ESRF	**Experiment title:** Carbon speciation in the Earth's lower mantle.	**Experiment number**: HS-3828
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Shifts:	**Local contact(s)**: Mr Jean Philippe PERRILLAT	*Received at ESRF:*

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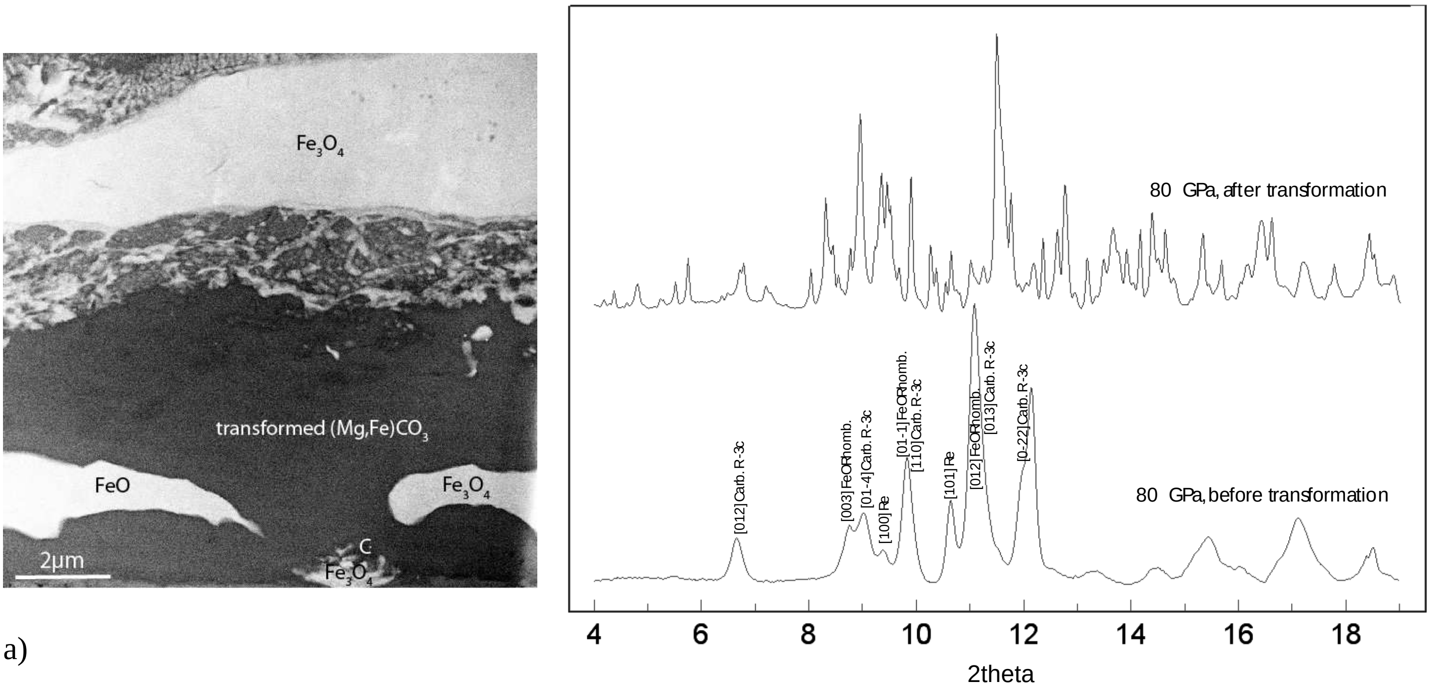
Report:

The mantle is thought to be the largest carbon reservoir. Carbon (C) is mainly found in two different states at the surface: oxidized in carbonates and reduced in the organic matter. C is recycled into the mantle through subduction but its oxidation state at depths remains unknown. Mantle oxygen fugacity (fo_2) is the major parameter used for defining the stability of C-bearing phases in Earth, such as diamonds and carbonates.

Measurements on mantle natural samples (*e.g.* 1) and experimental works (*e.g.*2) have evidenced a general decrease in fo_2 with depth resulting from the effect of pressure on the Fe^{3+}/Fe^{2+} equilibrium at a level where iron metal becomes stable in a large portion of the deep mantle. Moreover, the early Earth's mantle redox state has probably evolved from reducing conditions during core segregation to more oxidized present-day conditions (3). Thus, the influence of fo_2 heterogeneous spatial and temporal conditions in the Earth's mantle has important implications for the speciation and cycling of C phases in Earth today and during its early evolution.

In order to evaluate the major mantle inter-conversion reactions between reduced C and oxidized C at relevant pressure and temperature conditions, fine powders of either "FeO + carbonates" or "Si metal + carbonates" were loaded into the laser heated diamond anvil.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 100 GPa, and 1500-2500 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).

An exemple of a STEM picture of the recovered sample are represented bellow, these were obtained afeter transformation of FeO + $FeCO_3$ assemblage at about 80 GPa-2200K.TEM observations yielded a mineralogy composed of wustite (FeO), siderite ($(Mg,Fe)CO_3$) or tranformed siderite (at pressure above 80 GPa), magnetite (Fe_3O_4) and nano-diamonds.
The XRD pattern collected *in situ* at pressure above 80 GPa is more complex because of the presence of high pressure phases not reported yet. An exemple of a XRD pattern is shown bellow. We tentatively interpreted this XRD pattern as a mineral assemblage of a high pressure phase of magnetite (nce 4), wustite, and a high pressure phase of carbonate.



a)

b)

Figure 1. a) STEM picture of the recovered sample in which one can see the mineral assemblage
b) XRD pattern of FeO + $FeCO_3$ assemblage before and after laser heatig anealing

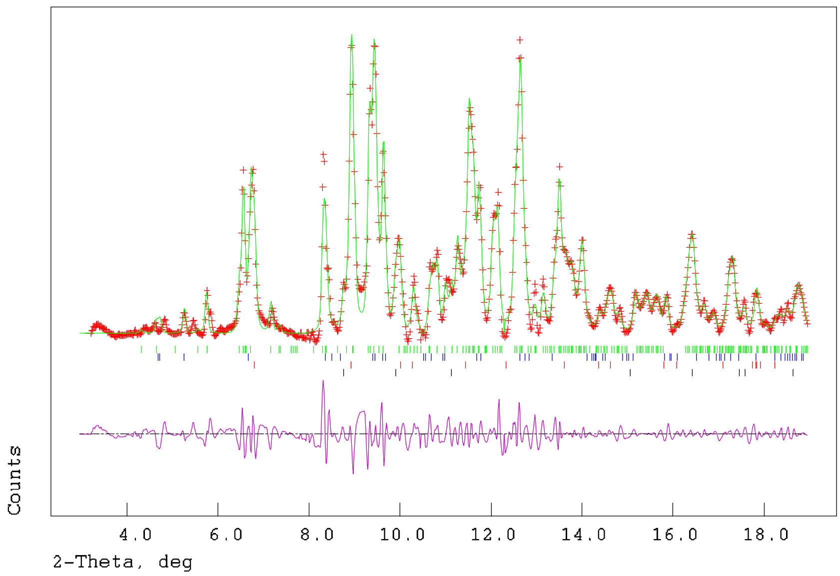


Figure 2. X-ray diffraction pattern of FeO + $FeCO_3$ assemblage transformed at 80 GPa and room temperature. Crosses represent observed diffraction data and solid line the profile refinement. The background has been subtracted. For the refinement we used an assemblage of high pressure carbonate phase – upper tick, high-pressure phase of magnetite (4) – tick bellow, untransformed siderite (space group R-3c) – middle ticks, and the untransformed wustite (lower ticks). Residual between observations and fit is shown below the spectrum

References :

(1) A.B. Woodland, J. Kornprobst & A. Tabit, ferric iron in orogenic lherzolite massifs and controls of oxygen fugacity in the upper mantle Lithos, vol. 89: 222–241, 2006.

(2) D.J. Frost, C. Liebske, F. Langenhorst, C.A. McCammon, R. G. Trønnes & D. C. Rubiel, experimental evidence for the existence of iron-rich metal in the Earth’s lower mantle, Nature, vol.428: 409-412, 2004.

(3) B. J. Wood, M. J. Walter, J. Wade, accretion of the Earth and segregation of its core, Nature, vol. 441 (7095): 825-833, 2006

(4) C. Haavik, S. Stolen, H. Fjellvag, M. Hanfland, D. Hausermann, Am. Miner. 85, 514 (2000).