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The effect of carbonate solid solution on the elasticity of natural fluorapatites

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Apatite is an important mineral and knowledge of its stability at the Earth's interior is essential to understand its role as potential repository of phosphorous at the mantle depth. In biomedical field its mechanical properties are also important as apatite is a dental enamel constituent. Changes in the chemical and physical properties of apatite are observed when carbonate is incorporated into the apatite structure. Incorporation of carbonate can occur by substitution for both the channel anion and the phosphate ion with different effects on unit-cell parameters. Substitution of hydroxyl (OH) by type A carbonate results in progressive increase in a and decrease in c , whereas substitution of phosphate by type B carbonate results in progressive decrease in a and increase in c . So far several compression experiments have been carried out to investigate the compressibility of synthetic samples of fluorapatite, hydroxylapatite, and chlorapatite. A study of natural fluorapatite was performed by [1], who found a lower value of K_T than previous work (using a BM2, $K_T = 91.6(1.0)$ GPa by [1] versus $97.9(1.9)$ GPa [2] and $97.8(1.0)$ GPa by [3]). Recently [4] have studied the effect of carbonate substitution on the compressibility of hydroxylapatite: the substitution of carbonate (both type A and B) lowers the value of K_T . However, it is difficult to assess if the softening is due to type-A or type-B or both types of substitution. Among the available data, only [3] have performed a single crystal diffraction study.

In order to clarify such discrepancies, we have performed a single crystal diffraction study of two natural fluorapatite and type-B carbonate fluorapatite ("francolite") samples coming from Muséum National d'Histoire Naturelle, Paris. Two crystals were mounted together in a DAC using quartz as pressure calibrant and a 16:3:1 mixture of methanol:ethanol:water as pressure-transmitting medium. We used SINGLE program [5] to collect data on a Siemens P4 four-circle diffractometer and EosFit7c [6] to fit the data.

Our data (16 pressure points up to 5.8 GPa), fit to a 3rd order Birch-Murnaghan Equation of State (BM3-EoS) show that type-B carbonate substitution effectively decreases the bulk modulus from $K_T = 88.41(1.9)$ GPa [with $K_T' = 5.8(0.8)$] to $K_T = 85.3(1.4)$ GPa [with a K_T' of $5.6(0.6)$]. However, careful inspection of the $F-f$ plot shows that two different elastic regimes (low-P < 3.25 GPa and high-P ≥ 3.25 GPa) should be actually taken into account for fluorapatite. Moreover, collecting more data during decompression will allow to better constrain both pressure ranges. So far we have used a BM2 EoS for both the low-P and the high-P regimes obtaining K_T of $91.94(99)$ and $98.9(1.6)$ GPa for the low-P and the high-P regimes respectively. This preliminary result agrees well with previous findings for fluorapatite as the value obtained by [2] were probably biased by high pressure regime (although high pressure data > 9 GPa was probably not hydrostatic) while the value obtained by [1] did not have enough observations at high pressure. In both cases the authors fitted the whole observed pressure range as a unique pressure regime.

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Unraveling the structural complexity of high-pressure orthorhombic iron oxides

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Occurring as accessory minerals in most rocks and forming large deposits of considerable economical importance, iron oxides have a key petrological importance. Their role as oxygen buffers, in differentiation processes and as magnetic phases summarizes the iron oxides critical importance in most geological contexts, independently of their abundance.

The recent discovery of a new compound in the Fe-O system, Fe₄O₅ [1], reshaped our assumptions on the behavior of iron oxides in the Earth's deep interior, where phases of FeO and Fe₃O₄ were considered the sole plausible players. Fe₄O₅ is stable at pressures greater than about 10 GPa and, with an iron average valence state of 2.5+, is a plausible accessory mineral of the deep Earth. Other studies found that Fe₄O₅ may be stable in a wide stoichiometry range [2] and can accept a wide extent of isomorphous substitutions [3]. Finding a new compound in one of the most investigated binary systems and in a pressure and temperature range that is experimentally accessible for decades is surprising. The discovery of Fe₄O₅ relies on high resolution high pressure microdiffraction mapping using highly focused high energy x-ray only available at synchrotron sources. We will present the procedures that led to the discovery of Fe₄O₅ [4], in particular how powder, single crystal and multigrain diffraction strategies may be combined within samples that are yet only about 100 μm large and less than 10 μm thick. This strategy can provide more robust identification and characterization of phases synthesized at high P-T and a characterization of samples heterogeneity.

We will present some of the latest results revealing an Fe-O system that shows at high pressure an unexpected complexity including important degrees of disorder, as evidenced by diffuse scattering effects.

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