Paper Number: 5205

Nano-entity formation prior to the crystallisation of platinum-group minerals: fundamental control by electron cloud interaction?

Tredoux, M.

Geology Dept, Univ. of the Free State, PO Box 339, Bloemfontein, South Africa, mtredoux@ufs.ac.za

---

The possibility that the behaviour of the platinum-group elements (PGE) in magmatic systems might be primarily controlled by metallic nano-entities (whether *bone fide* clusters or nano-xenocrysts) was first mooted more that two decades ago [e.g. 1]. However, the analytical technology at that time was not yet sophisticated enough to test the hypothesis. More recent work, using high resolution transmission electron microscopy, and double quadrupole laser ablation inductively coupled mass spectrometry for elemental analysis, illustrated that Pt-As nano-entities do indeed form in experimental melts, which are undersaturated with respect to sperrylite ($PtAs_2$, a common platinum-group mineral (PGM)), at >900^{o}C [2]. From these findings the authors concluded that such clustering between the PGE and selected stabilising ligands, prior to the formations of PGMs, might also occur in natural magmas. In collaboration of this, natural nano-entities have been found in PGE ore from the Merensky reef, Bushveld complex, South Africa [3].

It has become clear that the nature of the available ligands are important [4]. The preferences found in PGE-rich Fe-S experimental charges doped with As and Te (ibid.) are shown in Table 1. Such associations account for 36% of the PGMs which do not contain Pd as a major element.

Table 1. Preferred bonding ligands for the PGE, as identified by Helmy et al [2]. Note that Pd was not included in their experiment.

PGE	**Ligand(s)**	**Typical mineral(s)**
Os	Other PGE, Fe	Alloys such as osmiridium
Ir	Other PGE, As	Alloys such as above, irarsite
Pt	Fe, As,Te	Sperrylite, moncheite, isoferroplatinum
Ru	S	Laurite
Rh	As, S	Hollingsworthite

Perhaps the statement that the geochemical behaviour of the PGE is controlled by their outer electron configurations sounds like a *sine qua non* to be worthy of investigation. However, it is nevertheless intriguing to explore why the PGE display such a propensity for selective cluster formation, not least because it may lead to a better understanding of intra-PGE fractionation, which is not well understood. This presentation will consider how experimental results can be explained by the anomalous outer electron arrangements (i.e. not according to the Aufbau Principle) of 4 of the PGE. The shielding of the outer (valency) electrons in the sixth level because of the filling of inner 4F and 5d orbitals will also be considered, as it may explain why the PGE of row 6 are more siderophile that the PGE in the preceding row.

References:

[1] Tredoux et al. (1993) Chemical Geology

[2] Helmy et al. (2013) Nature Communications, 4, DOI: 10.1038/ncomms3405.

[3] Wirth R et al. (2013) Canadian Mineralogist 51, 143–155.

[4] Helmy et al. (2015) Goldschmidt2015 abstract 1226.