Rhenium data from shales confirms ferruginous Proterozoic deep oceans

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A new view of Proterozoic ocean chemistry is emerging from sedimentary Fe speciation and Mo abundance and isotope data from black shales. Fe speciation has revealed examples of anoxic/sulfidic (euxinic) mid-depth waters that were underlain by anoxic/ferruginous (Fe^{2+}-rich) deep waters. Mo data indicate a moderate-sized oceanic Mo inventory, consistent with pervasive oxidative weathering but a pronounced Mo sink into euxinic sediments. However, Fe speciation is strictly a local redox proxy. Furthermore, the high efficiency of Mo burial in sulfidic environments relative to oxygenated and ferruginous settings renders the oceanic Mo inventory sensitive to small changes in the extent of water column euxinia.

To test the hypothesis of ferruginous Proterozoic deep oceans we turned to Re abundances in black shales. Like Mo, Re is oxidatively mobilized from the upper crust and accumulates in oxygenated seawater. Re and Mo have long oceanic residence times (~10^5 years today) that enable their use as global redox proxies. Both metals are removed in sulfidic marine settings. In contrast, Re burial rates in O_2-deficient sediments beneath low-O_2/ferruginous and mildly oxygenated bottom waters are high and low, respectively, whereas Mo burial rates in these settings are low and negligible, respectively.

We found that Re abundances in most Paleoproterozoic and Mesoproterozoic shales are similar to those in Late Archean shales. Re (up to 50 ppb) is enriched relative to upper crust (~1 ppb), indicating that dissolved Re was supplied to the oceans via oxidative weathering. However, the low Re abundances in Proterozoic shales point to widespread low-O_2/ferruginous conditions that maintained a low oceanic Re inventory. Higher Mo (but not Re) abundances in Proterozoic relative to Late Archean shales is consistent with increased oxidative weathering, limited extent of sulfidic conditions, and low Mo burial rates beneath ferruginous deep waters. Re is a global redox proxy, so our data confirm the widespread ferruginous Proterozoic deep oceans inferred from local Fe speciation data.

Exceptions to the Late Archean-to-Mesoproterozoic baseline are found in black shales deposited during the Paleoproterozoic Lomagundi positive carbon isotope excursion (the later stage of the Great Oxidation Event) and the late Mesoproterozoic. Re abundances in these shales reach 200 ppb, similar to the lower end of the range observed in Ediacaran and Phanerozoic shales, and hence suggests a greater extent of ocean oxygenation at these times.

Microbial hydrogen sulfide generation within Syncrude composite tailings

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Surface mining of Alberta's Oil Sands has led to significant land disturbance, making reclamation one of the largest challenges facing the industry today. With increased production from Alberta's Oil Sands, sustainable development of this resource has emerged as a substantial environmental issue facing Canadians. Syncrude Canada Ltd. has developed an innovative technique to reclaim composite tailings (CT) through constructed wetland landscapes and is currently investigating the viability of a pilot-scale freshwater fen built over sandcapped CT. Episodes of hydrogen sulfide (H_2S) gas release have been encountered during the initial stages of fen construction; these occurrences were not predicted by abiotic geochemical models, thus highlighting the likely importance of microbial metabolic activity in controlling H_2S generation. Previous research in our group has demonstrated the occurrence of H_2S within CT and sandcap porewaters. The interfacial surficial sandcap between the CT and fen has revealed a widespread presence of diverse microbial communities capable of Fe and S metabolisms, suggesting that microbial Fe and S activity within the deeper CT itself is likely. However, to date, no systematic study of CT Fe and S biogeochemistry has occurred. The objectives of this study are to: (1) characterize the mineralogy, microbial Fe and S metabolisms and biologically accessible Fe and S pools with depth in the CT (over 40m) and; (2) constrain microbial and geochemical variables affecting H_2S generation throughout laboratory experimentation. Microcosm experiments are being conducted in an effort to monitor H_2S generation in CT collected from 2 different depths under varying microbial Fe and S metabolic influence. Preliminary results of these experiments will be presented in conjunction with the field based mineralogical, geochemical and microbial CT characterization to identify the constraining variables of the system.