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Redox reactions caused by exsolution: A potential factor influencing mantle redox state and diamond formation

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Exsolution phenomena are not uncommon in solid solution minerals of crustal rocks that cooled from magmatic or high grade metamorphic conditions, but they are preserved only if the cooling history was not too slow as then exsolutions segregate to the rock matrix. Until recently, exsolution phenomena have not been linked to changes in redox conditions, but Proyer et al. [1] have shown that some types of exsolution, like that of rutile or ilmenite in garnet and some other rock-forming minerals requires additional (diffusional) exchange of ions with the rock matrix and that the fastest potential mechanism found to date is actually a redox mechanism. Ti on the octahedral site of garnet is replaced by a Fe^{2+} from the dodecahedral site, which, in the process, oxidized to Fe^{3+}. The net result of the entire complex reaction is release of Fe^0 (or Fe^{2+} + 2 e^-) from garnet, causing reduction in the environment.

This is supported by observations that primary rutile inclusions in garnet and sometimes matrix rutiles obtain a bluish to purplish black colour, which is a sign of increasing amounts of Ti^{3+} in the structure. Other evidence might be in some cases the formation of nano-diamonds or graphite in CO_2-bearing fluid inclusions.

If we consider the above observations and their interpretation valid, we can envision on a broader scale that any unmixing of Ti from a high-grade Fe-bearing mineral where Ti substitutes (mainly) for Al might operate in a similar fashion, i.e. the energy of lattice strain generates a diffusional reducing current to the matrix. If matrix reduction is very localized as by the formation of a few nuclei of a diamond from carbonate or CO_2-bearing pore fluid, a few larger crystals of diamond would buffer and accomodate the reduction reaction.

All minerals in an upwelling mantle current or convective flow would be subject to decompression, some cooling and an unknown degree of compositional adjustment. Exsolution phenomena can be expected in the uppermost asthenosphere where cooling starts to predominate over decompression effects. Material caught by deep and relatively cool cratonic roots might be a case in point. Hence this could be a place where exsolution of Ti-minerals (rutile or ilmenite) could create a transient reducing environment in which diamond formation could be favoured if oxidised carbon is present in some form. Ti-rich garnet could also be generated within cool lithospheric roots by the infiltration of hot Ti-rich fluids or melts from whatever mantle source, and later exsolve Ti again during cooling.

Even if later annealing or mantle metasomatism recrystallizes or dissolves Fe^{3+}-enriched garnet (as one example), that process might not result in the entire destruction of the reduced minerals formed, particularly if a mobile medium, like a kimberlite melt, gets extracted from the region.

References:

[1] Proyer A et al. (2013) Contrib. Mineral. Petrol. 166:211-234