.g., Mg in BO ₃ - <i>i</i> , Mg, Fe in BO ₃ - <i>j</i> , F in BO ₃ - <i>k</i> ,
255	Ca, Li in BO ₃ - <i>l</i> , Mg, Al in BO ₃ - <i>m</i> , Al in BO ₃ - <i>n</i> , Fe in BO ₃ - <i>o</i> and Fe, Mg in BO ₃ - <i>p</i>). The clusters for
256	the BO4 unit were constructed on the basis of the crystal structure of phyllosilicate minerals (e.g.,
257	muscovite, biotite, phlogopite and serpentine), in which different chemical compositions were
258	considered (^[6] Al in BO ₄ - <i>i</i> , ^[4] Si in BO ₄ - <i>j</i> and BO ₄ - <i>k</i> , ^[4] Al in BO ₄ - <i>l</i> , ^[6] Fe in BO ₄ - <i>m</i> , ^[6] Mg in BO ₄ - <i>n</i>).



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Figure 2. Cluster models representing BO₃ and BO₄ units in silicate melts with variable chemical compositions.

262 2.3. Calculation of the reduced partition function ratio (RPFR)

The vibrational frequency shifts due to isotopic substitution can lead to equilibrium isotope fractionation (Bigeleisen and Mayer, 1947; Urey, 1947). Under the harmonic approximation, the isotope fractionation factor between phase A and an ideal X atoms gas β_A) can be expressed as:

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$$RPFR(A) = \frac{Q^*}{Q} = \prod_{i}^{N_m} \frac{u_i^*}{u_i} \frac{\exp(-u_i^*/2)}{1 - \exp(-u_i^*)} \frac{1 - \exp(-u_i)}{\exp(-u_i/2)}$$
(1)

where * represents the heavier isotope, Q^* and Q refer to the vibrational partition function for the heavy and light isotopes, respectively, *i* is the index of the vibration modes and N_m represents the number of vibration modes. For convenience, we used the relationship $\beta = \text{RPFR}^{1/n}$, in which the exponent 1/n is a normalizing factor to account for multiple substitutions in a phase A that contains more than one atom of X (Schauble, 2004). The term of u_i was calculated by:

272
$$u_i = \frac{hv_i}{kT}$$
(2)

where *h* and *k* are Plank's and Boltzmann's constants, respectively, *T* is temperature in Kelvins and v_i is the vibration frequency of the *i*th mode. The isotope fractionation at equilibrium between phases A and B can be expressed as (Wang et al., 2019; Li et al., 2019):

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$$\Delta_{A-B} \approx 1000 ln \alpha_{A-B} = 1000 ln \beta_A - 1000 ln \beta_B \tag{3}$$

Calculation details for the reduced partition function ratio of tourmaline and aqueous fluids were provided in Li et al. (2020). In the current study, the cluster models of BO₃ and BO₄ units were calculated using the B3LYP exchange-correlation functional with 6-31G(d) basis set using the GAUSSIAN 16 software package (Frisch et al., 2016). All the calculations for white micas were carried out using the Cambridge Serial Total Energy Package (CASTEP) in Material Studio 7.0 (Clark et al., 2005). The Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional and norm-

283 conserving pseudopotentials were employed in calculations of both the geometry optimization and the 284 phonon frequency of the white mica models. The parameter sets of k-points, cut-off energy, and q-285 points for 'Fine' quality level recommended by Material Studio 7.0 are summarized in Table 1. When 286 applying a scaling factor of 0.9614 for frequencies calculated with a combination of the B3LYP 287 functional and 6-31G(d) basis set, the overall root-mean-square error between the fundamental and 288 theoretical harmonic frequencies is small (Merrick et al., 2007). To obtain more accurate frequencies, 289 we use 0.9614 to scale the harmonic vibrational frequency of the cluster models. The β values of the 290 minerals, melts and fluids are listed in the Appendix (Table A1).

291 2.4. Error estimation

292 As emphasized by Kowalski and Wunder (2018), an important aspect of reliable theoretical 293 predictions is an error estimation of the computed fractionation factors. Previous studies have indicated 294 that the errors in the computed β and Δ values could be estimated from an average error of vibrational 295 frequencies (Méheut et al., 2007; Kowalski and Jahn, 2011; Kowalski et al., 2013). Different 296 functionals or more sophisticated and time-consuming post-Hartree-Fock methods, such as MP2, can 297 also yield similar error estimates (Kowalski et al., 2013). The PBE calculations reproduce the 298 frequencies with a systematic underestimation of 2 to 5% (Méheut et al., 2007) and the BLYP 299 functional systematically overestimates the harmonic frequencies by 3.5±1% (Kowalski et al., 2013). 300 Consequently, the β and Δ values are systematically overestimated by 7.0±2% with the BLYP 301 functional (Kowalski and Wunder, 2018). The consistency in the error estimates for β and Δ values 302 between minerals and fluid from Kowalski et al. (2013) and Li et al. (2020) shows the robustness of 303 the error estimation scheme proposed by Kowalski et al. (2013). It is noteworthy that in the error 304 estimation method of Méheut et al. (2009), a systematic error of n% on the phonon frequencies can

induce a relative error on the ln β factors of n% (at low temperatures) and 2n% (at high temperature). Hence, we conclude that the relative error in ln β factors induced by DFT or anharmonicity should not exceed 1.5n% (about 5% in ln β). The overall absolute errors for 1000ln β and 1000ln α in ‰ are estimated by the relationships $\frac{1000ln\beta \times 5\%}{2}$ and $\frac{(1000ln\beta_A + 1000ln\beta_B) \times 5\%}{2}$, respectively.

309

310 **3. RESULTS**

311 *3.1.* β factors of white mica with variable B/Si ordering and chemical composition

For the 56 types of muscovite structures given in the American Mineralogist crystal structure 312 313 database (Downs and Hall-Wallace, 2003), each tetrahedron contains approximately 0.75 Si and 0.25 314 Al in muscovite (KAl₂[AlSi₃O₁₀](OH)₂), with a disordered Al/Si arrangement in the tetrahedral layer. Because of the reduction in the bond length from 1.64 Å for (Si,Al)-O in albite to 1.47 Å for B-O in 315 316 reedmergnerite, a disordered structure is more favorable than an ordered structure for the substitution 317 of B for Al (Christ, 1965). In the boromuscovite structure (KAl₂[BSi₃O₁₀](OH)₂) defined by Liang et al. (1995), each tetrahedral position also contains approximately 0.75 Si and 0.25 B, if ^[4]Al is replaced 318 by B in muscovite. Because ^[4]B-O-^[4]B linkages are relatively unfavorable energetically as are ^[4]Al-319 O-^[4]Al linkages in aluminosilicates (Du et al., 2004), the possible distributions of boron and silicon 320 321 can be represented by two arrangements of boron atoms in the B-Si tetrahedral layer in white mica 322 models: 1) Type-I, which contains one or two boron atoms in any six-membered ring of the layer; and 323 2) Type-II, in which the arrangement comprises three boron atoms in any six-membered ring of the B-324 Si tetrahedral layer (as illustrated in the inset of Figure 1 and 3a). Given the variety of polytypes, lattice 325 parameters, chemical compositions, and the B/Si ordering in the tetrahedral layer of white mica, five 326 models for boromuscovite and two models for phengite were constructed in this study (Figure 1). The

327 minerals, boromuscovite-A-2M1, boromuscovite-A-1M, phengite-A-2M1 and phengite-B-2M1 have 328 Type-I arrangements of boron atoms, whereas boromuscovite-B-1M, boromuscovite-B-2M1 and 329 boromuscovite-C-2M1 have Type-II arrangements. The calculated β factors for the boromuscovite 330 models in Figure 3 reveal that polytypes of the same minerals (e.g., boromuscovite-B-1M and 331 boromuscovite-B-2M1) have very similar β factors at 600 K, with a difference of ≤ 1 % between this 332 study with the PBE functional and Kowalski et al. (2013) with the BLYP functional (Figure 3a). This 333 observation suggests that the effect of the orientation of OH⁻ groups in the inter-layers on boron isotope fractionation is insignificant. In addition, phengite-A-2M1 and phengite-B-2M1, which have the same 334 335 lattice parameters and are of the same polytype, but differ in chemical composition (replacement of Si 336 by Al in a six-membered ring of the B-Si tetrahedral layer), have similar β factors (0.39‰ at 600K; Figure 3a). With the same B/Si ordering, the differences of β factors are less than 1.2% for Type-I 337 338 white mica and 0.83‰ for Type-II white mica at 600K (Figure 3a). By contrast, boromuscovite-A-1M 339 (Type-I) and boromuscovite-B-1M (Type-II) share the same polytype and chemical composition, but differ more in their β factors (2.5‰ at 600 K; Figure 3a). Similarly, the β factor of boromuscovite-C-340 341 2M1 (Type-II) differs from those of phengite-A-2M1 (Type-I) and phengite-B-2M1 (Type-I) (which 342 share the same lattice parameters and polytypes) by as much as 3.5-3.9‰ at 600 K. Therefore, the 343 differences in the B/Si ordering (i.e., Type-I and Type-II white micas) may cause obvious changes in 344 β factors (average 2.9‰ at 600 K). The consistency in the above behavior suggests that the B/Si 345 ordering in the inter-layers and in the B-Si tetrahedral layer is more important in controlling the boron 346 isotope fractionation than other factors, such as chemical compositions and polytype difference. The 347 driving force behind the phenomenon is considered to be the B-O bond length (Kowalski et al., 2013),

with a longer B-O bond leading to a smaller β factor (1.53±0.05 Å for Type-I and 1.58±0.02 Å for
Type-II).

350 As shown in Figure A1, the difference in β factors of tourmaline calculated with the PBE, B3LYP functional (Li et al., 2020) and the BLYP functional (Kowalski et al., 2013) are ~±0.5‰ at 1000 K 351 352 and $\sim \pm 1.0\%$ at 600 K, reflecting negligible differences in the β factors of minerals obtained using 353 different exchange-correlation functionals. In contrast, the β factors with Type I and Type II white 354 mica determined in this study are $\sim 5\%$ and $\sim 1\%$ larger than those of Kowalski et al. (2013) at ~ 600 K, despite the consistency of the different boromuscovite-types in their cell volume and chemical 355 356 composition. It is important to note, however, that all the studies (Liang et al., 1995; Kowalski et al., 357 2013 and this study) used cell parameters that lie well within the wide range observed in natural white 358 micas as a consequence of isomorphous substitutions (e.g., Deer et al., 2013). Hence, any discrepancies 359 between the results from this study and those of Kowalski et al. (2013) may be mirrored in natural 360 systems, due to the B/Si ordering diversity in the tetrahedral layer of white mica minerals.

In addition to the B/Si ordering, the influence of the chemical composition of mica minerals on β factors has been evaluated. This evaluation indicates that the difference in 1000ln β is < 1.2‰ for boromuscovite and phengite (type I), and < 0.8‰ for mica fragments with variable chemical composition at 600 K (Figure 3b). Taken in combination with the small difference (< 1.8‰) in 1000ln β for tourmaline group minerals at 600 K (Li et al., 2020), this indicates that the chemical composition of boron-bearing minerals has a minor effect on the β factor.

Li, Y.-C., Wei, H.-Z., Palmer, M. R., Jiang, S.-Y., Liu, X., Williams-Jones, A. E., Ma, J., Lu, J.-J., Lin, Y.-B., and Dong, G., 2021, Boron coordination and B/Si ordering controls over equilibrium boron isotope fractionation among minerals, melts, and fluids: Chemical Geology, v. 561, p. 120030.



Figure 3. Calculated β values for (a) white micas with variable B/Si ordering and (b) mica fragments
with different chemical compositions.

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371 3.2. β factors of melts and fluids with variable proportions of BO₄

As stressed above, the proportions of BO₃ and BO₄ are highly variable in both melt and fluid. The temperature-dependent β values of silicate melt and aqueous fluid are shown in Figure 4 for temperatures > 600 K. The large difference in the β values of silicate melt and aqueous fluid with variable BO₃ and BO₄ demonstrates that an understanding of the coordination of boron in the interacting phases (i.e., fluids, minerals, and melts) is essential for a first-order quantification of boron isotope fractionation in natural systems. The dataset of β factors is given in the Appendix (Table A2).



Figure 4. Calculated β factors with variable proportions of the BO₄ unit in silicate melt (a) and aqueous fluid (b). The β factors of BO₃ units in silicate melt were taken from Li et al. (2020), whereas those of aqueous fluids were taken from Kowalski et al. (2013) and Li et al. (2020).

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383 **4. DISCUSSION**

384 4.1. Boron isotope fractionation between white mica and aqueous liquid

The calculated boron isotope fractionation factors ($1000\ln\alpha$) between white mica (only including 385 BO₄) and aqueous liquid are shown in Figure 5. In general, the value of $1000 \ln \alpha_{mica-fluid}$ for an acidic 386 387 fluid is higher than for a basic fluid, based on the similarity of the results of this study to those of 388 Kowalski et al. (2013). The temperature dependence of boron isotope fractionation in the range of 600 389 K to 1000 K for a basic fluid (largely tetrahedral boron coordination) is described by the equation $1000 \ln \alpha_{\text{mica-basic fluid}} = 0.8-2.4 \times (1000/\text{T}) - 0.8 \times (1000/\text{T})^2$ and for an acidic liquid (largely trigonal boron 390 coordination) by the equation $1000 \ln \alpha_{\text{mica-acidic fluid}} = 7.0-14.0 \times (1000/T) - 1.2 \times (1000/T)^2$. Wunder et al. 391 392 (2005) determined the boron isotopic fractionation between boromuscovite and fluid at 3 GPA and 773 and 973 Kelvin for near neutral fluids and 0.4 GPA and 673 and 773 Kelvin for strongly basic 393 394 fluids. As the amount of fluid in their run products was too low to measure the pH, it was not possible 395 for them to determine the proportions of $B(OH)_3$ and $B(OH)_4^-$ in their fluids. Our theoretical 396 calculations, however, suggest that there was ~10% B(OH)₃ in the basic fluid and ~33% B(OH)₄⁻ in 397 the near neutral fluid. Given the large effect of pH on the boron speciation, it is therefore important, in 398 comparing experimental determinations of boron isotope fractionation with theoretical estimates, to 399 correct ambient temperature measurements to the in-situ pH. Finally, Raman spectra indicate that the 400 relative proportions of B(OH)₃ and B(OH)₄⁻ in fluids depend not only on pH, but also on temperature 401 and pressure at high P-T conditions (Schmidt et al., 2005).

Li, Y.-C., Wei, H.-Z., Palmer, M. R., Jiang, S.-Y., Liu, X., Williams-Jones, A. E., Ma, J., Lu, J.-J., Lin, Y.-B., and Dong, G., 2021, Boron coordination and B/Si ordering controls over equilibrium boron isotope fractionation among minerals, melts, and fluids: Chemical Geology, v. 561, p. 120030.



403 **Figure 5.** Comparison of theoretically and experimentally determined boron isotope fractionation 404 factors for white mica-basic fluid (a) and white mica-acid fluid (b). The species B(OH)₃ and B(OH)₄⁻ 405 are exclusively in the acid and basic aqueous liquid, respectively. The experimental and calculated 406 error bars correspond to 1 σ ; the data were fitted with linear regression. The β factors for the aqueous 407 liquid were derived from Li et al. (2020) and the study of Kowalski et al. (2013).

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409 4.2. Boron isotope fractionation between coexisting white mica and tourmaline

410 Based on the above discussion, boron isotope fractionation between minerals is likely dependent on both the coordination of the boron and the B/Si ordering within the minerals. For white mica and 411 412 tourmaline, there is a good agreement among the theoretical, empirical and corrected experimental 413 results (Figure 6). The overall temperature dependence of boron isotope fractionation between 414 tourmaline and white mica in the range 600 K to 1000 K was fitted by the equation of $1000 \ln \alpha_{mica-tur}$ = $1.9-5.4 \times (1000/T)-3.4 \times (1000/T)^2$ after taking into account the variation in the chemical composition 415 416 and the B/Si ordering of the minerals (i.e., Type-I and Type-II white micas). The minor discrepancies that remain between the theoretical predications and experimental determinations (Klemme et al., 2011; 417 418 Belley et al., 2014; Kutzschbach et al., 2016; Cao et al., 2018) may be due to heterogeneities in the 419 chemical composition (especially for natural zoned tourmaline) (Li et al., 2020) and the local atomic

420 environment (especially for the B/Si ordering in the B-Si tetrahedral layers of white mica). Another 421 factor may be the growth history of the minerals. For example, there is ~ 4‰ of offset for one $\Delta_{mica-tur}$ 422 value of dravite-phengite pairs from Syros (Greece) with retrograde growth-histories summarized by 423 Klemme et al. (2011) (Figure 6). This exceeds a compositional effect on boron isotope fractionation of tourmaline and mica (i.e., about 1.2 ‰ at 400-430 °C, Li et al., 2020) and might be due to retrograde 424 overprinting of δ^{11} B in tournaline or mica. The overall consistency between the two individual 425 theoretical studies (Kowalski et al., 2013 and this study) and the experimental/empirical data strongly 426 supports the hypothesis that boron coordination plays a key role in controlling isotope fractionation 427 428 among coexisting minerals under equilibrium conditions. In addition, this study emphasizes that the local heterogeneity in the δ^{11} B of white mica is mainly due to the B/Si disorder in the tetrahedral layer 429 430 rather than differences in chemical composition.



Figure 6. A comparison of theoretically and experimentally determined factors for boron isotope fractionation (1000ln $\alpha_{mica-tur}$) between mica and tourmaline. The data for natural samples are from (Klemme et al., 2011; Belley et al., 2014; Kutzschbach et al., 2016; Cao et al., 2018). These data were fitted with a quadratic polynomial. The experimental fractionation was calculated from the experimental data of Meyer et al. (2008) and Wunder et al. (2005). The corrected experimental results

were obtained by adjusting the original experimental fractionation factors using the difference betweenthe experimental and theoretical fractionation factors for white mica-acid fluid in Figure 5b.

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440 4.3. Comparison of measured and calculated α factors in mineral-melt and fluid-melt systems

441 Prior to discussion of the boron isotope fractionation in systems that contain complex silicate melts, 442 we assess here the applicability of a simplified treatment of boron coordination structures in silicate 443 melts by comparing the theoretical and experimental data. Tonarini et al. (2003) experimentally 444 determined the proportion of BO₄ (i.e., R(BO₄)) of volcanic glass (liquid) in equilibrium with biotite 445 from Roccastrada, Mt. Amiata and Mt. Cimini (Italy) to be 8% at 1028 ~ 1093 K, 15% at 1023 ~ 1073 446 K and 26% at 1123 ~ 1153 K, respectively. With the known parameters of R(BO₄) and T, the calculated 447 boron isotope fractionation factors between silicate melts and white micas are compared with the 448 measured values in Figure 7a. The calculated boron isotope fractionation is consistent with the 449 measured values for samples from Roccastrada and Mt. Amiata. For the Mt. Cimini sample, the theoretically predicted Δ^{11} B_{melt-mica} ranges from 4.6±0.8‰ to 4.3±0.7‰ in the temperature range 1123 450 451 to 1153 K, and is greater than the measured boron isotope fractionation value of 2.8±0.8‰. One 452 explanation for this difference may be that the crystallization temperature of the Mt. Cimini sample is 453 less well-constrained than for the other samples (Tonarini et al., 2003). Alternatively, the silicate melt 454 may have undergone fluid exsolution after mica crystallization. This would have led to the measured 455 Δ^{11} B_{melt-mica} value being less than the true value (as shown schematically in Figure 8), if the temperature 456 estimate of Mt. Cimini sample is reliable. Because boron partitions preferentially into aqueous liquid-457 like supercritical fluids as BO₃ (London et al., 1988), the R(BO₄) of the residual melt increases, which lowers the δ^{11} B in the melt. In the case of Mt. Cimini, the δ^{11} B measured in the glass may therefore 458 459 not represent the boron isotopic composition of the initial melt from which the biotite crystallized, but

rather a degassed melt. After correcting the boron isotope fractionation between the final melt and biotite in the Mt. Cimini sample with the boron isotope fractionation factor ($\Delta^{11}B_{melt-fluid}$) of -1.7±0.9‰ and -1.8±0.9‰ during fluid exsolution at 1153 K and 1123 K, the $\Delta^{11}B_{initial melt-mica}$ is 4.5±0.8‰ ($\Delta^{11}B_{melt-mica}$ corrected = $\Delta^{11}B_{melt-mica}$ measured - $\Delta^{11}B_{melt-fluid}$ predicted value (Figure 7a).

465 In contrast to the case of Mt. Cimini, a study of quartz-hosted melt inclusions and degassed glassy groundmass of the Long Valley rhyolite revealed that aqueous phase separation did not affect the 466 467 isotope composition of the melt; i.e., the melt inclusions and the degassed glass had the same boron 468 isotopic composition (Schmitt and Simon, 2004). This conclusion is supported by other studies of 469 volcanic suites in which strong positive correlations were observed between the concentrations of 470 boron and immobile incompatible elements (e.g., Nb, Be, La, Zr), implying that boron losses from 471 magma by volatile exsolution are small (Ryan et al., 1996; Tonarini et al., 2004). The differences in 472 the behavior between the magmatic systems discussed above may relate to their boron concentrations; 473 the Long Valley rhyolites contain <70 ppm boron (Schmitt and Simon, 2004), whereas the Mt. Cimini 474 glasses contain >500 ppm boron (Tonarini et al., 2003). At higher boron concentration, boron may exceed the amount that can be dissolved in the melt and be more strongly partitioned into the aqueous 475 476 phase. It may thus be lost from the melt during volatile exsolution (London et al., 1996; Dingwell et 477 al., 1996).

Boron isotope fractionation between silicate melts and fluids in the temperature range 1023 K to 1373 K was determined experimentally by Hervig et al. (2002). It was assumed that the trace boron dissolved in fluids is predominantly in trigonal coordination, whereas that in the silicate melts is tetrahedrally coordinated (Hervig et al., 2002). A systematical investigation of the partitioning and

482 isotope fractionation of boron between granitic melt and aqueous fluids at 973 and 1073 K and 0.2 483 GPa confirmed that the fraction of tetrahedral BO₄ coordination in hydrous granitic melt is 484 considerably (Maner and London, 2018). Therefore, we calculated the β factors of silicate melt models 485 with $R(BO_4)$ varying from 0.5 to 1 at the different temperatures. The theoretical estimates of boron isotope fractionation factors between silicate melts and fluids, made using the ß factors in fluids 486 487 derived by extrapolating the theoretical lines of Li et al. (2020) and Kowalski et al. (2013), are 488 generally in a good agreement with the experimental values of Hervig et al. (2002) and Maner and London (2018) (Figure 7ab). 489

490 In addition, the theoretical estimates also confirm the dominant tetrahedral boron coordination in 491 the melts; the exact proportion of BO₄ in each sample was constrained. It is worth noting that there is a ~3‰ of difference in Δ^{11} B_{melt-fluid} values measured for the 'High B' and 'Low B' melts at 1073 K in 492 the experiment by Maner and London (2018), and that the calculated $\Delta^{11}B_{melt-fluid}$ data are more 493 consistent with the measured $\Delta^{11}B_{melt-fluid}$ values for the 'Low B' melt than the 'High B' melt, assuming 494 495 $R(BO_4) = 1$ (Figure 7b). As the isotopic fractionation factors and partition coefficients reported in their study represent near-equilibrium values (Maner and London, 2018), the difference of $\sim 3\%$ in Δ^{11} B_{melt}-496 497 fluid values at 1073 K might reflect a difference in the internal bonding structure of boron in melts with different boron contents. Raman and NMR (¹⁷O, ²⁷Al, ²⁹Si) spectra of albite glass (NaAlSi₃O₈) with 498 499 $4.8 \sim 16.7$ wt% B₂O₃ (14880 ~ 51770 ppm B) demonstrate that B interacts strongly with the 500 aluminosilicate network forming Si-O-B and perhaps Al-O-B units and that the proportion of 501 interconnected borate units (B-O-B) is relatively small (Schmidt et al., 2004). Considering the high B content in the 'High B' melt (i.e., 7950 ~ 8975 ppm, 1073 K) in the experiments of Maner and London 502 503 (2018), complex boron structures with B/Si ordering similar to type-I or type-II in white micas may

504 have formed. As shown in Table A1, there is an average difference of $1.9 \pm 0.7\%$ in 1000ln β between 505 BO₄ clusters and type-II white micas (i.e., 13.5‰ for type-II white micas vs. 15.4‰ for BO₄ cluster in mica fragments) at 1073 K, which is equivalent to the observed difference in Δ^{11} B_{melt-fluid} between 506 507 'High B' and 'Low B' melts in the experiments of Maner and London (2018). 508 As demonstrated by London (1997), the B content of even the most enriched melt rarely exceeds 509 ~1 wt % B_2O_3 (i.e., 3100 ppm) and in most natural silicate magmas B is a trace or minor component. The theoretical understanding from this study will be therefore applicable to most natural systems. In 510 addition, a small proportion of $B(OH)_4^-$ in the fluid (e.g., 10%) only produces a minor shift of < +0.5%511 512 in Δ^{11} B_{melt-fluid} at temperatures above 1000 K. The analytical uncertainty of ±0.04 in the determined R(BO₄) of silicate melt (Tonarini et al., 2003) would only cause a shift of $< \pm 0.2\%$ in Δ^{11} B_{melt-mica}. 513



Figure 7. (a) Comparison of measured and calculated 1000ln α factors for natural melt-mica systems and experimental melt-fluid systems; (b) Comparison of measured and calculated 1000ln α factors for melt-fluid systems with different boron contents. The fraction of tetrahedrally coordinated boron in silicate melt is expressed as R(BO₄) = BO₄/(BO₄+BO₃) and the vertical component of the shaded boxes shows the range of 1000ln α _{calculated} with R(BO₄) values varying from 0.5 to 1.

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522 **Figure 8.** A schematic diagram showing the paths of boron isotope variation with magma evolution.

523 The superscripts III and IV refer to the boron coordination structures, BO₃ and BO₄ in the different 524 phases.

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526 4.4. Application to natural systems

527 4.4.1 Boron isotope geothermometers for magmatic-hydrothermal ore deposits

Reconstructing the thermal evolution of hydrothermal ore deposits using the fluid inclusion record is limited by the difficulty of reliably estimating the trapping conditions (independent estimates of temperature or pressure are generally required). However, the coexistence of mica and tourmaline in many granite-hosted hydrothermal ore deposits and the fractionation of boron isotopes between these minerals provides a reliable means of estimating temperature in such magmatic-hydrothermal systems.

Li, Y.-C., Wei, H.-Z., Palmer, M. R., Jiang, S.-Y., Liu, X., Williams-Jones, A. E., Ma, J., Lu, J.-J., Lin, Y.-B., and Dong, G., 2021, Boron coordination and B/Si ordering controls over equilibrium boron isotope fractionation among minerals, melts, and fluids: Chemical Geology, v. 561, p. 120030.





Figure 9. A plot of δ^{11} B for tournaline versus δ^{11} B in mica showing isotherms (solid lines) for the 534 equilibrium fractionation between the two minerals, based on the theoretical model presented in this 535 study (Table 2, Figure 6). The dashed lines correspond to isopleths of $\delta^{11}B_{\text{fluid}}$ for different 536 temperatures based on equilibrium boron isotope fractionation among white mica, tourmaline and fluid 537 (Figure 5; Li et al., 2020; Kowalski et al., 2013). Areas shaded with grey, red, orange and green 538 539 represent a quartz-chalcopyrite-wolframite vein (Sample PN30C), a quartz-mica-wolframite vein 540 (Samples PN46B, PN33A), a cassiterite-quartz vein (Sample PN26AB) and a late fault zone (Sample 541 PN37-2), all from the Panasqueira deposit, Portugal. The boron isotope SIMS data for the mica-542 tourmaline pairs were taken from Codeço et al. (2019).

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Table 2. Equations describing boron isotope-geothermometers in coexisting



white	e mica-tourmaline
Description	$y = 1000/T$ (K), $x = \Delta^{11}B_{mica-tur}$
Average temperature	$y = 0.360 - 0.098x - 0.0013x^2$
Upper-limit temperature	$y = 0.360 - 0.114x - 0.0016x^2$
Lower-limit temperature	$y = 0.360 - 0.086x - 0.0010x^2$

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547 The granite-hosted Panasqueira W-Sn deposit in Central Portugal, is the largest tungsten deposit 548 in Europe, and likely formed from magmatic hydrothermal fluids. It is characterized by a paragenetic 549 sequence comprising a pre-ore crack seal stage, a pre- to synore white mica selvage formation stage, 550 an oxide-silicate ore stage, the main ore stage, a pyrrhotite alteration stage and a post-ore late carbonate 551 stage (Codeço et al., 2019). White mica is one of the most abundant phases, in all stages of the vein 552 system, whereas tournaline is a major mineral phase in the wall-rock alteration zones and occurs in 553 some vein selvages (Codeço et al., 2019). A variety of geothermometers have been employed to 554 estimate the temperature of formation of the Panasqueira deposit and have produced a wide range of 555 values. For example, fluid inclusion homogenization temperatures have been used to infer a minimum 556 mineralization temperature of 230 to ~360°C (Kelly and Rye, 1979; Bussink, 1984; Jaques and Pascal, 557 2017; Lecumberri-Sanchez et al., 2017). In contrast, arsenopyrite geothermometry yielded 558 temperatures ranging from 380-640°C (Kelly and Rye, 1979; Sharp et al., 1985; Mignardi et al., 1995; 559 Jaques and Pascal, 2017), and Ti-in-quartz thermometry, temperatures of ~400 to 550 °C (assuming a 560 pressure of 100 MPa; Codeço et al., 2017).

561 Codeço et al. (2019) re-evaluated the temperature of mineralization and alteration at Panasqueira using the experimentally determined muscovite-tournaline boron isotope fractionation of Meyer et al. 562 (2008) and Wunder et al. (2005) (i.e., Δ^{11} Bmica-tourmaline = -6.49 × 1000/T(K) + 0.36). This involved the 563 564 following samples: PN46B, PN22B and PN33A from a quartz-mica-wolframite vein with a mica-rich 565 selvage, PN30C from a quartz-chalcopyrite-wolframite vein with a mica-poor selvage, PN26AB from 566 a cassiterite-quartz vein and PN37-2 from a late fault. The temperatures obtained for these samples 567 were in the range 350 to 500°C for the vein selvages (i.e., PN33A, PN46B, PN30C) and 220 to 320°C 568 for the late fault zone (PN37-2).

569	As discussed in Sections 4.1 and 4.2, the temperature dependence of $1000 ln \alpha_{mica-tur}$ derived from
570	experimental $1000 ln \alpha_{mica-fluid}$ values (Meyer et al., 2008; Wunder et al., 2015) is less than that from
571	theoretical predictions (Kowalski et al., 2013 and this work) and measurement of natural samples. We
572	re-estimated the temperature ranges for the above samples using the equation for boron isotope
573	fractionation between white mica and tourmaline derived in this study (Table 2). From these equations,
574	the mean temperatures for the quartz-chalcopyrite-wolframite vein (PN30C) is 653±76°C, for the
575	quartz-mica-wolframite veins (PN33A, PN46B) are 581±72°C(PN37-2) and 621±74°C (PN46B), and
576	for the cassiterite-quartz vein (PN26AB) and late fault zone are 480±65°C and 468±64°C, respectively
577	(Figure 9). A high temperature of 673±77°C for sample PN22B from a quartz-mica-wolframite vein is
578	not reliable because it is uncertain that tourmaline and mica are cogenetic in this sample.
579	The analytical uncertainties in the SIMS boron isotope ratios for tourmaline and mica in these
580	samples are ± 0.6 and $\pm 1.5\%$ (1 σ), respectively, which corresponds to an uncertainty in the temperature
581	of $\pm 50^{\circ}$ C to $\pm 94^{\circ}$ C after error propagation for the low- and high- temperature range, respectively. These
582	errors are similar to those for the white mica-tourmaline fractionation equations and relate to
583	differences in the chemical composition and structures of the minerals ($\pm 64^{\circ}C$ and $\pm 77^{\circ}C$). In addition
584	to the analytical uncertainties in boron isotope analysis, it is noteworthy that Codeço et al. (2019)
585	reported variations in $\delta^{11}B$, of up to $\pm 5\%$ for multiple analyses of the same tourmaline and mica
586	crystals. The heterogeneity in $\delta^{11}B$ within individual crystals likely reflects compositional zonation
587	which, in turn, could reflect fluctuations in the temperature, pH, and composition of the fluid. Given
588	the uncertainties referred to above, the temperatures of crystallization of the Panasqueira samples are
589	most reliably estimated by the median values.

590 Codeço et al. (2019) calculated lower temperatures than estimated by us because they used the 591 temperature dependence of muscovite-tournaline fractionation developed from the experimental data 592 of tourmaline-fluid by Meyer et al. (2008) and muscovite-fluid by Wunder et al. (2005). Whereas the 593 tourmaline experiments were conducted under acidic conditions for which the fluid contained 594 essentially 100% BO₃ (Meyer et al., 2008), the fluid used in the muscovite experiments contained 595 varying proportions of both BO₃ and BO₄ (Wunder et al., 2005). This difference in the boron speciation 596 of the aqueous fluids has a strong influence on boron isotope fractionation between minerals and fluid and, in turn, on the tourmaline-mica fractionation (as illustrated in Figure 5). In contrast, the theoretical 597 598 approach employed in our study does not make any assumptions concerning the fluid speciation 599 (although both species must be present if muscovite and tourmaline are to precipitate 600 contemporaneously from the same fluid). Instead, the calculated fractionation factor depends solely on 601 the difference in boron co-ordination between the two minerals. Moreover the theoretical $\Delta^{11}B_{mica-tur}$ 602 values are close to those measured in natural samples (e.g., Klemme et al., 2011), but greater than those estimated from the experimental $\Delta^{11}B_{mica-fluid}$ and $\Delta^{11}B_{tur-fluid}$ data. Finally, we caution that before 603 604 applying the boron isotope geothermometer, direct evidence of the attainment of equilibrium between the mineral pairs of interest needs to be demonstrated. 605

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607 4.4.2 Reconstruction of the original boron isotope signatures of fluids and melts

The calculations presented above make it possible to quantitatively assess equilibrium boron isotope fractionation among minerals, fluid and melt. If the $\delta^{11}B_{mica}$, $\delta^{11}B_{tur}$ and R(BO₄)_{melt} values are known, the temperature of the crystallization of the minerals as well as $\delta^{11}B_{melt}$, $\delta^{11}B_{fluid}$ can be determined, as shown schematically in Figure 10.

612	On the basis of δ^{11} B in muscovite and tourmaline in the granite-hosted Panasqueira W-Sn deposit,
613	the δ^{11} B of the fluid is estimated to have varied from -5.0 to -9.0‰, as illustrated in Figure 9. Assuming
614	the R(BO ₄) in the melt to be 0, 0.3 and 0.5, the δ^{11} B in the melts are estimated to have been -6.8 to -
615	10.8‰, -9.3 to -13.3‰ and -10.9 to -14.9‰, at a temperature of 800 K, which is consistent with the
616	δ^{11} B distribution in S-type silicate rocks (-11 ± 4‰) (Trumbull et al., 2018). Thus, the boron isotope
617	data imply that the tungsten deposit at Panasquiera was produced by fluids exsolved from the adjacent

618 S-type Panasqueira granite.



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620 **Figure 10.** An illustration of how the boron isotope compositions of fluids and melts can be determined 621 from the δ^{11} B values of the tournaline and white mica that crystallized from them.

622

623 4.4.3 Additional factors influencing boron isotope fractionation

In addition to chemical composition and the B/Si ordering in mineral lattices, the effect of pressure on boron isotope fractionation among aqueous fluid, melt and minerals needs to be considered. The effect of pressure on the fractionation of isotopes between two minerals depends mainly on the coordination environment (e.g., channels, layers of polyhedra, face-centered and body-centered), and

628	varies from negligible (e.g., sulfur isotope fractionation among sulfide minerals, Hamann et al., 1984)
629	to significant (e.g., magnesium isotope fractionation among mantle minerals, Huang et al., 2013).
630	In mineral-fluid systems at high pressure, both the structure and density of the fluids change far
631	more than the minerals do, and in principle, this could significantly affect isotopic fractionation. In the
632	case of hydrogen, the effect is considerable (Polyakov and Kharlashina, 1994; Horita et al., 1999),
633	whereas for oxygen, it is negligible ($\leq 0.2\%$) for many minerals (e.g., quartz, calcite, albite and
634	wollastonite) in aqueous systems at pressures as high as 2.2 GPa (Horita et al., 2002).
635	On the basis of spectral measurements and force field simulations, Sanchez-Valle et al. (2005)
636	concluded that the effect of pressure on boron isotope fractionation in aqueous fluids is negligible up
637	to 10 GPa and 723 K relative to temperature or speciation (pH) effects. For mineral-fluid systems,
638	Kowalski et al. (2013) showed that, although there is a pressure effect on the β factors for boron
639	isotopes in aqueous solutions, after correcting for the effects of high T and P, the resulting isotope
640	fractionation factor between boromuscovite and aqueous fluid is very similar to that at ambient
641	pressure. Meyer et al. (2008) showed that there is also no measurable pressure dependence on the
642	isotope fractionation of boron between tourmaline and fluid at 500°C and up to 500 MPa. As the effect
643	of pressure on boron isotope fractionation is still unclear, we recommend that the results of this study
644	not be applied to systems for which the pressure is higher than 1 GPa, especially if the system contains
645	an aqueous fluid.

For pressures ≤ 1 GPa, the boron isotope fractionation equations developed in this study can be applied to most systems containing the mineral pair of tourmaline and white mica in equilibrium, and may help in further understanding systems such as those forming magmatic hydrothermal deposits particularly for issues relating to the sources of the fluids and magmas (e.g., Trumbull et al., 2013). It

is important to note, however, that in natural systems, the boron isotope evolution of silicate melts is
complicated by the fact that it is influenced by crystallization, fluid exsolution and the introduction of
boron from external reservoirs.

In addition to equilibrium boron isotope fractionation, the kinetic effects on the evolution of $\delta^{11}B$ 653 654 in residual melts because of the removal boron by the crystallization of minerals and fluid exsolution 655 must be considered, as there is a significant boron loss during phase separation. Using the same conditions as Trumbull et al. (2013) (i.e., a starting condition with $\delta^{11}B$ of -14‰ and T of ~500°C), 656 657 the impact of the R(BO₄) values of silicate melts and aqueous fluid on boron isotope evolution in 658 magmas during Rayleigh fractionation has been evaluated (Figure 11). The maximum boron 659 partitioning coefficient, D_{fluid-melt}, observed in experiments between melts and fluids is 4.6 (Schatz et al., 2004). Assuming a R(BO₄) value of 0.5 in the melt, the 6% of shift in δ^{11} B_{melt} from the outer to 660 661 the inner zones of the Borborema pegmatite (Trumbull et al. 2013) may have resulted from about 70% 662 removal of boron by tournaline crystallization or by an exsolved acid fluid having a R(BO₄) of 0.1. By contrast, even 90% removal of boron by an exsolved neutral fluid with a R(BO₄) of 0.5, cannot 663 664 cause a large decrease in δ^{11} B_{melt}.



665

Figure 11. Model curves illustrating the variations in δ^{11} B values in residual melt with a reduced fraction of boron (F) due to crystallization of tourmaline or mica, after exsolution of aqueous fluid. The starting composition, δ^{11} B of -14‰, corresponds to that in the Borborema leucogranite (Trumbull et al., 2013), whereas the boron isotope fractionation factors at 800 K were taken from this study.

670

671 **5. CONCLUSIONS**

672 Representative models of the BO3 and BO4 units in silicate melts for a wide range of chemical 673 composition were developed in this study, and can be used to assess equilibrium boron isotope fractionation in magmatic-hydrothermal systems. After assessing the applicability of the simplified 674 treatment of boron coordination structures in silicate melts, the principal conclusions of the study are: 675 (i) In co-existing boron-bearing minerals, chemical replacement reactions play a relative minor role in 676 boron isotope fractionation (< 2‰ at 600 K); (ii) B/Si disorder in the tetrahedral layer of boron-677 enriched silicate minerals, such as white mica, result in within crystal δ^{11} B variations that average 2.9% 678 679 at 600 K; (iii) In muscovite-fluid systems, the temperature dependency of boron isotope fractionation

680	is greater for acidic fluids than for basic fluids, reinforcing the conclusion that the difference in the
681	coordination of boron in trigonal/tetrahedral structures in the two phases dominates boron isotope
682	fractionation; (iv) In silicate magmas, boron coordination controls boron isotopic fractionation
683	between melt and crystallizing minerals. At magmatic temperatures, the proportion of the BO4 unit is
684	highly variable and the Δ^{11} B values between mineral/fluid and melt vary with R(BO ₄) unit in the melt;
685	(v) Theoretical predictions for boron isotope fractionation among muscovite, tourmaline, silicate melt
686	and aqueous liquid facilitate the application of white mica-tourmaline geothermometry to magmatic-
687	hydrothermal ore-forming systems and the evaluation of fluid/melt source in these systems.

688

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696

697 **Appendix A.** Supplementary data associated with this article can be found, in the online version.

698

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1013 CAPTIONS OF FIGURES AND TABLES

- **Figure 1**. A series of periodic boundary cell (PBC) models for white mica (left) and the arrangement of boron atoms in silica tetrahedral layers (right). The letters A, B, and C represent possible distributions of boron and silicon in the inter-layers of mica structures along the *c*-axis.
- 1017
- Figure 2. Cluster models representing BO₃ and BO₄ units in silicate melts with variable chemical
 compositions.

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1021 **Figure 3.** Calculated β values for (a) white micas with variable B/Si ordering and (b) mica fragments 1022 with different chemical compositions.

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Figure 4. Calculated β factors with variable proportion of BO₄ unit in silicate melt (a) and aqueous fluid (b). The β factors of BO₃ units in silicate melt were cited from Li et al. (2020) while that of aqueous fluids were cited from Kowalski et al. (2013) and Li et al. (2020).

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Figure 5. Comparison of theoretically and experimentally determined boron isotope fractionation factors for white mica-basic fluid (a) and white mica-acid fluid (b). The species $B(OH)_3$ and $B(OH)_4^$ are exclusively in the acid and basic aqueous liquid, respectively. The experimental and calculated error bars correspond to 1σ ; the data were fitted with linear regression. The β factors for the aqueous liquid were derived from Li et al. (2020) and the study of Kowalski et al. (2013).

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Figure 6. A comparison of theoretically and experimentally determined boron isotope fractionation factors ($1000\ln\alpha_{mica-tur}$) between mica and tourmaline. The data from natural samples are cited from (Klemme et al., 2011; Belley et al., 2014; Kutzschbach et al., 2016; Cao et al., 2018). The data were fitted with the quadratic polynomial. The experimental fractionation was calculated from the experimental data by Meyer et al. (2008) and Wunder et al. (2005). The corrected experimental results were obtained by correcting to the original experimental fractionation factors with the difference between the experimental and theoretical fractionation factors for white mica-acid fluid in Figure 5b.

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Figure 7. (a) Comparison of measured and calculated 1000ln α factors for natural melt-mica system and experimental melt-fluid system; (b) Comparison of measured and calculated 1000ln α factors for melt-fluid system with different boron contents. The fraction of tetrahedral boron coordination in silicate melt is expressed as R(BO₄) = BO₄/(BO₄+BO₃) and the longitudinal boundary of shadow box indicates the range of 1000ln α _{calculated} with variable R(BO₄) from 0.5 to 1.

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- Figure 8. A schematic diagram showing the paths of boron isotope variation with magma evolution.
 The superscripts III and IV refer to the boron coordination structures, BO₃ and BO₄ in the different
 phases.
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Figure 9. A plot of δ^{11} B for tournaline versus δ^{11} B in mica showing isotherms (solid lines) for the 1052 1053 equilibrium fractionation between the two minerals, based on the theoretical model presented in this 1054 study (Table 2, Figure 6). The dashed lines correspond to isopleths of $\delta^{11}B_{\text{fluid}}$ for different temperatures based on equilibrium boron isotope fractionation among white mica, tourmaline and fluid 1055 1056 (Figure 5; Li et al., 2020; Kowalski et al., 2013). Areas shaded with grey, wine-red, orange and green represent a quartz-chalcopyrite-wolframite vein (Sample PN30C), a quartz-mica-wolframite vein 1057 (Samples PN46B, PN33A), a cassiterite-quartz vein (Sample PN26AB) and a late fault zone (Sample 1058 PN37-2), all in the Panasqueira deposit, Portugal. The boron isotope SIMS data for the mica-1059 1060 tourmaline pairs were taken from Codeço et al. (2019).

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1062 **Figure 10.** An illustration of how the boron isotope compositions of fluids and melts can be determined 1063 from the δ^{11} B values of the minerals of tourmaline and white mica that crystallized from them.

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Figure 11. Model curves illustrating the variations in δ^{11} B values in residual melt with a reduced fraction of boron (F) due to crystallization of tourmaline or mica, and after exsolution of aqueous fluid. The starting composition, δ^{11} B of -14‰, corresponds to that in the Borborema leucogranite (Trumbull

- 1068 et al., 2013), whereas the boron isotope fractionation factors at 800 K were taken from this study.
- 1069
- 1070 **Table 1**. The lattice parameters and calculation sets for the white mica model

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1072	Table 2. Equations describing boron isotope-geothermometers in coexisting muscovite-tournaline
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1092	GRAPHICAL ABSTRACT
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Li, Y.-C., Wei, H.-Z., Palmer, M. R., Jiang, S.-Y., Liu, X., Williams-Jones, A. E., Ma, J., Lu, J.-J., Lin, Y.-B., and Dong, G., 2021, Boron coordination and B/Si ordering controls over equilibrium boron isotope fractionation among minerals, melts, and fluids: Chemical Geology, v. 561, p. 120030.



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Appendix

Boron coordination and B/Si ordering controls over equilibrium boron isotope fractionation among minerals, melts, and fluids

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1. Calculated β factors for melts, mica and fluid

Table A1. β factors of BO₃ and BO₄ unit in melts, white micas and aqueous fluids at

				β facto	ors in whi	te micas				
Models	600K	800K	1000K	1073K	1093K	1123K	1223K	1353K	1500K	References
Boromuscovite-A-2M1	1.0443	1.0254	1.0165	1.0143	1.0138	1.0131	1.0111	1.0091	1.0074	
Boromuscovite-A-1M	1.0449	1.0258	1.0167	1.0146	1.0140	1.0133	1.0113	1.0092	1.0075	
Phengite-A-2M1	1.0451	1.0259	1.0168	1.0146	1.0141	1.0134	1.0113	1.0093	1.0075	
Phengite-B-2M1	1.0455	1.0262	1.0170	1.0148	1.0143	1.0136	1.0115	1.0094	1.0076	
Boromuscovite-B-2M1	1.0420	1.0241	1.0156	1.0136	1.0131	1.0124	1.0105	1.0086	1.0070	This study
boromuscovite-B-1M	1.0423	1.0243	1.0157	1.0137	1.0132	1.0125	1.0106	1.0086	1.0071	
boromuscovite-C-2M1	1.0414	1.0238	1.0154	1.0134	1.0129	1.0123	1.0104	1.0085	1.0069	
M. 1.1.			β	factors i	n BO3 an	d BO4 uni	its			Defe
wodels	600K	800K	1000K	1073K	1093K	1123K	1223K	1353K	1500K	Kelerences
BO ₃ -i	1.0610	1.0356	1.0232	1.0203	1.0196	1.0186	1.0157	1.0129	1.0105	
BO ₃ -j	1.0614	1.0359	1.0234	1.0205	1.0197	1.0187	1.0159	1.0130	1.0106	
BO ₃ -k	1.0612	1.0358	1.0233	1.0204	1.0196	1.0186	1.0158	1.0130	1.0106	
BO ₃ - <i>l</i>	1.0613	1.0358	1.0234	1.0204	1.0197	1.0187	1.0158	1.0130	1.0106	Listal 2020
BO3- <i>m</i>	1.0614	1.0359	1.0234	1.0204	1.0197	1.0187	1.0158	1.0130	1.0106	Li et al., 2020
BO ₃ -n	1.0626	1.0366	1.0239	1.0209	1.0202	1.0191	1.0162	1.0133	1.0109	
BO ₃ -o	1.0626	1.0366	1.0239	1.0208	1.0201	1.0191	1.0162	1.0133	1.0108	
BO ₃ - <i>p</i>	1.0621	1.0363	1.0237	1.0207	1.0199	1.0189	1.0160	1.0132	1.0107	
BO4-i	1.0479	1.0276	1.0179	1.0156	1.0150	1.0142	1.0120	1.0099	1.0080	
BO ₄ -j	1.0483	1.0278	1.0180	1.0157	1.0151	1.0143	1.0121	1.0099	1.0081	
BO ₄ -k	1.0474	1.0273	1.0177	1.0154	1.0149	1.0141	1.0119	1.0098	1.0080	This study
$\mathrm{BO}_{4} ext{-}l$	1.0474	1.0274	1.0177	1.0154	1.0149	1.0141	1.0119	1.0098	1.0080	This study
BO ₄ - <i>m</i>	1.0474	1.0273	1.0177	1.0154	1.0148	1.0141	1.0119	1.0097	1.0079	
BO4-n	1.0475	1.0273	1.0177	1.0154	1.0148	1.0141	1.0119	1.0097	1.0079	
Modela				βf	actors in	fluid				Doforonoos
widdels	600K	800K	1000K	1023K	1073K	1123K	1153K	1223K	1373K	Kelerences
HaBOa	1.0662	1.0395	1.0256	1.0244	1.0220	1.0199	1.0188	1.0164	1.0122	Li et al., 2020
113003	1.0626	1.0362	1.0237	1.0226	1.0207	1.0189	1.0180	1.0160	1.0128	Kowalski et al., 2013
B(OH)-	1.0528	1.0308	1.0199	1.0190	1.0173	1.0157	1.0149	1.0131	1.0101	Li et al., 2020
D (011)4	1.0460	1.0265	1.0175	1.0167	1.0153	1.0141	1.0134	1.0121	1.0099	Kowalski et al., 2013

different temperatures

2. Calculated β factors for melts and fluid with variable temperature and *R*(*BO*₄)

				β factor	s in melt						
R(BO4)	600K	800K	1000K	1093K	1123K	1223K	1353K	1500K			
0	1.0617	1.0361	1.0235	1.0198	1.0188	1.0159	1.0131	1.0107			
0.1	1.0603	1.0352	1.0230	1.0193	1.0183	1.0155	1.0128	1.0104			
0.2	1.0589	1.0344	1.0224	1.0188	1.0179	1.0151	1.0124	1.0101			
0.3	1.0575	1.0335	1.0218	1.0184	1.0174	1.0147	1.0121	1.0099			
0.4	1.0561	1.0326	1.0212	1.0179	1.0170	1.0144	1.0118	1.0096			
0.5	1.0547	1.0318	1.0207	1.0174	1.0165	1.0140	1.0114	1.0093			
0.6	1.0533	1.0309	1.0201	1.0169	1.0160	1.0136	1.0111	1.0091			
0.7	1.0519	1.0300	1.0195	1.0164	1.0156	1.0132	1.0108	1.0088			
0.8	1.0505	1.0292	1.0189	1.0159	1.0151	1.0128	1.0105	1.0085			
0.9	1.0491	1.0283	1.0184	1.0154	1.0146	1.0124	1.0101	1.0083			
1	1.0477	1.0275	1.0178	1.0149	1.0142	1.0120	1.0098	1.0080			
		B factors in fluid									
K(BO4)	600K	800K	1000K	1023K	1123K	1153K	1223K	1373K			
0	1.0644	1.0379	1.0246	1.0235	1.0194	1.0184	1.0162	1.0125			
0.1	1.0629	1.0370	1.0240	1.0230	1.0190	1.0180	1.0158	1.0122			
0.2	1.0614	1.0360	1.0234	1.0224	1.0185	1.0175	1.0155	1.0120			
0.3	1.0599	1.0351	1.0228	1.0218	1.0181	1.0171	1.0151	1.0117			
0.4	1.0584	1.0342	1.0222	1.0213	1.0176	1.0167	1.0148	1.0115			
0.5	1.0569	1.0333	1.0217	1.0207	1.0172	1.0163	1.0144	1.0112			
0.6	1.0554	1.0324	1.0211	1.0201	1.0167	1.0158	1.0140	1.0110			
0.7	1.0539	1.0314	1.0205	1.0196	1.0163	1.0154	1.0137	1.0107			
0.8	1.0524	1.0305	1.0199	1.0190	1.0158	1.0150	1.0133	1.0105			
0.9	1.0509	1.0296	1.0193	1.0185	1.0154	1.0146	1.0130	1.0102			
1	1.0494	1.0287	1.0187	1.0179	1.0149	1.0142	1.0126	1.0100			

Table A2. Calculated β factors of melt and fluid at different temperatures



Figure A1. Comparison of calculated RPFRs (β) of dravite with PBE, B3LYP functional (Li et al.,

2020) and BLYP functional (Kowalski et al., 2013).





Figure A2. Relationship between 1000lnβ and average B-O bond length of BO₃ cluster, BO₄ cluster,

type-I white mica and type-II white mica.



Figure A3. Muscovite supercells containing only one boron atom. The Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional and the norm-conserving pseudopotentials were employed in the geometry optimization. The cut-off energy is 800eV. During optimization, the cell parameters were fixed. k-points mesh is $1 \times 1 \times 1$.

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