

The conditions of sublithospheric diamond formation constrained from ferric iron-rich exsolution from ferropericlyase inclusions.

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Ferropericlyase is apparently one of the more common inclusions to be found in sub-lithospheric diamonds, which are considered to form in the convecting mantle. Although relatively rare, these inclusions have been examined in a number of studies in the hope of providing information on the formation conditions of such deep diamonds, which could potentially be in the transition zone or lower mantle. The wide range of oxide Fe/(Fe+Mg) ratios found has raised the idea that they may form through the oxidation of iron metal. During TEM investigations, however, evidence for the exsolution of Fe₂O₃-rich phases such as magnesiowüstite have been found, which implies that a more complex scenario may be involved. Ferropericlyase-magnesiowüstite diamond inclusions are most likely some of the deepest available samples from the mantle and they potentially provide the most direct evidence for deep mantle carbon transport processes. The ferric iron contents of such inclusions alone may not provide a direct estimate for the oxygen fugacity at which the inclusions were trapped, particularly if pressure has a strong effect on the f_{O_2} - Fe³⁺/Fe_{tot} relationship. However, using experimental data it is possible to determine the oxygen fugacity at which the exsolution observed in the diamond inclusions occurred and coupled with the oxide Fe³⁺/Fe_{tot} ratio this could be used to estimate the pressure of formation.

The ferropericlyase- magnesiowüstite system has been investigated by several studies at room pressure but the stability field of the two components has been shown to become more complicated at high pressure due to the formation of mixed valence oxides. We have combined experimental measurements with thermodynamic modelling in order to address two main questions: at which P, T, f_{O_2} conditions do Fe₂O₃-rich phases exsolve from ferropericlyase? And what is the maximum Fe³⁺/Fe_{tot} ratio of ferropericlyase. To answer these questions, multianvil experiments have been performed between 6 –25 GPa and 1200-1800°C using a starting composition of (Mg₈₆Fe₁₄)O plus 20 % Fe₂O₃. Pt powder was added to the experiments to act as a redox sensor and minor amounts of Ni, Cr, Mn and Na were also added. Samples were then analyzed with the scanning electron microscope, electron microprobe, Mössbauer spectroscopy and X-ray diffraction. In the recovered experiments ferropericlyase coexists with magnetite-magnesiowüstite solid solution up to 10 GPa and Mg₂Fe₂O₅-Fe₄O₅ solid solution at higher pressures. In the calculation of the oxygen fugacity a ferropericlyase model in the FeO-Fe_{2/3}O-MgO system was employed and exchange of Mg and Fe²⁺ in magnetite was accounted for. Oxygen fugacities at which the phases coexist can be calculated in the magnetite-magnesiowüstite field using three different equilibria and a quite simple ferropericlyase mixing model results in calculated oxygen fugacities that are within 0.1 log units of each other for all three equilibria. The results show that magnetite-magnesiowüstite solid solution should not be in equilibrium with ferropericlyase in the diamond stability field. Our results imply that the exsolution of Fe³⁺ rich phases observed in natural samples likely occurred at pressures corresponding to the transition zone or deeper.