

A window into metal availability in Late Archean seawater

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Thermodynamic models and phylogenomics suggest that metal availability in seawater has changed dramatically over geological time, but confirming these predictions in the rock record is challenging. Fe(II)-silicate minerals, such as greenalite, are abundant in Archean sediments and are interpreted to be primary precipitates [1]. Recent experimental work has demonstrated that several key metals enter Fe(II)-silicates, thought to be a precursor to crystalline greenalite, during precipitation and are largely retained in the structure during heating and crystallisation [2]. Sorption of silica (SiO₂) to Fe(II)-silicate nanoparticles during transport, followed by early lithification in chert, could have protected primary geochemical signals from alteration [3]. Greenalite therefore represents an excellent potential archive of ancient marine geochemistry. Here, we present mineral-specific metal contents for natural greenalite from ~2.46 Ga chert beds from the Kuruman Iron Formation, Transvaal Supergroup, South Africa and place these into a quantitative framework to calculate marine metal concentrations in a Late Archean shelf environment. Patterns of metal availability were radically different to the modern ocean: Zn and V were extremely scarce, whereas Ni levels were similar and Co was slightly enriched. Intriguingly, our data imply Mn concentrations reached 7 mmol kg⁻¹, making Mn a major element in Archean seawater. Our data are largely consistent with predictions based on thermodynamic models, and in places, overlap with constraints from other geological archives. These patterns of metal availability would have had a profound impact on the evolution of early microbial life and are consistent with phylogenomic and proteomic data which indicate that Mn and Co were selected over Zn by early microbes. Our approach demonstrates the utility of greenalite as a palaeo-archive and raises the possibility of exploring the Archean and Proterozoic record to reconstruct metal concentrations in different settings over geological time.

¹Rasmussen, Muhling and Krapež, 2021, *Earth Science Reviews* 217, 103613.

²Tostevin & Ahmed, 2023, *Nature Geoscience* 16(12), 1188-1193.

³Rasmussen and Muhling, 2021, *Precambrian Research* 353, 106003.