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P-mediated crystal-fluid interaction in ERI and OFF topology

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The intrusion of molecules or ions into the structural voids of open-framework minerals (i.e. zeolites) was extensively investigated during last decades, due to the potential exploitability in creating new multifunctional materials or to boost industrial catalytic processes [1;2]. These phenomena can have potential implications in Earth Sciences: zeolites are widely spread in the upper oceanic crust; therefore, they may play an important role as fluid carriers during the early stages of subduction, especially considering a potential over-hydration effect governed by the physical-chemical conditions of the subduction zones.
The present study describes the high-pressure behaviour and crystal-fluid interaction of two natural zeolites: offretite and erionite (OFF and ERI topologies). Both species are members of the ACB-6 family, sharing a similar framework sequence (AABAAC for ERI and AAB for OFF), which results in a quite common intergrowth in natural samples [3]. Erionite, the most abundant in nature, was observed in the volcaniclastic deep-sea sediments collected in the framework of the Oceanic Drilling Program (ODP) [4]. Investigation were conducted by means of in-situ high-pressure single-crystal synchrotron X-ray diffraction, using a diamond anvil cell (DAC), at the ID15b beamline of ESRF (Grenoble, France) and P02.2 of PETRA-III (Hamburg, Germany). Samples were compressed using different hydrostatic P-transmitting fluids (PTFs), both non-penetrating (silicone oil and daphne oil 7575) and potentially penetrating (methanol:ethanol:water mixture 16:3:1, distilled H2O and ethanol:water 1:1). Offretite was also investigated using Ne as PTF.
The P-V patterns show different trends with penetrating and non-penetrating PTFs, revealing the unambiguously occurrence of an intrusion of molecules within the structural nanocavities, and the magnitude of this phenomenon was surprisingly high in natural erionite. Results from the Ne experiment in offretite showed a similar trend to potentially penetrating PTFs, suggesting a P-induced adsorption of this noble gas within the structural voids. Thank to single crystal X-ray refinements, the deformation-mechanisms at the atomic scale, as well as the location of the new atomic sites, are here described.

Primary author: Mr BATTISTON, Tommaso (Università degli Studi di Milano)

Co-authors: Dr COMBONI, Davide (ESRF); Mr PAGLIARO, Francesco (Università degli Studi di Milano); Dr LOTTI, Paolo (Università degli Studi di Milano); Prof. GATTA, G.Diego (Università degli Studi di Milano)

Presenter: Mr BATTISTON, Tommaso (Università degli Studi di Milano)

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