Earth and Planetary Science Letters 335–336 (2012) 25–35

Contents lists available at SciVerse ScienceDirect

Earth and Planetary Science Letters

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

Late Ediacaran redox stability and metazoan evolution

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ARTICLE INFO

Article history:
Received 30 December 2011
Received in revised form
10 April 2012
Accepted 7 May 2012
Editor: G. Henderson
Available online 13 June 2012

Keywords:
evolution
animals
atmospheric oxygen
Neoproterozoic
Russia
Ediacaran

ABSTRACT

The Neoproterozoic arrival of animals fundamentally changed Earth's biological and geochemical trajectory. Since the early description of Ediacaran and Cambrian animal fossils, a vigorous debate has emerged about the drivers underpinning their seemingly rapid radiation. Some argue for predation and ecology as central to diversification, whereas others point to a changing chemical environment as the trigger. In both cases, questions of timing and feedbacks remain unresolved. Through these debates, the last fifty years of work has largely converged on the concept that a change in atmospheric oxygen levels, perhaps manifested indirectly as an oxygenation of the deep ocean, was causally linked to the initial diversification of large animals. What has largely been absent, but is provided in this study, is a multi-proxy stratigraphic test of this hypothesis. Here, we describe a coupled geochemical and paleontological investigation of Neoproterozoic sedimentary rocks from northern Russia. In detail, we provide iron speciation data, carbon and sulfur isotope compositions, and major element abundances from a predominantly siliciclastic succession (spanning >1000 m) sampled by the Kel'tminskaya-1 drillcore. Our interpretation of these data is consistent with the hypothesis that the $p\mathrm{O}_2$ threshold required for diversification of animals with high metabolic oxygen demands was crossed prior to or during the Ediacaran Period. Redox *stabilization* of shallow marine environments was, however, also critical and only occurred about 560 million years ago (Ma), when large motile bilaterians first enter the regional stratigraphic record. In contrast, neither fossils nor geochemistry lend support to the hypothesis that ecological interactions altered the course of evolution in the absence of environmental change. Together, the geochemical and paleontological records suggest a coordinated transition from low oxygen oceans sometime before the Marinoan ($\sim$635 Ma) ice age, through better oxygenated but still redox-unstable shelves of the early Ediacaran Period, to the fully and persistently oxygenated marine environments characteristic of later Ediacaran successions that preserve the first bilaterian macrofossils and trace fossils.

1. Introduction

The hypothesis that increased oxygen availability facilitated Ediacaran (635–542 Ma) metazoan evolution dates back more than half a century (Cloud and Drake, 1968; Nursall, 1959). This hypothesis posits that an increase in the oxygen content of shallow-marine environments was physiologically necessary for the emergence of large, highly energetic animals (Raff and Raff, 1970; Rhoads and Morse, 1971). Ecological and physiological observations place lower dissolved oxygen (DO) limits for ocean waters in which different types of animals can live (e.g., (Diaz and Rosenberg, 1995; Levin, 2003)). They further make predictions about body shape in early animals, based on diffusion length-scales for organisms that lack a circulatory system for bulk oxygen transport (Knoll, 2011; Payne et al., 2011; Raff and Raff, 1970; Runnegar, 1991). Together, then, these physiological requirements for oxygen predict that geochemical evidence for well-oxygenated marine waters should coincide with or slightly antedate fossil records of animals with high oxygen demand.

A growing suite of redox-related geochemical tools is now available to test the oxygen-facilitation hypothesis. For instance, reconstructions of the iron and sulfur cycles in Ediacaran strata of Newfoundland suggest a broad consistency between oxygenation and animal diversification (Canfield et al., 2007). There, deep-water

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http://dx.doi.org/10.1016/j.epsl.2012.05.010

axial turbidites with low overall organic carbon contents preserve a shift in the distribution of iron minerals that bespeaks increased DO. This inferred change in redox structure is placed atop the ~580 Ma glacial deposit of the Gaskiers Formation and is followed by the appearance of Ediacaran macrofossils through the overlying Drook, Briscal and Mistaken Point formations. A similar geochemical formula was applied to fossil-bearing sections from South China and the Yukon (McFadden et al., 2008; Narbonne and Aitken, 1990), however the relationship between the fossil record and redox transitions in these basins, especially as they relate to Newfoundland (Canfield et al., 2007), is less clear cut. Correlations among these basins and their stratigraphic successions are challenging, and the postulated role of sulfide as a key toxin in basins developed along the continental margin of the South China craton further complicates physiological interpretations (Li et al., 2010).

Thus, the lack of first-order geochemical coherence among these localities, perhaps due in part to locally variable biogeochemical fluxes (Johnston et al., 2010; Kah and Bartley, 2011), means that the direct role that oxygen played in the timing of both local and global animal diversification remains to be fully elucidated. Given this, it is important to acknowledge models of eumetazoan innovation that bypass oxygen entirely and call upon ecology as the primary driver (Butterfield, 2009; Peterson and Butterfield, 2005; Stanley, 1973). In addressing the role of oxygen through the application of robust geochemical techniques, both hypotheses can ultimately be tested.

Environmental and ecological hypotheses make distinct predictions about the sequence of biological and geochemical changes, which can be tested through detailed geochemical analyses of fossil-bearing Ediacaran strata. This forms the premise for our current study of Ediacaran marine sediments from the Eastern European Platform (EEP). This succession hosts some of the most exquisite examples of early animal life (Fedonkin et al., 2007; Fedonkin and Waggoner, 1997; Martin et al., 2000) and offers a prime opportunity to reconstruct oceanic redox conditions through the application of a range of geochemical methods. Here, we thus revisit both the oxygen facilitation and ecology hypotheses through the application of iron, sulfur, and carbon geochemistry, bulk elemental data, and rigorous statistical analysis.

2. Geological setting

The Kel'tminskaya-1 drillhole, located near the Dzhezhim–Parma uplift in northern Russia records ~5000 m of upper Neoproterozoic and Paleozoic strata that accumulated along the northeast margin of the East European Platform (Fig. 1). The lowermost 2000 m of the core contains a mixed carbonate and siliciclastic succession deposited in a shallow-marine setting, correlated bio- and chemo-stratigraphically to the Cryogenian (850–635 Ma) Karatau Group in the Ural Mountains (Raaben and Oparenkova, 1997; Sergeev, 2006; Sergeev and Seong-Joo, 2006). Age constraints for this part of the succession are limited, but stromatolites, vase-shaped microfossils (Maslov et al., 1994; Porter et al., 2003) and correlation to Pb–Pb dated carbonate rocks of the Min'yar Formation in the Ural Mountains suggest an age of 780 ± 85 Ma (Ovchinnikova et al., 2000).

Unconformably overlying Cryogenian strata, and thus separated by >100 million years, are siliciclastics of the Vychegda, Redkino and Kotlin formations. The Vychegda Formation, a 600 m thick succession, is dominated by interbedded sandstone, siltstone and shale suggestive of mid-shelf deposition. Diverse large ornamented microfossils first appear low in this unit (at 2779 m) and indicate an Ediacaran age (Vorob'eva et al., 2009b) (Fig. 1). No Sturtian or Marinoan-aged diamictites are present in the drillcore, complicating placement of the Cryogenian–Ediacaran boundary. However, typically pre-Ediacaran microfossils occur in mixed coastal siliciclastic rocks in the lowermost six meters of the Vychegda Formation, suggesting that the period boundary is marked by a cryptic unconformity just above these beds (Vorob'eva et al., 2009a,b).

The exact duration of the proposed hiatus is unclear; however, overlying Vychegda shales, interpreted as mid-shelf deposits (Vorob'eva et al., 2009a, b), contain a diverse assemblage of large, highly ornamented organic-walled microfossils akin to the Ediacaran Complex Acanthomorph-dominated Palynoflora (ECAP (Grey, 2005)). In central and southern Australia (Grey and Calver, 2007; Grey et al., 2003), the ECAP assemblage populates a restricted temporal interval, occupying beds that overlie the ca. 580 Ma Acraman impact layer, but underlie the strongly negative C-isotopic excursion of the Wonoka Formation (correlated with the Shuram anomaly in Oman). Well above this interval, diverse Ediacaran macrofossils appear. The same is true in China (Jiang et al., 2007; McFadden et al., 2008), Subhimalayan India (Kaufman et al., 2006), and the Patom region of Siberia (Pokrovskii et al., 2006; Sergeev et al., 2011). Detrital zircons also constrain ECAP acritarchs in the Hedmark Group, Norway to be younger than 620+/−14 Ma (Bingen et al., 2005), consistent with other results. Taken together, these observations most conservatively suggest that the Vychegda Formation was deposited during the Ediacaran Period, before 558 Ma, a U–Pb constraint provided from the Redkino Formation and discussed below. Given the distribution of ECAP microfossils elsewhere, we suggest that the majority of Vychegda Formation deposition took place between 580 and 558 Ma.

Siliciclastic rocks in the upper 1000 m of the Kel'tminskaya-1 drillhole correlate with the Redkino and Kotlin successions preserved across the EEP (Sokolov and Fedonkin, 1990). Redkino rocks lack highly ornamented microfossils but preserve an exceptional record of Ediacaran macrofossils, including *Kimberella*, widely considered to be the earliest known bilaterian animal (Fedonkin et al., 2007; Fedonkin and Waggoner, 1997; Rogov et al., 2012) (Fig. 1). Additional information about the paleobiology of Kel'tminskaya-1 core material can be found in (Vorob'eva et al., 2009a,b). U–Pb dates on zircons in Redkino ash beds indicate ages of 555.3 ± 0.3 Ma near the top of the succession (Martin et al., 2000) and 558 ± 1 Ma toward its base (Grazhdankin, 2003). Biostratigraphy places the Proterozoic–Cambrian boundary at or near the top of the Kotlin succession.

3. Methods

Iron speciation was performed following a calibrated extraction technique (Poulton and Canfield, 2005). This method targets operationally defined iron pools, such as iron carbonate (Fe_{carb}: ankerite and siderite), Fe^{3+} oxides (Fe_{ox}: goethite and hematite) and mixed valence iron minerals (Fe_{mag}: magnetite). Pyrite iron (Fe_{py}) and sulfur, as well as acid volatile sulfur (AVS; below detection in these samples) were extracted via traditional distillation techniques (Canfield et al., 1986). Together, these pools define a suite of minerals that can be considered biogeochemically available, or highly reactive (FeHr) towards reductive dissolution in surface and near-surface environments ($FeHr = Fe_{carb} + Fe_{ox} + Fe_{mag} + Fe_{py}$) (Poulton et al., 2004a). Total Fe (FeT) additionally comprises a largely unreactive silicate iron pool (FeU), delivered to the marine environment via weathered detrital fluxes (i.e., FeHr + FeU = FeT). Both pools are classically defined in relation to their reactivity toward dissolved sulfide (Canfield et al., 1992; Poulton et al., 2004b). Total Fe contents were derived from both $HF–HClO_4–HNO_3$ extractions and standard XRF analyses. X-ray fluorescence also provided major element chemistry, most notably Al, Ti, K, Na, Si,