

## Subcontinental lithospheric mantle and mantle plume controls on crustal PGE abundance: A case study of Palaeogene magma conduits from Western Scotland, UK

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A strong correlation can be demonstrated between plume magmatism, ancient cratonic lithosphere, and the occurrence of magmatic sulphide Ni-Cu-PGE deposits [1]. Such deposits are typically located proximal to Archaean craton margins. A highly desirable combination of plume-related mafic/ultramafic igneous systems and Archaean cratons, underlain by their associated subcontinental lithospheric mantle (SCLM) keel, occur within the North Atlantic Igneous Province (NAIP). Significant mineralization has been discovered in the western portion of the NAIP (e.g. Skaergaard and Paleogene macrodykes [2,3]). Therefore, the British Palaeogene Igneous Province (BPIP) is potentially the most prospective PGE province in Western Europe.

This research focuses on the Scottish sector of the BPIP. Isolated platinum group mineral occurrences are documented on the Isles of Rum, Mull and Skye, but with limited assessment of its relationship to the province as a whole. To assess the geochemical inputs of asthenospheric (plume) vs. lithospheric 'reservoirs', a temporal and spatial evaluation of PGE abundance across the region must be adopted. This study incorporates the Paleoproterozoic Scourie dyke swarm, Caledonain lavas and small-scale intrusions, mantle xenoliths, and Palaeogene lavas and magma conduits.

Whole-rock grab samples were analysed for major and trace elements by ICP-OES and ICP-MS and NiS fire assay with ICP-MS analysis to determine PGE and Au abundances. Whole-rock PGE+Au concentrations from the 2.4 Ga Scourie Dyke swarm suggest no major removal of PGE from mantle 'reservoirs' at this time, leaving residual Archaean SCLM as 'fertile'. Permian dyke-hosted lherzolite xenoliths are in support of the shallow mantle remaining 'fertile' during this period, and may have undergone some degree of subduction-related enrichment of Au during Caledonian orogenesis. Lithochemical indicators (e.g. Cu/Pd ratio) highlight the occurrence of both S-saturated and -unsaturated magma batches across the BPIP, however there is no clear correlation with MgO, which may infer variable Cu/Pd of parental magmas instead. Pd/Ir suggest variable coeval SCLM contamination.

[1] Begg, G. C. *et al* 2010. *Econ. Geol.*, **105**, 1057-1070. [2] Andersen, J. C. Ø. *et al* 1998. *Econ. Geol.*, **93**, 488-509. [3] Holwell, D.A. *et al* (2012). *Mineral. Dep.*, **47**, 3-21.

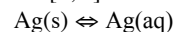
## Dissolved metals in redox-state zero: A gap in thermodynamic databases

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Dissolution of metals like silver is usually considered solely as oxidative dissolution  $\text{Ag(s)} \rightleftharpoons \text{Ag}^+ + \text{e}^-$ .

Whereas the solubility of zero-valent mercury is well known [1], experimental data about the solubility of other metals like silver is scarce [2, 3]. The explicit equilibrium



although published and discussed in [2], is not included in any thermodynamic database. The same is true for Hg(aq).

The myth that heavy metals are "insoluble" seems to be so powerful that dissolved metal atoms do not exist in geochemical considerations. This blind spot of chemical equilibrium thermodynamics has consequences: (1) The calculated "solubility abyss" of heavy metals under reducing conditions does not exist. (2) "Unclear differences" in experimental data sets and strange model parameters are due to the ignorance of zero-valent metal species.

(1) In the field of radioactive waste disposal solubility limits of contaminants are important safety issues. In the case of metals like silver, conventional model calculations lead to a "solubility abyss" under strong reducing conditions. There, silver metal is the thermodynamically stable phase and the concentration of dissolved silver virtually drops to zero. This is an artefact due to the omission of Ag(aq).

(2) Experimental determinations of the solubility of silver sulphide,  $\text{Ag}_2\text{S(s)}$ , lead to large differences between data sets in acidic solutions. "The reason for this is unclear" [4]. However, these differences can be explained by considering Ag(aq) and assuming that the data sets have been measured under slightly different redox conditions. Measurements of the solubility of gold in water have been interpreted in terms of extremely strong AuOH(aq) complex formation [5]. Assuming a solubility of zero-valent gold similar to Ag(aq) the experiments can be interpreted as governed by the formation of Au(aq).

Experimental data or good estimates for Au(aq), Cu(aq), Ni(aq), Pd(aq), Pt(aq) are needed to fill the database gap.

[1] Clever *et al* (1985) *J. Phys. Chem. Ref. Data* **14**, 631-680. [2] Kozlov & Khodakovskiy (1983) *Geochem. Inter.* **20**, 118-131. [3] Dobrowolski & Oglaza (1963) *Nucleonika* **8**, 79-81. [4] Stefánsson & Seward (2003) *Geochim. Cosmochim. Acta* **67**, 1395-1413. [5] Stefánsson & Seward (2003) *Geochim. Cosmochim. Acta* **67**, 1677-1688.