

In situ Raman Study of Wairakite and Dawsonite Interaction with Water at High P – T Parameters

S. V. Goryainov^a, A. S. Krylov^b, A. N. Vtyurin^b, A. Yu. Likhacheva^a, and P. S. R. Prasad^c

^a*Sobolev Institute of Geology and Mineralogy, Siberian Branch, Russian Academy of Sciences, Novosibirsk, 630090 Russia*

^b*Kirensky Institute of Physics, Siberian Branch, Russian Academy of Sciences, Krasnoyarsk, 660036 Russia*

^c*National Geophysical Research Institute, Council for Scientific and Industrial Research, Hyderabad, 500007 India*

e-mail: svg@igm.nsc.ru

Abstract—The behavior of wairakite $\text{CaAl}_2\text{Si}_4\text{O}_{12} \cdot 2\text{H}_2\text{O}$ and dawsonite $\text{NaAlCO}_3(\text{OH})_2$ in a water medium is studied by means of in situ Raman spectroscopy at the simultaneously high temperatures and pressures (up to $T = 723$ K and $P = 1$ GPa). After the initial minerals are partially dissolved, phillipsite forms in the wairakite–water system, and a glass-like phase is generated in the dawsonite–water system. These minerals show no signs of overhydration. The amorphization of the wairakite structure that occurs at high temperatures and pressures was reversible.

DOI: 10.3103/S1062873816050087

INTRODUCTION

Using in situ means to study the behavior of minerals under conditions of their interaction with a water medium at simultaneously high temperatures and pressures is important to modeling the processes of mineral transformation in zones of the subduction of lithospheric slabs [1]. We are especially interested in mineral processes that proceed in a water medium in cold subduction zones at moderate P – T parameters, as this conforms to the beginning of oceanic crust submersion and to the bottom of the ocean near geothermal sources [1, 2].

Zeolite wairakite $\text{CaAl}_2\text{Si}_4\text{O}_{12} \cdot 2\text{H}_2\text{O}$ and carbonate dawsonite $\text{NaAlCO}_3(\text{OH})_2$ have been used selected in studies as examples of hydrated and hydroxylated minerals that might participate in oceanic crust submersion. According to the P – T phase plot constructed using the results from studies with different ex situ means [2], the region of wairakite stability lies in the range of ~ 523 – 673 K at pressure values of 0 – 0.4 GPa. As the temperature rises, wairakite is transformed into anorthite; as the temperature falls, it is converted into laumontite. When the pressure rises to 0.4 GPa, wairakite disintegrates into lawsonite + quartz + fluid. Wairakite has been studied by Raman means at high P values and room T in such quasihydrostatic media as water and glycerol [3].

Dawsonite remains stable up to a temperature of 813 K at a pressure of 1 GPa [4]. The processes in these minerals at simultaneously high P – T parameters have yet to be studied by in situ Raman means.

Compared to ex situ means, in situ methods have several advantages, since they allow us to observe such different unannealed states and transformations as

polymorphous transitions, overhydration, dehydration, and reversible amorphization [5]. Note that the overhydration initially discovered in zeolites [6] is observed in certain hydrated minerals when excess water molecules penetrate structural channels and cavities under the action of a water-containing medium [7–11]. The state of overhydration is anomalous, since it is accompanied by considerable (50 to 100 times) growth in the diffusive mobility of water molecules and cations inside the mineral channels, as opposed to normal behavior when diffusion is suppressed under the Arrhenius law as P increases [7, 11].

The aim of this work was an in situ Raman study of possible unannealed phases of zeolite wairakite and hydroxyl-carbonate dawsonite at simultaneously high temperatures and pressures of a water medium that correspond to the conditions in cold zones of lithospheric slab subduction (up to $P = 1$ GPa and $T = 723$ K). In this case, as was assumed in constructing phase plot [2], wairakite can gradually disintegrate into lawsonite and quartz, while dawsonite can retain its crystalline structure as the P – T parameters grow.

EXPERIMENTAL

High pressures and temperatures (up to 723 K and 4.5 GPa) were generated by a resistively heated device with HT-DAC (EasyLab) diamond anvils. The Raman spectra were excited by laser irradiation (514.5 nm) and were recorded by a T64000 (Horiba Jobin Yvon) spectrometer with a resolution of 2 cm^{-1} [8, 12]. Natural samples of wairakite $\text{CaAl}_2\text{Si}_4\text{O}_{12} \cdot 2\text{H}_2\text{O}$ (from Taupo, New Zealand) and dawsonite $\text{NaAlCO}_3(\text{OH})_2$ (from Slany, Czech Republic) submerged into a water medium were studied. The chem-

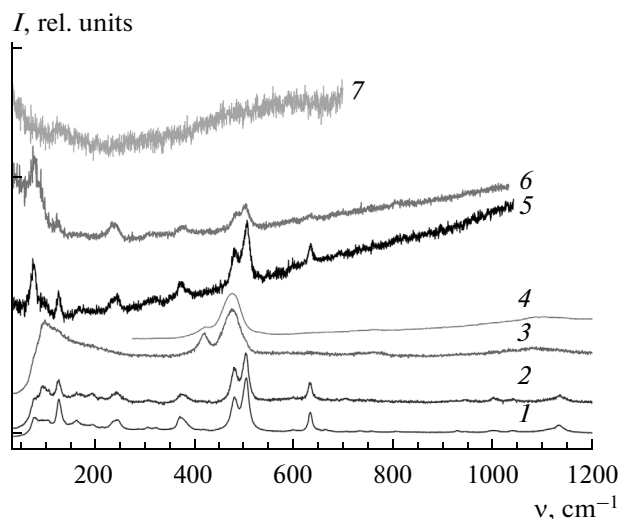


Fig. 1. Raman spectra obtained in the wairakite–water system at different P – T parameters: (1) 10^5 Pa, with 293 K as the initial temperature; (2) 10^5 Pa, with 293 K for wairakite after the experiment; (3) 10^5 Pa, with 293 K for phillipsite after the experiment in the wairakite–water system; (4) natural Ca–phillipsite; and wairakite compressed in a water medium in DAC at (5) 0.14 GPa, 293 K, (6) 0.37 GPa, 523 K and (7) 0.95 GPa, 673 K.

ical composition of the minerals was similar to the above idealized formulas.

RESULTS AND DISCUSSION

Figures 1 and 2 present the Raman spectra of wairakite and dawsonite recorded under laboratory conditions for the both initial and ex situ samples and under in situ conditions at high P – T parameters in the HT-DAC device. Wairakite $\text{Ca}_3\text{Al}_6\text{Si}_{12}\text{O}_{36} \cdot 6\text{H}_2\text{O}$ was first dissolved during the experiment; approximately 20–40% of different crystalline blocks were dissolved over four hours at 723 K. A different mineral, phillipsite $\text{Ca}_3\text{Al}_6\text{Si}_{10}\text{O}_{32} \cdot 12\text{H}_2\text{O}$, was then crystallized from the solution (Fig. 1, spectrum 3).

We expected lawsonite to appear in the wairakite–water system but instead witnessed the formation of phillipsite. This was unexpected but conformed to the data from dredging the ocean bottom where such zeolites as phillipsite (Ca–Na form [13]) and analcime (Na-form) are found. Phillipsite was crystallized in the region of the upper baric boundary of wairakite stability, which is more likely associated with the fast kinetics of this transition. It is probable that the reaction of wairakite decomposition into lawsonite and quartz was not recorded because of its low kinetic capability, and because the conditions and length of exposure could not result in the equilibrium mineral composition.

No polymorphous transformations were observed in dawsonite (Fig. 2). During the experiment, dawso-

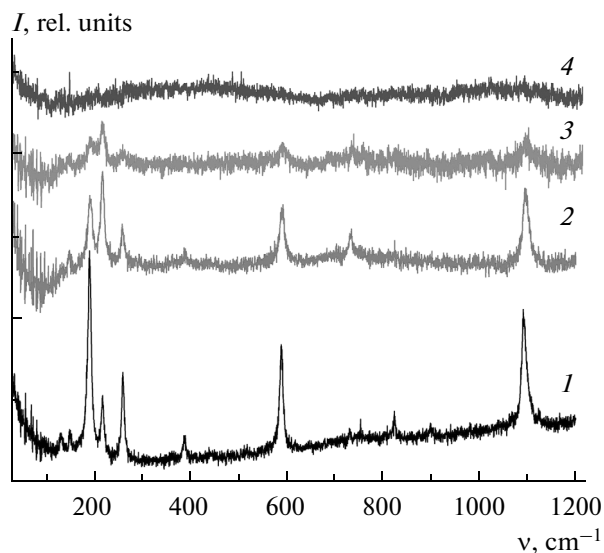


Fig. 2. Raman spectra of dawsonite compressed in a water medium at different P – T parameters: (1) 0.23 GPa, 295 K; (2) 0.47 GPa, 473 K; (3) 0.65 GPa, 573 K; and (4) 0.95 GPa, 723 K.

nite first began to dissolve; as the temperature fell, an amorphized (glasslike) phase emerged in the solution.

The Raman spectrum of crystalline dawsonite was recorded up to a temperature of 573 K. After this was reached, the spectrum diffused, indicating amorphization of the structure (Fig. 2). Exposing dawsonite for 2 h at 573 K led to the gradual reduction and disappearance of the Raman spectra of the crystalline phase. Under laboratory conditions ($P = 10^5$ Pa, $T = 295$ K), the frequency of the carbonate valence band ($\nu = 1091 \text{ cm}^{-1}$) gradually grew along with P and T (Fig. 3a). In both cases, this was due to a rise in pressure accompanying the heating of the operating volume. As a rule, the frequencies of the valence oscillating bands fell when a crystal was heated [14] (except for several bands in crystals with anomalous coefficients of thermal expansion and O–H bands). For dawsonite, the expected drop in frequency as T rose was excessively compensated for by an increase in frequency due to a rise in P (Fig. 3a).

The bandwidth of the symmetric valence C–O oscillations of dawsonite at 1091 cm^{-1} demonstrates the temperature dependence (Fig. 3b) approximated by relation [14]:

$$\Delta\nu = A(2n_2 + 1) + B(3n_3^2 + 3n_3 + 1) + d(T - T_r),$$

where $n_2 = 1/[\exp(\hbar\nu_0/2k_B T) - 1]$ and $n_3 = 1/[\exp(\hbar\nu_0/3k_B T) - 1]$ are the populations of the Bose–Einstein statistical distribution that conform to the channels of characteristic oscillation ν_0 disintegrating into two and three phonons, respectively; A and B are coefficients of band thermal broadening; and d is coefficient of band broadening $\Delta\nu_{PT} = d(T - T_r)$ due to the rise in pressure ΔP caused by the heating of the quasi-

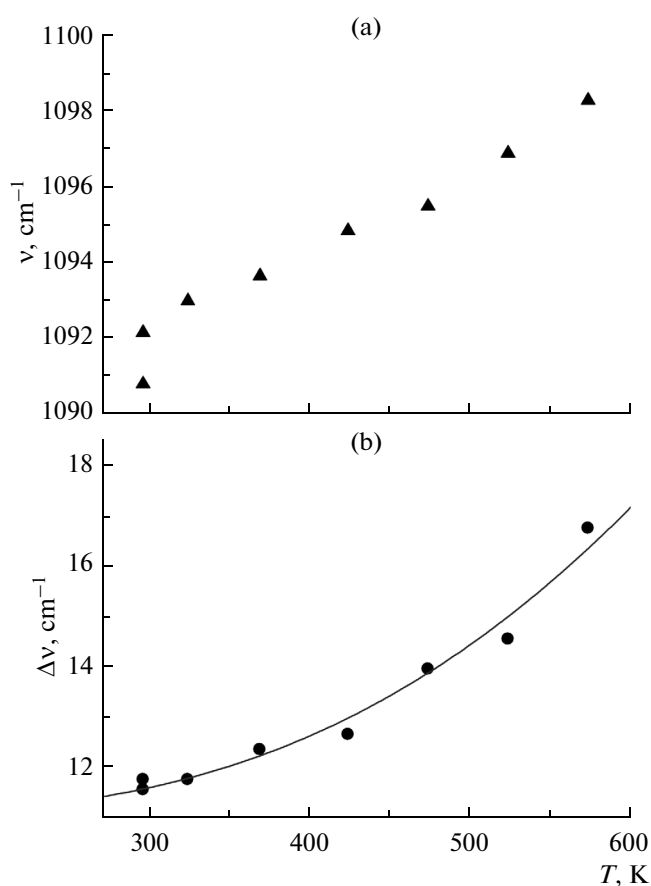


Fig. 3. Temperature T dependences of carbonate Raman band (a) frequency and (b) width ($\sim 1091\text{ cm}^{-1}$ at $P = 10^5\text{ Pa}$, $T = 295\text{ K}$) for dawsonite compressed in a water medium with simultaneous growth of parameters $P(\text{GPa})-T(\text{K})$: $\sim 0, 295$; $0.23, 295$; $0.27, 323$; $0.33, 368$; $0.4, 423$; $0.47, 473$; $0.55, 523$; and $0.65, 573$ in the sequence corresponding to the rise in frequency at each point in Fig. (a).

hydrostatic cell volume obtained in the form $d = CD$ when using linear approximations $\Delta P \approx C(T - T_r)$ and $\Delta v_{PT} \approx D\Delta P$, where the heating starts at room temperature T_r .

CONCLUSIONS

Wairakite and dawsonite compressed in a water medium do not undergo polymorphous transformation as the $P-T$ parameters increase (the crystals remain in the initial phase). At temperatures of 573–673 K ($P = 1\text{ GPa}$), however, the Raman spectra of these minerals virtually disappear, which could indicate structural amorphization. The partial reversible amorphization of wairakite is observed.

The above minerals partially dissolved during the experiment; this was followed by the formation of other minerals. As a result, an additional zeolite phase, phillipsite, formed in the wairakite–water system, and

a glass-like phase appeared in the dawsonite–water system. The formation of phillipsite recorded at $P-T$ parameters in the region of the upper baric boundary of wairakite stability could explain the wide occurrence of phillipsite in marine sediments.

The width of the dawsonite C–O stretching band obeys the temperature dependence at 1091 cm^{-1} , as was described with respect to the mechanism of this oscillation disintegrating into two and three phonons.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research, project nos. 14-05-00616 and 15-55-45070-IND, and the Russian Science Foundation, project no. 15-17-30012.

REFERENCES

1. Pawley, A.R., Chinnery, N.J., Clark, S.M., and Walter, M.J., *Contrib. Mineral. Petrol.*, 2011, vol. 162, p. 1279.
2. Rashchenko, S.V., Likhacheva, A.Yu., Chanyshev, A.D., and Ancharov, A.I., *J. Struct. Chem.*, 2012, vol. 53, p. S43.
3. Goryainov, S.V., Fursenko, B.A., and Belitskii, I.A., *Dokl. Phys. Chem.*, 1999, vol. 369, p. 307.
4. Von der Gönna, J., Nover, G., and Lathe, C., *Proc. EGU General Assembly*, 2013, vol. 15, p. EGU2013-9391.
5. Goryainov, S.V., *Eur. J. Mineral.*, 2005, vol. 17, no. 2, p. 201.
6. Hazen, R.M., *Science*, 1988, vol. 219, p. 1065.
7. Moroz, N.K., Kholopov, E.V., Belitsky, I.A., and Fursenko, B.A., *Microporous Mesoporous Mater.*, 2001, vol. 42, p. 113.
8. Goryainov, S.V., Krylov, A.S., Likhacheva, A.Yu., and Vtyurin, A.N., *Bull. Russ. Acad. Sci.: Phys.*, 2012, vol. 76, no. 7, p. 804.
9. Likhacheva, A.Yu., et al., *J. Raman Spectrosc.*, 2012, vol. 43, p. 559.
10. Goryainov, S.V., Krylov, A.S., and Vtyurin, A.N., *Bull. Russ. Acad. Sci.: Phys.*, 2013, vol. 77, no. 3, p. 313.
11. Goryainov, S.V., Secco, R.A., Huang, Y., and Likhacheva, A.Y., *Microporous Mesoporous Mater.*, 2013, vol. 171, p. 125.
12. Goryainov, S.V., Krylov, A.S., Vtyurin, A.N., and Pan, Yu., *Bull. Russ. Acad. Sci.: Phys.*, 2015, vol. 79, no. 6, p. 794.
13. Bowers, T.S. and Burns, R.G., *Am. Mineral.*, 1990, vol. 75, p. 601.
14. Surovtsev, N.V. and Kupriyanov, I.N., *J. Raman Spectrosc.*, 2015, vol. 46, p. 171.

Translated by L. Mukhortova