

HIGH-PRESSURE BEHAVIOR OF MICROPOROUS MATERIALS: CRYSTAL-FLUID INTERACTIONS AND DEFORMATION MECHANISMS AT THE ATOMIC SCALE

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INTRODUCTION

Zeolites are crystalline, hydrated aluminosilicates characterized by a tetrahedral framework of TO_4 units connected in such a way that sub-nanometric channels and cages occur. These structural cavities host the so-called extra-framework population (e.g., Fig. 1), which mainly consists of alkali and alkaline-earth cations and small molecules, such as H_2O (Baerlocher *et al.*, 2007.; Pabalan *et al.*, 2011).

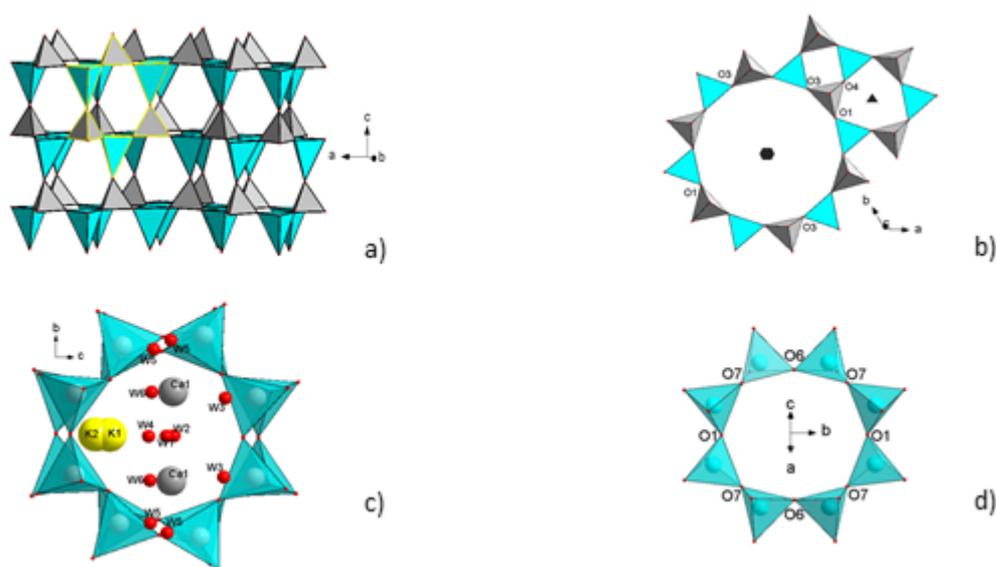


Fig. 1 - a) Alternation of the upward AlO_4 and downward PO_4 tetrahedra in AlPO_4 -5 structure (in grey and light blue respectively), underlined in yellow the 6-mRs $[hk0]$; b) secondary building units (6-mRs $[001]$ and 12-mRs) shown down the c crystallographic axis; c) configuration of the 8-mR $[100]$ -1, 8mR $[100]$ -2, 8-mR $[010]$ and 8-mR(001) at $P1$ and of the extra-framework population in phillipsite, as viewed down $[100]$; d) configuration of the 8-mRs in armstrongite.

In the last decades, the scientific community showed a rising interest on the behavior of microporous and mesoporous compounds (e.g., zeolites) at high-pressure conditions, and on the crystal-fluid interaction phenomena occurring at extreme conditions (Gatta & Lee, 2014; Gatta *et al.*, 2018). As zeolites could act as an ideal carrier of H_2O and others small molecules or monoatomic species (e.g., CO_2 , CH_4 , H_2S , He, Ar, Kr, Xe), experiments on zeolites compressed (and ambient to low/high T) in aqueous mixtures have important implications in the Earth Sciences (e.g., Comboni *et al.*, 2018). Furthermore, high-pressure experiments on synthetic zeolites may pave the way for new routes of tailoring new functional materials (made by hybrid host-guest architecture), bearing a potentially relevant technological impact (Eroshenko *et al.*, 2002).

In this experimental research, the high-pressure behavior and the crystal-fluid interaction at the atomic scale of a selected series of natural and synthetic zeolites (*i.e.*, AlPO_4 -5, leonhardite, laumontite, phillipsite) and a zeolites-like mineral (*i.e.*, armstrongite) have been investigated by means of *in-situ* single-crystal X-ray diffraction, using “penetrating” and “non-penetrating” pressure-transmitting fluids. The main aims were: 1) to describe the deformation mechanisms induced by pressure at the atomic scale in the studied microporous

compounds; 2) to draw the geological implications about the H₂O load carried by these minerals in relevant geologic environments (*e.g.*, first km of the subducted oceanic crust and oil reservoir); 3) to investigate the potential of zeolites (enhanced by pressure) as energy storage materials.

MATERIALS AND METHODS

All the crystals studied were selected *via* optical investigation and tested using an Xcalibur Oxford Instruments 4-circle X-ray diffractometer equipped with a CCD, using graphite-monochromatized MoK α radiation, and operating at 50 kV and 30 mA at the Earth Science Department of Milan (ESD-MI). The high-pressure experiments were performed in large-scale facilities, at the ID09A and ID15b beamline (Merlini & Hanfland, 2013) of the European Synchrotron Radiation Source (ESRF), Grenoble, France, and at the Extreme Conditions Beamline P02.2 at PETRA III/DESY, Hamburg, Germany. These beamlines are entirely dedicated to high-pressure experiments using diamond anvil-cell devices: the sample, along with the pressure calibrant, is placed in a pressure chamber which is delimited on the top and on the bottom by flat parallel faces (culets) of two opposed diamond anvils. Laterally, the pressure chamber is confined by a metal foil. The pressure chamber is flooded with a pressure-transmitting fluid, a liquid which, ideally, exerts hydrostatic pressure onto the sample (Fig. 2). The pressure is applied by forcing the diamonds together. This causes the extrusion of the gasket around the diamond culets, sealing in this way the pressure chamber. The extrusion of the gasket compresses the pressure-transmitting fluid which, in turn, compresses both sample and pressure calibrant under hydrostatic conditions. The X-ray beam penetrates across the first diamond, hits the crystal in the pressure chamber and the diffracted beams pass through the second diamond. In these experiments is therefore possible to study, *in-situ*, the deformation mechanisms occurring at an atomic level.



Fig. 2 - Components of an ETH-type diamond anvil cell with the four screws used to load to the diamonds

RESULTS

Fig. 3 shows the evolution of the unit-cell volumes and axial parameters with pressure, normalized to the room-*P* values, of the studied open-framework materials. The refined elastic parameters, based on second- or third-order Birch-Murnaghan equations of state fits, are reported in Table 1. The comparative analysis of these parameters shows that the studied materials display a high diversity as far as the bulk compressibility (at ambient temperature) is concerned.

The reported compressibility of zeolites (*e.g.*, Gatta 2008) is variable, as their bulk moduli range between 18 and 70 GPa. $\text{AlPO}_4\text{-5}$ is the most compressible microporous material studied in this research project, with a K_{V0} of only 13.2(11) GPa, which makes it one of the softest zeolites reported so far.

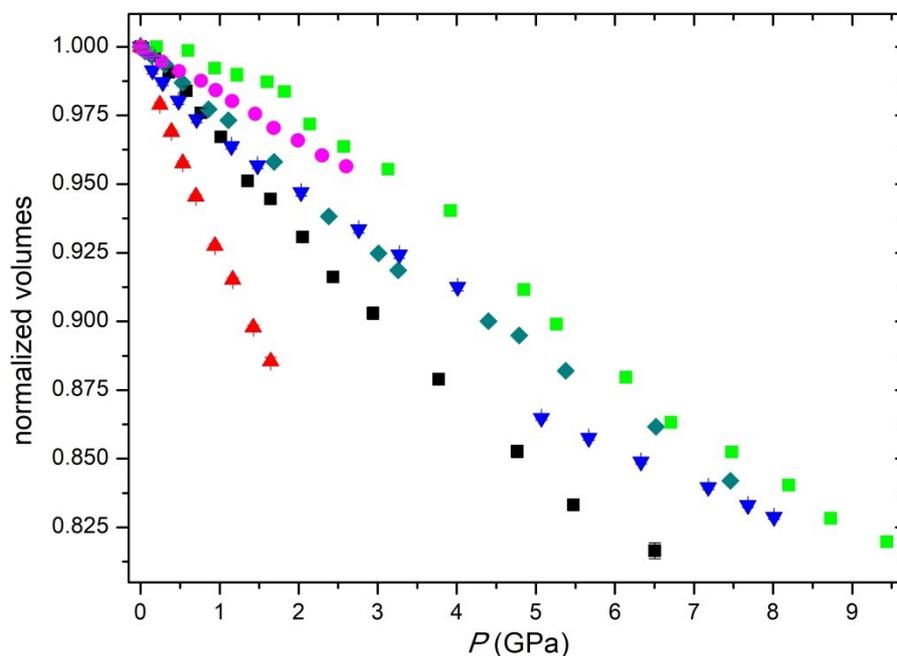


Fig. 3 - Evolution of the normalized (to P_0) unit-cell volumes of $\text{AlPO}_4\text{-5}$ (silicon oil in red triangles, *m.e.w.* in black squares), phillipsite (green squares), armstrongite (blue triangles), laumontite (purple circles) and leonhardite (dark green diamonds)

The other minerals species here studied, *i.e.*, laumontite, leonhardite, phillipsite and armstrongite, are far less compressible with respect to $\text{AlPO}_4\text{-5}$ (see Table 1).

A visual inspection of Table 1 highlights that the studied materials are characterized by a pronounced elastic anisotropy. This is rather expectable since all the studied open-framework materials, with the only exception of $\text{AlPO}_4\text{-5}$, have low symmetry. Nevertheless, it is worth to note that such an anisotropy is usually not preserved when changes in the extra-framework configuration occur. In $\text{AlPO}_4\text{-5}$, for instance, for the sample compressed in silicone oil, K_c is considerably lower than K_a (15.5(3) vs. 9.6(2) GPa, respectively). This reverses when the crystal is compressed in *m.e.w.* (*i.e.*, methanol:ethanol:water 16:3:1 mixture) as, in response to the “pillar effect” induced by the adsorbed H_2O molecules, the *bulk modulus* along the *c* direction triplicates, whereas K_a only increases by 50% (*i.e.*, 19.7(7) and 29.3(10) GPa, respectively).

IMPLICATIONS OF THE STUDIES

As reported previously, microporous materials can be useful as storage of mechanical energy; in this light, it is worth to examine the decompression path of $\text{AlPO}_4\text{-5}$ (Fig. 3). In $\text{AlPO}_4\text{-5}$, the unit-cell parameters refined from the data collected in decompression reveal that the bulk compression is not fully recovered at these pressures. This fact, along with the results here reported (which show that the zeolite $\text{AlPO}_4\text{-5}$ is a promising material for the *P*-induce selective sorption of a relatively high number of H_2O molecules per unit cell), suggest that this zeolite could represent a system for the storage/dissipation of mechanical energy. Because the volume of $\text{AlPO}_4\text{-5}$ after decompression is lower than its initial value (before compression), it seems that this microporous compound could be used as a *bumper*, thus as a sink of mechanical energy. The fact that the *P*-induced hydration occurs already at very low pressure is also promising for potential industrial applications, as the use of modest pressures would be highly desirable for practical applications (Gatta *et al.*, 2018).

Table 1 - Elastic parameter of the studied compounds

	AlPO ₄ -5	AlPO ₄ -5	Leonhardite	Laumontite	Phillipsite low-pressure regime	Phillipsite high-pressure regime	Armstrongite low-pressure form	Armstrongite high-pressure form
Space group	<i>P6cc</i>	<i>P6cc</i>	<i>C2/m</i>	<i>C2/m</i>	<i>P2₁/m</i>	<i>P2₁/m</i>	<i>C2/m</i>	<i>C2/m</i>
Pressure medium	<i>s. oil</i>	<i>m.e.w. (16:3:1)</i>	<i>m.e. (4:1)</i>	<i>m.e.w. (1:1:2)</i>	<i>m.e.w. (16:3:1)</i>	<i>m.e.w. (16:3:1)</i>	<i>m.e.w. (16:3:1)</i>	<i>m.e.w. (16:3:1)</i>
<i>P</i> - range (GPa)	0.25-1.65	0.0001-6.51	0.0001-7.46	0.0001-2.65	0.0001-1.82	3.1-9.4	0.0001-4	5-8.01
EoS	3-BM EoS	3-BM EoS	3-BM EoS	2-BM EoS	2-BM EoS	2-BM EoS	3-BM EoS	2-BM EoS
<i>V</i> ₀ (Å ³)	1376(3)	1360(2)	1348(1)	1393.9(6)	1005(1)	1098(2)	1465(1)	4185(8)
<i>K</i> _{VO} (GPa)	13.2(11)	22.2(9)	36(1)	54.8(10)	89(8)	18.8(7)	31.2(6)	45(1)
<i>K</i> '	5.1(14)	3.0(3)	2.4(3)	4*	4*	4*	8.6*	4*
<i>a</i> ₀ (Å)	13.759(5)	13.734(9)	14.76(1)	14.923(3)	9.914(7)	10.07(2)	14.028(1)	13.17(2)
<i>K</i> _{ao} (GPa)	15.5(3)	19.7(7)	37(2)	66(3)	81(12)	30(2)	78(4)	35(1)
<i>K</i> _a '	4*	3.0(3)	1.1(5)	4*	4*	4*	2(2)	4*
<i>b</i> ₀ (Å)	-	-	13.055(4)*	13.174(2)**	14.201(9)	14.8(1)	14.131(4)	13.87(1)
<i>K</i> _{b0} (GPa)	-	-	95(9)*	85(4)**	50(5)	11(1)	23(2)	50(2)
<i>K</i> _b '	-	-	4*	4*	4*	4*	10*	4*
<i>c</i> ₀ (Å)	8.369(4)	8.453(3)	7.559(7)	7.537(2)	8.707(2)	8.94(2)	7.844(2)	23.62(4)
<i>K</i> _{c0} (GPa)	9.6(2)	29.3(10)	20(2)	40(1)	107(8)	21(1)	26(2)	46(3)
<i>K</i> _c '	7*	2.9(4)	6.6(8)	4*	4*	4*	10*	4*

*= fixed parameter; **= fitted up to 2.1 GPa

As far as the geological implications are concerned, the experiments here reported suggest that the penetration phenomenon is likely to be active even at very low pressures (2 kbar or lower, for instance in AlPO₄-5 and in leonhardite). This is very interesting because zeolites (some Ca-zeolites as laumontite) are believed to be stable at those pressures. Geological fluids can, therefore, interact efficiently with zeolites, enhancing a significant fluid-to-crystal mass transfer. Thus, pressure can promote the ability of zeolites, as microporous materials, to act as geochemical traps of small molecules, even at room temperature. In this light, the role of zeolites as fluids-carrier in geological environments, such as oceanic crust subductions, should be carefully re-considered in geophysical modelling, especially in view of the recent findings of the Ocean Drilling Project: zeolites are pervasively diffused in oceanic basalts, which will be subducted at *P* and *T* in which they can uptake and then release significant mass of fluids.

As pointed out by several studies (*e.g.*, Lotti *et al.*, 2016; Gatta *et al.*, 2018), and observed in this article, there must be several variables that govern the sorption phenomena at high pressure beyond the “free diameters” of the framework cavities. This is probably the case of the chemical nature and the configuration of the extra-framework population and the partial pressure of the penetrating molecule in the fluid (if mixed with other non-penetrating molecules, *e.g.*, the *P*(H₂O) in a mixture of alcohol–H₂O, as shown for hydration of leonhardite). Moreover, it is also likely that the rate of the *P*-increase, the surface/volume ratio of the crystallites under investigations, and the temperature at which the experiment is conducted play a critical role in the hydration process. It is highly likely that the combined effect of pressure and temperature would improve the magnitude of the pressure-induced hydration, as previously observed in other zeolites (Gatta & Lee 2014, and references therein, Kong *et al.*, 2018). The results and the implications of this work can be found in Lotti *et al.* (2016), Comboni *et al.* (2017, 2018, 2019).

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