ESRF	**Experiment title:** CO$_4$ tetrahedra-bearing carbonates stability in the lower mantle	**Experiment number**: ES-94
Beamline: ID27	**Date of experiment**: from: 27/11/ 2013 to: 04/12/ 2013	**Date of report**:
Shifts: 18	**Local contact(s)**: Gaston Garbarino, Volodymyr Svitlyk	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

E. Boulard[1] *, W.L. Mao[1], G. Fiquet[2]*,G. Morard [2]*, A-L Auzende[2]*,

[1]Stanford University, Stanford, U.S.A.

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

Report:

The aim of this experiment was to study carbonate stability and its solubility within mantle silicate phases. Mg,Fe-rich carbonates play a key role on the geodynamic carbon cycle as they are the main oxidized carbon-bearing phase deep in the Earth. In our previous studies on iron-bearing carbonates stability, two new high P-T phases were observed for two compositions: (1) the (Mg,Fe)CO$_3$ system above 85 GPa – 2000 K (. Boulard et al., 2011) and (2) the FeCO$_3$ composition above 40 GPa – 1500 K (E. Boulard et al., 2012). In both structures *ex situ* analyses showed drastic changes in the crystal chemistry : 1) a change in the carbon environment as carbon formed CO$_4$ tetrahedra instead of the CO$_3$ groups normally seen in carbonates 2) the two new high P-T phases are Fe^{3+} bearing phases (E. Boulard et al., 2012; E. Boulard et al., 2011). Such changes may influence carbonate –silicate reactivity at lower mantle conditions. Here, we used *in situ* XRD in order to study the stability of the Fe^{2+}-rich carbonate and Fe^{3+}-rich high-pressure phases of carbonate in equilibrium with bridgmanite at lower mantle conditions.

Starting materials were mixtures of powdered synthetic silicate (enstatite, $Mg_{0.8}Fe_{0.2}SiO_3$) and natural carbonate. We used four different mixtures compositions. The goal of the present study was to investigate the effect of the Fe-content, for that we used three different composition of carbonate: $Mg_{0.25}Fe_{0.75}CO_3$, $Mg_{0.44}Fe_{0.56}CO_3$ (Mg-siderite) and MgCO$_3$ (magnesite). In addition, in order to study the effect of the amount of Fe^{3+} in the silicate phase, we performed experiments with $Mg_{0.25}Fe_{0.75}CO_3$ together with synthetic Al-bearing bridgmanite glass prepared by aerodynamic levitation at I.M.P.M.C. (cf Auzende et al., 2011).
For each composition, XRD have been collected at high pressure and high temperature in three different pressure ranges:
- below 50 GPa: below the Fe spin transition in siderite
- between 50 and 80 GPa : above the Fe spin transition in siderite
- above 80 GPa: above the phase transition of magnesite and siderite.

At pressure below 50 GPa, bridgmanite together with carbonate are observed in the XRD patterns during and after laser heating. Little differences are observed between mixture with Al-bearing silicate and Al-free silicate. However, all experiments conducted with Mg-siderite result in the formation of magnetite which was not observed in the case of magnesite as the starting carbonate (Figure 1).

Above 80 GPa, magnesite and siderite transformed into a high pressure phase. In agreement with our previous study (see report HS3697, Eglantine Boulard et al., 2011), we observed the transformation of magnesite into the post-magnesite phase with a monoclinic structure. As shown in Figure 2, $MgCO_3$ + $Mg_{0.8}Fe_{0.2}SiO_3$ experiments led to the formation of the post-magnesite together with bridgmanite. Again, experiments conducted with Fe-rich carbonate led to redox reaction hence a more complex mineral assemblage is observed. Further *ex situ* analyses are under process in order to obtain information on these mineral assemblages.

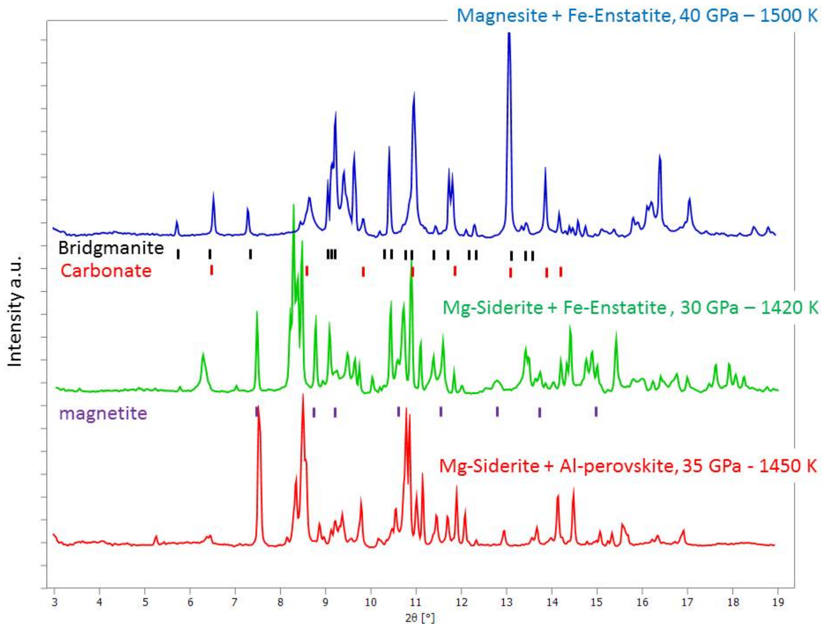

Figure 1:
XRD patterns of three different starting material mixtures at pressure between 30 and 40 GPa (below the Fe spin transition in siderite).

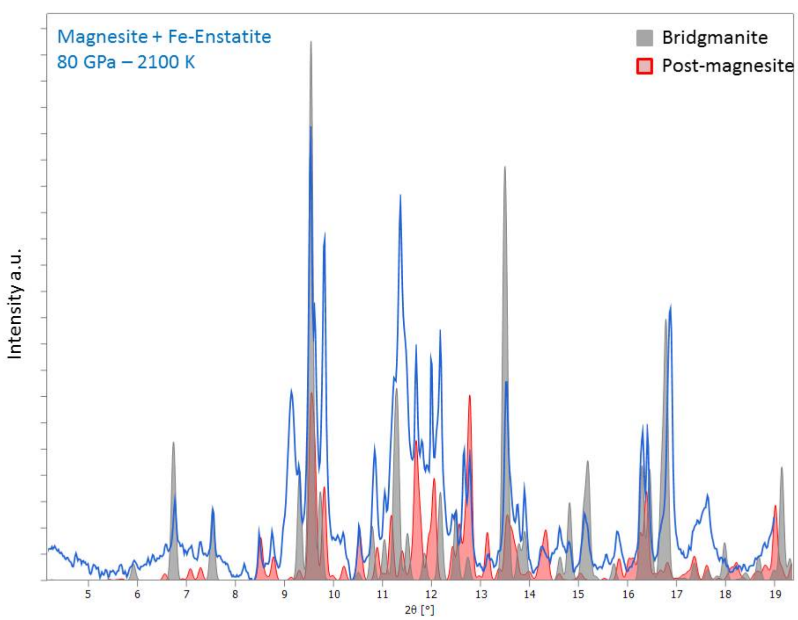

Figure 2:
XRD pattern of $MgCO_3$ + $Mg_{0.8}Fe_{0.2}SiO_3$ at about 80 GPa and 2100 K(above the carbonate high pressure phase transition).

References:

Auzende, A.-L., Gillot, J., Coquet, A., Hennet, L., Ona-Nguema, G., Bonnin, D., … Fiquet, G. (2011). Synthesis of amorphous MgO-rich peridotitic starting material for laser-heated diamond anvil cell experiments – application to iron partitioning in the mantle. *High Pressure Research*, *31*(1), 199–213. doi:10.1080/08957959.2011.556631

Boulard, E., Gloter, A., Corgne, A., Antonangeli, D., Auzende, A., Perrillat, J.-P., … Fiquet, G. (2011). New host for carbon in the deep Earth. *PNAS*, *108*(13), 5184–5187. doi:10.1073/pnas.1016934108/-/DCSupplemental.www.pnas.org/cgi/doi/10.1073/pnas.1016934108

Boulard, E., Menguy, N., Auzende, a. L., Benzerara, K., Bureau, H., Antonangeli, D., … Fiquet, G. (2012). Experimental investigation of the stability of Fe-rich carbonates in the lower mantle. *Journal of Geophysical Research*, *117*(B2), 1–15. doi:10.1029/2011JB008733