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## The influence of cation disorder on the mineral physics of ankerite: new HP synchrotron X-ray diffraction data

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### 1. Introduction and methodology

Carbonates are the most important carbon (C) – bearing minerals being key phases in the Earth's carbon cycle.

The most abundant carbonates in nature are the rhombohedral calcite ( $\text{CaCO}_3$  - space group R-3c), magnesite ( $\text{MgCO}_3$  - space group R-3c) and dolomite [ $\text{CaMg}(\text{CO}_3)_2$  - space group R-3]. Ankerite [ $\text{Ca}(\text{Mg}_{1-x}\text{Fe}_x)(\text{CO}_3)_2$ ,  $0 \leq x \leq 0.7$ ] is isostructural with dolomite and the Mg substitution by Fe has important effects on the high pressure (HP) behavior of the mineral, in terms of compressibility, structural stability and thermoelastic properties (e.g., [1]). In natural occurring R-3 carbonates, cations distribute in alternated layers (ordered crystal structures). At high temperature conditions cations start to randomly distribute among cationic sites giving rise to disordered crystal structures [2][3]. Structural parameters such as chemical composition and cation disorder strongly influence the carbonate's stability under non ambient conditions. Synchrotron single crystal X-ray Diffraction experiments were carried out at the ID-15B beamline at ESRF (Grenoble, France) up to approximately 23 GPa, in order to study the HP behavior of ordered (hereafter ank-ord) and disordered (hereafter ank-dis) ankerite, eventually locate the occurrence of phase transition, and analyze the influence of disorder on the ankerite mineral physics. Collected data were treated to study the crystal structure evolution as well as the compressibility behavior of the analyzed samples.

### 2. Results

The crystal structure refinements of both ank-ord and ank-dis at increasing P showed that ank-ord undergoes phase transition to ankerite-II (hereafter ank-II) in the P range 12-13.5 GPa. Upon phase transition, the coordination number of Ca increases from 6 to 8 and the space group varies from R-3 to P-1, in analogy with dolomite-II [4]. The ank-ord crystal structure regularizes with increasing P up to phase transition and, after that, distortion strongly increases, i.e., ank-II is strongly deformed with respect to ank-ord. Ank-dis regularizes too as P increases, reaching full regularization at approximately 19 GPa. However, no phase transition was observed up to the highest analyzed P. Disorder has a small but significant influence on the compressibility of ankerite, being ank-dis less compressible than ank-ord. After the phase transition, compressibility of ankerite drastically changes and ank-II is considerably less compressible than ank-ord and shows almost incompressible  $\text{MgO}_6$  octahedra. In all the three crystal structures, the a parameter has the lowest compressibility and it even expands in ank-II (Fig 1). This behavior is strictly related to the observed increase in  $\gamma$  angle as P increases (Fig. 1), that is a consequence of the shear of cation layers in the (0 1 -1) plane (Fig. 2).

Fig. 1: Pressure dependence of cell parameters for ank-ord, ank-II and ank-dis.

Fig. 2: Crystal structure of ank-II at 21.97 GPa.

### 3. References

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