The Possibility of Survival of PGM Micro-Xenocrysts in Mantle Melts

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Solubilities of the PGE in mafic magma are still inaccurately known, since they depend upon many variables such as sulfur and oxygen fugacity, the exact nature of the chemical system being studied, and accurate determination of true concentrations in melts. Quoted values for PGE solubility can vary by orders of magnitude, sometimes even within systems which appear to be geochemically similar. Here we suggest that the key to PGE enrichment in magmatic ore bodies may lie, not in their solubility, but rather in the insolubility of the PGE phases in silicate systems.

In the literature the PGE are described as having a dual nature, both siderophile (e.g. in meteorites) or chalcophile - this latter behaviour forms the basis of the most popular models for PGE ore formation. It is thus appropriate for this discussion to examine the behaviour of PGE with respect to sulfides during fractional melting of the mantle. The PGE in mantle assemblages may occur either with the sulfide (perhaps in solid solution) or as discrete PGMs. Because of low solubility, as discussed below, the latter may never be melt significantly, and might enter the melt as microxenocrysts. As to the former, geochemical modelling indicates that the magma will initially be sulfur-saturated, and therefore that the proportion of sulfide in the restite will decrease as the melt fraction increases. However, the sulfide will not melt congruently, especially with respect to the PGE (Lindsay 1994). As long as there is residual sulfide left, most of the PGE in the system will probably remain associated with it. Thus, as the proportion of host sulfide decreases, the relative concentration of the PGE associated with it is likely to increase.

Ultimately, if the mantle melting event continues for long enough, a point will be reached when the remaining sulfide grains melt (this process has been described by O'Hara et al., 2001) and the PGE are likely to become liberated primarily at this point. Most mafic melts, such as the parental melts of the Bushveld complex, are generated at temperatures which are considerably lower than the melting points of mantle PGMs (probably mainly inter-PGE metallic alloys (McDonald, 1993)). Given the low solubility of

PGE in silicate melts, it is not unlikely that at least a portion of the PGE might enter the melt as unreacted micro- or even nano-crystals, "rather like diamonds in a kimberlite" (Tredoux et al, 1995, p. 163). This possibility was pointed out more than 20 years ago by Hiemstra (1979).

Because of extensive overlap of the dorbitals in the metallic bonds that would predominate in typical PGMs, phase surfaces of these micro-xenocrysts would be very different from the more rigid covalent structures in the surrounding silicate melt. This would restrict the interaction between the PGE micro-xenocrysts and the magma. The bonding energy within such metallic clusters are very high (Cohen and Knight, 1990) and it is unlikely that a Pt (or other PGE) atom at the surface of the clusters will 'leave' the structures. Therefore, the solubility of PGE in the silicate melt may be extremely small (Lindsay, 1989), in which case the concentrations of PGE being liberated by the final decomposition of sulfide may exceed their solubilities in the system. Hence, all of the PGE liberated from the mantle will not dissolve in the magma, but a significant proportion might remain as micro-xenocrysts of PGM or clusters of PGE atoms (Tredoux et al., 1995). Given their small size (in the order of tens of nanometers or even less (Buffat and Borel, 1976)). they will be suspended in the magma due to Brownian movement. Thus, the PGE are liberated from the mantle, but never fully dissolved in the magma. In this way, apparent supersaturation in the magma is created because the insoluble material is so extremely fine-grained. For example, the parent magma to the Bushveld Complex is considered to contain over 30 ppb of PGE (Davies and Tredoux, 1986). Such high values may exceed the true PGE saturation limits for these reasons. Tiny PGM grains or clusters may survive indefinitely in the magma, and may be finally extracted by physical, rather than chemical, processes (Hiemstra, 1986, Tredoux et al., 1995). They may be extracted by physical adherence to accumulating material, probably in the order sulfide > chromite >> silicate. Once attached to chromite or sulfide they may react and re-equilibrate, and so their original identity would be lost.

We conclude that the PGE might exist in some form of high-pressure micro-xenocrysts (PGM or metallic clusters) in the magma until physically incorporated into the crystal pile at the base of a magma chamber.

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