

High-pressure behaviour and crystal-fluid interaction of the ABC-6 zeolites: the case of erionite, offretite and bellbergite

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INTRODUCTION

Zeolites are a large group of hydrated aluminosilicates, widely spread in the first kilometres of the Earth's crust. They are characterized by an open aluminosilicate framework formed by the interconnection of channel and cage systems with "free-diameters" lower than 20 Å. Polar molecules (i.e., mainly H₂O) and alkali/alkaline-earth cations are hosted within the structural nanocavities, composing the extraframework population. The peculiar crystal structure of zeolites provides them with unique properties, among them: *i*) molecular sieving, *ii*) reversible hydration, *iii*) cation exchange, and *iv*) catalytic activity for the fractioning of hydrocarbon chains (Ghobar-kar et al., 1999; Li et al., 2021). The *International Zeolite Association* (IZA) recognizes the existence of more than 250 compounds with zeolitic structures, among those more than 80 found as natural species, highlighting the considerable crystallographic diversity and the scientific and industrial interest in zeolites.

In the last decades, the scientific community has shown a rising interest in the high-pressure behaviour (ranging from a few kbar to GPa) of zeolites, both natural and synthetic, in particular about the crystal-fluid interactions enhanced by pressure (e.g., Gatta & Lee, 2014; Gatta et al., 2018; Gigli et al., 2019; Comboni et al., 2020; Arletti et al., 2011). Given the zeolite's capacity to host and exchange H₂O, other small molecules or monoatomic species (e.g., noble gases), *in situ* experiments involving hydrostatically compressed zeolites, in potentially-penetrating mixtures of molecules, can provide a description of the *P*-induced crystal-fluid interaction phenomena in zeolites.

This Ph.D. project aimed at the investigation of the *P*-mediated crystal-fluid interaction in erionite (ERI framework type), offretite (OFF framework type) and bellbergite (EAB framework type), three members of the "ABC-6 group" of zeolites. The investigations were also performed on the synthetic counterpart of bellbergite, a polycrystalline sample with an EAB framework. The

purpose of this project is twofold, including both geological and industrial implications. From a geological perspective, studying the high-pressure behaviours of minerals, and the interactions between fluids and zeolites, represent a crucial initial step to better understand complex geological processes. Zeolites, found as alteration species in marine basalts or sediments, exhibit markedly higher H₂O content compared to commonly widespread hydrous minerals of the Earth's crust (i.e., amphiboles, micas, chlorites, ...) (Kastner, 1979). Considering the ability of zeolites to over-hydrate and dehydrate in response to *P-T* variation, it is reasonable to suppose that they act as fluid carriers during the early stage of subduction. In this light, a comprehensive description of the *P*-mediated over-hydration of commonly found natural erionite, along with the structurally similar offretite and bellbergite, was performed. On the other hand, from an industrial perspective, studies on the interaction between zeolites and various alcohol molecules represent a necessary step to open a new route in, for example, methanol chemistry. Under this light, applying a pressure gradient could serve as an effective route to enhance zeolites' adsorption capacity and then promote interaction and transformation of the sorbates. The experiments performed on synthetic EAB allowed direct observations of the different high-pressure behaviour and *P*-mediated crystal fluid interaction among isotopic materials: synthetic and natural zeolite. Additionally, the two investigated isotopic samples (i.e., natural and synthetic) were characterized by a different Si/Al ratio, unveiling the effect of crystal chemistry on the material behaviour. Furthermore, no crystallographic data at high-pressure were available so far for erionite, offretite and bellbergite, along with their elastic parameters. This study aims even to shed new light on the pressure-induced deformation mechanisms, at the atomic scale, of three representative species of the ABC-6 group.

MATERIALS AND METHODS

Zeolites belonging to the ABC-6 group include hexa-

Table 1 Chemical formulae by EMPA-WDS analysis of the investigated samples. For the synthetic Na- and K-EAB, the charge imbalance is likely compensated by silanols and H^+ .

Sample	Chemical Formula
Erionite	$(K_{2.39}Ca_{1.99}Mg_{1.02})[Al_{9.02}Si_{27.05}]O_{72} \cdot 26.84H_2O$
Offretite	$(K_{0.93}Ca_{1.12}Mg_{0.67})[Al_{4.77}Si_{13.26}]O_{36} \cdot 10.50H_2O$
Bellbergite	$(Na_{0.76}K_{1.73}Sr_{2.28}Ca_{4.93})[Al_{17.46}Si_{18.63}]O_{72} \cdot 28.03H_2O$
Na-EAB	$(Na_{9.9})[Al_{12.4}Si_{23.6}]O_{72} \cdot 17.3H_2O$
K-EAB	$(K_{11.2})[Al_{12.4}Si_{23.6}]O_{72} \cdot 16.4H_2O$

gonal structures that can be generated by the overlap of six-membered rings among three different positions (namely A, B, or C) by pure translation along the a and b axes. The rings are superposed along the c-axis direction with a characteristic stacking sequence in the A, B, and C positions, which is diagnostic of the framework.

The crystal structure of erionite (ERI framework type, stacking sequence AABAAC) is characterized by the presence of three different types of cages superposed along the c-axis (Fig. 1). Similarly, in bellbergite (EAB framework, stacking sequence ABBACC) three different cages with a shorter length along the c-axis direction with respect to those of ERI framework occur (Fig. 1). Conversely, in offretite (OFF framework type, AAB stacking sequence) the absence of a six-membered ring in C position lead to the presence of a large 12-membered ring channel, absent in ERI and EAB framework (Fig. 1).

The three natural crystal samples and the two synthetic powders with EAB framework were chemically characterized by electron microprobe analysis in wavelength dispersive mode (EMPA-WDS). The chemical formulas are reported in Table 1.

The structure of the samples has been characterized with X-ray diffraction, to build a reliable structural model based on data collected at ambient conditions.

Experiments at non-ambient conditions

In situ high-pressure single crystal X-ray diffraction experiments were conducted at the ID15b beamline of the European Synchrotron Radiation Facility (ESRF) in Grenoble (France) and the P02.2 beamline at PETRA-III, Deutsches Elektronen-Synchrotron (DESY) in Hamburg (Germany). The beamlines setup is described in Poreba et al. (2022) and Liermann et al. (2015). The non-ambient conditions were reached using a Diamond-Anvil-Cell (DAC) to generate hydrostatic pressure on the samples. The experimental protocol involved using different pressure-transmitting fluids to assess the intrinsic compressibility of the species and to stimulate the pressure-induced crystal-fluid interaction. In detail:

1. Experiments using 'non-penetrating' *P*-transmitting fluids, such as *daphne oil* (hereafter *d.o.*) or *silicone oil* (hereafter *s.o.*), aimed at determining the compressibility path and the elastic parameters of the minerals, without any interference of the *P*-transmitting fluid, setting a benchmark for the second-step.

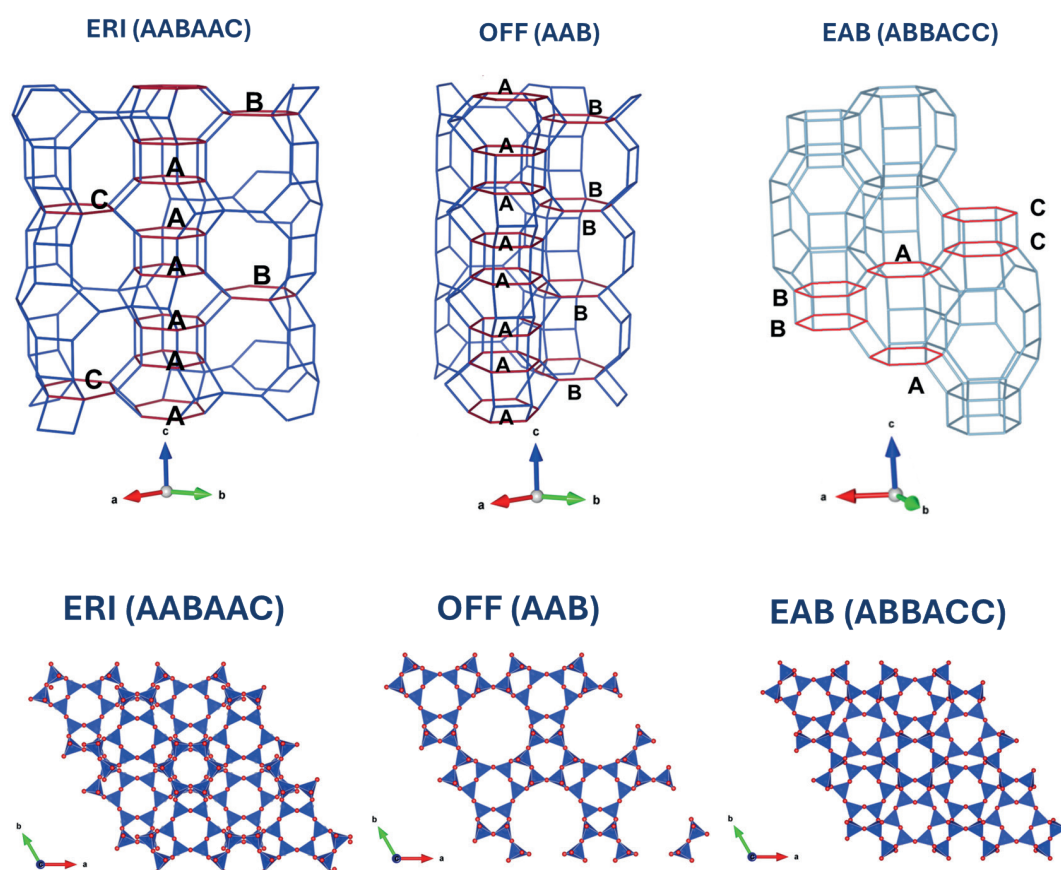


Figure 1 (top) Skeletal representation of the three investigated frameworks, in red the six-membered rings, the repetition of which generates the different topologies; (bottom) tetrahedral representation of the three frameworks, viewed down the c-axis.

- Experiments using ‘potentially-penetrating’ P -transmitting fluids, such as alcohols-water mixtures (i.e., distilled H_2O , methanol:ethanol: $H_2O = 16:3:1$ hereafter *m.e.w.*, ethanol: $H_2O = 1:1$ hereafter *e.w.*, methanol) or noble gases (i.e., Ne in its liquid state), to promote the P -mediated crystal-fluid interaction.

The experimental P - V data were modelled with an isothermal Birch-Murnaghan equation of state, using the EoSFit 7.0 GUI software, to calculate the bulk modulus $K_{V_0} = -V_0(\delta P/\delta V) = \beta_{V_0}^{-1}$, where β_{V_0} is the volume compressibility at room conditions (Angel et al., 2014).

RESULTS

Erionite

The compressional data obtained from the experiment using the non-penetrating silicone oil provide insights into the intrinsic elastic behaviour of natural erionite. The refined bulk modulus, calculated with a II order Birch-Murnaghan equation of state (Angel et al., 2014), resulted to be $K_{V_0} = 47(2)$ GPa. Interestingly, an increase in compressibility was observed in the *silicone oil* experiment above ~ 0.5 GPa due to the saturation of a peculiar deformation mechanism of the erionite cage (detailed discussion in Battiston et al., 2022).

The P - V analysis of the unit-cell evolution between the experiments using non- and potentially-penetrating PTFs suggested the occurrence of P -induced intrusion of H_2O . Therefore, the over-hydration of the structural cavities leads to a sort of ‘‘pillar’’ effect, resulting in lower bulk compressibility with respect to the pristine sample (Gatta & Lee, 2014; Gatta et al., 2018). The intrusion likely involves the erionite cage, showing the first evidence at relatively low pressure ($P \sim 0.2$ GPa), with an increase in

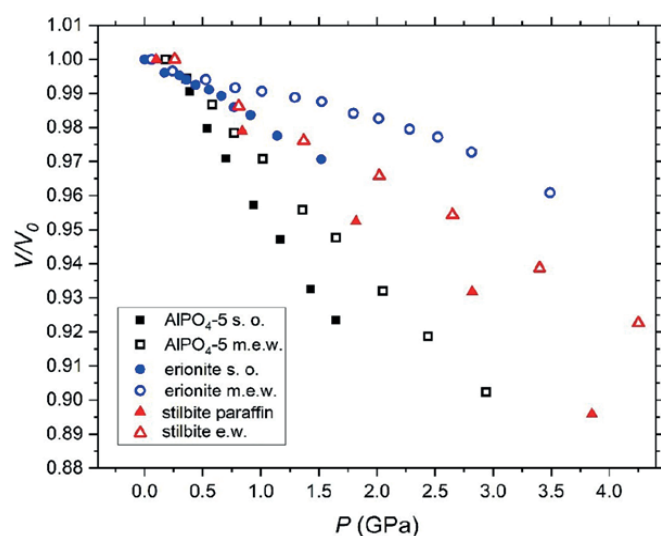


Figure 2 P -induced evolution of the normalized unit-cell volumes of the natural erionite of this study vs. synthetic $AlPO_4-5$ (Lotti et al., 2016) and natural stilbite (Seryiotkin et al., 2021), compressed in non-penetrating (full symbols) and potentially-penetrating (empty symbols) pressure-transmitting fluids.

magnitude at higher pressure.

A comparison with reported crystal-fluid interactions in other natural and synthetic zeolites reveals that the magnitude of the intrusion phenomena observed in erionite is surprisingly high for a natural zeolite with stuffed cavities (Fig. 2).

Offretite

The P - V data obtained using the non-penetrating *daphne oil* reflect the intrinsic compressibility of this zeolite. Interestingly, offretite exhibited a change of the compressional behaviour at ca. 1.83 GPa, without any pressure-induced phase transition. This change was marked by a significant decrease in bulk compressibility, being the refined bulk modulus, calculated with a II order Birch-Murnaghan equation of state (Angel et al., 2014), equal to $K_{V_0} = 59(2)$ GPa at pressures below 1.83 GPa, and $K_{V_0} = 28(2)$ GPa at pressures above 1.83 GPa. This variation is ascribable to a rearrangement of the extraframework configuration involving the migration of H_2O molecules, which enhances bulk compressibility (details in Battiston et al. 2023).

Experiments with potentially penetrating PTFs demonstrated the P -induced adsorption of new molecules within the large 12-membered ring (12 mRs) channels of offretite, resulting in an overall decrease of its bulk compressibility (Fig. 3). Comparing these findings on natural offretite with those of the structurally similar erionite, we observed that erionite is more efficient in P -induced adsorption of H_2O molecules, despite lacking a continuous large channel along the c -axis direction.

Neon (Ne) atoms can access the 12 mRs channels of offretite under the applied pressure, occupying the same atomic sites as the newly adsorbed H_2O molecules in experiments with potentially penetrating aqueous mixtu-

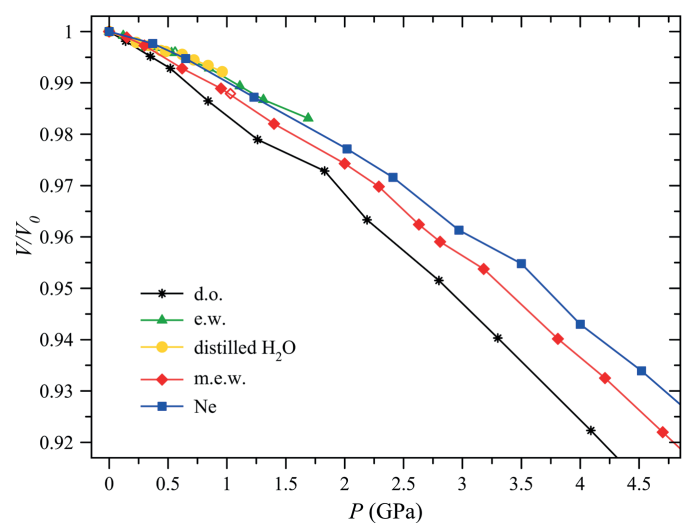


Figure 3 P -induced evolution of the normalized unit-cell volumes of the natural offretite of this study vs. synthetic $AlPO_4-5$ (Lotti et al., 2016) and natural stilbite (Seryiotkin et al., 2021), compressed in non-penetrating (d.o.) and potentially-penetrating (e.w., distilled H_2O , m.e.w. and Ne) pressure-transmitting fluids.

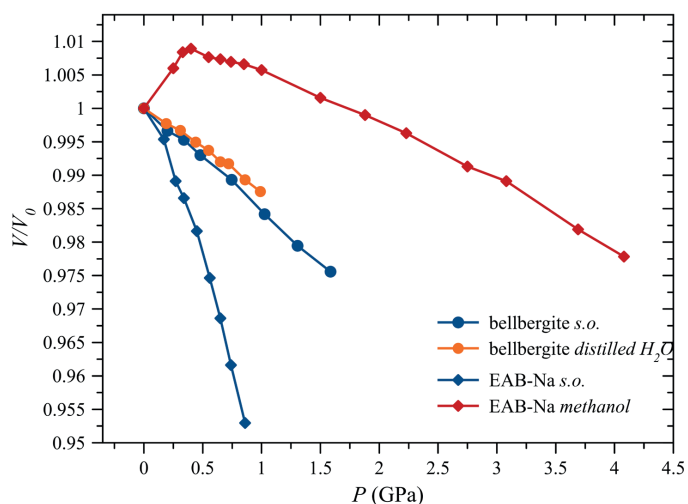


Figure 4 P-induced evolution of the normalized unit-cell volumes of the natural bellbergite and synthetic Na-EAB zeolite, compressed in non-penetrating (s.o.) and potentially-penetrating (distilled H₂O and m.e.w.) pressure-transmitting fluids.

res. These findings open a new route about the Ne cycle in nature, highlighting the potential of open-framework silicates to trap Ne under the combined pressure and temperature conditions, making zeolites potential carriers of Ne at shallow depths.

Bellbergite and synthetic analogues

In a non-penetrating fluid, the refined isothermal bulk modulus of natural bellbergite, calculated with an II order Birch-Murnaghan equation of state (Angel et al., 2014), resulted to be $K_{V0} = 62(1)$ GPa, while the synthetic samples showed markedly higher intrinsic compressibility, being their bulk moduli equal to 16(4) and 19(5) for K and Na end-member, respectively. The different compressional behaviour reflects the different nature of cationic and molecular extraframework populations among the samples (Battiston et al., 2024).

This is also evident from experimental data with potentially penetrating fluids, where the magnitude of crystal-fluid interaction is significantly higher in synthetic EAB, while it is modest in natural bellbergite and seems to occur only under compression in distilled H₂O (Fig. 4). Furthermore, both synthetic EAB samples show a remarkable unit-cell volume increase within the first 0.4 GPa when compressed in methanol, indicating a significant interaction with this molecule. In contrast, methanol does not significantly penetrate natural bellbergite.

DISCUSSION

The key role of the extraframework population on the bulk compressibility of a microporous structure with channels or cavities has already been widely described (e.g., Gatta & Lee, 2014; Gatta et al., 2018; Arletti et al., 2010). The experiments here performed made it possible to calculate the intrinsic compressibilities of the three

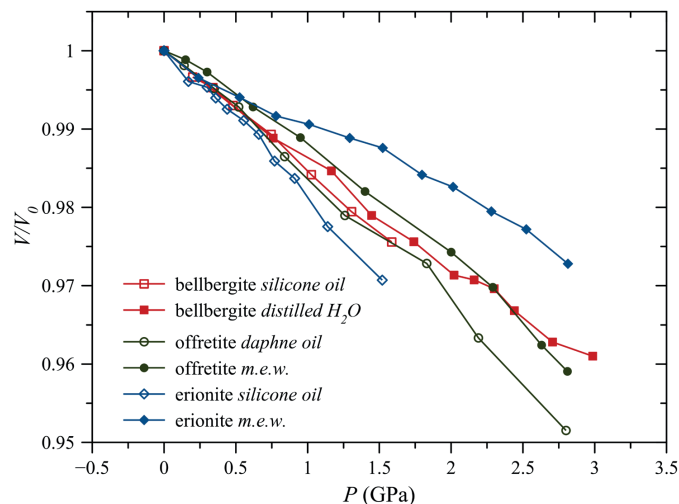


Figure 5 Comparative P-induced evolution of the normalized unit-cell volumes of the three natural zeolites here investigated, compressed in non-penetrating (s.o.) and potentially-penetrating (distilled H₂O and m.e.w.) pressure-transmitting fluids.

zeolites never investigated so far, revealing that erionite has the highest compressibility, followed by offretite and then bellbergite. The lower compressibility of bellbergite is likely a consequence of the high aluminium content in the framework, which requires a large number of extraframework cations within the structural cavities to balance the negative charge of the framework. Conversely, the higher compressibility of erionite, if compared to the structurally similar offretite, is ascribable to the higher structural flexibility of the framework (Battiston et al., 2023), governed by tilting of the tetrahedra, which act as rigid units around the O-hinges (Gatta, 2008), even in the first kilobar.

Regarding the crystal-fluid interactions, the experimental data reveal a higher pressure-induced adsorption capacity for natural erionite, followed by offretite and then bellbergite (Fig. 5).

Comparing the results of zeolites with EAB frameworks, the higher pressure-induced adsorption capacities of synthetic zeolites can be ascribed to some factors, including: *i*) a higher surface/volume ratio in synthetic zeolites, if compared to natural samples (i.e., powder vs. single-crystal); *ii*) a lower Si/Al ratio in the natural sample, resulting in a lower occupiable volume available for the new guest sites (Battiston et al., 2024).

The higher pressure-induced adsorption capacity of erionite compared to offretite, despite a lower occupiable volume within the unit-cell (11% vs 17%), is attributed to the different geometry of their frameworks. In offretite, the large 12-ring channels are not connected to each other on the (001) plane and are only accessible along the direction of the crystallographic *c*-axis. In contrast, the cages in erionite, although having a smaller occupiable volume than the channels, are interconnected, allowing higher accessibility and pervasiveness for the adsorption process (Battiston et al., 2022; 2023).

IMPLICATIONS

The crystal-fluid interaction experiments on natural zeolites revealed that all three species investigated here can increase and decrease their H₂O content in response to pressure. Notably, natural erionite exhibited the highest magnitude of over-hydration ever observed in a natural zeolite when compressed in an aqueous medium. This finding is significant, given erionite's widespread occurrence in various natural environments, including oceanic basalts as an alteration product (Hay & Sheppard, 2001; Kastner, 1979). Although less common than other hydrous minerals like amphiboles and micas, zeolites contain a higher H₂O content (even up to 20 wt.% at ambient conditions). Overhydration occurs at moderate pressure (~0.5 GPa) and ambient temperature, within the zeolite stability range, indicating that geological fluids can interact with these zeolites, enabling them to act as water (or other small molecules) carriers. Zeolite-rich basalts, subducted under moderate pressure and temperature conditions, can efficiently absorb and subsequently release molecules and cations. Therefore, the role of zeolites in fluid transportation within geological systems should be carefully reconsidered.

The remarkable methanol adsorption observed in synthetic EAB is particularly promising for methanol chemistry. This suggests that EAB-type zeolites could be suitable for MTH (i.e., *Methanol-To-Hydrocarbons*) processes, enabling the production of hydrocarbon products without the use of fossil oils as raw precursors. Considering the findings of this study, a dealuminated EAB sample with an increased Si/Al ratio could be a promising candidate for future research into pressure-mediated zeolite-methanol interactions.

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