

REDOX-SENSITIVE TRACE METAL CONCENTRATIONS IN LATE ARCHEAN ORGANIC-RICH MUDROCKS FROM THE GRIQUALAND WEST BASIN, SOUTH AFRICA: IMPLICATIONS FOR EARLY EARTH MARINE GEOCHEMICAL CYCLES AND METAL SOURCES. B. Kendall, Department of Earth & Environmental Sciences, University of Waterloo, 200 University Avenue West, Waterloo, Ontario N2L3G1, Canada (bkendall@uwaterloo.ca).

The concentrations and/or isotopic compositions of redox-sensitive trace metals (RSTM), especially Mo, Cr, and Re, in sedimentary archives have been used as evidence for episodes of mild environmental oxygenation on land and along ocean margins more than 500 Myr before the 2.45-2.32 Ga Great Oxidation Event [e.g., 1-6]. Other RSTMs such as V, Co, Ni, Cu, and Zn have generally received less attention in paleoredox studies because their marine geochemical behavior is not as well understood, and because modern organic-rich sediments contain smaller enrichments of these metals relative to background detrital concentrations [7-9]. However, recent studies of modern anoxic marine environments are leading to a better understanding of the geochemical behavior of the less commonly used RSTMs [9]. This modern framework provides the basis for exploring ancient marine geochemical cycles of RSTM and their implications for biological evolution on the early Earth.

The concentrations of V, Co, Ni, Cu, and Zn were measured in 2.6-2.5 Gyr-old organic-rich mudrocks of the Nauga Formation and overlying Klein Naute Formation (Ghaap Group, Transvaal Supergroup) recovered from two drill cores in the Griqualand West Basin, South Africa. The GKF01 and GKP01 cores represent the slope and slope-to-basin transition of a large carbonate platform, respectively [10-11]. Local bottom water redox conditions during deposition of these organic-rich mudrocks were constrained previously by sedimentary Fe speciation and Re/Mo ratios [3]. Organic-rich mudrocks of the Nauga Formation represent deposition from oxygenated and anoxic/ferruginous waters, whereas the Klein Naute Formation was deposited from anoxic/euxinic and anoxic/ferruginous deeper waters after the carbonate platform drowned [3].

Similar to modern environments, the euxinic mudrocks contain generally higher enrichments of RSTMs compared to mudrocks deposited from oxygenated and anoxic/ferruginous bottom waters. Hence, the euxinic mudrocks from the Klein Naute Formation are most suitable for comparing metal enrichments in the shallower GKF01 and deeper GKP01 for the purpose of inferring metal sources to the sediments.

The metal enrichment factor is defined as $EF_{\text{metal}} = [\text{metal}/\text{Al}]_{\text{sample}} / [\text{metal}/\text{Al}]_{\text{average upper crust}}$ [8]. In the euxinic Klein Naute Formation, the relative order of metal EF is $\text{Zn} > \text{Cu} > \text{Ni} > \text{Co} > \text{V}$. Both V and Co

have persistently low enrichments with no clear difference between the two cores. By contrast, Ni exhibits mild enrichments that are higher in the euxinic mudrocks of the shallower GKF01 core. A moderate correlation exists between Ni and Fe enrichment, suggesting that Ni enrichments may be tied to a benthic Fe flux, as in modern anoxic settings [9].

Copper sequestration in organic-rich sediments is thought to be sensitive to water column sulfide availability, whereas Zn is primarily associated with organic matter [8-9]. However, both Cu and Zn are enriched to a greater extent in the deeper GKP01 core compared to the shallower GKF01 core despite the higher total organic carbon contents and higher ratios of biogeochemically highly reactive iron to total iron ($\text{Fe}_{\text{HR}}/\text{Fe}_{\text{T}}$) in GKF01 [3]. Furthermore, there is no significant difference in the ratio of pyrite Fe to Fe_{HR} between the two cores [3]. Hence, the higher Cu and Zn enrichments in GKP01 suggests a deep-sea hydrothermal source for these metals to late Archean seawater. Hence, Cu and Zn would have been available at this time to support any primitive eukaryotic life, although the use of Zn in eukaryotic metallomes appears delayed by evolutionary factors [12-15]. By contrast, Re and Mo are more enriched in the shallower GKF01, suggesting that oxidative crustal weathering of sulfide minerals, not deep-sea hydrothermal inputs, is the major source of Re and Mo to late Archean seawater [3].

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