DIAMOND FORMATION IN CORE SEGREGATION EXPERIMENTS. J. Siebert[1], F. Guyot[1], V. Malavergne[2] and M. Chaussidon[3], [1] Laboratoire de minéralogie-cristallographie et institut de physique du globe de Paris, 4 place jussieu, 75252 Paris cedex 05, France. *julien.siebert@lmcp.jussieu.fr*, *François.Guyot@lmcp.jussieu.fr*, [2] Université de Marne-La-Vallée, Laboratoire des géomatériaux, cité Descartes, Champs-sur-Marne, 77454 Marne-La-Vallée cedex, France. *malaverg@univ-mlv.fr* ,[3] CRPG-CNRS, BP 20, 54501 Vandoeuvre-lès-Nancy cedex, France. *chocho@crpg.cnrs-nancy.fr*

Introduction: Heterogeneous accretion models imply a first accretion stage with highly reduced materials e.g. [1]. The presence of silicon in the metal that segregates to form the core is a simple way to obtain such reducing conditions [2,3]. During this stage of accretion (80-90 % of the final Earth), the terrestrial accreting material might be a mixture of reduced, volatile-free components and oxidized, volatile-rich components in minor proportions (e.g., mixture of EH and CI chondrites). Mixing carbonates with silicon-rich alloys is relevant to such Earth's primitive conditions. This could bring constraints on carbon evolution during core-mantle differentiation and permit to discuss if the combination of carbon and silicon is relevant for core composition.

Results and implications: Multi-anvil press experiments were performed on different assemblages of siderite ($FeCO_3$) and silicon-rich metal systems, between 10 and 25 GPa and up to 1800°C. Different reducing conditions were tested by varying the starting silicon proportions in metal. The following reactions describe the recovered samples observations (Fig.1):

$$2\,FeCO_3 + 3\,Si = 2\,Fe + 3\,SiO_{2\ \text{stishovite}} + 2\,C_{\text{diamond}} \quad (1)$$

or in a simplest way:

$$CO_{2\ \text{(in siderite)}} + Si_{\text{in metal}} = SiO_{2\ \text{stishovite}} + C_{\text{diamond}}$$

Euhedral diamonds have thus been synthesized using a carbonate as an unique carbon source. These experiments provide a new possible mechanism for spontaneous growth of diamond in the Earth's primitive mantle. The redox conditions of our experiments are very reduced because of the high initial silicon content in metal. The fO_2 conditions of experiments were then estimated relative to the Si-SiO_2 buffer (Fig. 2) and present a good coherence with the observations.

Some geochemical mass balance calculations imply core models with significant silicon amounts (e.g. 7 wt % of silicon are required for explaining the Mg/Si ratio of the Earth's primitive mantle relative to CI chondrites) [4, 5]. Such silicon content in the metal phase combined with P, T, fO_2 conditions relevant for core formation scenario implies low oxygen fugacities in the primitive Earth under which no carbonates would thus be stable (Fig. 3). Our experiments show that reduced carbon is in the form of diamond and not Fe_3C, suggesting that incongruent melting of Fe_3C occurs below 2000 K at 10 GPa and 25 GPa.

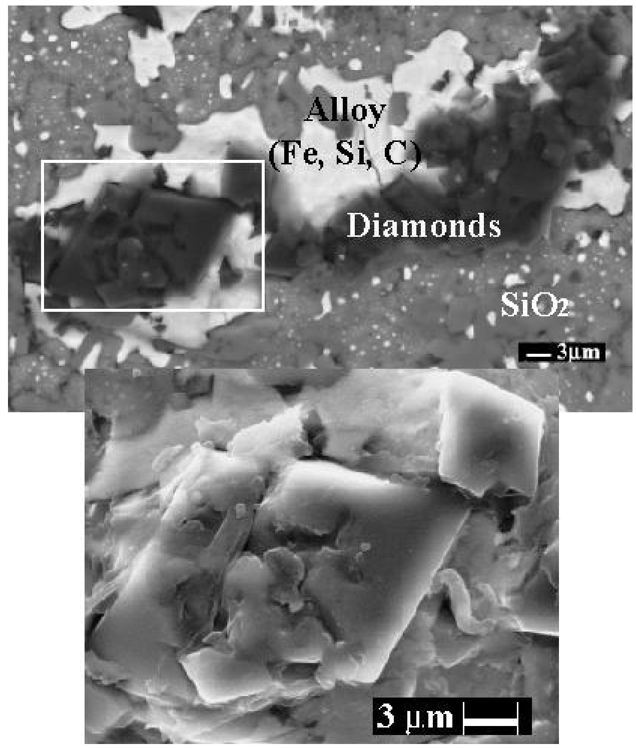

Figure 1. Backscattered and secondary electron images of sample S3264 (20 GPa, 1700 °C) and enlargement of the region enclosed by the white frame showing the products of experiments described in reaction (1). The size of diamonds can reach up to 20 µm. Diamonds have crystallized in the form of octahedral.

Moreover, the presence of diamond embedded in metal is a proof of carbon saturation. Thus, the observed diamond saturation is a good way for estimating the carbon solubility in metal under high pressure conditions. Preliminary results on carbon contents in metal were obtained by ion microprobe measurements and found to be close to 1.5 wt % (±0.3 wt %) at 20 GPa and 1800 °C. These first measurements show a discrepancy with thermodynamic calculations of carbon solubility at high pressure [6]. If confirmed, this would imply a possible loading of carbon in metal at upper mantle conditions and a subsequent exsolution of diamonds (and not Fe_3C) at higher pressures. This could provide mechanisms for a primitive diamond reservoir in the mantle or for diamond formation at the core-mantle boundary. However, further measurements of carbon concentrations in metal with alternative analytical techniques are necessary to confirm or infirm this hypothesis.

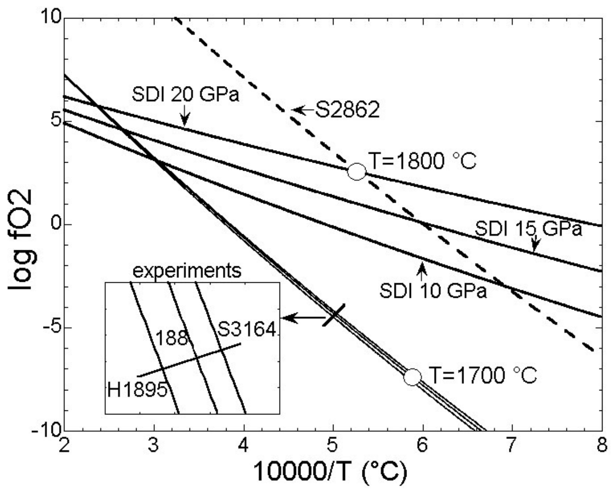

Figure 2. Oxygen fugacities in four experiments: S2862 and S3164 at 20 GPa; 188 at 15 GPa; H1895 at 10 GPa. The fO_2 (P, T) of experiments are calculated relative to the Si-SiO_2 [a] buffer using the measurements of silicon contents in Fe-rich metal alloy. The fO_2 are then plotted at the temperature of experiments. Large calculated variations of Si contents in metal phases (S2862 contains trace of silicon in metal while H1895, 188, S3164 contain amounts >20 wt %) are consistent with the observations. The stability of siderite is described by the position of the SDI [b] buffer determined at 10, 15 and 20 GPa. In the temperature range studied, presence of silicon in the metal phase is not compatible with stable siderite.

[a] $Si + O_2 = SiO_2$
[b] $FeCO_3 = Fe + C_{diamond} + 3/2\ O_2$
(Siderite-Diamond-Iron)

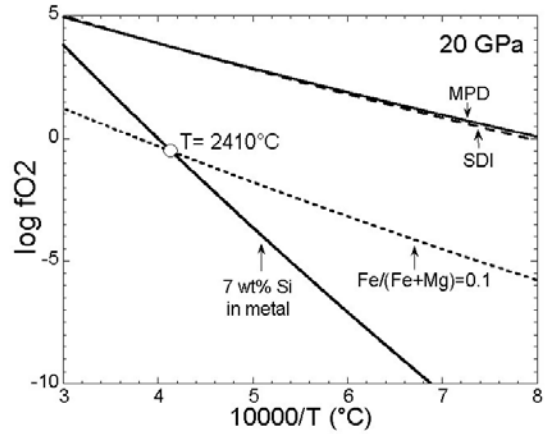

Figure 3. fO_2 conditions plotted at temperatures required for generating a core containing 7 wt % Si and a FeO content in silicates consistent with the current FeO content of the mantle. The buffers are calculated relative to Si-SiO_2 and IW [c] at 20 GPa. This redox condition estimated for the primitive Earth is well below the field of fO_2 at which carbonates would be stable, as represented by the SDI and MPD buffers.

[c] $FeO = Fe + 1/2\ O_2$
(Iron-Wüstite)
[d] $MgCO_3 = MgO + C_{diamond} + O_2$ (Magnesite-Periclase-Diamond)

References: [1] Wänke H. and Dreibus G. (1988), *Phil. Trans. Roy. Soc. Lond.*, *A325*, 545-557. [2] Malavergne et al. *GCA*, *(in press)*. [3] Siebert et al. *PEPI, (in press).* [4] Allègre et al. (2001) *EPSL*, *185*, 49-69. [5] Javoy M. (1995), *GRL*, *22*, 2219-2222. [6] Wood B.J. (1993). *EPSL*, *117*, 593-609.