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Crystal-fluid interactions in laumontite

Davide Comboni[1], G. Diego Gatta[1,2], Paolo Lotti[1*], Marco Merlini[1], Michael Hanfland[3]

[1] Dipartimento di Scienze della Terra, Università degli Studi di Milano, Via Botticelli 23, 20133 Milano, Italy

[2] CNR – Istituto di Cristallografia, Sede di Bari, Via G. Amendola 122/O, Bari, Italy

[3] ESRF – European Synchrotron Radiation Facility, 71 Avenue des Martyrs, CS40220, 38043 Grenoble Cedex, France.

* Corresponding Author**:**
Phone: +39-0250315598; e-mail: paolo.lotti@unimi.it

Abstract

The elastic behavior and the structural evolution at high pressure of a natural Ca-laumontite and Ca-leonhardite, the partially dehydrated form of Ca-laumontite, have been investigated by *in situ* single-crystal synchrotron X-ray diffraction up to 2.7 GPa and 7.5 GPa, respectively, using a diamond anvil cell. Despite no phase transitions have been observed within the *P*-range investigated, an anomalous stiffening of the structure along the *b* crystallographic axis occurs at about 2.1 GPa in Ca-laumontite and 2.4 GPa in Ca-leonhardite. The isothermal bulk elastic parameters of Ca-laumontite, refined by a second order Birch–Murnaghan equation of state (BM-EoS) fit, are: V_0 = 1393.9(6) Å^3 and K_{V0} = 54.8(10) GPa; whereas the isothermal bulk elastic parameters of Ca-leonhardite, refined by a third order BM-EoS fit, are: V_0 = 1348(1) Å^3, K_{V0} = 36(1) GPa and K_{V}' = 2.4(3). The hydration process, at ambient *P-T* conditions, of Ca-leonhardite has also been studied by means of *in-situ* single crystal X-ray diffraction in several H_2O-based mixtures. The results show that the hydration process is influenced by the fraction of

H_2O in the aqueous mixtures in which leonhardite is immersed, and an almost linear correlation between the occupancy of the crystallographic W1 site and the unit-cell volume has been found. The structure deformation mechanisms that govern the compression of Ca-laumontite and Ca-leonhardite at the atomic scale, as well as those related to the hydration process of Ca-leonhardite, are described.

Keywords: laumontite, leonhardite, high pressure, X-ray diffraction, molecules intrusion.

1. Introduction

Laumontite, $[(Ca_{4-x}Na_x)K_x][Al_8Si_{16}O_{48}]\cdot(H_2O)_n$ ($0 \leq x \leq 2$ and $12 \leq n \leq 18$), space group $C2/m$, is one of the most common natural zeolites, adopted as a reference mineral for the "zeolite facies" of low-grade metamorphism [1]. Laumontite occurs in a wide range of natural environments, including sedimentary deposits or volcanoclastic sequences interested by burial diagenesis/metamorphism, as well as in hydrothermal vugs of intrusive and volcanic rocks ([2-4] and references therein). According to Jove and Hacker [5], laumontite can represent up to 20% in volume of the rocks forming oil reservoirs, where, due its cementing action, it can dramatically decrease the porosity of the host rock [6-7].

The aluminosilicate framework of laumontite [8] is characterized by chains of four- and six-membered rings (hereafter 4-mRs and 6-mRs, respectively), also referred to as secondary building units (SBU 4-6, Fig. 1). The Si and Al atoms are ordered among three distinct tetrahedral sites (namely Si1, Si2 and Al) leading to a constant 2:1 = Si:Al ratio in most of the natural laumontite samples. The 4-mRs and 6-mRs chains, running along the *c* axis, form ten-membered rings (Fig. 1), hereafter 10-mRs, which host Ca and other cations, mainly K and Na as well as H_2O molecules [9]. The main difference between (Na,K)- and Ca-laumontite is the presence, in the former, of an additional cation position (M2) occupied by K^+ or Na^+, whereas the tetrahedral framework and the H_2O molecules arrangement (at least at room-*P*) are almost identical in both the varieties. Fully hydrated laumontite contains 18 H_2O molecules per unit

formula [10-11], but if it is exposed to atmosphere at low humidity rate (< 50% of relative humidity, RH), up to 4 H_2O molecules per unit formula are lost. This partially-dehydrated laumontite (*i.e.* $Ca_4Al_8Si_{16}O_{48}\cdot 14H_2O$) is formally referred to as leonhardite [1,10,12-13]. Following this nomenclature, hereafter the term leonhardite will refer to a partially-dehydrated laumontite (LAU·$14H_2O$), for which the W1 crystallographic site is missing and a partial occupancy is found for the W2 and W5 H_2O sites.

Artioli et al. [14], in a single-crystal neutron diffraction experiment performed at 15 K, identified 11 H_2O sites. However, some of these sites were found to merge with increasing temperature. Based on a single-crystal X-ray diffraction experiment at 100 K, Armbuster et al. [15], identified 7 H_2O sites, whereas only four (referred to as W1, W2, W5, W8) can be distinguished in the fully hydrated Ca-laumontite at ambient conditions [12-13, 16]. The W2 and W8 oxygens are bonded to the Ca^{2+} ion, whereas W1 and W5 are hydrogen bonded to the framework oxygen atoms and to other H_2O molecules. Yamazaki et al. [10], based on a X-ray powder diffraction data, investigated the hydration process of Ca-laumontite reporting a final unit-cell volume of about 1388 $Å^3$ at RH > 80%. Fridriksson et al. [17] studied the response of a quasi-stoichiometric Ca-laumontite to hydration/dehydration paths by controlling the partial pressure of H_2O (P_{H2O}) at ~301.7 K, reporting that the dehydration of W1 allows W2 to move off the special position and split in two half-occupied subsites.

White et al. [18], using computational methods, hypothesized that fully hydrated laumontite (LAU·$18H_2O$) is stable up to ~ 5.5 GPa, whereas leonhardite only up to ~ 3.5 GPa. Above these pressures, the simulations showed that both the structures undergo a phase transition. The high-pressure behavior of Ca-laumontite was experimentally investigated by Lee et al. [11], by means of a synchrotron powder diffraction experiment using a diamond anvil cell (DAC) with a 16:3:1 methanol-ethanol-H_2O mixture (referred to as *m.e.w.*), as pressure-transmitting fluid. These authors observed that the partially-hydrated Ca-laumontite with ~12 H_2O per formula unit used in their experiment (V_0 ~ 1356 $Å^3$ at room pressure), underwent a full hydration already at 0.2 GPa. In this experiment, an order–disorder transition of the hydrogen-bonded H_2O

molecules, followed by a tripling of the *b* axis above 3 GPa, was observed. The latter phenomenon has been interpreted as a result of a different ordering of either the H_2O molecules or the Ca cations in the channels along the *b*-axis. Such a phase transition, occurring above 3 GPa, could be related to the predicted transition theorized by White et al. [18].

More recently, the hydration of a partially hydrated (Na,K)-rich laumontite has been investigated either at room pressure (at different RH rates) and at high pressure, using pure water as pressure-transmitting medium [19-20]. Rashchenko et al. [19] observed that (Na,K)-rich laumontite hydrates continuously if exposed to increasing RH rates, in contrast to Ca-laumontite, in which the hydration or dehydration of the W1 site induces an abrupt increase or decrease of the unit-cell volume [10, 17]. Rashchenko et al. [20] investigated the high-pressure behavior of the same (Na,K)-rich laumontite observing a continuous hydration up to 0.75 GPa.

To the best of our knowledge, no single crystal study has been performed on Ca-laumontite at high-pressure conditions. In addition, the elastic behavior and the *P*-induced structure evolution of leonhardite is still unknown, despite thermodynamic calculations, as well as experimental and geological observations, suggest that it should be the stable form of laumontite at diagenetic and low- grade metamorphic conditions (*e.g* [1, 21-22]). The crystal-fluid interactions induced by pressure on microporous compounds are being object of a raising interest especially in the field of materials science, as they proved feasible the *P*-induced intrusion, into the structural voids of zeolites, of small or complex molecules [23-25]. In the framework of a long-term project on the crystal-fluid interactions occurring in microporous compounds [26-28], we here report the 1) elastic parameters, 2) the structural re-arrangement occurring at the atomic scale and 3) the crystal-H_2O interactions induced by pressure on natural samples of Ca-laumontite and leonhardite, by means of *in situ* single-crystal synchrotron X-ray diffraction using a diamond anvil cell (DAC). A comparative description of the high-*P* behavior of Ca-laumontite and Ca-leonhardite is provided. In addition, in order to better constrain our knowledge of the hydration process in laumontite, the kinetics of molecules sorption by single

crystals of leonhardite immersed in water-based mixtures at ambient (*P*,*T*)-conditions has been investigated by means of single-crystal X-ray diffraction.

2. Experimental methods

2.1 Samples and chemical analysis

Crystals of laumontite from a natural rock sample from Nashik (India), were selected for the experiments of this study. Preliminary single-crystal X-ray diffraction data collections were performed using a KUMA-KM4 four-circle diffractometer, equipped with a point-detector and Mo*K*α radiation, at the Earth Sciences Department of the University of Milano (ESD-MI). All the selected crystals had similar size and shape (prismatic, ~ 400 x 200 x 200 μm^3) and were found to be free of twinning and optical defects.

The chemical compositions of the selected crystals have been determined by electron-microprobe analysis in wavelength dispersive mode (EPMA-WDS), using a Jeol JXA-8200 microprobe at the ESD-MI. The system was operated with an accelerating voltage of 15 kV, a beam current of 5 nA, a counting time of 30 s on the peaks and 10 s on the backgrounds and a beam diameter of 10 μm. Natural mineral samples (grossular for Si, Al and Ca; K-feldspar for K and omphacite for Na) were used as standards. The raw data were corrected for matrix effects using the φρZ method as implemented in the JEOL suite of programs. Overall, the selected crystals were found chemically homogeneous; only minor differences were found in the amount of Na and K, which were anyway negligible. The samples were always significantly enriched in Ca and the average chemical formula (based on 10 crystal fragments and 100 point analyses), calculated on the basis of 48 oxygen atoms, is: $[Na_{0.04}K_{0.04}Ca_{3.80}]_{\Sigma 3.88}[Al_{7.95}Si_{16.11}]_{\Sigma 24.06}O_{48}\cdot 13.85H_2O$. In order to perform the high pressure experiment on a fully hydrated laumontite, and based on the results obtained at ambient pressure (see section 4), few crystals have been immersed in pure H_2O for six months.

2.2 Hydration of leonhardite at ambient (P,T) conditions

Single crystals with prismatic habit were selected to investigate the hydration process of leonhardite by means of *in-situ* single crystal X-ray diffraction. The crystals were stuck (with epoxy resin) on a glass fibre, located in a 5 mm (in diameter) glass vial (Fig. 2). All the samples so prepared were mounted on a goniometer head for X-ray diffraction data collections (firstly) in air performed with an Xcalibur Oxford Diffraction diffractometer equipped with a CCD detector, graphite-monochromatized Mo-Kα radiation, and operating at 50 kV and 30 mA at the ESD-MI. A combination of ω and φ scans, in order to maximize the reciprocal space coverage, with a step size of 1° and an exposure time of 25 s per frame, was adopted. Data reductions, including Lorenz-polarization and absorption correction based on the implemented semi-empirical ABSPACK routine, were performed using the software CrysAlis [29]. After the measurement in air, aimed to obtain the initial cell parameters, the vials were flooded with a H_2O-ethanol mixture containing 100%, 15%, 10% and 5% of H_2O, the samples being named Wat100, Wat15, Wat10 and Wat5, respectively. The open side of each vial was carefully closed with a plastic cap stuck with epoxy resin, in order to avoid a change in the H_2O-ethanol ratio. In order to primary investigate the role of the fraction of H_2O in the fluid, in which leonhardite is immersed during the hydration process, the selected samples were chosen with similar size and habit, to minimize the effects induced by shape, surface/volume ratio, etc. Consecutive short data collections were performed for the samples Wat100 and Wat5 adopting the following strategy: a 180° φ scan, with a step size of 1.5° and an exposure time of 20 s per frame. Such a data collection required only 120 minutes. In this way, it was possible to study the evolution of the unit-cell parameters as a function of the hydration process. On the other hand, for the samples Wat15 and Wat10, longer data collections (similar to those with the crystal in air) were performed, in order to obtain sufficient Bragg reflections to perform structure refinements.

2.3 High-pressure experiments

In order to perform high-pressure experiments on laumontite and leonhardite, a few single crystals with a prismatic habit (~60x25x25 μm^3 in size) were selected on the basis of their

optical quality. The high-pressure diffraction experiments were performed at the ID15B beamline of the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. A parallel monochromatic beam (E = 30.16 KeV, $\lambda \sim 0.411$ Å) was used. In the case of leonhardite, a first data collection was performed with the crystal in the DAC without the pressure-transmitting medium. In the case of hydrated laumontite this was not possible as the data collections performed in air showed that the dehydration process starts as soon as the sample was exposed to the atmosphere (or even if the crystals were submerged into a mixture with a low content of H_2O), in fair agreement with the observations of Fridriksson et al. [17]. For these reasons, a single crystal was selected and immediately placed in a DAC along with a 1:1:2 methanol:ethanol:H_2O mixture. Due to the high H_2O content, the experiment was performed up to 2.7 GPa, in order to prevent the crystallization of ice, and five data collections were performed during the decompression. In the case of leonhardite, a nominally anhydrous methanol:ethanol mixture (4:1), which is hydrostatic up to 9.8 GPa [30], was used as *P*-transmitting fluid. In both the experiments, membrane-driven diamond anvil cells (DACs), mounting Boehler-Almax designed diamonds (culet diameter 600 μm), were used. A 250-μm-thick foil of stainless steel, which served as a gasket, was pre-indented to ~70 μm and then drilled using a spark-erosion device, leading to a *P*-chamber ~200 μm in diameter. The ruby fluorescence method was used for pressure calibration ([31]; pressure uncertainty ±0.05 GPa). A stepwise ω-rotation in the range ±32°, with 1° step width and 1s exposure time per step, was adopted for the data collection strategy; the diffraction patterns were collected by a MAR555 flat-panel detector, at a 287.43 mm distance from the sample position. Further details on the beamline experimental setup are reported in Merlini and Hanfland [32]. Indexing of the diffraction patterns, unit-cell parameters refinement and integration of the intensities data were performed using the CrysAlis package [29]. Corrections for absorption (due to the DAC components) and background were applied by the semiempirical ABSPACK routine implemented in CrysAlis [29].

3. Structure refinement protocol

All the structure refinements (pertaining to the hydration experiments at ambient conditions and to the high-*P* experiments) were performed using the software JANA2006 [33] in the space group *C*2/*m*, as suggested by the diffraction patterns and by the reflection conditions. The fractional coordinates of the framework sites were obtained using the SUPERFLIP program [34]. The positions of the extra-framework sites were obtained by a careful analysis of the difference-Fourier maps of the electron density.

In the structure refinement based on the data collected in air, one Ca site along with four independent sites assigned to the H_2O-oxygen atoms were identified and named W2, W5, W8 and W8', respectively. This notation is consistent with that of Lee et al. [11] and Fridriksson et al. [17], with the difference that W8, in the present study, is modelled as two mutually exclusive sites, namely W8 and W8'. Notably, Fridriksson et al. [17] reported that refining W8 with anisotropic displacement parameters yielded to a significant improvement of the refined model and also suggested that W8 could have been refined as 2 partially occupied sites. This is also consistent with the structure refinements reported by Ståhl et al. [14] and Armbruster et al. [15]. In order to reduce the number of the refined variables, the displacement parameters (D.P.) were restrained as isotropic, the H_2O-oxygen sites were restrained to share the same D.P value, except for the structure refinement of leonhardite based on the X-ray data collected with the crystal in the DAC without *P*-medium, where two D.P.'s were refined (one for W8-W8' and one for W5-W2, respectively). In addition, due to mutual exclusiveness, the sum of the W8 and W8' occupancies was kept ≤ 1.

The refined unit-cell parameters pertaining to the experiments at high pressure are listed in Tables 1 and 2.

The unit-cell parameters of the H_2O adsorption experiments performed at ambient conditions are listed in Table 3 and shown in Fig. 3. The principal statistical parameters of the structure refinements are listed in Table S1 (supplementary materials, SM). Atomic coordinates and site occupancies of selected structure refinements are given in Table S2 (SM). The relevant bond

distances pertaining to the H_2O sites are reported in Tables 4 and 5, whereas further relevant structural parameters pertaining to leonhardite and hydrated laumontite are listed in Table 6.

4. Results

4.1 Hydration of leonhardite at ambient conditions

The evolution of the unit-cell parameters as a function of H_2O fraction of the mixture and time (Fig. 3; Table 3) suggests that the adsorption rate of H_2O into the structural voids of laumontite is enhanced by increasing its concentration in the fluid interacting with the sample, in fair agreement with the observations reported in previous studies (*e.g.* [10,17]).

4.2 High-pressure behavior of leonhardite and hydrated Ca-laumontite

The *P*-induced evolution of the unit-cell parameters of both leonhardite and hydrated laumontite, shown in Fig. 4 and Fig. 5, is monotonic, without any evidence of phase transition up to the highest pressure investigated. In both the cases, the unit cell edges *a* and *c* decrease over the entire *P*-range, whereas the monoclinic β angle markedly increases. The *b* unit-cell edge of leonhardite, on the other hand, slightly increases between 2.38 GPa and 3.01 GPa, after which a significant stiffening along that direction occurs, leading to an almost uncompressible behavior (Fig. 5 and Table 1). This anomalous behavior was also observed for hydrated laumontite between 2.1 and 2.5 GPa.

To describe the (isothermal) compressional behavior of leonhardite and hydrated-laumontite, the unit-cell volume *vs.* pressure data were fitted to a Birch-Murnaghan equation of state (BM-EoS) truncated to the third and to the second order, for leonhardite and hydrated laumontite, respectively. The BM-EoS relies on the assumption that the strain energy of a solid under compression can be expressed as a Taylor series in the Eulerian finite strain [35]. The experimental *V-P* data, weighted by their uncertainties, have been fitted to the BM EoS using the *EoSFit 7.0* software [36-37], leading to the refined elastic parameters listed in Table 7. The refined bulk modulus at ambient conditions ($K_{V0} = \beta_{V0}^{-1}$, where β_{V0} is the volume

compressibility) of the hydrated laumontite is 54.8(10) GPa, similar, but slightly lower, to that obtained for a powder sample by Lee et al. [11], who reported K_{V0} = 59(1) GPa, whereas the refined bulk modulus of leonhardite at ambient conditions was found to be 36(1) GPa. Overall, both leonhardite and hydrated laumontite show a significant anisotropic compressibility with $K(c)_{P0,T0} < K(a)_{P0,T0} < K(b)_{P0,T0}$, even though the anisotropy is particularly pronounced in the former, being $K(b)_{P0,T0}$ ~2.5 $K(a)_{P0,T0}$ ~ 5$K(c)_{P0,T0}$ in leonhardite and $K(b)_{P0,T0}$ ~1.3 $K(a)_{P0,T0}$ ~ 2$K(c)_{P0,T0}$ in hydrated laumontite.

5. Discussion

5.1 Hydration of leonhardite at ambient conditions

The experiments on the hydration at ambient conditions of Ca-laumontite performed so far (*e.g* [10-11,16-17]) were based on the use of powder samples, which almost immediately increase or decrease their unit-cell volume in response to different RH rate or submersion in pure H_2O or hydrous mixtures. On the contrary, to the best of our knowledge, this is the first experiment that investigates the hydration of Ca-laumontite at ambient conditions by means of *in-situ* single-crystal XRD. The results reported in section 4.1 indicate that the adsorption of H_2O depends not only on the size of the crystals, or on the timescale of immersion, but also on the fraction of H_2O of the mixture, similarly to the results obtained with laumontite in air at varying the RH conditions (*e.g* [10,17]). The hydration of leonhardite can take a few hours before affecting the unit-cell volume: for instance, the unit-cell volume of the sample Wat10, immersed in a 10% H_2O mixture, increases of only 5 $Å^3$ after 4 hours. In addition, the results suggest that there is a critical fraction of H_2O under which the full occupancy of the H_2O-oxygen site W1 is not fulfilled (at least at the timescale of the experiment). In fact, the sample Wat5, after a quick volume increase (identical within 3σ to that observed in the samples Wat10 and Wat15), does not complete the hydration process, with final unit-cell volume of 1364.3(4) $Å^3$ (Table 3). On the contrary, the unit-cell volumes of the samples Wat10 and Wat15 continuously increase up to 1385.7(4)$Å^3$ and 1384.1(3)$Å^3$, respectively (Table 3, Fig. 3). It is noteworthy to underline that

the latter are consistent with the final unit-cell volume of the sample Wat100 (1383(1)Å^3), which was submerged in pure H_2O. As can be seen in Fig. 3, the higher the fraction of H_2O in the fluid interacting with the crystal, the quicker the hydration process. The structure refinements performed on the sample Wat10 and Wat15, in which long data collections were performed for each point (see section 2.2), show that the volume variation is coupled with an increase of the W1 site occupancy, which is initially nil. After 48 hours, the occupancy of W1 site in the sample Wat10 (0.83(2)) and Wat15 (0.89(2)), reaches the saturation and, at the same conditions, the unit-cell volumes do not increase anymore (see Table 3 and Fig. 3). A structure refinement based on a data collection performed on the Wat100 sample after 40 hours of immersion in pure H_2O revealed that W1-$s.o.f._{(Wat100)}$ ~ W1-$s.o.f._{(Wat10)}$ ≤ W1-$s.o.f._{(Wat15)}$. This suggests that either a saturation in the W1-occupancy is reached at ambient *P/T* conditions or, most likely, the W1-occupancy is also influenced by other variables, such as the presence of structural defects hindering the molecules diffusion through the channels, the surface/volume ratio, etc.

During the hydration process, the *a* and *b* unit-cell edges increase whereas *c* decreases, although the hydration process mainly affects the β monoclinic angle (Table 3). It is interesting to note that, as the W1-occupancy increases, the H_2O-oxygen sites W2 and W5 move toward the mirror plane, reducing the W2-W2 and W5-W5 interatomic distances, respectively (Fig. 6).

5.2 High-pressure behavior of leonhardite and hydrated Ca-laumontite

Due to its anhydrous nature and the high hydrostatic pressure limit [30], the methanol:ethanol 4:1 mixture has been adopted as *P*-transmitting fluid to investigate the high-pressure behavior of leonhardite.

The higher compressibility shown by leonhardite (K_{V0} = 36(1) GPa) with respect to the hydrated Ca-laumontite here studied (K_{V0} = 54.8(10) GPa) and that reported by Lee et al. [11] (K_{V0} = 59(1) GPa, based on the compression of a polycrystalline sample in the methanol:ethanol:H_2O 16:3:1 mixture), may be ascribed to the absence of the W1 H_2O-oxygen site, acting as a "filler"

of the cavities, and to the partial occupancy of W2 in the crystal structure of leonhardite. Comparing the (slightly) different compressibility between the Ca-laumontite of this study and that reported by Lee et al. [11] is less trivial. However, we can note that: 1) contrary to the structure model of by Lee et al. [11], the W5 H_2O-oxygen site of the Ca-laumontite of this study is only partially occupied (Table S2) and 2) the larger surface/volume ratio of the powder sample used for the previous experiments may promote the *P*-induced intrusion of H_2O molecules, which is hindered in single crystals, as already observed in SiO_2-ferrierite and $AlPO_4$ zeolites [26-27]. It is noteworthy that, based on a compression in pure water, Rashchenko et al. [20] reported a higher compressibility (K_{I0} = 39(3) GPa) for the (Na,K) counterpart of laumontite. In both hydrated laumontite and leonhardite, a dramatic stiffening along the *b* crystallographic axis was detected at about 2.2-2.5 GPa whereas no tripling of the same axis has been observed, in contrast to what reported by Lee et al. [11]. As common for open-framework materials [25,38], the $(Si,Al)O_4$ tetrahedra behave as quasi-rigid units in response to pressure, and the bulk compression is mainly accommodated through the tilting of the TO_4 units around the shared oxygen hinges. This mechanism gives rise to a pronounced increase of the ellipticity of the 10-mRs with pressure. The ellipticity ratio ε, defined as the ratio between the shortest (O1-O1) and the longest (O7-O7) diameters of the ring (Fig. 1), is almost constant up to 2.38 GPa, whereas at higher pressures significantly decreases (Table 6), revealing that the bulk compression is initially accommodated isotropically by the 10-mRs channels and, in the higher pressure range, the deformation occurs mainly along the O1-O1 diameter parallel to the *a* crystallographic axis. Consistently, up to the highest pressure investigated of 2.65 GPa, no significant changes in the ε parameter of the 10-mRs of hydrated laumontite are observed, suggesting an isotropic compression of this channel (Table 6).

One of the most relevant deformation mechanism induced by pressure consists in the distortion of the 6-mRs (Fig. 1). In leonhardite, this distortion is driven by a significant decrease of the O5-O5 diameter coupled with an increase of the O4-O4 one (Fig. 1 and Table 6). The same

distortion mechanism is observed also in the fully hydrated laumontite, although less pronounced (Table 6). Overall, the higher H_2O content in laumontite induces an expansion of the unit-cell volume that is reflected in the tetrahedral framework. In leonhardite, as the absence of H_2O molecules act as a sort of "chemical pressure", the ellipticity of the 10-mRs is higher and the interatomic distances are shorter than in laumontite (Table 6). The H_2O molecules also act as fillers, partially counteracting the effect of pressure by leading, in hydrated laumontite, to a lower magnitude of the same deformation mechanisms observed in leonhardite, which is also reflected at the macroscopic scale by the different isothermal bulk moduli.

The *P*-induced compression in leonhardite affects the extraframework population mainly through the significant shortening of the W8-Ca, W8-O5, W8-O7, W2-Ca and W2-W5 interatomic distances (Table 5). On the contrary, it is worth to note that the W8'-O4 distance undergoes only a moderate contraction, whereas an expansion of the W8'-Ca distance is observed (Table 5). This is coupled with a reduction in the occupancy of the W8′ H_2O-oxygen site at 1.69 GPa (Table S2), whereas at 2.38 GPa no peak could be detected in the difference-Fuorier synthesis of the electron density at the position formerly occupied by the W8′ site. It is noteworthy that the disappearance of the W8′ site is coupled with an increase in the occupancy of W8 (Table S2). A similar *P*-induced re-arrangement of the H_2O molecules, without any phase transition, was recently also observed in the natural zeolite phillipsite [28]. Finally, as pressure increases, a significant shortening in the W5-W2 interatomic distance is observed (Table 5).

A different *P*-induced evolution of the extraframework population has been observed in the hydrated laumontite, where a minor shortening (less than 1%) of the W8-O7, W2-Ca, W8'-Ca and W1-O7 interatomic distances occurs, along with a more pronounced compression of the W8-O5, W5-W2 and W1-W2 distances, which decrease by about 4%, 6% and 5%, respectively (see Table 5). It is worth to report that the W8′ H_2O-oxygen site, in the crystal structure of fully hydrated laumontite, occupies a position slightly different with respect to that of leonhardite, which likely governs the different behavior at high pressure of this H_2O-oxygen site in the two

compounds. Unfortunately, the low hydrostatic *P*-limit of the 1:1:2 methanol-ethanol-H_2O mixture, adopted as *P*-transmitting fluid for hydrated laumontite, prevented to investigate the behavior of this compound at higher pressures, where we cannot exclude that a similar merging to that observed in leonhardite might occur.

6. Concluding remarks and implications

The hydration process of Ca-leonhardite, a partially dehydrated form of Ca-laumontite, in aqueous solution has been studied by *in situ* single-crystal XRD. The results show that: 1) in order to enhance a complete hydration process, a critical fraction of H_2O of the solution (between 5% and 10%) is required and 2) the higher the fraction of H_2O in the mixture, the quicker the hydration of the crystals.

The high-pressure behaviors of Ca-leonhardite and Ca-laumontite show that, despite a significant stiffening along the *b* axis at ~2.4 GPa, no phase transition occurs up the highest pressure investigated. The lower compressibility of Ca-laumontite (β_{V0} = 0.0184(3) GPa^{-1}),with respect to Ca-leonhardite (β_{V0} = 0.0278(8) GPa^{-1}), highlights the "pillar effect" played by the extraframework H_2O molecules, which counteract the *P*-induced framework deformation and, therefore, the bulk compression.

The hydration process here described underlines that laumontite behaves as an "open system" when immersed in an aqueous fluid, with a continuous uptake or release of structural H_2O molecules as a function of its relative abundance in the fluid (as well as of *T* and *P*). This observation bears a large relevance if we consider that laumontite can be a major component of oceanic sediments and basalts, where it forms as an alteration product of Ca-bearing aluminosilicate minerals at the conditions of burial diagenesis and low-grade metamorphism [2,39]. Modeling the stability of mineralogical assemblages by thermodynamic calculations can be largely biased by the choice of Ca-laumontite or Ca-leonhardite [21]. The drastically different refined bulk compressibilities of the two polymorphs, here reported, further confirm

this conclusion. The choice of suitable thermodynamic parameters is, therefore, fundamental for modeling the stability of this hydrous mineral, for example during the subduction process of the oceanic crust, or for predicting its occurrence in geological environments of economic relevance, as oil reservoirs, where cementing laumontite degrades the potential of the country rocks for hosting hydrocarbons [6,7].

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Table 1. Unit-cell parameters of leonhardite with pressure (* in decompression).

P (GPa)	*V* (Å^3)	*a* (Å)	*b* (Å)	*c* (Å)	*β* (°)
0.0001	1346.9(6)	14.7342(19)	13.0562(7)	7.5533(5)	112.035(11)
0.06(5)	1344.6(5)	14.7262(9)	13.0524(3)	7.5501(3)	112.096(5)
0.14(5)	1342.6(5)	14.7240(10)	13.0485(3)	7.5435(2)	112.126(5)
0.31(5)	1338.3(7)	14.7192(11)	13.0435(4)	7.5273(2)	112.175(6)
0.53(5)	1329.2(6)	14.7025(13)	13.0280(4)	7.5004(3)	112.298(7)
0.86(5)	1316.3(6)	14.6745(15)	13.0069(4)	7.4633(3)	112.476(8)
1.11(5)	1310.8(6)	14.6603(12)	13.0009(4)	7.4464(3)	112.549(7)
1.69(5)	1290.4(5)	14.592(3)	12.9919(9)	7.3886(6)	112.895(16)
2.38(5)	1263.6(5)	14.4842(13)	12.9848(4)	7.3228(3)	113.433(7)
3.01(5)	1245.6(5)	14.3866(18)	12.9949(5)	7.2861(4)	113.872(11)
3.37(5)	1237.2(5)	14.3381(10)	12.9947(3)	7.2696(2)	114.015(6)
4.40(5)	1212.2(5)	14.2038(12)	12.9866(4)	7.2217(3)	114.495(8)
4.79(5)	1205.3(5)	14.1660(12)	12.9851(3)	7.2083(3)	114.630(8)
5.38(5)	1187.9(5)	14.0783 (12)	12.9766(3)	7.1729(3)	114.975(7)
6.52(5)	1160.6(5)	13.9584(18)	12.9754(4)	7.1184(4)	115.818(12)
7.46(5)	1134(6)	13.863(5)	12.9795(13)	7.0707(13)	116.960(4)
*4.01(5)	1227(2)	14.17(2)	13.02(7)	7.239(5)	113.23(13)

Table 2. Unit-cell parameters of hydrated laumontite with pressure (* in decompression).

P (GPa)	*V* (Å^3)	*a* (Å)	*b* (Å)	*c* (Å)	*β* (°)
0.00(5)	1394.4(3)	14.9193(6)	13.1805(5)	7.54296(13)	109.939(3)
0.03(5)	1393.1(4)	14.9132(11)	13.1775(9)	7.5405(2)	109.932(5)
0.11(5)	1391.1(3)	14.9096(10)	13.1708(8)	7.5319(2)	109.854(4)
0.27(5)	1386.8(4)	14.9036(6)	13.1542(5)	7.51924(13)	109.813(3)
0.49(5)	1382.0(4)	14.8932(10)	13.1422(9)	7.5048(2)	109.806(4)
0.67(5)	1377.1(3)	14.8789(6)	13.1358(5)	7.49105(13)	109.850(3)
0.90(5)	1372.4(4)	14.8644(7)	13.1268(6)	7.4789(2)	109.878(3)
1.10(5)	1366.8(4)	14.8445(6)	13.1169(6)	7.46626 (14)	109.918(3)
1.40(5)	1360.3(4)	14.8202(13)	13.1067(11)	7.4517(3)	109.987(5)
1.72(5)	1353.1(4)	14.796(2)	13.090 (2)	7.4361(4)	110.032(9)
2.03(5)	1346.8(7)	14.777(4)	13.0810(11)	7.4236(7)	110.19(2)
2.35(5)	1339.2(5)	14.7337(9)	13.0792(7)	7.4069(2)	110.242(4)
2.65(5)	1333.7(6)	14.703(2)	13.0917(5)	7.3974(3)	110.500(9)
*2.36(5)	1339.5(7)	14.737(2)	13.0865(5)	7.4083(3)	110.354(9)
*1.99(5)	1347.0(7)	14.778(2)	13.0810(4)	7.4233(2)	110.170(7)
*1.69(5)	1352.8(6)	14.8009(12)	13.0859(3)	7.4367(2)	110.080(6)
*0.58(5)	1380.7(5)	14.8914(9)	13.1374(8)	7.5008(2)	109.795(4)
*0.05(5)	1392.2(8)	14.928(3)	13.1573(7)	7.5339(6)	109.81(2)

Table 3. Evolution of the unit-cell parameters of leonhardite as a function of time of immersion for the samples Wat100, Wat15, Wat10 and Wat5, respectively (see text for further details).

Leonhardite Wat100 sample					
time* (min)	V(Å^3)	a (Å)	b (Å)	c (Å)	β (°)
0	1351.56(17)	14.7372(8)	13.0754(5)	7.5604(3)	111.916(5)
78	1356(2)	14.75(2)	13.120(2)	7.532(11)	111.42(15)
198	1364.9(10)	14.758(1)	13.151(6)	7.525(4)	110.84(6)
305	1367(1)	14.788(12)	13.140(14)	7.526(6)	110.80(8)
428	1368(1)	14.795(11)	13.142(13)	7.523(6)	110.70(8)
545	1374(1)	14.849(13)	13.134(13)	7.533(6)	110.72(8)
979	1378(7)	14.813(6)	13.149(7)	7.562(3)	110.67(4)
1502	1383(1)	14.807(12)	13.213(10)	7.552(6)	110.62(8)
1708	1383(1)	14.809(13)	13.211(11)	7.551(6)	110.63(8)
2054	1383(1)	14.806(11)	13.220(11)	7.551(5)	110.60(7)
Leonhardite Wat15 sample					
time* (min)	V(Å^3)	a (Å)	b (Å)	c (Å)	β (°)
0	1349.1(7)	14.764(7)	13.072(5)	7.555(2)	112.29(4)
240	1360.2(6)	14.757(7)	13.134(5)	7.5505(16)	111.65(4)
1710	1385.6(4)	14.886(4)	13.180(3)	7.5321(9)	110.35(2)
2370	1385.7(4)	14.880(4)	13.184(3)	7.5302 (9)	110.29(2)
Leonhardite Wat10 sample					
time* (min)	V(Å^3)	a (Å)	b (Å)	c (Å)	β (°)
0	1350.18(18)	14.7568(11)	13.0649(5)	7.5574(5)	112.080(8)
250	1354.8(4)	14.755(4)	13.0962(13)	7.5618(8)	111.99(2)
812	1360.6(3)	14.769(5)	13.1232(15)	7.562(14)	111.83(3)
1998	1384.1(4)	14.861(3)	13.1772(11)	7.5455(7)	110.497(16)
2464	1384.1(3)	14.860(3)	13.1798(12)	7.5419(8)	110.446(18)
Leonhardite Wat5 sample					
time* (min)	V(Å^3)	a (Å)	b (Å)	c (Å)	β (°)
0	1349.6(5)	14.856(3)	13.063(3)	7.5554(15)	112.07(2)
95	1351.4(8)	14.757(3)	13.072(2)	7.556(14)	112.00(2)
212	1354.7(3)	14.763(3)	13.083(3)	7.5655(16)	112.02(2)
351	1357.7(3)	14.779(3)	13.088(2)	7.570(15)	111.99(2)
493	1359.6(3)	14.785(3)	13.099(2)	7.5708(13)	111.98(2)
623	1360.8(4)	14.786(7)	13.104(5)	7.575 (3)	112.01(4)
1468	1361.4(6)	14.776(5)	13.120(4)	7.567 (2)	111.87(3)
1734	1361.7(5)	14.776(6)	13.123(4)	7.569 (2)	111.90(4)
1878	1361.5(7)	14.767(6)	13.121(4)	7.571 (3)	111.85(4)
2184	1362.4(5)	14.778(6)	13.123(4)	7.569 (3)	111.85(4)
2637	1363.8(5)	14.784(7)	13.135(4)	7.566 (3)	111.85(4)
3266	1364.0(6)	14.785(7)	13.135(5)	7.565 (3)	111.80(4)
3479	1363.8(5)	14.786(8)	13.125(6)	7.568 (3)	111.78(5)

3933	1364.3(4)	14.782(6)	13.138(4)	7.565 (2)	111.78(3)

Table 4. Refined interatomic distances (in Å) pertaining to the samples Wat15 and Wat10 as a function of time.

Wat15 sample							
time (min)	O1-O1	O7-O7	W2-W2	W5-W5	W2-Ca	W8-O7	W1-07
0	6.68(4)	8.12(3)	1.010(4)	1.753(7)	2.487(14)	3.208(10)	-
240	6.75(4)	8.14(3)	0.802(3)	1.333(5)	2.471(14)	3.219(10)	2.907(8)
1710	6.96(4)	8.16(3)	0.475(2)	0.780(3)	2.396(14)	3.384(11)	2.802(8)
2370	7.00(4)	8.15(3)	0.494(2)	0.801(3)	2.398(14)	3.377(10)	2.792(8)

Wat10 sample							
time (min)	O1-O1	O7-O7	W2-W2	W5-W5	W2-Ca	W8-O7	W1-O7
0	6.67(4)	8.11(3)	0.928(8)	1.715(7)	2.48(1)	3.20(1)	-
250	6.73(4)	8.13(3)	0.933(8)	1.591(6)	2.47(1)	3.22(1)	2.89(5)
812	6.74(4)	8.14(3)	0.706(6)	1.298(5)	2.44(1)	3.23(1)	2.84(8)
1998	6.92(4)	8.16(3)	0.445(4)	0.778(3)	2.40(1)	3.28(1)	2.79(8)
2464	6.93(4)	8.16(3)	0.471(4)	0.727(3)	2.40(1)	3.47(1)	2.78(8)

Table 5. Relevant interatomic distances (in Å) of leonhardite and hydrated laumontite pertaining to the H_2O sites at different pressure (* in decompression).

Leonhardite									
P (GPa)	W2-W2	W2-Ca	W5-W8	W5-W2	W8-Ca	W8-O5	W8-O7	W8'-Ca	W8'-O4
0.0001	0.979(2)	2.525(4)	2.480(2)	3.133(5)	2.424(1)	2.927(4)	3.265(2)	2.358(5)	2.867(6)
0.06(5)	0.902(2)	2.493(4)	2.595(2)	3.126(5)	2.364(1)	2.905(4)	3.278(2)	2.351(5)	2.807(6)
0.14(5)	0.925(2)	2.489(4)	2.610(2)	3.120(5)	2.368(1)	2.925(4)	3.238(2)	2.353(5)	2.789(6)
0.31(5)	0.896(2)	2.475(4)	2.625(2)	3.110(5)	2.368(1)	2.920(4)	3.224(2)	2.363(5)	2.780(6)
0.53(5)	0.883(2)	2.483(4)	2.618(2)	3.081(5)	2.381(1)	2.912(4)	3.177(2)	2.377(5)	2.759(6)
0.86(5)	0.840(2)	2.485(4)	2.667(2)	3.030(5)	2.363(1)	2.900(4)	3.148(2)	2.384(5)	2.759(6)
1.11(5)	0.848(2)	2.512(4)	2.662(2)	3.003(4)	2.370(1)	2.894(4)	3.127(2)	2.345(5)	2.727(6)
1.69(5)	0.693(2)	2.438(4)	2.750(2)	2.960(5)	2.344(1)	2.846(4)	3.100(2)	2.402(5)	2.711(6)
2.38(5)	0.676(2)	2.421(4)	2.857(2)	2.877(4)	2.329(1)	2.844(4)	3.040(2)		
3.01(5)	0.659(2)	2.423(4)	2.918(2)	2.813(4)	2.334(1)	2.795(4)	3.000(2)		
3.26(5)	0.623(2)	2.408(4)	2.901(2)	2.808(4)	2.339(1)	2.788(4)	2.975(2)		
4.40(5)	0.612(2)	2.394(4)	2.928(2)	2.754(4)	2.327(1)	2.750(4)	2.913(2)		
4.79(5)	0.646(2)	2.356(4)	2.940(2)	2.756(4)	2.310(1)	2.745(4)	2.929(2)		
5.38(5)	0.604(2)	2.370(4)	2.928(2)	2.698(4)	2.323(1)	2.749(4)	2.876(2)		
6.52(5)	0.630(2)	2.330(4)	2.921(2)	2.619(4)	2.289(1)	2.755(4)	2.871(2)		
7.46(5)	0.497(2)	2.243(4)	3.006(2)	2.540(4)	2.316(1)	2.855(4)	2.857(2)		
Laumontite									
P (GPa)	W2-Ca	W5-W8	W5-W2	W8-Ca	W8-O5	W8-O7	W8'-Ca	W1-W2	W1-O7
0.00(5)	2.355(3)	3.117(2)	3.515(5)	2.392(1)	2.935(4)	3.293(2)	2.391(1)	2.739(1)	2.813(2)
0.03(5)	2.337(3)	3.211(2)	3.529(5)	2.3881)	2.898 (4)	3.320(2)	2.408(1)	2.737(1)	2.817(2)

0.11(5)	2.345(3)	3.366(2)	3.528(5)	2.356(1)	2.903(4)	3.395(2)	2.421(1)	2.746(1)	2.816(2)
0.27(5)	2.341(3)	3.266(2)	3.523(5)	2.388(1)	2.889(4)	3.317(2)	2.407(1)	2.739(1)	2.809(2)
0.49(5)	2.335(3)	3.208(2)	3.512(5)	2.389(1)	2.869(4)	3.303(2)	2.386(1)	2.746(1)	2.807(2)
0.67(5)	2.342(3)	3.176(2)	3.482(5)	2.396(1)	2.853(4)	3.270(2)	2.390(1)	2.741(1)	2.806(2)
0.90(5)	2.344(3)	3.136(2)	3.469(5)	2.395(1)	2.864(4)	3.254(2)	2.383(1)	2.727(1)	2.815(2)
1.10(5)	2.345(3)	3.130(2)	3.448(5)	2.389(1)	2.842(4)	3.260(2)	2.391(1)	2.733(1)	2.808(2)
1.40(5)	2.351(3)	3.145(2)	3.431(5)	2.385(1)	2.821(4)	3.263(2)	2.379(1)	2.721(1)	2.810(2)
1.72(5)	2.346(3)	3.203(2)	3.409(5)	2.381(1)	2.832(4)	3.239(2)	2.361(1)	2.724(1)	2.801(2)
2.03(5)	2.336(3)	3.073(2)	3.384(5)	2.334(1)	2.832(4)	3.238(2)	2.377(1)	2.732(1)	2.779(2)
2.35(5)	2.335(3)	3.258(2)	3.360(5)	2.256(1)	2.816(4)	3.396(2)	2.380(1)	2.737(1)	2.820(2)
2.65(5)	2.346(3)	3.084(2)	3.312(5)	2.332(1)	2.812(4)	3.207(2)	2.368(1)	2.739(1)	2.771(2)
*2.36(5)	2.345(3)	3.132(2)	3.343(5)	2.299(1)	2.820(4)	3.276(2)	2.370(1)	2.731(1)	2.776(2)
*1.99(5)	2.362(3)	3.095(2)	3.366(5)	2.324(1)	2.831(4)	3.271(2)	2.391(1)	2.728(1)	2.777(2)
*1.69(5)	2.340(3)	3.123(2)	3.405(5)	2.318(1)	2.861(4)	3.284(2)	2.406(1)	2.736(1)	2.779(2)
*0.58(5)	2.342(3)	3.191(2)	3.505(5)	2.412(1)	2.871(4)	3.270(2)	2.378(1)	2.728(1)	2.819(2)
*0.05(5)	2.325(3)	3.186(2)	3.549(5)	2.427(1)	2.914(4)	3.292(2)	2.371(1)	2.742(1)	2.834(2)

Table 6. Relevant interatomic distances (in Å) and ε parameter (see Section 5.2) of leonhardite and hydrated laumontite pertaining to the 6- and 10-mRs at different pressure $\left[\varepsilon_{10-\mathrm{mRs}} = \frac{\mathrm{O1-O1}}{\mathrm{O7-O7}}\right]$ (* in decompression).

Leonhardite							
P (GPa)	O3-O3	O4-O4	O5-O5	O1-O6	O1-O1	O7-O7	$\varepsilon_{10\text{-mRs}}$
0.0001	4.859(3)	4.841(6)	5.339(5)	3.162(2)	6.683(8)	8.095(6)	0.826(3)
0.06(5)	4.856(3)	4.841(6)	5.316(5)	3.208(2)	6.661(8)	8.092(6)	0.823(3)
0.14(5)	4.850(3)	4.862(6)	5.294(5)	3.224(2)	6.662(8)	8.078(6)	0.825(3)
0.31(5)	4.841(3)	4.872(6)	5.269(5)	3.219(2)	6.651(8)	8.074(6)	0.824(3)
0.53(5)	4.843(3)	4.897(6)	5.217(5)	3.210(2)	6.663(8)	8.050(6)	0.828(3)
0.86(5)	4.842(3)	4.939(6)	5.131(5)	3.226(2)	6.638(8)	8.018(6)	0.828(3)
1.11(5)	4.839(3)	4.961(6)	5.083(5)	3.256(2)	6.608(8)	8.010(6)	0.825(3)
1.69(5)	4.832(3)	5.042(6)	4.930(5)	3.254(2)	6.598(8)	7.980(6)	0.827(3)
2.38(5)	4.823(3)	5.198(7)	4.708(4)	3.312(2)	6.548(8)	7.942(6)	0.824(3)
3.01(5)	4.804(3)	5.277(7)	4.554(4)	3.409(2)	6.409(8)	7.921(6)	0.801(3)
3.26(5)	4.781(3)	5.362(7)	4.492(4)	3.399(2)	6.406(8)	7.902(6)	0.811(3)
4.40(5)	4.744(3)	5.474(7)	4.399(6)	3.450(2)	6.300(8)	7.837(6)	0.804(3)
4.79(5)	4.739(3)	5.495(7)	4.298(6)	3.445(2)	6.261(8)	7.835(6)	0.799(3)
5.38(5)	4.729(3)	5.557(7)	4.204(4)	3.444(2)	6.212(8)	7.789(6)	0.797(3)
6.52(5)	4.707(3)	5.576(7)	4.060(4)	3.449(3)	6.081(8)	7.777(6)	0.782(3)
7.46(5)	4.847(3)	5.659(7)	3.943(4)	3.422(3)	6.026(8)	7.851(6)	0.768(3)
Laumontite							
P (GPa)	O3-O3	O4-O4	O5-O5	O1-O6	O1-O1	O7-O7	$\varepsilon_{10\text{-mRs}}$
0.00(5)	4.971(3)	5.113(6)	5.230(5)	3.279(2)	7.008(8)	8.147(6)	0.860(3)
0.03(5)	4.973(3)	5.118(6)	5.218(5)	3.266(2)	7.010(8)	8.161(6)	0.860(3)
0.11(5)	5.000(3)	5.109(6)	5.226(5)	3.267(2)	7.026(8)	8.160(6)	0.861(3)
0.27(5)	4.975(3)	5.098(6)	5.202(5)	3.235(2)	7.030(8)	8.115(6)	0.866(3)
0.49(5)	4.973(3)	5.095(6)	5.191(5)	3.247(2)	7.011(8)	8.128(6)	0.863(3)
0.67(5)	4.964(3)	5.119(6)	5.170(5)	3.243(2)	7.032(8)	8.110(6)	0.867(3)
0.90(5)	4.962(3)	5.121(6)	5.154(5)	3.251(2)	6.989(8)	8.105(6)	0.862(3)
1.10(5)	4.969(3)	5.125(6)	5.143(5)	3.233(2)	6.969(8)	8.096(6)	0.861(3)
1.40(5)	4.950(3)	5.129(6)	5.105(5)	3.222(2)	6.962(8)	8.088(6)	0.861(3)
1.72(5)	4.933(3)	5.140(6)	5.092(5)	3.232(2)	6.957(8)	8.079(6)	0.861(3)
2.03(5)	4.915(3)	5.162(6)	5.057(5)	3.226(2)	6.948(8)	8.057(6)	0.862(3)
2.35(5)	4.887(3)	5.167(6)	5.032(5)	3.210(2)	6.933(8)	8.124(6)	0.853(3)
2.65(5)	4.873(3)	5.230(6)	4.980(5)	3.242(2)	6.881(8)	8.055(6)	0.854(3)

*2.36(5)	4.888(3)	5.200(6)	5.018(5)	3.229(2)	6.937(8)	8.063(6)	0.860(3)
*1.99(5)	4.908(3)	5.164(6)	5.058(5)	3.191(2)	6.999(8)	8.057(6)	0.869(3)
*1.69(5)	4.915(3)	5.132(6)	5.123(5)	3.244(2)	6.925(8)	8.060(6)	0.859(3)
*0.58(5)	4.952(3)	5.114(6)	5.178(5)	3.256(2)	6.997(8)	8.137(6)	0.860(3)
*0.05(5)	4.947(3)	5.108(6)	5.242(5)	3.269(2)	6.994(8)	8.176(6)	0.855(3)

Table 7. Refined isothermal elastic parameters of leonhardite and hydrated laumontite based on III- and II-BM equation of state fits (see the Section 4.2 for further details).

	V_0, x_0 (Å^3, Å)	K_0 (GPa)	K'	$\beta_{V,I}$ (GPa^{-1})
Elastic parameters of leonhardite fitted with a third-order Birch-Murnaghan EoS				
V	1348(1)	36(1)	2.4(3)	0.0278(8)
a	14.76(1)	37(2)	1.1(5)	0.0090(5)
b	13.055(4)*	95(9)*	4*	0.0035(4)*
c	7.559(7)	20(2)	6.6(8)	0.017 (1)
* *b*-*V* data fitted up to 2.38 GPa				

	V_0, x_0 (Å^3, Å)	K_0 (GPa)	K'	$\beta_{V,I}$ (GPa^{-1})
Elastic parameters of fully hydrated laumontite fitted with a second-order Birch-Murnaghan EoS				
V	1393.9(6)	54.8(10)	4	0.0184(3)
a	14.923(3)	66(3)	4	0.0050(2)
b	13.174(2)**	85(4)**	4**	0.0039(2)**
c	7.537(2)	40(1)	4	0.0083(3)
** *b*-*V* data fitted up to 2.1 GPa				

Figure captions

Fig. 1. Configuration of the 6-mRs at ambient pressure (a) and at 7.5 GPa (b) and of the 10-mRs, as viewed down [100] in Ca-leonhardite (c, d) and Ca-hydrated laumontite (e, f) based on the structural refinements at ambient and high pressure (7.5 and 2.7 GPa for Ca-leonhardite and Ca-hydrated laumontite, respectively).

Fig. 2. A leonhardite (partially dehydrated laumontite) crystal stuck with epoxy resin on a glass capillary and in a glass vial.

Fig. 3. Evolution of the normalized unit-cell volume of leonhardite *vs* time of immersion (Wat5 in black squares, Wat10 in blue triangles, Wat15 in green triangles and Wat100 in red circles).

Fig. 4. (top) High-pressure evolution of the normalized (to P_0) unit-cell volume and axial parameters of leonhardite compressed in the 4:1 methanol:ethanol mixture. V/V_0 in *black squares*, a/a_0 *red circles*, b/b_0 *blue triangles*, c/c_0 *cyan triangle.* (bottom) High-pressure evolution of the normalized (to P_0) β angle; black squares points taken during compression, red circle taken during decompression.

Fig. 5. (top) High-pressure evolution of the normalized (to P_0) unit-cell volume and axial parameters of hydrated laumontite compressed in the 1:1:2 methanol-ethanol-H_2O mixture. V/V_0 in *black squares*, a/a_0 *red circles*, b/b_0 *blue triangles*, c/c_0 *cyan triangle.* (bottom) High pressure evolution of the normalized (to P_0) β angle; black squares points taken during compression, red circle taken during decompression.

Fig. 6. W2 and W5 migration towards the mirror plane as a function of W1 occupancy. As W1 *s.o.f* increases, both W2 and W5 migrates towards the mirror plane (W2 in black squares, W5 in red circles).

Fig. 7. Evolution of the normalized diameters (O5-O5 black squares, O4-O4 red circles, O3-O3 blue triangles) of the 6-mRs in leonhardite (top) and hydrated laumontite (bottom).