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1 Revision 2

2 **Impact of fluorine on the thermal stability of phlogopite**

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12 **ABSTRACT**

13 Knowledge of volatile cycling is vital to understand evolution of the planet and  
14 the life it supports. Although it is gradually accepted that the mantle is a vast store  
15 house of H<sub>2</sub>O and other volatiles, the impact of co-existing volatiles on the thermal  
16 stabilities of OH and the lattice of the host mineral is still poorly understood.  
17 Phlogopite is one of the few hydrous minerals capable of carrying both water and  
18 halogens into the mantle. Previous observations from both experiments and textural  
19 relationships in natural samples have indicated that F-rich phlogopite can be stable  
20 under ultra-high-temperature conditions. Here, the impact of F on the thermal stability  
21 of phlogopite was investigated via XRD, Raman, and IR spectroscopy from room  
22 temperature to 1000 to 1200 °C. Based on the experimental results from a F-poor and  
23 a F-rich natural phlogopites, we show that about 4 wt% F can increase the breakdown  
24 temperature of phlogopite by 100 °C under ambient pressure. The impact mechanism  
25 mainly involves preventing OH and lattice softening<sup>2</sup> at high temperatures. This study  
26 reveals the links between F and the behavior of OH and phlogopite lattice, which is  
27 important for constraining volatile cycling as well as F's role in the physical and  
28 chemical properties of the upper mantle.

29 **Keywords:** Fluorine, water, thermal stability, phlogopite, mantle

30

## INTRODUCTION

31 Volatiles (e.g., hydrogen, nitrogen, carbon, and halogens) are not only present on  
32 the surface of the Earth, but also in the deep Earth. Volatile exchange between the  
33 surface and mantle plays a critical role in the evolution and habitability of the Earth.  
34 Although a large number of studies have investigated volatile cycling in the deep Earth,  
35 it is still unclear how these volatiles are transported. Volatile transport in the deep Earth  
36 mainly depends on the thermal stabilities of the host minerals (van Keken et al. 2011).  
37 Most hydrous minerals are not only important water carriers, but carry also other  
38 volatiles such as nitrogen and the halogens (Williams et al. 1992; Bebout 1997; Hall  
39 1999; Sadofsky and Bebout 2000; Yokochi et al. 2009; John et al. 2011; Palya 2011;  
40 Kendrick et al. 2013; Halama et al. 2014; Pagé et al. 2016; Grützner et al. 2017a). Few  
41 studies have paid attention to the possible links between the volatiles when evaluating  
42 volatile transport by the host minerals. It has been noticed that fluorine (F) substituting  
43 for hydroxyl (OH) can extend the pressure-temperature stability field of the hydrous  
44 minerals such as amphibole, talc, and clinohumite (Foley 1991; Chibisov 2011;  
45 Grützner et al. 2017a). Recent studies have also pointed out the intimate links between  
46 nitrogen and hydrogen diffusion in phengite (Yang et al. 2017; Liu et al. 2019),  
47 providing new insights into water release in the Earth's interior. Therefore, exploring  
48 the effects of specific volatiles on water release from the host hydrous minerals is  
49 greatly needed in order to understand the associated cycling of volatiles and H<sub>2</sub>O.

50 Phlogopite is a sheet silicate frequently found in mantle nodules brought to the  
51 Earth's surface mainly by alkaline basalt and kimberlite lavas (Frey and Prinz 1978;  
52 Erlank et al. 1987; Fritschle et al. 2013). Fluorine has been experimentally proven to be  
53 compatible in phlogopite, with a F partition coefficient between phlogopite and melt  
54 larger than 1 (Flemetakis et al. 2021). Thus, phlogopite acts as an important reservoir  
55 and carrier of water and F in the upper mantle despite the fact that it is volumetrically  
56 insignificant when compared to olivine and pyroxenes (Frost 2006). Many studies have

57 focused on the  $P$ - $T$  stability field of phlogopite in different systems. Most importantly,  
58 observations from both experiments and textural relationships in natural samples have  
59 shown that F-rich phlogopite can be stable up to ultra-high-temperature conditions  
60 (Peterson et al. 1991; Dooley and Patiño Douce 1996; Motoyoshi and Hensen 2001).  
61 However, the impact of F on the stability of phlogopite has never been explored further  
62 and many unknowns still exist. For instance, what is the relationship between the  
63 proportion of F (F/(F+OH) ratio) in phlogopite and the breakdown temperature down to  
64 the atomic level? In addition, it has been reported that dehydrogenation could happen at  
65 low temperatures, such as 500 °C, before the breakdown of phlogopite (Chon et al.  
66 2006; Ventruti et al. 2009; Zema et al. 2010). But it remains unclear whether F has an  
67 impact on the dehydrogenation of phlogopite. These unknowns limit a full  
68 understanding of volatile release from phlogopite.

69 In this study, we systematically investigate the effect of F on the thermal stability  
70 and dehydrogenation of phlogopite, using high temperature Raman spectroscopy and  
71 X-ray diffraction (XRD) to monitor the breakdown processes of the lattice, and high  
72 temperature Fourier transform infrared (FTIR) spectroscopy to reveal the behavior of  
73 OH with increasing temperature.

## 74 MATERIALS AND METHODS

### 75 Samples

76 The two starting samples are phlogopite crystals from two different localities  
77 described in Li et al. (2017). The F-rich phlogopite is a 10 × 5 mm, golden-brown  
78 crystal from Franklin, New Jersey, United States. The F-poor phlogopite is a 70 × 50  
79 mm, reddish-brown crystal from Badakhshan, Afghanistan. The chemical  
80 compositions were obtained using a shimadzu electron probe microanalyzer (EPMA  
81 1720) at 15 kV and 10 nA beam with a 5 μm beam diameter. Counting time was 10 s on  
82 the peak and 10 s on the background for all elements except F, which was 60 s on peak  
83 and 30 s on background. Four to seven points were measured on each phlogopite grain.

84 The average chemical compositions of the two samples are listed in Table 1. Structure  
85 formula was calculated on the basis of 22 cation charges, assuming an anion framework  
86 of 10 oxygens and 2(OH+F+Cl), and all Fe as Fe<sup>2+</sup> (Dymek 1983; Rieder et al. 1998).  
87 This results in the following formula  
88  $(K_{0.963}Na_{0.015})(Mg_{2.677}Fe_{0.166}Al_{0.059}Mn_{0.002}Ti_{0.015}Cr_{0.009}Ni_{0.003})(Si_{3.067}Al_{0.933})O_{10}[F_{0.905}C$   
89  $l_{0.016}OH_{1.079}]$  for the F-rich phlogopite ( $X_F = 0.45$ ), and  
90  $(K_{0.911}Na_{0.047})(Mg_{2.723}Fe_{0.026}Al_{0.111}Mn_{0.001}Ti_{0.062}Cr_{0.002}Ni_{0.001})(Si_{2.955}Al_{1.045})O_{10}[F_{0.053}C$   
91  $l_{0.002}OH_{1.945}]$  for the F-poor phlogopite ( $X_F = 0.026$ ).

## 92 **X-ray diffraction spectroscopy (XRD)**

93 To monitor the breakdown processes of the two samples, high temperature X-ray  
94 diffraction measurements were carried out on a PANalytical X'Pert PRO Multipurpose  
95 Diffractometer (MPD), powered by a Philips PW3040 generator and equipped with an  
96 X'Celerator detector using CuK $\alpha$  radiation ( $\lambda=1.5406 \text{ \AA}$ ). The measurements were  
97 operated at 40 kV and 40 mA with 2 $\theta$  ranging from 7 to 70°. Both samples were finely  
98 pulverized in an agate mortar for over 3 h and then passed through a 74  $\mu\text{m}$  sieve.  
99 Powders were mounted on a platinum resistive heating stage and placed in an evacuated  
100 chamber. For each run, the temperature was increased from room temperature to  
101 1100 °C at 100 °C intervals and with a heating rate of 10 °C/min. The temperature was  
102 monitored by a TCU1000N (2604 unit) controller with a temperature error of less than  
103 1 °C. The XRD spectra were collected at each temperature. Each 100 °C temperature  
104 step consisted of a 15 min dwell time and a 30 min detection time. All data were  
105 analyzed using the Jade 6 software.

## 106 **Raman spectroscopy**

107 To further characterize phlogopite breakdown processes, high temperature Raman  
108 spectra of the phlogopites in the frequency range 50 to 1200  $\text{cm}^{-1}$  were collected using a  
109 LABRAM-HR spectrometer with an 1800 grooves/mm grating. The sample was  
110 excited by a 532 nm green light from a Spectra Physics Ar ion laser for a total time of

111 100 s for each data point. Single-crystal silicon was used as the reference spectrum.  
112 High temperatures were produced by a Linkam TS1500 heating stage, equipped with a  
113 resistance heater and a S type thermocouple. Temperatures were determined with an  
114 uncertainty of less than 1 °C. The powder samples (grain size < 74 µm) were heated  
115 while continuously purged by Ar and held for 30 min at the desired temperatures of 900,  
116 1000, 1100, and 1200 °C. Raman spectra were measured on the samples after they have  
117 been quenched to room temperature. In order to investigate the evolution of lattice  
118 vibrations as a function of increasing temperature, temperature-dependent Raman  
119 spectra, from room temperature to 1000 °C, were measured on crystal samples in the  
120 heating stage. The heating rate was set to be 10 °C/min, and an idle time of 5 min was  
121 applied to each experimental temperature.

#### 122 **Fourier transform infrared (FTIR) spectroscopy**

123 To reveal the behavior of OH and dehydrogenation in the two samples at high  
124 temperatures, thin cleavage flakes perpendicular to the (001) plane with a thickness of  
125 50 to 130 µm were used for the temperature-dependent FTIR measurements. Polarized  
126 and unpolarized FTIR spectra in the frequency range 1000-4000 cm<sup>-1</sup> were collected  
127 with an IR beam direction perpendicular to the (001) plane (i.e., to the layers) using a  
128 Nicolet iS50 FTIR spectrometer coupled with a Continuum microscope. A KBr  
129 beam-splitter and a liquid-nitrogen cooled MCT-A detector were applied. A total of  
130 128 scans were accumulated for each spectrum at a 4 cm<sup>-1</sup> resolution. The aperture size  
131 was set to 50 × 50 µm.

132 High temperatures were produced using an Instec HS1300 heating stage with CaF<sub>2</sub>  
133 windows, equipped with a resistance heater and a S type thermocouple. The phlogopite  
134 grains were placed on a sapphire plate in the heating stage continuously purged with N<sub>2</sub>  
135 gas. The sample temperature was determined with an uncertainty of less than ±1 °C.  
136 The FTIR measurements were performed from room temperature to 100 °C and then  
137 1000 °C using an interval of 100 °C. Samples were heated at a rate of 10 °C/min and

138 held at the desired temperature for 5 min. Background spectra and sample spectra were  
139 collected on the same selected area, respectively, for each grain and each temperature.

## 140 **RESULTS**

### 141 **Stability of F-rich and F-poor phlogopites at high temperatures**

142 Studies on the stabilities of phlogopite in complex systems have long been carried  
143 out (Frost 2006 and references therein). They proposed that the stability field and  
144 decomposition products depend on the initial chemical compositions of the systems. In  
145 this study, the focus is on the role of F during the breakdown of individual phlogopite  
146 crystals.

147 X-ray diffraction patterns at elevated temperatures are shown in Figure 1. With  
148 increasing temperature, the intensities of the original diffraction peaks (005) and (003)  
149 of the phlogopite decrease, whereas the intensities of the diffraction peaks for forsterite,  
150 such as (222), (031) and (120), grow concomitantly (Figs. 1c-d). Both phlogopite  
151 samples began to decompose at 1000°C, as indicated by the appearance of the forsterite  
152 diffraction peaks. Moreover, most of the phlogopite diffraction peaks disappear at  
153 1100 °C for the F-poor phlogopite, whereas the sharp diffraction peaks (005) and (003)  
154 persist for the F-rich phlogopite, indicating the different degrees of breakdown for the  
155 two samples. Comparison of the XRD patterns from the two samples before and after  
156 the run shows more clearly the different degrees of breakdown (Fig. 1e). These X-ray  
157 diffraction results demonstrate that breakdown starts at 1000 °C for both samples, but  
158 the F-poor phlogopite completely decomposes at 1100°C, whereas the F-rich  
159 phlogopite has only partly decomposed at the same temperature. The breakdown  
160 process of the two phlogopites was further characterized by Raman spectra from the  
161 quenched powder samples after annealing at different temperatures (Fig. 2). In  
162 accordance with observations from the XRD results, the Raman spectra show that both  
163 phlogopites start to decompose at 1000 °C as illustrated by the appearance of the  
164 characteristic peaks of forsterite at 825 and 857 cm<sup>-1</sup>. But the breakdown degrees were

165 different between the two samples. After annealing at 1100 °C, the F-poor phlogopite  
166 completely decomposed as indicated by the disappearance of the initial characteristic  
167 peaks of phlogopite, while there still exist remnants of these peaks for the F-rich  
168 phlogopite. By 1200 °C, the F-rich phlogopite had completely decomposed, according  
169 to the Raman spectra in Figure 2, indicating that the breakdown process is faster for the  
170 F-poor phlogopite than for the F-rich one.

### 171 **Lattice of the F-rich and F-poor phlogopites at various temperatures**

172 The thermal behavior of the crystal lattice for the two samples were investigated  
173 using temperature-dependent Raman spectra in the range of 50-1200  $\text{cm}^{-1}$  up to 1000°C  
174 (Fig. 3). Raman modes of the two phlogopite samples are similar to those observed in  
175 previous studies (Loh 1973; Clemens et al. 1987; Tlili et al. 1989; McKeown et al. 1999;  
176 Tutti et al. 2000), but minor differences exist in band positions of some modes (Fig. 3a).  
177 The predominant modes are 193, 281, 327, 358, and 682  $\text{cm}^{-1}$  for the F-poor phlogopite,  
178 and 193, 277, 320, and 682  $\text{cm}^{-1}$  for the F-rich phlogopite. Modes at 193, 277 to 281,  
179 320 to 327, and 682  $\text{cm}^{-1}$  appear to correspond to the same modes in both phlogopites.  
180 The intensity of the 358  $\text{cm}^{-1}$  mode is much stronger for the F-poor phlogopite than the  
181 F-rich one, which is in agreement with the fact that it has only been reported in the  
182 synthetic pure OH phlogopite (Clemens et al. 1987). Modes at frequencies less than 350  
183  $\text{cm}^{-1}$  are generally classified as the lattice modes where long-range  $\text{T}_4\text{O}_{10}$  sheet motions  
184 can mix with M2 and (F, OH) displacements. Modes between 350 and 850  $\text{cm}^{-1}$  have  
185 bond stretch and bend motions with the  $\text{T}_4\text{O}_{10}$  sheets and M2 octahedra. The mode at  
186 682  $\text{cm}^{-1}$  is assigned to O3-T-O1 band, which reflects motion along the  $z(c)$  direction in  
187 the structure (McKeown et al. 1999).

188 No new band in the spectra appears nor disappears at elevated temperatures (Figs.  
189 3b-c). Most lattice modes shift continuously toward lower wavenumbers without  
190 apparent turning points, except for some small accidents around 400 to 500 °C for the  
191 193 and 682  $\text{cm}^{-1}$  modes (Figs. 3d-h). These small breaks do not support any structural



192 phase transitions occurring during the heating process, although phlogopite has been  
193 found to undergo a structural phase transition at temperatures of around 400 °C (Tutti  
194 and Lazor 2008). Similarly, Zhang et al. (2016) found that the phonon modes of  
195 phlogopite all exhibited gradual changes with increasing temperature except for the  
196 Al-O and Si-O stretching vibrations, which show a discontinuity near 327 °C. This was  
197 suggested by the authors to be related to the alteration of the OH environment. The  
198 small accidents around 400 to 500 °C for the 193 and 682 cm<sup>-1</sup> modes observed in this  
199 study could be related to dehydrogenation processes, which is evidenced by the  
200 behavior of OH at elevated temperatures (Fig. 4).

### 201 **Behavior of OH in F-rich and F-poor phlogopites as a function of temperature**

202 Figures 4a-b show the temperature-dependent unpolarized IR spectra of OH  
203 vibrations in the 3500 to 3750 cm<sup>-1</sup> range up to 1000 °C for the F-rich and F-poor  
204 phlogopites. For both samples, the absorptions of OH stretching bands recorded  
205 through IR beam perpendicular to the (001) plane have isotropic properties, thus, the  
206 spectra with polarizer rotating to different angles are similar (Fig. 4c). Some  
207 differences in OH wavenumbers between the two samples can nevertheless be observed.  
208 For the F-poor phlogopite, there are mainly three OH bands at 3714, 3671, and 3621  
209 cm<sup>-1</sup>. In contrast, three OH bands at 3707, 3665 and 3599 cm<sup>-1</sup> are shown in the IR  
210 spectra of the F-rich phlogopite. Vedder (1964) divided the OH bands in phlogopite  
211 into three groups: type N band (normal) corresponding to OH bonding to three  
212 octahedrally coordinated divalent cations, type I band (impurity) related to OH bonding  
213 to two divalent and one trivalent cations, and type V band (vacancy) due to an OH  
214 adjacent to an octahedral vacancy. All previous studies assign the bands at 3714 and  
215 3707 cm<sup>-1</sup> to the type N OH (Vedder and Wilkins 1969; Zhang et al. 2016). Bands at  
216 3671 and 3665 cm<sup>-1</sup> were assigned to the type I OH, relating to Mg<sub>2</sub>(Al, Fe<sup>3+</sup>)-OH  
217 species (Robert and Kodama 1988; Ventruti et al. 2009; Zhang et al. 2016). The bands  
218 at 3621 and 3599 cm<sup>-1</sup> are generally associated with the type V OH, corresponding to a

219 vacancy with two divalent ions in the octahedral sheet and a vacancy with one divalent  
220 ion and one trivalent ion, respectively (Vedder 1964). The relative intensity of the type  
221 N OH to the other two groups is larger for the F-poor phlogopite than the F-rich  
222 phlogopite, which is consistent with the conclusion that F prefers to substitute for the  
223 type N OH based on analyses of synthetic F-rich phlogopites (Papin et al. 1997).

224 Since the IR spectra exhibit isotropic features independent of the polarizer  
225 orientation in (001) plane, we used only unpolarized IR spectroscopy to study the OH in  
226 phlogopite at elevated temperatures. Comparison between the IR spectra of the F-poor  
227 phlogopite before heating and after quenching shows no evident decrease of the  
228 absorbance for the type N OH ( $3714$  and  $3707\text{ cm}^{-1}$ ), and a small decrease for the type I  
229 OH ( $3671$  and  $3665\text{ cm}^{-1}$ ), while the type V OH ( $3621$  and  $3599\text{ cm}^{-1}$ ) almost  
230 disappears. These variations in the absorbances suggest dehydrogenation, especially  
231 for the type V OH (Figs. 4a-b). We could not tell from the spectra whether  
232 dehydrogenation happened at elevated temperatures for the F-rich phlogopite, because  
233 the spectrum of the quenched sample from  $1000\text{ }^{\circ}\text{C}$  is seriously distorted. But  
234 dehydrogenation could be inferred from the evolution of the OH band wavenumbers  
235 with temperature. The three OH band groups shift to lower wavenumbers with  
236 increasing temperature, but with discontinuities at  $400$  to  $500\text{ }^{\circ}\text{C}$  for the type I OH and  
237 the type V OH bands (Fig. 4d). The abrupt shift in the temperature-induced OH  
238 wavenumber for type I OH and type V OH, observed around  $400$  to  $500\text{ }^{\circ}\text{C}$ , occurs in  
239 the temperature range where dehydrogenation is generally observed in phlogopite (e.g.,  
240 Vedder and Wilkins 1969; Tutti et al. 2000; Zhang et al. 2016). Thus, both phlogopites  
241 experienced dehydrogenation of type I OH and type V OH at around  $400$  to  $500\text{ }^{\circ}\text{C}$   
242 during heating, further confirming the IR spectra before heating and after quenching,  
243 although we cannot confirm it with the spectrum from the quenched F-rich  
244 phlogopite.

245

## DISCUSSION

## 246 **The effects of F on the thermal stability of phlogopite**

247 It has already been documented that F may markedly extend the thermal stability  
248 of phlogopite. For example, the experimental study by Hensen and Osanai (1994)  
249 demonstrated that synthetic phlogopite with about 6 wt% F decomposed at 1045 °C and  
250 9 kbar. Moreover, Dooley and Patiño Douce (1996) found that the synthetic phlogopite  
251 with 8.7 wt% F can be stable at 1263 °C at 10 kbar. Accordingly, F-rich phlogopite was  
252 reported as a stable constituent in ultra-high-temperature rocks (Motoyoshi and Hensen  
253 2001). To reveal the relationship between F and the breakdown temperature of  
254 phlogopite, we plotted the breakdown temperature to proportion of F (F/(F+OH) ratio)  
255 in Figure 5 based on the data from this study and previous studies. It shows that  
256 addition of F can increase the breakdown temperature, confirming the higher stabilities  
257 of F-rich phlogopites previously observed. The F-poor and F-rich phlogopite samples  
258 start to decompose at 1000 °C under ambient pressure. But the breakdown process is  
259 faster for the F-poor phlogopite compared to the F-rich phlogopite, since the complete  
260 breakdown temperature is at least 100 °C lower for the F-poor phlogopite compared  
261 with the F-rich phlogopite.

262 It should be noted that in addition to F, the chemical compositions of these two  
263 phlogopites differ. Previous studies have suggested that Ti can stabilize biotite both at  
264 high *P-T* and at low H<sub>2</sub>O activity (Henry et al. 2005; Harlov et al. 2006; Hansen and  
265 Harlov 2007). As basically the Mg endmember of the biotite series, phlogopite should  
266 also be stabilized by Ti. To check the effect of Ti on the thermal stability of phlogopite,  
267 we plotted the Ti contents vs. the breakdown temperatures of the samples from Figure 5  
268 in the supplementary material (Fig. S1). Indeed, a high Ti content can increase the  
269 thermal stability of phlogopite as well. Although the F-poor phlogopite contains more  
270 Ti than the F-rich phlogopite, F content still plays an important role in phlogopite  
271 stability as shown in Figure 5. Therefore, the actual effect of F on phlogopite could be  
272 even stronger if the Ti content was the same in both phlogopite samples. On the other

273 hand, pressure effect on the mineral stability is also important. To check the effect of F  
274 on the breakdown temperature of phlogopite under different pressures, compiled data  
275 previously reported for phlogopite and other hydrous minerals at high pressure is  
276 plotted in Figure 5. It is shown that F generally plays an important role on the thermal  
277 stabilities of the host minerals at the same pressure. For phlogopite, the breakdown  
278 temperature increases with the increasing F content no matter whether at ambient  
279 pressure or at 7 to 15 kbar. Moreover, the breakdown temperatures of phlogopites with  
280 the same amount of F are higher at ambient pressure than at high pressures. Considering  
281 the impact of Ti on the phlogopite samples with higher Ti contents used in experiments  
282 at 7 to 15 kbar, the breakdown temperatures may be even lower than those shown in  
283 Figure 5. Thus, it seems that pressure plays a negative role in the thermal stability of  
284 phlogopite, which is the reverse of F effect. However, this pressure effect for  
285 phlogopite is not applicable to other minerals. For example, for clinohumite, with a F  
286 fraction of 0.5, can be stable up to 1100 °C at 30 kbar (Fig. 5), and up to 1600 °C at 10  
287 GPa as inferred from Grützner et al. (2017).

### 288 **The effects of F on the breakdown process at high temperatures**

289 With increasing temperature, most Raman modes shift toward lower  
290 wavenumbers (Figs. 3d-h), indicating a temperature-induced softening of the  
291 phlogopite lattice for the two samples. So far, no one has reported the effect of F on the  
292 lattice vibrations of phlogopite at high temperatures. To investigate this, Figure 6a  
293 compares the temperature-induced shifts of the main Raman modes of the F-poor  
294 phlogopite and the F-rich one. It is seen that F has an impact on the  
295 temperature-induced shifts of the modes around 320 and 682  $\text{cm}^{-1}$ . The shifted  
296 amplitudes of these modes are drastically reduced for the F-rich sample. This suggests  
297 that incorporation of F retards the lattice softening at high temperatures.

298 Fluorine appears to have an impact on the thermal behavior of OH in phlogopite. It  
299 can be observed that wavenumbers of the three groups OH bands in the F-rich

300 phlogopite are generally lower than those in the F-poor phlogopite (Fig. 4d).  
301 Relationship between the OH wavenumbers for the three groups of OH bands and Al  
302 content has been reported by Robert and Kodama (1988). According to them, micas  
303 with higher Al contents show lower OH wavenumbers for the type N and I OH bands,  
304 which is in contrast with our study that the F-poor phlogopite with a higher Al content  
305 has a higher OH wavenumber for all the types of OH bands. Therefore, the Al content  
306 alone cannot explain the differences in OH wavenumbers between the two samples.  
307 Another factor may be the higher Fe content in the F-rich phlogopite which will  
308 decrease the OH wavenumber (Vedder 1964). In addition, the impact of F on the OH  
309 wavenumber has been reported for mica, amphibole, and talc (Robert et al. 1993, 1999;  
310 Rywak and Burlitch 1996), which is not difficult to understand considering the stronger  
311 electronegativity of F than oxygen (Pauling 1932). Thus, it may be expected that F  
312 substitution for OH in phlogopite will strengthen the hydrogen bonding (O-H $\cdots$ F),  
313 thereby reducing the OH wavenumber (Libowitzky 1999). This has been seen in the  
314 F-induced OH band shift to lower wavenumbers in apatite (e.g., Tacker 2004). To  
315 explore the correlation between F incorporation and hydrogen bonding strength, we  
316 plot wavenumbers of the type N OH against the F content represented by their  $X_F$   
317 values in Figure 6b, based on the data from this study and a compilation of data from  
318 literature. Although the data are somewhat scattered, mainly due to different chemical  
319 compositions besides F, the negative relationship is obvious. Consequently, with  
320 increasing F substitution, the strength of hydrogen bonding in phlogopite will be  
321 enhanced. This strengthened hydrogen bonding may influence the thermal stability of  
322 OH, which is seen in the different thermal behavior of OH for the F-poor phlogopite vs.  
323 F-rich phlogopite. With increasing temperature, the OH bands all become broader, and  
324 shift towards lower wavenumbers, suggesting temperature-induced OH softening (Figs.  
325 4a-b). There also exist some differences in the amplitudes of the temperature-induced  
326 wavenumber shifts of the OH bands between the two samples. The shift amplitudes are  
327 generally larger for the F-poor phlogopite than for the F-rich one (Fig. 6c). In other

328 words, despite the fact that a higher temperature induces OH softening for all the  
329 phlogopite samples, phlogopite will experience less softening with addition of F. Thus,  
330 dehydrogenation may be more difficult for the F-rich phlogopite, and this needs to be  
331 verified by dehydrogenation kinetics studies in future.

332 From the vibrational spectra, the isobaric Grüneisen parameters of the lattice and  
333 OH modes in the two samples are calculated via the equation  $\gamma_{iP} = -\frac{1}{\alpha v_i} \left( \frac{\partial v_i}{\partial T} \right)_P$ , where  
334  $\gamma_{iP}$  is isobaric Grüneisen parameter of a mode ( $v_i$ ), and  $\alpha$  is the thermal expansion  
335 coefficient. Since there has been no report of the effects of F on the thermal expansion  
336 coefficient of phlogopite, we here refer to the thermal expansion coefficient of  $6.26 \times$   
337  $10^{-5} \text{ K}^{-1}$  from Tutti et al. (2000). The calculated isobaric Grüneisen parameters of the  
338 two samples are listed in Tables 2 and 3. The parameters are generally larger for the  
339 F-poor phlogopite than the F-rich phlogopite, indicating that the OH and lattice of the  
340 F-poor phlogopite are more sensitive to temperature. Therefore, our study reveals that  
341 both OH and the lattice of F-rich phlogopite have a higher thermal stability, compared  
342 with those of the F-poor phlogopite. Hydrogen diffusion from the lattice has been  
343 suggested to control the stability of muscovite (Gaines and Vedder 1964). The impact  
344 of F on the lattice and the OH are thus probably responsible for the different breakdown  
345 processes of the F-rich and F-poor phlogopites at high temperatures. To date, one study  
346 has reported on the high-pressure Raman spectra of phlogopite (Williams et al. 2012).  
347 They reported that both OH and lattice stiffened with increasing pressure, whereas the  
348 impact of F is unknown. Considering that pressure is another important parameter,  
349 future experimental work should focus on high pressures to explore the effects of F on  
350 the behavior of OH and the lattice of the phlogopite.

## 351 **IMPLICATIONS**

352 Because of the size similarity between F and OH, it is generally supposed that  
353 the incorporation of F into both nominally hydrous and anhydrous silicate minerals is  
354 mainly through the substitution for OH (e.g., Robert et al. 1999; Crépeisson et al. 2014;

355 Roberge et al. 2015; Beyer et al. 2016; Grützner et al. 2017b; Yoshino and Jaseem  
356 2018; Hughes and Pawley 2019). This substitution inevitably causes variations in the  
357 structure and property of the phlogopite. The data from this study demonstrates that  
358 increasing the F substitution in phlogopite can prevent O-H bonding weakening and  
359 lattice softening at high temperatures, and consequently stabilize the phlogopite,  
360 which has an impact on the stability of phlogopite at high temperatures.

361 It is well known that the mantle is a major water reservoir in the Earth because of  
362 the storage of hydrogen defects in nominally anhydrous mantle minerals such as  
363 olivine (e.g., Bell and Rossman 1992; Pearson et al. 2014). Recent studies have also  
364 indicated that the mantle has acted as a reservoir for F (e.g., Beyer et al. 2016;  
365 Grützner et al. 2018; Yoshino and Jaseem 2018). A close association between F and  
366 OH has been demonstrated via their coupled incorporation mechanism in olivine  
367 (Crépeisson et al. 2014). To date, only one study has reported on the impact of F on  
368 nominally anhydrous mantle minerals, mainly focusing on F storage and phase  
369 stability (Grützner et al. 2018). Phlogopite is a F-rich and hydrous key mineral in the  
370 upper mantle. Experimental studies have suggested that F concentrates preferentially  
371 in phlogopite compared to other minerals (Edgar and Charbonneau 1991). The F  
372 contents in mantle phlogopites are mostly from 0 to ~5 wt% and some are up to  
373 ~8-9.5 wt% (Li et al. 2016). Figure 5 indicates that  $X_F > 0.5$  can increase the  
374 breakdown temperature of phlogopite to over 100 °C under ambient pressure.  
375 Considering the high-pressure conditions in the upper mantle and the impact of other  
376 elements, such as Ti, the specific breakdown temperature for phlogopite would be  
377 affected. For example, a phlogopite with 8 wt% F ( $X_F = 0.9$ ) is expected to be stable  
378 up to 1350 °C under ambient pressure, while it is expected to be stable up to a  
379 temperature lower than 1300°C at 7-15 kbar (Fig. 5). Indeed, high-Ti phlogopite  
380 containing 8 wt% F has been found in an ultra-high-temperature (UHT) metamorphic  
381 terrane (980-1120 °C, below 9 kbar) (Motoyoshi and Hensen 2001) suggesting that  
382 F-rich samples can be stable at higher temperatures at ambient pressure than at a

383 higher pressure. Consequently, the increased stability and hydrogen bonding of  
384 F-bearing phlogopite makes it an excellent candidate for the storage and transport of  
385 both H<sub>2</sub>O and the halogens in the upper mantle. In the lithospheric mantle, F can be  
386 stored both in hydrous minerals and nominally anhydrous minerals. Although  
387 amphibole, phlogopite, and apatite are accessory mantle phases, they are dominant F  
388 carriers because F is likely a compatible element in these minerals (Klemme and  
389 Stalder 2018). Furthermore, the transport of F in the mantle is dependent on the  
390 thermal stabilities of F-bearing minerals. Previous studies showed that phlogopite can  
391 be stable up to 1100 °C under 6 GPa, amphibole (K-richterite) can be stable up to  
392 1300 °C, and apatite can be stable up to 1100 °C under 6 to 8 GPa (Konzett and  
393 Ulmer 1999; Konzett et al. 2012). Since F plays an important role in stabilizing  
394 phlogopite, amphibole, and apatite (e.g., Frost 2006), F-bearing phlogopite,  
395 amphibole, and apatite act as important repositories of F in the mantle, dependent on  
396 their distributions in some regional zones.

397 The effect of F on the hydrogen bonding may have some implications on the  
398 dehydrogenation and electrical conductivity of phlogopite. Although it has been  
399 reported that dehydrogenation will occur before phlogopite breaks down (e.g., Vedder  
400 and Wilkins 1969; Tutti et al. 2000; Zhang et al. 2016), our study shows that the  
401 addition of F may make dehydrogenation more difficult. Furthermore, Li et al. (2017)  
402 has reported that increasing the F content can significantly enhance the electrical  
403 conductivity of phlogopite. Our study shows that F incorporation can prevent O-H  
404 bonds from weakening at high temperatures, which may impede hydrogen mobility.  
405 Therefore, the contribution of hydrogen conductivity should decrease with increasing  
406 F content in phlogopite.

407

408

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- 647

648 **Table 1.** Chemical compositions of the two phlogopite samples (in wt%, dash = below 0.01 wt%).

	<b>F-poor phlogopite (from Badakhshan)</b>						<b>F-rich phlogopite (from Franklin)</b>								
	Phl1	Phl2	Phl3	Phl4	Average	SD	Phl5	Phl6	Phl7	Phl8	Phl9	phl10	phl11	Average	SD
SiO <sub>2</sub>	42.39	43.23	42.67	42.31	42.65	0.42	43.16	43.68	43.51	43.69	43.87	43.41	43.52	43.55	0.23
TiO <sub>2</sub>	1.15	1.13	1.24	1.20	1.18	0.05	0.33	0.42	0.18	0.25	0.24	0.23	0.21	0.27	0.08
Al <sub>2</sub> O <sub>3</sub>	14.31	14.18	14.14	14.03	14.16	0.11	12.16	11.84	11.87	12.00	12.13	11.85	11.77	11.95	0.15
FeO	0.48	0.47	0.41	0.48	0.46	0.04	2.80	2.47	2.70	2.73	2.86	2.98	3.17	2.82	0.22
MnO	-	0.04	-	0.06	0.02	0.03	0.01	0.04	0.01	0.09	0.03	-	0.05	0.03	0.03
MgO	26.62	26.34	26.02	26.48	26.37	0.26	25.77	25.58	25.88	25.59	25.06	25.36	25.29	25.50	0.29
CaO	-	0.01	-	-	-	-	-	-	-	-	-	-	-	-	-
Na <sub>2</sub> O	0.30	0.39	0.36	0.35	0.35	0.03	0.07	0.09	0.14	0.10	0.12	0.12	0.15	0.11	0.03
K <sub>2</sub> O	10.36	10.27	10.22	10.41	10.31	0.09	10.76	10.77	10.70	10.63	10.71	10.69	10.76	10.72	0.05
F	0.23	0.26	0.24	0.24	0.24	0.01	3.98	4.10	4.10	4.01	3.97	4.03	4.24	4.06	0.09
Cl	-	0.03	0.04	0.02	0.02	0.02	0.12	0.12	0.13	0.14	0.16	0.17	0.14	0.14	0.02
Cr <sub>2</sub> O <sub>3</sub>	0.03	-	0.08	0.04	0.04	0.03	0.20	0.14	0.13	0.15	0.16	0.14	0.16	0.15	0.02
NiO	-	-	-	0.05	0.01	0.03	0.07	-	0.05	0.04	0.05	0.08	-	0.04	0.03
H <sub>2</sub> O*	4.22	4.23	4.19	4.19	4.21		2.34	2.28	2.28	2.33	2.34	2.29	2.20	2.30	
Subtotal	100.08	100.57	99.60	99.85	100.03		101.77	101.52	101.66	101.75	101.70	101.36	101.65	101.63	
O=F,Cl	0.10	0.12	0.11	0.11	0.11		1.70	1.75	1.76	1.72	1.71	1.74	1.81	1.74	
Total	99.99	100.45	99.49	99.74	99.92		100.06	99.77	99.90	100.03	99.99	99.62	99.84	99.89	

*Note:* \*H<sub>2</sub>O and OH estimated on the basis of 22 cation charges, assuming 10 oxygen and 2(OH+F+Cl) (Rieder et al. 1998).

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652 **Table 2.** Evolutions of wavenumbers of the lattice modes ( $\text{cm}^{-1}$ ) with temperature and the isobaric Grüneisen parameters. The data in italics are the  
 653 uncertainties.

Temperature (°C)	F-poor phlogopite Lattice mode ( $\text{cm}^{-1}$ )					F-rich phlogopite Lattice mode ( $\text{cm}^{-1}$ )			
	20	192.8 <i>0.29</i>	281.3 <i>0.39</i>	326.9 <i>0.73</i>	357.7 <i>0.42</i>	681.6 <i>0.28</i>	192.6 <i>0.20</i>	276.6 <i>0.22</i>	320.4 <i>0.70</i>
100	191.7 <i>0.20</i>	280.8 <i>0.29</i>	325.3 <i>0.26</i>	356.4 <i>0.08</i>	680.6 <i>0.27</i>	191.3 <i>0.12</i>	275.2 <i>0.33</i>	320.1 <i>0.35</i>	681.2 <i>0.31</i>
200	190.5 <i>0.20</i>	279.9 <i>0.17</i>	323.3 <i>0.26</i>	354.4 <i>0.30</i>	679.7 <i>0.01</i>	190.0 <i>0.02</i>	274.5 <i>0.21</i>	319.1 <i>0.53</i>	680.3 <i>0.67</i>
300	189.0 <i>0.06</i>	278.5 <i>0.28</i>	321.2 <i>0.62</i>	352.7 <i>0.21</i>	678.2 <i>0.24</i>	188.9 <i>0.09</i>	273.3 <i>0.65</i>	318.3 <i>0.10</i>	679.3 <i>0.69</i>
400	188.2 <i>0.23</i>	277.7 <i>0.44</i>	319.6 <i>0.21</i>	349.9 <i>0.13</i>	676.9 <i>0.36</i>	187.3 <i>0.35</i>	272.0 <i>0.52</i>	317.0 <i>0.73</i>	678.7 <i>0.23</i>
500	186.5 <i>0.26</i>	276.3 <i>0.07</i>	316.8 <i>0.39</i>	347.9 <i>0.10</i>	674.3 <i>0.42</i>	185.5 <i>0.32</i>	270.8 <i>0.27</i>	315.8 <i>0.37</i>	676.9 <i>0.40</i>
600	185.4 <i>0.21</i>	275.5 <i>0.34</i>	314.4 <i>0.76</i>	346.0 <i>0.19</i>	673.3 <i>0.21</i>	184.7 <i>0.29</i>	270.0 <i>0.39</i>	314.9 <i>0.48</i>	675.5 <i>0.07</i>
700	184.5 <i>0.24</i>	274.1 <i>0.20</i>	311.9 <i>0.23</i>	344.0 <i>0.05</i>	671.8 <i>0.21</i>	183.9 <i>0.20</i>	269.0 <i>0.66</i>	314.2 <i>0.37</i>	674.5 <i>0.04</i>
800	183.2 <i>0.39</i>	273.5 <i>0.22</i>	308.6 <i>0.54</i>	342.3 <i>0.02</i>	670.1 <i>0.38</i>	183.1 <i>0.19</i>	267.7 <i>0.42</i>	312.2 <i>0.57</i>	672.8 <i>0.40</i>
900	181.8 <i>0.19</i>	272.4 <i>0.71</i>	306.0 <i>0.22</i>	340.6 <i>0.13</i>	668.6 <i>0.26</i>	182.0 <i>0.50</i>	266.4 <i>0.51</i>	310.8 <i>1.02</i>	671.2 <i>0.09</i>
1000	180.6 <i>0.20</i>	271.3 <i>0.91</i>	304.0 <i>0.60</i>	338.7 <i>0.07</i>	667.5 <i>0.22</i>	180.7 <i>0.09</i>	265.7 <i>0.03</i>	309.6 <i>0.48</i>	669.2 <i>1.25</i>
Wavenumber shift with temperature ( $\text{cm}^{-1}/^\circ\text{C}$ )	-0.0128 (20-400°C)	-0.0108 (20-1000°C)	-0.0242 (20-1000°C)	-0.0197 (20-1000°C)	-0.0123 (20-400°C)	-0.0125 (20-400°C)	-0.0109 (20-1000°C)	-0.0114 (20-1000°C)	-0.0097 (20-400°C)
Isobaric Grüneisen parameters	1.061	0.613	1.179	0.880	0.288	1.039	0.630	0.567	0.227

654

655 **Table 3.** Evolutions of wavenumbers of the three groups of OH bands ( $\text{cm}^{-1}$ ) with temperature and the isobaric Grüneisen parameters of the OH modes. The  
 656 data in italic are the uncertainties.

Temperature ( $^{\circ}\text{C}$ )	F-poor phlogopite OH wavenumber ( $\text{cm}^{-1}$ )			F-rich phlogopite OH wavenumber ( $\text{cm}^{-1}$ )		
	20	3714.2 <i>0.18</i>	3671.3 <i>0.25</i>	3621.7 <i>0.20</i>	3706.8 <i>0.22</i>	3665.5 <i>0.51</i>
100	3711.5 <i>0.26</i>	3670.6 <i>1.65</i>	3620.8 <i>0.11</i>	3704.4 <i>0.08</i>	3664.6 <i>0.87</i>	3598.0 <i>0.91</i>
200	3708.7 <i>0.14</i>	3670.0 <i>0.69</i>	3619.9 <i>0.08</i>	3701.7 <i>0.12</i>	3664.1 <i>0.75</i>	3597.5 <i>0.33</i>
300	3705.1 <i>0.18</i>	3668.0 <i>0.31</i>	3618.6 <i>0.16</i>	3698.8 <i>0.14</i>	3663.0 <i>0.46</i>	3596.0 <i>0.88</i>
400	3701.6 <i>0.12</i>	3666.4 <i>0.75</i>	3616.6 <i>0.68</i>	3695.2 <i>0.16</i>	3661.8 <i>1.52</i>	3596.0 <i>0.60</i>
500	3698.5 <i>0.04</i>	3662.7 <i>1.41</i>	3614.4 <i>1.79</i>	3691.6 <i>0.28</i>	3659.3 <i>1.92</i>	3594.8 <i>0.56</i>
600	3694.8 <i>0.17</i>	3658.9 <i>2.25</i>	3607.6 <i>4.06</i>	3687.9 <i>0.33</i>	3658.1 <i>1.64</i>	3583.9 <i>0.55</i>
700	3691.6 <i>0.23</i>	3653.2 <i>1.74</i>	3594.4 <i>2.91</i>	3685.6 <i>0.16</i>	3655.2 <i>2.37</i>	3580.4 <i>1.42</i>
800	3688.2 <i>0.34</i>	3650.7 <i>0.35</i>	3586.5 <i>1.53</i>	3682.8 <i>0.27</i>		3581.4 <i>2.19</i>
900	3684.6 <i>0.48</i>			3680.9 <i>0.16</i>		
1000	3681.0 <i>0.49</i>					
Wavenumber shift with temperature ( $\text{cm}^{-1}/^{\circ}\text{C}$ )	-0.0336 (20-1000 $^{\circ}\text{C}$ )	-0.0119 (20-400 $^{\circ}\text{C}$ )	-0.0111 (20-500 $^{\circ}\text{C}$ )	-0.0304 (20-900 $^{\circ}\text{C}$ )	-0.0089 (20-400 $^{\circ}\text{C}$ )	-0.0089 (20-500 $^{\circ}\text{C}$ )
Isobaric Grüneisen parameters	0.145	0.052	0.049	0.131	0.039	0.040

657

658 **Figure captions:**

659 Figure 1. (a-b) X-ray diffraction patterns of phlogopite powders at elevated  
660 temperatures (“RT” represents room temperature). (c-d) Enlarged regions showing the  
661 breakdown processes. (e) Comparison of phlogopite samples before and after the  
662 heating and cooling runs.

663 Figure 2. Comparisons of Raman spectra of lattice vibrations between the initial and  
664 quenched powder samples from 900, 1000, 1100, and 1200 °C, respectively. (a-d)  
665 F-poor phlogopite; (e-h) F-rich phlogopite. The red arrows indicate the appearance of  
666 the characteristic modes of forsterite at 825 and 857  $\text{cm}^{-1}$ .

667 Figure 3. (a) Raman spectra of phlogopites at ambient conditions. (b) Raman spectra  
668 at various temperatures from 20 to 1000 °C of the F-poor phlogopite. (c) Raman  
669 spectra at various temperatures from 20 to 1000 °C of the F-rich phlogopite. (d-h)  
670 Evolution of Raman shifts of lattice modes of the phlogopites (data are in Table 2).

671 Figure 4. (a) Unpolarized IR spectra of OH stretching vibrations from the F-poor  
672 phlogopite at elevated temperatures and quenched from 1000 °C. (b) Unpolarized IR  
673 spectra of OH stretching vibrations of F-rich phlogopite at various temperatures and  
674 quenched from 1000 °C. The spectrum at 1000 °C of the F-rich phlogopite was  
675 corrupt due to serious interference, is not presented here. (c) Unpolarized and  
676 polarized IR spectra of OH stretching vibrations at ambient conditions, with the

677 polarizer rotated to  $0^\circ$  and  $90^\circ$  in (001) plane. (d) Wavenumbers of the three groups  
678 from unpolarized OH bands with temperature (data from Table 3).

679 Figure 5. Breakdown temperature of phlogopite and other hydrous minerals (pargasite,  
680 K-richterite, and clinohumite) as function of F content at different pressures. The blue  
681 field represents the phlogopite stability field. Data are from this study and the  
682 literature. Phlogopite at ambient pressure: Rimsaite (1970, 1972), Prost and Laperche  
683 (1990), Hammouda et al. (1995), Ogorodova et al. (2009). Phlogopite at high  
684 pressures: Hensen and Osanai (1994), Dooley and Patiño Douce (1996). Pargasite:  
685 Holloway and Ford (1975), Oba (1990). K-richterite: Foley (1991). Clinohumite:  
686 Weiss (1997). The open square represents the poorly constrained breakdown  
687 temperature of fluorphlogopite in Hammouda et al. (1995). It is probably higher than  
688  $1403^\circ\text{C}$  because it completely melts without breakdown at this temperature. The red  
689 and blue filled squares represent F-poor and F-rich phlogopites in this study,  
690 respectively.

691 Figure 6. (a) Temperature-induced wavenumber shifts of the lattice modes. (b)  
692 Wavenumbers of the type N OH at ambient conditions versus  $X_F$ . Two data are from  
693 this study, and the others are from previous studies (Vedder 1964; Prost and Laperche  
694 1990; Xu and Shen 2005; Chon et al. 2006; Piccinini et al. 2006; Scordari et al. 2006;  
695 Ventruti et al. 2009; Lacalamita et al. 2011; Zhang et al. 2016). (c)  
696 Temperature-induced wavenumber shifts of the OH bands. Since there exist

- 697 discontinuities in the wavenumber evolutions of some lattice modes and OH bands, the
- 698 dotted squares indicate the temperature range of the linear fit.

Figure 1

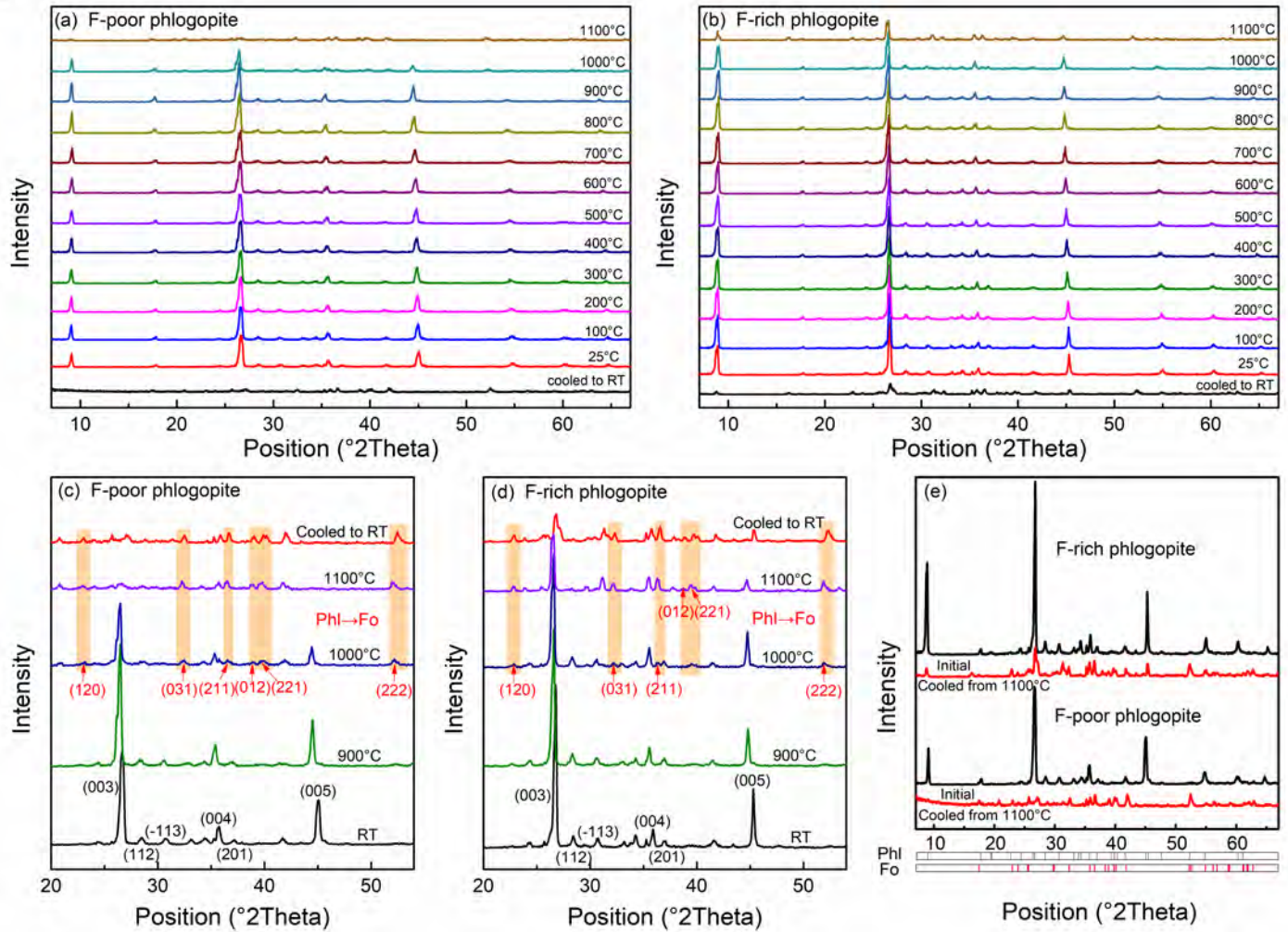


Figure 2

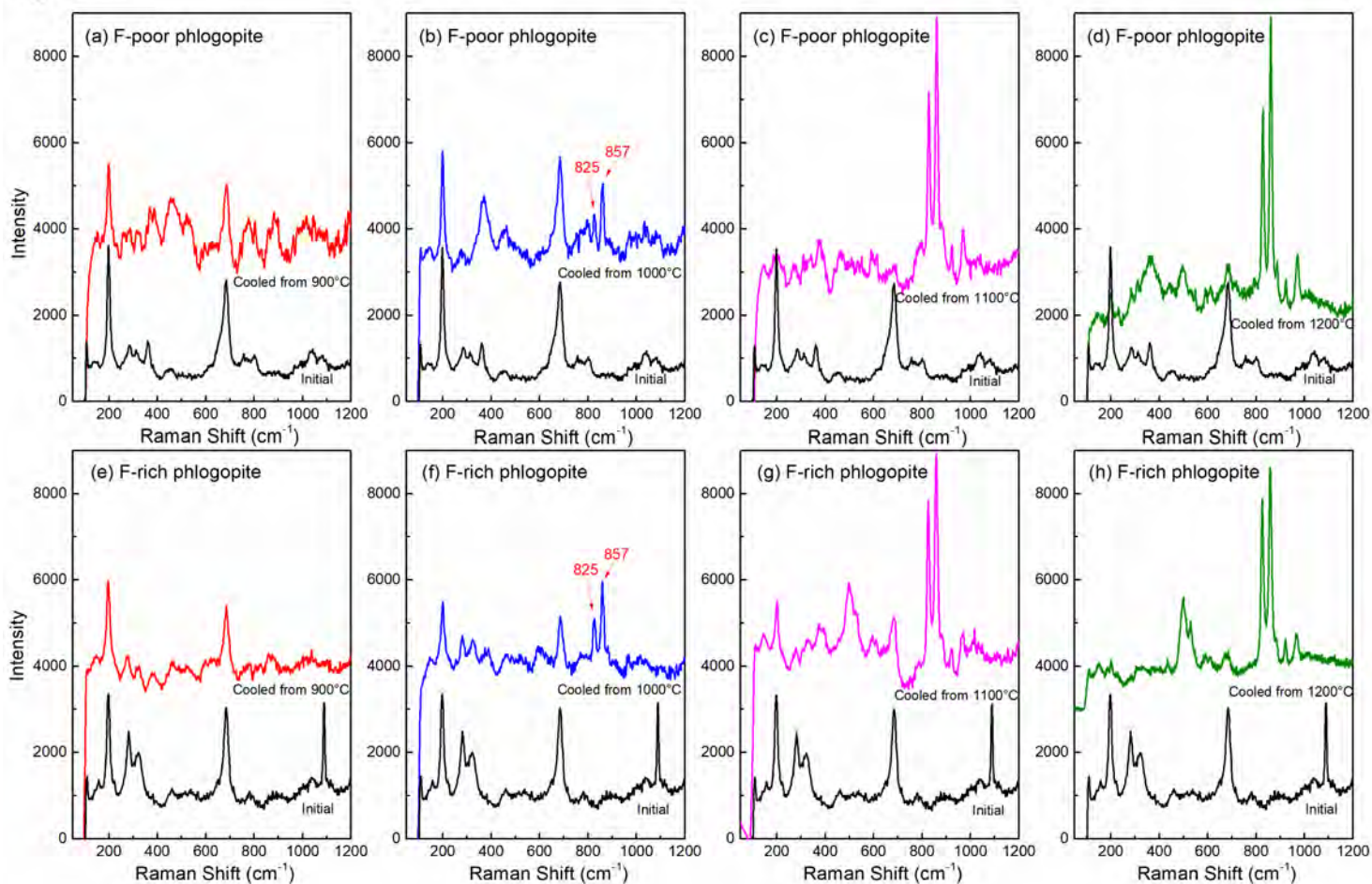


Figure 3

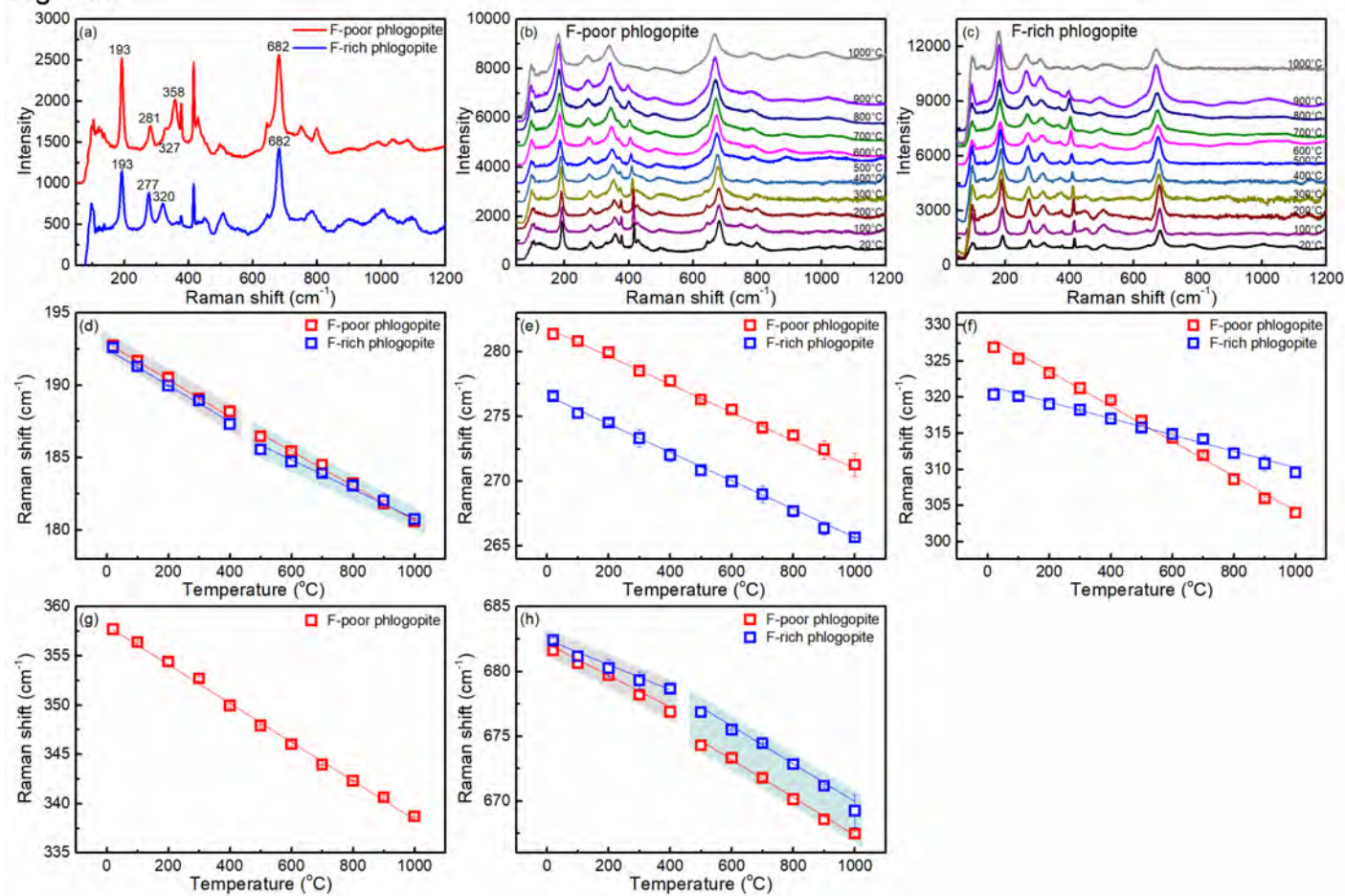




Figure 4

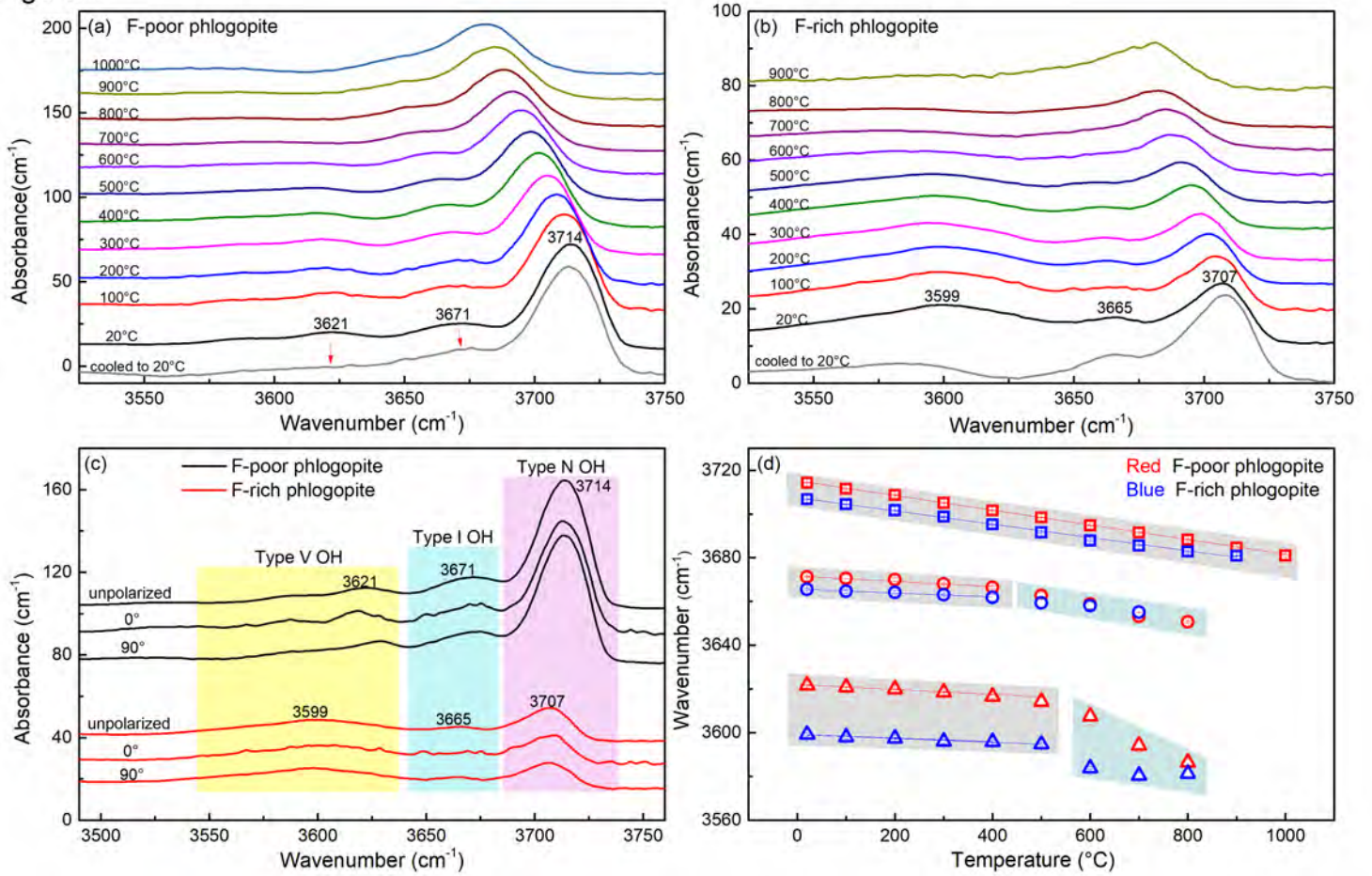


Figure 5

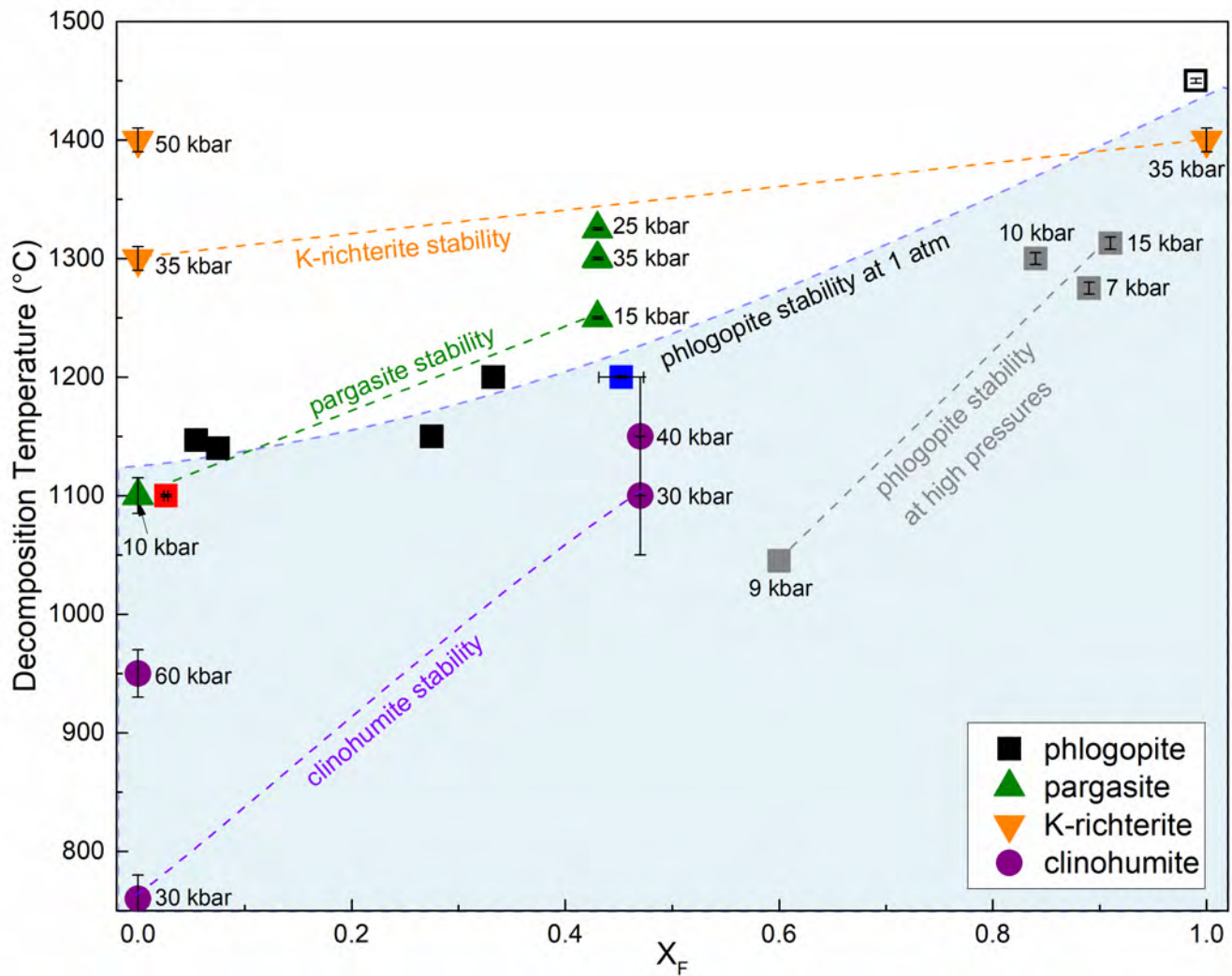


Figure 6

