



	Experiment title: Ultra-high pressure crystal structure of dolomite and magnesite	Experiment number: HS- 4712
Beamline:	Date of experiment: from: 27 set 2012 to: 02 ott 2012	Date of report:
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Report:

We performed four high pressure single crystal experiments on the following samples:

- 1- pure dolomite, $\text{CaMg}(\text{CO}_3)_2$
- 2- pure magnesite, MgCO_3
- 3- Fe-bearing magnesite [siderite: $(\text{Mg}_{0.4}\text{Fe}_{0.6})\text{CO}_3$]
- 4- Rhodocrosite, MnCO_3

We performed single crystal diffraction analysis up to Mbar pressures for samples 1 and 3, and up to 60 GPa for samples 2 and 4, using tiny samples (apx $10 \times 10 \times 5 \mu\text{m}^3$ size) contained in ESRF membrane type DAC equipped with bevelled diamonds and 125 μm culet diameter (samples 1 and 3) and 300 μm culet diameter (samples 2 and 4). The main results achieved for the different samples are here below summarised.

- 1- dolomite.

At 15 GPa (2 GPa lower than Fe-dolomite previously analysed [1]) we observed dolomite to dolomite-II polymorphic transition. Dolomite-II in Fe-free sample presents the same crystallographic features as dolomite-II observed in Fe-bearing sample.

At 40 GPa (5 GPa higher than in Fe-bearing sample), we observed dolomite-II /dolomite-III transition. Dolomite-III, contrary to dolomite-II, has a different structure in Fe-free compared to Fe-bearing sample. It is triclinic, with similar unit cell volume, 80 atoms in the unit cell, but different unit cell axis length. Dolomite-III is observed up to the maximum pressure investigated, 110 GPa, without any further transition (figure 1). The absence of Fe prevented laser heating. The results indicate a complex polymorphism in dolomite-ankerite compositional join and therefore a possible very complex behaviour in natural lower mantle environments.

2- Magnesite

High pressure at ambient temperature did not indicate any phase transition up to the maximum pressure investigated, confirming therefore that steric considerations based on ionic radii are unaccurate at very high pressures. In fact, considering that rhombohedral calcite structure is stable up to 2 GPa in CaCO₃ and up to 15 GPa in CaMgCO₃, we would expect in MgCO₃ a phase transition around 40 GPa, but this is not the case. Crystal structure refinements indicate a regularisation of MgO₆ coordination polyhedra as pressure is increased, differently from Fe bearing compounds (see below). The lack of Fe in the sample prevented laser heating experiments.

3- Fe-magnesite (siderite)

Natural crystals of Fe-bearing magnesite [siderite: (Mg_{0.4}Fe_{0.6})CO₃] were compressed above the Mbar. On increasing pressures up to 130 GPa, we observed the Fe- high to low spin transition at 45 GPa. No further transitions were observed. Crystal structure refinements indicate a progressive distortion of Fe coordination polyhedra as function of pressure, contrary to pure MgCO₃, despite Fe in low spin state presents a similar ionic radii as Mg. This confirms that geometrical approach is useful to predict structural behaviour only in a relatively low pressure range. At significant high pressures, electronic configuration of cations may therefore significantly change the structural behaviour and, consequently, the sequence of structural transitions. The structure refinements allowed also to extract accurate Fe-O bond distances (figure 2) and, for the first time, a direct Fe ionic radii estimation of Fe in low spin state from structure relevant to Earth's lower mantle mineralogy [2]

The sample was then laser-heated and X-ray diffraction indicated the presence of single crystal spots. Indexing of the diffractions revealed the presence of two different phases, and crystal structure solution, performed with charge-flipping algorithm and Fourier analysis, allowed establishing both stoichiometry and crystals structure of these new phases. Both were unpredicted and unreported. They consist in Mg₂Fe₂C₄O₁₃ carbonate, with tetrahedral carbonate groups arranged in truncated C₄O₁₃ chains, and in Fe₁₃O₁₉, with a stoichiometry intermediate between magnetite and hematite.

4- rhodocrosite

Sample of MnCO₃ was compressed up to 60 GPa. Mn present similar ionic radii as Mg and Fe, and electronic transition are also reported for this compound. Differently from magnesite, the compression of MnCO₃ at ambient temperature determine a polymorphic transition above 40 GPa, with transition from calcite structure to CaCO₃-VI structure [3]

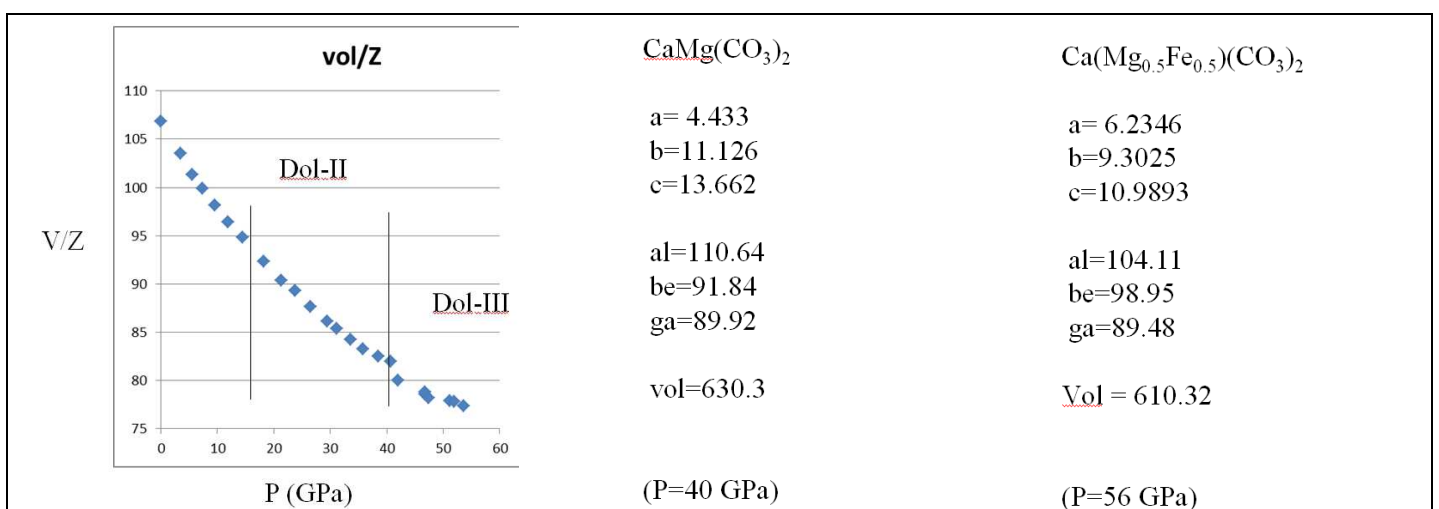


Figure 1- Volume data of dolomite (up to 50 GPa) and unit cell of dolomite-III in pure dolomite and in Fe-dolomite [ref. 1]

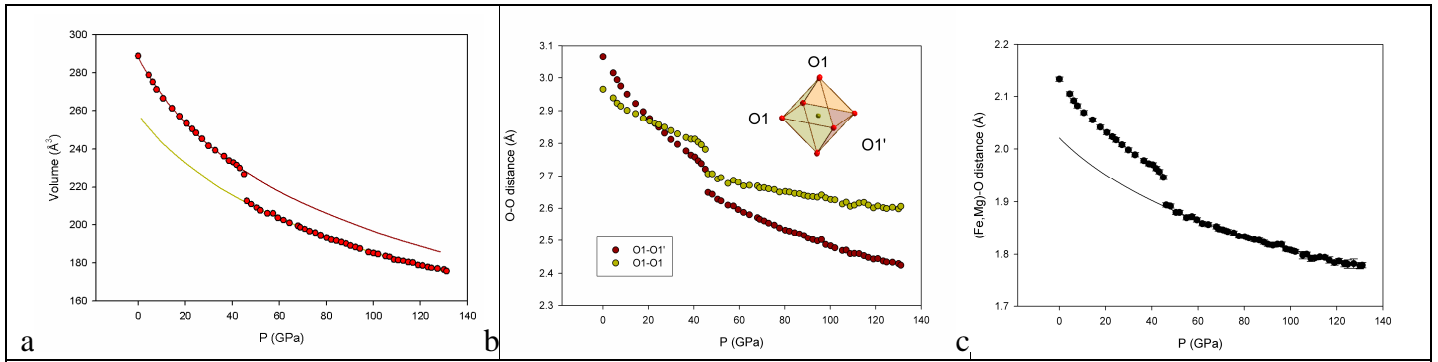


Figure 2 – Volume data for Fe-magnesite (a); structural distortion of coordination polyhedra, indicated by the O-O distances (b); (Fe,Mg)-O distances (c)

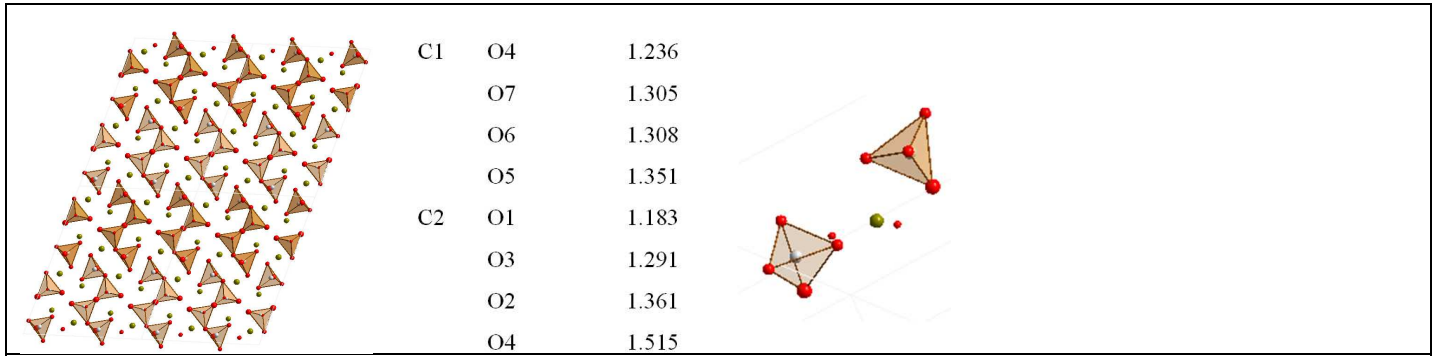


Fig 3 – Crystal structure and CO₄ polyhedra with reported interatomic distances of Mg₂Fe₂C₄O₁₃ at 130 GPa

References

- [1] Merlini et al. (2012). Structures of dolomite at ultrahigh pressure and their influence on the deep carbon cycle. PNAS, 109(34), 13509-13514.
- [2] Merlini & Hanfland (2013). Single-crystal diffraction at megabar conditions by synchrotron radiation. High pressure research, on-line first
- [3] Merlini et al. (2012). CaCO₃-III and CaCO₃-VI, high-pressure polymorphs of calcite: Possible host structures for carbon in the Earth's mantle. Earth and Planetary Science Letters, 333-334(1), 265-271