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Searching for an oxygenation event in the fossiliferous Ediacaran of northwestern Canada

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ABSTRACT

Late Neoproterozoic (Ediacaran) strata from northwestern Canada provide a thick and rich sedimentological record, preserving intercalated carbonates and shale extending from the ~635 million year old Marinoan glacial deposits up through the ~541 million year old Precambrian–Cambrian boundary. This region also holds one of the classic localities for the study of early animal life, with the ensuing suggestion that this temporal interval captures a gross change in the O_2 content of the Earth's atmosphere. To test this hypothesis and bring records of northwestern Canada into line with other Ediacaran, fossil-bearing basins, we provide a detailed geochemical reconstruction from the Wernecke Mountains of the Yukon. Where possible, we also extend these records to the Ogilvie Mountains to the west and previously published data from the Mackenzie Mountains to the east.

Our work in the Wernecke Mountains is set against a composite $\delta^{13}C$ record for carbonate that preserves three distinct Ediacaran isotope excursions, the lowermost of which (preserved in the Gametrail Formation) is a putative Shuram excursion equivalent. What emerges from a multi-proxy (Fe speciation, sulfur isotopes, major and trace element analyses) reconstruction is a picture of a persistently anoxic and ferruginous Ediacaran ocean. Notably absent is geochemical evidence for a prominent oxygenation event, an expectation given the appearance of animals and large swings in $\delta^{13}C$. The new insight gained through these data challenges the idea of an Ediacaran jump in atmospheric oxygen, which in turn muddles the link between animal evolution and local geochemical environments.

1. Introduction

Interest in understanding Earth surface change in the late Proterozoic is rooted in trying to pinpoint the mechanisms and feedbacks associated with the origin of animals (Nursall, 1959; Cloud and Drake, 1968; Holland, 1984; Canfield et al., 2007; McFadden et al., 2008). Decades of work have combed Neoproterozoic successions and provide a robust paleontological roadmap for both the distribution of classic Ediacaran-type fossils as well as the underlying, earlier Ediacaran acritarch record (Hofmann et al., 1990; Narbonne and Aitken, 1990b; Fedonkin and Waggoner, 1997; Grey, 2005). Despite numerous models for the mechanisms driving the transition in biological systems (Canfield et al., 2007; Butterfield, 2009; Johnston et al., 2012b), the clues about the critical events that led to the emergence of animals remain at least partially locked within marine sediments. As a result, a suite of studies employing redox sensitive proxies have developed a framework whereby it is proposed that roughly coincident with the first animals, the deep ocean became oxygenated (Fike et al., 2006; Canfield et al., 2007; Canfield et al., 2008; Scott et al., 2008); this was Earth's canonical second great oxidation (Holland, 1984; DesMarais et al., 1992; Och and Shields-Zhou, 2012).

Assaying large-scale changes in atmospheric oxygen and geochemical cycles is classically a problem resolved through carbon isotope reconstructions (Broecker, 1970; Knoll et al., 1986; DesMarais et al., 1992; Fike et al., 2006; Johnston et al., 2012a). Here, the isotopic composition of carbonate and bulk organic carbon ($\delta^{13}C_{carb}$ and $\delta^{13}C_{org}$, respectively), when placed in a steady-state framework for the operation of the carbon cycle (Hayes et al., 1999), provides insight on the net production of oxygen. This O_2 then propagates throughout surface environments, often leaving an imprint directly on pO_2, but equally as important it controls sulfate delivery to the oceans and ferric oxide production on the continents (Holland, 1984; Holland et al., 1986; Hayes and Waldbauer, 2006; Holland, 2006). The net gain in these three oxidized reservoirs is the true measure of surface oxidation, and requires an expansion of the geochemical toolbox. Fortunately, the sulfur cycle can be indirectly tracked through isotopic reconstructions of sedimentary pyrite records and where possible, sulfates from evaporites, fluid inclusions,

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or that trapped within the carbonate lattice (Canfield and Teske, 1996; Canfield, 1998; Kampschulte and Strauss, 2004; Fike et al., 2006; Fike and Grotzinger, 2008). The influence of oxygen on global Fe budgets is more difficult to measure, as much of the ferric iron resides on the continents and in crustal materials. However, a refined extraction scheme provides a snapshot of iron cycling along a continental margin and serves as a powerful proxy for this budget. If the commonly posited increase in pO_2 accompanies or slightly predates the Ediacaran appearance of animals, it should be detectable in the C–S–Fe geochemistry of strata in northwestern Canada.

The last decade has seen the pervasive application of a revised sedimentary iron extraction scheme capable of diagnosing the chemical structure of the marine water column (Poulton et al., 2004; Canfield et al., 2007; Canfield et al., 2008; Johnston et al., 2010; Li et al., 2010; Poulton et al., 2010; Planavsky et al., 2011; Johnston et al., 2012b). Through quantifying the partitioning of iron into different Fe-bearing minerals, it is possible to identify anoxia and further distinguish between ferruginous (ferrous iron bearing) and euxinic (sulfide bearing) conditions (Poulton and Canfield, 2005). Applied to shale facies from a number of Neoproterozoic basins, Fe geochemistry is revealing a complicated picture of marine redox between the end of the Marinoan glaciation roughly 635 million years ago (Ma) and the Precambrian–Cambrian boundary at 541 Ma. Reconstructions of fossiliferous basins in modern day Russia and Newfoundland provide internally consistent pictures of a water column that is sometimes oxygenated, but when anoxic, is always ferruginous (Canfield et al., 2007; Johnston et al., 2012b). As it relates to the origin of metazoans, up-section changes in the redox state of the EEP basin (targeting transitions that antedate or that are coincident with the first appearance of animals) are not profound, leading to the subtler hypothesis that the geochemical/redox *stabilization* of these environments may have also been important to the development of more complex life and ecologies (Johnston et al., 2012b). In contrast, condensed fossil-bearing stratigraphic sections from South China capture much more reducing marine conditions, with an almost episodic fluctuation between ferruginous and euxinic conditions (Shen et al., 2008a; Li et al., 2010) and even some indication of oxic conditions (Sahoo et al., 2012). Inferentially, marine chemical evolution through the Ediacaran appears to be a basin-by-basin affair (Kah and Bartley, 2011; Johnston et al., 2012b). Interestingly, and appreciating that taphonomy is also variable, the distribution of fossil-bearing assemblages is similarly heterogeneous.

Marine redox/geochemical variability will always reflect the interplay between equilibrium with the overburden of atmospheric oxygen and the move toward disequilibria in water column dissolved oxygen (DO) as a result of differential nutrient inputs and productivity-remineralization regimes. How this context then feeds back on the link to animals and their unique physiological requirements is less clear, but must be related. Finding continuity between the geochemical and biological records through Ediacaran successions, especially those containing early metazoan records, requires high-resolution sampling, detailed and explicit correlations to fossil bearing horizons, and an expansion of geochemical reconstructions to include an understanding of sediment protolith.

One of the cornerstone Ediacaran paleontological records comes from mixed siliciclastic and carbonate sequences in northwestern Canada (Hofmann et al., 1990; Narbonne and Aitken, 1990b; Narbonne et al., 1994; Kaufman et al., 1997; Pyle et al., 2004; Macdonald et al., 2013–in this issue). Work on C–S–Fe in early Ediacaran stratigraphy from the Mackenzie Mountains has already hinted at evolving water column chemistry (Canfield et al., 2008; Shen et al., 2008b), but how that geochemical setting varies spatially (across the basin) or in time (up toward the Precambrian–Cambrian boundary) is unclear. In what follows we describe a detailed geochemical study, in conjunction with a revised stratigraphic context (Macdonald et al., 2013–in this issue), where we track major and trace element geochemistry and key isotopic metrics. Taken together, and when assimilated with data from other Ediacaran paleo-basins, a more lucid picture of Earth surface change and biological innovation is realized.

2. Geological setting

2.1. The Wernecke Mountains

In northwestern Canada, Ediacaran strata begin with micropeloidal dolomite of the Ravensthroat Formation (James et al., 2001), which caps a lowstand system tract at the top of the Cryogenian Keele Formation (Day et al., 2004) and glacigenic diamictite wedges of the Marinoan Icebrook Formation (Aitken, 1991b). The Ravensthroat is up to 30 m thick and is locally overlain by $\leq$10 m of limestone with pseudomorphosed aragonite fans of the Hayhook Formation (James et al., 2001). In the central Mackenzie Mountains, sea-floor barite discontinuously mantles the contact between the Ravensthroat and Hayhook formations, which together comprise the 'cap carbonate' (Hoffman and Halverson, 2011). Above the cap carbonate, the Ediacaran stratigraphy is a mix of siliciclastic and carbonate rocks (defined as the Sheepbed, Gametrail, Blueflower, and Risky formations, along with the informal, newly described Sheepbed carbonate and June beds (Macdonald et al., 2013–in this issue)) preserving large lateral variability in exposure and thickness (Fig. 1).

In the Wernecke Mountains, the lower Sheepbed Formation consists of shale with thin limestone interbeds and measures ~350 m thick. Similar to exposures in the Mackenzie Mountains, the lower ~100 m of shale is the darkest and most fissile and likely contain the maximum flooding surface (MFS) of the glacio-eustatic marine transgression. A distinct coarsening occurs roughly 180 m into the Sheepbed in our Wernecke section (same as Goz A from Pyle et al. 2004), where siltstone interbeds and platform-derived debris flows begin to appear. Upsection from this surface, limestone is increasingly more abundant and finally gives way to shallow water dolostone of the informal Sheepbed carbonate (Aitken, 1991a; Macdonald et al., 2013–in this issue). This carbonate unit was previously correlated with the Gametrail Formation (Pyle et al., 2004), but a recent examination of this correlation has identified an additional sequence boundary between the Sheepbed carbonate and the Gametrail Formation at its type locality (Macdonald et al., 2013–in this issue). The lower ~150 m of the Sheepbed carbonate consists of a monotonous, massive dolomite with rare cross-bedding and giant ooids. This is capped by a major karst surface, and is succeeded by ~40 m of coarse-grained sandstone and calc-arenite, which are assigned to the informal June beds. The overlying Gametrail Formation (peritidal member of Pyle et al. (2004)) consists of ~50 m of peritidal dolomite stacked in ~10 m thick parasequences capped by exposure surfaces. These surfaces culminate in a major unconformity that defines the base of the Blueflower Formation (Yuletide member of Pyle et al. (2004)) and is incised by multiple beds of cobble-clast quartzite conglomerate. The conglomerates are succeeded by a major flooding surface and shale with interbedded normally graded beds of sand and silt (interpreted as turbidites) that host simple bedding plane traces and Ediacaran disk fossils (Narbonne and Aitken, 1990a). The Blueflower Formation shallows upwards into hummocky cross-stratified sandstone and pink sandy dolomite of the Risky Formation. The top of the Risky Formation is marked by a karstic unconformity. Above this unconformity, small shelly fossils and a diverse microfossil assemblage have been described in phosphatic carbonates in the Ingta Formation near the southern Wernecke Mountain sections at Goz C and D (Nowlan et al., 1985; Pyle et al., 2006). This stratigraphic framework is presented in Fig. 1 and discussed in detail in a companion study (Macdonald et al., 2013–in this issue).

2.2. Correlation to the Mackenzie and Ogilvie Mountains

Correlative Ediacaran strata have been measured both to the east (in the central and southeast Mackenzie Mountains) and to the west (Ogilvie