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Carbon-silicate-Fe metal reactions at high pressures: New experimental constraints on deep volatile cycles

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Carbon and hydrogen are most important and are among the most uncertain constituents in the Earth's deep interior. Due to significant solubility in the Fe-metal these volatiles can be strongly partitioned to the Earth's core during its formation, if present in significant amounts in the early Earth. In this presentation we would like to review our resent results on carbon-hydrogen-metal and carbonate-silicate-metal equilibria at pressures up to about 30 GPa using multianvil technique. In situ X-ray diffraction experiments were performed at the synchrotron radiation facility SPring-8. We studied following systems: $MgCO_3$+SiO_2, $CaCO_3$+SiO_2, $MgCO_3$+Fe, and $CaCO_3$+Fe. Preliminary results for in situ data for the $Mg(OH)_2$+C+Fe and $Ca(OH)_2$+C+Fe systems and laboratory experiments on peridotite and eclogite coexisting with reduced C-O-H fluid are also discussed.
The reaction of $MgCO_3+SiO_2= MgSiO_3+CO_2$was studied using both the multianvil and diamond anvil cell (DAC) technique. We observed melting reaction at pressures up to about 32 GPa. Decarbonation was observed at pressures below 6 GPa and, surprisingly, in the short pressure interval of wadsleyite + stishovite stability (in $MgSiO_3$system) near 16 GPa. In all other experiments reaction proceeds with the formation of $MgSiO_3$phase and melt. The Mg/Si ratio of partial melt, coexisting with Mg-perovskite, was 1.7-2.0 whereas at lower pressures this ratio is 2.3-2.5. Formation of Mg-perovskite was observed in DAC experiments at pressures 25-100 GPa, however, $CO_2$was not detected by in situ X-ray diffraction or in situ Raman spectroscopy, which may indicate melting reaction at higher pressure also. The reaction $CaCO_3+SiO_2= CaSiO_3+CO_2$was studied at pressures 3-22 GPa. In contrast to the Mg-system we observed the formation of CO_2 fluid at 6-10 GPa and melting at 16-17 GPa. The partial melt has a Ca/Si ratio of 2.3-3.0. The reactions $MgCO_3$+Fe and $CaCO_3$+Fe were also studied at 6 and 15-16 GPa. We observed fast formation of Fe3C in the Mg-system at 900-1000°C, according to the reaction $MgCO_3+5Fe = Fe_3C+3(Fe_{0.67}Mg_{0.33})O$. In the Ca-system the reaction proceeds with formation of Fe_3C and Ca-rich melt with a Ca/Fe ratio of near 4.
In discussion, we outline (a) relative stability of Fe-hydride and Fe-carbide and their role in core formation and metal precipitation, (b) possibility of carbonate reduction during deep subduction, (c) possible role of melting in COH-fluid equilibria with mantle assemblages, (d) comparison of mantle solidi under reduced and oxidized conditions up to lower mantle P-T conditions.

Keywords: carbon, hydrogen, iron, carbonate, mantle, core