Experimental report for proposal CH-5604

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Beamline: ID15B

In the last years, pressure-induced crystal-fluid interaction in microporous and microporous-like materials (e.g., heterosilicates) has shown a raising interest, especially in the fields of materials science and mineralogy. Up to know, among minerals, only zeolites and recently, a few phyllosilicates have shown the ability to adsorb small molecules, thus possessing the potential for tailoring new materials or new properties. Heterosilicates, among them armstrongite ($CaZrSi_6O_{15}\cdot 3H_2O$) and narsarsukite ($Na_2(Ti,Fe^{3+})Si_4(O,F)_{11}$), due to their peculiar crystal structures, similar in some regards to those of zeolites, are eligible candidates to adsorb small molecules of geologic and/or technological interest, in particular H_2O and CO_2. During the beamtime we started to investigate the behavior of those minerals when compressed in potentially penetrating media. Armstrongite, compressed in a mixture of methanol, ethanol and water up to ca. 8 GPa, undergoes a phase transition at 4.50 GPa, likely connected to the tilting of the Zr-octahedra (similarly to what shown in elpidite, its Na-analogue). Unfortunately, the triplication of the unit-cell volume following the phase transition, and the related increase in the number of independent variables, prevented the structure solution of the high-*P* polymorph of armstrongite, hindering a comparison between the high-pressure structures of armstrongite and elpidite. A second set of data has been collected after the phase transition, rotating the DAC at $\chi = 0$ and 90° at the same pressure conditions, in order to allow a sufficient reciprocal space coverage for the structure solution. Analysis of these data is currently in progress. Nevertheless, this study highlighted the wider *P*-range of stability of armstrongite (in which the phase transition occurs only between 4 and 5 GPa) in comparison with its Na-analogue elpidite, confirming the higher *P*-stability of Ca-phases in comparison of Na-phases. No clear evidences of *P*-induced fluid molecules intrusion have been observed.
Narsarsukite has been compressed in a mixture of methanol:ethanol:water, up to ca 1.5 GPa. Preliminary data suggest the absence of any *P*-induced intrusion of the fluid molecules, with a significant bulk compressibility. Structure refinements are in progress, in order to disclose the structural mechanisms accommodating the volume compression.

The results obtained in these experiments provide a fundamental benchmark to which base future investigations, as it clearly appears that a cold compression in fluids bearing water and small alcohol molecules does not trigger the *P*-induced intrusion phenomenon shown by several zeolites. The use of a small or moderate amount of heat (moderate temperature) should be tested, combined with pressure, in order to check if these heterosilicates (armstrongite and narsarsukite) may show a zeolite-like ability in adsorbing small molecules into their structural nanopores.