

In situ Raman Spectroscopic Study of Interaction between Phengite and Water under P – T Conditions Typical of Subduction Zones

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Abstract—In situ Raman spectroscopy is used to study the layered mineral phengite $K(\text{Al}, \text{Mg})_2(\text{Si}, \text{Al})_4\text{O}_{10}(\text{OH})_2$ in water under the high temperature and pressure conditions typical of cold subduction zones (T up to 373°C and $P = 12.5$ GPa). High pressure and temperature were created in a resistively heated diamond anvil cell. Raman spectra show the high P – T stability of phengite. No reversible polymorphic transitions (overhydration or notable amorphization) are observed.

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INTRODUCTION

It is important that we study the interaction between silicates and water under the pressure and temperature conditions characteristic of subduction zones if we are to understand the geobalance of materials, the transport of water, and other volatile components in subduction zones [1, 2]. The transport of water to great depths is mostly due to the enormous quantity of serpentinous rocks in the subducting oceanic crust. In addition to serpentinous rocks, other high-pressure minerals are believed to participate in water transport, e.g., phengite [3, 4], datolite [5], and talc [6]. Phengite remains poorly studied today.

Phengite $K(\text{Al}, \text{Mg})_2(\text{Si}, \text{Al})_4\text{O}_{10}(\text{OH})_2$ is a potassic dioctahedral mica. Its crystal structure is similar to that of muscovite, differing from the latter by a higher number of Mg cations. According to the IMA list of minerals [4], phengite is a solid solution with the abovementioned chemical composition. It belongs to the mica group, which includes the dioctahedral mica minerals muscovite $\text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2$, aluminoceladonite $\text{KAlMgSi}_4\text{O}_{10}(\text{OH})_2$, and celadonite $\text{KMgFe}^{3+}\text{Si}_4\text{O}_{10}(\text{OH})_2$. Compared to other ultrahigh-pressure complexes, phengite contains more Si than complexes found at shallower depths.

Phengite is believed to be responsible for water transport in subduction zones. It is one of the deepest hydrated minerals [1], due to its high stability with respect to pressure and temperature. Phengite and its P – T diagram have only been studied ex situ: phengite samples have been analyzed after high-pressure experiments. The structure and vibrational properties of

phengite have never been studied under conditions of high pressure and temperature using in situ structural and spectroscopic techniques. In [3], it was reported that up to 7.4 GPa, the pressure dependence of phengite unit cell parameters (a/a_0 and b/b_0) exhibits slight deviations from the Birch–Murnaghan equation of state, though the coordinates of atoms in 2M1 phengite were not specified. The structural evolution of 2M1 phengite at high pressures (up to 11 GPa) was described in [7]. It was found that phengite retains its original crystal symmetry, while its polyhedra deform as the pressure rises.

In situ techniques can be used to study such phengite transitions as reversible polymorphism, changes in the degree of hydration, and amorphization. Since phengite has a layered structure, it is believed that additional groups of H_2O or OH^- could be incorporated into the interlayer space under high pressure [8–10].

The aim of this work was to ascertain whether phengite is likely to undergo reversible polymorphism, overhydration, and amorphization under the pressure and temperature conditions typical of cold subduction zones. We used in situ Raman spectroscopy to study phengite samples at high pressures and temperatures generated in a resistively heated apparatus with diamond anvils.

EXPERIMENTAL

Raman spectra were excited using a Spectra-Physics Ar^+ Laser (wavelength, 514.5 nm; power, 5 mW)

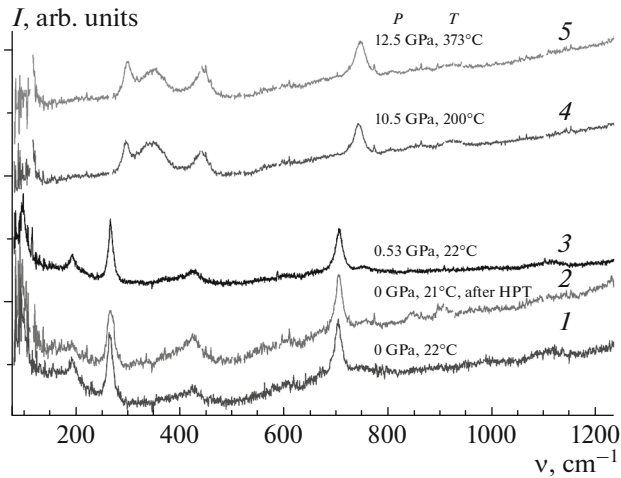


Fig. 1. Raman spectra for the area up to 1200 cm^{-1} of phengite compressed in water at specific pressures and temperatures.

and recorded with a Horiba Jobin Yvon T64000 triple spectrometer [5] in the range of $10\text{--}4000\text{ cm}^{-1}$ with a spectral resolution of 2 cm^{-1} . The experiment was conducted in a resistively heated, water-cooled apparatus with gas membrane-driven diamond anvil cells (Diacell μ ScopeDAC HT (G), EasyLab, UK) fed with a constant flow of a mixture of Ar with 1% of H_2 . The gasket used in the DAC was a $250\text{ }\mu\text{m}$ thick Inconel film, compressed to a thickness of $80\text{ }\mu\text{m}$, with a $150\text{ }\mu\text{m}$ -diameter hole drilled by an electric discharge spark drill. Fluorescent sensors were $1\text{ }\mu\text{m}$ thick slices of borate $\text{SrB}_4\text{O}_7\text{: Sm}^{2+}$ and ruby. The temperature of the thermocouple was calibrated as described in [11, 12]. Samples of phengite from eclogite were taken from the Maksyutov metamorphic complex, Southern Urals, Russia. The composition of the phengite $\text{K}(\text{Mg, Fe})_{0.5}\text{Al}_2\text{Si}_{3.5}\text{O}_{10}(\text{OH})_2$ was determined in [13].

RESULTS AND DISCUSSION

As pressure P changed, monotonous changes were observed in the Raman spectra with respect to vibrations of the cations inside and outside the framework, and to O–H stretching vibrations (Figs. 1 and 2). Raman bands at $96, 191, 264, 424$ and 703 cm^{-1} shifted monotonously to higher frequencies as pressure P increased. Note that the intensity of the main Raman bands at 264 and 703 cm^{-1} remains virtually unchanged, while the bands at 191 and 424 cm^{-1} diminish in intensity as P rises.

The Raman spectrum of phengite exhibits three very strong bands with similar intensity: the first two are below 1200 cm^{-1} , and the third band of O–H stretching oscillations of hydroxyls is at 3612 cm^{-1} . The

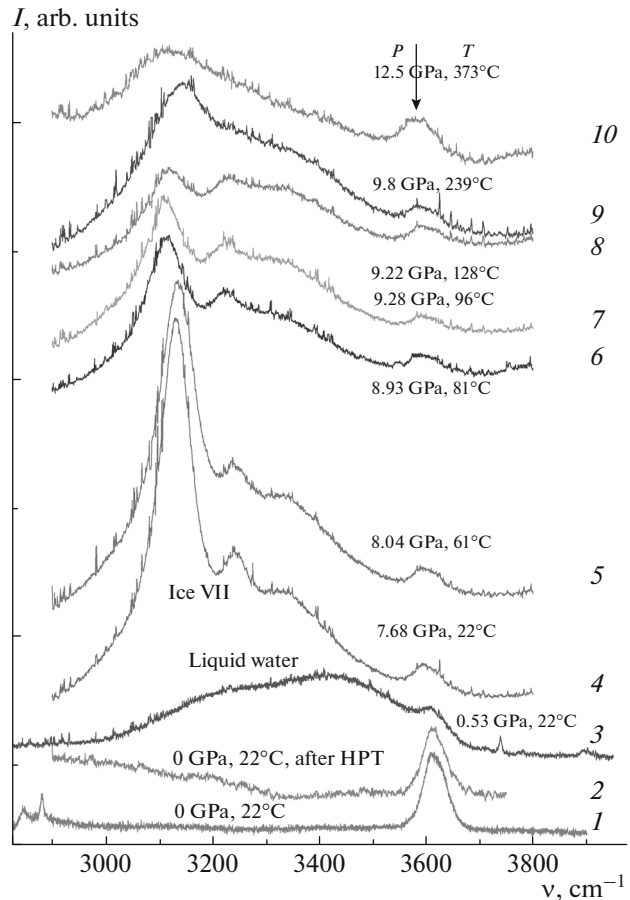


Fig. 2. Raman spectra in the area of stretching O–H oscillations of phengite compressed in water at specific pressures and temperatures.

first band at 264 cm^{-1} corresponds to external oscillations of the TO_4 tetrahedra that form an aluminosilicate layer. The second band at 703 cm^{-1} is associated with the bending O–T–O vibrations of TO_4 tetrahedra, which is similar to the interpretation of the vibrational modes of phlogopite [14]. These two bands testify to the stability of phengite at high pressures and temperatures: their intensity and frequency change very little as the pressure and temperature rise. We assume, however, that the bands at 191 and 424 cm^{-1} are due to the oscillations of K cations inside the layers: K cations are more likely to change with pressure and temperature because they form a more mobile sublattice. Their intensity thus falls considerably (Fig. 1). These conclusions regarding the great deformability of K -polyhedra are consistent with the structural data in [7].

The Raman spectra also exhibit liquid-water and ice vibration bands that appear and disappear, depending on the pressure and temperature (Figs. 1 and 2), e.g., the

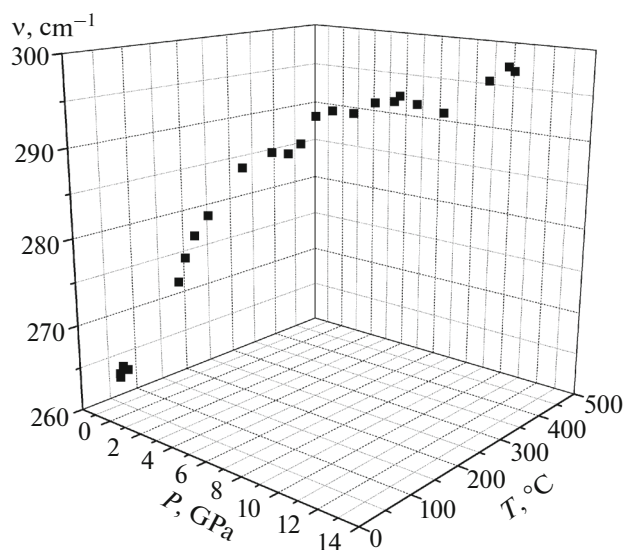


Fig. 3. Frequency of the 264 cm^{-1} Raman band of phengite vs. pressure P (from 105 Pa to 12.5 GPa) and temperature T (from 22 to 373°C).

strong 350 cm^{-1} band of the high-pressure phase of H_2O ice VII, which corresponds to external oscillations of H_2O (Fig. 1, spectra 4 and 5).

No additional O–H stretching oscillation bands appear as the pressure rises, indicating that no additional water molecules or OH^- groups penetrate into the phengite's interlayer space. Since the Raman spectrum of phengite changes little with pressure and temperature, and the number of its bands remained the same throughout the experiment, this could indicate that the initial crystalline phase is retained and there are no reversible polymorphic transitions, none of the superhydration observed earlier in zeolites [8–10], and no visible amorphization. Upon cooling and a reduction in pressure, the Raman spectrum of phengite almost regains its initial appearance, including the band of O–H oscillations of hydroxyls, which resumes its position at 3612 cm^{-1} (Figs. 1 and 2).

When $T = 22^\circ\text{C}$, the frequency of the 264 cm^{-1} Raman mode grows almost linearly with pressure P until $P \sim 10\text{ GPa}$ (Fig. 3). Subsequent heating of the DAC chamber at constant pressure on the membrane results in almost isochoric conditions and a slight increase in P (Fig. 3). At this stage, the frequency of this band grows slightly along with temperature and pressure; this increase is due to the rising pressure. The frequency usually falls as the temperature grows, but this does not compensate for the frequency shift due to the rise in pressure.

At room temperature and ambient air pressure, the bandwidths at 264 cm^{-1} and 703 cm^{-1} are 12 and 15.3 cm^{-1} , respectively. The width of the bands first grows slightly along with P (until $P \sim 10\text{ GPa}$) when

$T = 22^\circ\text{C}$. When the DAC chamber is heated, the width of these bands grows rapidly along with P (up to $20\text{--}25\text{ cm}^{-1}$ at maximum P and T), due to two mechanisms broadening the band under the influence of both T and P when the latter rises at a constant volume.

According to [1], phengite can transform into *K*-hollandite at high pressures and temperatures ($P \sim 11\text{--}12\text{ GPa}$; $T \sim 500^\circ\text{C}$). We observed no such transformation in our experiment, during which $P \sim 12.5\text{ GPa}$ and $T \sim 373^\circ\text{C}$ were reached; phengite was stable under these conditions. Note that the P – T parameters of the stability threshold of phengite can vary, depending on its chemical composition (primarily replaceable cations (Si, Al) and (Al, Mg)). No notable partial dissolution of phengite crystals was observed in liquid water.

CONCLUSIONS

Our Raman spectroscopic examination of phengite compressed in water at pressures and temperatures specific to subduction zones (up to 12.5 GPa and 373°C for 4 h) demonstrated the stability of its crystal structure, explaining the invariable number of Raman bands and the absence of reversible polymorphic transitions, overhydration, and notable amorphization.

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