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Associazione Italiana Zeoliti
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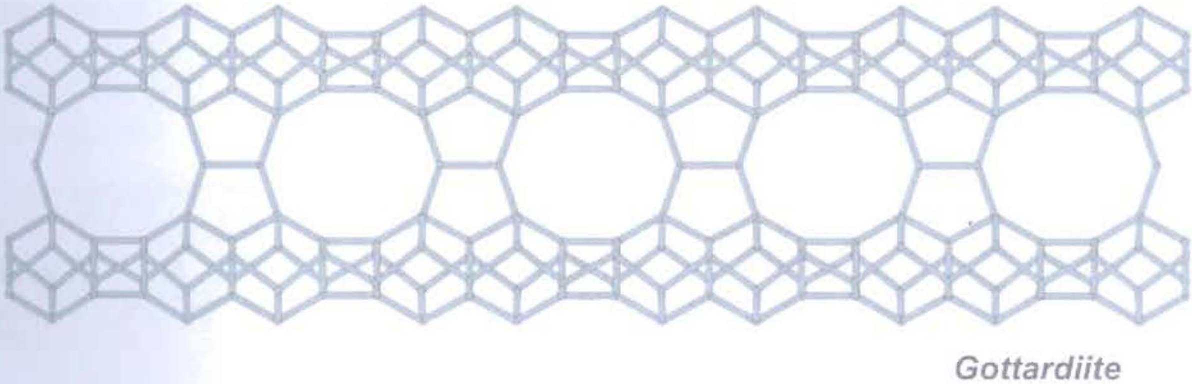

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On the crystal-fluid interactions in laumontite

Davide Comboni,[a] G. Diego Gatta[a], Marco Merlini[a], Paolo Lotti[a], Michael Hanfland[b]

[a] *Dipartimento di Scienze della Terra, Università degli Studi di Milano, Via Botticelli 23, 20133 Milano, Italy,*
[b] *ESRF -European Synchrotron Radiation Facility, 71 Avenue des Martyrs, CS40220, 38043 Grenoble Cedex, France.*

Laumontite, $|(Ca_{4-x}Na_x)K_x(H_2O)_n|$ $[Al_8Si_{16}O_{48}]$, space group *C2/m*, is one of the most common natural zeolite occurring in a wide range of geological environments, including sedimentary deposits, deep-sea sediments and in sedimentary deposits related to oil reservoirs. Remarkbly, it is also present in oceanic basalts, as well as in vugs of plutonic and volcanic rocks. Fully hydrated laumontite contains 18 H_2O molecules per formula unit. If exposed to air at relative humidity (RH) $< 50\%$, laumontite can lose up to 4 H_2O molecules per formula unit. Such a partially-dehydrated laumontite is formally referred as leonhardite [1]. Lee et al. [2] investigated the high-pressure behavior of laumontite up to 7.5 GPa, by *in-situ* synchrotron powder diffraction with a diamond anvil cell, using the 16:3:1=methanol-ethanol-H_2O mix as pressure-transmitting fluid, and observed an instantaneous over-hydration effect at a relatively low pressure (< 0.3 GPa), with a potential additional phase transition at about 3 GPa [2]. Others authors have investigated, mainly by *in-situ* X-ray powder diffraction, the processes of hydration/dehydration, controlling the RH or submerging samples in pure water or increasing temperature [1, 3].

However, no experiments have so far been devoted to the elastic behavior of leonhardite, which both thermodynamic calculation and geological observations suggest being the stable form of laumontite under diagenetic and low-grade metamorphic conditions [4]. Furthermore, the bulk modulus K_V of leonhardite is a critical parameter needed in order to model the thermodynamic stability of this mineral in geological environments of economic relevance (*i.e.*, deposits related to oil reservoirs). Moreover, some questions are still open about e.g. the single-crystal hydration kinetics in H_2O mixture and the possible phase transition observed by Lee et al. [2] at about 3 GPa.

In order to unveil the open questions, we performed a series of *in-situ* single-crystal synchrotron X-ray diffraction experiments using different pressure-transmitting fluids, as well as *in-situ* single-crystal X-ray experiments at ambient pressure in different H_2O rich-mixture. On the basis of these studies, we are were to describe: 1) the hydration mechanisms and kinetics of laumontite in single crystals, 2) the bonding configuration of the adsorbed H_2O molecules and the structural deformation of the framework in response to the overhydration at ambient pressure; 3) the elastic parameters of leonhardite; 4) the different deformation behavior between leonhardite and the fully-hydrated laumontite.

[1] Yamazaki A., Shiraki T., Nishido H., Otsuka R. 1991. Clay Science. Phase change of laumontite under relative humidity-controlled conditions. Clay Scien., 8, 79-86.

[2] Lee Y., Hrilja A.J., Vogt T. 2004. Pressure-induced migration of zeolitic water in laumontite. Phys. Chem. Miner., 31, 421–428.

[3] Fridriksson T., Bish D.L, Bird D.K 2004. Hydrogen-bonded water in laumontite I: X-ray powder diffraction study of water site occupancy and structural changes in laumontite during room-temperature isothermal hydration/dehydration. Am. Mineral., 88, 277- 287.

[4] Neuhoff P.S. and Bird D.K. 2001. Partial dehydration of laumontite: thermodynamic constraints and petrogenetic implications. Mineral. Mag., 65, 59-70.

P6. High-pressure behaviour of B-MFI zeolite in methanol: a preliminary study

Enrico Catizzone,[a] Massimo Migliori,[a] Alfredo Aloise,[a] Girolamo Giordano,[a] Davide Comboni,[b] Paolo Lott
Marco Merlini,[b] G. Diego Gatta,[b]

[a]*Dipartimento di Ingegneria per l'Ambiente e il Territorio e Ingegneria Chimica, Università della Calabria, Rende, Ita*
[b]*Dipartimento di Scienze della Terra, Università degli Studi di Milano, Milano, Italy.*

The high-pressure (*P*) behavior of a home-made sample of MFI-zeolite, with chemical form $Na_{1.6}B_{1.6}Si_{94.4}O_{192}{\cdot}nH_2O$, has been investigated by *in situ* synchrotron powder X-ray diffraction with a diam anvil cell, using silicone oil as a non-penetrating fluid and pure methanol as penetrating fluid [1]. Rietveld profile fit was used to obtain the unit-cell parameters of the investigated sample at varying pressure conditi The aim of the experiment was to check the occurrence and the effects induced by the intrusion of methanol the zeolite's structural voids in response to the applied pressure, by comparison with the behavior in a penetrating fluid.

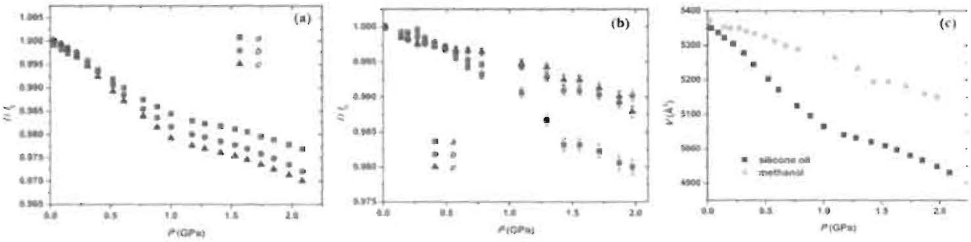

Figure 1. H pressure evolution of unit-cell parameters o Na-B-MF zeolite in n penetratin silicone oil and penetra methanol (b). The effect of pressure on unit-cell volume (c).

The experimental data obtained from the *P*-ramp in methanol showed that: i) the compressibility of Na-B MFI in methanol is significantly lower than that in silicone oil (Fig. 1c) and ii) the elastic anisotrop drastically different as well (Figs 1a and 1b), from which we can infer that the intrusion of the meth molecules into the structural voids of investigated sample occurred. The *P*-intruded methanol molecules a "pillars", reducing drastically the voids and then the MFI-type structure compressibility. Future investigat will be extending to Al- and Fe-containing MFI-type crystals, in order to describe the control of the framew components on the crystal-fluid interaction at high pressure.

[1] Gatta G.D., Lee Y. (2014) Zeolites at high pressure: a review. Mineral. Mag., 78, 267-291.