Rare Earth Element evidence for redox structure evolution

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Rare Earth Element (REE) systematics have long been used as tool to understand the genesis of banded iron formations (BIFs) and the evolution of the ocean redox structure. The conclusions of many previous REE studies on BIFs, however, are complicated by analytical inaccuracies, incomplete measurements, and measurements on samples from extremely altered formations. We conducted REE analysis of samples from 26 formations and provide a revaluation of trace element analyses of detrital-free BIFs.

There are several temporal trends in our dataset that appear to reflect ocean redox stratification evolution. No BIFs contain statistically significant shale-normalized negative Ce anomalies and there are not positive Ce anomalies in our dataset until ~1.9 Ga. Low Y/Ho and high shale normalized light to heavy REE (LREE/HREE) ratios are only present in ~1.9 Ga and younger BIFs. Both low Y/Ho and high LREE/HREE ratios develop in seawater below the redoxcline in the modern ocean, therefore, the lack of similar trends in ≥2.4 Ga BIFs is most consistent with the absence of significant redox cycling across a redoxcline. In a stratified ocean, metal oxides, Ce oxides, and organic matter from oxic waters will be transported below the redoxcline. Oxide dissolution and organic matter remineralization in an anoxic water column will lower the Y/Ho ratio, raise the light to heavy REE ratio, and increase the concentration of Ce relative to neighboring REE (La and Pr). The lack of evidence for an oxide shuttle, redox stratification, and the apparently low oxidizing potential of shallow-water environments in Archean oceans question the plausibility of classical models for BIF deposition that invoke oxidation at or above a redoxcline.

Accessory minerals in the subduction zone

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Recent laboratory experiments [1-3] predict a dominant role for accessory minerals (e.g., rutile, allanite, monazite and zircon) in controlling trace element transfer out of the subducting plate. At face value, the prevalence of residual accessory minerals, with their very high partition coefficients for many trace elements (e.g., REE, U, Th), is at odds with efficient elemental recycling from slab to arc. Trace element fractionations between sediment input and arc magma output provide insights into this problem.

The low solubility of allanite and monazite in low-temperature melts/fluids predict that most subduction zone fluids will be saturated in one of these phases. Because LREE are essential components in these minerals, their concentrations in fluids should be set by the solubility limits, and not by the bulk composition of incoming material. Nonetheless, there is a strong correspondence between Th/La in local subducting sediment and nearby volcanic output [4], which can only be maintained if monazite is the major REE-phase, given its sub-equal effects on Th and La. The presence of monazite instead of allanite may be a natural consequence of the low Ca/P of marine pelitic sediments.

The predicted saturation of rutile, coupled with its very high partition coefficients for Nb and Ta, provides a ready explanation for the common HFSE depletion observed in arc magmas. Sediments themselves, however, enter the subduction zone with Nb anomalies, the magnitude of which is sufficient to create the Nb depletion observed in some arcs. In fact, only those sedimentary sections with high Ti/Fe bulk compositions require residual rutile to explain arc patterns, and thus rutile may not be a ubiquitous phase in the slab.

It is difficult to resolve whether all arc magmas require residual zircon, because subducting terrigneous sediments have La/Zr already set by accessory mineral saturation in the upper continental crust. Thus, arc magmas inherit some chemical feautures from sediments, and some from accessory mineral fractionation in the subduction zone.

[1] Klimm *et al.* (2008, in press) *J. Pet.* [2] Rubatto & Hermann (2007) *Chem. Geol.* **241**, 38-61. [3] Schmidt *et al.* (2004) *Earth Planet. Sci. Lett.* **226**, 415-432. [4] Plank (2005) *J.Pet.* **46**, 921-44.