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PHILLIPSITE AT HIGH PRESSURE: A SINGLE-CRYSTAL X-RAY SYNCHROTRON DIFFRACTION STUDY

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Phillipsite is a low Si/Al natural zeolite, often found as autogenic mineral in both "close" and "open" hydrologic system or in vugs of basalt, as an alteration product of volcanic glass. Along with laumontite, it is one of the most common zeolites found in oceanic basalts. In order to investigate the high-pressure behavior of phillipsite and its structural evolution at the atomic scale, we performed an *in situ* single-crystal synchrotron X-ray diffraction experiment up to 10 GPa with a diamond anvil cell, using a nominally penetrating pressure-transmitting fluid (methanol:ethanol:H₂O = 16:3:1 mix) (Gatta, 2010). The unit-cell parameters and the structure refinements within the *P*-range investigated show that: 1) phillipsite does not adsorb further H₂O molecules from the penetrating-transmitting fluid within the *P*-range investigated; 2) the configuration of the extra-framework population changes with pressure (between 2 and 3 GPa), affecting the elastic behavior of the mineral. More in details, two distinct compressional regimes have been observed, in which the bulk moduli differs drastically (i.e., $K_V = 89(8)$ GPa between 0 and 2 GPa, $K_V = 18.8(7)$ GPa between 3 and 9 GPa); 3) phillipsite is crystalline at least up to 10 GPa, and this is surprising if we consider its microporous nature; 4) all the *P*-induced effects are completely reversible in decompression. The structural refinements allowed us to describe the mechanisms, at the atomic scale, that govern its elastic behavior, which are mainly governed by inter-tetrahedral tilting. The relatively low compressibility of phillipsite at room-*P* and its relatively wide *P*-stability shown in this experiment suggests that this zeolite is a potential H₂O carrier during the first phase of the oceanic crust subduction or, toward the industrial front, its potential use in systems for the mechanical energy storage/dissipation (Eroshenko et al., 2001; Soulard et al., 2004).

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HIGH-*P* BEHAVIOR OF ZEOLITES IN “PENETRATING” FLUIDS: RECENT INSIGHTS AND NEW OPPORTUNITIES FROM Xpress, THE HIGH-*P* DEDICATED DIFFRACTION BEAMLINE AT ELETTRA

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The high-pressure behavior of zeolites when compressed in potentially “penetrating” fluids, i.e. those whose molecules can be intruded into the zeolitic structural micropores, has recently been a subject of growing research interest. Pressure-mediated intrusion of molecules can induce changes in the physical and chemical properties of zeolites, thus offering an excellent tool for the tailoring of the properties of these industrially relevant materials. *In situ* experiments on SiO₂-ferrierite (FER; Lotti et al., 2015) and AlPO₄-5 (AFI; Lotti et al., 2016) zeolites, conducted in diamond anvil cells (DACs) using “penetrating” pressure-transmitting fluids, showed that the *P*-induced intrusion of molecules can be readily recognized from the synchrotron single-crystal and powder diffraction data. In case of FER, the complex patterns of phase-transitions at increasing pressure reveal the intrusion, whereas for AFI, the drastically different compressibilities provide evidence of this process. In this scenario, recently commissioned dedicated high-pressure diffraction beamline *Xpress*, at the Elettra synchrotron light-source (Trieste, Italy), represents a new facility for high-pressure investigations in the field of geomaterials, using X-ray diffraction. *Xpress* is part of a scientific partnership between Italy and India (Indian Institute of Science, Bangalore). At *Xpress*, a liquid nitrogen cooled silicon single crystal, cut along the [111] direction, intercepts the beam from multipole superconducting wiggler source and deflects it at a fixed energy of 25 keV. The beam is focused using a toroidal mirror of 1.4 m length and 2.9 mrad grazing angle. The mirror is Pt coated to achieve 80% reflectivity at 25 keV. Focused beam from the mirror is further optimized by collimators (ranging from 30 to 200 micrometer in diameter), in order to have intense and well defined monochromatic beam for the HP-XRD experiments. On-line pressure monitoring is achieved through a ruby fluorescence microscope. The present experimental stage is equipped to host different kinds of DACs, in order to permit room-temperature - high-pressure experiments in the pressure range 0-50 GPa. An image plate MAR345 with a controllable linear movement along the beam direction is available for the collection of the diffraction pattern. The setup for hosting *in-situ* high-*P* single-crystal X-ray diffraction experiments is under development and will be available for users in the near future.

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CANDIDATE CARBONATE PHASES IN THE EARTH

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With the current state of art of experimental facilities, we conducted studies on carbonates at the variable pressures and temperatures existing from the Earth's crust to the mantle/core region conditions. The quality of the diffraction data (single crystal and powder) allow full structural analysis for all the phases encountered. We present an updated overview of all the possible candidate carbonate phases in the inner Earth, based on model carbonate system and on most-likely composition in the ternary diagram $\text{CaCO}_3\text{-MgCO}_3\text{-FeCO}_3$. The model BaCO_3 studied at high temperatures and high pressures present the sequence of transition from aragonite-type phase to disorder-calcite phase and finally NaCl structure. At high pressure, the aragonite-type transform into the post-aragonite above 8 GPa. A similar scenario is observed in CaCO_3 , but new high-pressure polymorphs denser than aragonite are present above 15 GPa. Dolomite, previously considered unstable at mantle conditions, is demonstrated to be stable above 30 GPa at the high pressures and temperatures existing in the Earth's interior up to the mantle/core boundary. It transforms to dense polymorphs based on distorted calcite-type structure at intermediate pressures, and, above the Mbar, transforms into new polymorphs featuring ring-carbonate C_3O_9 groups. This structure is likely the candidate phase for carbon storage in a carbonate in the Earth's mantle, and may form complete solid solution with CaCO_3 and MgCO_3 . Fe-magnesite, stabilized at high pressures and temperatures, undergoes complex red-ox reactions, with the formation of Fe^{3+} bearing carbonates with stoichiometry different from ABO_3 .

CHARACTERIZATION OF NEWLY-FORMED CALCIUM PHOSPHATES STRATIGRAPHIES CRYSTALLIZED ON CALCIUM CARBONATE SUBSTRATES: A MULTI-ANALYTICAL APPROACH

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The diammonium hydrogen phosphate [DAP, (NH₄)₂HPO₄] treatment is an effective and promising consolidating agent for carbonatic substrates (Matteini et al., 2011, 2013). The reaction with calcite [CC, CaCO₃] at room temperature is non-stoichiometric and induces the formation of hydroxyapatite [HAP, Ca₅(PO₄)₃(OH)] (Ni & Ratner, 2003) and other metastable phases (Possenti et al., 2016). Due to the complexity of the DAP reaction mechanism, several studies have been focused on the interaction between the consolidating product and the carbonatic substrate, in order to define the crystallization sequence and the identification of the formed calcium phosphates.

We have recently been carried out a series of experiments on Carrara marble specimens treated by capillarity, paper poultice and immersion in DAP solutions with different molarities. The first experimental findings showed that the treatment involves the formation of a *shell*-like layer around the calcite grains, composed by a mixture of crystalline and amorphous calcium phosphates. These phases are arranged in layers, with different crystals size and morphology. Since the straightforward characterization of calcium phosphates mixture is challenging (Drouet, 2013; Karampas & Kontoyannis, 2013), we have developed and improved a new multi-analytical approach (based on the combination of X-ray diffraction techniques, vibrational spectroscopies and morphological-microchemical analyses). In addition, the reaction kinetics has been investigated (with a non-destructive protocol) with time-resolved experiments performed at the MCX beamline at Elettra (Trieste, Italy). Our first experimental results suggest a correlation between the specific crystalline phase to the morphology and the position of the newly-formed products of the *shell* structure. The reaction products and their position into the porous matrix govern the performance of the mineral-inorganic treatment. The obtained data of this study provide useful recommendation concerning the treatment methodologies in the conservation works (DAP molarities and treatment time).

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