Understanding Ediacaran environmental change

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The latest Proterozoic has long captured the imagination of Earth historians, as sedimentary rocks of this age contain the first evidence for complex multi-cellular life (*1*). The oxygen requirement of animals further provides a unique perspective on the partial pressure of Ediacaran atmospheric oxygen (*2*). In search of geochemical evidence of oxygenation, numerous studies have targeted reconstructing C, S, and Fe chemostratigraphies [e.g.(*3*)]. These data are provocative, yet scaling local or basinal observations to a global ocean, and uniquely identifying specific mechanism (s) driving surface and deep ocean oxygenation remains a topic of much debate. We look to test previous hypotheses and build a more integrative geochemical model using new sedimentological and geochemical records from multiple sections through the Ediacarn of the Yukon, Canada.

In this study we begin by reconstructing the Ediacaran carbon cycle (via $\delta^{13}C$ of organic carbon and carbonate) as recroded in mixed shale and carbonate sequences. With a quantitative grasp on organic carbon export (e^- donation), we turn to constraining the oxidants driving dominant anaerobic remineralization reactions; namely ferric iron (via Fe-speciation) and seawater sulfate (via multiple sulfur isotope data on pyrite and carbonate associated sulfate). These cycles can be linked through numerous shared processes, such as the metabolisms noted above as well as pyrite burial; these links are critical to our integrated modeling approach. Central to this quantification is the inclusion of new perspectives on rates of Ediacaran sediment burial. These results shed new light on the severity of Ediacaran geochemical change, help to constrain the mechanisms driving the marine redox budget and provide an environmental context for interpreting the rise of animals.

[1] L. M. Yin *et al.* (2007) *Nature* **446**, 661. [2] B. Runnegar (1991) *Palaeogeography Palaeoclimatology Palaeoecology* **97**, 97. [3] Fike, Grotzinger, Pratt & Summons (2006) *Nature* **444**, 744.

Seawater inundation of Fe-rich coastal lowlands – Hydrogeochemical coupling and hysteresis at the tidal fringe

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Over 17 million ha of coastal lowlands contain acid sulfate soils (CASS). These soils are rich in meta-stable, redox-sensitive Fe (III)-minerals. Large areas of CASS are at risk of increased saline tidal inundation due to sea-level rise. Field-based CASS remediation trials reveal that tidal seawater inundation initiates radical changes in sediment hydro-geochemistry, stimulating Fe and SO_4 reducing conditions, generating alkalinity and greatly decreasing the acidity hazard. However, these changes also have profound consequences for the fate, mobilisation, redistribution and transformation of Fe minerals and co-associated trace elements. Here, we examine the consequences for iron and arsenic by investigating the hydrology, *in situ* porewater geochemistry, solid-phase Fe and As fractions and Fe mineralogy across a tidally inundated CASS toposequence.

Reductive dissolution of As (V)-bearing Fe (III) minerals, including jarosite ($KFe_3 (SO_4)_2 (OH)_6$), resulted in elevated concentrations of porewater Fe^{2+} (2000 mg L^{-1}) and As (~400 μg L^{-1}) in former sulfuric horizons in the upper-intertidal zone. Oscillating hydraulic gradients caused by tidal pumping promoted upward advection of this As and Fe^{2+}-enriched porewater. This led to accumulation of As (V)-enriched Fe (III) (hydr)oxides at the oxic sediment-water interface and some flux of As_{aq} and $Fe^{2+}{}_{aq}$ to overtopping tidal surface waters. Fe (III) (hydr)oxides at the surface-water interface were poorly crystalline and displayed a diverse mineralisation sequence related to tidal zonation. Whilst these Fe (III) (hydr)oxides act as a natural reactive-Fe barrier, they represent a transient phase that is prone to future reductive dissolution. This has uncertain consequences regarding the potential release of co-associated trace elements.

The extreme enrichment of poorly crystalline Fe (III) (hydr)oxides (~40% Fe w/w) near the surface is a function of the interplay between tidally influenced hydrology, topography and geochemistry. This enrichment not only affects As partitioning, it strongly influences contemporary SO_4 reduction products and pathways. It also represents a substantive hysteresis in the geochemical trajectory of the CASS landscape as it undergoes remediation. Conceptual models are presented to explain the observed landscape-scale patterns of Fe and As hydro-geochemical zonation. These findings have broad geochemical relevance to the saline tidal inundation of low lying Fe-rich landscapes.