1	<b>REVISION 3</b>
2	Influence of anisotropy on the electrical conductivity of apatite
3	at high temperatures and high pressures
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#### Abstract

13 The *in-situ* electrical conductivity of apatite single crystals along three main 14 crystalline directions were measured using the YJ-3000t multi-anvil apparatus and a 15 combined system consisting of the impedance/gain-phase analyzer (Solartron 1260) 16 and dielectric interface (Solartron 1296) at conditions of 973-1373 K and 1.0-3.0 GPa. Experimental results indicate that the relationship between the electrical 17 18 conductivity of sample and temperature conforms to the Arrhenius relation. At 2.0 19 GPa, the electrical conductivity of apatite with relatively high activation enthalpies of 20 1.92–2.24 eV shows a significant anisotropy with the extremely high anisotropic 21 degree ( $\tau = -8-16$ ) value. For a given [001] crystallographic orientation, the electrical 22 conductivity of apatite slightly decreases with increasing pressure, and its 23 corresponding activation energy and activation volume of charge carriers are 24 calculated as  $2.05 \pm 0.06$  eV and  $9.31 \pm 0.98$  cm<sup>3</sup>/mole, respectively. All of these 25 observed anomalously high activation enthalpy and positive activation volume values 26 suggest that the main conduction mechanism of sample is related to the monovalent 27 fluorine anion at high temperature and high pressure. Furthermore, three 28 representative petrological average schemes including the parallel, Hashin–Shtrikman 29 upper bound and average models were selected to establish the functional relation for the electrical conductivity of the phlogopite-apatite-peridotite rock system along with 30 the volume percentages of apatite ranging from 1% to 10% at conditions of 973–1373 31 32 K and 2.0 GPa. For a typical Hashin-Shtrikman upper bound model, the electrical

33	conductivity-depth profile for peridotite containing the 10% volume percentage of
34	apatite was successfully constructed in conjunction with our acquired anisotropic
35	electrical conductivity results and available temperature gradient data (11.6 K/km and
36	27.6 K/km) at depths of 20-90 km. Although the presence of apatite in peridotite
37	cannot explain the high conductivity anomalies in western Junggar of Xinjiang
38	autonomous region, it can provide a reasonable constraint on those of representative
39	apatite-rich areas.
40	Keywords: Apatite; electrical conductivity; anisotropy; fluorine conduction; high

41 pressure

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### Introduction

43 Previously available field geophysical magnetotelluric (MT) results revealed that 44 there existed phenomena of widespread high conductivity anomalies and highly 45 electrical conductivity anisotropy in many areas of the lithosphere and asthenosphere 46 (Hamilton et al. 2006; Naif et al. 2013; Selway 2014, 2015, 2019; Selway and O'Donnell 2019; Selway et al. 2019; Förster and Selway 2021; Özaydın and Selway 47 2022). For a typical geotectonic unit in western Junggar of Xinjiang autonomous 48 49 region, the remnants of subducted oceanic slab with the anomalous high conductivity 50 range of  $\sim 10^{-2}$ -1 S/m have been reported on the basis of recent MT data (Xu et al. 2016, 2020; Zhang et al. 2017; Liu et al. 2019a). In-situ electrical conductivity 51 52 measurements of relevant minerals and rocks under high-temperature and high-53 pressure conditions can be applied to reasonably interpret the observed MT results. As 54 pointed out by Xu et al. (2020), the high conductivity anomalies in the western 55 Junggar of Xinjiang autonomous region can be caused by the presence of volatile-56 bearing metasomatic minerals (VMMs), such as apatite, phlogopite, lawsonite and 57 amphibole in the residual oceanic plate.

Generally, the volatile–bearing metasomatic minerals are the ordinary constituent materials to mantle magma, which also exist as a disseminated type in the mantle peridotite. As a research hotpoint, the electrical properties of VMMs at high temperature and high pressure have attracted great attention in the recently several years (Manthilake et al. 2015, 2016, 2021a, b; Li et al. 2016, 2017; Hu et al. 2018; Liu

63 et al. 2019b; Ye et al. 2022). For a representative water-bearing and fluorine-bearing 64 silicate mineral, Li et al. (2016) investigated the electrical conductivity of phlogopite 65 single crystals along three main crystalline directions at temperature range of 473-1173 K and pressure of 1.0 GPa with an end-loaded piston cylinder press. They 66 67 observed anomalously high conductivity and significant electrical conductivity 68 anisotropy of phlogopite, which can account for the regional high conductivity 69 anomalies in the continental upper mantle. As far as a typically hydrous silicate 70 mineral in oceanic subduction slab, Manthilake et al. (2015) performed the electrical 71 conductivity measurements of lawsonite at 298-1320 K and 7.0 GPa by virtue of the Kawai-1500t multi-anvil high-pressure apparatus. They found that the highly 72 73 conductive fluid from the dehydration of lawsonite can lead to those of regional high 74 conductivity anomalies of northern Chilean subduction zone, central Chilean 75 subduction zone and northeastern Japan within the depth range of 150-275 km. For a 76 predominant rock-forming mineral in the mid-lower Earth crust and subduction zone, 77 the electrical conductivity of iron-bearing amphibole single crystals was 78 systematically investigated by Hu et al. (2018) at temperatures of 523-1173 K and 79 pressures of 0.5–2.0 GPa using the YJ–3000t multi–anvil high–pressure apparatus. All 80 of these acquired experimental results from Hu et al. (2018) indicated that the 81 electrical conductivity of amphibole was highly sensitive to temperature, pressure and 82 oxidation-dehydrogenation process. Due to the occurrence of oxidation-83 dehydrogenation, the enhanced electrical conductivity of amphibole can reasonably

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explain the high conductivity anomalies in the stable continental lowermost mid–crust and slab–mantle wedge interfaces. However, as a crucial volatile–bearing metasomatic mineral, so far, there is no reported data about the electrical conductivity of apatite under high temperature and high pressure conditions.

88 Apatite is a type of important calcium-bearing and volatile-bearing phosphate 89 mineral, which widely exists as an accessory mineral in a large number of igneous, 90 sedimentary and metamorphic rocks. As the major source of phosphorous ore, the 91 high-pressure physiochemical investigations on apatite are essential to explore the 92 geological cycle of global phosphorus element in the deep Earth's interior. Most of 93 reported data about the high-pressure compressibility, thermal expansion coefficient 94 and P-T phase diagram on apatite were obtained by *in-situ* synchrotron X-ray 95 diffraction and Raman spectroscopy measurements (Murayama et al. 1986; Brunet et 96 al. 1999; Comodi et al. 2001a, b; Matsukage et al. 2004; Konzett and Frost 2009). It is 97 well known that apatite is a representative hexagonal mineral with the relatively low-98 symmetric crystalline structure. All of these data including the high-pressure thermal 99 expansion coefficient and compressibility reported by Brunet et al. (1999) and 100 Comodi et al. (2001a), as well as the element diffusivity reported by Brenan (1994) 101 and Li et al. (2020), have indicated the significant effect of crystallographic orientation on the physiochemical properties of the low-symmetric apatite single crystal. 102 103 Electrical conductivity is also highly sensitive to the crystallographic orientation for 104 some typical low-symmetric silicate minerals (e.g., olivine, pyroxene, phlogopite, K-

105	feldspar, etc.), which widely outcrop in the regions of mid-lower Earth crust and
106	upper mantle (Huebner and Voigt 1988; Yang 2012; Dai and Karato 2014a; Li et al.
107	2016; Dai et al. 2018a, 2022). Nevertheless, until now, the effect of high-pressure
108	crystallographic orientation on the electrical conductivity of apatite remains unclear.
109	In the present study, the <i>in-situ</i> electrical conductivity of apatite single crystals
110	along three main [001], [100] and [010] crystalline directions were investigated at
111	temperatures of 973-1373 K and pressures of 1.0-3.0 GPa. The influences of
112	temperature, pressure and crystallographic orientation on the electrical conductivity
113	were explored in detail. Furthermore, the functional dependence relation for the
114	volume percentages of apatite on the electrical conductivity of the phlogopite-apatite-
115	peridotite rock system was successfully constructed. Finally, the electrical
116	conductivity-depth profile for peridotite containing the 10% volume percentage of
117	apatite was established, and profoundly discussed its geophysical implications.

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### **Experimental procedures**

119 Sample preparation

In this study, a natural gem–grade apatite single crystal with the perfect hexagonal structure and its dimension of  $\sim 20 \times 15 \times 15$  mm<sup>3</sup> was collected from Lianyungang city, Jiangsu province, China. Apatite single crystal was fresh with the transparent yellow surface color, vitreous luster and no evidences of twinning, exsolution or alteration. The chemical composition of sample was checked by the

125	JEOL JXA-8230 electron microprobe analyzer (EPMA) operated at the State Key
126	Laboratory of Ore-Deposit Geochemistry, Institute of Geochemistry, Chinese
127	Academy of Sciences (CAS), as shown in Table 1. It is obvious that our sample
128	belongs to a representative calcium-bearing, volatile-bearing (fluorine-containing
129	and chloride-containing) and nominally anhydrous phosphate fluorapatite with the
130	relatively high fluorine content up to $4.33 \pm 0.02$ wt.%. In this study, the hexagonal
131	apatite single crystal along the long crystallographic orientation is nominated as the
132	[001] crystalline direction, and other two mutually perpendicular crystallographic
133	orientations are nominated as the [100] and [010] crystalline directions. Accordingly,
134	the representative optical microscopic observation and its corresponding crystalline
135	structure of apatite are also displayed in Figure 1. Then, the crystal was cut and
136	polished to circular columns (Spec: 6.0 mm of diameter and 4.0 mm of height) along
137	three main [001], [100] and [010] crystalline directions. After that, the cylindrical
138	samples were rinsed using the acetone, ethanol and de-ionized water in an ultrasonic
139	cleaner. Finally, the samples were kept in a muffle furnace at 423 K for 10 hrs to
140	eliminate the absorbed water for subsequent electrical conductivity measurements.

141 Sample characterization

142 The water content of samples before and after the electrical conductivity 143 measurements was investigated by using a Vertex–70V vacuum Fourier transform 144 infrared (FT–IR) spectroscopy analyzer. Samples were cut and doubly polished to a

145 thickness of less than 150 µm using the diamond blade for subsequent FT-IR analysis. 146 The FT-IR spectra were collected according to the total absorbance of OH groups between wavenumbers of 3000-4000 cm<sup>-1</sup> with the accumulation of 512 scans for 147 148 each sample. As shown in Figure 2, the representative FT-IR spectra for initial and 149 recovered samples exhibit a sharp absorbance peak at the characteristic wavenumber 150 position of ~3560 cm<sup>-1</sup>, which is in good agreement with previously reported FT-IR 151 results of apatite single crystal for Wang et al. (2011). According to the Beer–Lambert 152 law, the water content  $(C_w)$  in apatite single crystals can be calculated by the 153 following formula,

154 
$$C_w = \omega A / \varepsilon \rho d$$

(1)

where *A* is the total integrated absorbance (1/cm),  $\omega$  represents the molar mass of H<sub>2</sub>O (18.02 g/mole),  $\rho$  is the density of sample (3.20 g/cm<sup>3</sup>), *d* is the thickness of sample (cm), and  $\varepsilon$  is the molar absorptivity of sample [2.31×10<sup>4</sup> L/(mole·cm<sup>2</sup>)] to be reported by Wang et al. (2011). The water contents of starting and recovered apatite single crystals were calculated as 176.69 ppm wt and 134.87 ppm wt, respectively, which suggests no clear water loss during the process of electrical conductivity measurements.

### 162 High-pressure cell and complex impedance measurements

163 Complex impedance measurements of samples were conducted using the YJ– 164 3000t multi–anvil apparatus and a combined system consisting of the

165 impedance/gain-phase analyzer (Solartron 1260) and dielectric interface (Solartron 166 1296). Experimental principles and measurement procedures were described by Dai et 167 al. (2012) and Hu et al. (2017) in detail. Figure 3 displays the cross-section diagram of the sample assemblage for high-pressure impedance spectroscopy measurements. 168 Pressure-transmitting medium of cubic pyrophyllite with a dimension of 169 32.5×32.5×32.5 mm<sup>3</sup> was baked at 1073 K for 8 hrs to avoid the influence of 170 171 dehydration on the electrical conductivity results. Some components of the 172 experimental assemblage (alumina sleeve, magnesia sleeves and ceramic tube) were 173 kept at 423 K in a muffle furnace for 10 hrs to remove the absorbed water. The heater 174 was consisted of three-layer stainless steel sheets with a total thickness of 0.5 mm. 175 Alumina and magnesia sleeves were employed to provide an excellent insulation 176 environment during the process of high-pressure electrical conductivity 177 measurements. The nickel foil with its corresponding thickness of 25 µm connected to 178 the ground was installed between alumina and magnesia sleeves, which can efficiently 179 prevent the current leakage of high-pressure experimental assemblage. A cylindrical 180 sample (Spec: 6.0 mm  $\times$  4.0 mm) was laid in the center of electrical conductivity 181 assemblage. Two symmetric nickel slices with each thickness of 0.5 mm at both ends of 182 sample were adopted as electrodes, which also can be adopted to control and adjust the 183 oxygen fugacity in the sample chamber. The experimental temperatures were monitored by a Ni<sub>90</sub>Cr<sub>10</sub>-Ni<sub>97</sub>Al<sub>3</sub> thermocouple. Measurement uncertainties from the 184 185 experimental temperature and pressure were  $\pm 5$  K and  $\pm 0.1$  GPa, respectively.

186 During the experiment, pressure was raised to the designated value at a rate of 1.0 187 GPa/h. Under constant pressure condition, temperature was gradually increased to the 188 desired value at an interval of 50 K. Subsequently, the complex impedance spectra of 189 apatite were continuously collected within the temperature range from 973 K to 1373 190 K. The fixed signal voltage of 1.0 V and frequency range of  $10^{-1}$ – $10^{6}$  Hz were applied, 191 respectively. To obtain reproducible data, the complex impedance spectra of the 192 samples were measured in two subsequent heating-cooling cycles. In order to check 193 the insulation property of the assemblage background, the electrical conductivity of a 194 cylindrical magnesium oxide with the diameter of 6.0 mm and height of 4.0 mm was 195 investigated at a wider temperature range from 1073 K to 1523 K and 2.0 GPa. At a 196 relatively low temperature of 1073 K, the electrical conductivity of magnesium oxide 197 is approximately 3.2 times lower than that of [010] crystallographic orientation, and approximately 29.4 times lower than that of [001] crystallographic orientation, as 198 199 detailedly displayed in Figure 7. With the rise of temperature, the discrepancy of the 200 electrical conductivity in apatite and magnesium oxide increases, and thus, the 201 insulation property of assemblage background becomes better. At a relatively high 202 temperature of 1373 K, the electrical conductivity of magnesium oxide is 203 approximately 32.3 times lower than that of [010] crystallographic orientation, and 204 more than 500 times lower than that of [001] crystallographic orientation. As a typical 205 insulation material of magnesium oxide, it can provide an extremely good insulation, 206 especially among the high-temperature electrical conductivity of apatite.

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### Results

208	In the present experiments, the electrical conductivity of apatite single crystals
209	along three main [001], [100] and [010] crystalline directions was measured in the
210	temperature range of 973-1373 K and pressure of 2.0 GPa. To deeply explore the
211	influence of pressure on the electrical conductivity, measurements of samples along a
212	fixed [001] crystallographic orientation were also carried out within the pressure
213	range from 1.0 GPa to 3.0 GPa.
214	Representative complex impedance spectra for apatite single crystal of the [010]
215	crystallographic orientation at conditions of 973-1373 K and 2.0 GPa are shown in
216	Figure 4. All of the complex impedance spectra at each corresponding temperature
217	point are composed of an almost ideal semicircular arc within the high-frequency
218	range and a tiny tail at low frequency. According to the theory of AC complex
219	electrochemical impedance spectroscopy (Huebner and Dillenburg 1995; Yang and
220	McCammon 2012; Saltas et al. 2013, 2020; Sivakumar et al. 2018, 2021, 2022; Dai
221	and Karato 2020), our acquired semicircular arc and additional tiny tail stand for the
222	electrical transport process of grain interior and polarization process at the sample-
223	electrode interface, respectively. Therefore, an equivalent circuit composed of the
224	series connection of parallel $R_{\rm S}$ -CPE <sub>s</sub> and parallel $R_{\rm E}$ -CPE <sub>E</sub> was employed to fit the
225	impedance semicircular arc and determine the electrical resistance of apatite single
226	crystal, where the symbols of $R_{\rm S}$ and CPE <sub>S</sub> represent the electrical resistance and
227	constant phase element for the sample, respectively; $R_E$ and $CPE_E$ represent the

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electrical resistance and constant phase element for the polarization process at the sample–electrode interface, respectively. Then, the electrical conductivity of the sample ( $\sigma$ ) was calculated as follows,

 $\sigma = L/RS \tag{2}$ 

where L, S and R are the length of sample (m), the cross-section area of electrode ( $m^2$ ),

and the electrical resistance of sample ( $\Omega$ ), respectively.

234 Figure 5 shows the logarithmic electrical conductivity of apatite in the [001] 235 crystallographic orientation against the reciprocal temperature for two continuous 236 heating-cooling cycles ranging from 973 K to 1373 K and 3.0 GPa. It is clear that the 237 electrical conductivity in the first heating cycle is higher than those in the subsequent 238 cooling and second heating-cooling cycles at a relatively low temperature range from 239 973 K to 1173 K. In the following first cooling and second heating-cooling cycles, the 240 electrical conductivity values show a good reproducibility over the whole measured 241 temperature range, which indicates that a completely stable and equivalent state is 242 reached in the sample chamber during the process of electrical conductivity 243 measurement. The reproducible data attained from the first cooling and subsequent 244 second heating-cooling cycles are used to fit the electrical conductivity results. The 245 relationship between the electrical conductivity of apatite and temperature can be 246 expressed by the Arrhenius relation,

247 
$$\sigma = \sigma_0 \exp(-\Delta H/kT) \tag{3}$$

248 where  $\sigma_0$ , k and T are the pre–exponential factor (S/m), the Boltzmann constant (eV/K)

249 and the absolute temperature (K), respectively.  $\Delta H$  is the activation enthalpy (eV). 250 The dependence relation of activation enthalpy on the pressure can be described as, 251  $\Delta H = \Delta U + P \Delta V$ (4)where  $\Delta U$  and  $\Delta V$  are the activation energy (eV) and activation volume (cm<sup>3</sup>/mole), 252 253 respectively. Figure 6 displays the influence of pressure on the electrical conductivity of 254 255 apatite along the [001] crystallographic orientation at conditions of 973-1373 K and 256 1.0-3.0 GPa. The detailed electrical conductivity of apatite single crystals along three 257 main [001], [100] and [010] crystalline directions at 973-1373 K and 2.0 GPa are 258 illustrated in Figure 7. In addition, the background electrical conductivity of 259 magnesium oxide is also included in Figure 7 over a wider temperature range from 260 1073 K to 1523 K at 2.0 GPa. All the fitting parameters for the electrical conductivity 261 of apatite single crystals are detailedly listed in Table 2.

262

#### **Discussions**

263 Effect of pressure on electrical conductivity

For a fixed [001] crystallographic orientation, the pressure-dependent electrical conductivity of apatite is clearly displayed in Figure 6. It is clear that the electrical conductivity of the sample decreases by approximately 2.5 times at a certain temperature point as the pressure increases from 1.0 GPa to 3.0 GPa. Whereas, the magnitude of pre-exponential factor rises from  $8.91 \times 10^5$  S/m to  $2.09 \times 10^6$  S/m, and

269 the activation enthalpy value increases from 2.14 eV to 2.33 eV, respectively. With the 270 rise of pressure, the crystalline framework of apatite is gradually compressed, which 271 leads to a narrower pathway of charge carrier, and thus, the relatively high energy is 272 required for charge carrier to cross the energy barrier. This is reflected in the reduced 273 electrical conductivity and increased activation enthalpy of samples at higher pressure 274 conditions. The negative influence of pressure on the electrical conductivity was also 275 observed for some silicate minerals, such as olivine, anorthite, plagioclase, kaolinite, 276 etc. (Xu et al. 2000; Dai and Karato 2014b; Hu et al. 2015, 2022a; Hong et al. 2022). 277 According to equation (4) and Table 2, the activation energy and the activation volume 278 of charge carriers are calculated as  $2.05 \pm 0.06$  eV and  $9.31 \pm 0.98$  cm<sup>3</sup>/mole, 279 respectively. In light of the available pressure-dependent electrical conductivity, we 280 can also extrapolate the relationship between the electrical conductivity of apatite and 281 temperature at atmospheric pressure, as illustrated in Figure 6.

### 282 Effect of crystallographic orientation on electrical conductivity

For a fixed pressure of 2.0 GPa, the influence of crystallographic orientation on the electrical conductivity of apatite single crystal at temperatures of 973–1373 K is detailedly depicted in Figure 7. The electrical conductivity of the background of magnesium oxide is included at a wider temperature range from 1073 K to 1523 K and 2.0 GPa. It is clear that the electrical conductivity of sample increases along an order of [010], [100] and [001] crystallographic orientations, and their corresponding

289 activation enthalpies are determined to be 1.92-2.24 eV. Figure 8 displays the degree 290 of electrical conductivity anisotropy ( $\tau = \sigma_{Max}/\sigma_{Min}$ ) for apatite single crystals and 291 apatite polycrystalline aggregates as a function of temperature from 900 K to 1700 K. Our present obtained electrical conductivity results for olivine containing the 10% 292 293 volume percentage of apatite, and previously available results for the electrical 294 conductivity of hydrous olivine single crystals reported by Dai and Karato (2014a), as 295 well as the electrical conductivity of the field geophysical observations in 296 asthenosphere from Evans et al. (2005) and Naif et al. (2013) are also clearly illustrated in Figure 8. The degree of electrical conductivity anisotropy ( $\tau = \sigma_{Max}/\sigma_{Min}$ ) 297 298 for olivine containing the 10% volume percentage of apatite is calculated using our 299 present anisotropic electrical conductivity data and the Hashin-Shtrikman upper 300 bound model, which is detailedly presented as,

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$$\tau_{\rm HS+} = \tau_{\rm OI} + \frac{f_{\rm Ap}}{(\tau_{\rm Ap} - \tau_{\rm OI})^{-1} + f_{\rm OI}(3\tau_{\rm OI})^{-1}}$$
(5)

where  $\tau_{Apa}$  and  $\tau_{Ol}$  are the degrees of electrical conductivity anisotropy of apatite single crystal and olivine single crystal, respectively;  $f_{Apa}$  and  $f_{Ol}$  are the volume percentages of apatite single crystal and olivine single crystal, respectively.

As detailedly described in Figure 8, the degree of electrical conductivity anisotropy for apatite single crystal displays an available positive linear dependence relation with temperature at 2.0 GPa. With increasing temperature from 700 K to 1700 K, the degree of electrical conductivity anisotropy for apatite single crystal increases from ~7 to ~23. Accordingly, the degree of electrical conductivity anisotropy for

310 apatite polycrystalline aggregates is also enhanced from ~0.50 to ~1.65, which reveals 311 the existence of more significant electrical conductivity anisotropy for apatite single 312 crystal under condition of the higher temperature of deeper Earth's interior. On the 313 other hand, the degree of electrical conductivity anisotropy for apatite becomes higher 314 than that of hydrous olivine at temperatures below ~1320 K, and lower than that of 315 hydrous olivine in the temperature range of 1320-1700 K. The degrees of electrical 316 conductivity anisotropy for olivine containing the 10% volume percentage of apatite 317 and hydrous olivine single crystal exhibit similar tendency with the variation of 318 temperature. These results can be transformed into the degree of electrical 319 conductivity anisotropy for polycrystalline aggregates using the numerical research on 320 olivine single crystals to be reported by Simpson and Tommasi (2005). As pointed out 321 by McKenzie and Bickle (1988), the temperature in the region of mantle 322 asthenosphere falls within the range of 1550-1650 K. Previous geophysical 323 observations have indicated that the degree of electrical conductivity anisotropy in the 324 asthenosphere can be up to a factor of  $\sim 2-3$  higher along the flow direction on the 325 horizontal plane (Evans et al. 2005; Naif et al. 2013). For the representative 326 peridotite-dominated asthenospheric temperature condition, it is clear that the 327 obtained degree of electrical conductivity anisotropy value for apatite is much lower than those of field geophysical observations. The degree of conductivity anisotropy 328 329 observed in the asthenosphere is dominated by the anisotropic electrical conductivity 330 of hydrous olivine.

331 The acquired highly electrical conductivity anisotropy of apatite may be resulted 332 in by the anisotropic mobility of charge carrier, which is possibly correlated with its 333 low-symmetric crystalline structure (Fig. 1b). In combination with the measured 334 anisotropic electrical conductivity results, three spatial averaging schemes were 335 employed to extrapolate the isotropic electrical conductivity of randomly oriented 336 apatite polycrystalline aggregates at high temperature and high pressure. In the 337 present study, three representative averaging schemes on the electrical conductivity of 338 apatite single crystals including series ( $\sigma_{\rm S}$ ), parallel ( $\sigma_{\rm P}$ ), and average ( $\sigma_{\rm A}$ ) models are 339 presented as follows,

340 
$$\sigma_{\rm S} = \frac{3}{1/\sigma_{[001]} + 1/\sigma_{[100]} + 1/\sigma_{[010]}} \tag{6}$$

341 
$$\sigma_{\rm P} = \frac{\sigma_{[001]} + \sigma_{[100]} + \sigma_{[010]}}{3}$$
(7)

342 
$$\sigma_{\rm A} = \frac{\sigma_{\rm s} + \sigma_{\rm p} + \sqrt{(\sigma_{\rm s} + \sigma_{\rm p})^2 + 32\sigma_{\rm s}\sigma_{\rm p}}}{8} \tag{8}$$

By virtue of three above-mentioned isotropic average schemes, the acquired anisotropic electrical conductivity results on apatite along the [010], [100] and [001] crystalline directions were transformed into isotropic conductivity values for randomly oriented apatite polycrystalline aggregates. As pointed out by Dai and Karato (2014a) and Hu et al. (2022b), the electrical conductivity results from the series and parallel models represent the lower and upper boundary values in the isotropic average schemes of polycrystalline aggregates, respectively.

#### 350 Comparisons with other VMMs

351 For the representative geotectonic unit in western Junggar of Xinjiang 352 autonomous region, Xu et al. (2020) proposed that there existed four interconnected 353 VMMs of apatite, phlogopite, lawsonite and amphibole, which can be employed to explain the anomalously high conductivity from the field geophysical MT results. 354 355 Therefore, investigations on the electrical properties of VMMs at elevated 356 temperature and pressure conditions are crucial in deeply exploring the origin of high 357 conductivity anomalies in western Junggar of Xinjiang autonomous region. In this 358 study, we systemically investigated the electrical conductivity of apatite along three 359 main [001], [100] and [010] crystallographic orientations at conditions of 973–1373 K 360 and 1.0-3.0 GPa. Thus, our absolutely new results for the anisotropic electrical 361 conductivity of apatite single crystals were compared with the previously available 362 data of other VMMs (i.e., phlogopite, lawsonite and amphibole), which is displayed in 363 Figure 9. As a whole, the anisotropic electrical conductivity of apatite single crystals 364 at 2.0 GPa are abnormally lower than those of three other representative VMMs for 365 phlogopite from Li et al. (2016), lawsonite from Manthilake et al. (2015) and 366 amphibole from Hu et al. (2018) at temperature range of 973-1373 K. As a hydrous 367 and fluorine-bearing silicate mineral, Li et al. (2016) investigated the electrical 368 conductivity of phlogopite single crystals along various crystalline directions at 369 temperatures of 473–1173 K and pressure of 1.0 GPa. In comparison, the degree of 370 electrical conductivity anisotropy in apatite ( $\tau = -8-16$ ) is much higher than that of phlogopite ( $\tau = -4-12$ ) at temperatures of 973–1373 K, which implies a stronger 371 19

372 dependence relation of anisotropic conductivity in the apatite single crystal at high 373 temperature and high pressure. Meanwhile, the acquired activation enthalpies of 1.92-374 2.24 eV for the anisotropic electrical conductivity of apatite are slightly higher than 375 those of phlogopite (1.37–2.08 eV). For a representative hydrous silicate mineral in 376 the oceanic subducted slab, Manthilake et al. (2015) performed the electrical 377 conductivity measurements of lawsonite at temperature range of 298-1320 K and 7.0 378 GPa. As reported by Manthilake et al. (2015), a sharp enhancement in electrical 379 conductivity was observed as the temperature exceeding 1258 K, which can be 380 ascribed to the dehydration of lawsonite. Their acquired activation enthalpies of 0.21-381 0.98 eV on lawsonite are much lower than those of our present results for apatite. As 382 far as a predominant rock-forming mineral in the mid-lower Earth crust and subduction zone, the electrical conductivity of iron-bearing amphibole single crystals 383 384 was measured by Hu et al. (2018) at conditions of 623-1173 K and 0.5-2.0 GPa. 385 During their experiment, the occurrence of oxidation-dehydrogenation reaction was 386 put forward at a temperature of ~843 K, which greatly enhanced the electrical 387 conductivity of amphibole. The dominant conduction mechanism of amphibole was small polaron conduction with the relatively low activation enthalpies of 0.70–0.80 eV, 388 389 which are much lower than our acquired activation enthalpy results of apatite. In 390 summary, the electrical conductivity of apatite along different crystalline directions is 391 much lower than those of other representative VMMs (i.e., phlogopite, lawsonite and 392 amphibole) at temperature range of 973-1373 K. Likewise, our observed highly 20

anisotropic electrical conductivity of apatite single crystals with relatively high
activation enthalpies (1.92–2.24 eV) are possibly correlated with the unique
hexagonal crystalline structure, as well as its mineralogical composition of the
calcium–bearing and high–fluorine fluorapatite.

### 397 Conduction mechanism

398 The activation enthalpy for each conduction mechanism strongly depends on 399 charge mobility, and the electrical transport mechanism can be distinguished by the 400 variation in slope at given temperature range of the Arrhenius relation (Hu et al. 2015; 401 Dai et al. 2016; Sun et al. 2017). For the newly attained data of apatite, only a linear 402 relationship between the logarithmic electrical conductivity and reciprocal 403 temperature is exhibited in the Arrhenius diagram, implying that only one dominant conduction mechanism, or several mechanisms with similar activation energy 404 405 dominate the electrical transport of apatite within the limited temperature range of 973–1373 K and pressure range of 1.0–3.0 GPa. 406

In the present study, the relatively high activation enthalpies up to 1.92–2.24 eV were obtained for the electrical conductivity of apatite single crystals along three main [001], [100] and [010] crystalline directions at conditions of 973–1373 K and 2.0 GPa. Due to the existence of trace amount of water in our samples, the proton may be the dominant conduction mechanism for apatite at high temperature and high pressure. It is well known that the proton conduction is the most common defect species in many

413 hydrous silicate minerals with a relatively low activation enthalpy of less than 1.0 eV, 414 such as hydrous amphibole, chlorite, glaucophane, etc. (Saltas et al. 2013; Manthilake 415 et al. 2016, 2021b). In view of the noticeable discrepancy in activation enthalpy 416 between proton conduction and our results, it cannot be the dominant conduction 417 mechanism for apatite. The small polaron conduction is considered to be an important 418 conduction mechanism for some anhydrous iron-bearing silicate minerals, such as 419 garnet, biotite and clinopyroxene (Dai et al. 2013; Saltas et al. 2020; Sun et al. 2020). 420 All of these obtained results have confirmed that small polaron conduction is 421 characterized by the activation enthalpy of <1.5 eV. Thus, the iron-free apatite single 422 crystals with relatively high activation enthalpies of 1.92–2.24 eV in this study can 423 rule out any contribution of small polaron. The observed values of high activation 424 enthalpy and positive activation volume for apatite conform to the characteristics of 425 ion conduction (Hu et al. 2015, Li et al. 2016, 2017). As shown in Table 1, calcium and 426 fluorine are two important constituent elements in our sample. According to the high-427 temperature diffusion results reported by Cherniak (2010a), the diffusivity of calcium 428 cation is much lower than that of fluorine anion at the same temperature condition. 429 Therefore, the contribution of calcium cation to the electrical conduction of apatite 430 can be neglected. The most promising charge carrier in apatite is the fluorine anion, which has a relatively small effective ionic radius ( $\sim 1.17 - 1.25$  Å) and high mobility at 431 elevated temperatures and pressures (Shannon 1976; Cherniak 2010b; Liu et al. 2019b). 432 433 In summary, on the basis of these obtained relatively high activation enthalpies,

434 positive activation volume and appreciable fluorine content for the apatite sample, the
435 monovalent fluorine anion was considered to be the main charge carrier for apatite
436 under high-temperature and high-pressure conditions.

437

### Implications

438 All of the previously available evidences from experimental petrology, isotopic 439 geochemistry and field geophysics have revealed that apatite is a typical volatile-440 bearing mineral formed on the geotectonic environments of hydrothermal metasomatism (Roden et al. 1984; O'Reilly and Griffin 2000; Morishita et al. 2008; 441 442 Marocchi et al. 2009; Efimov et al. 2012). As two correlated volatile-bearing 443 accessory minerals, apatite and phlogopite are mutually accompanied, which are 444 mainly enriched in the peridotite-predominated Earth mantle. As pointed out by 445 Morishita et al. (2003, 2008), the field petrological observations and ion microprobe 446 isotopic dating results have already confirmed that the highly metasomatized Finero phlogopite-peridotite massif was widely existed as an apatite-rich peridotite layer 447 448 with its volume percentage of apatite up to 10% in the region of Italian Western Alps. 449 For the representative electrical conductivity anomaly from the field geophysical 450 magnetotelluric results in western Junggar of Xinjiang autonomous region, the high 451 electrical conductivity with the corresponding magnitude of  $\sim 10^{-2}$ -1 S/m from Xu et 452 al. (2020) is caused by the existence of four main volatile-bearing metasomatism 453 minerals (i.e., apatite, phlogopite, lawsonite and amphibole).

454 In order to explore the effect of the volume percentage of apatite on the electrical conductivity of accessory mineralogical associations for the volatile-bearing 455 456 metasomatism minerals in the peridotite-predominated Earth mantle, we constructed a phlogopite-apatite-peridotite rock system at high temperature and high pressure. 457 458 Previously available field petrological results indicated that the variation of 459 mineralogical volume fraction for two coexisting mineralogical associations of apatite 460 and phlogopite falls within the range of 1-10% in mantle peridotite (Griffin et al. 461 1984; O'Reilly 1987; O'Reilly and Griffin 2000; Morishita et al. 2003, 2008). To 462 efficiently assess the contribution of apatite on the electrical conductivity of the 463 phlogopite-apatite-peridotite rock system, three typical petrological average schemes 464 including the parallel, Hashin-Shtrikman upper bound and average models were 465 selected to calculate the electrical conductivity of sample at temperature range of 466 973–1373 K and 2.0 GPa. As noted by Xu et al. (2000), the parallel model stands for 467 the maximum value among the petrological average schemes from the laboratory-468 based electrical conductivity results on three-phase (or two-phase) system at high 469 temperature and high pressure. A detailed parallel model ( $\sigma_P$ ) can be described as,

470

$$\sigma_{\rm P} = f_{\rm Ap} \sigma_{\rm Ap} + f_{\rm Phl} \sigma_{\rm Phl} + f_{\rm Peri} \sigma_{\rm Peri} \tag{9}$$

471 where  $f_{Ap}$ ,  $f_{Phl}$  and  $f_{Peri}$  are the volume fractions of apatite single crystal, phlogopite 472 single crystal and peridotite, respectively; Ap, Phl and Peri represent apatite single 473 crystal, phlogopite single crystal and peridotite, respectively;  $\sigma_{Ap}$ ,  $\sigma_{Phl}$  and  $\sigma_{Peri}$  are the 474 electrical conductivity of apatite single crystal, phlogopite single crystal and peridotite,

### 475 respectively.

The middle Hashin–Shtrikman upper bound model ( $\sigma_{HS+}$ ) is an efficient petrological average scheme to fit and calculate the electrical conductivity results of three–phase (or two–phase) system (Hashin and Shtrikman 1962; Hu et al. 2022a), which is described as,

480 
$$\sigma_{\rm HS^+} = \sigma_{\rm Phl} + \frac{A_1}{1 - A_1 (3\sigma_{\rm Phl})^{-1}}$$
(10)

481 
$$A_{1} = \frac{f_{Ap}}{(\sigma_{Ap} - \sigma_{Phl})^{-1} + (3\sigma_{Phl})^{-1}} + \frac{f_{Peri}}{(\sigma_{Peri} - \sigma_{Phl})^{-1} + (3\sigma_{Phl})^{-1}}$$
(11)

As usual, the lower average model ( $\sigma_A$ ) is adopted to transform the electrical conductivity results of three constituent mineral single crystals (or two mineral single erystals) into the electrical conductivity of rock system (Dai and Karato 2014a; Dai et al. 2018a). Detailed average model for three–phase (or two–phase) system is exhibited as follows,

487 
$$\sigma_{\rm A} = \frac{\sigma_{\rm p} + \sigma_{\rm s} + \sqrt{(\sigma_{\rm p} + \sigma_{\rm s})^2 + 32\sigma_{\rm p}\sigma_{\rm s}}}{8} \tag{12}$$

488 
$$\sigma_{\rm S} = \frac{f_{\rm Ap}\sigma_{\rm Phl}\sigma_{\rm Peri} + f_{\rm Phl}\sigma_{\rm Ap}\sigma_{\rm Peri} + f_{\rm Peri}\sigma_{\rm Ap}\sigma_{\rm Phl}}{\sigma_{\rm Ap}\sigma_{\rm Phl}\sigma_{\rm Peri}}$$
(13)

489 where  $\sigma_P$  is the parallel model for the electrical conductivity of the phlogopite– 490 apatite–peridotite rock system from equation (9);  $\sigma_S$  is the series model for the 491 electrical conductivity of the phlogopite–apatite–peridotite rock system.

Figure 10 shows the functional dependence relation for the volume percentages of apatite ranging from 1% to 10% on the electrical conductivity of the phlogopite– apatite–peridotite rock system under three controlled petrological average schemes at temperature range of 973–1373 K and 2.0 GPa. Wherein, the electrical conductivity

496 of apatite is chosen from the average model of our present obtained anisotropic 497 electrical conductivity results. In order to profoundly illustrate the variation of volume 498 percentage on the electrical conductivity of the phlogopite-apatite-peridotite rock 499 system, previously classic electrical conductivity results on phlogopite single crystals 500 reported by Li et al. (2016) and dry peridotite originated from Dai et al. (2008) were 501 also adopted. As a whole, with increasing temperature, the electrical conductivity of 502 the phlogopite-apatite-peridotite rock system increases at each fixed petrological 503 average scheme, accordingly. Under conditions of three typical temperature points 504 (i.e., 973 K, 1173 K and 1373 K) and a constant volume percentage, the electrical 505 conductivity of the phlogopite-apatite-peridotite rock system of Hashin-Shtrikman 506 upper bound model ( $\sigma_{\text{HS}+}$ ) is slightly lower than that of parallel model ( $\sigma_{\text{P}}$ ), and ~2.8 507 times higher than that of average model ( $\sigma_A$ ). As far as different petrological average 508 schemes, the electrical conductivity of the phlogopite-apatite-peridotite rock system 509 exhibits a similar tendency with the variation of volume percentages for apatite, i.e. 510 the electrical conductivity of the phlogopite-apatite-peridotite rock system increases 511 with the reduction in the content of apatite.

512 For a typical Hashin–Shtrikman upper bound model, the electrical conductivity– 513 depth profile for peridotite containing the 10% volume percentage of apatite was 514 established by converting the conductivity–temperature data into conductivity–depth 515 results. At the same time, the electrical conductivity results on other three 516 representative volatile–bearing metasomatism mineral single crystals (i.e., phlogopite,

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517 lawsonite and amphibole) were also compared in detail. The electrical conductivity 518 results on the single crystals of phlogopite, lawsonite and amphibole originated from 519 Li et al. (2016), Manthilake et al. (2015) and Hu et al. (2018), respectively. In order to 520 simplify the electrical conductivity-depth profile model, some indispensable 521 assumptions and extrapolations were proposed as follows, (1) the effects from water 522 of VMMs either the existing species of hydroxyl (i.e., apatite, phlogopite and 523 amphibole) or molecular structure (lawsonite) on the electrical conductivity of 524 peridotite containing the volume percentage of 10% VMMs, and their corresponding 525 partitioning coefficients between VMMs (i.e., apatite, phlogopite, amphibole and 526 lawsonite) and peridotite are inevitable, however, they are beyond our present 527 research range; (2) a feeble influence of pressure on the electrical conductivity of 528 apatite was observed ranging from 1.0 GPa to 3.0 GPa in the present study, which was 529 ignored during the construction of electrical conductivity-depth profile; (3) our 530 present high-temperature and high-pressure impedance spectroscopy measurements 531 were conducted under the control of Ni-NiO solid buffer, which was employed to 532 represent the oxygen fugacity in the upper Earth mantle (Dai et al. 2013); (4) 533 previously available results have indicated that grain boundary electrical conductivity 534 is negligible when compared with grain interior electrical conductivity and total 535 electrical conductivity (Dai et al. 2008; Yang and Heidelbach 2012), and thus, we need not consider the influence of grain boundary on the electrical conductivity for 536 537 the system of the peridotite plus the individual VMMs (i.e., apatite, phlogopite,

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538 amphibole and lawsonite); (5) the chemical compositions of dry peridotite from Dai et 539 al. (2008), and four typical volatile-bearing metasomatism mineral single crystals for 540 phlogopite from Li et al. (2016), lawsonite from Manthilake et al. (2015), amphibole 541 from Hu et al. (2018), as well as our present measured apatite with its corresponding 542 stoichiometric composition of Ca5.25(PO4)3F1.23Cl0.05 were adopted to represent the 543 mineralogical compositions of peridotite and various VMMs in western Junggar of 544 Xinjiang autonomous region, respectively, and the volume percentage of each VMM 545 in the dry peridotite is fixed at 10%; (6) the electrical conductivity results of peridotite 546 and various VMMs were properly extended on the basis of their respective electrical 547 conductivity-temperature dependence relation, as well as previously observed 548 temperature-induced dehydration of lawsonite from Manthilake et al. (2015) and 549 oxidation-dehydrogenation reaction of amphibole from Hu et al. (2018) were fully 550 considered; (7) previously available geothermal results suggested that the geothermal 551 gradients in western Junggar of Xinjiang autonomous region fall within the range of 552 11.6-27.6 K/km (Rao et al. 2013), therefore, we adopted 11.6 K/km and 27.6 K/km to 553 stand for the lower boundary and upper boundary of geothermal gradients in the 554 western Junggar of Xinjiang autonomous region, respectively; (8) except for our 555 present detailed investigation on the orientation-related electrical conductivity of apatite, some representative high-conductivity accessory minerals (such as magnetite, 556 557 chromite and ilmenite) have an important influence on the electrical conductivity of 558 dry peridotite (or olivine polycrystalline aggregates), which have been deeply

investigated in our recently reported results (Dai et al. 2019; Sun et al. 2021, 2022),
thus, we need not consider them in this study.

561 Figure 11 displays the electrical conductivity-depth profile of peridotite containing the 10% volume percentage of apatite under two geothermal gradients of 562 563 11.6 K/km and 27.6 K/km at depth range of 20-90 km. Previously available results 564 for the field MT data in western Junggar of Xinjiang autonomous region from Zhang 565 et al. (2017) and Xu et al. (2020), as well as the electrical conductivity results for other 566 three VMMs (i.e., phlogopite, amphibole and lawsonite) are comprehensively 567 considered. As a whole, the electrical conductivity of peridotite containing the 10% 568 volume percentage of apatite increases gradually with the depth under two 569 representative geothermal gradients of 11.6 K/km and 27.6 K/km. For the electrical 570 conductivity of peridotite containing the 10% volume percentage of lawsonite, an 571 abrupt change is observed at depths of ~30 km and ~76 km for the corresponding 572 geothermal gradients of 27.6 K/km and 11.6 K/km, respectively, which can be 573 resulted in by the temperature-induced dehydration effect of lawsonite. The electrical 574 conductivity of peridotite containing the 10% volume percentage of amphibole also 575 exhibits a sudden discontinuity at the temperature of ~873 K due to the oxidation-576 dehydrogenation reaction of amphibole. At a certain depth, when the geothermal gradient is increased from the lower boundary of 11.6 K/km to the upper boundary of 577 27.6 K/km, there exists the differentiation of ~4 orders of magnitude in the electrical 578 579 conductivity of the 10% volume percentage of VMMs-containing peridotite. At a

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580 constant geothermal gradient, the electrical conductivity of peridotite containing the 581 10% volume percentage of apatite is lower than those of peridotite containing other 582 various 10% volume percentage of VMMs (i.e., phlogopite, lawsonite and amphibole), 583 and their conductivity-depth curves gradually converge with increasing depth. For the 584 lower boundary geothermal gradient of 11.6 K/km in the western Junggar of Xinjiang 585 autonomous region, it is evident that the electrical conductivity of peridotite with the 10% volume percentage of apatite is close to  $\sim 10^{-2}$  S/m at a depth of 90 km, which is 586 lower than that of the high conductivity zone. Therefore, the presence of the 10% 587 588 volume percentage of apatite in peridotite cannot explain the high conductivity 589 anomalies at a low geothermal gradient of 11.6 K/km, which may be closely related to 590 the presences of phlogopite and lawsonite. As far as the upper boundary geothermal 591 gradient of 27.6 K/km in the western Junggar of Xinjiang autonomous region, the 592 electrical conductivity of peridotite with the 10% volume percentage of apatite reaches  $\sim 10^{-1.8}$  S/m at a depth of  $\sim 40$  km, which corresponds to the highest 593 594 measurement temperature of 1373 K in this study. The maximum electrical 595 conductivity of peridotite containing the 10% volume percentage of apatite is also 596 slightly lower than that of the high conductivity zone. Thus, the presence of the 10% 597 volume percentage of apatite in peridotite still cannot explain the high conductivity anomalies at the geothermal gradient of 27.6 K/km, which may be closely related to 598 599 the presences of phlogopite, lawsonite and amphibole. In summary, the presence of 600 apatite in peridotite cannot explain the high conductivity anomalies for the lower

boundary of 11.6 K/km and upper boundary of 27.6 K/km in western Junggar of
Xinjiang autonomous region, it can provide a reasonable constraint on those of
apatite-rich areas with relativity high resistivity.

Although our present obtained anisotropic electrical conductivity results of 604 605 apatite single crystals cannot explain the high conductivity anomalies, it is crucial to 606 deeply understand the geological cycle of halogen family element in the deep interior. 607 As the most important endmember among phosphate minerals, fluorapatite contains a large number of volatile components. Previously available geological evidences have 608 609 already confirmed that the average concentration of fluorine element in the deep 610 Earth's crust is approximate to 800 ppm wt, which mainly existed as the fluorine-rich 611 minerals of apatite and fluorspar (Barth 1947). As a predominated fluorine-bearing 612 phosphate mineral, apatite is widely distributed in a large number of basic-acid 613 igneous rocks (e.g., basalt, gabbro, granite, etc.) and regional metamorphic rocks (e.g., 614 schist, gneiss, carbonaceous slate, etc.). In the recent several years, in order to explain 615 the high electrical conductivity anomalies in some representative geotectonic units of 616 the Tibetan Plateau, southern India and Dabie-Sulu ultrahigh-pressure metamorphic 617 belt, there are a large quantity of electrical conductivity results to be reported on those 618 of basic-acid igneous rocks and regional thermal metamorphic rocks under high-619 temperature and high-pressure conditions (Dai et al. 2014, 2015, 2018b; Sun et al. 2019a, b, c). In comprehensive consideration of our present obtained anisotropic 620 621 electrical conductivity results on apatite at high temperature and high pressure, it is

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622 crucial to deeply understand the geochemical cycle of fluorine element in the deep 623 interior of the Earth. In addition, owing to the unique chemical and mineralogical 624 compositions for the existence of multi-component magmatic volatiles (e.g., fluorine, 625 chlorine and hydroxyl) in apatite, it is extremely widely applied in the field of many 626 regional magmatic hydrothermal deposits, such as the porphyry-type copper deposit 627 in the region of the American southwestern New Mexico, the porphyry-skarn type of 628 gold-copper deposit in the region of the Chinese southwestern Ailaoshan-Red River 629 belt and the porphyry-skarn type of iron-gold-copper deposit in the region of the 630 southern Peru's Andahuaylas-Yauri batholith (Huang et al. 2023). As a crucial 631 mineralization tracer, all of these volatile-related parameters including fluorine 632 content, chlorine content, as well as the ratio of fluorine and chlorine in apatite can be 633 used to efficiently explain the petrogenetic-metallogenic mechanism during the deep-634 related fluid exsolution processes in the regions of synsubduction, continental 635 collision and intracontinental environments (Huang et al. 2023). Whereas, it is well 636 known that the electrical conductivity of relevant minerals and rocks is also highly 637 sensitive to the variations of volatile content at high temperature and high pressure. In 638 conclusion, more and more researches on high-pressure electrical conductivity 639 experiments for those of apatite family minerals are indispensable to be deeply investigated in the future. 640

641

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659	References
660	Barth, T.F. (1947) On the geochemical cycle of fluorine. The Journal of Geology, 55, 5,
661	420–426.
662	Brenan, J. (1994) Kinetics of fluorine, chlorine and hydroxyl exchange in fluorapatite.
663	Chemical Geology, 110, 195–210.
664	Brunet, F., Allan, D.R., Redfern, S.A.T., Angel, R.J., Miletich, R., Reichmann, H.J.,
665	Sergent, J., and Hanfland, M. (1999) Compressibility and thermal expansivity of
666	synthetic apatites, $Ca_5(PO_4)_3X$ with $X = OH$ , F and Cl. European Journal of
667	Mineralogy, 11, 1023–1035.
668	Cherniak, D.J. (2010a) Diffusion in carbonates, fluorite, sulfide minerals, and diamond.
669	Reviews in Mineralogy and Geochemistry, 72, 871–897.
670	Cherniak, D.J. (2010b) Diffusion in accessory minerals: Zircon, titanite, apatite,
671	monazite and xenotime. Reviews in Mineralogy and Geochemistry, 72, 1, 827-
672	869.
673	Comodi, P., Liu, Y., Zanazzi, P.F., and Montagnoli, M. (2001a) Structural and
674	vibrational behaviour of fluorapatite with pressure. Part I: in situ single-crystal
675	X-ray diffraction investigation. Physics and Chemistry of Minerals, 28, 219–224.
676	Comodi, P., Liu, Y., and Frezzotti, M. L. (2001b) Structural and vibrational behaviour
677	of fluorapatite with pressure. Part II: in situ micro-Raman spectroscopic
678	investigation. Physics and Chemistry of Minerals, 28, 225-231.
679	Dai, L.D., and Karato, S. (2014a) High and highly anisotropic electrical conductivity of
680	the asthenosphere due to hydrogen diffusion in olivine. Earth and Planetary
681	Science Letters, 408, 79–86.
682	Dai, L.D., and Karato, S. (2014b) The effect of pressure on the electrical conductivity
683	of olivine under the hydrogen-rich conditions. Physics of the Earth and Planetary
684	Interiors, 232, 51–56.
685	Dai, L.D., and Karato, S. (2020) Electrical conductivity of Ti-bearing hydrous olivine

aggregates at high temperature and high pressure. Journal of Geophysical
Research: Solid Earth, 125, e2020JB020309.

- Dai, L.D., Li, H.P., Hu, H.Y., and Shan, S.M. (2008) Experimental study of grain
  boundary electrical conductivities of dry synthetic peridotite under
  high-temperature, high-pressure, and different oxygen fugacity conditions.
  Journal of Geophysical Research: Solid Earth, 113, B12211.
- Dai, L.D., Li, H.P., Hu, H.Y., Shan, S.M., Jiang, J.J., and Hui, K.S. (2012) The effect of
  chemical composition and oxygen fugacity on the electrical conductivity of dry
  and hydrous garnet at high temperatures and pressures. Contributions to
  Mineralogy and Petrology, 163, 4, 689–700.
- Dai, L.D., Li, H.P., Hu, H.Y., Jiang, J.J., Hui, K.S., and Shan, S.M. (2013) Electrical
  conductivity of Alm<sub>82</sub>Py<sub>15</sub>Grs<sub>3</sub> almandine-rich garnet determined by impedance
  spectroscopy at high temperatures and high pressures. Tectonophysics, 608, 1086–
  1093.
- Dai, L.D., Hu, H.Y., Li, H.P., Jiang, J.J., and Hui, K.S. (2014) Effects of temperature,
  pressure and chemical composition on the electrical conductivity of granite and its
  geophysical implications. American Mineralogist, 99, 1420–1428.
- Dai, L.D., Jiang, J.J., Li, H.P., Hu, H.Y., and Hui, K.S. (2015) Electrical conductivity of
  hydrous natural basalts at high temperatures and pressures. Journal of Applied
  Geophysics, 112, 290–297.
- Dai, L.D., Hu, H.Y., Li, H.P., Wu, L., Hui, K.S., Jiang, J.J., and Sun, W.Q. (2016)
  Influence of temperature, pressure, and oxygen fugacity on the electrical
  conductivity of dry eclogite, and geophysical implications. Geochemistry,
  Geophysics, Geosystems, 17, 6, 2394–2407.
- Dai, L.D., Hu, H.Y., Li, H.P., Sun, W.Q., and Jiang, J.J. (2018a) Influence of anisotropy
  on the electrical conductivity and diffusion coefficient of dry K-feldspar:
  Implications of the mechanism of conduction. Chinese Physics B, 27, 2, 028703.
- 713 Dai, L.D., Sun, W.Q., Li, H.P., Hu, H.Y., Wu, L., and Jiang, J.J. (2018b) Effect of

- chemical composition on the electrical conductivity of gneiss at high temperatures
  and pressures. Solid Earth, 9, 233–245.
- 716 Dai, L.D., Hu, H.Y., Sun, W.Q., Li, H.P., Liu, C.C., and Wang, M.Q. (2019) Influence
- of high conductive magnetite impurity on the electrical conductivity of dry olivine
  aggregates at high temperature and high pressure. Minerals, 9, 44.
- Dai, L.D., Hu, H.Y., He, Y., and Sun, W.Q. (2022) Some new progress in the
  experimental measurements on electrical property of main minerals in the upper
  mantle at high temperatures and high pressures. In Mineralogy edited by Miloš
  René, IntechOpen, London, United Kingdom, pp. 15–38.
- Evans, R.L., Hirth, G., Baba, K., Forsyth, D., Chave, A., and Makie, R. (2005)
  Geophysical evidence from the MELT area for compositional control on oceanic
  plates. Nature, 437, 249–252.
- Efimov, A.A., Ronkin, Y.L., Malich, K.N., and Lepikhina, G.A. (2012) New Sm-Nd
  and Rb-Sr (ID-TIMS) isotope data for apatite-phlogopite clinopyroxenites from
  the dunite "Core" of the Konder Massif, Aldan Shield, Yakutia. Doklady Earth
  Sciences, 445, 956–961.
- Förster, M.W., and Selway, K. (2021) Melting of subducted sediments reconciles
  geophysical images of subduction zones. Nature Communications, 12, 1320.
- Griffin, W.L., Wass, S.Y., and Hollis, J.D. (1984) Ultramafic xenoliths from
  Bullenmerri and Gnotuk maars, Victoria, Australia: Petrology of a subcontinental
- crust-mantle transition. Journal of Petrology, 25, 53–87.
- Hamilton, M.P., Jones, A.G., Evans, R.L., Evans, S., Fourie, C.J.S., Garcia, X.,
  Mountford, A., and Spratt, J.E. (2006) Electrical anisotropy of South Africa
  lithosphere compared with seismic anisotropy from shear-wave splitting analyses.
  Physics of the Earth and Planetary Interiors, 158, 226–239.
- Hashin, Z., and Shtrikman, S. (1962) A variational approach to the theory of the
  effective magnetic permeability of multiphase materials. Journal of Applied
- 741 Physics, 33, 10, 3125–3131.

- 742 Hong, M.L., Dai, L.D., Hu, H.Y., and Zhang, X.Y. (2022) Pressure-induced structural
- phase transitions in natural kaolinite investigated by Raman spectroscopy and
  electrical conductivity. American Mineralogist, 107, 385–394.
- Hu, H.Y., Dai, L.D., Li, H.P., Hui, K.S., and Li, J. (2015) Temperature and high
  pressure dependence of electrical conductivity in synthetic anorthite. Solid State
  Ionics, 276, 136–141.
- Hu, H.Y., Dai, L.D., Li, H.P., Hui, K.S., and Sun, W.Q. (2017) Influence of dehydration
  on the electrical conductivity of epidote and implications for high conductivity
  anomalies in subduction zones. Journal of Geophysical Research: Solid Earth, 122,
  2751–2762.
- Hu, H.Y., Dai, L.D., Li, H.P., Sun, W.Q., and Li, B.S. (2018) Effect of dehydrogenation
  on the electrical conductivity of Fe-bearing amphibole: Implications for high
  conductivity anomalies in subduction zones and continental crust. Earth and
  Planetary Science Letters, 498, 27–37.
- Hu, H.Y., Dai, L.D., Sun, W.Q., Wang, M.Q., and Jing, C.X. (2022a) Constraints on
  fluids in the continental crust from laboratory-based electrical conductivity
  measurements of plagioclase. Gondwana Research, 107, 1–12.
- 759 Hu, H.Y., Dai, L.D., Sun, W.Q., Zhuang, Y.K., Liu, K.X., Yang, L.F., Pu, C., Hong,
- 760 M.L., Wang, M.Q., Hu, Z.M., Jing, C.X., Li, C., Yin, C.Y., and Paramasivam, S.
- (2022b) Some remarks on the electrical conductivity of hydrous silicate minerals
  in the earth crust, upper mantle and subduction zone at high temperatures and high
  pressures. Minerals, 12, 161.
- Huang, M.L., Zhu, J.J., Chiaradia, M., Hu, R.Z., Xu, L.L., and Bi, X.W. (2023) Apatite
  volatile contents of porphyry Cu deposits controlled by depth-related fluid
  exsolution processes. Economic Geology, in press,
  https://doi.org/10.5382/econgeo.5000.
- 768 Huebner, J.S., and Voigt, D.E. (1988) Electrical conductivity of diopside: Evidence for
- 769 oxygen vacancies. American Mineralogist, 73, 1235–1254.

770	Huebner, J.S., and Dillenburg, R.G. (1995) Impedance spectra of hot, dry silicate
771	minerals and rock: Qualitative interpretation of spectra. American Mineralogist,
772	80, 46–64.

- 773Konzett, J., and Frost, D.J. (2009) The high P-T stability of hydroxylapatite in natural774and simplified MORB-an experimental study to 15 GPa with implications for775transport and storage of phosphorus and halogens in subduction zones. Journal of776Petrology, 50, 2043–2062.
- 777 Li, W., Chakraborty, S., Nagashima, K., and Costa, F. (2020) Multicomponent diffusion
- of F, Cl and OH in apatite with application to magma ascent rates. Earth andPlanetary Science Letters, 550, 116545.
- Li, Y., Yang, X.Z., Yu, J.H., and Cai, Y.F. (2016) Unusually high electrical conductivity
  of phlogopite: The possible role of fluorine and geophysical implications.
  Contributions to Mineralogy and Petrology, 171, 37.
- Li, Y., Jiang, H.T, and Yang, X.Z. (2017) Fluorine follows water: Effect on electrical
  conductivity of silicate minerals by experimental constraints from phlogopite.
  Geochimica et Cosmochimica Acta, 217, 16–27.
- 786 Liu, Y., Junge, A., Yang, B., Löwer, A., Cembrowski, M., and Xu, Y.X. (2019a)
- Electrically anisotropic crust from three–dimensional magnetotelluric modeling in
  the western Junggar, NW China. Journal of Geophysical Research: Solid Earth,
  124, 9474–9494.
- Liu, H.Y., Zhu, Q., and Yang, X.Z. (2019b) Electrical conductivity of fluorite and
  fluorine conduction. Minerals, 9, 72.
- 792 Manthilake, G., Mookherjee, M., Bolfan-Casanova, N., and Andrault, D. (2015)
- Electrical conductivity of lawsonite and dehydrating fluids at high pressures and
  temperatures. Geophysical Research Letters, 42, 18, 7398–7405.
- 795 Manthilake, G., Bolfan–Casanova, N., Novella, D., Mookherjee, M., and Andrault, D.
- 796 (2016) Dehydration of chlorite explains anomalously high electrical conductivity
- in the mantle wedges. Science Advances, 2, e1501631.

798	Manthilake, G., Koga1, K.T., Ye, P., and Mookherjee, M. (2021a) Halogen bearing
799	amphiboles, aqueous fluids, and melts in subduction zones: Insights on halogen
800	cycle from electrical conductivity. Journal of Geophysical Research: Solid Earth,
801	126, 3, 021339.
802	Manthilake, G., Ye, P., Koga1, K.T., and Mookherjee, M. (2021b) Tracking slab surface
803	temperatures with electrical conductivity of glaucophane. Scientific Reports, 11,
804	18014.
805	Marocchi, M., Mair, V., Tropper, P., and Bargossi, G.M. (2009) Metasomatic reaction
806	bands at the Mt. Hochwart gneiss-peridotite contact (Ulten Zone, Italy): Insights
807	into fluid-rock interaction in subduction zones. Mineralogy and Petrology, 95,
808	251–272.
809	Matsukage, K.N., Ono, S., Kawamoto, T., and Kikegawa, T. (2004) The
810	compressibility of a natural apatite. Physics and Chemistry of Minerals, 31, 580-
811	584.
812	McKenzie, D., and Bickle, M.J. (1988) The volume and composition of melt generated
813	by extension of the lithosphere. Journal of Petrology, 29, 625-679.
814	Morishita, T., Araic, S., and Tamura, A. (2003) Petrology of an apatite-rich layer in
815	the Finero phlogopite-peridotite, Italian Western Alps; implications for evolution
816	of a metasomatising agent. Lithos, 69, 37–49.
817	Morishita, T., Hattori, K.H., Terada, K., Matsumoto, T., Yamamoto, K., Takebe, M.,
818	Ishida, Y., Tamura, A., and Arai, S. (2008) Geochemistry of apatite-rich layers in
819	the Finero phlogopite-peridotite massif (Italian Western Alps) and ion microprobe
820	dating of apatite. Chemical Geology, 251, 99–111.
821	Murayama, J.K., Nakai, S., Kato, M., and Kumazawa, M. (1986) A dense polymorph of
822	Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> : A high pressure phase of apatite decomposition and its geochemical
823	significance. Physics of the Earth and Planetary Interiors, 44, 293–303.
824	Naif, S., Key, K., Constable, S., and Evans, R.L. (2013) Melt-rich channel observed at
825	the lithosphere–asthenosphere boundary. Nature, 495, 356–359.

- 826 O'Reilly, S.Y. (1987) Volatile-rich mantle beneath eastern Australia. In: Nixon, P. H.
- 827 (Ed.), Mantle Xenoliths. Wiley London, pp. 661–670.
- O'Reilly, S.Y., and Griffin, W.L. (2000) Apatite in the mantle: Implications for
  metasomatic processes and high heat production in Phanerozoic mantle. Lithos, 53,
  217–232.
- Özaydın, S., and Selway, K. (2022) The relationship between kimberlitic magmatism
  and electrical conductivity anomalies in the mantle. Geophysical Research Letters,
  49, e2022GL099661.
- Rao, S., Hu, S.B., Zhu, C.Q., Tang, X.Y., Li, W.W., and Wang, J.Y. (2013) The
  characteristics of heat flow and lithospheric thermal structure in Junggar basin,
  northwest China. Chinese Journal of Geophysics, 56, 2760–2770.
- Roden, M.F., Frey, F.A., and Francis, D.M. (1984) An example of consequent mantle
  metasomatism in peridotite inclusions from Nunivak Island, Alaska. Journal of
  Petrology, 2, 546–577.
- Saltas, V., Chatzistamou, V., Pentari, D., Paris, E., Triantis, D., Fitilis, I., and
  Vallianatos, F. (2013) Complex electrical conductivity measurements of a KTB
  amphibolite sample at elevated temperatures. Materials Chemistry and Physics,
  139, 169–175.
- 844 Saltas, V., Pentari, D., and Vallianatos, F. (2020) Complex electrical conductivity of
- 845 biotite and muscovite micas at elevated temperatures: A comparative study.846 Materials, 13, 3513.
- Selway, K. (2014) On the causes of electrical conductivity anomalies in tectonically
  stable lithosphere. Surveys in Geophysics, 35, 219–257.
- Selway, K. (2015) Negligible effect of hydrogen content on plate strength in East
  Africa. Nature Geoscience, 10, 1038.
- 851 Selway, K. (2019) Electrical discontinuities in the continental lithosphere imaged with
- 852 magnetotellurics. In: Lithospheric Discontinuities, 239, AGU Geophysical
- 853 Monograph edited by Huaiyu Yuan and Barbara Romanowicz, pp. 89–110.

854 Selway, K., and O'Donnell, J.P. (2019) A small, unextractable melt fraction as the cause

- for the low velocity zone. Earth and Planetary Science Letters, 517, 117–124.
- 856 Selway, K., O'Donnell, J.P., and Özaydin, S. (2019) Upper mantle melt distribution
- 857 from petrologically constrained magnetotellurics. Geochemistry, Geophysics,
  858 Geosystems, 20, 3328–3346.
- Shannon, R.D. (1976) Revised effective ionic radii and systematic studies of
  interatomic distances in halides and chalcogenides. Acta Crystallographica,
  Section A, 32, 751–767.
- 862 Simpson, F., and Tommasi, A. (2005) Hydrogen diffusivity and electrical anisotropy of
  863 a peridotite mantle. Geophysical Journal International, 160, 1092–1102.
- 864 Sivakumar, A., Suresh, S., Pradeep, J.A., Balachandar, S., and Martin Britto Dhas, S.A.
- 865 (2018) Effect of shock waves on dielectric properties of KDP crystal. Journal of
  866 Electronic Materials, 47, 4831–4839.
- Sivakumar, A., Dhas, S.S.J., Almansour, A.I., Kumar, R.S., Arumugam, N., Prabhu, S.,
  Sivashanmugan, K., Ramesh, R., and Martin Britto Dhas, S.A. (2021) Shock
  waves induced enhancement of electrochemical properties of CoFe<sub>2</sub>O<sub>4</sub>
  nanoparticles for energy storage applications. Surfaces and Interfaces, 27, 101539.
- Sivakumar, A., Mowlika, V., Dhas, S.S.J., Prabhu, S., Ramesh, R., Robert, R., and
  Martin Britto Dhas, S.A. (2022) Shock wave induced switchable electrical
- resistance of ZnFe<sub>2</sub>O<sub>4</sub> nanoparticles. Solid State Sciences, 125, 106843.
- Sun, W.Q., Dai, L.D., Li, H.P., Hu, H.Y., Wu, L., and Jiang, J.J. (2017) Electrical
  conductivity of mudstone (before and after dehydration at high *P*–*T*) and a test of
  high conductivity layers in the crust. American Mineralogist, 102, 2450–2456.
- 877 Sun, W.Q., Dai, L.D., Li, H.P., Hu, H.Y., and Liu, C.C. (2019a) Effect of temperature,
- pressure and chemical composition on the electrical conductivity of granulite and
  geophysical implications. Journal of Mineralogical and Petrological Sciences, 114,
  880 87–98.
- 881 Sun, W.Q., Dai, L.D., Li, H.P., Hu, H.Y., Liu, C.C., and Wang, M.Q. (2019b) Effect of 41

- temperature, pressure and chemical compositions on the electrical conductivity of
  schist: Implications for electrical structures under the Tibetan plateau. Materials,
  12, 961.
- Sun, W.Q., Dai, L.D., Li, H.P., Hu, H.Y., Jiang, J.J., and Liu, C.C. (2019c)
  Experimental study on the electrical properties of carbonaceous slate: A special
  natural rock with unusually high conductivity at high temperatures and pressures.
  High Temperatures-High Pressures, 48, 455–467.
- Sun, W.Q., Dai, L.D., Li, H.P., Hu, H.Y., Jiang, J.J., and Wang, M.Q. (2020) Electrical
  conductivity of clinopyroxene–NaCl–H<sub>2</sub>O system at high temperatures and
  pressures: Implications for high-conductivity anomalies in the deep crust and
  subduction zone. Journal of Geophysical Research: Solid Earth, 125,
  e2019JB019093.
- Sun, W.Q., Jiang, J.J., Dai, L.D., Hu, H.Y., Wang, M.Q., Qi, Y.Q., and Li, H.P. (2021)
  Electrical properties of dry polycrystalline olivine mixed with various chromite
  contents: Implications for the high conductivity anomalies in subduction zones.
  Geoscience Frontiers, 12, 5, 101178.
- 898 Sun, W.Q., Dai, L.D., Hu, H.Y., Wang, M.Q., Hu, Z.M., and Jing, C.X. (2022)
- Experimental research on electrical conductivity of the olivine–ilmenite system at
  high temperatures and high pressures. Frontiers in Earth Sciences, 10, 681003.
- Wang, K.L., Zhang, Y., and Naab, F.U. (2011) Calibration for IR absorbance
  measurements of OH in apatite. American Mineralogist, 96, 1392–1397.
- Xu, Y.S., Shankland, T.J., and Duba, A.G. (2000) Pressure effect on electrical
  conductivity of mantle olivine. Physics of the Earth and Planetary Interiors, 118, 1,
  149–161.
- 906 Xu, Y.X., Yang, B., Zhang, S., Liu, Y., Zhu, L.P., Huang, R., Chen, C., Li, Y.T., and Luo,
- 907 Y.H. (2016) Magnetotelluric imaging of a fossil Paleozoic intraoceanic subduction
  908 zone in western Junggar, NW China. Journal of Geophysical Research: Solid
- 909 Earth, 121, 4103–4117.

42

- 910 Xu, Y.X., Yang, B., Zhang, A.Q., Wu, S.C., Zhu, L., Yang, Y.J., Wang, Q.Y., and Xia,
- 911 Q.K. (2020) Magnetotelluric imaging of a fossil oceanic plate in northwestern
- 912 Xinjiang, China. Geology, 48, 4, 385–389.
- 913 Yang, X.Z. (2012) Orientation-related electrical conductivity of hydrous olivine,
- clinopyroxene and plagioclase and implications for the structure of the lower
  continental crust and uppermost mantle. Earth and Planetary Science Letters, 317–
  318, 241–250.
- 917 Yang, X.Z., and McCammon, C. (2012) Fe<sup>3+</sup>-rich augite and high electrical
  918 conductivity in the deep lithosphere. Geology, 40, 2, 131–134.
- Yang, X.Z., and Heidelbach, F. (2012) Grain size effect on the electrical conductivity of
  clinopyroxene. Contributions to Mineralogy and Petrology, 163, 939–947.
- Ye, P., Manthilake, G., and Mookherjee, M. (2022) Electrical conductivity of
  metasomatized lithology in subcontinental lithosphere. American Mineralogist,
  107, 413–420.
- 924 Zhang, S., Xu, Y.X., Jiang, L., Yang, B., Liu, Y., Griffin, W.L., Luo, Y., Huang, R.,
- 925 Zhou, Y., and Zhang, L.L. (2017) Electrical structures in the northwest margin of
- 926 the Junggar basin: Implications for its late Paleozoic geodynamics.
  927 Tectonophysics, 717, 473–483.

### 928 Figure captions:

Figure 1. The optical microscopic observation (a) and the corresponding crystallinestructure (b) of apatite single crystal.

**Figure 2.** Fourier transform infrared (FT–IR) spectroscopy of apatite single crystals before and after electrical conductivity measurements at the wavenumber range of 3000–4000 cm<sup>-1</sup>. The water contents for starting and recovered samples were calculated as 176.69 ppm wt and 134.87 ppm wt, respectively, which suggested no clear water loss during the process of electrical conductivity measurements.

936 Figure 3. Cross-section diagram of the sample assemblage for high-pressure
937 impedance spectroscopy measurements.

938 Figure 4. Representative complex impedance spectra for apatite single crystal along 939 the [010] crystallographic orientation at conditions of 973-1373 K and 2.0 GPa. 940 Wherein, Z and Z' are the real and imaginary parts of the complex impedance 941 spectroscopy, respectively. An equivalent circuit composed of the series conjunction of 942 parallel  $R_{\rm S}$ -CPE<sub>S</sub> and parallel  $R_{\rm E}$ -CPE<sub>E</sub> was selected to fit the impedance semicircular 943 arc.  $R_{\rm S}$  and CPE<sub>S</sub> stand for the electrical resistance and the constant phase element of 944 the sample, respectively;  $R_{\rm E}$  and  $CPE_{\rm E}$  represent the electrical resistance and the 945 constant phase element from the polarization effect of the sample-electrode interface, 946 respectively.

Figure 5. Logarithmic electrical conductivity of apatite single crystal along the [001]
crystallographic orientation as a function of reciprocal temperature in two continuous
heating-cooling cycles at 973–1373 K and 3.0 GPa.

Figure 6. Influence of pressure on the electrical conductivity of apatite single crystals
along the [001] crystallographic orientation at temperature range of 973–1373 K.

**Figure 7.** Electrical conductivity of apatite single crystals along three main [001], [100] and [010] crystallographic orientations at conditions of 973–1373 K and 2.0 GPa. We also compared it with the fitting conductivity results by virtue of three representative averaging schemes of series model ( $\sigma_{\rm S}$ ), parallel model ( $\sigma_{\rm P}$ ) and average model ( $\sigma_{\rm A}$ ) in detail. The electrical conductivity of the background of magnesium oxide is also included under conditions of wider temperature range from 1073 K to 1523 K and 2.0 GPa.

959 Figure 8. The degree of electrical conductivity anisotropy for apatite single crystal as 960 a function of temperature from 900 K to 1700 K, and the comparison with hydrous 961 olivine single crystal from Dai and Karato (2014a) and olivine with the 10% volume 962 percentage of apatite calculated using our present anisotropic electrical conductivity 963 data and Hashin-Shtrikman upper bound model. The brown region stands for the 964 temperature range of 1550–1650 K in the asthenosphere (McKenzie and Bickle 1988). 965 The blue region represents the degree of electrical conductivity anisotropy in the 966 asthenosphere by a factor of  $\sim 2-3$  higher along the flow direction on the horizontal 967 plane (Evans et al. 2005; Naif et al. 2013). These conductivity anisotropy results for 968 the mineral single crystals can be transformed into the conductivity anisotropy of 969 anisotropic aggregates by using numerical research to be reported by Simpson and 970 Tommasi (2005).

**Figure 9.** Comparisons of the anisotropic electrical conductivity results of apatite single crystals and other three VMMs (i.e., phlogopite, amphibole and lawsonite). The lines are labeled as follows: (1) Black solid lines represent our present results for the anisotropic electrical conductivity of apatite single crystals along three main [001], [100] and [010] crystallographic orientations; (2) Blue dashed lines represent the electrical conductivity of phlogopite along three main crystalline directions from Li et al. (2016); (3) Green dashed line represents the electrical conductivity of lawsonite

measured by Manthilake et al. (2015), as well as (4) Red dashed line represents the
electrical conductivity of iron-bearing amphibole single crystals investigated by Hu et
al. (2018).

981 Figure 10. Three typical petrological average schemes for the electrical conductivity 982 of the phlogopite-apatite-peridotite rock system with the variation of the volume 983 fractions of apatite ranging from 1% to 10% at temperatures of 973–1373 K and 2.0 984 GPa. All of these solid lines, dashed lines and dotted lines stand for the average model 985  $(\sigma_A)$ , Hashin–Shtrikman upper bound model  $(\sigma_{HS^+})$  and parallel model  $(\sigma_P)$  for the 986 electrical conductivity of the phlogopite-apatite-peridotite rock system, respectively. 987 Electrical conductivity data for apatite single crystals, phlogopite single crystals and 988 dry peridotite were adopted from the average model for our present anisotropic 989 electrical conductivity results, Li et al. (2016) and Dai et al. (2008), respectively.

990 Figure 11. Laboratory-based electrical conductivity-depth profile for peridotite 991 containing the 10% volume percentage of apatite on the basis of our average model 992 for the anisotropic electrical conductivity of apatite and two different geothermal 993 gradients of 11.6 K/km and 27.6 K/km at depth range of 20-90 km. The field MT data 994 in western Junggar of Xinjiang autonomous region from Zhang et al. (2017) and Xu et 995 al. (2020), as well as the previously reported electrical conductivity results for dry 996 peridotite reported by Dai et al. (2008), and other three VMMs of the mineral single 997 crystals (i.e., phlogopite, lawsonite and amphibole) from Li et al. (2016), Manthilake 998 et al. (2015) and Hu et al. (2018) are also included. Wherein, red and blue lines stand 999 for the upper boundary of 27.6 K/km and lower boundary of 11.6 K/km for the 1000 geothermal gradients in the western Junggar of Xinjiang autonomous region, 1001 respectively (Rao et al. 2013); solid, dotted, dash-dot and dashed lines stand for the electrical conductivity of peridotite containing the 10% volume percentage of apatite, 1002 1003 peridotite containing the 10% volume percentage of phlogopite, peridotite containing

1004 the 10% volume percentage of lawsonite and peridotite containing the 10% volume 1005 percentage of amphibole, respectively; the green region stands for the high 1006 conductivity zone with its electrical conductivity values of  $\sim 10^{-2}$ –1 S/m under the 1007 western Junggar of Xinjiang autonomous region at depths of 20–90 km (Xu et al. 1008 2020).

- 1009 TABLE 1. Chemical compositions of the starting and recovered apatite single crystals before and
- 1010 after electrical conductivity measurements.

Compositions	Starting sample (wt.%)	Recovered sample (wt.%)		
$SiO_2$	$0.43\pm0.05$	$0.37\pm0.06$		
FeO	$0.03\pm0.01$	$0.02\pm0.01$		
CaO	$54.93\pm0.05$	$54.88\pm0.10$		
$P_2O_5$	$39.55\pm0.30$	$39.75\pm0.16$		
$SO_3$	$0.67 \pm 0.03$	$0.64\pm0.03$		
SrO	$0.09\pm0.02$	$0.08\pm0.02$		
F	$4.33\pm0.02$	$4.36\pm0.05$		
Cl	$0.23\pm0.01$	$0.24\pm0.02$		
Ce <sub>2</sub> O <sub>3</sub>	$0.43\pm0.02$	$0.42\pm0.07$		
$Nd_2O_3$	$0.13\pm0.03$	$0.16\pm0.04$		
Total	$98.99 \pm 0.24$	$99.03\pm0.30$		

1011

### 1012 TABLE 2. Fitting parameters of the Arrhenius relation for the electrical conductivity of apatite

1013 single crystals along three main crystallographic orientations under conditions of 973–1373 K and

1014 1.0–3.0 GPa.

Run No.	Orientation	<i>T</i> (K)	P (GPa)	$\log \sigma_0$	$\Delta H(\mathrm{eV})$	$R^2$	$\Delta U ({ m eV})$	$\Delta V$
Ap01	[001]	973–1373	1.0	$5.95\pm0.33$	$2.14\pm0.07$	0.9911		-
Ap04	[001]	973–1373	2.0	$6.12\pm0.29$	$2.24\pm0.06$	0.9940	$2.05\pm0.06$	$9.31\pm0.98$
Ap06	[001]	973–1373	3.0	$6.32\pm0.20$	$2.33\pm0.05$	0.9972	-	-
Ap09	[100]	973–1373	2.0	$3.85\pm0.16$	$1.92\pm0.04$	0.9974	_	_
Ap10	[010]	973–1373	2.0	$4.18\pm0.19$	$2.04\pm0.05$	0.9967	_	_

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## Figure 2.



## Figure 3.



## Figure 4.



## Figure 5.



## Figure 6.



## Figure 7.



## Figure 8.



## Figure 9.



# Figure 10.



## Figure 11.

