

## Distinct PGM assemblages in a mantle tectonite at Unst: Evidence for robustness of Os-isotope system

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This study presents the first extensive data set of Os isotopic compositions of 'primary' and 'secondary' platinum-group mineral (PGM) assemblages derived from ophiolite-type ultramafic complex at Unst (Shetland Islands, UK), considered to form at ~473 Ma. The study 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 characterize an isolated chromitite pod in dunite at Harold's Grave, about 0.5 km below the transition zone harzburgite and petrological Moho. A 'primary' magmatic euhedrally shaped (up to 55 µm in size) PGM assemblage mainly composed of laurite and osmium iridium occur as composite inclusions in chromite. A 'secondary' subeuhedral to anhedral PGM assemblage (up to 300 µm), dominated by laurite, Os-rich laurite, irarsite, osmium and Ru-penlandite, has been documented in cracks filled by chlorite or serpentine, interstitially to chromite grains. This alteration assemblage is likely to reflect processes such as *in situ* serpentinisation, alteration during emplacement or regional greenschist metamorphism.

Whole-rock PGE concentrations give negatively sloped chondrite-normalized PGE patterns, typical of podiform chromitite, where IPGE prevail over PPGE. The osmium isotope results identify similar 'unradiogenic' <sup>187</sup>Os/<sup>188</sup>Os values for 'primary' and 'secondary' PGM assemblages (e.g., 0.12043-12558 with median of 0.12441, n=33 and 0.12345-0.12763, median=0.12448 and n=59, respectively), being within uncertainty of the chromitite composition (0.1240±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 (e.g., suprachondritic) during later thermal events, as frequently invoked, has been observed.

## Isotopic fractionation of Sn due to methylation and demethylation reactions in aqueous solution

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Laboratory experiments, modeling the methylation of inorganic Sn(II) by methylcobalamin and the decomposition of methyltin under irradiation with UV light in aqueous solution, have been performed. Methyltin has been separated from inorganic Sn using ion-exchange chromatography and subjected to Sn isotope ratio measurements by multicollector inductively coupled plasma mass spectrometry (MC-ICPMS). The methylation of Sn(II) in the dark was accompanied by mass-dependent Sn isotopic fractionation, which resulted in preferential partitioning of the lighter Sn isotopes into the organic phase, with a shift of ~0.6±0.1‰ in terms of δ<sup>124</sup>Sn/<sup>116</sup>Sn between methylated and inorganic Sn. The methylation of Sn(II) by methylcobalamin under UV irradiation resulted in the accelerated formation of methyltin in the beginning of the process, but was followed by the photolytic degradation of methyltin until its complete mineralization. The photolytic degradation of methyltin in the presence of methylcobalamin and inorganic Sn(II) was slower than that of pure solutions of commercially obtained monomethyltin. This is attributed to the methylating action of methyl radicals produced from photolytically decomposing methylcobalamin. Both synthesis and decomposition of methyltin under UV irradiation were accompanied by both mass-dependent and mass-independent Sn isotopic fractionation, with the latter due to the magnetic isotope effect. As a result of this, the lighter Sn isotopes preferentially partition into reaction products, while the odd isotopes, <sup>117</sup>Sn and <sup>119</sup>Sn, are selectively enriched relative to the other isotopes in the starting molecules. The extent of the observed variations in the isotopic composition of Sn is larger than that documented previously for geological and archeological samples. These results indicate that Sn isotopic fractionation between various chemical forms of Sn in the natural aquatic systems may be significant and can provide new insights into the biogeochemical cycling of the element.