



## **The speciation of carbon in the Earth's mantle as a function of oxygen fugacity**

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The residence time of carbon in the mantle depends crucially on the conditions under which it is stable within melts or fluids, compared with conditions under which it forms solid phases. At a given pressure and temperature the stability of carbonate-bearing minerals and melts (carbonatites and kimberlites) relative to graphite/diamond depends on oxygen fugacity. In this study, the oxygen fugacity buffered by equilibria involving both elemental carbon (graphite or diamond) and carbonate (minerals or melts) were determined in a simplified Fe-Ca-Mg-Si-O-C model peridotite composition at pressures between 2.5 and 25 GPa and temperatures at and above the carbonated peridotite solidus (1100-1600°C). Oxygen fugacities were measured using iridium-iron alloy as a sliding redox sensor. Above the carbonate peridotite solidus the silicate component of the melt increases with increasing temperature. The results show that this dilution of the carbonate melt with increasing temperature drives the equilibrium oxygen fugacity down compared to the extrapolation of carbon/carbonate equilibrium from previous studies.

In addition we have performed experiments in the Fe-Ca-Mg-Al-Si-O-C system to determine the Fe<sup>3+</sup> content of garnet at an oxygen fugacity buffered by the carbon-carbonate equilibria in a peridotite assemblage. The ferric iron contents of the garnet in the run products were determined by <sup>57</sup>Moessbauer spectroscopy. The results from these experiments allow the redox conditions of carbon and carbonate stability to be compared directly to the expected Fe<sup>3+</sup>/Fe<sup>tot</sup> ratios of mantle rocks. Further experiments were performed at pressures compatible with the Earth's mid lower mantle (approximately 50 GPa) and 1600-1700 °C using sintered diamond anvils. Such runs allowed us to estimate the likely redox conditions occurring in the lower mantle at which elemental carbon (diamond) might be equilibrated with carbonate, ferropericlasite and a metal phase.

Our results imply that: (1) in up-welling mantle beneath mid-ocean ridges, the relative oxygen fugacity of peridotitic rocks will increase on decompression. Diamond and then graphite are the dominant C-bearing phases at depth, but become oxidized by ferric Fe in garnet as a result of decompression. Only once graphite is oxidized, which will occur at relatively shallow depths, can small degree carbonate-rich melts form; (2) measurements of Fe<sup>3+</sup>/Fe ratios of garnets in equilibrium with graphite and carbonate are inconsistent with extrapolations of previously published oxythermobarometers; (3) the effect of pressure on the carbonate/carbon buffer indicates that the diamond stability field may not persist deep into the lower mantle, with carbonates being the stable host for carbon, probably in equilibrium with Fe-Ni carbide.