Temporal trends in the seawater osmium inventory and $^{187}Os/^{188}Os$

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Recently, several studies have used compilations of redox-sensitive metal abundances (e.g., Mo, Ni, Zn) from organic-rich sedimentary rocks (ORS) and iron formations to infer first-order temporal trends in oceanic metal inventories. These trends provide critical information about atmosphere and ocean oxygenation and associated changes in biogeochemical cycles and biological evolution. Osmium (Os) is a redox-sensitive metal that can provide information about redox conditions and crustal vs hydrothermal fluxes.

Most of the Os supplied to the modern oceans is derived from rivers (via oxidative weathering of the upper crust), with the remainder coming from cosmic dust dissolution and hydrothermal alteration of oceanic crust and peridotites. Osmium accumulates in modern oxygenated seawater (residence time of 10^4 years) but is sequestered into anoxic, organic-rich sediments. Seawater $^{187}Os/^{188}Os$ (= initial $^{187}Os/^{188}Os$ of ORS at the time of sediment deposition) also constrains the relative importance of radiogenic crustal versus unradiogenic hydrothermal (and extraterrestrial) inputs to seawater. Temporal trends in $^{187}Os/^{188}Os$ have been explored, whereas Os abundances in ORS have received less attention.

Here, we present a compilation of ^{192}Os abundances in ORS (total Os abundances are not used because of ^{187}Os contributions from ^{187}Re decay). We find that ^{192}Os abundances in pre-Ediacaran shales are low, typically <300 ppt, but still elevated above average upper crust (~10-20 ppt). The ^{192}Os enrichments and chondritic initial $^{187}Os/^{188}Os$ from Archean ORS require a oceanic Os inventory dominated by hydrothermally sourced Os. However, there is no clear change in ^{192}Os abundances across the Great Oxidation Event. This observation contrasts with a shift from chondritic seawater $^{187}Os/^{188}Os$ in the Archean to moderately radiogenic seawater $^{187}Os/^{188}Os$ in the Proterozoic, which points to an increase in the riverine flux of radiogenic Os to the oceans. To reconcile these obesrvations, we suggest that continued widespread Proterozoic deep ocean anoxia and declining hydrothermal Os fluxes kept the oceanic Os inventory broadly similar to Archean levels. Higher ^{192}Os abundances (>300 ppt) and instances of highly radiogenic seawater $^{187}Os/^{188}Os$ in the Ediacaran Period and Phanerozoic Eon point to an increase in the riverine Os flux and oceanic Os inventory in response to late Neoproterozoic oxygenation.

Possible PGE nano structures, in magmatic systems

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The retention of platinum-group elements (PGE) in the mantle restite is difficult to explain by conventional chalcophile models. PGE nano-structures (clusters of 10-100nm), might be the cause that magma can become enriched in PGE, during the early stages of magmatic differentiation. The study focused on the possible formation of these entitites in a magmatic system. If these entities do form, to what extend might they contribute to ore forming processes in ultra mafic deposits, like the Bushveld complex.

A synthetic sulphide system was used to replicate the sulphide portion of a Cu-Ni-S ± PGE system. Sulphides are of the first ore minerals to crystallize in a magmatic environment and thus the ideal place to look for clusters. Experiments were run, using the dry powder silica charge technique. A base mixture of Cu, S and Fe, was doped with variable concentration of PGE (Pt, Pd and Ru) and As. As was chosen as stabilising chalcogene ligand. The systems were manipulated to form a mono sulphide or pyrrhotite phase (Fe_xS_x) and a melt ($Fe_xCu_xS_x$) phase.

Nano scale PGE-ligand phases, ranging from 10-1000 nm, were measured in the synthetic samples, by high resolution SAM and TOF-SIMS. This observation indicated that the PGE may form phases, on a nano level, without sulphide saturation having been achieved. The clusters form due to the physio-chemical association of the PGE with chalcogene ligands, such as As, Fe and Cu, before formal chemical bonding, to from PGMs. A fraction of the clusters are reabsorbed into the melt, while a fraction may act as nucleation points to form nano-crystals and minerals in the incompatible sulphide, oxide or silicate phases. The clusters form during the early stages of magmatic differentiation.

Chemical behaviour may govern the secondary distribution of PGE-phases, but clustering is potentially the primary (physical) enrichment mechanism. This behaviour cannot be explained by sub-solidus immiscibility properties as has been suggested to account for the frequent presence of PGE in base metal sulphide minerals.

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