Bio-essential trace metal cycling in a ferruginous, silica rich ocean

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All microbes have a requirement for micro-nutrients (e.g. Zn, Co, Mo, Ni), but the availability of these metals in the oceans may have varied dramatically through Earth history. The oceans in the Archean and Paleoproterozoic were dominantly anoxic and Fe rich (ferruginous), and the stratigraphic distribution of early diagenetic chert and syndepositional granular silica (Fischer & Knoll, 2009; Stefurak et al., 2014) indicates that silica concentrations were commonly elevated. Trace metal cycling under these conditions would have been radically different to today because Fe-rich authigenic precipitates likely exerted a strong geochemical control on the bioavailability of these nutrients. Greenalite, a pervasive component of banded iron formation forming close to the sediment-water interface, is one such marine precpitate (Tosca et al., 2015), and is an ideal candidate to preserve a record of coeval seawater metal concentrations.

Here, we explore the uptake, retention, and recycling of trace metals by greenalite during crystal growth, early diagenesis and low grade metamorphism. Laboratory experiments were carried out under strict anoxic conditions using solutions that attempt to mimic ancient seawater. Solution and solid-phase analyses indicate significant partitioning of trace metals, including Ni, Zn, and Cu, into the greenalite surface during its nucleation and growth from anoxic seawater. X-ray absorption spectroscopy (EXAFS and XANES) was used to probe the local environment surrounding the Fe-atom in the greenalite structure and the sorbed trace metals, and we find significant changes in structure and oxidation state as the solid phase is allowed to oxidize.

Our results suggest that greenalite is a promising archive of trace metal availability under favorable precipitation conditions. Basin-scale greenalite growth, as recorded by several iron formation deposits, may have been an important control on the availability of bio-essential trace metals in Precambrian basins featuring both anoxia and elevated silica.

Fischer, W. & Knoll, A. (2009) *GSA Bulletin*, 121, 222.

Stefurak, E., et al. (2014) *Geology*, 42, 283.

Tosca, N. et al. (2015) *GSA Bulletin*,.B31339-1.