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Behavior of phengite at high temperature and high pressure: In situ IR and Raman spectroscopic studies

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Key Points:

- Vibrations of hydroxyl and lattice of phengite at high temperature and high pressure were analyzed.
- High pressure induces O-H bond weakening and hydrogen disordering.
- Ammonium incorporated has potential effects on thermodynamic properties and stability of phengite.

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20 Abstract

21 Water release in subduction zones is not only an important part of the deep Earth's water cycle,
22 but also plays an essential role in the physical and chemical properties of rocks constituting the
23 deep Earth. To understand water release processes, it is important to know properties of
24 dehydration in hydrous phases of the downgoing slab. Although it is widely accepted that
25 phengite can be stable to greater depth in subduction environment, behavior of hydroxyl and
26 lattice of it at high temperature and high pressure are less investigated in contrast to other
27 hydrous phases. Here, using *in situ* IR and Raman spectroscopy, we characterize hydroxyl and
28 lattice of ammonium-bearing and ammonium-free phengite at high temperature and high
29 pressure. No proton transferring and structural phase transition in phengite were observed over
30 the measured temperature and pressure range. Both pressure and temperature induce hydroxyl
31 band shifting to lower frequencies, and pressure has a greater impact. The band width of
32 hydroxyl increases with temperature and pressure. Hydroxyl bond weakening and hydrogen
33 disordering at high temperature and high pressure should be responsible for the spectra
34 variations. On the other hand, the lattice modes soften with increasing temperature whereas
35 stiffen under compression, and ammonium plays an important role in the Grüneisen parameters
36 of the lattice modes, especially the K-O mode. These features of hydroxyl and lattice at high
37 temperature and high pressure could benefit for further understanding dehydration,
38 thermodynamic properties and stability of phengite in subduction zones.

39 1 Introduction

40 Dehydration of hydrous minerals in subduction zones not only determines the transport
41 efficiency of water to the deep Earth, but also can trigger magmatism and earthquakes, cause
42 oxidization of the sub-arc mantle wedge, and lead to rheological heterogeneities and large
43 conductivity anomalies (e.g., Green et al., 2010; Grove et al., 2012; Schmidt & Poli, 2014;
44 Debret et al., 2015; Manthilake et al., 2016; Okazaki & Hirth, 2016; Chen et al., 2017; Ferrand et
45 al., 2017; Behr et al., 2018). Dehydration of hydrous minerals has therefore been extensively
46 investigated over the years (Ono, 1998; Mibe et al., 1999; Hattori & Guillot, 2003; Wallace,
47 2005; Tokiwa & Nakashima, 2010; Van Keken et al., 2011; Hu et al., 2017; Hwang et al., 2017;
48 Liu et al., 2019). Several recent studies provide new insights into dehydration of hydrous
49 minerals in subduction zones. For example, Hu et al. (2017) reported dehydrogenation rather

than dehydration of goethite, revisiting the general concept of hydrogen circulation by hydration and dehydration. Our recent study (Liu et al., 2019) reported intimate links between other volatiles such as nitrogen and dehydration of phengite, highlighting the need to re-evaluate dehydration of hydrous minerals, in particular phengite. Most importantly, the role of super-hydrated kaolinite formed under high pressures in the deep Earth's water cycle was recently evaluated by Hwang et al. (2017). They suggest that other hydrous minerals in the oceanic sediment and crust may undergo similar super-hydration during subduction.

Phengite is the most common high-pressure white mica observed in subducted metasediments, being stable in subduction zones to depths of about 300 km (Schmidt, 1996). It is a good candidate for transporting both hydrogen and nitrogen into the deep Earth (Busigny et al., 2003; Watenphul et al., 2009). Noteworthy, residing as ammonium (NH_4^+) in the interlayer sites in phengite, nitrogen is intimately linked to the kinetics and mechanism of dehydration in phengite at high temperatures (Yang et al., 2017, Liu et al., 2019). Most interestingly, in contrast to other hydrous minerals (Hwang et al., 2017), there is no hydration of phengite compressed in water, as indicated by *in situ* Raman spectroscopic studies (Goryainov et al., 2017). To understand the stability and dehydration of phengite in subduction zones, the behavior of hydroxyl in phengite and the lattice properties of phengite at high temperature and pressure should be examined in detail. However, in contrast to other hydrous minerals in subduction zones, *in situ* high-T-P vibrational spectroscopy has been rarely applied to phengite. In this study, we present new data of the structural stability of hydroxyl and variation of lattice feature in phengite at high temperature and pressure.

2 Materials and Methods

2.1. Samples

Single crystals of natural ammonium-bearing and ammonium-free phengite from a previous study (Liu et al., 2019) were selected for this study. The chemical composition and unit-cell parameters are listed in Table S1.

2.2. *In situ* high temperature IR and Raman spectroscopy

For *in situ* high temperature IR spectra measurements, an Instec HS1300 heating stage with CaF_2 windows was used to generate high temperatures. The samples were heated in the stage purged

with Ar. IR spectra in the frequency range 4000-1000 cm^{-1} were collected at every temperature at Zhejiang University, China, using a Nicolet iS50 FTIR spectrometer coupled with a Continuum microscope. A KBr beam-splitter and a liquid nitrogen-cooled MCT-A detector were applied. A total of 128 scans were accumulated for each spectrum at a 4 cm^{-1} resolution. The aperture size was set to be 50×50 μm . For *in situ* Raman spectra measurements, a Linkam 600 heating stage was used to generate high temperatures. Raman spectra were collected from a range of 50 cm^{-1} to 1200 cm^{-1} at every temperature employing a HPRIBA LABRAM-HR spectrometer at Zhejiang University, China. Single-crystal silicon was used as a reference. The sample was excited by the 514.5 nm green line of a Spectra Physics Ar laser. A 50× objective was used to focus the incident laser light on the sample and to collect the scattered light. The diameter of the focused laser light spot was estimated to be 1 μm .

2.3. *In situ* high pressure IR and Raman spectroscopy

For *in situ* high pressure IR and Raman spectra measurements, hydrostatic high-pressure conditions were generated in a symmetric piston-cylinder diamond anvil cell (DAC) with diamonds of 300 μm culet size. Prior to sample loading, pieces of stainless steel foil or Re gasket were pre-indented in the cell down to a thickness of about 20-30 μm . A 100 to 150 μm diameter hole was then drilled into the gasket. A thin sample section was loaded into the sample chamber between two diamond anvils together with ruby for pressure calibration. The sample chamber was then filled with KBr as a pressure medium. During the experiments, pressure variations within the samples were monitored with the multiple ruby clips located near the sample. At the peak pressures on compression, these variations did not exceed 10% of the total pressure.

Using a Bruker VERTEX 70v spectrometer coupled with a Bruker Hyperion 3000 microscope, IR spectra from 4000-1000 cm^{-1} were collected at every pressure at the Infrared spectroscopy and microscopic imaging beamline (BL01B) of the National Synchrotron Radiation Laboratory (University of Science and Technology of China). A KBr beam-splitter and a liquid nitrogen-cooled MCT-A detector were applied. The aperture size was set to 30×30 μm . A total of 128 scans were accumulated for each spectrum at a resolution of 4 cm^{-1} . Raman spectra were collected from 50 to 1200 cm^{-1} and from 3000 to 4000 cm^{-1} at every pressure using a HPRIBA LABRAM-HR spectrometer. Single-crystal silicon was used as a reference. The sample was excited by the 514.5 nm green line of a Spectra Physics Ar laser. A 50× objective was used to

focus the incident laser light on the sample and to collect the scattered light. The diameter of the focused laser light spot was estimated to be 1 μm .

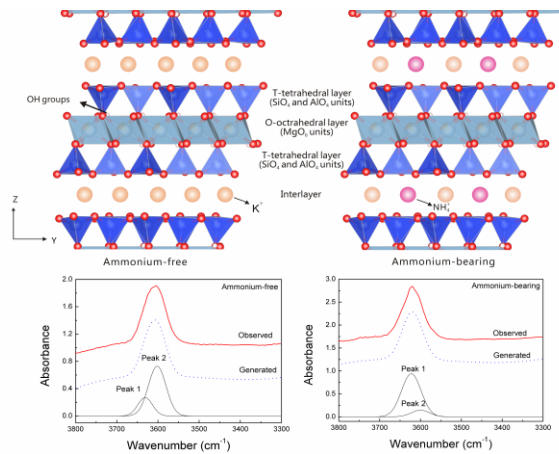
All the parameters of IR and Raman spectra at elevated temperatures and pressures are listed in Tables S2-S5.

3 Results and discussion

3.1. Hydroxyl in phengite at ambient conditions

Phengite is a common high pressure white mica, with chemical compositions between muscovite end-member and celadonite end-member. Muscovite is comprised of an octahedral sheet sandwiched between two tetrahedral sheets (SiO_4), forming tetrahedral-octahedral-tetrahedral (T-O-T) layer structure. Although structure of muscovite has been extensively investigated, hydrogen sites in muscovite lattice are still not well known. Liang et al. (1998) reported two independent but closely separated hydrogen sites within muscovite based on the neutron spectroscopy at -261°C , which is consistent with the IR spectrum of muscovite and electrostatic calculations (Serratosa & Bradley, 1958; Rouxhet, 1970; Abbott et al., 1989; Liang & Hawthorne, 1998). However, Gatta et al. (2011) argued for the presence of a single hydrogen site in muscovite based on neutron diffraction at -261°C . Hydrogen disordering in muscovite at high pressure, indicated by IR spectra, also suggests multiple hydrogen sites (Williams et al., 2012). Because of these discrepancies, only one band around 3620 cm^{-1} in the IR spectra of hydroxyl in muscovite is generally considered. Recently, Tuladhar et al. (2019) detected multiple distinct peaks in the O-H stretching vibration region using vibrational sum frequency generation spectroscopy. In this study, we also find the broad and asymmetric O-H stretching bands of the phengite samples at ambient conditions (Fig. 1). Band deconvolution indicates two OH bands around 3600 and 3620 cm^{-1} . Therefore, the broad and asymmetric OH bands should be assigned to hydrogen sites with different environments.

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135 **Figure 1. IR spectra of hydroxyl in the phengite at ambient conditions. The crystal structures of the two samples are**
 136 **illustrated.**

137 3.2. Hydroxyl in phengite at high temperatures

138 Evolutions of hydroxyl in ammonium-bearing and ammonium-free phengite samples at elevated
 139 temperatures to 800 °C are displayed in Figure 2. The frequency of hydroxyl appears insensitive
 140 to temperature for both phengite types. The hydroxyl band gradually broadens with increasing
 141 temperature, with a discontinuous broadening taking place at about 400 °C, indicating
 142 disordering of the different hydrogen sites. Comparing the spectra at 20 °C before and after
 143 heating, it is apparent that the integral absorbance decreases for the ammonium-bearing phengite
 144 but does not change for the ammonium-free phengite. This is in accordance with our previous
 145 study showing that ammonium promotes dehydration of phengite at high temperatures (Liu et al.,
 146 2019). Figure 3 compares temperature-induced frequency shifts of some hydrous phases in
 147 subduction zones. Hydroxyl bands in these phases generally have negative frequency shifts with
 148 increasing temperature. In contrast to nominally anhydrous minerals (Yang et al., 2019), there
 149 appears no relationship between the frequency shift and room-temperature frequency of these
 150 hydrous phases. However, it is obvious that hydroxyl in phengite is most insensitive to
 151 temperature, which is distinct to other hydrous minerals especially muscovite and pyrophyllite.
 152 The frequency of a hydroxyl reflects strength of the O-H bond. Thus, negative frequency shifts
 153 are caused by lengthening of the O-H bond during heating. The contrasting behavior of O-H
 154 bond between phengite and other hydrous minerals at high temperatures is compatible with the
 155 better thermal stability of the former.

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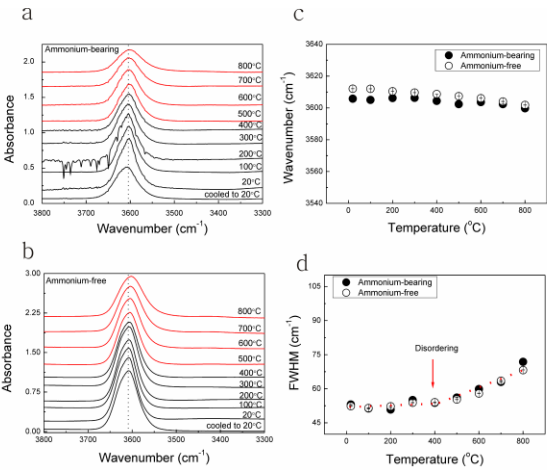


Figure 2. Temperature evolutions of hydroxyl in phengite: (a) and (b) *in situ* high temperature IR spectra of ammonium-bearing phengite and ammonium-free phengite, respectively; (c) variation of the hydroxyl frequency with increasing temperature; (d) variation of the width of hydroxyl band the full width at half-maximum, FWHM) with increasing temperature.

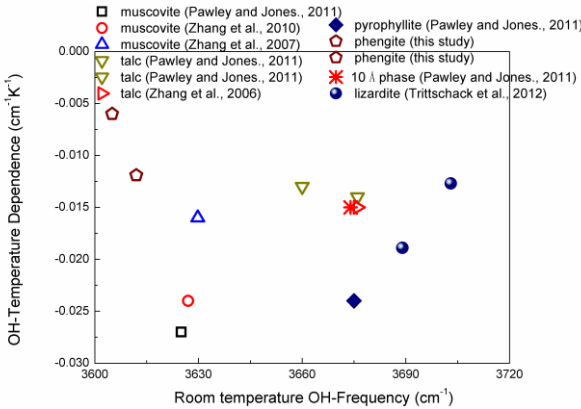


Figure 3. Temperature-induced frequency shifts of the hydroxyl band in hydrous minerals.

3.3. Hydroxyl in phengite at high pressures

Evolutions of hydroxyl in ammonium-bearing and ammonium-free phengite under compression are shown in Figure 4. We did not find pressure-induced hydrogen transferring similar to that observed for brucite by Shinoda et al. (2002), but pressure can indeed induce dramatic variations of hydroxyl. The hydroxyl band broadens with increasing pressure. Interestingly, there is a discontinuity at around 10 GPa in the evolution of band width with pressure, for both IR band and Raman band. The band broadening indicates pressure-induced hydrogen disordering, which is similar to the behavior of hydroxyl in muscovite (Williams et al., 2012). In addition, pressure also induces hydroxyl band shifting to lower frequencies, and the frequency shift is much greater

175 than temperature-induced shift. Hydroxyl in phengite continuously shifts to lower frequencies
176 under compression, without displaying a discontinuity in the pressure-induced frequency shift as
177 hydroxyl in lawsonite (Scott & Williams, 1999). Figure 5 includes pressure-induced frequency
178 shifts of hydroxyl in hydrous phases of subduction zones. Some bands shift to higher
179 frequencies, while others shift to lower frequencies. There seems to be no general relationship
180 between frequency shift and room-pressure frequency for the minerals. However, this
181 relationship indeed exists within the same mineral. For example, there is a positive relationship
182 between the frequency shift and room-pressure frequency for most of the minerals except for
183 lawsonite and phase D displaying a negative relationship. The pressure-induced negative
184 hydroxyl frequency shift is generally ascribed to shortening and strengthening of the hydrogen
185 bonding (an attractive interaction between a hydrogen atom from a hydroxyl and a neighboring
186 oxygen atom, O-H...O), thereby lengthening and weakening of the O-H bond with increasing
187 pressure (e.g., Pawley & Jones, 2011; Williams et al., 2012). Therefore, the negative frequency
188 shift of hydroxyl in phengite under compression indicates weakening of the hydroxyl bonds at
189 high pressures. The frequency shift range of hydroxyl in phengite is relatively small compared to
190 other minerals, especially lawsonite and brucite.

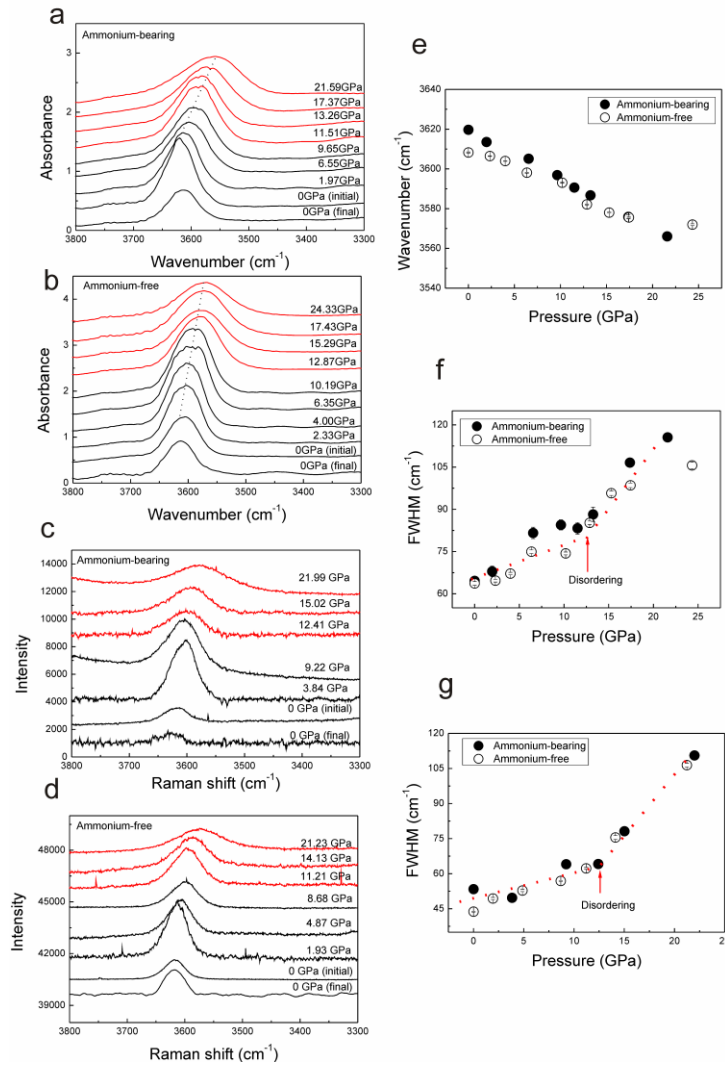
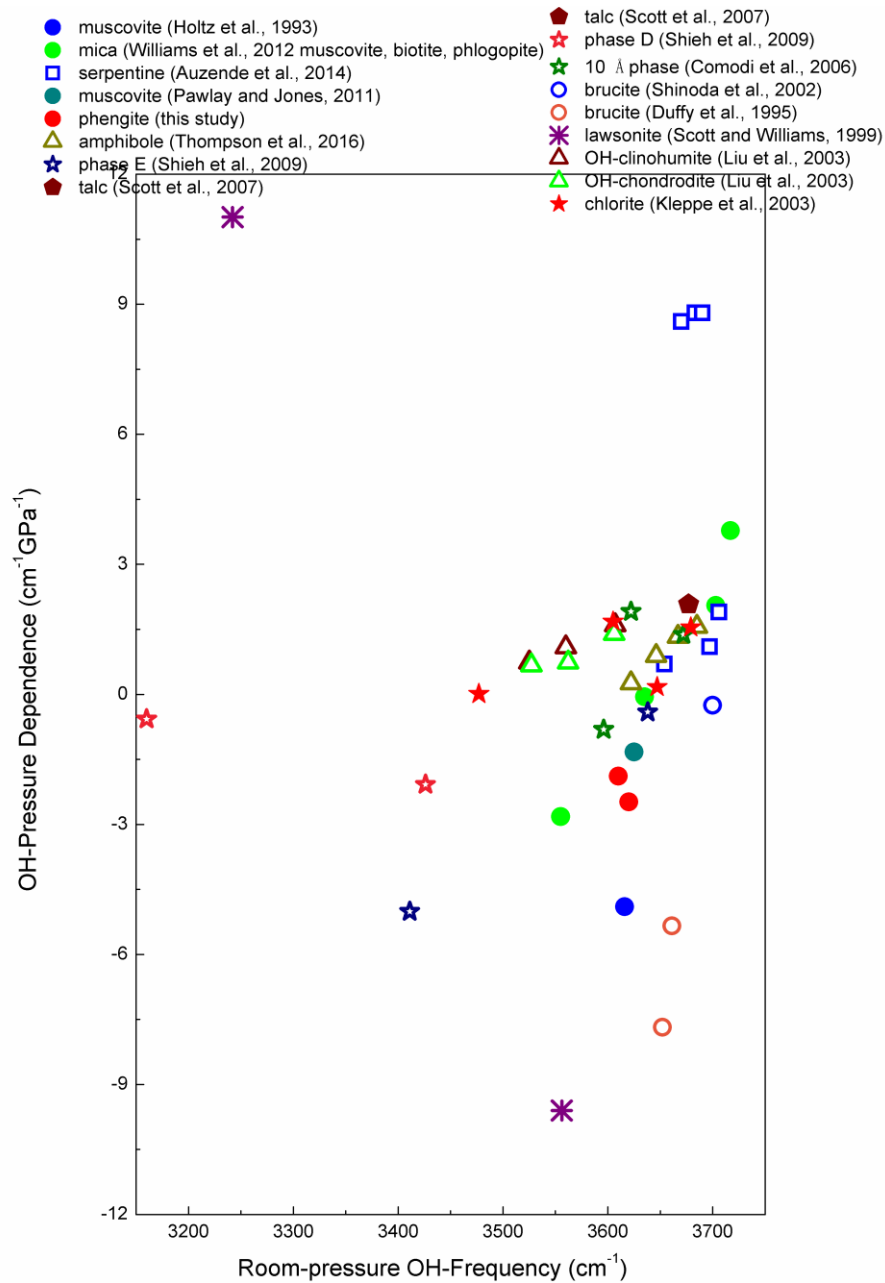


Figure 4. Evolutions of hydroxyl in phengite under compression: (a) and (b) *in situ* high pressure IR spectra of ammonium-bearing phengite and ammonium-free phengite, respectively; (c) and (d) *in situ* high pressure Raman spectra of ammonium-bearing phengite and ammonium-free phengite, respectively; (e) variation of the hydroxyl frequency with increasing pressure; (f) variation of the width of hydroxyl IR band with increasing pressure; (g) variation of the width of hydroxyl Raman band with increasing pressure.



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198 **Figure 5. Pressure-induced frequency shifts of hydroxyl bands in hydrous minerals.**

199 **3.4. Lattice of phengite at high temperature/high pressure**

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There are about five prominent bands around 95, 190, 260, 420 and 706 cm^{-1} in the spectra of phengite at ambient conditions. McKeown et al. (1999) suggested that the modes between 800

and 360 cm^{-1} had internal tetrahedral sheet motions mixed with K and octahedral Al displacements, and the modes at frequencies less than 360 cm^{-1} had lattice motions. The evolutions of lattice vibrations with increasing temperature to 500°C are shown in Figure 6. The spectra at high temperatures suggest no disordering of the lattice within this temperature range. The frequencies of most of the lattice modes slightly shift to lower frequencies with increasing temperature. Inversely, the 435 cm^{-1} mode in the ammonium-bearing phengite slightly shifts to higher frequencies. In addition, the frequency shift of the 95 cm^{-1} mode is much smaller for the ammonium-bearing phengite than the ammonium-free phengite. According to the band assignment of previous studies (Holtz et al., 1993, McKeown et al., 1999, Mookherjee & Redfern, 2002, Zhang et al., 2010), the band at 95 cm^{-1} in the present study should be due to K-O stretching vibration. The temperature-induced lower frequency shift of the lattice modes indicates expansion of the microstructure with increasing temperature. When the isobaric Grüneisen parameter of the five modes of the ammonium-bearing phengite, the ammonium-free phengite and muscovite are compared, the isobaric mode Grüneisen parameters of muscovite are obviously different from those of phengite. Furthermore, the distinct behavior of some modes, especially the 95 cm^{-1} mode, between the ammonium-bearing phengite and the ammonium-free phengite may suggest some effects of ammonium on the thermodynamic properties and stability of the phengite lattice.

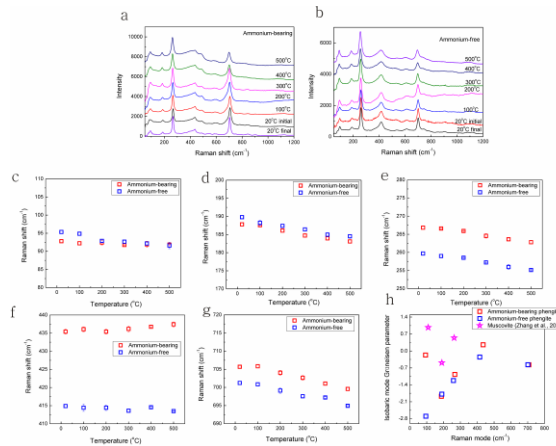


Figure 6. Temperature evolutions of phengite lattice: (a) and (b) *in situ* high temperature Raman spectra of ammonium-bearing phengite and ammonium-free phengite, respectively; (c)-(g) variations of Raman shifts with increasing temperature; (h) isobaric Grüneisen parameters of the Raman modes. The isobaric Grüneisen parameters of phengite were calculated using the equation of Fujimori et al. (2002), and the thermal expansion coefficient was taken from Gemmi et al. (2008).

Based on high pressure Raman and XRD spectroscopic studies of muscovite, lattice disordering of muscovite occurs at pressures around 15-18 GPa (Faust & Knittle, 1994; Williams et al., 2012). However, the Raman spectra of phengite suggest no lattice disordering within the pressure range of this study (Fig. 7), which is in agreement with the observations of phengite made by Goryainov et al. (2017). In contrast to temperature, pressure causes modes significantly shifting to higher frequencies for both the ammonium-bearing and ammonium-free phengite samples. There is little difference between the pressure-induced mode shifts of the two phengite species. The pressure-induced stiffening of the Raman modes indicates strengthening of the K-O, M-O and T-O bonds. The shortening of these bonds is compatible with the compressed structure of phengite (Gatta et al., 2009, 2010). The isothermal mode Grüneisen parameters of muscovite are similar to those of phengite, except for the 112 cm^{-1} mode assigned to K-translation (Williams et al., 2012). Comparison between the ammonium-bearing phengite and the ammonium-free phengite indicates that ammonium has little effect on the isothermal mode Grüneisen parameters. Nevertheless, ammonium effects on the compression of phengite still need to be investigated.

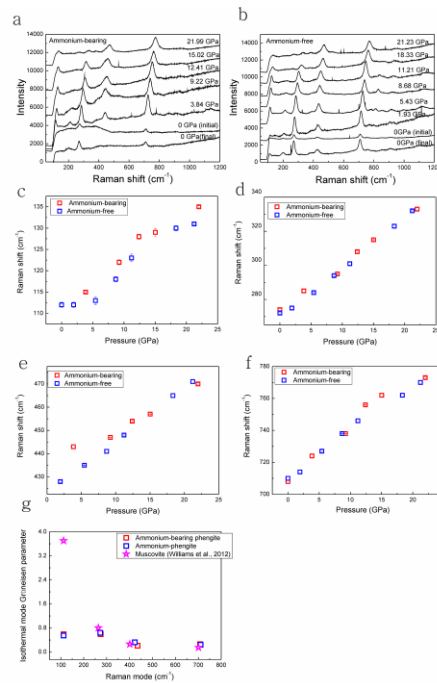


Figure 7. Evolutions of phengite lattice under compression: (a) and (b) *in situ* high pressure Raman spectra of ammonium-bearing phengite and ammonium-free phengite, respectively; (c)-(f) variations of Raman shifts with increasing pressure; (g) isothermal Grüneisen parameter of the Raman modes. The isobaric Grüneisen parameters of

phengite were calculated using the equation of Fujimori et al. (2002), and the isothermal bulk modulus was taken from Curetti et al. (2006).

4. Implications

4.1. Dehydration before phengite breakdown

Water release in subduction zones provides the main source for fluids triggering flux melting in the mantle wedge, formation of volcanoes and earthquakes (e.g., Van Keeken et al., 2011). In studying dehydration of hydrous minerals in subducting slabs, much more attention has been paid to mineral breakdown than water diffusion in the mineral lattice. However, it was recognized by Gaines & Vedder (1964) that the rate of muscovite breakdown may be limited by hydroxyl diffusion from its lattice. Indeed, many subsequent experimental studies focused on dehydroxylation of muscovite without breakdown during heating at room pressure (e.g., Gaines & Vedder, 1964; Mazzucato et al., 1999; Tokiwai & Nakashima, 2010; Zhang et al., 2010; Heller-Kallai & Lapides, 2015; Liu et al., 2019). Whether dehydroxylation without mineral breakdown can happen at high pressures need to be further clarified. Our study concerns the behavior of hydroxyl in phengite at high pressure and high temperature, revealing hydroxyl bonds weakening and hydrogen disordering. For brucite, any modulation of the O...O distance as a result of thermal motions will effectively lower the height of the potential barrier between proton sites of hydroxyl (Martens & Freund, 1976). On the other hand, pressure-induced hydrogen disordering in hydroxide has been extensively reported. It can trigger destabilization of the oxygen substructure, and enhancement of electrical conductivity (e.g., Duffy et al., 1995; Guo & Yoshino, 2014). According to Mazzucato et al. (1999), the process of dehydration in muscovite encompasses the following three steps: condensation of two adjacent hydroxyls in the octahedral layer to form a water molecule, diffusion of the water molecule throughout the tetrahedral layer, and diffusion of the water molecule in the interlayer region to be releases. Since the formation of water from structural hydroxyl in the lattice is the primary step, dehydroxylation in the lattice is vital for the whole dehydration process. We propose that pressure-induced shortening of the O...O distance (weakening of hydroxyl bond) and hydrogen disordering in phengite should favor condensation of two adjacent hydroxyls in the octahedral layer to form water molecules. These results may shed new light on dehydration in phengite. Water may be continuously released from the lattice before the phengite breakdown with increasing temperature and pressure. To further compare the properties of hydroxyl of the

hydrous phases under compression in subduction zones, we display the available isothermal Grüneisen parameters of hydroxyl in several hydrous minerals in Figure 8. It is clear that the isothermal Grüneisen parameters for hydroxyl in most phases in subduction zones are positive, except for phengite, phase E and phase D showing negative isothermal Grüneisen parameters. Although water content in phengite is not very high relative to other hydrous phases in subduction zones, phengite can be stable at a wide range of pressure in the subduction environment. Therefore, dehydroxylation from the lattice before its breakdown can not be neglected in the evaluation of water release in subduction zones.

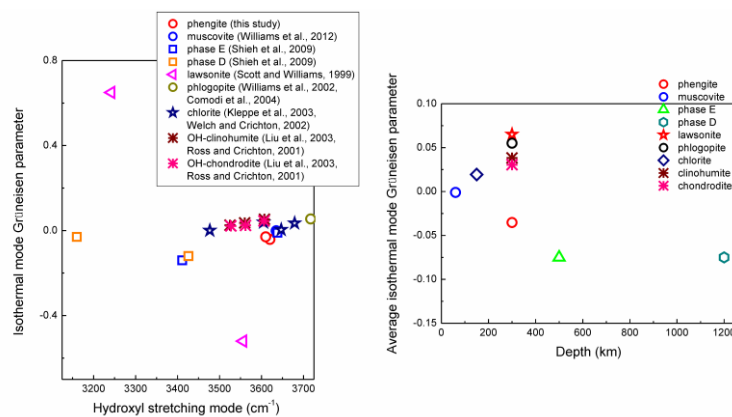


Figure 8. Comparison of isothermal Grüneisen parameters of hydroxyl between different minerals in subduction zones: (a) isothermal Grüneisen parameters of hydroxyl in hydrous minerals. The parameters of muscovite, phase E, phase D and lawsonite were taken from the references listed in the figure. The parameters of the other minerals were calculated using the equation of Fujimori et al. (2002). The frequency shifts were adopted for phlogopite from Williams et al. (2012), for chlorite from Kleppe et al. (2003), and for clinohumite and chondrodite from Liu et al. (2003). The isothermal bulk modulus values were taken for phengite from Curetti et al. (2006), for phlogopite from Comodi et al. (2004), for chlorite from Welch and Crichton (2002), and for clinohumite and chondrodite from Ross and Crichton (2001). (b) average isothermal Grüneisen parameters of hydroxyl in minerals that are stable to different depths, with the maximum stability depths taken from Litasov and Ohtani (2007).

4.2. Potential effects of ammonium on thermodynamic properties and stability of phengite

Mineral stability under equilibrium conditions is governed by the lowest free energy. Lattice vibrations are related to thermodynamic properties of minerals, thus, mineral stabilities can be studied from lattice vibrations (Kieffer, 1979; Ross, 1992). Our study found that temperature and pressure have opposite impacts on the properties of the phengite lattice. Temperature induces softening of the framework, while pressure makes the framework stiffer. Based on the mode Grüneisen parameters of the ammonium-bearing and ammonium-free phengite samples (Figs. 6 and 7), the absolute value of the average isobaric Grüneisen parameter is much smaller for

ammonium-bearing phengite (0.67) than the ammonium-free phengite (1.30), while the absolute value of the average isothermal Grüneisen parameter is not much different between the two samples. It should be noted that the mode Grüneisen parameters in this study were calculated on the basis of the thermal expansion coefficient and isothermal bulk modulus of ammonium-free phengite (Curetti et al., 2006, Gemmi et al., 2008). Even so, ammonium impacts on the mode Grüneisen parameters can still be observed. Therefore, the effects of ammonium on the thermodynamic properties and stability of phengite deserve careful consideration.

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