

Crustal versus hydrothermal sources to 2.7-2.3 Ga seawater: Constraints from Os isotopes and Re, Mo abundances in black shales

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Re-Os geochronology and redox-sensitive metal abundances (e.g., Re, Mo) in black shales have great potential to constrain Early Earth marine geochemical cycles and the chronology of atmosphere and ocean oxygenation. Seawater ¹⁸⁷Os/¹⁸⁸Os (as recorded by the initial ¹⁸⁷Os/¹⁸⁸Os [I_{Os}] of Re-Os isochron regressions) reflects a balance between the riverine flux of radiogenic Os from oxidative weathering of upper continental crust (present-day value of ~ 1.0-1.5) and the flux of unradiogenic Os from hydrothermal alteration of oceanic crust and peridotites, and cosmic dust (~ 0.11-0.13). Chondritic I_{Os} obtained from the 2.70 Ga Joy Lake Sequence (Superior Province, Minnesota, USA) [1], 2.50 Ga Mt. McRae Shale (Hamersley Group, western Australia) [2], and 2.32 Ga Rooihooft and Timeball Hill Formations (Transvaal Supergroup, South Africa) [3] are consistent with dominance of the Late Archean to Early Paleoproterozoic marine Os budget by hydrothermal and extraterrestrial inputs. However, an interval of elevated Re and Mo abundances in the Mt. McRae Shale together with elevated Re abundances in the Joy Lake sequence may record mild shallow water oxygenation (whether local or global) prior to the 2.45-2.32 Ga Great Oxidation Event [2]. Thus, oxidative weathering of crustal sulfides may represent a measurable, albeit minor source of Re and Mo to Late Archean seawater relative to the hydrothermal and extraterrestrial fluxes. New high-resolution chemostratigraphic profiles through black shale intervals in the 2.6-2.5 Ga Ghaap Group (Transvaal Supergroup, South Africa) are consistent with this hypothesis.

[1] Yang *et al.* (2007) *GSA Abstr. Prog.* **39**, 274. [2] Anbar *et al.* (2007) *Science* **317**, 1903-1906. [3] Hannah *et al.* (2004) *EPSL* **225**, 43-52.

Cell-mineral surface origins of the biogeophysical response

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Successful bioremediation schemes rely on effective monitoring of subsurface biogeochemical processes and cell transport. Recent laboratory results show induced polarization (IP) geophysical measurements are sensitive to microbial activity in porous media. This presents the potential for high-resolution, non-invasive, long term monitoring of biogeochemical conditions over large subsurface volumes using low-frequency electrical techniques. Critical to future field-scale implementation, however, is a fundamental understanding of the bioelectric IP effect, which we believe is rooted in cell-mineral surface processes. Key parameters are surface ion mobility, local dielectric, and surface potential, which we probe using polarization force microscopy. Polarization forces over a bacterium are higher than those over a mica surface at low relative humidities. This is suggestive of differential water retention and increased surface ion mobility at the cell interface, both of which represent possible polarization mechanisms (*viz.* IP effects), at least for partially saturated conditions. Moreover, low-frequency dispersions of the local permittivity inferred from polarization force data collected over cells correspond to dispersions modeled for a bacterium in aqueous conditions. Specifically, frequency cut-off values increase with increasing ion mobility in a pattern that is consistent with the modeled values. Further polarization force measurements and nanoscale mapping of the heterogeneous electrical layout at the mineral-microbe interface should provide much needed molecular-level insight into column and field-scale bio-IP phenomena.