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Reducing environment in chromitites: possible causes for PGE and diamond formation

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At least two interesting problems exist with regard to chromitites of different origin: One is exemplified by chromite-rich layers in layered intrusions which are also characterized by abundant sulfides and PGE enrichment. The other one are ophiolite-related chromitite pods, reported particularly from the Chinese part of the Himalayan mountain belt, where elaborate mineral separation efforts have led to the recovery of not only diamonds but also a great variety of highly reduced minerals like moissanite and metals. In addition to existing models, an alternative view is presented here, which highlights the potential crucial role of chromite itself as a trigger of reduction reactions in its vicinity.

This model is based on the evidence of high-grade garnets exsolving rutile and ilmenite which requires and open system behavior of the mineral, i.e. diffusional ion exchange with the matrix in order to accomplish exsolution [1]. Importantly the fastest exsolution reaction envisaged is a redox-reaction: Ti on the octahedral site 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 $\text{Fe}^{2+} + 2 e^-$) from garnet, causing reduction in the environment. This mechanism is possible because Fe can occur in garnet in two possible structural positions demanding different valence states. The same holds true for the spinel group.

More than 50 years ago the oriented intergrowths of magnetite with ilmenite were proven by experiment to result from unmixing of former Ti-rich magnetites (containing an ulvospinel component) by an oxidation reaction: $3 \text{TiFe}^{2+}\text{O}_4 + \text{O} = 3 \text{FeTiO}_3 + \text{Fe}_3\text{O}_4$. Such a reaction would reduce the environment. A potential ulvospinel component in chromite might exsolve in a similar way, but most chromites from the above mentioned occurrences do not show ilmenite lamellae. An alternative mechanism can be envisaged though, which also requires open system behaviour, perhaps in a slowly cooling environment: Lattice strain caused by reduced miscibility of ulvospinel causes Ti to diffuse out of the crystal, most likely in reduced form, while Fe is oxidized internally and a divalent ion from the matrix replaces Ti on its site: $\text{TiFe}^{2+}\text{O}_4 + \text{Fe}^{2+} = \text{Fe}_3\text{O}_4 + \text{Ti}^{3+} + e^-$.

A chromite-dominated rock could thus cause significant reduction in the rock matrix, which could result in PGEs precipitating, as well as available volatile species getting very reduced, thus potentially contributing to the formation of metals and elemental carbon, e.g. as diamond. The validity of this theory can be tested in several ways: The exsolved Ti should be found in some form in the vicinity and a significant difference in Ti-content and/or P-T history must exist between chromitites with and without reduced phases.

An entirely different alternative explanation is to assume the source of particular chromite occurrences and its PGEs or reduced minerals in the D'' layer at the bottom of the mantle, entrained by an ascending plume and deposited where this plume material is inserted into the crust. This hypothesis assumes that the D'' layer is largely a product of the differentiation of the metallic outer core and its interaction with

the lowermost mantle. As virtually nothing is known about the D'' layer, its chemical composition, processes and isotopic characteristics, this scenario is much more difficult to verify or falsify at this point.

References:

- [1] Proyer A et al. (2013) *Contrib. Mineral. Petrol.* 166:211-234
- [2] Buddington R and Lindsley P (1964) *J. Petrol* 5(2):310-357

