



“NANO-REACTORS” UNDER HP: THE INFLUENCE OF FRAMEWORK/EXTRAFRAMEWORK COMPOSITION IN CHA TOPOLOGY

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Shifts: 12	Local contact(s): Vladimir Dmitriev	

Names and affiliations of applicants (* indicates experimentalists):

Simona Quartieri, *Dip. Scienze della Terra, Messina (Italy)*

Giovanna Vezzalini and Rossella Arletti, *Dip. Scienze della Terra, Modena (Italy)*

Lara Leardini, *Dip. Scienze della Terra, Ferrara (Italy)*

Vladimir Dmitriev, *ESRF.*

Introduction

In recent experiments performed by our group a survey of the HP behaviour of a number of zeolites of environmental and technological interest was performed. We observed very different deformation mechanisms depending on both zeolite framework structure and on the framework content. **It is now essential to understand, chosen a particular topology, the role of framework/extraframework composition on the deformation mechanisms.** A series of microporous materials with chabazite framework topology (CHA), largely applied in industrial applications and characterized by a high thermal stability, were selected for this purpose. We have studied natural chabazite from Vallerano (Italy), SAPO-34 and ALPO-34 as synthesized and ALPO-34 calcinated. The four phases are characterized by different tetrahedral composition: Si,Al in natural chabazite; Al,P in ALPO-34 and Si,Al,P in SAPO-34, respectively. Moreover, ALPO-34 as synthesized contains one third of the Al atoms in octahedral coordination. Concerning the extraframework content, ALPO-34 as synthesized and SAPO-34 contain morpholinium/ morpholine as structure directing agent, while chabazite contains alkaline/earth alkaline cations and water molecules.

Experimental details

The diffraction experiments were performed at BM01a beamline, at the fixed wavelength of 0.7 Å, using a modified Merrill-Basset Diamond Anvil Cell and silicon oil as non penetrating P-transmitting medium (P-range= Pamb - 7 GPa). Patterns were collected by means of a MAR 345 IP detector (pixel size 150 µm), and the two-dimensional images were turned into 2θ-scan with the FIT2D software. The 2θ accessed range was 0 – 47°. The unit cell parameters were extracted from the powder patterns by means of the Rietveld or LeBail method using GSAS package.

Results

All the studied samples show weakening and broadening of the diffraction peaks with increasing P, but no complete amorphization was observed up to the highest investigated P. The P-induced effects are reversible. Natural chabazite (Figure 1a), SAPO-34 and ALPO-34 calcinated do not exhibit a symmetry change while ALPO-34 as synthesized shows a phase transition from the triclinic to the monoclinic symmetry between 3.4

and 3.9 GPa. The P -induced effects on this porous material are completely reversible but an hysteresis effect is evident because at 2.8 GPa the structure is still monoclinic (Figure 1b).

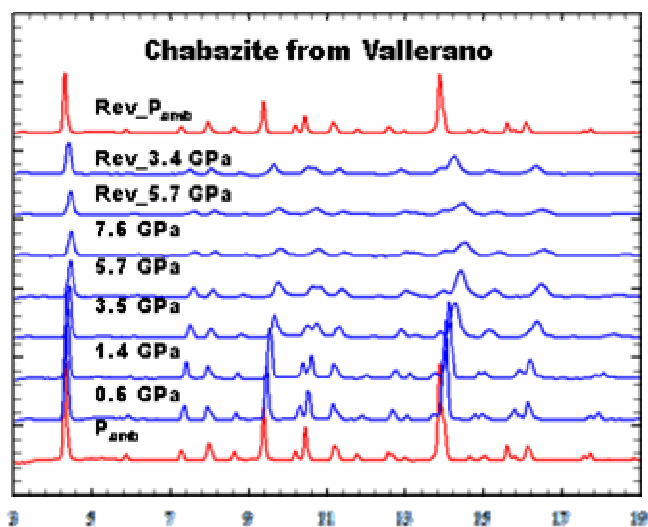


Figure 1a

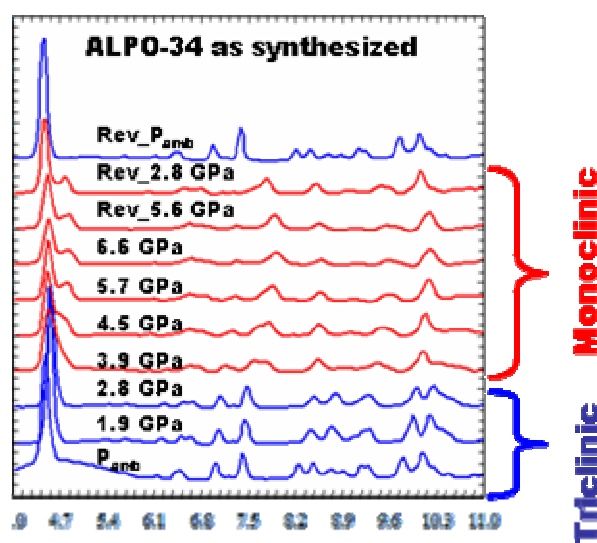


Figure 1b

Figure 2 reports the P -dependence of the normalized lattice parameters for the four samples.

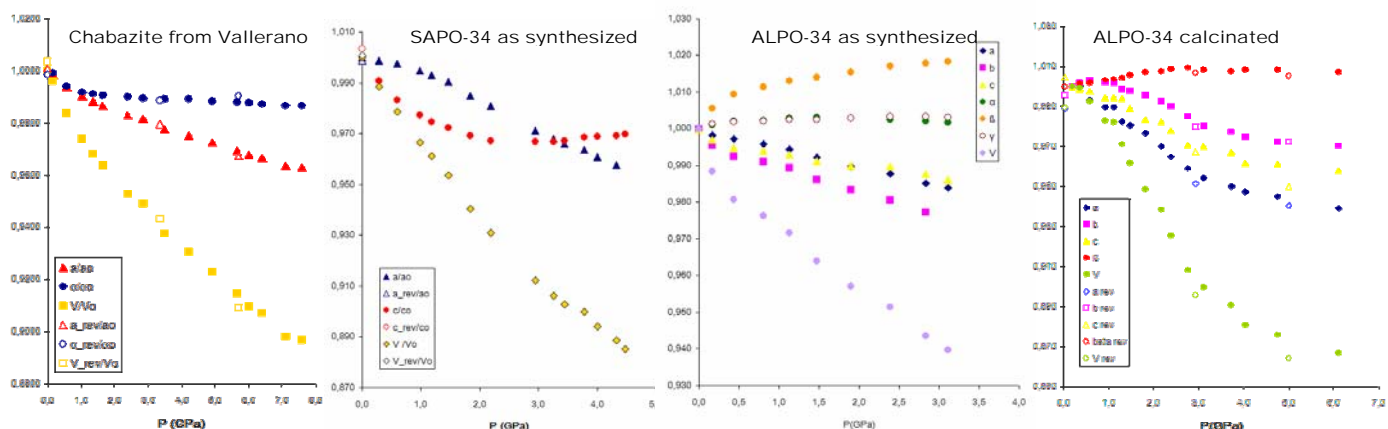


Figure 2

The volume decreases observed for the four phases in the same pressure range (0-4.5 GPa) are the following:

	$\Delta V\%$ at 4.5 GPa
Natural chabazite (Vallerano, Italy):	6.9
ALPO-34 as synthesized	9.0
SAPO-34 as synthesized	11.5
Calcinated ALPO-34	12.4

The less compressible phase is the natural chabazite, which is characterized by the most complex extraframework content. On the other side, the most compressible phase is the calcinated ALPO-34, whose pores are completely free. Both phases with the intermediate compressibility contain the template morpholine molecules in the cavities, but ALPO-34 has a lower compressibility due to the octahedral coordination of some Al cations. This makes the structure more rigid than the tetrahedral framework.