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PRESSURE-DRIVEN CRYSTAL-FLUID INTERACTION IN NATURAL ERIONITE-K

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The high-pressure behaviour of crystalline compounds with a microporous structure, e.g. zeolites, has experienced a boosted interest in the last two decades, especially due to the *P*-induced intrusion of molecules and solvated ions into the structural nano-cavities [1]. The control of these phenomena in zeolites may expand their utilizations: opening new way in tailoring functional materials or in improving catalytic performance in industrial processes. In this study, we have investigated the behaviour of the natural zeolite erionite when compressed either in non-penetrating and potentially penetrating fluids (i.e. those fluids made by molecules with a kinetic diameter that may allow their *P*-mediated adsorption into the zeolite structural cavities).

Erionites represent a series belonging to the zeolites group, which is defined among three end-members: erionite-Ca, erionite-Na and erionite-K.

The natural sample object of this study, is classified as erionite-K and has the average chemical formula: $(K_{2.95}Ca_{1.99}Mg_{1.02}Na_{0.10})(Al_{9.01}Si_{26.99}O_{72.14}) \cdot 26.78(H_2O)$.

The erionite framework is characterized by the presence of large cages (23-hedron, called “erionite-cage”) superposed along the *c* axes, and a channel made by the alternation of cancrinite cages (CAN-cage) and double six rings (D6R).

Experiments by single-crystal synchrotron X-ray diffraction at *in-situ* high-pressure conditions, using diamond anvil cells, were conducted at the ID15B beamline of ESRF (Grenoble, France). Two *P*-ramps were performed: the first using the non-penetrating silicone oil, up to 1.52(5) GPa, and the second with the potentially penetrating methanol:ethanol:H₂O = 16:3:1 mixture, up to 3.58(5) GPa. A comparison of the *P-V* data obtained by the two ramps unambiguously shows the occurrence of a *P*-induced intrusion of H₂O (and possibly alcohol) molecules within the structural voids of erionite. The magnitude of the intrusion appears comparable with that previously observed in synthetic zeolites (e.g. SiO₂-ferrierite or AlPO₄-5 zeolites) [2; 3], that is quite surprising if we consider that the studied erionite is a natural zeolite with the structural voids stuffed by extraframework cations and H₂O. Structure refinements allowed us to locate two new (H₂O)-oxygen atomic positions and, at a first approximation, to model at the atomic scale the *P*-induced molecules adsorption. In addition, for the first time, the main deformation mechanisms in response to the applied pressure, at the atomic scale, have been described in a natural erionite.

References:

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