Carbon speciation and mantle metasomatism

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Three intensive parameters constrain the speciation of carbon in the Earth's mantle: temperature, pressure and oxygen fugacity (fO_2). The conditions of diamond stability are bounded in pressure and temperature by the diamond-graphite equilibrium curve. The upper fO_2 limit for stability of elemental carbon in peridotite is constrained by the reaction: Enstatite + Magnesite = Forsterite + C + O_2 (EMOD/G) [1]. In P-T-fO_2 space the intersection of these planar boundaries defines three volumes of mantle carbon speciation – diamond stability at high pressure and low fO_2, graphite stability at low pressure and low fO_2, carbonate stability at high fO_2.

We calculated the fO_2 of peridotite xenolith samples from the Kimberley Mines, South Africa based on ferric iron concentrations in pyropic garnets obtained by adapting a recently developed electron microprobe technique [2] to garnets with low total Fe concenrations. The fO_2 of these rocks ranges from ~5 log units below the fayalite-magnetite-quartz reference buffer (FMQ) to greater than FMQ-1. Kimberley peridotite samples are present in each of the three carbon speciation volumes.

The oxidation state of the peridotite samples is correlated with trace element evidence for mantle metasomatism. Three distinct chondrite-normalized rare earth element (REE_N) patterns are observed in garnets from the studied Kimberley xenoliths – sinusoidal, humped and normal. The sinusoidal pattern indicates metasomatic re-enrichment by an agent with a high $LREE_N$ to $HREE_N$ ratio.. Humped patterns have a positive slope from $LREE_N$ to $MREE_N$ with a plateau at ~10-20 times chondritic abundance from Sm to Gd followed by a negative slope to the $HREE_N$. Normal patterns show a positive slope in the $LREE_N$ towards flat $MREE_N$ to $HREE_N$ at ~10 times chrondritic abundance. The Gd/Sm ratio is a measure of the degree of sinuosity of REE_N patterns. The Gd_N/Sm_N ratio is <1 for sinusoidal patterns, ~1 for humped patterns, and >1 for normal patterns. The most reduced samples have the lowest Gd/Sm ratio and therefore, have garnets with sinuous REE_N patterns. The humped and normal patterns are observed in garnets from the more oxidized lherzolites, including those that lie in the carbonate stability volume. This suggests that metasomatic re-enrichment of the lithospheric mantle beneath Kimberley lead to oxidation of the lithosphere and destruction of diamond.

References

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[2] Höfer, H., et al., (2000) *Eur. J. Min.* **12,** 63-71