Precambrian Research 263 (2015) 232–245

Contents lists available at ScienceDirect

Precambrian Research

journal homepage: www.elsevier.com/locate/precamres

Chemostratigraphy of the Shaler Supergroup, Victoria Island, NW Canada: A record of ocean composition prior to the Cryogenian glaciations

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ARTICLE INFO

Article history:
Received 12 February 2014
Received in revised form 1 February 2015
Accepted 2 February 2015
Available online 12 February 2015

Keywords:
Neoproterozoic
Carbon isotopes
Chemostratigraphy
Redox-sensitive trace metals
Fe speciation
Bitter Springs carbon isotope excursion

ABSTRACT

A new $\delta^{13}C_{carb}$ curve combined with $\delta^{13}C_{org}$ values is presented for the upper Shaler Supergroup (~900 to ~720 Ma), Amundsen Basin, northwestern Canada. The dataset fills gaps in the existing stratigraphic record and makes correlations with adjacent basins more robust. There is a pronounced negative $\delta^{13}C$ excursion in the Wynniatt Formation that can be correlated with a putative worldwide negative carbon isotope excursion, namely the Bitter Springs stage. However, in the Amundsen Basin, the $\delta^{13}C_{carb}$ excursion drops to anomalously negative values (−14‰), which we attribute to local overprints wherein isotopically light carbon in pore waters, released by oxidation of methane and organic matter during sulphate and iron reduction, was incorporated into authigenic carbonate cement. We document basin euxinia and anoxia during the same time interval using a multi-proxy approach; specifically, Fe-speciation and redox-sensitive trace metal data. Patterns of pronounced enrichment in Mo, V, and U concentrations in euxinic black shales suggest that the Bitter Springs stage was a transitional period in Earth's redox evolution, from the more reduced global oceans during the mid-Proterozoic to the more oxygenated oceans during the Phanerozoic.

1. Introduction

The Neoproterozoic Era records dramatic changes in seawater chemistry that eventually led to emergence of Phanerozoic surface conditions. Various isotopic systems have been employed to interpret secular changes in Neoproterozoic ocean chemistry, most commonly carbonate and organic carbon isotopes (e.g. Halverson et al., 2005, 2010; Swanson-Hysell et al., 2010; Walter et al., 2000), strontium isotopes (e.g. Halverson et al., 2007a; Thomas et al., 2004; Veizer, 1989), and sulphur isotopes (e.g. Kaufman et al., 2007; Loyd et al., 2012). Much of the work has focused on the period of the late Neoproterozoic glaciations and the Ediacaran–Cambrian transition, although attention is now being drawn to older successions and a broader array of redox proxies (e.g. Canfield et al., 2008; Johnston et al., 2010; Sperling et al., 2013).

In contrast to the Phanerozoic, the Neoproterozoic is characterized by intervals with sustained positive $\delta^{13}C_{carb}$ values punctuated by abrupt shifts to negative $\delta^{13}C_{carb}$ values (e.g. Halverson et al., 2010). The majority of the large, negative perturbations to the Neoproterozoic carbon cycle are associated with glaciations, but there are exceptions. One of them, the Bitter Springs stage, is defined by a negative excursion in the global carbon isotope record reported from many localities, including Australia (Walter et al., 2000), Zambia (Bull et al., 2011), Svalbard (Halverson et al., 2007b), Scotland (Prave et al., 2009), and northern Canada (e.g. Jones et al., 2010; Macdonald et al., 2010). A U–Pb age from an interbedded tuff in carbonate rocks preserved below the base of the Bitter Springs stage in the Ogilvie Mountains, Canada, yielded an age of 811.5 ± 0.25 Ma (Macdonald et al., 2010). Although the Bitter Springs stage is not associated with a glaciation, it is interpreted to mark a large perturbation to the global carbon cycle.

It is commonly assumed that the deep ocean became permanently oxygenated in the terminal Neoproterozoic and that this global redox shift was a driving force behind the diversification of multicellular life (e.g. Canfield and Teske, 1996; Des Marais et al.,

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http://dx.doi.org/10.1016/j.precamres.2015.02.007
0301-9268/

1992). Many studies have sought to characterize the redox state of the deep ocean and specifically pinpoint when the oceans became fully oxygenated (e.g. Sahoo et al., 2012; Scott et al., 2008; Sperling et al., 2013). However, despite a surge of work over the past decade, there is still debate about Neoproterozoic marine redox evolution. Several independent studies suggest ocean oxygenation around 580 Ma (Canfield et al., 2007; Fike et al., 2006; McFadden et al., 2008). More recent work suggests at least temporary pervasive ocean oxygenation earlier in the Ediacaran (ca. 635–630 Ma), in the immediate aftermath of the Marinoan 'Snowball Earth' glaciation (Sahoo et al., 2012).

Sedimentary rocks of the Shaler Supergroup were deposited in the Amundsen Basin and are exposed in the Minto Inlier, Victoria Island, Northwest Territories, Canada (Fig. 1). The upper Shaler Supergroup was deposited between ~900 and 720 Ma and is exceptionally well preserved, providing an ideal target for marine paleoredox studies of the time interval leading up to the Sturtian glaciation. Further, this succession provides an opportunity to further explore $\delta^{13}C_{carb}$ and $\delta^{13}C_{org}$ trends through this important period of time. Herein, we present new C isotope, Fe-speciation, trace metal, and pyrite sulphur isotope data to interpret marine redox conditions and carbon cycle dynamics, including their global implications.

2. Geologic setting

The Tonian (1000–850 Ma) to Cryogenian (850–635 Ma) Shaler Supergroup (~1100–723 Ma) is a >4-km-thick sedimentary succession composed of predominantly shallow-marine carbonate rocks interstratified with mudstones, sandstones, and sulphate evaporites (Fig. 1) deposited in the Amundsen Basin, a shallow embayment within a larger epeiric sea that developed after the assembly of Rodinia (Rainbird et al., 1996, 1998; Young, 1981). The maximum age of the Shaler Supergroup is constrained by detrital zircon geochronology at <1151 Ma (Rayner and Rainbird, 2013). The minimum age is 723 +4/−2 Ma based on U–Pb geochronology of diabase sills that intrude the sedimentary succession and feed overlying flood basalts, part of the Franklin Large Igneous Province (Heaman et al., 1992). Three depositional ages of 892 ± 13 Ma (Boot Inlet Formation), 849 ± 48 Ma (Black Shale member of the Wynniatt Formation), and 761 ± 41 Ma (Upper Carbonate member of the Wynniatt Formation) based on Re–Os black shale geochronology provide additional chronostratigraphic constraints (Fig. 1, van Acken et al., 2013). The strata are relatively undeformed, with dips typically less than 10°, and have experienced only low-grade contact metamorphism by the diabase sills (Fig. 2).

The Boot Inlet Formation is characterized by large stromatolitic bioherms that formed along a carbonate ramp, with interstratified inner and mid-ramp deposits (Narbonne et al., 2000). An upward-shallowing trend is preserved in the overlying Fort Collinson Formation, an interval of fluvial and marine-reworked sandstones (Rainbird et al., 1994). The overlying Jago Bay Formation is an upward-shallowing succession of carbonate-rich sedimentary rocks deposited in intertidal/lagoonal to supratidal and restricted intertidal depositional environments (Rainbird et al., 1994). Overlying the Jago Bay Formation, the Minto Inlet Formation consists of sedimentary rocks deposited under alternating restricted and open-marine conditions as reflected in bedded gypsum deposits and shallow subtidal limestones, respectively (Rainbird et al., 1996; Young, 1981). The overlying Wynniatt Formation, interpreted as a storm-dominated carbonate ramp, is divided into four informal members: (1) Lower Carbonate member, an upward-deepening succession of supra- to sub-tidal carbonate rocks; (2) Black Shale member, a recessive interval of dark-grey siltstone and silty shale deposited in a pro-delta setting; (3) Stromatolitic Carbonate member, comprising stacked upward-shallowing cycles of subtidal to supratidal carbonate rocks and, (4) Upper Carbonate member, an upward-shallowing succession from subtidal black calcareous shale to peritidal, cross-bedded intraclastic grainstone and stromatolitic limestone (Thomson et al., 2014). The Kilian Formation is characterized by cyclically alternating shallow sub- to intertidal carbonate rocks and sabkha-related evaporite facies (Rainbird, 1993).

Asmerom et al. (1991) reported several Sr isotope values for the Shaler Supergroup, however the lack of good age control hindered robust global correlation. Jones et al. (2010) published the first $\delta^{13}C_{carb}$ detailed chemostratigraphic curve for the Shaler Supergroup. A negative excursion reported from the Wynniatt Formation was correlated with the global Bitter Springs stage, and a younger negative excursion documented in the Kilian Formation was tentatively correlated to the 'Islay' excursion (Brasier and Shields, 2000; Jones et al., 2010).

3. Methods

3.1. Geochemical approach to paleoredox interpretation

We applied a multi-proxy approach using iron speciation, redox-sensitive trace metals, and pyrite sulphur isotope ratios to estimate the paleoredox conditions in the Amundsen Basin. The Fe speciation proxy provides a fingerprint for the presence of anoxic water column conditions. It is typically accepted that in average continental and slope deposits, iron that is highly reactive towards hydrogen sulphide on short time scales (Fe_{HR}) accounts for less than ~40% of the total iron (Fe_T) pool (Poulton and Raiswell, 2002; Raiswell and Canfield, 1998). In contrast, stratigraphically persistent, highly reactive iron enrichments develop when there is Fe scavenging under an anoxic water column (Poulton and Canfield, 2011). Therefore, typical continental margin sediments with Fe_{HR}/Fe_T ratios greater than ~0.4 are interpreted to have been deposited under an anoxic water column. However, it should be noted that sediments deposited close to large anoxic zones can also have highly reactive iron enrichments (Scholz et al., 2014), but these settings are unlikely to leave a laterally and stratigraphically persistent record.

If Fe speciation data suggests that sediments were deposited under anoxic water column conditions, one can explore further whether ferruginous ($Fe^{2+} > H_2S$) or euxinic ($Fe^{2+} < H_2S$) water column conditions prevailed based on the ratio of pyrite (Fe_{Py}) to Fe_{HR}. If the Fe_{Py}/Fe_{HR} ratio is >0.7, the anoxic shales can be attributed to iron-limited, sulphide-rich (euxinic) depositional conditions, while a Fe_{Py}/Fe_{HR} ratio <0.7 indicates ferruginous conditions (Poulton and Canfield, 2011).

The Fe proxies were calibrated in modern and ancient rocks that are predominately siliciclastic. However, several carbonate-rich rocks (e.g., Black Sea sediments) were used in the initial calibration. Further, there was recently a detailed study gauging the utility of the Fe proxies for carbonate-rich rocks that provided support for the use of proxies when there is significant amount (>1%) of total Fe (Clarkson et al., 2014). Therefore, the Fe proxies should be valid for the examined rocks despite significant TIC in some samples.

The degree of redox-sensitive trace metal enrichment (Mo, U, V) for shales deposited under euxinic conditions, based on the Fe speciation proxies, can be used to make first-order inferences about the global marine redox state (e.g. Algeo and Lyons, 2006; Lyons et al., 2009; Partin et al., 2013; Reinhard et al., 2013; Scott et al., 2008). This idea builds from three key principles. First, because these elements are more soluble under oxic than anoxic conditions, the global ratio of oxic-to-anoxic marine conditions controls the magnitude of the marine burial fluxes and ultimately the size of