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Compressional behaviour of paulingite - A sub-nanosponge?

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Introduction

Paulingite is a rare zeolite, found in vesicles in basalt flows, with ideal chemical formula: $(K,Na,Ca_{0.5},Ba_{0.5},)_{10}(Al_{10}Si_{32}O_{84})\cdot 30H_2O$ (Z = 16). Its crystal structure was solved and refined by Gordon et al. (1966) in the space group *Im3m*, showing the complex framework topology of this zeolite designated with the IZA-code "PAU". A structural re-investigation was carried out later by Lengauer et al. (1997). The tetrahedral framework topology of paulingite is characterized by a connecting double 8-ring (D8R), which links alternatively the α-cage (truncated cuboctahedron) and the γ-cage (gmelinite-type cage). The D8R, the α-cage and the γ-cage represent the building-block units of the PAU framework. The main voids systems of the PAU framework are represented by two parallel (and independent) sets of a three-dimensional channel systems oriented along the principal axes and shifted ½, ½, ½ against each other. Along the threefold axis of the PAU framework, a second type of a channel system exists, which is built up by the α-cage and a modified form of the levyne-cage only observed in the paulingite topology (*i.e.*, π-cage) (Lengauer et al. 1997). The PAU framework type is considered as one of the most complex in the mineral world. In all the structure refinements so far reported, the Si/Al-distribution was modelled as completely disordered. A series of extra-framework sites were located. The long "free diameters" of the channel systems make this zeolite a good candidate to explore the *P*-induced penetration of external molecular species in response to hydrostatic compression (*e.g.*, Gatta 2008, 2010).

Experimental Methods

A sample of paulingite from Vinařická hora Hill near Kladno (Czech Republic) was used for our experiments. A sample from the same locality was previously used by Lengauer et al. (1997) for their chemical and crystallographic study. Electron microprobe analysis (in wavelength dispersive mode) along with thermo-gravimetric data yielded the following chemical formula: $(Ca_{2.57}K_{2.28}Ba_{1.39}Na_{0.38})(Al_{11.55}Si_{30.59}O_{84})\cdot 27H_2O$ (Lengauer et al. 1997).

A single-crystal of paulingite, free of defects under polarized microscope, was selected for the *in-situ* diffraction experiment with a diamond anvil cell (DAC). Intensity diffraction data were first collected at room-conditions with a Stoe StadiVari diffractometer with an high-brilliance Incoatec Mo Iμs X-ray-source and a Dectris Pilatus 300K pixel detector. The structure refinement was performed in the space group *Im3m* using the structural model of Lengauer et al. (1997) to a R_1 = 0.0802 for 2477 $Fo > 4\sigma(Fo)$ and 255 refined parameters. The same crystal was used for the high-pressure (*HP*) experiment performed using an ETH-type DAC. The experiment was conducted using a mixture of methanol:ethanol = 4:1 as hydrostatic *P*-transmitting medium, along with a few ruby chips serving as *P*-calibrant. Unit-cell parameters were measured between 0.0001 (crystal in the DAC with no pressure medium) and 3.3(1) GPa.

Two further *in-situ* *HP* synchrotron X-ray powder diffraction experiments were performed at the X7A beamline at the national synchrotron light source (NSLS) at Brookhaven National Laboratory (BNL). A gas-proportional position-sensitive detector was used. The wavelength of the incident beam was 0.60046(1) Å as determined from a CeO_2 standard. A modified Merrill–Bassett DAC was used to generate *HP*-conditions.

Two compression experiments with two different *P*-fluids were performed, *i.e.*, with silicon-oil and a mix of methanol:ethanol:water = 16:3:1. The evolution of the cell parameters with *P* for all three pressure-transmitting media is shown in Fig. 1.

Results and Discussion

The evolution of the unit-cell parameters of paulingite with *P* based on our experiments with different *P*-media show a dramatic role played by the compression-fluid on the behavior of this zeolite (Figure 1). Due to its polymeric nature, silicon-oil can be unambiguously considered as a "non-penetrating" *P*-medium. The

compressional pattern obtained with silicon-oil describes the actual elastic behavior of paulingite (*i.e.*, without any interference of the *P*-fluid). The Birch-Murnaghan equation of state truncated to the second-order was used to fit the experimental *P-V* data within the *P*-range investigated (*i.e.* 0.0001-2.5(1) GPa), giving the following isothermal bulk modulus: $K_0 = \beta_0^{-1} = V_0(\partial P/\partial V) = 18(1)$ GPa ($\beta_0 = 0.055(3)$ GPa^{-1}). Paulingite appears to be one of the softest crystalline inorganic materials reported so far. The H*P*-data obtained using the mix methanol:ethanol = 4:1 and methanol:ethanol:water = 16:3:1 suggest that these molecules act as "penetrating" media in response to the applied pressure. The *P*-induced penetration of external molecules through the cavities leads to a lower bulk compressibility of paulingite. The different compressibility of paulingite in methanol:ethanol = 4:1 and methanol:ethanol:water = 16:3:1 mix reflects the different penetrability of the media. Water is clearly the most penetrating molecule in response to the applied pressure, and so in general an hydrous medium tends to decrease significantly the compressional pattern of a porous material (Gatta 2008, 2010). Interestingly, the *P*-induced penetration of external molecules in paulingite structure does not lead to spectacular expansion (with a drastic discontinuity in the *P-V* behaviour), as observed for example in natrolite (Lee et al. 2002).

The complexity of the paulingite structure did not allow to perform structure refinement at high pressure, hindering a description of the penetration mechanisms at the atomic scale. A series of further experiments are in progress in order to explore: 1) the reversibility of the *P*-induced penetration of aforementioned molecules and 2) the behavior of this zeolite as a "sub-nanosponge" for other small molecules in response to hydrostatic pressure.

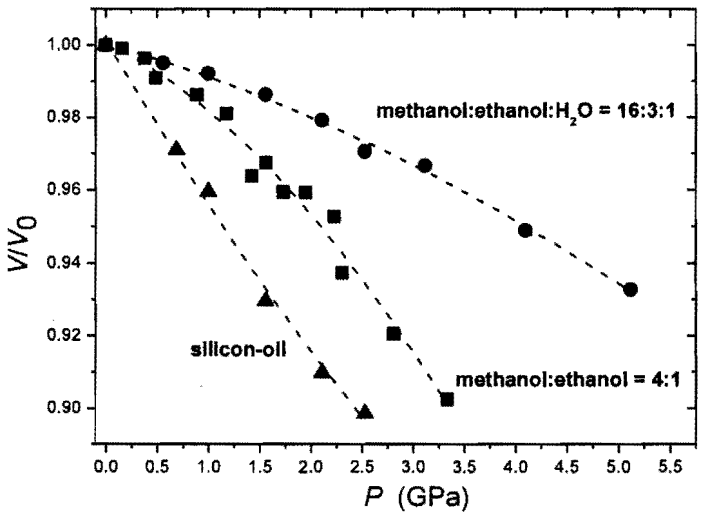

Figure 1. Evolution of the unit-cell volume of paulingite (normalized to the value at 0.0001 GPa) with *P* compressed in three different *P*-media. The polynomial fit shows an anomalous softening when methanol-ethanol or methanol-ethanol-H_2O mix are used as *P*-transmitting fluids

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Effects of low temperature and high pressure on the structure of gobbinsite

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Introduction

Gobbinsite is a rare zeolite, typically found in amygdaloidal vugs of massive volcanic rocks, where it crystallizes as a hydrothermal post-magmatic product.Gobbinsite typically forms radiating aggregates of sub-microscopic elongated crystals, often associated with phillipsite, gmelinite, natrolite, and calcite. It was first described from the type locality of Co. Antrim, N. Ireland, but other occurrences were later reported from a few other localities. Its ideal formula is $Na_5[Al_5Si_{11}O_{32}]\cdot 12H_2O$, but evidence of a Ca,K-enriched form has been reported, so that the general chemical formula can be re-written as: $(Na_{2-2x},Ca_x)_2K_2[Al_6Si_{10}O_{32}]\cdot 12H_2O$. Gobbinsite has a GIS (gismondine) framework type, which can be described as a stacking of two perpendicular double-crankshaft chains, the first running along [100] and the second along [010]. Two secondary building units are present, namely 8- and 4-membered rings, with two perpendicular and interconnecting sets of channels: 8mR[100] and 8mR[010]. The ideal symmetry for the GIS framework type is tetragonal $I4_1/amd$ (idealized unit-cell parameters: a = 9.8 Å, c = 10.2 Å), but zeolites with GIS topology often show a lower symmetry (*e.g.*, gismondine; garronite; amicite; gobbinsite; Na-P1; Na-P2; TMA-gismondine). The lack of crystals large enough (and free of twinning and defects) forced early studies on the crystal structure of gobbinsite to use X-ray powder diffraction techniques. Solution and refinement of the structure led to an orthorhombic unit cell (a = 10.108(1), b = 9.766(1) and c = 10.171(1) Å) and space group $Pmn2_1$. However, such a model showed unusually low coordination for the extra-framework cations (CN = 4 for K and 5 for Na). Discovery of sub-mm crystals from Bundoora, Melbourne, Victoria, Australia, allowed us to re-investigate the gobbinsite crystal structure by X-ray single-crystal methods. The analysis of reflection conditions and statistics of distribution of normalized structure factors suggested the centrosymmetric space group *Pmnb* as highly likely, with unit-cell parameters a = 10.1035(15), b = 9.7819(10) and c = 10.1523(9) Å. Single-crystal structure refinement showed two extra-framework sites partially occupied by Na and Ca, respectively (though inter-site chemical disorder could not be ruled out), five partially occupied sites for H_2O molecules, and a disordered (Si,Al)-distribution in the tetrahedral framework.

In addition to re-investigation of the crystal structure of gobbinsite from Bundoora (Australia), we have investigated the low-temperature (L*T*) and the high-pressure (H*P*) behavior of this zeolite by means of in-situ single-crystal X-ray diffraction. The L*T* experiments were performed in order to minimize the effects of atomic thermal libration and positional disorder. The presence of many centers of motion for a single site (positional disorder) results in large and unusual anisotropic displacement parameters. L*T* conditions were expected to reduce such effects, leading to a clearer picture of the extra-framework configuration. Moreover, comprehension of L*T*-behavior could provide more information about chemical disorder in extra-framework cationic sites. The H*P* experiments were performed following a series of experiments on microporous materials aimed to describe the response of open-framework materials under hydrostatic pressure of the order of GPa.

Experimental Methods

Chemical analysis, by means of electron microprobe in the wavelength dispersive mode and elemental CHN analysis, yielded the following chemical formula:

$$(Na_{4.97}K_{0.07}Ca_{0.48})\Sigma_{5.52}[Al_{5.62}Si_{10.29}]_{\Sigma 15.91}O_{32}\cdot 11.9H_2O \ (Z = 1) \ (E(\%) = -6.3)$$

Two single-crystals, free of defects under polarized microscope, were used for the L*T* and H*P* experiments, respectively.

Diffraction intensity data were collected at 293 (room temperature), 250, 200, 150 and 100 K using an Oxford Diffraction Gemini diffractometer operating at 50 kV and 40 mA with Mo$K\alpha$ radiation, equipped with a Ruby CCD detector positioned at 50 mm from the sample, and an Enhance X-ray Optics graphite

monochromator. Low-*T* data were collected with the crystal cooled by an Oxford Cryosystems 700 open-flow nitrogen gas system.

The high-pressure experiment was performed using an ETH-type diamond anvil cell (DAC). The experiment was conducted using a mixture of methanol: ethanol = 4:1 as the hydrostatic *P*-transmitting medium along with a few ruby chips as *P*-calibrant. Unit-cell parameters were measured between 0.0001 (crystal in the DAC with no pressure medium) and 4.3(1) GPa, using a list of 36 Bragg peaks centered with a KUMA KM4 point-detector diffractometer, operating at 50 kV and 40 mA, with Mo*K*α radiation (graphite monochromator). Seven intensity data collections were performed at 0.0001, 0.8(1), 1.5(1), 2.5(1), 3.0(1), 3.7(1) and 4.3(1) GPa using an Xcalibur diffractometer equipped with a CCD detector. All datasets showed reflections conditions consistent with space group *Pmnb*. Structure refinements using L*T* and H*P* data were performed with the SHELX-97 program.

Results and Discussion

a) Low Temperature

Reflection conditions confirmed that the space group *Pmnb* is maintained within the *T*-range investigated. At room temperature, the extra-framework population consists of one site partially occupied by Na, one site partially occupied by Ca, and five sites partially occupied by H_2O. At low-*T*, partial dehydration, likely induced by the N_2-flow, was observed, with a significant rearrangement of the extra-framework configuration. Low-*T* induced deformations of the 8- and 4-membered rings were observed

b) High Pressure

No evidence of amorphization was observed within *P*-range investigated. Two changes of the elastic behavior occurred, one at 1.1 - 1.3 GPa and a second at 2.7 - 3.2 GPa. Birch-Murnaghan equations of state truncated to the second order were used to fit the experimental *P-V* data within the three *P*-ranges (*i.e.*, 0.0001-1.1, 1.3 - 2.7 and 3.2 - 4.3 GPa), giving the following isothermal bulk moduli: 46.3(9), 52(8) and 28(6) GPa, respectively. The unit-cell compression is significantly anisotropic. In response to the applied pressure, the 8-membered ring channel perpendicular to [100] underwent a significant increase of ellipticity, whereas the channel perpendicular to [010] shrank towards a circular shape at $P \geq 1.3$ GPa. Partial re-organization of the H_2O sites occurred between 1.1 and 1.3 GPa, and new framework deformational modes were observed at $P \geq 3.2$ GPa, coupled with a change in the coordination environment of the extraframework cations.

If we compare the elastic behavior and the H*P* structural evolution of gobbinsite with those so far reported for other zeolites, we can make some generalizations: 1) The range of compressibility among this class of open-framework silicates is large, with bulk moduli ranging between 15 - 70 GPa; 2) Microporosity does not necessarily imply high compressibility – gobbinsite has large channels, compared with other zeolites, but its compressibility is not significantly low; 3) The flexibility observed in zeolites under hydrostatic compression is mainly governed by tilting of rigid tetrahedra around O atoms that behave as hinges within the framework; 4) Deformation mechanisms in response to applied pressure are generally dictated by the topological configuration of the framework rather than the Si/Al-distribution or the extra-framework content. The channel content governs the compressibility of the cavities.

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