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5	Experimental study on the kinetics of magnesiohornblende
6	dehydration and its implications
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13	ABSTRACT
14	Magnesiohornblende dehydration was studied using both high-temperature
15	thermogravimetric analysis and high-pressure differential thermal analysis (HP-DTA).
16	The high-temperature thermogravimetric analysis results revealed that
17	magnesiohornblende dehydration at high temperatures could be divided into three steps:
18	848-1058 K, 1058-1243 K, and 1243-1473 K, and each step followed an <i>n</i> -order
19	reaction $(Fn)$ . The dehydration process is characterized by an oxidation-
20	dehydrogenation mechanism, and the dehydration of the last step can be explained as
21	the direct decomposition of the hydroxyl groups connected to the magnesium ions. The
22	HP-DTA of magnesiohornblende dehydration under pressures of 0.5, 1.0, 2.0, and 3.0

23	GPa revealed the occurrence of two endothermic peaks, indicating that the dehydration
24	occurs in two steps at high temperature and pressure. Our experimental results reveal
25	that during subduction, the fluid released during the dehydration of
26	magnesiohornblende may trigger earthquakes and cause high electrical
27	conductivity anomalies in the subduction zones.
28	Keywords: magnesiohornblende; dehydration; thermogravimetric analysis; high-
29	pressure differential thermal analysis (HP-DTA); subduction zones
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## **INTRODUCTION**

46 As one of the most complex and active zones in the Earth's interior, subducted 47 slabs carry water into the deep parts of the Earth where it can form different types of 48 hydrous minerals at different depths (Tatsumi and Kogiso, 2003). The dehydration of 49 hydrous minerals influences many geological processes and the geodynamics of the 50 Earth, such as partial melting and earthquakes (Marschall and Foster, 2018). The 51 dehydration of hydrous minerals in subduction zones is of great significance to 52 understanding the physical and chemical properties of minerals and rocks, such as high 53 electrical conductivity anomalies and seismic wave velocity anomalies (Dai et al., 2020; 54 Hu et al., 2018; Ji et al., 2013; Ji et al., 2015; Jung et al., 2014; Kim and Jung, 2019; 55 Wang et al., 2012).

56 Amphibole is an important double chain silicate mineral (AB<sub>2</sub>C<sub>5</sub>T<sub>8</sub>O<sub>22</sub>W<sub>2</sub>) in the 57 oceanic crust, subducting slab, and metamorphic and igneous rocks (Hawthorne and 58 Oberti, 2007). The mineralogical model of the continental crust indicates that the 59 amphibole content of rocks can reach 35-40% (by volume) within 15-30 km of the 60 surface (Christensen and Mooney, 1995). As one of the important reservoirs of fluids 61 and volatiles, the amphibole content of amphibole-eclogite facies and amphibolite 62 facies can reach 50-60% in subduction zones (Poli and Schmidt, 1995). Amphibole 63 undergoes a series of metamorphic dehydration reactions during subduction, which 64 affects the oxidation of the iron in the amphibole and the release of fluids into the lower 65 crust and mantle.

66	The thermal decomposition of amphibole group minerals has been previously
67	studied and some progress (Kusiorowski et al., 2015; Kusiorowski et al., 2012; Li et al.,
68	2022) has been made. As one of the common minerals with the a complex structure,
69	Fe-dominant amphibole has mainly been used for technological applications such as
70	insulation from heat and fire (Addison et al., 1962a; Addison et al., 1962b; Addison and
71	Sharp, 1962; Addison and White, 1968; Ernst and Wai, 1970; Hodgson et al., 1965).
72	Accordingly, the oxidation-dehydrogenation mechanism of crocidolite at high
73	temperatures, structural changes, and the influences of the $Fe^{2+}$ and $Mg^{2+}$ contents have
74	been widely studied (Phillips et al., 1988; Phillips et al., 1991; Ungaretti, 1980). Recent
75	studies on the stability of amphibole have focused on riebeckite in sodic amphibole,
76	which is a typical high-pressure mineral (Della Ventura et al., 2018; Oberti et al., 2016;
77	Oberti et al., 2018; Ventura et al., 2017). The oxidation-dehydrogenation reaction of
78	iron-bearing amphibole can occur as follows:

79 
$$2Fe^{2+} + 2^{W}(OH)^{-} \rightarrow 2Fe^{3+} + 2^{W}O^{2-} + e^{x}H_{2}$$

80 where W is the W(hydroxyl)-site anions in the formulae  $AB_2C_5T_8O_{22}W_2$ , <sup>ex</sup>H<sub>2</sub> means 81 the external H<sub>2</sub>. This reaction reveals the oxidation of ferrous iron is coupled with a loss 82 of protons from the W(hydroxyl)-site simultaneously to balance the charge in the local 83 region and produce external H<sub>2</sub>. In the oxidation-dehydrogenation of iron-bearing 84 amphibole, dehydrogenation often occurs within a few hours (Hu et al., 2018; 85 Manthilake et al., 2021; Ungaretti, 1980). Fourier transform infrared (FTIR)

86	spectroscopy and Raman spectroscopy studies have suggested that the oxidation
87	dehydrogenation reaction is reversible within a definite but broad range of temperatures
88	for iron-bearing amphibole (Della Ventura et al., 2018; Mihailova et al., 2021).
89	Compared with Fe-bearing amphibole, the dehydration temperature of Mg-rich
90	amphibole is thought to be 200-600 K higher, but the dehydration temperature of
91	magnesiohornblende under high-temperature and high-pressure conditions is not well
92	defined. In addition, the dehydration kinetics of Mg-rich amphibole at high
93	temperatures has not been fully studied. Moreover, as the ferrous content increases, the
94	$C2/m \rightarrow P2_1/m$ phase transition may occur during the heating of Mg-dominated
95	amphibole (Welch et al., 2007), and the critical temperature decreases from ~600 K to
96	200 K (Ballaran et al., 2004; Marschall and Foster, 2018; Welch et al., 2007).

In this study, thermogravimetric analysis and high-pressure differential thermal
analysis (HP-DTA) were used to study the kinetics of magnesiohornblende dehydration,
and the dehydration temperature and kinetics of magnesiohornblende were confirmed.

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#### **EXPERIMENTAL METHODS**

101 Sample Material

102 The material used in the experiments was magnesiohornblende crystals collected 103 from Liaoning Province, China. The chemical compositions of the magnesiohornblende 104 crystals were analyzed using an electron probe microanalyzer (Table 1). The 105 magnesiohornblende crystals were washed and ultrasonicated for 30 min and then 106 ground into powder using an agate mortar. Various grains with different sizes were 107 separated from the powdered materials according to Stokes's law (Ferguson and Church,

- 108 2004). Particles with diameters ranging from 5 to 10  $\mu$ m were selected for use in the
- 109 experiments and were stored above 393 K in a vacuum oven for one week to fully
- 110 remove the absorbed molecular  $H_2O$ .

#### 111 Thermal Analysis and Determination of Kinetic Parameters

- 112 Thermogravimetric (TG) analysis was performed to determine the reaction 113 mechanisms and kinetic parameters using the STA449 F5 device at the University of Chinese Academy of Sciences. Magnesiohornblende dehydration was measured using 114 115 non-isothermal and constant heating rates (10, 20, and 40 K/min). The samples were 116 placed in corundum sample holders and heated at 303-1573 K in a constant air 117 atmosphere (20 ml/min). The purge gas was nitrogen, with a flow rate of 60 ml/min. 118 The sample weight of each non-isothermal experiment was 20 mg, and the error of the 119 weight was less than 0.1 mg. The data were collected at an interval of 1 s.
- In the thermal analysis of the kinetics, isothermal or non-isothermal conditions
  were adopted to study the kinetics of the dehydration of the materials (Liu et al., 2019;
  Wang et al., 2015). To describe the dehydration progress under non-isothermal
  conditions, the mass fraction of the released volatiles (α) is defined as:

124 
$$\alpha = \frac{m_0 - m_t}{m_0 - m_f},\tag{1}$$

where  $m_t$  is the mass at time t, and  $m_0$  and  $m_f$  are the initial and final masses of the sample.

127 The general rate equation and integral form of the rate equation are as follows:

128 
$$Rate = \frac{d\alpha}{dt} = kf(\alpha), \qquad (2)$$

129 
$$G(\alpha) = kt,$$
 (3)

130 where *t* is time; k is the rate constant; and  $f(\alpha)$  and  $G(\alpha)$  are the mechanism function 131 and integral form of the mechanism function, respectively. k depends on the 132 temperature *T*, and the relationship between k and *T* can be expressed using the 133 Arrhenius equation:

134 
$$\mathbf{k} = A \exp(-E/\mathbf{R}T). \tag{4}$$

135 Under non-isothermal conditions, the heating rate  $\beta = dT/dt$  can be substituted into 136 Equation 2 to obtain the non-isothermal rate equation:

138 
$$\frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \exp\left(-E/RT\right) dT.$$
 (5)

142 
$$G(\alpha) = \frac{A}{\beta} \int_0^T \exp\left(-\frac{E}{RT}\right) dT,$$
 (6)

143 where 
$$E$$
 is the apparent activation energy,  $A$  is a pre-exponential factor and R is the

- 144 gas constant. The Flynn-Wall-Ozawa (FWO) method (Flynn and Wall, 1967; Ozawa,
- 145 1965; Ozawa, 1986), a model-free method, was used to determine the kinetic
- 146 parameters including apparent activation energy (E), and pre-exponential factor (A)
- 147 of magnesiohornblende dehydration:

148 
$$ln\left(\frac{d\alpha}{dT}\beta\right) = ln\left[Af(\alpha)\right] - \frac{E}{RT}.$$
 (7)

149	The apparent activation energy <i>E</i> can then be determined by plotting $\ln(d\alpha/dt)$
150	versus $1/T$ for each activation energy. Apparent activation energy is based on many
151	effects that produce a cumulative result, which is similar to the concept of activation
152	energy but relates to the probability of not exceeding some measurable attribute
153	(Calderon-Cardenas et al., 2020). Dehydration reaction involves several processes,
154	therefore, the overall apparent activation energy of the reaction need to be determined
155	by averaging the apparent activation energy derived from $\ln(d\alpha/dt)$ versus $1/T$ at
156	different $\alpha$ . {{auth: The authors need to make clear how the apparent activation
157	energy is found from the (presumably true) activation energy and why this
158	calculation is necessary. DB}}
159	Another kinetic calculation method for thermal analysis is the model method, in
160	which different reaction mechanisms are selected to fit the TG data, and then, the best
161	reaction mechanism is determined based on the obtained apparent activation energy $E$ ,
162	{{The authors need to either explain the difference between E and E_a or be
163	consistent in there terminology. DB}} pre-exponential factor A, linear correlation
164	coefficient, and standard deviation.

# 165 High-Pressure Differential Thermal Analysis

166 All of the high-pressure experiments conducted in this study were conducted using167 the cubic-anvil high-pressure apparatus installed at University of Chinese Academy of

168	Sciences. The pressure calibrations were performed using the melting temperatures of
169	sodium at different pressures (Akella et al., 1969), and the uncertainty in the pressure
170	was estimated to be less than 0.11 GPa (Shen et al., 2020). A schematic diagram of the
171	experimental apparatus used for the HP-DTA is shown in Figure 1. A pyrophyllite cube
172	with a side length of 32.5 mm and a central hole diameter of 14.2 mm was used as the
173	pressure transfer medium. Two layers of stainless steel foil were selected as the furnace,
174	and a layer of Al <sub>2</sub> O <sub>3</sub> insulating tube was placed between the stainless steel foil and the
175	soaking pipe for insulation purposes. The H-type soaking tube was constructed of nickel
176	(Ni) to ensure heat stability at high temperatures. Alumina powder was used as a
177	reference sample for the thermoelectric potential measurement of the
178	magnesiohornblende. The alumina powder and the magnesiohornblende were loaded in
179	the upper and bottom parts of the H-type tube. A welded K-type thermocouple (NiCr-
180	NiSi) was symmetrically inserted into the center of the magnesiohornblende and
181	alumina powder at an interval of 8 mm to measure the temperature, and the uncertainty
182	of the temperature was less than $\pm 5$ K. Before the experiment, the pyrophyllite,
183	pyrophyllite plugs, and $Al_2O_3$ insulating tube were heated at 1173 K for 10 h to ensure
184	complete dehydration.

185 Two digital multimeters were used to record the thermoelectric potential difference 186 between the magnesiohornblende and alumina powder at 0.5, 1.0, 2.0, and 3.0 GPa. The 187 temperature of the alumina powder during the heating was also recorded using one of 188 the digital multimeters. The two digital multimeters automatically recorded the

temperature, and their accuracy reached  $10^{-13}$  V and  $10^{-5}$  K. In the four experiments, the materials were heated to 773 K at a uniform rate for 2 h and then heated to 1473 K at a rate of 20 K/min.

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# RESULTS

Figure 2 shows the TG and DTG (the first derivative of TG curve over time) curve of the magnesiohornblende in the air atmosphere. Magnesiohornblende dehydration occurred in the temperature range of 848–1473 K, while the TG curve shifts regularly with increasing heating rates due to thermal hysteresis (Masumoto et al., 2018). The average mass loss under the different heating rates was 2.16 wt.% (the water content of amphibole was approximately 2.20 wt.%).

199 Combining the mass loss of the TG curve and the mass loss rate of the DTG curve, 200 our study suggests that the first stage of magnesiohornblende dehydration occurs at 201 848-1058 K, which accounts for 25% of total mass loss (Table 2), where the lowest position of the DTG curve is the temperature at which the dehydration rate is fastest. 202 203 As the DTG curve flattens out, the first stage of the reaction ends. The same 204 phenomenon can be observed for the second and third stages of magnesiohornblende 205 dehydration at 1058-1243 K and 1243-1473 K, yielding a total mass loss of 25% and 206 60%, respectively (Table 2). It is noteworthy that the experimental temperature has 207 already prompted the start of the third stage of the reaction before the end of the second 208 stage, so we did not observe the end of the second stage.

209 The fitting results for the kinetic parameters (Table 2) of the different reaction

210 mechanisms indicate that our TG data for the three steps are best fit by an *n*-order

211 reaction (*Fn*) for magnesiohornblende, with a correlation coefficient of 99.953%.  $f(\alpha)$ 

212 =  $(1 - \alpha)^n$  and  $G(\alpha) = (1 - (1 - \alpha)^{(1-n)})/(1 - n)$  are the differential and integral forms of

213 the *n*-order reaction, respectively.

214 Table 2 presents the fitting results of the model method. As is shown in Table 2, 215 the activation energy E of step 1 is 416.6 kJ/mol, the pre-exponential factor A is  $1.58 \times$  $10^{22}$  s<sup>-1</sup>, and the reaction order *n* is 4.23. The activation energy *E* of step 2(1) is 411.4 216 kJ/mol, the pre-exponential factor A is  $2.82 \times 10^{15}$  s<sup>-1</sup>, and the reaction order n is 2.3. 217 218 The activation energy E of step 2(2) is 720.9 kJ/mol, the pre-exponential factor A is  $2.51 \times 10^{27}$  s<sup>-1</sup>, and the reaction order *n* is 1.95. Using these fitting parameters, we 219 220 recalculated the reaction progress at different heating rates and compared the results 221 with the experimental TG data (Fig. 3(a)). The experimental data are in good agreement 222 with the calculated results, despite there being small differences at high temperatures. 223 The differences may be caused by the nucleation rate of the products. Therefore, we 224 concluded that the kinetics of magnesiohornblende dehydration in three steps are well 225 modeled by *n*-order reaction (Fn).

The activation energy of magnesiohornblende dehydration in air obtained using the model-free method is 437–812 kJ/mol ( $\alpha = 0.1-0.85$ ) (Table 3). The model-free method uses the first-order reaction ( $F_1$ ) to fit the entire process of magnesiohornblende dehydration, with a correlation coefficient of 99.945%.  $f(\alpha) = 1 - \alpha$  and  $G(\alpha) = -\ln(1 - \alpha)$  are the differential and integral forms of the first-order reaction, respectively. We

231 compared the experimental and calculated curves for the magnesiohornblende 232 dehydration (Fig. 3(b)). Except for the deviation from the fitting results at high 233 temperatures (>1350 K), the overall fit is relatively good. A problem that arises is that 234 in the Arrhenius equation (Eq. 4) the activation energy is a fixed value for a single 235 reaction mechanism, but the activation energy of magnesiohornblende calculated using 236 the Friedman method fluctuates greatly. Therefore, a first-order reaction cannot 237 reasonably describe the thermal decomposition of magnesiohornblende. We conclude 238 that the model method fits the experimental data better than the model-free method.

239 differential Figure shows the high-pressure thermal 4 curve for 240 magnesiohornblende at 0.5, 1.0, 2.0, and 3.0 GPa. Within the experimental temperature 241 and pressure ranges, the alumina powder did not undergo physical and/or chemical 242 reactions and did not produce a thermal effect. Therefore, the two peaks of the curve 243 represent the two steps of magnesiohornblende dehydration. At low temperatures 244 (<1000 K), there was no obvious difference in the differential thermal voltage signals 245 of the magnesiohornblende and alumina powder. When the temperature and pressure 246 conditions for the experiments extended beyond the stability field of 247 magnesiohornblende, there was a temperature difference  $\Delta T$  ( $\Delta T < 0$ ) between the 248 magnesiohornblende and alumina, and endothermic valleys were visible in the 249 differential thermal curves of the experiments. The peak temperatures of the 250 endothermic valley at 0.5 GPa were 1090 K and 1235 K for magnesiohornblende and 251 alumina, respectively. The peak temperatures of the endothermic valley at 1.0 GPa were

252	1132 K and 1278 K. The peak temperatures of the endothermic valley at 2.0 GPa were
253	1161 K and 1313 K, and the peak temperatures of the endothermic valley at 3.0 GPa
254	were 1097 K and 1193 K.
255	Figure 5 shows the products at 3.0 GPa after quenching at the first and second
256	stages of magnesiohornblende dehydration at 1137 K and 1233 K, respectively. It can
257	be seen that products after dehydration are magnesiohornblende whose composition is
258	different from that of the starting material. The decomposition of magnesiohornblende
259	is involved in the oxidation-dehydrogenation process.

260 DISCUSSION

261 The dehydration temperature depends on the composition of the amphibole 262 (Fumagalli et al., 2009; Mandler and Grove, 2016; Phillips et al., 1988; Pirard and 263 Hermann, 2015; Ungaretti, 1980). For example, the different types of cations in position 264 B in the crystal structure of iron-poor and iron-bearing amphibole produce different 265 dehydration processes. Previous experiments on heat-treated amphibole (Phillips et al., 1991) have shown that the Fe<sup>2+</sup> at the M(1) and M(3) sites is oxidized during the 266 oxidation-dehydrogenation process to produce Fe<sup>3+</sup> and one electron. In addition, some 267 268 of the Fe<sup>2+</sup> ions at the M(2) and M(4) sites exchange with the Mg<sup>2+</sup> ions at the M(1) and 269 M(3) sites and are then oxidized similarly (Ishida, 1998). Accordingly, the H<sup>+</sup> connected 270 by O(3) is removed to ensure the charge balance in the local region. The reaction 271 products are  $H_2$  and  $O^{2-}$ . Previous studies have shown that the electrical conductivity 272 increases gradually as the iron content of the amphibole increases (Hu et al., 2018;

273	Schmidbauer et al., 2000; Shen et al., 2020; Wang et al., 2012; Zhou et al., 2011), and
274	the electrical conductivity is controlled by the electron produced by the oxidation of
275	$Fe^{2+}$ to $Fe^{3+}$ . The delocalization of the $e^{-}$ and $H^{+}$ and the subsequent jumping are the
276	main reasons for the electrical conductivity of amphibole (jump between W anions).
277	Mg-rich and Fe-poor crocidolite decompose in steps during the thermal decomposition
278	process, which is mainly reflected in the fact that the higher the $Fe^{2+}/Mg^{2+}$ ratio is, the
279	more $Fe^{2+}$ is oxidized during the oxidation-dehydrogenation process (Addison et al.,
280	1962a; Addison et al., 1962b; Addison and Sharp, 1962; Addison and White, 1968;
281	Ungaretti, 1980).

282 According to the result of the kinetics of magnesiohornblende dehydration, we can 283 describe the various stages of dehydration at different temperature ranges. As is shown 284 in Figure 2 and Table 2, magnesiohornblende dehydration can be divided into three 285 steps: 848-1058 K, 1058-1243 K, and 1243-1473 K (Table 2). The results of the 286 thermogravimetric measurements show that from 848 to 1058 K the activation energy 287 is approximately 416 kJ/mol, and the mass loss (approximately 25% of the total mass 288 loss) can be explained by the oxidation-dehydrogenation of the magnesiohornblende. 289 Approximately 20% of the total mass loss occurs in the temperature range of 1058– 290 1243 K and may be caused by the decomposition of the hydroxyl group connected to 291 the  $Fe^{2+}$  ion, which is not decomposed in the temperature range of 848–1058 K. The 292 activation energy of 411.4 kJ/mol is approximately equal to the activation energy of the 293 first step (416.6 kJ/mol), so the dehydration in this step is likely to be driven by

294 oxidation-dehydrogenation at high temperatures, which is probably due to the barrier 295 formed by the delocalized H in the migration process. The mass loss in the temperature 296 range of 1243-1473 K accounts for approximately 50% of the total mass loss and 297 corresponds to an activation energy of 720.9 kJ/mol, which is much larger than the 298 activation energy of the oxidation-dehydrogenation process. Therefore, the mass loss 299 in this step may be due to the direct decomposition of the -OH connected to the  $Mg^{2+}$ 300 ion in the inner part of the crystal. In this step, the dehydration associated with the 301 migration of the Mg ion requires a large activation energy. Compared with using 302 decomposition products to observe the decomposition steps in research on crocidolite, 303 in this study the form of the kinetic parameters was used to more intuitively explain the 304 changes in the decomposition mechanism during the dehydration.

305 Compared with the results of the thermogravimetric analysis, the 306 magnesiohornblende dehydration under high-temperature and high-pressure conditions 307 can be divided into two steps (Fig. 4): low- and high-temperature dehydration. The low-308 temperature dehydration curve is close to that of tremolite. In contrast, the high-309 temperature dehydration curve is much higher than that of tremolite. According to the 310 stability of magnesiohornblende under subduction zone conditions obtained from the dehydration peak temperature during the high-pressure differential thermal experiment 311 312 (Fig. 4), we found that magnesiohornblende may still partially exist within the stability 313 region of tremolite. When the research object is calcic amphibole, we can ignore the 314 factors that may affect the stability of amphibole, such as the alkaline content (Mandler

315	and Grove, 2016; Pirard and Hermann, 2015). The stability phase diagram of calcic
316	amphibole under high-temperature and high-pressure conditions shows that the stability
317	of calcic amphibole increases with increasing $Mg/(Mg+Fe^{2+})$ content (Fig. 6). Previous
318	studies (Gilbert, 1969; Oba, 1978; Thomas, 1982; Welch and Pawley, 1991) have
319	pointed out that the stability of tremolite is the highest, that of hastingsite is the lowest,
320	and that of tschermakite is between those of tremolite and hastingsite. Compared with
321	the decomposition of the hydroxyl groups connected to the $Mg^{2+}$ ions at high
322	temperatures, the decomposition of the hydroxyl groups connected to the $\mathrm{Fe}^{2+}$ ions
323	occur at relatively low temperatures, so the stability of tremolite, which has the highest
324	Mg/(Mg+Fe <sup>2+</sup> ) content, is the highest. Dehydration of calcic amphibole under high-
325	temperature and high-pressure conditions and the participation of oxygen should be
326	consistent with that of magnesiohornblende, and its dehydration process can be divided
327	into two steps, which has also been suggested by Shen et al. (2020), who identified the
328	two peaks corresponding to dehydration by FTIR.

329

#### IMPLICATIONS

Petrological studies have revealed that there is amphibole/chlorite saturated peridotite at the base of the mantle wedge, which is formed from the dehydration of the underlying slab, including the subducting oceanic crust and the serpentinized oceanic mantle (Ono, 1998; Peacock, 1996). These hydrous peridotite layers at the base of the mantle wedge under the northeastern part of the Japanese arc migrated along the subducting slab to form a hydrous layer. The fluid released by the dehydration of the

336 phlogopite (K-rich) and metasomatic amphibole in the hydrous layer caused the basaltic 337 magmatism of the Nasu and Chokai zones in northeast Japan (Ito and Tatsumi, 1995; Ujike, 1988). But Fumagalli et al. (2009) studied the phase relations between phlogopite 338 339 and amphibole in metasomatized peridotites and concluded that the decomposition of 340 peridotite leads to more K in phlogopite entering amphibole and generating Ca-341 amphibole. Tremolite (calcic amphibole) is considered stable at higher temperatures 342 than antigorite in the first ~180 km of depth (Mainprice and Ildefonse, 2009). So the 343 results of this study suggest that the upward migration of the fluids generated by the 344 dehydration of calcic amphibole (the Fe<sup>2+</sup> content is less than the H<sup>+</sup> content) led to the 345 formation of two parallel volcanic zones, Nasu and Chokai in northeast Japan. 346 Geophysical observations have revealed the presence of many high conductivity 347 anomalies in subduction zones, which are related to the dehydration of hydrous 348 minerals. Thus, these high electrical conductivity anomalies are formed by fluid 349 accumulation.

350 The liquids released from hydrous minerals may cause partial melting, seismic 351 events, low-velocity anomalies, and high electrical conductivity anomalies. It has been 352 suggested by previous studies (Hilairet et al., 2007; Liu et al., 2019) that earthquakes 353 will occur if the dehydration rates are higher than that of the viscous relaxation. 354 Therefore, calculated isothermal dehydration kinetic we models for 355 magnesiohornblende at different temperatures (Fig.7). It can be seen that the 356 dehydration time decreases with increasing temperature, and the

dehydration can finish within 40 mins at 1350 K. This fast dehydration could

- 358 supply sufficient fluid to form interconnected networks in subduction zones.
- 359 The dehydration rates  $(V_{1/2})$  of magnesiohornblende can be obtained from 360 the half-time of the reaction  $(t_{1/2})$ :

361 
$$V_{1/2} = \frac{C_{H_2O}}{t_{1/2}} \times \frac{\rho}{\rho_{H_2O}},$$

362 where  $C_{\rm H2O}$  is the water content of the amphibole,  $\rho$  and  $\rho_{\rm H2O}$  are the 363 densities of water and amphibole, and  $t_{1/2}$  is the half-time of the reaction 364 when  $\alpha$  is equal to 0.5. The half-time of the dehydrogenation and 365 dehydroxylation can be obtained from the isothermal model shown in Figure 7. The fluid production rate  $V_{1/2}$  under dehydrogenation is  $2.9 \times 10^{-4}$ ,  $1.7 \times$ 366  $10^{-3}$ , 5.4 × 10<sup>-3</sup>, 1.6 × 10<sup>-2</sup>, and 7.6 × 10<sup>-2</sup>  $m_{fluid}^3 m_{rock}^3 s^{-1}$  at temperatures of 367 368 900, 930, 950, 970, and 1000 K, respectively. The fluid production rate  $V_{1/2}$ under dehydroxylation is  $1.4 \times 10^{-4}$ ,  $4.3 \times 10^{-4}$ ,  $2.0 \times 10^{-3}$ ,  $9.0 \times 10^{-3}$ , and 369  $2.3 \times 10^{-2} m_{fluid}^3 m_{rock}^3 s^{-1}$  at temperatures of 1250, 1270, 1300, 1330, and 370 1350 K, respectively. Compared with the viscous relaxation of antigorite 371  $(3.0 \times 10^{-7} \text{ to } 3.0 \times 10^{-12} \text{ s}^{-1})$  (Hilairet et al., 2007), the fast dehydration of 372 373 magnesiohornblende could cause earthquakes in subduction zones.

Hu et al. (2018) measured the electrical conductivity of magnesiohornblende (0.5– 2.0 GPa and 623–1173 K) and concluded that the enhanced electrical conductivity of magnesiohornblende after dehydrogenation could explain the high electrical conductivity anomalies (>10<sup>-2</sup> S/m) observed in slab-mantle wedge interfaces (Fig. 8).

378	In this study, magnesiohornblende samples with similar compositions were used for the
379	experimental research (Table 1). It was found that as the temperature and pressure
380	continuously increased, after the oxidation-dehydrogenation of the
381	magnesiohornblende, the hydroxyl groups connected to the $Mg^{2+}$ ions in the structure
382	were subsequently decomposed. According to the research results for tremolite
383	conductivity (Shen et al., 2020), the dominant conductive mechanism in the
384	$Ca_2Mg_5Si_8O_{22}(OH)_2(tremolite) = 2CaMgSi_2O_6(diopside) + 3MgSiO_3(enstatite) +$
385	$SiO_2(quartz)$ + $H_2O(gas)$ reaction is the migration of $Mg^{2\scriptscriptstyle +}$ and $Ca^{2\scriptscriptstyle +}$ cations. The
386	dehydroxylation of tremolite may cause high electrical conductivity anomalies
387	(maximum value of 1 S/m). Therefore, the high electrical conductivity anomalies
388	caused by the magnesiohornblende dehydration in the slab-mantle wedge region may
389	be dominated by oxidation-dehydrogenation and dehydroxylation. When $Fe^{2+}$ and $Mg^{2+}$
390	exist in calcic amphibole and the $\mathrm{Fe}^{2+}$ content is less than the H <sup>+</sup> content, we believe
391	that calcic amphibole will dehydrate in two steps (similar to magnesiohornblende), and
392	the high electrical conductivity anomaly produced by this decomposition can be
393	explained by two mechanisms. Therefore, the dehydration of amphibole could explain
394	the high electrical conductivity anomalies at depths of $\sim 180$ km in subduction zones.

395

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- 600 Figure captions
- 601 FIGURE 1
- 602 Schematic diagram of the experimental setup of the high-pressure differential
- 603 thermal analysis.
- 604 The furnace was composed of two layers of stainless steel foil. The soaking tube was
- 605 constructed of nickel to ensure stability at high temperatures. A digital multimeter was
- 606 used to record the thermoelectric potential difference in the circuit and the temperature
- 607 of the alumina powder.
- 608 **FIGURE 2**
- 609 TG and DTG curves for magnesiohornblende at different heating rates.
- 610 The black, red, and green lines represent the reaction progress for heating rates of 10,
- 611 20, and 40 K/min, respectively. The numbers are the heating rates.
- 612 FIGURE 3
- 613 Experimental and calculated curves obtained using (a) the model method and (b)
- 614 **the model-free method.**
- 615 The solid line and dotted line represent the experimental data and calculated data,
- 616 respectively. For the model-free method, the experimental data are fit by the first-order
- 617 reaction (F1), which shows a large difference between the experimental and calculated
- data. In contrast, for the model method, the experimental and calculated data agree well.
- 619 FIGURE 4

#### 620 High-pressure differential thermal curves for magnesiohornblende at 0.5, 1.0, 2.0,

#### 621 and 3.0 GPa.

- 622 Magnesiohornblende dehydration is an endothermic reaction, and two peaks in the
- 623 curve at high temperatures and high pressures represent the two steps of the dehydration
- 624 process.
- 625 FIGURE 5
- 626 Backscattered electron (BSE) image of the products within the first and second
- 627 stages of magnesiohornblende dehydration under the 3.0 GPa.
- 628 (a) BSE image of the first stage (1137 K) of magnesiohornblende dehydration. (b) BSE
- 629 image of the second stage (1233 K) of magnesiohornblende dehydration.
- 630 FIGURE 6

#### 631 The stability of calcic amphibole under subduction zone conditions.

- 632 The red circles and blue squares represent the first and second peak values of the633 thermal decomposition in the high-pressure differential experiment, respectively.
- 634 Hastingsite,  $NaCa_2(Fe_4^{2+}Fe^{3+})Si_6Al_2O_{22}(OH)_2$ ; Tschermakite,

 $Ca_2(Mg_3AlFe^{3+})Si_6Al_2O_{22}(OH)_2$ ; and Tremolite  $Ca_2Mg_5Si_8O_{22}(OH)_2$ . The grey

- 636 lines denote the geothermal gradients at 10, 20, and 30 °C/km in subduction zones.
- 637 **FIGURE 7**

# 638 Isothermal dehydration kinetic models for magnesiohornblende at different

- 639 temperatures derived from the parameters of the non-isothermal experiments.
- 640 (a) decomposition rates at 848–1048 K based on the first dehydrogenation step and (b)
- 641 1243–1473 K based on the dehydroxylation step.

#### 642 FIGURE 8

# 643 The electrical conductivities and dehydration reactions of amphibole with

644 different Mg/(Mg+Fe<sup>2+</sup>) contents under subduction zone conditions.

645 electrical conductivities of Fe-dominant amphibole, Mg-Fe<sup>2+</sup>-bearing The 646 magnesiohornblende, and Fe-free tremolite increase significantly during 647 dehydrogenation and dehydroxylation (Hu et al., 2018; Shen et al., 2020). The blue and yellow areas are the electrical conductivity changes of amphibole with different 648 649  $Mg/(Mg+Fe^{2+})$  contents on the subducted slab. Dehydrogenation and dehydroxylation 650 occur during the magnesiohornblende dehydration, which may cause two electrical 651 conductivity changes. The Fe-dominated amphibole undergoes dehydrogenation, and 652 the Fe-free amphibole undergoes dehydroxylation. Dehydrogenation is the oxidation of  $Fe^{2+}$  on the M(1) and M(3) octahedra to  $Fe^{3+}$ , the loss of H<sup>+</sup> ions bonded to the O(3) 653 654 oxygen atom to balance the charge, and the reaction produces  $H_2$ . Dehydroxylation is 655 the migration of protons to OH<sup>-</sup> of O3 site and combine to form water molecule. The 656 upward migration of the fluids generated by the dehydration steps of calcic amphibole (the Fe<sup>2+</sup> content was less than the H<sup>+</sup> content) led to the formation of two parallel 657 658 volcanic zones, Nasu and Chokai, in northeast Japan. Mg-Hb-magnesiohornblende, 659 Amp—Amphibole, Tre—Tremolite.

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664	Table	1

- 665 Chemical composition of magnesiohornblende determined using an electron probe
- 666 microanalyzer. The chemical compositions of the magnesiohornblende and tremolite

667 used in the electrical conductivity studies are also list	ed.
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	Mg-Hb	Mg-Hb	Tremolite
Sample	[This study]	(Hu et al., 2018)	(Shen et al., 2020)
Na <sub>2</sub> O	1.56	0.38	0.12
MgO	16.33	14.29	25.65
$Al_2O_3$	5.65	3.66	0.09
$SiO_2$	49.77	50.56	58.28
K <sub>2</sub> O	0.42	-	0.15
CaO	11.45	20.43	12.99
FeO*	9.41	8.16	0.27
MnO	0.29	0.21	-
$TiO_2$	0.62	1.00	-
$Cr_2O_3$	0.02	-	-
Total	95.61	98.69	97.55
$\mathrm{Si}^{4+}$	7.29	7.29	7.92
$Mg^{2+}$	3.57	3.07	5.20
$100 \frac{Mg}{Mg + Fe}$	75.57	75.74	99.39

*Note*: Mg-Hb—magnesiohornblende. Twenty-three oxygen atoms were used to calculate the chemical formula of the crystal.

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# 686 **Table 2**

687 Kinetic parameters calculated using the model method.

Stage	T (K)	Mass loss (%)	E (kJ/mol)	A (1/s)	n
1	848-1058	25	416.60	$1.58\times10^{22}$	4.23
2(1)	1058-1243	20	411.40	$2.82 \times 10^{15}$	2.30
2(2)	1243–1473	55	720.90	$2.51 \times 10^{27}$	1.95

*Note: E*, *A*, and *n* are the apparent activation energy, pre-exponential factor, and the order of the reaction, respectively.

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# 702

# 703 **Table 3**

Stage	E		Α	
α	E (kJ/mol)	Δ	A (1/s)	Δ
0.1	437.83	2.67	$7.40 \times 10^{21}$	0.15
0.2	663.75	48.79	$1.28 \times 10^{31}$	2.55
0.3	600.37	5.44	$7.19 \times 10^{22}$	0.24
0.4	539.85	1.54	$6.46 \times 10^{19}$	0.06
0.5	622.92	23.59	$1.17 \times 10^{23}$	0.97
0.6	669.95	27.62	$7.14 \times 10^{24}$	1.12
0.7	709.50	39.98	$2.2 \times 10^{26}$	1.60
0.8	767.12	66.22	$2.51 \times 10^{28}$	2.62
0.85	811.85	102.97	$1.01 \times 10^{30}$	4.05
Average	647.02		$1.56 \times 10^{30}$	

E and A for different conversion rates calculated using the model-free method.

*Note*:  $\alpha$  is the reacted fraction; *E* is the apparent activation energy; *A* is the pre-exponential factor; and  $\Delta$  is an objective function, which was defined to describe the error between the experimental and fitting data.

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