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# Experimental study of carbonate-silicate-metal equilibria at pressures to 30 GPa: New insights into deep volatile cycles

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Carbon and hydrogen are among the most important, but uncertain constituents in the Earth's deep interior. In this presentation we will review resent results on 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 have studied the following systems: $MgCO_3$+$SiO_2$, $CaCO_3$+$SiO_2$, $MgCO_3$+Fe, and $CaCO_3$+Fe. Preliminary results from *in situ* measurements for the $MgCO_3$+$H_2O$+Fe and $CaCO_3$+$H_2O$+Fe systems and from laboratory experiments on peridotite and eclogite, coexisting with ultra-reduced C-O-H fluids, will also be 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 $Fe_3C$ in the Mg-system at 900-1000$^o$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.