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Origin of platinum-group mineral assemblages in a mantle tectonite at Unst deduced from mineral chemistry and osmium isotopes

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This study assesses textural and mineral chemistry data, whole-rock and mineral separate Os-isotope compositions for distinct platinum-group mineral (PGM) inclusion assemblages in an isolated chromitite pod at Harold's Grave, which occurrs in a mantle tectonite at Unst in the Shetland Ophiolite Complex, Scotland. The investigation employed a multi-technique approach and utilized a number of analytical techniques, including electron microprobe analysis, ID ICP-MS after high pressure acid digestion, and LA MC-ICP-MS.

Two distinct PGM assemblages have been recognized. They comprise a 'primary' euhedrally shaped (up to 15 μm in size) PGM assemblage, which occur as inclusions in chromite, and a modified 'secondary' subeuhedral to anhedral PGM assemblage (up to 100 μm) associated with Ru-rich pentlandite observed in cracks filled by chlorite or serpentine, interstitially to chromite grains.

A 'primary' PGM assemblage is represented by solitary grains of laurite or iridian osmium and composite grains that display well defined phase boundaries between two or three distinct PGM. The latter are dominated by laurite and iridian osmium, with subordinate laurite + osmian iridium + iridian osmium and rare laurite + Ir-Rh alloy + Rh-rich sulphide (possibly prassoite). The compositional variability of associated laurite and Os-rich alloys at Harold's Grave fit the predicted compositions of experiment W-1200-0.37 of *Andrews* and *Brenan* (2002) providing unequivocal information on conditions of their genesis, with the upper thermal stability of laurite in equilibrium with Os-rich alloys estimated at 1200 – 1250°C and $f(S_2)$ of $10^{-0.39}$–$10^{-0.07}$. The inconsistent grouping of different primary PGM grains argues against an origin by subsolidus exsolution from the chromite host, providing useful information on conditions of their genesis.

The 'secondary' PGM assemblage is polyphase, with dominant laurite, intimately intergrown with native osmium, irarsite and Ru-rich pentlandite. This assemblage is likely to reflect processes such as in-situ serpentinisation, alteration during emplacement or regional greenschist metamorphism.

Whole-rock platinum-group element (PGE) concentrations give negatively sloped chondrite-normalized PGE patterns, typical of podiform chromitite, where refractory PGE (Os, Ir and Ru) prevail over less refractory PGE (Rh, Pt and Pd). The osmium isotope results identify similarly 'unradiogenic' $^{187}Os/^{188}Os$ values for 'primary' and 'secondary' PGM assemblages (with mean $^{187}Os/^{188}Os$ values of 0.12419 and 0.12464, respectively), being within uncertainty of the chromitite composition (0.1240$\pm$0.0006). This implies that the whole-rock Os isotope budget is largely controlled by laurite-dominant assemblages, supporting the conclusion that the 'secondary' PGM assemblage inherited the subchondritic osmium isotope signature of the 'primary' PGM. No evidence for other source contributions during later thermal events has been observed. The Os-isotope data provide further support for an Enstatite Chondrite Reservoir model for the convective upper mantle as defined by *Walker* et al. (2002) and are consistent with origin of the complex as a Caledonian ophiolite formed in a supra-subduction zone.

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