# A comparative study of crystal-fluid interaction phenomena in ABC-6 zeolites group: the case of ERI, OFF and EAB topologies

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The pressure-mediated intrusion of molecules, along with solvated ions, into the nano-cavities of microporous or layered materials is one of the most spectacular routes to promote a mass transfer from fluids to crystalline solids. This phenomenon, observed for example in synthetic and natural zeolites, is now exploited in order to expand their industrial utilization, developing new functional materials and enhancing catalytic performance [1,2]. From a geological perspective, a full understanding of the P-induced crystal-fluid interaction could lead to a re-evaluation of the role played by zeolites as fluid carriers during the early stages of subduction, considering that this class of open-framework silicates can have even up to 20 wt.% $H_2O$. In this study, we have investigated the crystal-fluid interaction, promoted by pressure, of three different natural zeolites belonging to the ABC-6 group: erionite (ERI framework, 6-membered ring sequence of AABAAC), offretite (OFF, sequence of AAB), and bellbergite (EAB, sequence of AABCCB). The goals of the experiments were twofold: 1) to understand the potential role of erionite as a fluid carrier during subduction, given its status as one of the alteration minerals in oceanic floor basalts, and 2) to compare the mechanisms used by structurally similar frameworks in accommodating bulk compression and adsorbing new molecules. Synchrotron XRD experiments were conducted to investigate erionite, offretite, and bellbergite single crystals, using a diamond anvil cell and both potentially penetrating and non-penetrating P-transmitting fluids. The latter were used as a benchmark for evaluating crystal-fluid interaction, as the adsorption of new molecules decreases the bulk compressibility due to the "pillar" effect played by guest species in structural voids [1]. The results showed that erionite experiences the highest adsorption magnitude among the three zeolites. Furthermore, the occurrence and magnitude of the crystal-fluid interaction phenomena were found to be strongly governed by the $H_2O$ content of the hydrous P-transmitting fluids used for the experiments. Ne atoms were observed to penetrate into the offretite framework, making weak Van der Waals interactions with the extra-framework population. Natural bellbergite was found to be almost impenetrable for guest molecules from the P-transmitting fluids, highlighting the key role played by "secondary factors", such as the extra-framework content of the mineral, in crystal-fluid interaction phenomena.

[1] G.D. Gatta, G.D. et al. (2018): Phys. Chem. Miner., 45, 115-138.
[2] Comboni, D. et al. (2020): Catal. Today, 345, 88-96.