PRESSURE-INDUCED HYPERCONFINEMENT IN ZEOLITES: TODAY, TOMORROW

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How do supramolecular nanoaggregates form and behave under high pressure (*P*) conditions? And what can occur when they are confined in nanocavities? The *P*-induced penetration of "external" molecules through the zeolitic micropores was incidentally observed, and not entirely understood in the first experiments about 20 years ago [1]. Later, a series of experiments have been devoted to observe the *P*-induced penetration of "external" molecules in natural or synthetic zeolites with different framework, opening a new scenario in the crystal-chemistry of this class of materials [2 for a review].

A comparative study of the experimental and theoretical findings over the last years on zeolites compressed in "penetrating" and "non penetrating" fluids allow us to give new insights into 1) the "hyperconfinement" regime based on combined effects of applied pressure, spatial confinement and constraints in morphology at the nanoscale, and on 2) *P*-induced structural evolution of zeolitic frameworks. The *P*-induced penetration of new molecules through the zeolitic voids may create supramolecular organization, and so new nanosystems of controlled morphology with potential functional properties, which will be explored in the framework of ImPACT ("Impose pressure and change technology - Pressure-induced organized nanostructures and shape-driven segregation in zeolites"), a research project recently supported by the Italian Ministry of Education. The comparative elastic analysis and the high-*P* structural data of zeolites compressed in "non penetrating fluids" allow us to make some general considerations: 1) The range of compressibility among this class of open-framework silicates is significantly large, with bulk moduli ranging between 15 - 70 GPa; 2) Microporosity does not necessarily imply high compressibility, as several zeolites are less compressible than other non-zeolitic rock-forming minerals; 3) Compressibility of zeolites appears not directly related to the microporosity, at least if we model the microporosity with the "framework density"; 4) The flexibility observed in zeolites under hydrostatic compression is mainly governed by tetrahedral tilting of stiff tetrahedra around oxygens that behave as hinges. *P*-induced tetrahedral tilting usually leads to a continuous rearrangement of the framework without any phase-transition. More rarely, tilting induces "displacive" phase-transitions. *P*-induced reconstructive phase-transitions (without the concomitant effect of temperature), with a change in topology, do not occur in this class of materials; 5) The deformation mechanisms in response to the applied pressure are dictated by the topological configuration of the tetrahedral framework and are independent of the Si/Al-distribution and of the channels content. The channel population (with its different nature and bonding configuration) governs the compressibility of the cavities, leading to different unit-cell volume compressibility in isotypic structures.

References. [1] Hazen, R.M. (1983): *Science*, **219**, 1065-1067. [2] Gatta, G.D. (2010): *Zeitschrift für Kristallographie*, **223**, 160–170.