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Properties and Utilization of Natural Zeolites

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Edited by Wojciech Franus, Jarosław Madej

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Preface

It is a great honor to welcome you to the 10th International Conference on the Occurrence, Properties and Utilization of Natural zeolites – Zeolite 2018 that was organized under the auspices of the International Natural Zeolite Association – INZA and the following hosting institutions: Lublin University of Technology (Lublin, Poland), AGH University of Science and Technology (Kraków, Poland) and the Mineral and Energy Economy Research Institute, Polish Academy of Science (Kraków, Poland).

The primary focus of the INZA is to promote and encourage interest in natural zeolite materials throughout the scientific and technical community. INZA was officially organized in 2005 as a formal outgrowth from the International Committee on Natural Zeolites (ICNZ). Through the efforts of Dr. Frederick A. Mumpton, the ICNZ began as an *ad hoc* organization during the Zeolite '76 conference, the first International Conference on the Occurrence, Properties and Utilization of Natural Zeolites, held in Tucson, Arizona (USA) in 1976. The organization is open to any person interested in any aspect of natural zeolites.

In keeping with the primary purpose of the ICNZ and INZA, the organization encourages the advancement of natural zeolite science and technology, promotes research and scientific interest in natural zeolites and increases the diffusion of knowledge of natural zeolite science and technology.

Zeolite 2018 is the latest in a series of conferences organized under auspices of the ICNZ and INZA. Following the initial Zeolite '76 conference, subsequent conferences were held in Budapest, Hungary (Zeolite '85); Havana, Cuba (Zeolite '91); Boise, Idaho, USA (Zeolite '93); Ischia (Naples), Italy (Zeolite '97); Thessaloniki, Greece (Zeolite '02); Socorro, New Mexico, USA (Zeolite '06); Sofia, Bulgaria (Zeolite 2010) and Belgrade, Serbia (Zeolite 2014).

Every four years, researchers and students interested in natural zeolites present their results on all aspects of research on natural zeolites. It is a privilege to have participants from 40 countries around the world attending the Zeolite 2018 conference.

We wish you a pleasant stay in Krakow and hope that you will have a very successful and beneficial conference.

Aleksandra Daković, INZA President
Wojciech Franus
Magdalena Wdowin
Tomasz Bajda

Cracow, Poland
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Contents

New insights into crystal-fluid interactions in laumontite: A natural nanosponge

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Introduction

Laumontite, $|(Ca_{4-x}Na_x)K_x(H_2O)_n|$ $[Al_8Si_{16}O_{48}]$, space group *C*2/*m*, is one of the most common natural zeolites occurring in a wide range of geological environments, including oceanic basalts, in vugs of plutonic and volcanic rocks and in sedimentary rocks. Fully hydrated laumontite contains 18 H_2O molecules per formula unit (p.f.u.), although, if exposed to air at relative humidity (RH) < 50%, it can lose up to 4 H_2O molecules p.f.u.. Partially dehydrated laumontite is formally referred to as "leonhardite" (*e.g*., Yamazaki et al., 1991). To date, a number of studies have been devoted, mainly by *in-situ* X-ray powder diffraction, to the processes of hydration/dehydration, controlling the RH or exposing samples to pure water or increasing temperature (*e.g*., Yamazaki et al., 1991, Fridriksson et al., 2004). Lee et al. (2004) investigated the high-pressure behavior of a Ca-laumontite by *in-situ* synchrotron powder diffraction with a diamond anvil cell, using a 16:3:1 methanol-ethanol-H_2O mixture as the pressure-transmitting medium, up to 7.5 GPa. In that experiment an instantaneous over-hydration, occurring at a relatively low pressure (< 0.3 GPa), was observed. Furthermore, the authors noticed a tripling of the unit-cell edge along [010] at ~ 3 GPa, which was interpreted as a phase transition (Lee et al., 2004).The authors themselves suggested that single-crystal data were needed to unravel the questions still open.

Nowadays, a few open issues and missing information remain concerning: i) the possible phase transition observed by Lee et al. (2004) at about 3 GPa; ii) the elastic parameters of leonhardite, which both thermodynamic calculations and geological observations suggest is the stable form of laumontite under diagenetic and low-grade metamorphic conditions (*e.g*. Neuhoff and Bird 2001, Coombs et al., 1959); and iii) the single-crystal hydration kinetics in an H_2O-ethanol mixture. Laumontite's common occurrence in many geologic environments, for example in oceanic basalts, suggests that may be an important H_2O carrier in the very first kilometers of subduction zones. In addition, the isothermal bulk modulus (K_{V0}) of leonhardite, which is still unknown, is a critical parameter needed to model the thermodynamic stability of this mineral in geological environments of economic relevance (*i.e*., deposits related to oil reservoirs).

In this light, we performed a series of experiments aimed to describe the crystal-fluid interaction in laumontite-leonhardite by *in-situ* high-pressure single-crystal synchrotron X-ray diffraction using different pressure-transmitting fluids, as well as a number of *in-situ* single-crystal experiments at ambient pressure in different H_2O-ethanol mixtures.

Experimental Methods

In order to investigate the hydration process of leonhardite, single crystals were attached to a glass fiber located in a 5 mm (diameter) glass vial. 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. After the measurement in air, aimed to obtain the initial unit-cell parameters, the vials were flooded with different H_2O-ethanol mixtures containing 100%, 15%, 10% and 5% H_2O, samples Wat100, Wat15, Wat10 and Wat5, respectively. Consecutive short data collections (~120 minutes) were performed to study the evolution of the unit-cell parameters as a function of hydration.

High-pressure X-ray diffraction experiments were performed at the ID15B beamline of the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. In the case of fully hydrated laumontite, as explorative data collections revealed that the dehydration process begins as soon as the sample is exposed to the atmosphere (or even in DAC with a low H_2O mixture), in fair agreement with Yamazaki et al. (1991), a single crystal was selected and immediately placed in a diamond anvil cell (DAC) along with a 1:1:2 methanol:ethanol:H_2O mixture. Due to the high H_2O content, the experiment was performed only up to 2.7 GPa, to prevent the crystallization of ice. In the case of leonhardite, a nominally anhydrous methanol:ethanol mixture (4:1), was used as the *P*-transmitting fluid.

Results and Discussion

The evolution of the unit-cell parameters as a function of the H_2O fraction of the mixture and time (Fig. 1) suggests that the adsorption rate of H_2O into the structure 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.*,Yamazaki et al., 1991, Fridriksson et al., 2004). The *P*-induced evolution of the unit-cell parameters of both leonhardite and fully hydrated laumontite, shown in Fig. 2 and Fig. 3, is monotonic, without any evidence of phase transition up to the highest pressure investigated.The refined K_{V0} of fully hydrated laumontite is 54.8(10) GPa, similar to, but slightly lower than, that obtained for a powder sample by Lee et al. (2004), who reported K_{V0} = 59(1) GPa, whereas the refined bulk modulus of leonhardite at ambient conditions was found to be significantly lower: K_{V0} = 36(1) GPa. The higher compressibility shown by leonhardite, with respect to hydrated Ca-laumontite, may be ascribed to the empty W1 site (normally populated by H_2O), acting as a "filler", and to the partial occupancy of W2 (populated by H_2O) in the crystal structure of leonhardite.

Overall, the results here presented have important geological implications, considering that laumontite represents a valuable carrier of H_2O in the very first few kilometers of the subducting crust. Moreover, the stability of mineralogical assemblages, based on thermodynamic calculations, can be biased by the choice of Ca-laumontite or Ca-leonhardite (Neuhoff and Bird 2001). These parameters are also important to model the occurrence of leonhardite and laumontite in geological environments of economic relevance, such as oil reservoirs, where cementing laumontite decreases the potential of the country rocks for hosting hydrocarbons (*e.g.*, Galloway et al., 1979).

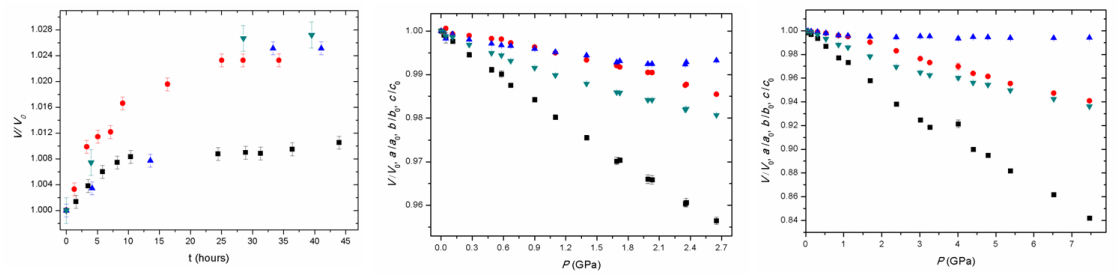

Figure 1. (left) Evolution of the normalized unit-cell volume of leonhardite *vs.* time of immersion (Wat5 in black squares, Wat10 in blue triangles, Wat15 in green triangles and Wat100 in red circles). High-pressure evolution of the normalized (to P_0) unit-cell volume and axial parameters of leonhardite and fully hydrated laumontite (middle and right side, respectively) 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 triangles.*

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