Raman spectroscopy in high-pressure research

Sergei GORYAINOV

Sobolev Institute of Geology and Mineralogy SB RAS, Novosibirsk, Russia

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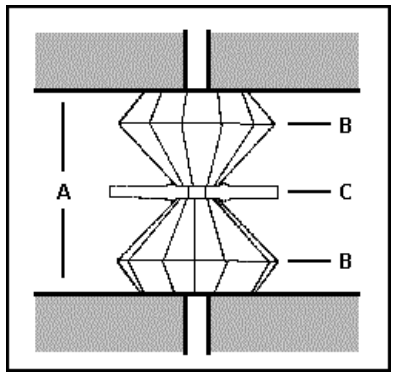
Lecture as the review of series of research works carried out by the group:

1 Goryainov S.V., 2 Krylov A.S., 1 Likhacheva A.Yu., 1 Rashchenko S.V. , 2 Vtyurin A.N.

In-situ Raman study of minerals at high pressure in diamond anvil cell: methods and achievements

- *1- Sobolev Institute of Geology and Mineralogy SB RAS, pr. Koptyug 3, Novosibirsk, Russia*
- *2- Kirensky Institute of Physics SB RAS, Akademgorodok, Krasnoyarsk, Russia*

Diamond anvil cell DAC



Scheme of DAC: A-solid supports, B-anvils, C- gasket

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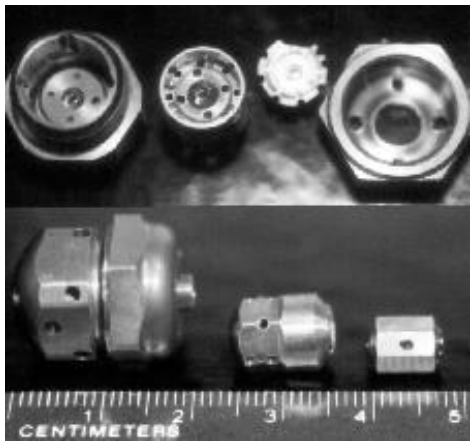
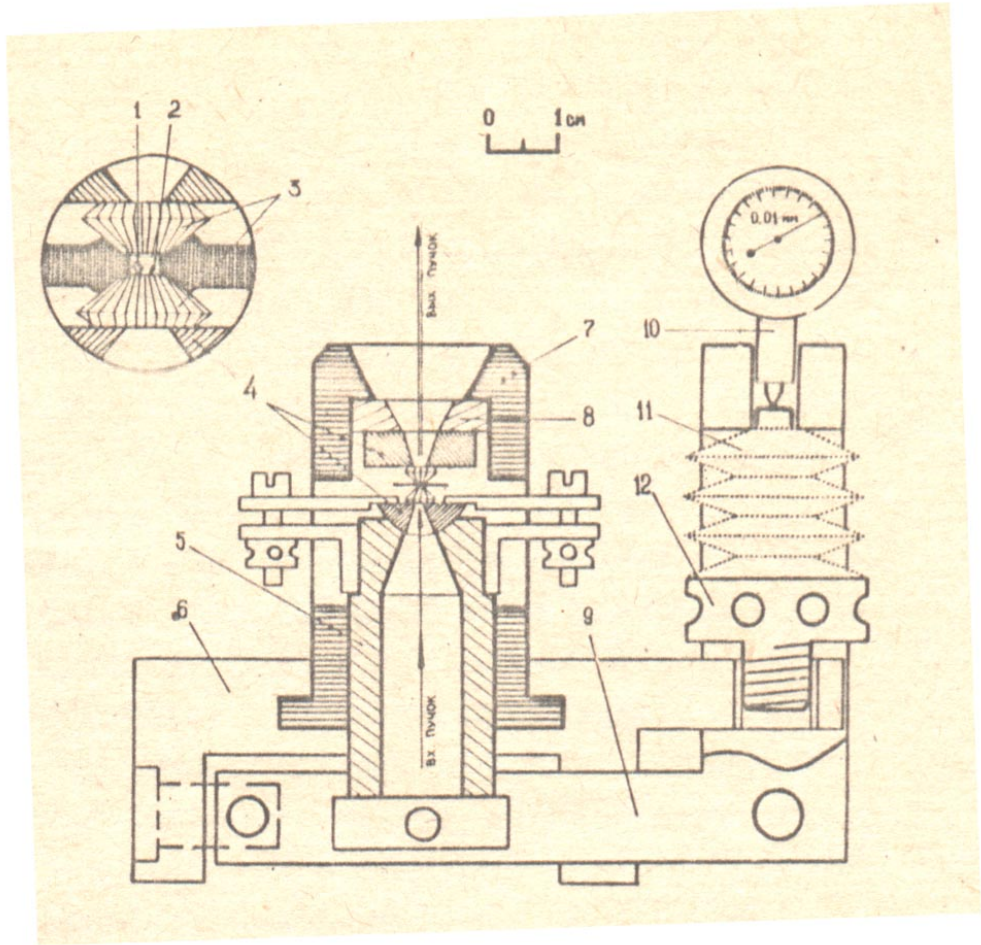




DAC cells, loaded with one or several screws:

- cell with one screw;
- cell with three screws;
- cell with lever arm and one screw.

- Raman spectrometers were used:
- Dilor OMARS 89,
- Horiba Jobin Yvon LabRam-HR800 and T64000,
- Spex Triplemate, Renishow Model 2000 RS

- Suitable gasket materials are hardened stainless-steel, tungsten, rhenium, inconel nickel alloy etc.
- Medium: alcohol (methanol/ ethanol 4/1), water, KBr, glycerol etc.

- P-indicators: ruby (R1 and R2 lines), Sm-borate

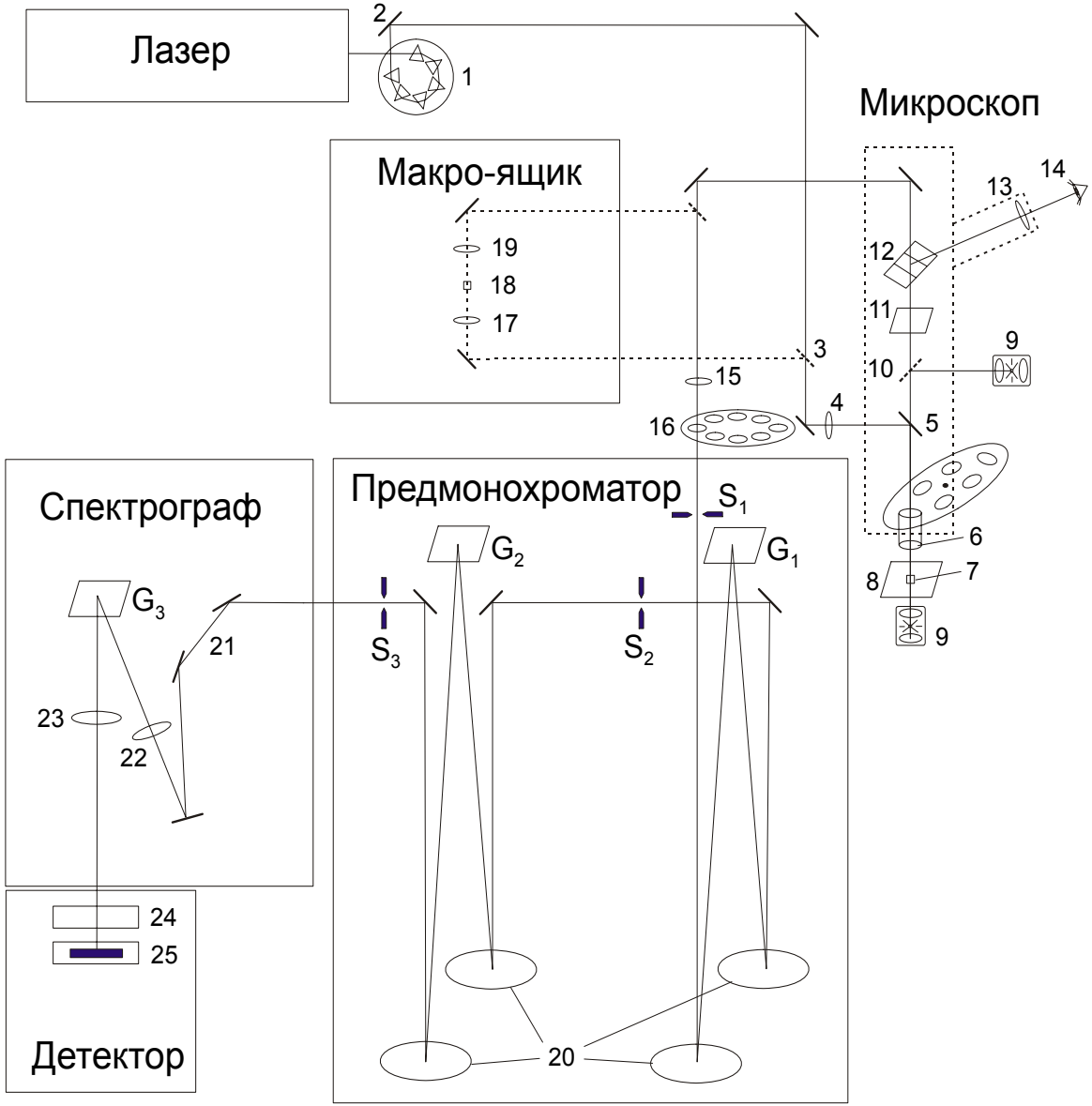


Fig. Scheme of Raman spectrometer (Dilor OMARS 89)

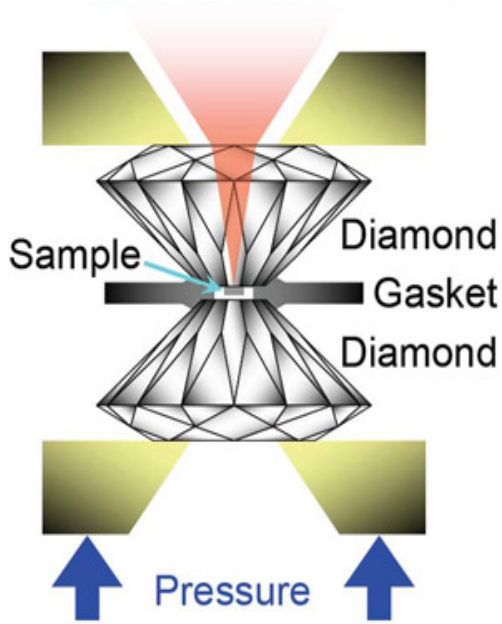
Horiba JobinYvon T64000

Raman spectrometer

- Horiba JobinYvon LabRam HR800 Raman spectrometer with DAC (IGM)

DAC at high P-T:

Raman equipment Horiba Jobin Yvon T64000 spectrometer with Olympus BX41 microscope with attached heated cell HT-DAC, EasyLab μScope .



Minerals at high pressure

- Using Raman spectroscopy in DAC-diamond anvil cell, several minerals were investigated at high P and room T:
- 1. Natrolite [20]
- 2. Thomsonite [13]
- 3. Scolecite [13]
- 4. Zeolite NaA [15]
- 5. Lawsonite [19]
- 6. H2O-cordierite [14]
- 7. Fluorapatite [20]
- 8. OH-apophyllite [7]
- 9. F- apophyllite [7]
- 10. Thaumasite [28]
- 11. Datolite [8]
- 12-13. Dehydrated and Hydrated analcimes
  - 14. Parasibirskite [29]; 15 Chibaite [25].

- Dependences $v(P)$ of stretching modes versus pressure can be estimated from potential model (Sherman, 1982) [18]:
- $U(r) = A - Br^{-n} + Cr^{-m}$,
- where *A, B, C, n (in power), m (in power)* – constants, r – inter-atomic distance.
- Effective force constant depends on r with rate: $dk/dr = -(n + m + 3)k_0/r_0$,
- where k_0, r_0 – constants are found at 0-pressure.
- Hence, for materials with Lennard-Jones potential ($n = 6$, $m = 12$):
- $dk/k_0 = -21\ dr/r_0$,
- that means the increase of force constant 21% at the decrease of inter-atomic distance 1%
- In alkali halides for ionic potential of 1-9 type ($n = 1$, $m = 9$):
- $dk/k_0 = -13\ dr/r_0$
- that means the increase of force constant 13% at the decrease of inter-atomic distance 1%.

- Using the noted potential, the band frequency versus P can be estimated by complex formula (Sherman, 1982) [18]. From that, hence, the dependence $v(P)$ is linear at small P and then $v(P)$ is nonlinear at large P with decreasing of the slope dv/dP.
- At zero pressure, the slope dv/dP:
- $$(dv/dP)_0 = v_0 (n+m+3)/6K_0,$$

- where K_0 is the bulk modulus, r_0 and v_0 at P=0. Curvature of the P-dependence of $v(P)$ is expressed:
- $$(d^2v/dP^2)_0 = -v_0 (m^2 + 14m + 14n + 4mn + n^2 + 29)/36(K_0)^2.$$

Hydrated NATROLITE

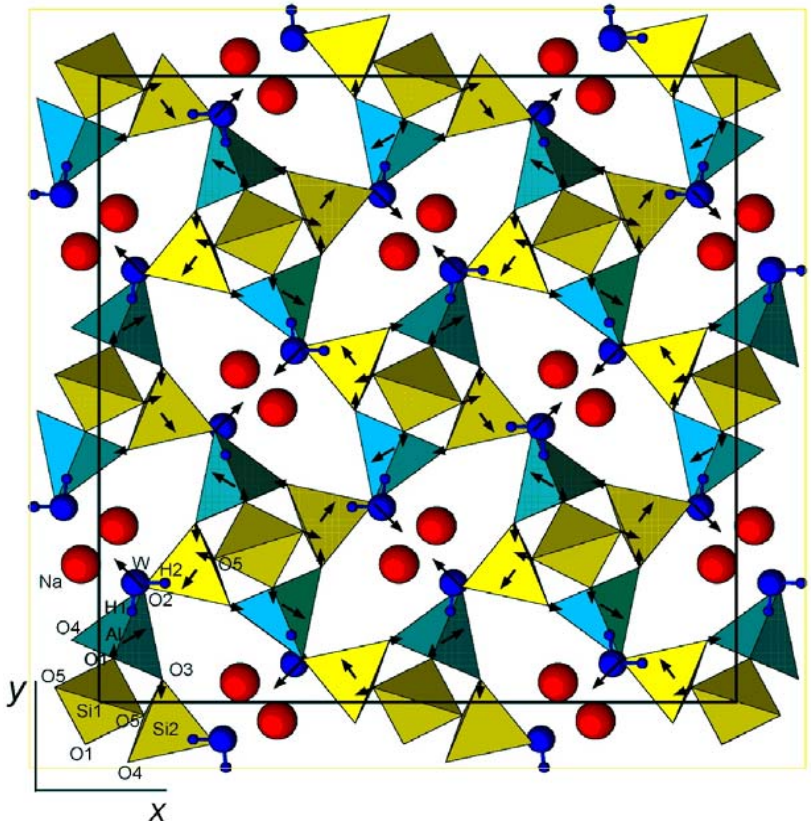


Fig. Crystal structure of initial phase of natrolite Na2Al2Si3O10 2H2O. Strong mode at 443 cm-1

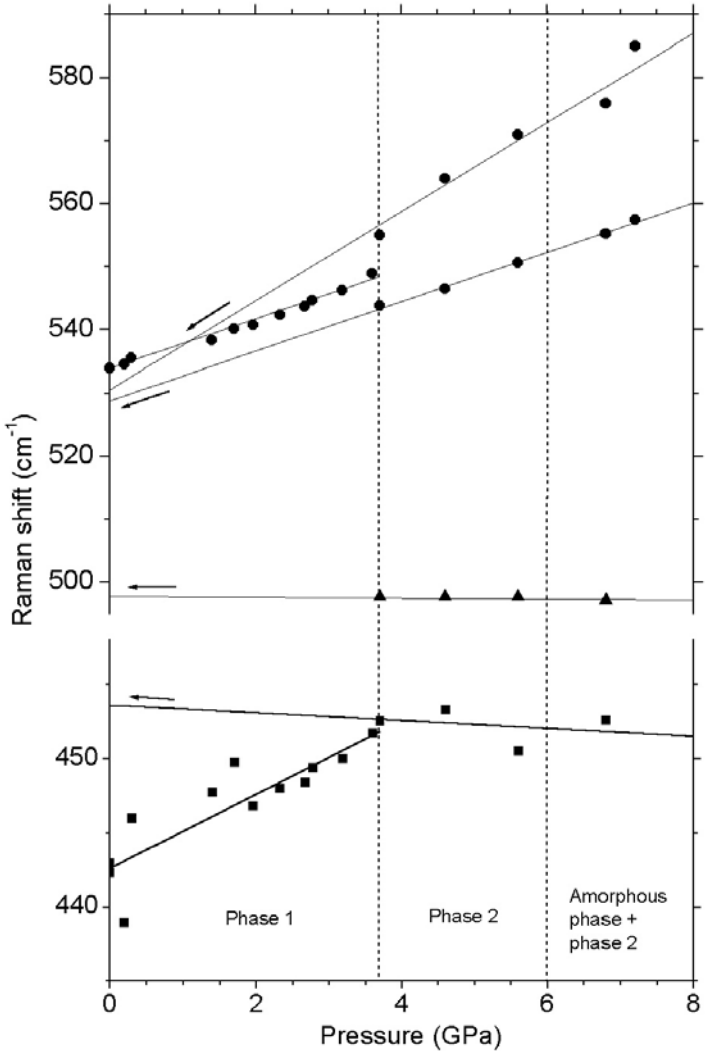
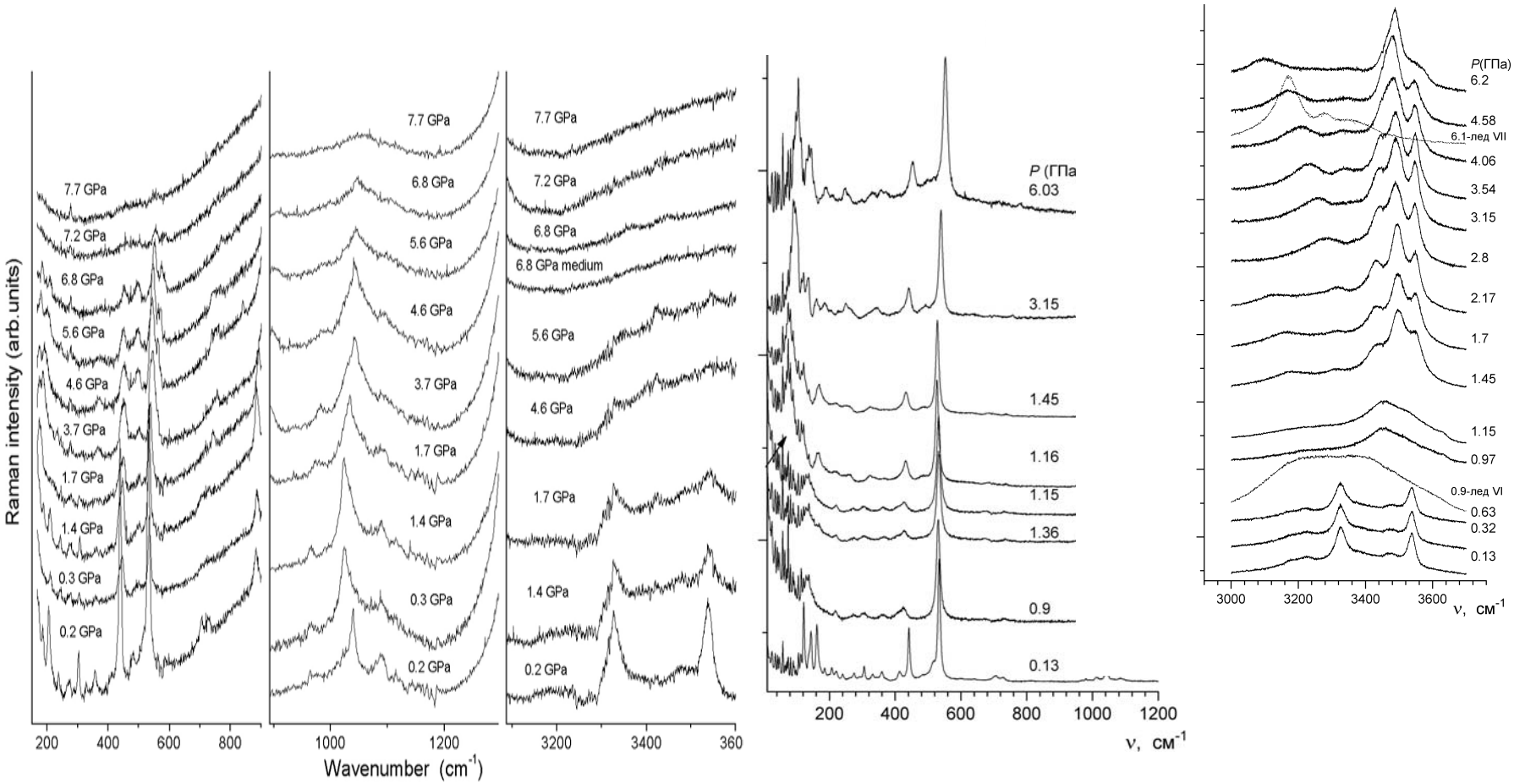


Fig. Baric dependence of wavenumber of natrolite Raman bands. Amorphization at 9 GPa and partial reconstruction of crystalline structure after decompression..

Hydrated and overhydrated natrolite at high pressure (Raman spectra with increasing *P*)



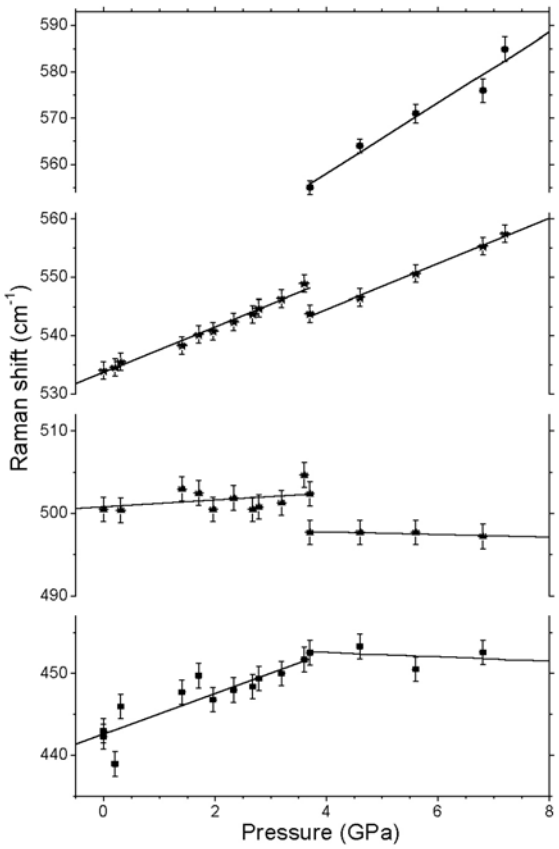
Hydrated natrolite starting from initial phase

Overhydrated natrolite starting from initial phase

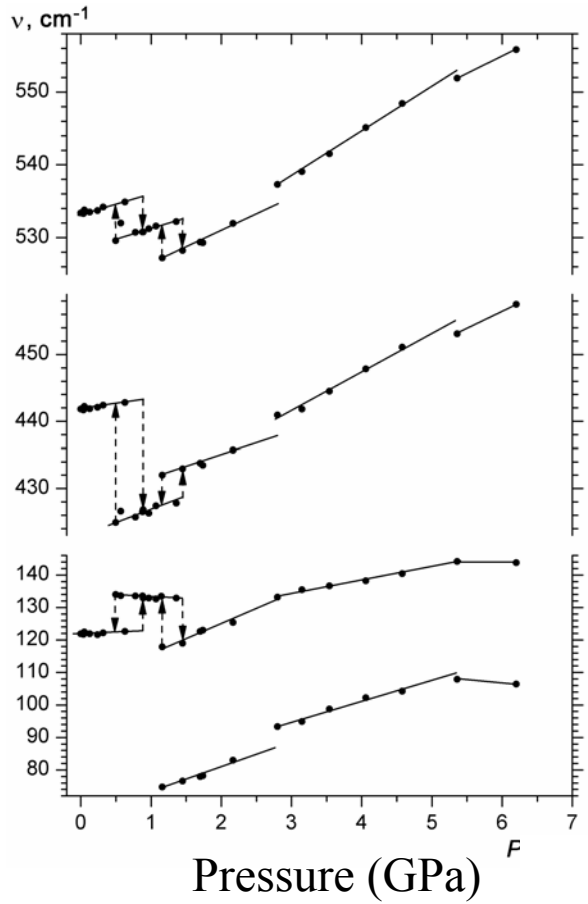
Overhydrated zeolites

Earlier data on overhydration of zeolites are presented in ref. [10-12,16].

Hydrated and overhydrated zeolite natrolite at high pressure. Our data [20].
Baric dependence of wavenumbers of the Raman bands



Hydrated

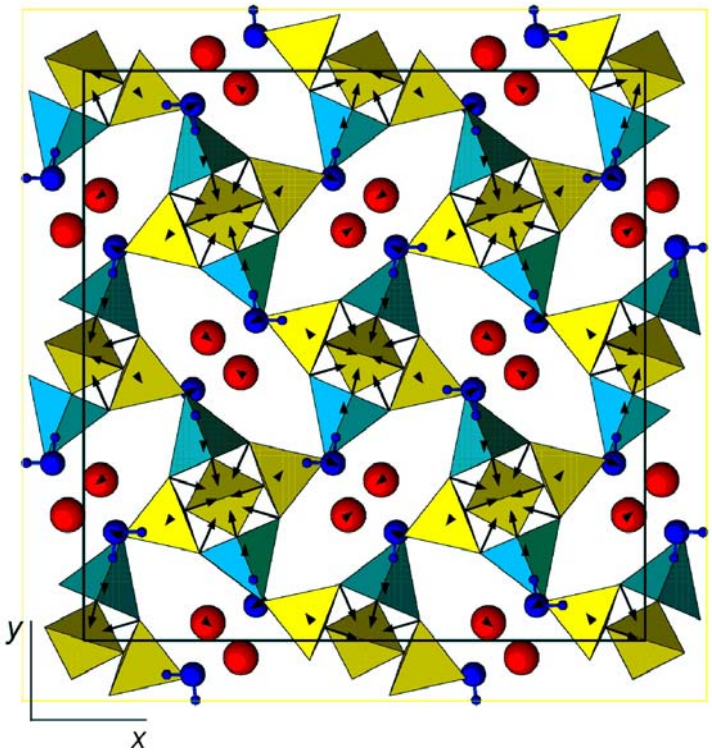


Overhydrated

Natrolite

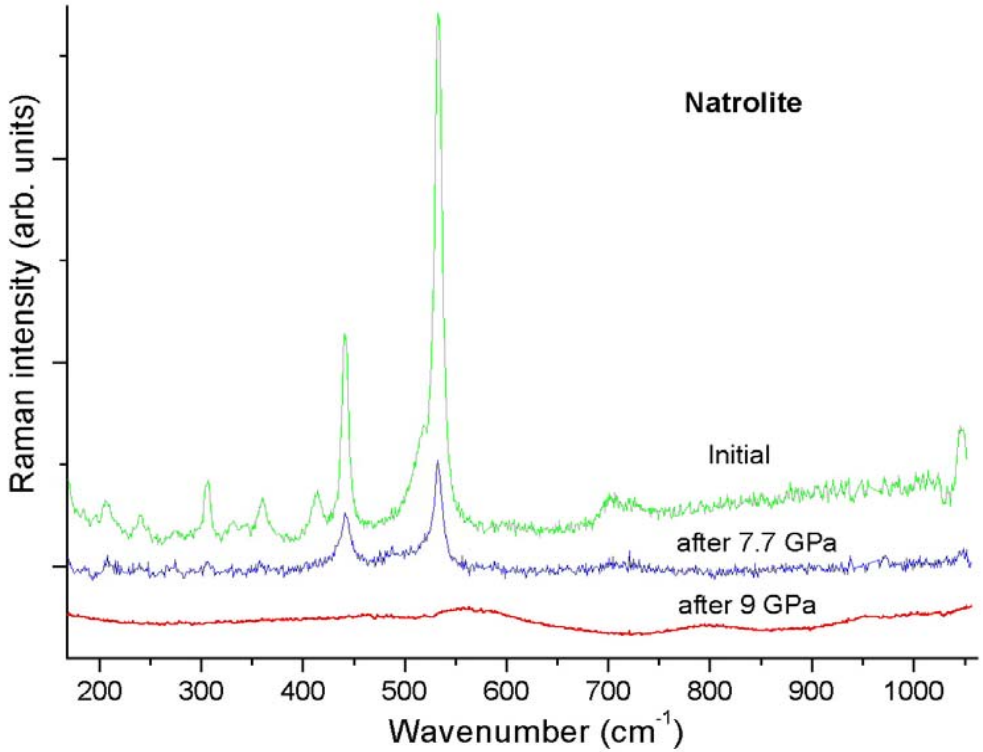
Reversibility of amorphization at compression up to 7.7 GPa

Irreversibility of amorphization at compression up to ~9 GPa.



Initial crystalline structure of natrolite Na2Al2Si3O10 2H2O.

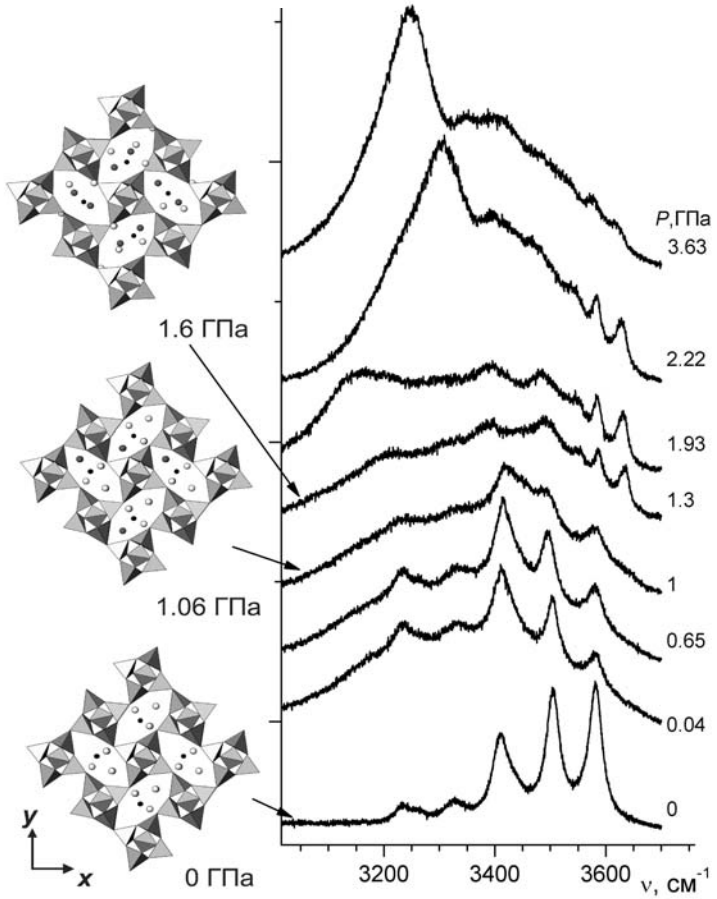
Mode vibration at 534 cm-1.



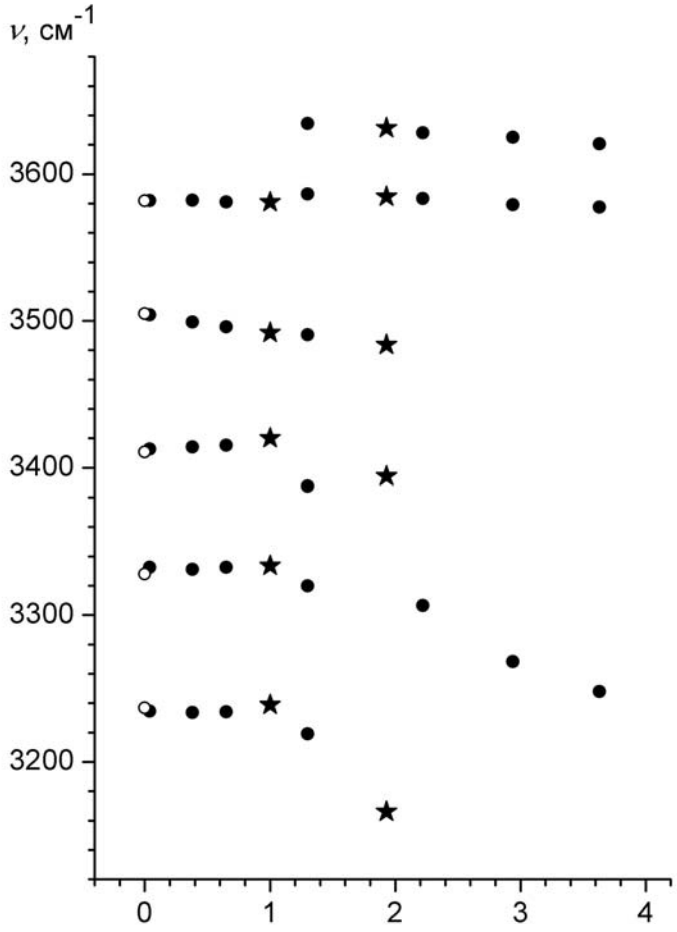
Raman spectra of natrolite Na2Al2Si3O10

Overhydrated zeolite scolecite at high pressure

(Raman spectra with increasing *P*). Our data [13].

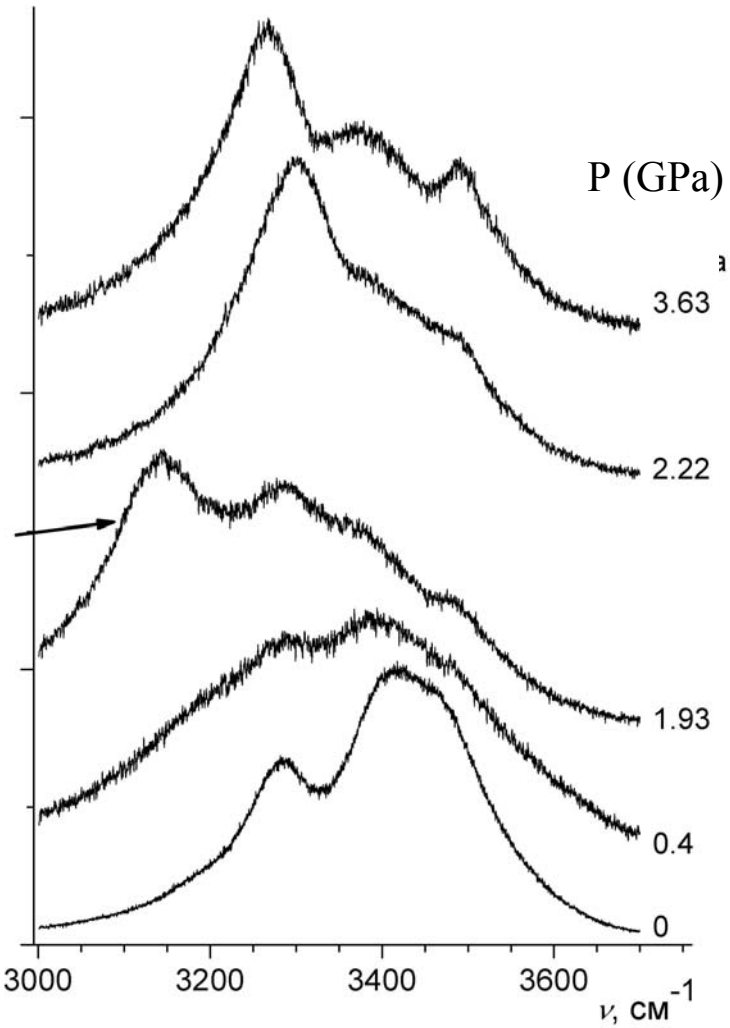


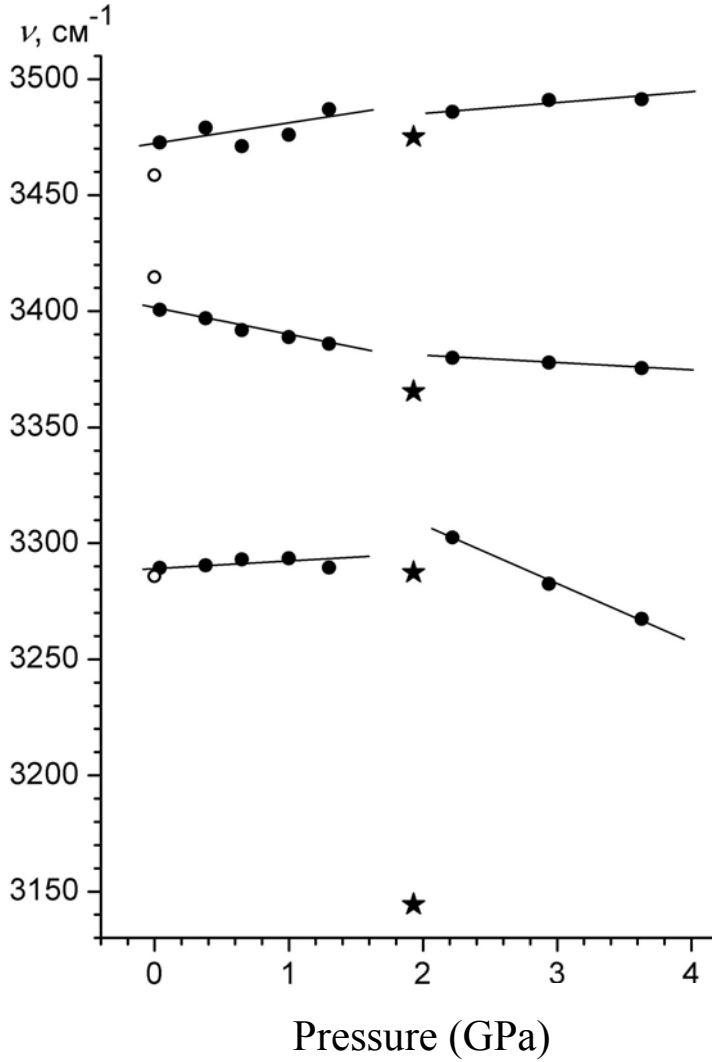
Wavenumber (1/cm)



Pressure (GPa)

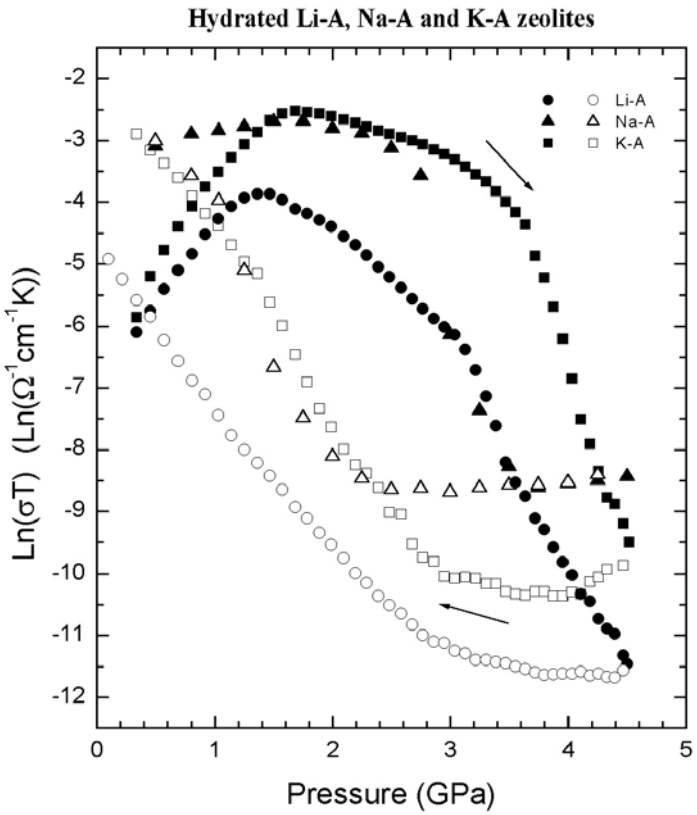
Overhydrated zeolite thomsonite at high pressure (Raman spectra with increasing P). Our data [13].

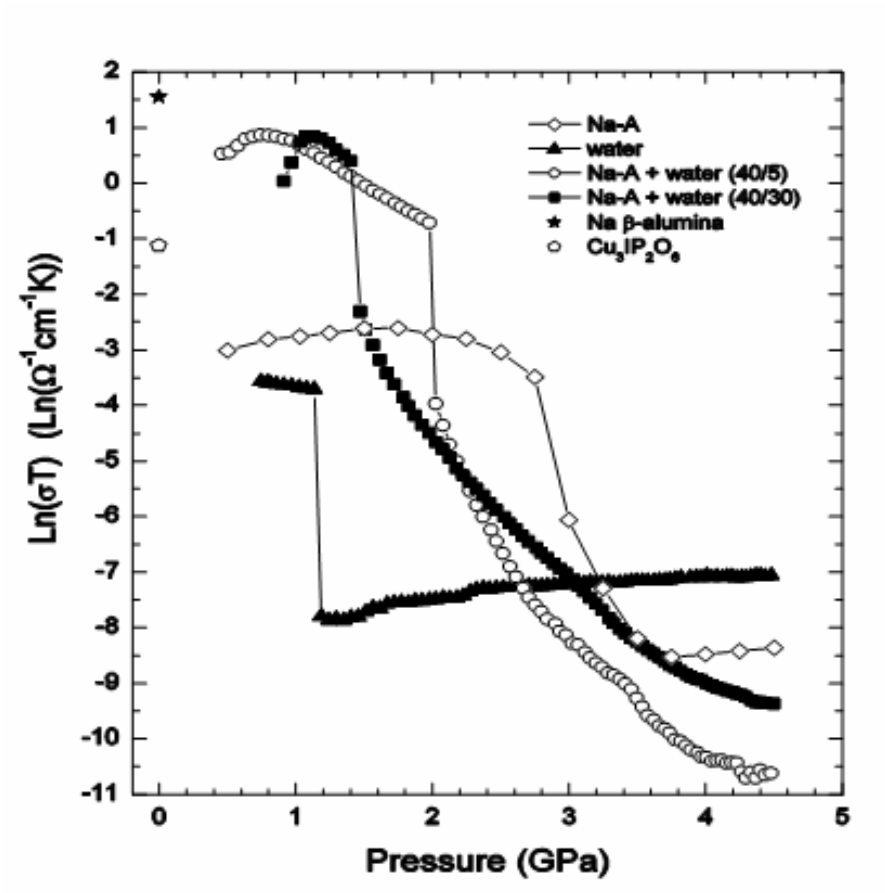




Ionic conductivity of overhydrated zeolite NaA

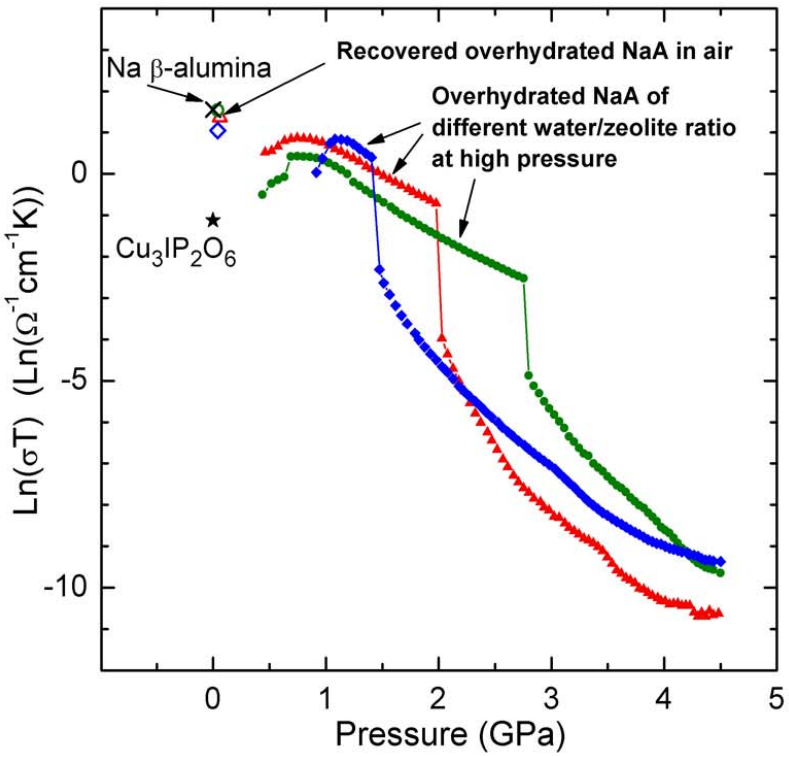
Ionic conductivity of hydrated zeolites: LiA, NaA and KA





NaA overhydrated zeolite:

ionic conduction (our data, Goryainov et al., *Micropor. Mesopor. Mater.* 2013 [15]) and calculated structure (Peral, Iniguez, *Phys. Rev. Lett.* 2006.)



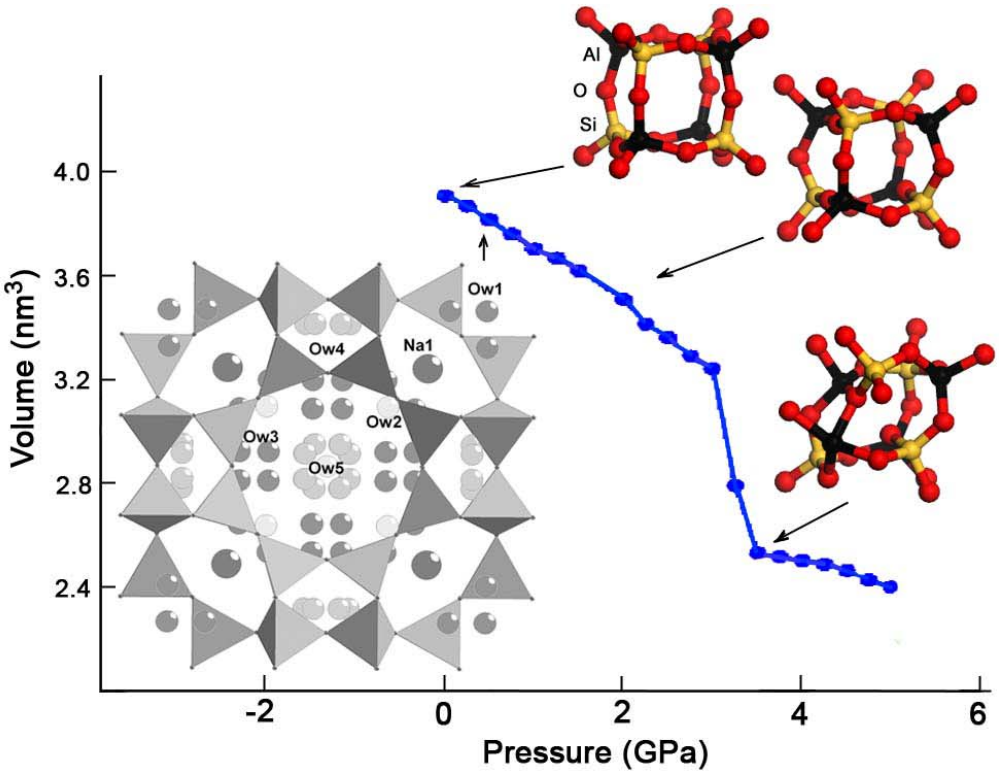
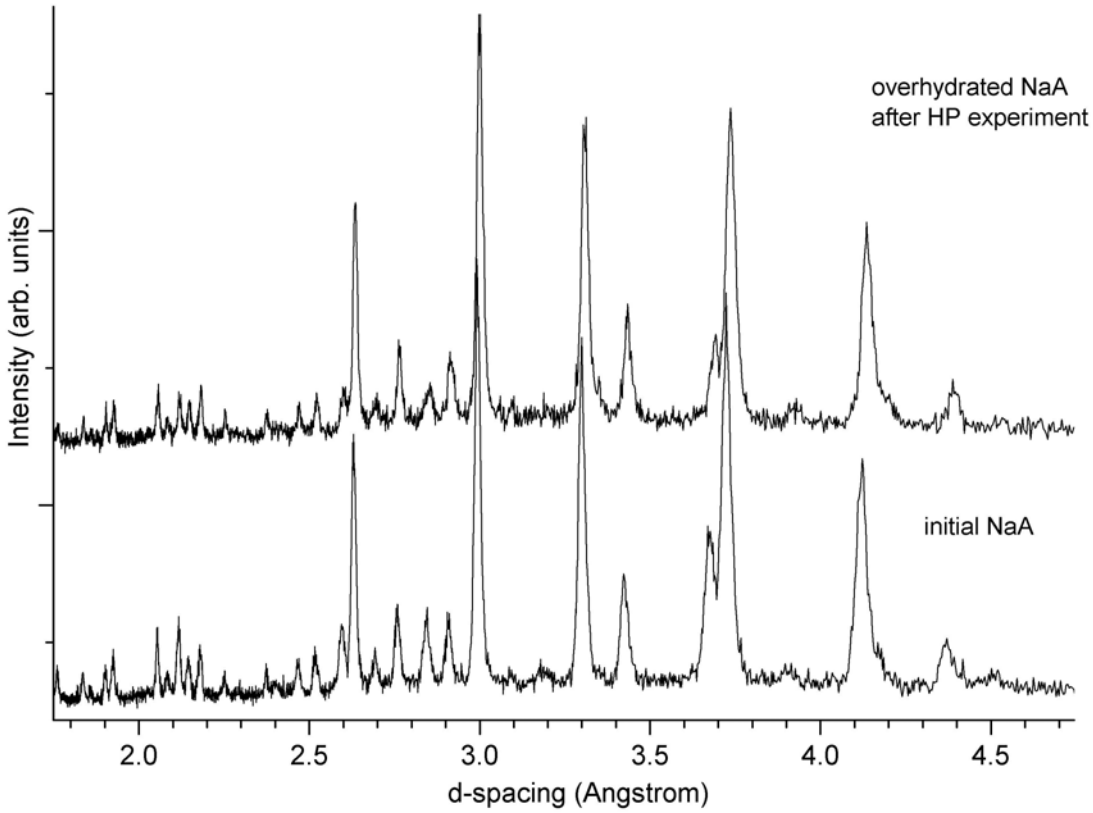
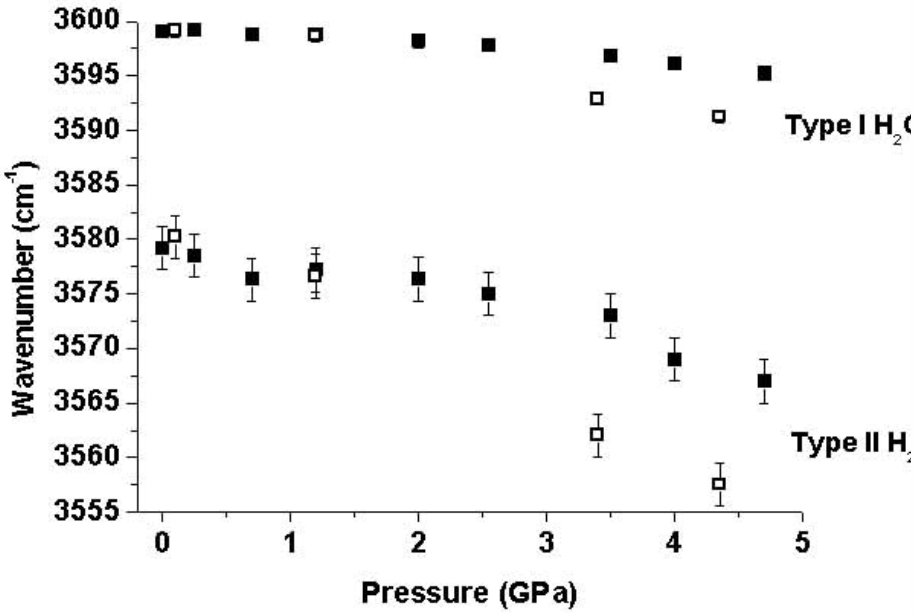
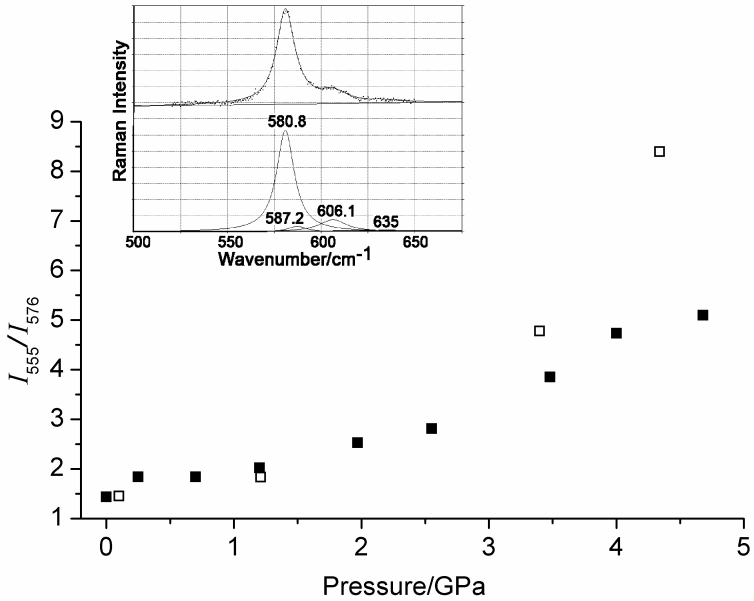


Fig. NaA zeolite XRD: initial (lower) and overhydrated (upper) zeolite, proved the conservation of partly overhydrated state for 12 h.

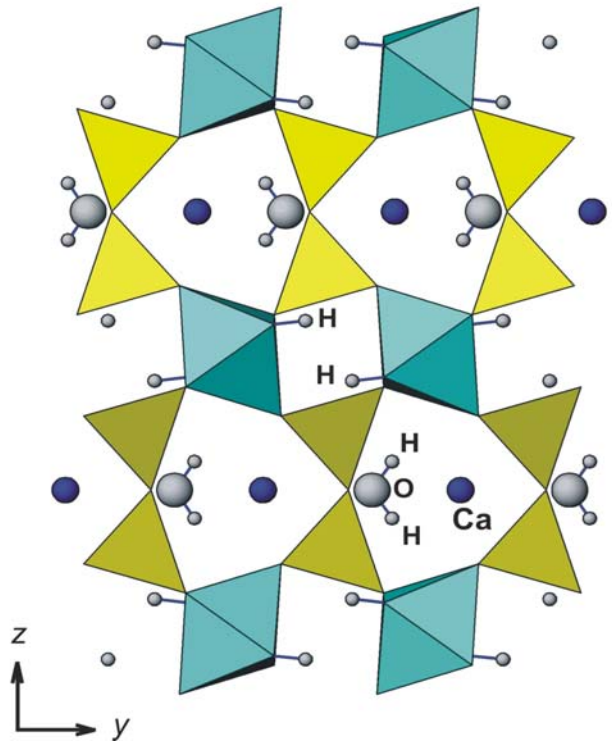


H2O-cordierite (Altai mountains)
Na0.07(Mg1.57Fe0.36Mn0.07) [Al3.96Fe0.06Si4.98O18]*0.45H2O
Sample compressed in water. Raman data [14].

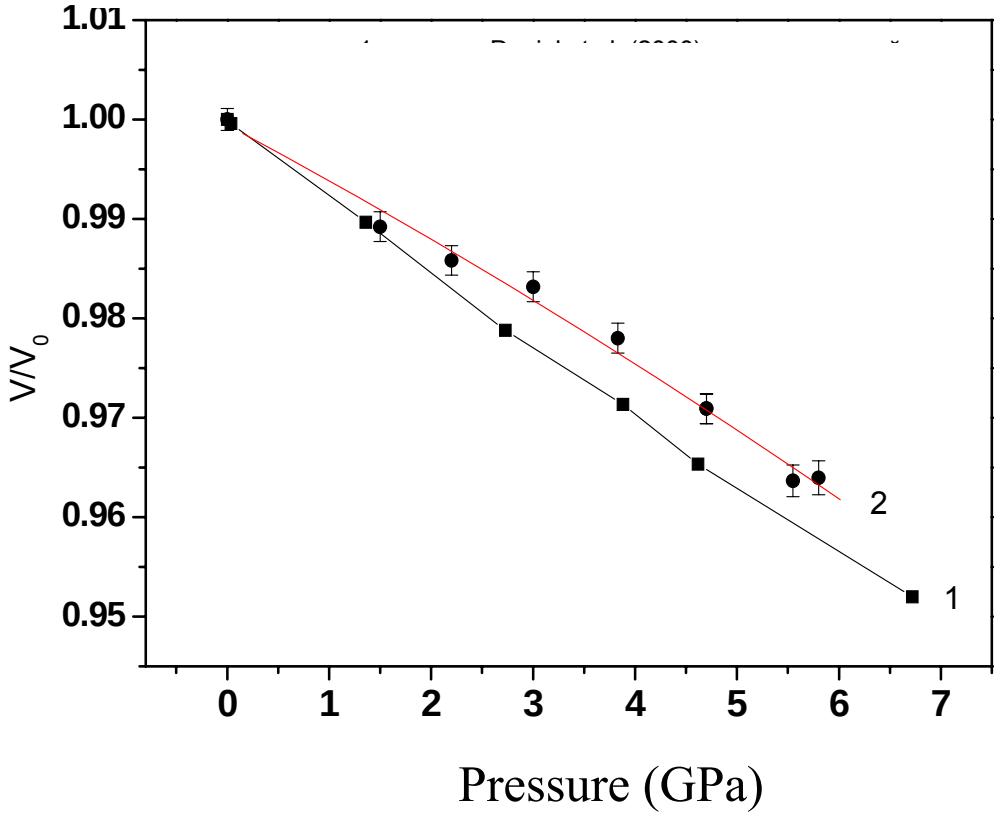




Lawsonite $CaAl_2Si_2O_7(OH)_2 * H_2O$ compressed in water and alcohol. X-ray diffraction [19]



Compressibility of lawsonite measured with synchrotron X-ray diffraction. 1- data of Daniel et al. (2000) [27] (black squares), compression in alcohol; 2- our data [19] (black circles), compression in water with alcohol admixture (water/ethanol 9/1). Lines are the approximations of the data.



Lawsonite CaAl2Si2O7(OH)2∗H2O compressed in water and alcohol. Raman and X-ray diffraction data 2009 [19].

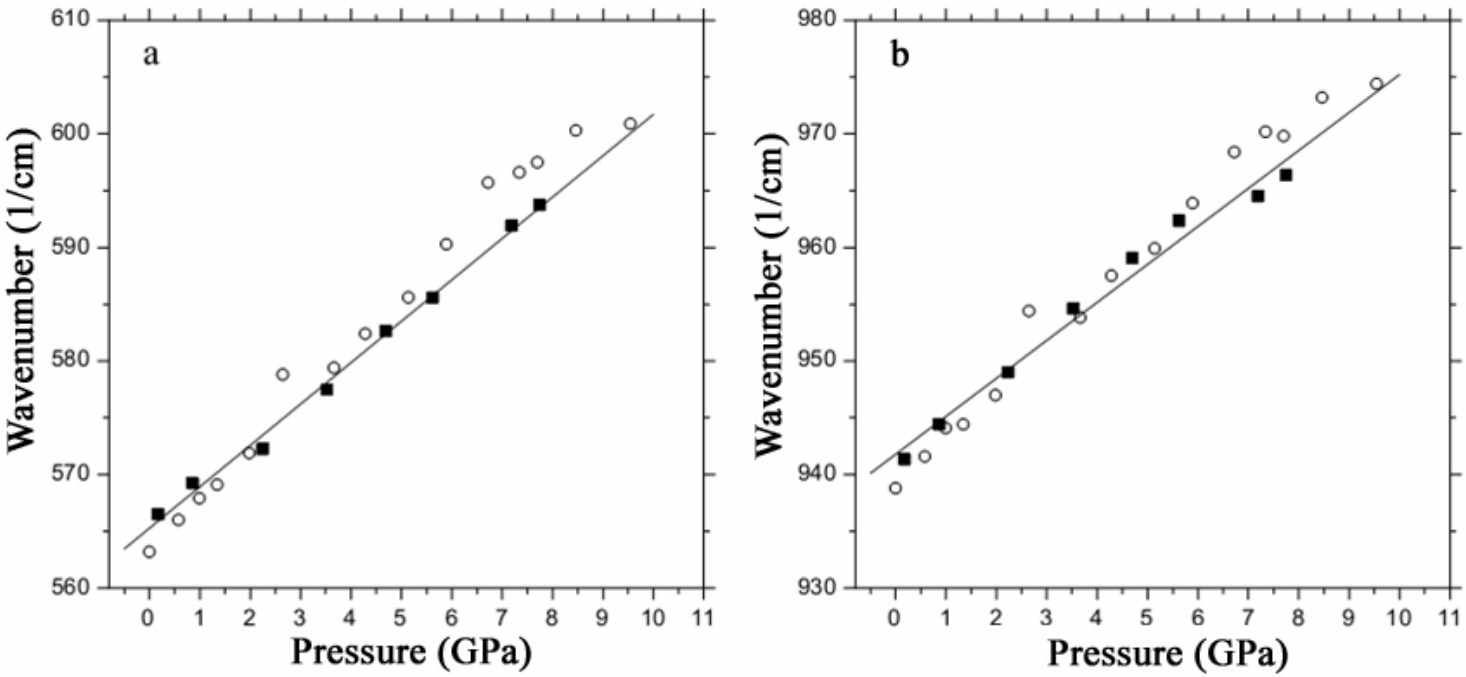
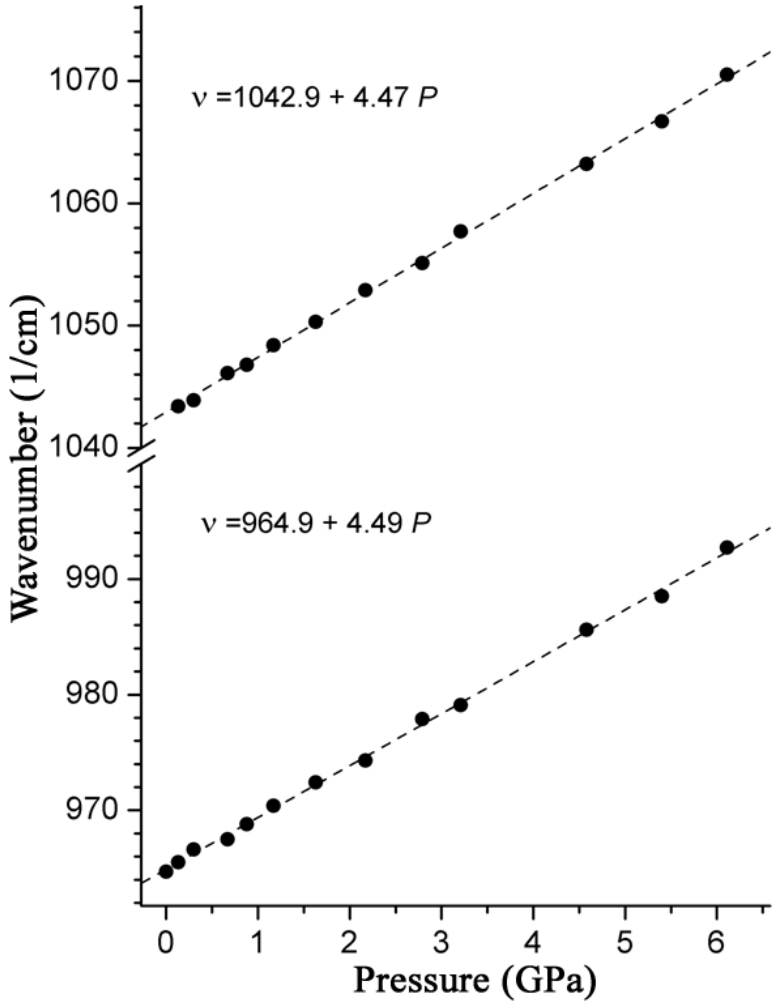


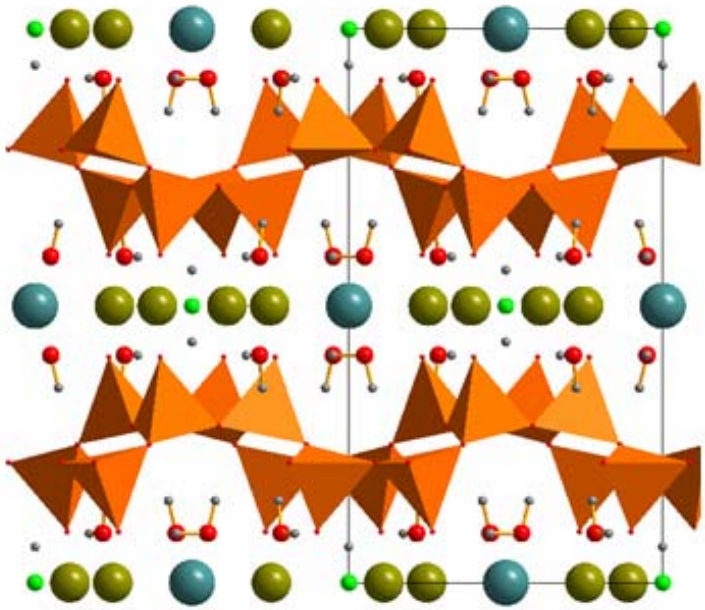
Fig. Pressure dependence of wavenumbers of lawsonite CaAl2Si2O7(OH)2∗H2O Raman bands at 566 **(a)** and 941 cm^{-1} **(b)**. Lawsonite crystals are compressed in water (circles) and methanol-ethanol 4:1 medium (squares). Linear approximation of experimental points for the last medium is plotted.

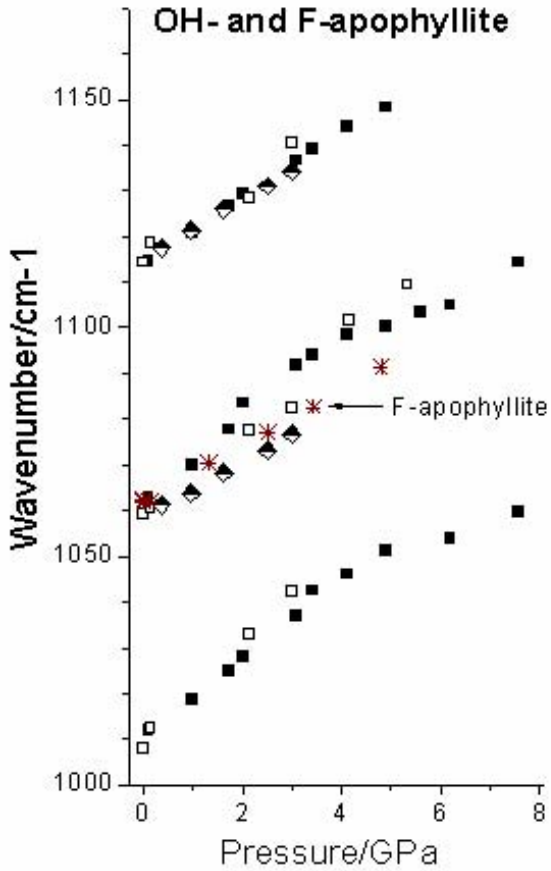
F-apatite compressed in water.

Raman data [20].



F-apophyllite **KCa4Si8O20(F, OH)·8H2O** compressed in alcohol.
Raman data (Goryainov et al., J. Raman Spec. 2012) [7].





- **Raman method at high P-T conditions**
- **Minerals: wairakite, dawsonite, talc and thaumasite**

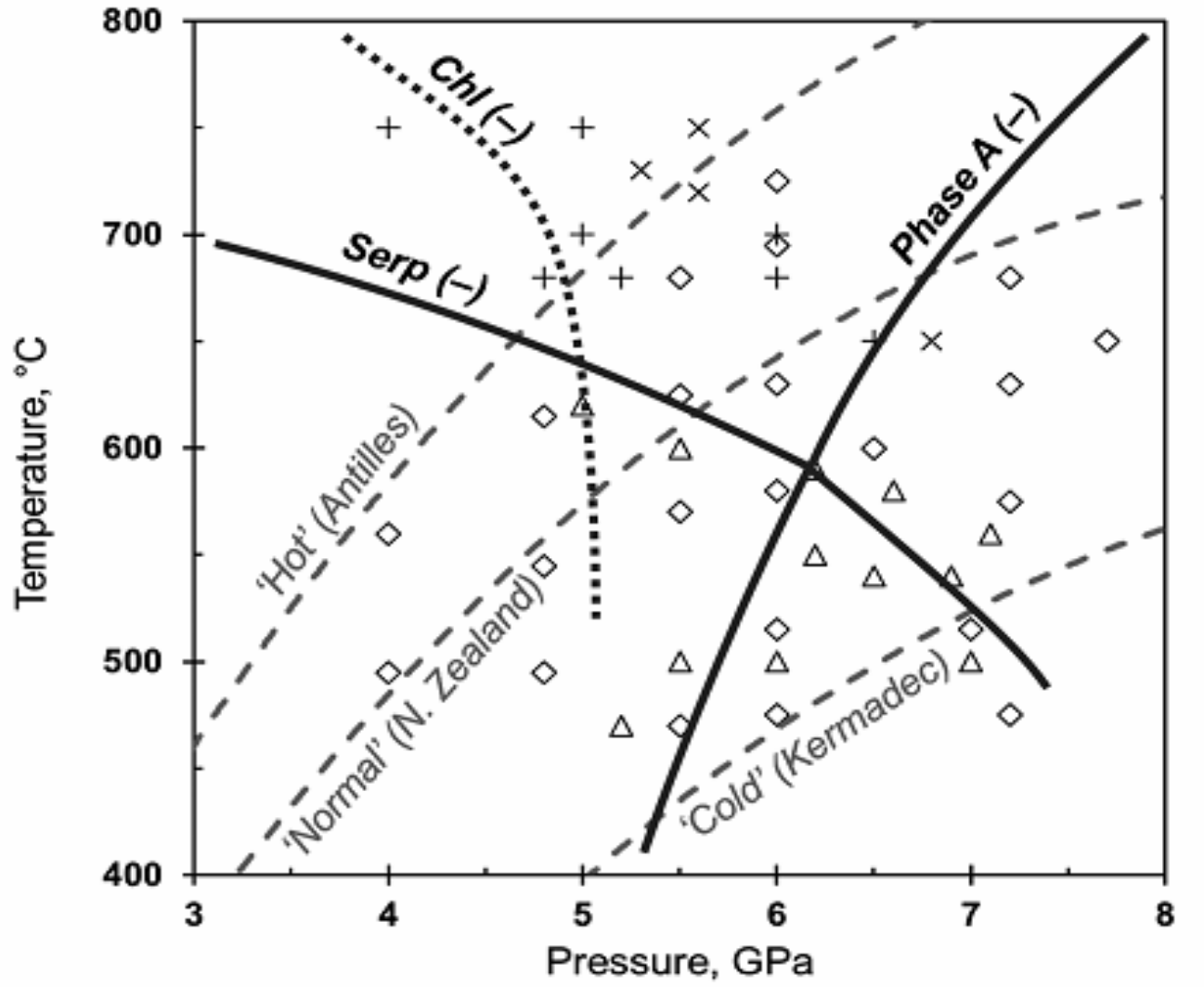


Fig. P-T phase diagram of serpentines at subduction conditions [9,24].

Talc – TAP transformation at high P-T. Our data [24].

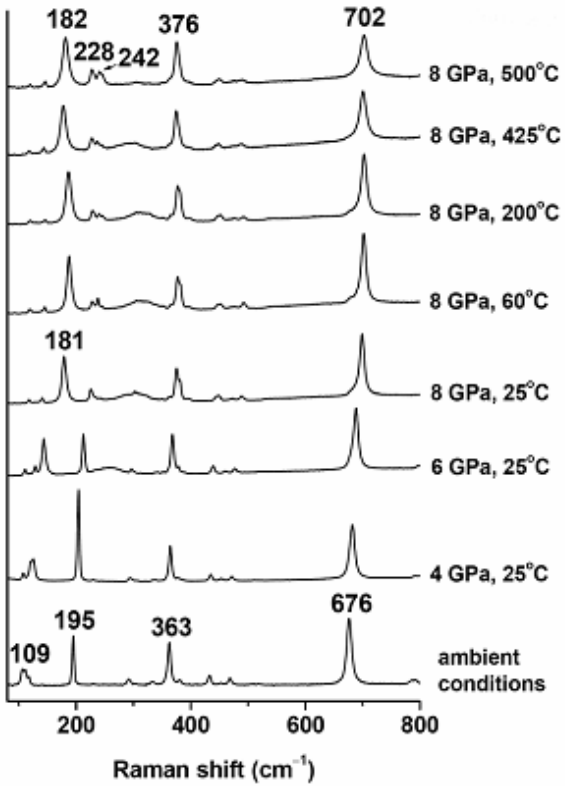


FIGURE 2. Raman spectra of *talc + H_2O* sample in the lattice-mode region collected during pressure and temperature increase from ambient conditions to 8 GPa/500 °C.

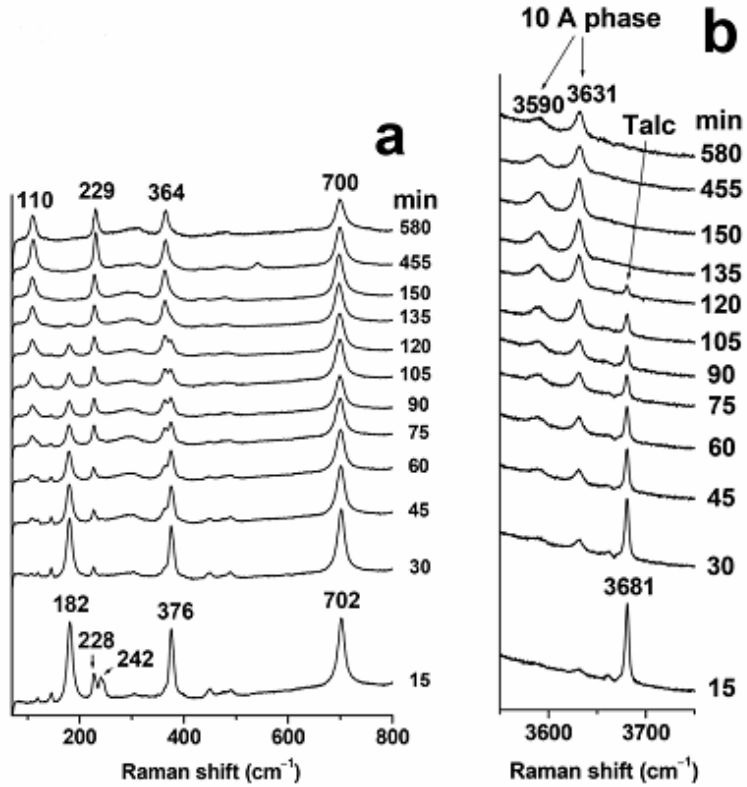


FIGURE 3. Raman spectra demonstrating *talc + H_2O → 10 Å phase* reaction process in (**a**) lattice-mode region and (**b**) O-H stretching region. Timing start corresponds to the achievement of 8 GPa/500 °C conditions.

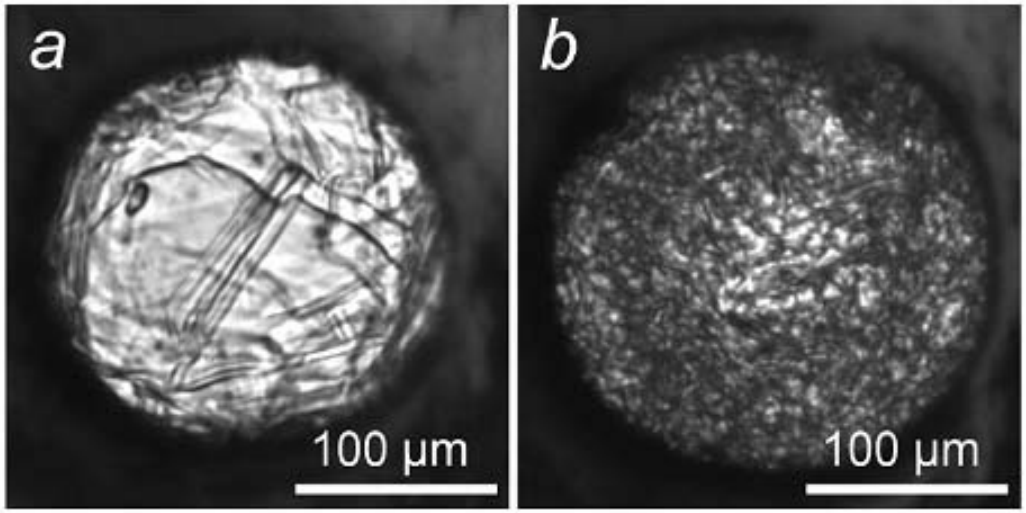


FIGURE 4. The sample at 8 GPa/500 °C before (**a**) and after (**b**) *talc + H_2O → 10 Å phase* transformation.

Talc – TAP transformation [24].

ABSTRACT

The synthesis of 10 Å phase via the reaction of talc plus water at 8 GPa and 500 °C was studied by in situ Raman spectroscopy using a diamond-anvil cell. The initial fast (2 h) incorporation of interlayer H_2O molecules into the talc structure is traced by gradual growth of new OH stretching bands at 3592 and 3621 cm^{-1} and the shift of several framework bands. Further monitoring at HP-HT conditions over 7 h reveals gradual weakening of the 3592 cm^{-1} band, which can probably be related to the onset of the formation of "long-run" 10 Å phase through the appearance of silanol groups following the model proposed by Pawley et al. (2010), influencing the interlayer hydrogen bonding.

Wairakite zeolite and OH-carbonate dawsonite at high P-T [26].

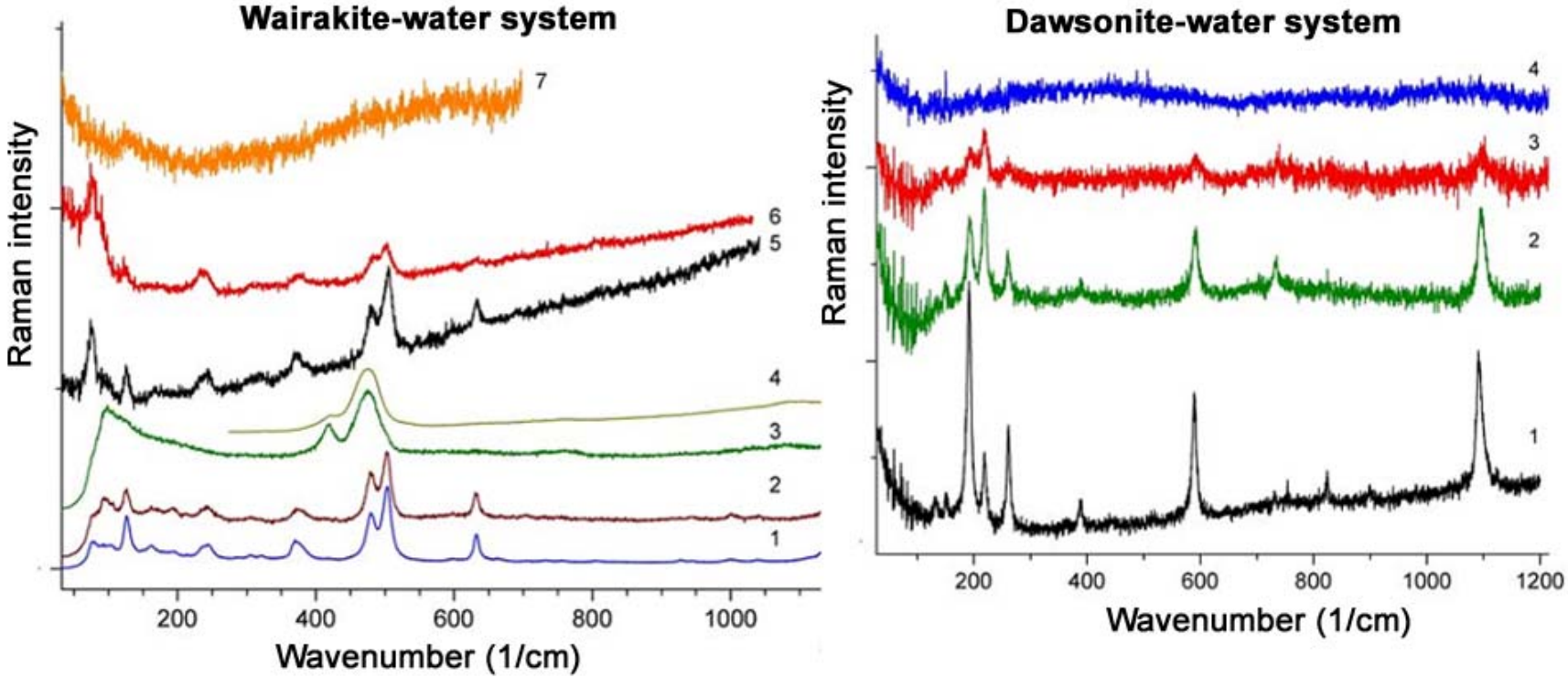


Fig. (left). Raman spectra obtained in the wairakite–water system at different P–T parameters:
(1) 1 bar, 293 K as the initial temperature; (2) 1 bar, 293 K for wairakite after the experiment;
(3) 1 bar, 293 K for phillipsite after the experiment in the wairakite–water system;
(4) natural Ca–phillipsite; 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.

Fig. (right). 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 GPà, 573 K; and (4) 0.95 GPa, 723 K.

Structure of thaumasite

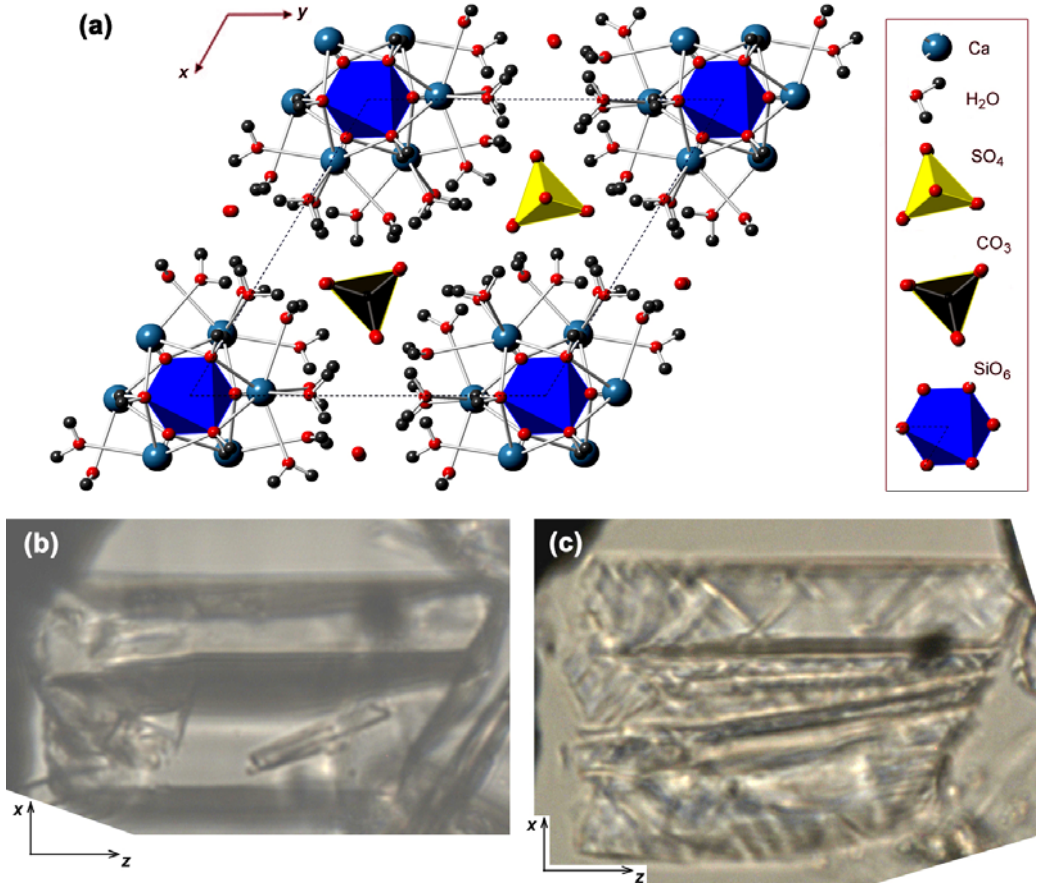


Figure 1. **(a)** The idealized crystal structure of thaumasite Ca3Si(OH)6(SO4)(CO3)*12H2O at room conditions. Groups of thaumasite Ca, SiO6, SO4, CO3 and H2O, where SiO6 polyhedron is a part of Si(OH)6, are plotted with CrystalMaker software.
(b) View of crystalline thaumasite I at water-alcohol pressure of 0.33 GPa (size of 94x170 μm2 along *xz*).
(c) View of the same crystalline phase-II thaumasite block at water-alcohol pressure of 4.6 GPa (Goryainov, J. Raman Spec. 2016) [28].
* Previous data on thaumasite are available in ref. [1-6].

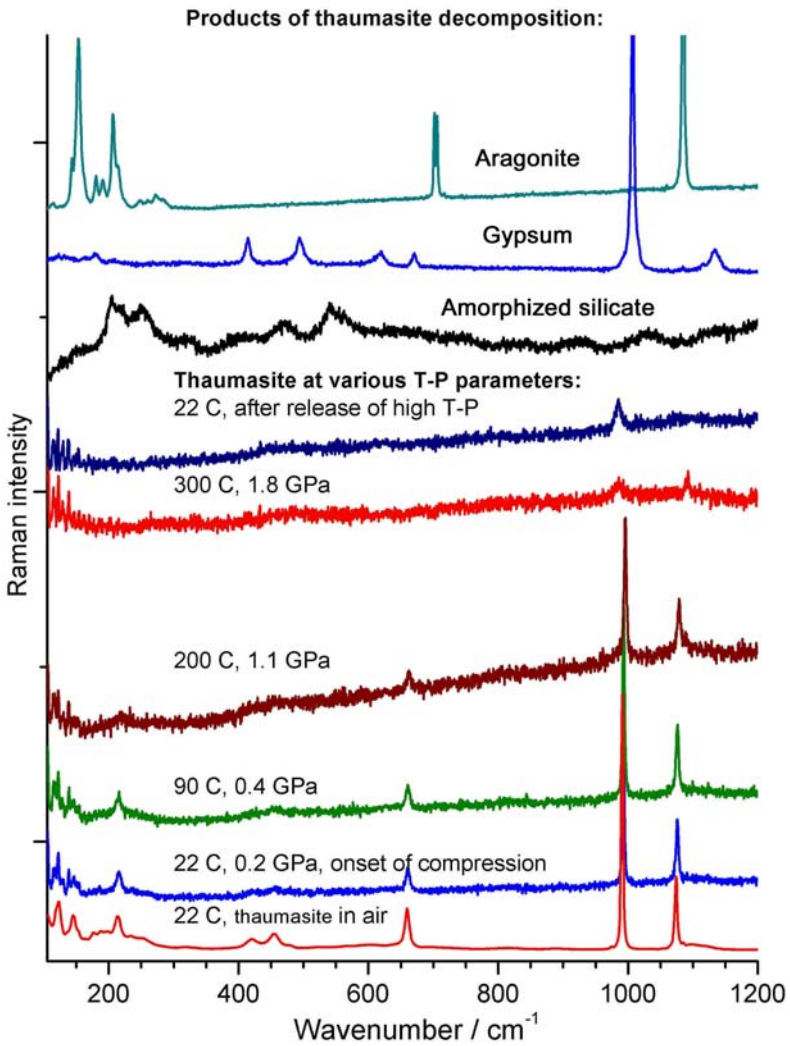


Figure. In-situ and ex-situ Raman spectra of thaumasite compressed in water at high P-T

– Remarks on the P-T study of thaumasite

- In the present Raman study [28], thaumasite samples were compressed in distilled water, alcohol-water and KBr media at high pressures up to ~7 GPa: several phase transformations were identified. In samples compressed in alcohol-water, the wavemunbers of intense Raman bands of S-O and C-O symmetric stretching vibrations at 991 and 1074 cm–1 proved to exhibit similar dependences on P: during first transition I→II at 4.4 GPa, the wavenumbers of both bands exhibited downward jump; at second transition II→III, which occurred at 4.9 GPa, each band split in doublet and, then at third transition III→IV at 5.4 GPa each doublet band transformed in singlet. In KBr medium, Raman bands of thaumasite showed similar (as at compression in alcohol-water) dependences on P.
- Transitions are assumed to be polymorphic: no noticeable overhydration in thaumasite compressed in water-alcohol occurred. In phase IV, gradual widening and weakening of each band were observed that is associated with amorphization.
- Considerable hysteresis was observed at thaumasite decompression. No overhydration of thaumasite was observed.
- Decomposition of thaumasite compressed in water is observed at 300 C, ~5 GPa. It transforms to aragonite + gypsum + (X-silicate) + fluid.
- After this HP-HT treatment, there is also remnant crystalline thaumasite having partially disordered structure.

- **CONCLUSION**
- **Method of in-situ Raman spectroscopy is effective tool to study the processes in minerals at high P:**
- **- determination of the P-range of crystalline stability; polymorphic transitions;**
- **- overhydration-hydration-dehydration at compression in water-containing medium;**
- **- disordering and amorphization.**
- **Method at high P-T conditions:**
- **- dissolution of the crystals;**
- **- recrystallization of initial phase and growth of new crystalline phases;**
- **- extraction of volatile components;**
- **- large variety of other processes.**

References

[1] Ardit M., Cruciani G., Dondi M., Garbarino G.L., Nestola F. Phase transitions during compression of thaumasite, Ca3Si(OH)6(CO3)(SO4)·12H2O: A high-pressure synchrotron powder X-ray diffraction study // Mineralogical Magazine, October 2014. V. 78(5). P. 1193–1208.

[2] Gatta, G.D., McIntyre, G.J., Swanson, J.G., Jacobsen, S.D. Minerals in cement chemistry: A single-crystal neutron diffraction and Raman spectroscopic study of thaumasite, Ca3Si(OH)6(CO3)(SO4)·12H2O. American Mineralogist, 2012, 97, 1060-1069.

[3] Barnett, S. J.; C. D. Adam; A. R. W. Jackson. Solid solutions between ettringite, Ca6Al2(SO4)3(OH)12·26H2O, and thaumasite, Ca3SiSO4CO3(OH)6·12H2O. Journal of Materials Science, 2000, 35 (16): 4109–4114.

[4] Barnett, S. J.; D. E. Macphee; E. E. Lachowski; N. J. Crammond. XRD, EDX and IR abalysis of solid solutions between thaumasite and ettringite. Cement and Concrete Research., May 2002, 32 (5), 719-730.

[5] Martucci, A. and Cruciani, G. In situ time resolved synchrotron powder diffraction study of thaumasite. Physics and Chemistry of Minerals, 2006, 33, 723-731.

[6] V.A. Drebushchak, Yu.V. Seryotkin, S.N. Kokh, E.V. Sokol. Natural specimen of triple solid solution ettringite-thaumasite-chromate-ettringite. J. Therm. Anal. Calorim. 2013, 114, 777–783.

[7] S.V. Goryainov, A.S. Krylov, Yu. Pan, I.A. Madyukov, M.B. Smirnov, A.N. Vtyurin. Raman investigation of hydrostatic and nonhydrostatic compressions of OH- and F-apophyllites up to 8 GPa. Journal of Raman Spectroscopy. 2012. V. 43. P. 439–447.

[8] Goryainov S.V., Krylov A.S., Vtyurin A.N., Pan Y. Raman study of datolite CaBSiO4(OH) at simultaneously high pressure and high temperature // J. Raman Spectrosc. 2015, 46, 177–181.

[9]. Schmidt M.W., Poli S. Generation of mobile components during subduction of oceanic crust. In: Treatise on Geochemistry. (Ed. R.L. Rudnick). Elsevier, 2003. V. 3. P. 567-591.

[10]. Moroz N.K., Kholopov E.V., Belitsky I.A., Fursenko B.A. Pressure-enhanced molecular self-diffusion in microporous solids. Microporous Mesoporous Mater. 2001. V. 42. P. 113-119.

[11] Lee Y., Vogt T., Hriljac J.A., Parise J.B., Hanson J.C., Kim S.J. Non-framework cation migration and irreversible pressure-induced hydration in a zeolite. Nature. 2002. V. 420. P. 485-489.

[12] Seryotkin Y.V., Bakakin V.V., Fursenko B.A., Belitsky I.A., Joswig W., Radaelli P.G. Structural evolution of natrolite during over-hydration: a high-pressure neutron diffraction study. Eur. J. Mineral. 2005. V. 17. P. 305–313.

[13] S.V. Goryainov, A.S. Krylov, A.Yu. Likhacheva, A.N. Vtyurin. Raman investigation of fibrous zeolites of natrolite group at high pressure of water medium.// Bulletin of the Russian Academy of Sciences: Physics. 2012. Vol. 76, N 7. P. 804-807.

[14]. A.Yu. Likhacheva, S.V. Goryainov, A.S. Krylov, T.A. Bul'bak, P.S.R. Prasad. Raman spectroscopy of natural cordierite at high water pressure up to 5 GPa.// Journal of Raman Spectroscopy. 2012. V. 43. Iss. 4. P. 559–563.

[15] Goryainov S.V., Secco R.A., Huang Y., Likhacheva A.Y. Pressure-induced ionic conductivity of overhydrated zeolite NaA at different water/zeolite ratios// Microporous Mesoporous Mater. 2013. V. 171. P. 125–130.

[16] Lee Y., Hriljac J.A., VogtT. Pressure-induced migration of zeolitic water in laumontite. Phys.Chem.Min.2004. V.41, 421-428.

References (continued)

[17] S.V. Goryainov. A model of phase transitions in double-well Morse potential: Application to hydrogen bond.// Physica B. 2012. V. 407. P. 4233–4237.

[18] Sherman W.F. Pressure-induced changes in mode Grüneisen parameters and general equations of state for solids // Journal of Phtsics C: Solid State Physics. 1982. V.15. P. 9-23; Sherman W.F. Vibrational spectroscopy under high pressures // Bulletin de la Societe Chimique de France. 1982. No. 9-10. P. I-347–I-369.

[19] Likhacheva A.Yu., Goryainov S.V., Madyukov I. A., Manakov A.Yu., Ancharov A.I. Powder diffraction and Raman spectroscopic study of lawsonite at high water pressure.// Bulletin of the Russian Academy of Sciences: Physics, 2009, 73, № 8. P. 1143-1146.

[20] Goryainov S.V., Krylov A.S., Vtyurin A.N. Behavior of natrolite zeolite and fluorapatite at high pressures in a water medium // Bulletin of the Russian Academy of Sciences. Physics. 2013, Vol. 77, No. 3, pp. 313–316.

[21] Khoury H.N., Sokol E.V., Kokh S.N., Seryotkin Yu.V., Nigmatulina E.N., Goryainov S.V., Belogub E.V., Clark I.D. Tululite, Ca14(Fe3+,Al)(Al,Zn,Fe3+,Si,P,Mn,Mg)15O36: a new Ca zincate-aluminate from combustion metamorphic marbles, central Jordan.// Mineralogy and Petrology. 2016. V. 110 (1). P. 125–140.

[22] Khoury H.N., Sokol E.V., Kokh S.N., Seryotkin Yu.V., Kozmenko O.A., Goryainov S.V., Clark I.D. Intermediate members of the lime-monteponite solid solutions (Ca1-xCdxO, x = 0.36-0.55): Discovery in natural occurrence.// American Mineralogist, 2016. V. 101. P. 132-147.

[23] Sokol E.V., Kokh S.N., Khoury H.N., Seryotkin Yu.V., Goryainov S.V. Long-term immobilisation of Cd2+ at the Tulul Al Hammam natural analogue site, central Jordan.// Applied Geochemistry. 2016. V. 70. P. 43-60.

[24] Rashchenko S.V., Likhacheva A.Yu., Goryainov S.V., Krylov A.S., Litasov K.D. In situ spectroscopic study of water intercalation into talc: New features of 10 Å phase formation.// American Mineralogist, 2016. V. 101. P. 431–436.

[25] Likhacheva A.Yu., Goryainov S.V., Seryotkin Yu.V., Litasov K.D., Momma K. Raman spectroscopy of chibaite, natural MTN silica clathrate, at high pressure up to 8 GPa. // Microporous and Mesoporous Materials. 2016. V. 224. P. 100-106.

[26] S.V. Goryainov, A.S. Krylov, A.N. Vtyurin, A.Yu. Likhacheva, P.S.R. Prasad. In situ Raman study of wairakite and dawsonite interaction with water at high P–T parameters.// Bulletin of the Russian Academy of Sciences. Physics, 2016. V. 80, No. 5. P. 522–524.

[27] Daniel, I., Fiquet, G., Gillet, P., Schmidt, M.W., Hanfland M., High-pressure behaviour of lawsonite: a phase transition at 8.6 GPa.// Eur. J. Miner., 2000, 12, 721-733.

[28] Goryainov S.V. Raman study of thaumasite Ca3Si(OH)6(SO4)(CO3)*12H2O at high pressure.// Journal of Raman Spectroscopy. 2016. V. 47. P. 984–992.

[29] S.V. Goryainov, Y. Pan, M.B. Smirnov, W. Sun, J.-X. Mi. Raman investigation on the behavior of parasibirskite CaHBO3 at high pressure.// Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy. 2017. V. 173. P. 46–52.

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