

Partitioning of P, V, Mo, and Ni during precipitation of ferric oxyhydroxides and implications for Archean ocean nutrient availability during BIF deposition

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During the Archean and Paleoproterozoic, large amounts of iron precipitated from seawater to yield Banded Iron Formations (BIF). It has been argued that during this time, the presence of abundant and highly reactive iron oxyhydroxides may have limited critical nutrients as a consequence of various adsorption and co-precipitation processes. These arguments have previously centred on the role of phosphorus, which is currently a major nutrient controlling the degree of ocean productivity. In this study, we add to the debate regarding nutrient availability in the ancient oceans at the time of BIF deposition by evaluating the degree to which ferric oxyhydroxides may sequester aqueous Mo, Ni, and V; these transition metals act as enzymatic co-factors that are critical, and at times limiting, for specific biological functions in modern microbes. Furthermore, it is generally assumed that dissolved silica was more abundant at the time of BIF deposition. As dissolved silica may influence elemental partitioning through a combination of competitive surface adsorption and co-precipitation processes, we also consider its role in the sequestration of these nutrients into iron oxyhydroxides. Finally, we evaluate our experimental data in light of the concentrations in which these elements are found in BIF, and estimate their degree of availability in ocean water at the time of BIF deposition.

The geochemical behaviour of Sb, Mo and W in subduction zones

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Due to their high charge-size ratio, Sb, Mo and W are part of the high field strength element (HFSE) group which is traditionally regarded as behaving immobile in subduction fluids. We present new high-precision W, Nb, Ta, Zr, Hf concentration data of lavas from various arc settings obtained by isotope dilution and MC-ICP-MS. Antimony and Mo were analysed in combination with other incompatible trace elements by conventional quadrupole ICP-MS measurements. Glasses from the UPL suite from Troodos, Cyprus permit to evaluate the mobilization of HFSE by fluids derived from subducting sediments (Cameron *et al.* 1985). The HFSE budget in these magmas is compared to that in Solomon arc lavas that have only been overprinted by fluids and melts derived from subducted oceanic crust (Schuth *et al.* 2004; König *et al.* 2007). Measured Ta/W in both suites are lower (<2.9) than values for MORB (ca. 5), indicating that W is more mobile in subduction components than Nb and Ta. Correlations between Ce/Pb, Sb/Ce and W/Th support an effective mobilization of Sb and W by slab-derived fluids and clearly resolve a more pronounced W and Sb enrichment in slab fluids originating from subducted sediments, reflecting the higher initial abundances of both elements in sediments. Tungsten and Mo abundances correlate well in the Solomon arc suite where negligible amounts of pelagic sediments were subducted, whereas both abundances are decoupled in the Cyprus suite with subducted pelagic sediments present in their sources. This difference possibly reflects variable redox conditions during dehydration processes in subducting oceanic plates.