Ocean redox changes in the wake of the Marinoan glaciation

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Metazoans first appeared in the fossil record shortly after the termination of the late Cryogenian (Marinoan) glaciation about 635 Myr ago [1]. It has been long hypothesized that an oxygenation event was the driving factor behind the rise and early diversification of metazoans [2], but there is little evidence for a direct link between animal and redox evolution. Here we report new geochemical data from early Ediacaran organic-rich black shales of the basal Doushantuo Formation in South China. These shales were deposited with a strong connection to the open ocean [3] and span the interval of the earliest metazoan fossil [1]. The temporal record of trace metal enrichments (particularly molybdenum) in euxinic shales currently provides one of the clearest signals for a significant redox shift in the Neoproterozoic [4,5]. However, prior to our study the oldest known occurrences of Phanerozoic-like trace metal enrichments are found near the end the Ediacaran (ca. 551 Ma) [4,5], long after the radiation of complex metazoans [1].

In contrast, we found very high, Phanerozoic-like, redox sensitive trace element (molybdenum, vanadium and uranium) abundances in euxinic shales (as identified by sedimentary Fe speciation) that were deposited between 635 and 630 Ma, within five million years of the Marinoan glaciation and coincident with the appearance of the earliest metazoan fossils. Moreover, highly negative pyrite sulphur isotope ($\delta^{34}S_{pyrite}$) values down to –35‰ from basinal samples also point toward an oxidizing ocean-atmosphere system. The isotope fractionation between pyrite and coeval sulphate in the deep basin section is >65‰—equivalent to the maximum fractionations observed in the Phanerozoic rock record [6]. As increase in the fractionation in the Neoproterozoic has been commonly linked to growth of the marine sulphate reservoir and surface oxidation [5], the large sulphur isotope fractionation, therefore, point toward a well oxidized ocean-atmosphere system. Our data provide the first direct evidence for a significant early Ediacaran postglacial oxygenation event. Our results support a casual link between one of the most severe glaciations in Earth's history, the oxygenation of the Earth's surface, and the earliest diversification of complex animals.

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Radium interactions with iron (oxy)hydroxide minerals.

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Typically, radium is the most significant contributor to dose in mining effluents from legacy uranium mining operations. However, little is known regarding the uptake of Ra^{2+} by iron (oxy)hydroxide minerals under environmental conditions representative of the mining wastes. Here, we assess the behaviour of Ra^{2+} (and Ba^{2+} as a chemical analogue of Ra^{2+}) to provide surface complexation constants that will be used in the prediction of Ra^{2+} speciation, mobility and fate across a range of environmental conditions.

Radium and barium uptake onto ferrihydrite and goethite was studied in the concentration range nM to mM and from pH 5 - 10, conditions commonly found in legacy U-mine wastes. For ferrihydrite, uptake of Ra^{2+} at nM concentrations was strong at pH > 7. At higher concentrations (μM - mM) Ba^{2+} sorption to ferrihydrite was slightly weaker than that of Ra^{2+}. Experiments with goethite showed weaker binding for both metal ions in all systems studied. Ongoing experiments are exploring the reversibility of these systems. In addition, we are exploring the behaviour of Ra^{2+} during transformation of ferrihydrite to goethite, a process of potential importance in the impacted environments.

Surface complexation modelling has successfully simulated Ra^{2+} and Ba^{2+} sorption across the pH and concentration ranges studied. These data will be used in underpinning the safety case for legacy mining sites.