ESRF	**Experiment title:** Carbonate structure in deep Earth's mantle.	**Experiment number**: HS-3697
Beamline:	**Date of experiment**: from: 23/10/2008 to: 28/10/2008	**Date of report**: 24/08/09
Shifts:	**Local contact(s)**: Mr Jean Philippe PERRILLAT	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

E. Boulard*, G. Fiquet*, F. Guyot*, J. Siebert*, D. Antonangeli*

IMPMC, Equipe de Minéralogie, UMR CNRS 7590, Campus Boucicaut, 140 rue de Lourmel, 75015 Paris

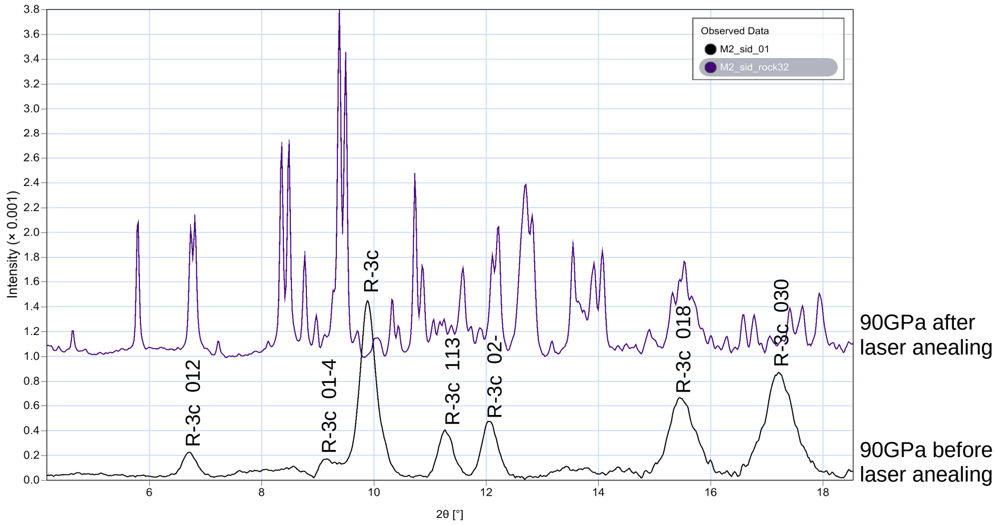
Report:

Carbonates such as magnesites ($MgCO_3$) and siderites ($FeCO_3$) are likely to be the carbon bearing phases in the deep mantle (see references (1) and (2)). The stability of these carbonates versus decarbonation and melting is therefore of great interest for understanding the global carbon cycle. Several phase transitions and reactions can affect the stability of these carbonates: (i) transformation to new crystalline phases, (ii) melting, (iii) decarbonation (iv) solubilization in silicates.

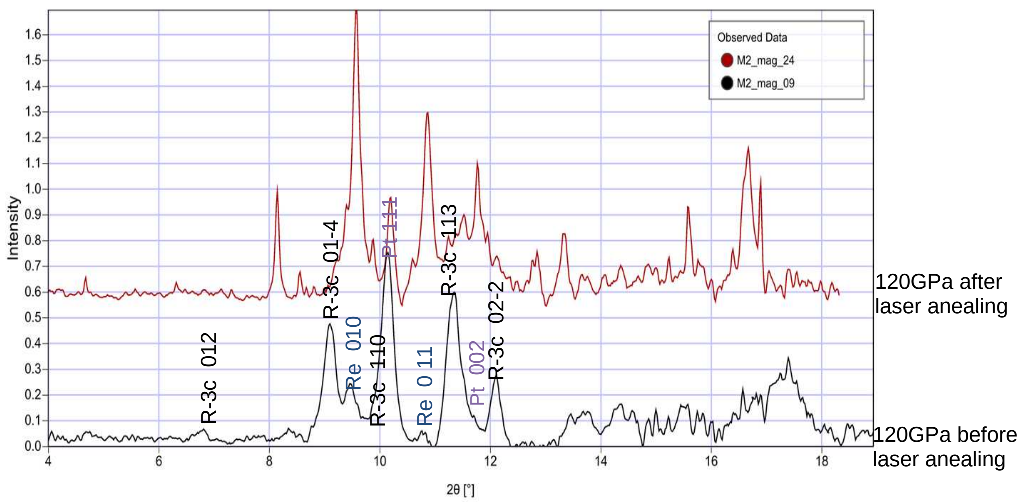
Thermodynamic properties and crystal structure of magnesite are already well documented for pressure under 80GPa (i.e reference (3) and experimental report HS622). At ambient conditions, magnesite crystallises in the calcite structure in the rhomboedral space group R-3c. Above 80GPa, G. Fiquet et al. (2002) observed a phase transition after laser-heating. A transition, possibly identical, was also observed by Isshiki et al. (see references (4)) above 115GPa, but the structure could not be identified with this experiment. Theoretical calculations attempted to solve this issue: several works showed that this post-magnesite structure could be a pyroxene-type structure either in the space group C2/c (see references (5)) or C2221 (see references (6)), thus demonstrating a possible new local environment for carbon in high-pressure structures. This question is central for the state of carbon in the deep Earth and the global carbon budget of our planet.

In order to study the pressure - temperature stability field of carbonate and study the possible high pressure phases, natural carbonates of different composition were loaded into laser heated diamond anvil cells : $(Fe_{0.6},Mg_{0.4})CO_3$ and $MgCO_3$.
Samples were subsequently transformed and analysed at hight pressure – high temperature by X-ray diffraction (XRD) collected on a CCD detector using the state-of-art double laser heating system available on the ID27 beamstation. Experiments were carried out between 55 and 120 GPa, and 1500-3000 K, covering lower mantle conditions. After the experiment recovered samples were prepared by focused ion beam milling (FIB) for scanning and transmission electron microscopy observations (SEM and TEM) and for scanning transmission X-ray microscopy analysis (STXM).

For both carbonate composition, an important change in the crystal structure was observed.



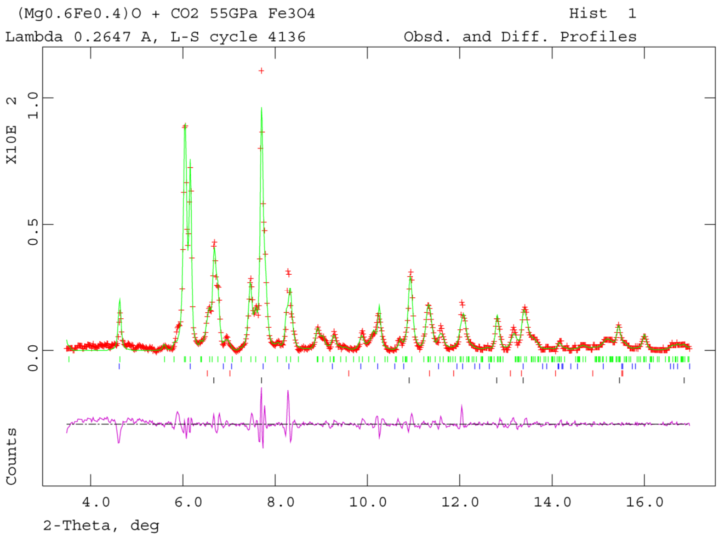
In the case of $(Fe_{0.6},Mg_{0.4})CO_3$ siderite, before laser heating the XRD pattern can be indexed in the R-3c structure, after laser heating a change of crystal structure occured, its structure refinement is still under process.

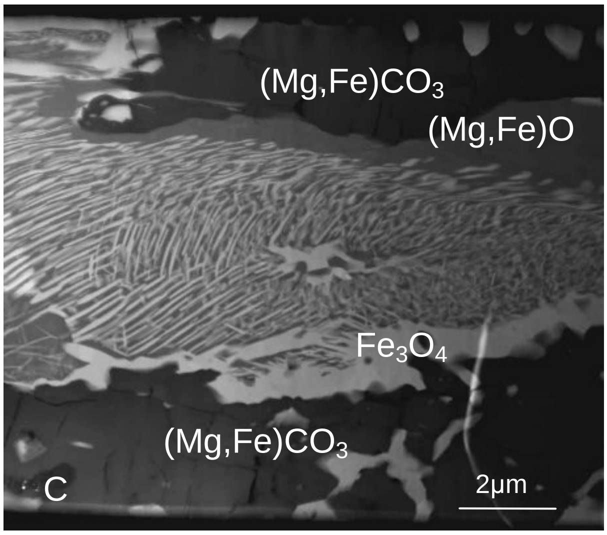


In the case of $MgCO_3$, the new structure obtained is in good agreement with the one observed by Fiquet et al (2002) and Isshiki et al (2004),the refinement is still under process.

In a second set of experiment we looked at the possibility of a reversal reaction of decarbonatation by loading Fe-Mg oxides (FeO, $(Fe_{0.4},Mg_{0.6})O$ and MgO) into CO_2 gas.

The recombination of oxides into a carbonate phase has been observed for the three different oxides composition, confirming the stability of carbonates up to 80GPa (i.e. reference 3). An exemple of a XRD diffraction and a STEM picture of the recovered sample are represented bellow, these were obtained at 55GPa-1500K from $(Fe_{0.4},Mg_{0.6})O$ loaded into CO_2. TEM obersvations and LeBail refinement yielded a mineralogy composed of ferro-periclase (Fe,Mg)O, magnesite $((Mg,Fe)CO_3)$, magnetite (Fe_3O_4) and nano-diamond.





References :

(1) Wood, Pawley and Frost, Water and carbon in the Earth's mantle, Phil. Trans. R. Soc. Lond. A, 354, 1495-1511,1996.

(2) Biellman, Guyot, Gillet, Peyronneau, Reynard , Experimental evidence for carbonate stability in the Earth's lower mantle, Earth Planet. Sci. Lett., 118, 31-41, 1993.

(3) Fiquet, Guyot, Kunz, Matas, Andrault and Hanfland, Structural refinements of magnesite at very high pressure, Am. Miner., 87, 1261-1265, 2002.

(4) Isshiki, Irifune, Hirose, Ono, Ohishi, Watanuki, Nishibori, Takata and Sakata, Nature, 427, 60-63,2004.

(5) Skorodumova, Belonoshko, Huang, Ahuja and Johansson, Stability of the $MgCO_3$ structures under lower mantle conditions, Am. Miner., 90, 1008-1011, 2005.

(6) Oganov, glass and Ono, Stability of magnesite and its high-pressure form in the lowermost mantle, Earth and Planet. Sci. Lett., 241, 95–103, 2006.