



Siderite breakdown and pressure induced Fe-C redox reactions

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Siderite, FeCO_3 , was investigated at high pressure (up to ~ 40 GPa) and high temperature (up to about 2400K) using a laser heated diamond anvil cell. The structure of the sample was probed with a synchrotron monochromatic beam; powder, multigrain and single crystal diffraction techniques were used according to changing size of the crystallites in the course of the experiment. At about 35 GPa we observed the breakdown of the carbonate into h- Fe_3O_4 (the orthorhombic high pressure phase of Fe_3O_4 [1]) and undetected carbon phases. We suggest the breakdown was achieved through a redox reaction where the iron formal valence is increased at the expense of the carbon reduction. This observation is in agreement with results of shock experiments on siderite [2-4] in which however the presence of hematite in the starting material prevented to discriminate among possible reactions determining the synthesis of Fe_3O_4 .

Oxygen fugacity and the crystal chemistry of deep Earth mineral assemblages exert a major control on ionic speciation, therefore experimental confirmation are necessary to determine the actual redox equilibrium between iron and carbon in the mantle. Remarkably, perovskite strongly favor the partitioning of Fe^{3+} [5] and so it might favor the C reduction. If the pressure effect on Fe-C redox equilibrium found in this experiment is active in the deep Earth, the speciation of carbon would be strongly affected, in particular, the stability of carbonates and CO_2 might be controlled by pressure induced reductions rather than by the stability of the pure phases. Carbon reduction at pressure might account for the greater subduction of carbon with respect to hydrogen [6]. On the other hand uplifting of reduced carbon assembly might release C-O fluids through reduction of Fe^{3+} . Our results suggest that Fe-C redox reactions might have a crucial role on the carbon speciation which has a major importance on deep Earth processes.

References

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