

COMPRESSIBILITY AND CRISTAL FLUID INTERACTIONS IN Si FERRITE

[P. Lotti](#)¹, R. Arletti², G.D. Gatta¹, G. Vezzalini³, S. Quartieri⁴, M. Merlini¹

¹Dip. di Scienze della Terra, Università degli Studi di Milano,
Via Botticelli 23, 20133 Milano, Italy

²Dip. di Scienze della Terra, Università di Torino, Via Valperga Caluso 35, 10125 Torino, Italy

³Dip. di Scienze Chimiche e Geologiche, Università di Modena e Reggio Emilia,
Via S. Eufemia 19, 41100 Modena, Italy

⁴Dip. di Fisica e Scienze della Terra, Università di Messina,
Viale Ferdinando Stagno d'Alcontres 31, 98166 Messina S. Agata, Italy

Introduction

The interest on the high-pressure (HP) behaviour of zeolites significantly increased during the last decade. The growing number of studies allowed the recognition of complex and variable responses to the applied pressure^{1,2}: a wide compressibility range, a remarkable structural flexibility and the relevant influence played by the framework (topology, cation ordering etc.) and extraframework components on the HP behaviour. Beside the intrinsic properties of the open-framework compounds, a significant number of experiments have been devoted to the high-pressure interactions between zeolites and the *P*-transmitting medium, as the so-called *P*-induced over-hydration: i.e. the *P*-induced penetration of H₂O molecules into the structural voids³. The *P*-driven penetration of molecules is not limited to H₂O, several “pore-penetrating” *P*-transmitting media may be involved in this process.

In this light, pressure may be applied not only to explore the elastic and structural properties of zeolites, but also as a tool to drive changes of these properties: e.g. improving the efficiency in the field of heterogeneous catalysis, favoring the access of reactants and products to/from the catalytically active sites; modifying the physical-chemical properties through irreversible phase transitions; or for the engineering of technological materials through irreversible molecules intrusion.

In this study, we explore (by both single-crystal and powder synchrotron X-ray diffraction) the high-pressure behaviour and crystal-fluid interactions of a synthetic siliceous matrix with ferrierite topology [Si-FER: Si₃₆O₇₂], using a number of penetrating and non-penetrating pressure-transmitting media.

Materials and experimental methods

The single crystals and powders used have all been selected from the same starting sample of synthetic pure Si-ferrierite (Si₃₆O₇₂)⁴. The *in-situ* high-pressure single-crystal (SC) and powder X-ray diffraction experiments have been performed at the ID09A and BM01-Swiss-Norwegian beamlines at ESRF (Grenoble), respectively, using diamond anvil cells. Four different *P*-transmitting media have been used for both SC and powder experiments: non-penetrating silicon oil and potentially penetrating methanol:ethanol:H₂O=16:3:1 mix (m.e.w.), ethylene glycol (egl) and 2methyl-2propen-1ol (mpo).

Results and discussion

The HP-study of Si-FER compressed in silicon oil evidenced the remarkable flexibility of this framework: a first displacive phase transition was observed from the orthorhombic *Pmnn* to the monoclinic *P12₁/n1* space group at ~ 0.7 GPa. A second displacive phase transition, involving a significant unit-cell volume contraction, was observed at ~ 1.24 GPa from the *P12₁/n1* to the *P2₁/n11* space group (through an intermediate *P-1* structure, “type-II” transition according to Christy⁵). The high-*P* *P2₁/n11* polymorph was found to be stable at least up to 3.00(7) GPa, whereas - upon pressure release - the starting *Pmnn* structure was fully recovered. The three polymorphs were found to share a virtually identical bulk elastic behaviour, being their average volume compressibility β_V : 0.051(4), 0.056(9) and 0.055(3) GPa⁻¹, respectively. The structure deformation is governed by the tilting of the tetrahedra around the shared oxygen hinges. The bulk *V*-contraction is mainly accommodated, after