# Behavior of CaBSiO$_4$(OH) Datolite at High Temperatures and Pressures of a Water Medium

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**Abstract**—The behavior of CaBSiO$_4$(OH) datolite compressed in a water medium at simultaneous high temperatures and pressures corresponding to the cold zones of tectonic plate subduction (up to $P \sim 5.3$ GPa and $T \sim 250°$C) is studied in situ via Raman spectroscopy. Two polymorphic transitions are found: (i) upon an increase of up to 2 GPa in pressure at a constant temperature of 22°C and (ii) upon heating to ~90°C at a constant pressure of ~5−5.3 GPa. Major trends of the variations in the Raman spectra are identified for all phases of the indicated $P–T$ parameters. No overhydration and amorphization of datolite is observed.

## INTRODUCTION

Experimental modeling of processes in the cold zones of the subduction of lithospheric slabs at high $P–T$ parameters ($P \sim 3−15$ GPa, $T \sim 300−600°$C) typically focuses on the state of hydroxyl-bearing silicate mineral in the structure. Several minerals (serpentine, lawsonite, talc, phengite, the 10 Å phase, and so on) are assumed to be the main transporters of water to subduction zones of the submerging plates. This water is extracted via dehydration and supports the main source of magmatism in these ranges [1, 2]. Borosilicate CaBSiO$_4$(OH) datolite can also participate in this process because of its high thermal stability [3]. Despite its relatively low abundance, datolite could contribute to the transport of water and its extraction in subduction zones. The behavior of datolite at the corresponding $P–T$ parameters has so far been studied only via ex situ quenching. It has yet to be investigated using in situ methods that could determine the presence of nonrecovered phases and states, including those with variable water and hydroxyl contents.

The monoclinic $P2_1/c$ crystal structure of datolite consists of layers of active corner-sharing [SiO$_4$] and [BO$_3$(OH)] tetrahedra (only hydroxyl corners are active in boron tetrahedra) [3]. A borosilicate layer is built by four-membered and eight-membered rings located at different heights and can be considered a 2-D framework. Ca$^{2+}$ cations are distributed throughout the interlayer space and are coordinated by six O anions and two OH groups along twisted cubes.

The aim of this work was to study the behavior of CaBSiO$_4$(OH) datolite in situ via Raman spectroscopy at high $P–T$ parameters in a water medium corresponding to cold subduction zones, and to determine the major trends of the change in its structure and vibrational spectrum.

## EXPERIMENTAL

Raman spectra were excited with radiation (wavelength, 514.5 nm; power, 5 mW) from a Spectra-Physics Ar laser and recorded on a Horiba Jobin Yvon T64000 triple spectrometer at the Institute of Physics, Siberian Branch, Russian Academy of Sciences. The spectra were registered in the range of 10−4000 cm$^{-1}$ with a spectral resolution of 2 cm$^{-1}$. A heated membrane-type Diacell μScope DAC HT(G) (EasyLab, UK) high-temperature diamond anvil cell (HT-DAC) with resistive heating, water-cooled casing, and Ar (with a 1% admixture of H$_2$) gas blowing was used for our Raman study of the processes that occur at simultaneous high hydrostatic pressures and high temperatures. A steel plate 250 μm thick, compressed to a thickness of 95 μm with a hole 150 μm in diameter obtained by spark drilling, was also used. The limiting $P–T$ parameters in the work volume of the HT-DAC device were 20 GPa and 500°C. The maximum $P–T$ values in our experiments with datolite were set at 5.3 GPa and 250°C. Calculations for the datolite lattice dynamic were performed using M.B. Smirnov's LADY (CRYME [4]) software package.
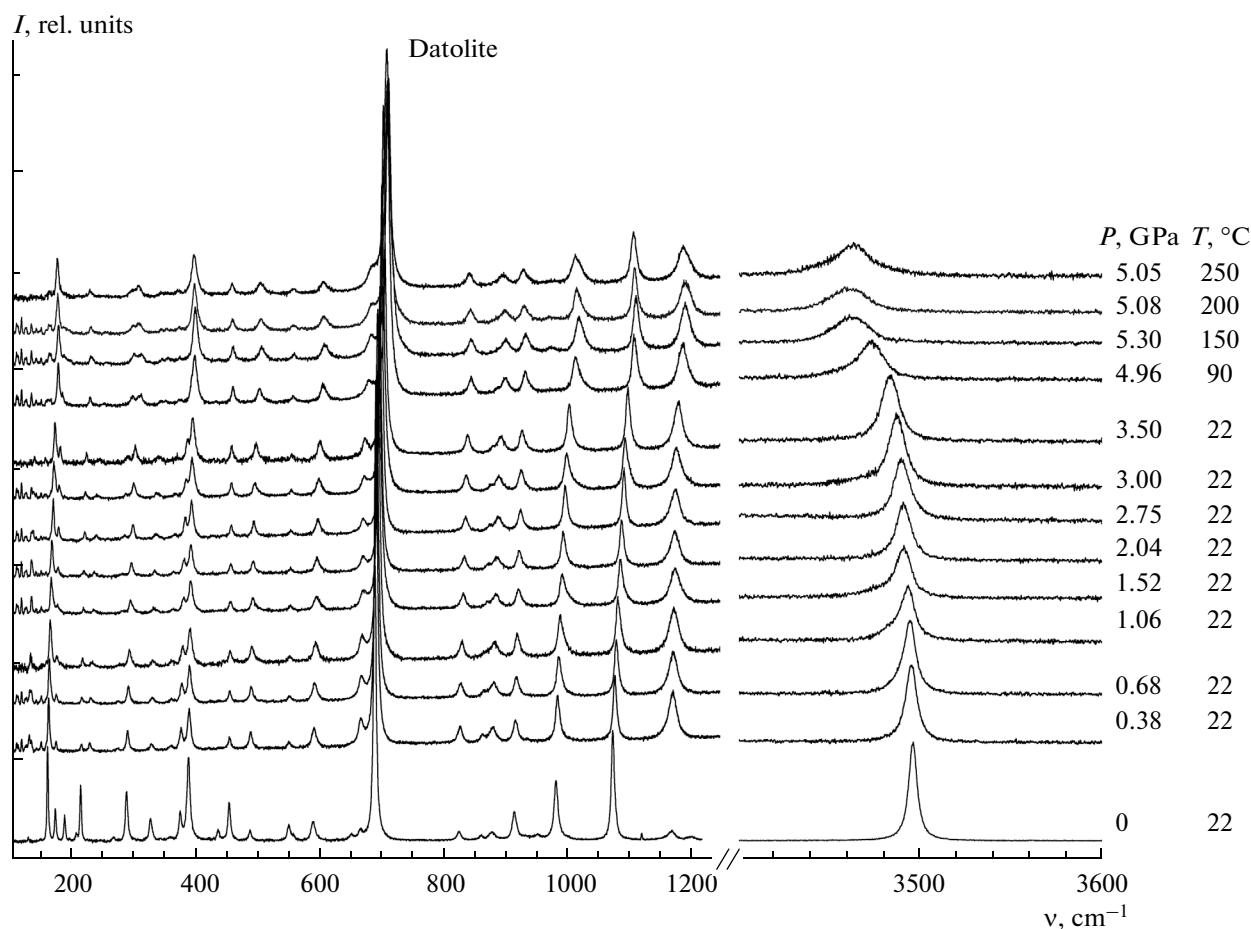
**Fig. 1.** Raman spectra of CaBSiO$_4$(OH) datolite under ambient conditions ($P = 10^5$ Pa ~ 0 GPa, $T = 22°C$) and high $P-T$ parameters of up to 5.05 GPa and 250°C. The weak narrow bands below 150 cm$^{-1}$ correspond to the Raman spectrum of air.

## RESULTS AND DISCUSSION

The Raman spectra of datolite vary when the $P-T$ conditions are elevated (Fig. 1). The main changes occur in the range of stretching O−H vibrations upon an increase in $P$, compared to the changes in both the stretching O−H vibrations and the range of external vibrations of borosilicate tetrahedra upon an increase in $T$.

Figure 2 shows the dependences of the Raman frequencies of some bands of datolite on pressure at a constant room temperature of 22°C. We can see stretching O−H vibrations at 3497 cm$^{-1}$, mixed antisymmetric stretching B−O and bending O−H vibrations at 1172 cm$^{-1}$, antisymmetric stretching B−O vibrations at 984.7 cm$^{-1}$, symmetric stretching B−O vibrations at 917.6 cm$^{-1}$, and vibrations of the borosilicate 2-D framework at 391.4 and 378 cm$^{-1}$. These bands were thus ascribed by comparing our experimental Raman spectra of datolite and ones calculated using the LADY program [4]. The frequencies of the Raman bands of the borosilicate layer and the Ca$^{2+}$ cations in the interlayer space that were registered in

the range of 150−1200 cm$^{-1}$ increase along with $P$ in an almost linear fashion with different slopes in two intervals (0−2 GPa and 2−3.5 GPa): $\nu_i(P) \sim \nu_{0i} + A_i P$ (Fig. 2), where $\nu_{0i}$ and $A_i$ are constants and 3.5 GPa is the maximum pressure at a given run with a constant $T$ of 22°C (a further rise in $P$ up to 5.3 GPa occurred simultaneously with an increase in $T$). Such Raman band $\nu_i(P)$ dependences with a frequency jump at 2.04 GPa indicate a phase transition (PT) of the first order between phases I and II. This transition was registered for the first time in our experiment. The structural changes that occur during the transition remain unclear.

We may assume that the PT is polymorphic and related to the change in the H bonds formed by H atoms of OH$^−$ group due to considerable anomalies in the $\nu(P)$ dependence of the band at 3497 cm$^{-1}$ from O−H vibrations in the range of 1.5−2.75 GPa (Fig. 2) and this transition seems longer than the $\nu(P)$ dependences for 2-D framework modes. Since no Raman bands of O−H vibrations are observed upon this transition and one O−H band is conserved, we may con-
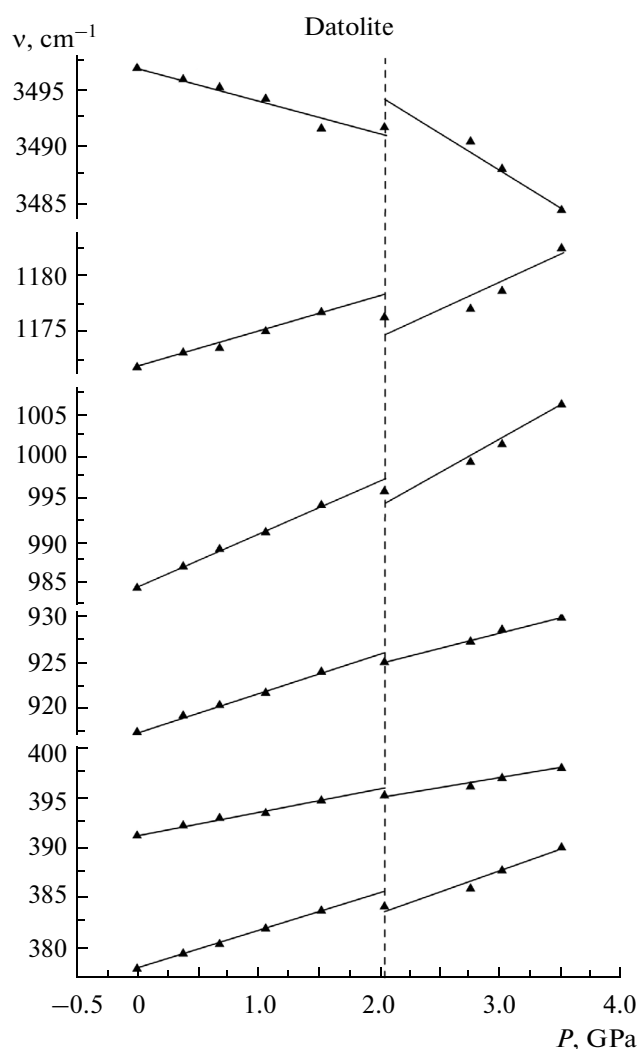
**Fig. 2.** Dependences of the wavenumbers of the Raman bands of CaBSiO$_4$(OH) datolite on pressure (from 10$^5$ Pa to 3.5 GPa) at a constant temperature of 22°C.

clude that the structural site of the OH-groups in the cell remains single in both phases I and II. The drop in the frequency of the O−H band upon an increase in $P$ (Fig. 2) indicates significant intensification of the H-bond in phases I and II, while the near stability of this band's frequency in the intermediate range of 1.5−2.75 GPa testifies to the stable energy and length of H-bonds according to the models in [5, 6].

According to the structural data in [3], datolite contains partly nonordered bifurcated H-bonds that vary upon a drop in temperature. Considering the shrinking of the datolite cell upon both hydrostatic compression and cooling, we may assume that the bifurcated H-bonds vary in a manner similar to cooling upon an increase in pressure. The PT in datolite at 2 GPa could in this case be related to similar nonmonotonic changes in structure upon a drop in $T$. The

symmetry of datolite is most likely invariable at high pressure PT, as is confirmed by the stable number of bands observed in the Raman spectra.

The absence of additional OH−bonds in high-pressure phase II could also indicate a lack of spasmodic overhydration (i.e., additional amounts of water penetrating into the structure), in contrast to some zeolites compressed in a water medium at high pressure [7−9]. No cracking of datolite upon the I−II transition or long-time diffusion processes were observed. The patterns of this transition are most likely polymorphic. In addition, none of the weak wide bands of OH vibrations that could form upon weak overhydration as H$_2$O molecules enter defect sites were observed in our Raman spectra of datolite in HT-DAC.

The Raman spectra of datolite vary considerably when $T$ rises from 22 to 90°C at fixed high $P$ (Figs. 1, 3), possibly indicating a second PT between phases II and III. The Raman bands at 176 and 232 cm$^{-1}$ disappear, a new band appears at ~300 cm$^{-1}$ (or the weak doublet band at ~271 cm$^{-1}$ grows stronger), and the singlet band at 292 cm$^{-1}$ (or the doublet band with a very weak component) becomes a doublet of bands of almost equal intensity. A new band appears at ~167 cm$^{-1}$ when $P \sim 5$ GPa and $T \sim 90$°C, and the PT doublet band that occurs at ~378 and 391cm$^{-1}$ becomes a singlet at 401 cm$^{-1}$. The Raman spectrum changes in the range of stretching O−H vibrations (Figs. 1, 3): the O−H band shifts (probably jumpwise) to the low-frequency range and grows much wider. The width of the O−H band varies weakly upon further heating from 150 to 250°C (Fig. 1). The symmetry of the datolite crystal most likely changes upon the high-temperature PT, as is probably reflected in the change in the number of Raman bands.

A comparison of the two transitions (the PT when pressure is raised to 2 GPa at constant temperature $T = 22$°C, and the high-temperature PT at 90°C and nearly constant pressure $P \sim 5.0$−5.3 GPa) shows that the high-temperature PT is distinguished by much stronger changes in the Raman spectra and thus the structure of its borosilicate 2-D framework and H-bonds.

The widths of the framework's Raman bands adhere to basic patterns: they grow almost linearly with the increase in $P$ at phase I, grow strongly with the increase in $T$ at the start of heating from 22 to 150°C in phase II at $P \sim 5$ GPa, and then grow weakly with the increase in $T$ in the range of 150−250°C at an almost constant pressure of ~5 GPa. The last pattern could be associated with the compensation effect of two opposite trends: the normal homogeneous widening of bands with an increase in $T$ and the reduction in the inhomogeneous widening of bands caused by high pressure.
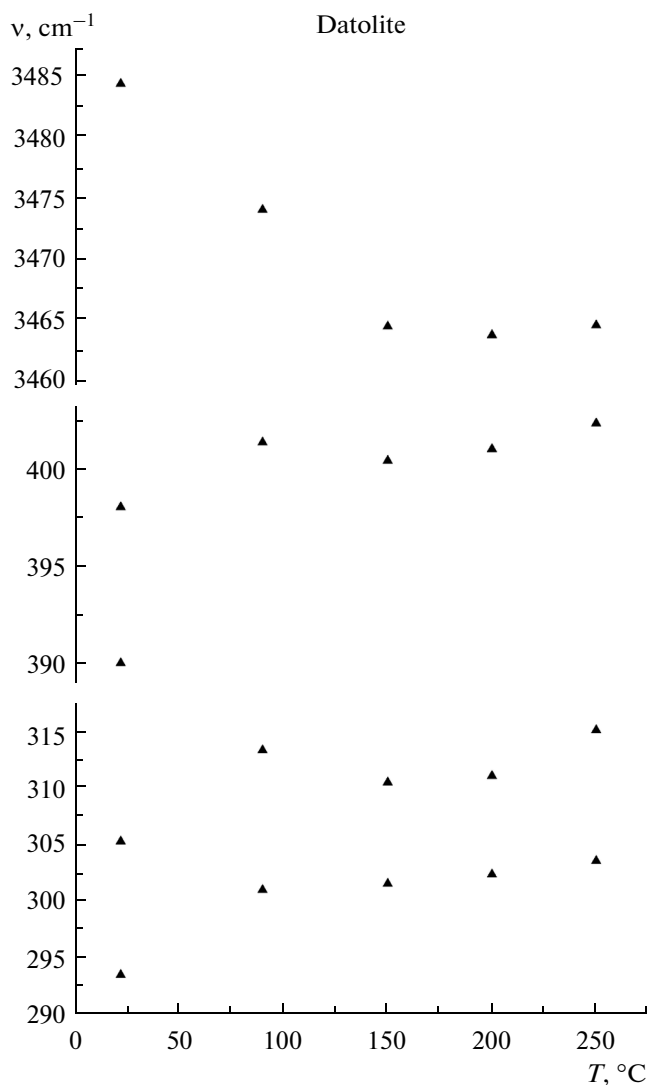
**Fig. 3.** Dependences of the wavenumbers of the Raman bands of CaBSiO$_4$(OH) datolite on temperature at high pressures (3.5−5.3 GPa). The pressure was constant upon signal acquisition at each point: 3.5 GPa (22°C), 4.96 GPa (90°C), 5.3 GPa (150°C), 5.08 GPa (200°C), 5.05 GPa (250°C).

No dehydration of datolite was observed at the investigated high $P{-}T$ parameters. We assume that the water is expelled (with the decomposition of hydroxyls) at the considerably higher temperatures of ~700−800°C corresponding to hot subduction zones [1−3].

## CONCLUSIONS

Our in situ Raman study of CaBSiO$_4$(OH) datolite in a water medium at simultaneous high pressures and temperatures revealed two polymorphic transitions: (i) transition I−II upon raising the pressure to ~2 GPa at a constant ambient temperature of 22°C and (ii) transition II−III upon heating to ~90°C at a fixed pressure of ~5.0−5.3 GPa. Both transitions were due primarily to the changes in hydrogen bonds. The wavenumbers of the datolite framework's Raman bands varied almost linearly in phases I and II in the range of our $P{-}T$ parameters.

No overhydration or amorphization of datolite compressed in our water medium were observed when the $P{-}T$ parameters were raised to values corresponding to cold subduction zones ($P$ ~ 5 GPa and $T$ ~ 250°C).

## ACKNOWLEDGMENTS

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