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Late Ediacaran redox stability and metazoan evolution

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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 > 1,000 meters) sampled by the Kel'tminskaya-1 drillcore. Our interpretation of these data is consistent with the hypothesis that the pO_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 (~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.

1.0 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 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.

2.0 GEOLOGICAL SETTING

The Kel'tminskaya-1 drillhole, located near the Dzhezhim–Parma uplift in northern Russia records ~5,000 meters 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, 2006; Sergeev et al., 2011). Detrital zircons also constrain ECAP acritarchs in the Hedmark Group, Norway to be younger than 620 $\pm$ 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) (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.

3.0 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 ($\text{FeHr} = \text{Fe}_{\text{carb}} + \text{Fe}_{\text{ox}} + \text{Fe}_{\text{mag}} + \text{Fe}_{\text{py}}$) (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., $\text{FeHr} + \text{FeU} = \text{FeT}$). 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 $\text{HF-HClO}_4\text{-HNO}_3$ extractions and standard XRF analyses. X-ray fluorescence also provided major element chemistry, most

notably Al, Ti, K, Na, Si, Mg, Mn, and P (performed at UMass Amherst). All aqueous Fe analyses were performed by AAS, with a RSD of <5% for all stages.

Sulfur isotope analyses were performed by combusting sulfide precipitates (see Fe_{py} above) to SO₂ and then run via continuous-flow on a Thermofinnigan Delta V with an analytical reproducibility of 0.2‰, normalized to VCDT. Carbon isotopes were performed on splits of the same bulk sample. Prior to carbon isotope analyses, samples were decalcified with a 10% HCl pre-treatment. Decalcified samples were analyzed for organic carbon isotopes ($\delta^{13}\text{C}_{\text{org}}$) and total organic carbon contents (TOC) via combustion to CO₂ with a Carlo Erba EA interfaced with a Thermofinnigan Delta V configured in continuous flow mode. Samples were run in duplicate with reproducibility of 0.2‰ and <0.05 wt%. Carbonate carbon isotope values ($\delta^{13}\text{C}_{\text{carb}}$) were measured on a Dual Inlet VG Optima gas source mass spectrometer interfaced with an Isocarb prep device. Reproducibility is roughly 0.1‰ and all carbon isotope data are normalized to a VPDB scale.

4.0 RESULTS AND DISCUSSION

We used iron speciation chemistry, major element abundances, and stable carbon and sulfur isotopic ratios to characterize oceanic redox conditions and biogeochemical cycling during deposition of the Kel'tminskaya-1 succession (Fig. 2). The distribution of reactive iron minerals in marine sediment has been calibrated in order to differentiate between oxic and anoxic water column conditions (Canfield et al., 1996; Lyons et al., 2003; Poulton and Canfield, 2011; Raiswell et al., 1988; Raiswell and Canfield, 1996; Raiswell et al., 1994; Raiswell et al., 2001). In keeping with these calibrations, we interpret highly reactive iron (Fe_{Hr})/total iron (Fe_T) >

0.38 as diagnostic of anoxia, with Phanerozoic and modern marine Fe_{Hr}/Fe_T values of 0.14±0.08 and 0.26±0.08 falling within a range characteristic of an oxic depositional environment (Anderson and Raiswell, 2004; Poulton and Raiswell, 2002; Raiswell and Canfield, 1998). Fe/Al provides additional paleoredox information, with the added value of circumventing dilution effects related to carbonate contents (Lyons et al., 2003). In the case of Fe/Al (here Fe refers to Fe_T), crustal values of ~0.5-0.6 commonly characterize oxic conditions, with anoxia generally giving rise to Fe/Al enrichments above this threshold (Lyons and Severmann, 2006).

We also report the chemical index of alteration (CIA) for siliciclastic samples in order to monitor the nature and maturity of terrigenous fluxes into the basin (Nesbitt et al., 1997; Nesbitt and Young, 1984; Nesbitt et al., 1996; Tosca et al., 2010). CIA, a measure of the degree of weathering, is expressed as $\text{Al}_2\text{O}_3/[\text{Al}_2\text{O}_3 + \text{CaO} + \text{Na}_2\text{O} + \text{K}_2\text{O}]$. Given the importance of clay minerals in organic matter burial and early diagenetic biogeochemistry (Hedges and Keil, 1995; Keil et al., 1994; Rothman and Forney, 2007), we provide these data to assay potential changes in source terrain for detrital siliciclastics that would in turn effect marine geochemical cycling, all presented against the backdrop of previous work on the Neoproterozoic (Kennedy et al., 2006; Tosca et al., 2010). Finally, reporting on the isotopic composition and abundances of carbon and sulfur allows the geochemical measures described above to be linked more directly to biogeochemical cycling. That is, the stoichiometry of heterotrophic remineralization reactions provides a means of relating organic carbon (and factors associated with production, export and burial) to electron accepting species within the Fe and S cycles (Fe-oxides and sulfate, in particular). Below we discuss the distribution of these data in the context of their specific geological setting, beginning with the oldest, Cryogenian-age samples. The full data are presented in the supplemental materials.

194

195 **4.1 Cryogenian records from the EEP**

196 Geochemical data for the carbonate-rich Cryogenian portion of the Kel'tminskya-1
197 drillhole mirror those of pre-Sturtian successions elsewhere (Canfield et al., 2008; Johnston et
198 al., 2010). Within the lower reach of the drillhole, $\delta^{13}\text{C}_{\text{carb}}$ varies stratigraphically from -4‰ to
199 4‰, consistent with earlier Neoproterozoic values from the Uralian Karatau Group (Podkovyrov
200 et al., 1998) and correlative carbonates on the Siberian Platform (Bartley et al., 2001). Organic
201 carbon content is generally low (< 0.4 wt%), and on average is higher in Cryogenian than in
202 younger intervals of the succession; $\delta^{13}\text{C}_{\text{org}}$ values for carbonate-rich Cryogenian samples vary
203 moderately around a mean of about -29‰. A monotonic $\sim 8\text{‰}$ rise in $\delta^{13}\text{C}_{\text{carb}}$ through the
204 Vapol' Formation may suggest an increase in organic carbon burial (Hayes et al., 1999), but a
205 tight, parallel change in $\delta^{13}\text{C}_{\text{org}}$ is lacking. This lack of isotopic covariance is not uncommon in
206 Neoproterozoic carbonates (Fike et al., 2006; Swanson-Hysell et al., 2010), with recent work
207 pointing to complexities associated with $\delta^{13}\text{C}_{\text{org}}$ as masking classic carbon isotope behavior
208 (Johnston et al., 2012; Knoll et al., 1986). In the case of the Cryogenian from Russia, the data
209 reported here support a stratigraphic link to the Ural Mountains and provide yet another example
210 of a pre-Sturtian carbon cycle with a large degree of variability. That is, the biogeochemical
211 picture provided by the Vapol' and Yskemess formations is consistent with those preserved
212 globally.

213 The Vapol' and Yskemess formations are carbonate dominated, with, on average, a
214 weight percent total iron (Fig. 2), much of which occurs as Fe-carbonate. The iron carbonate
215 fraction was determined via the first step of the normal Fe-speciation method, which is a weak

acid extract defined to access carbonate phases (ankerite and siderite). The further application of Fe-speciation data requires added discussion. It is important to appreciate that Fe-speciation methods are calibrated on fine-grained siliciclastic sediments and the threshold values that guide the reading of these metrics are similarly rooted. This, of course, complicates the direct and literal interpretation of Fe-speciation data on carbonates. However, a number of points require consideration. Foremost, the determination of iron carbonate, simply as a mass fraction and as presented above, is robust. Next, the logic of Fe speciation methods is based on the precipitation of Fe minerals under anoxic water column conditions and the subsequent settling of these minerals, enriching local sediments. This iron enrichment is only possible when bottom water conditions are anoxic. Thus, iron enrichment should occur in anoxic carbonate-rich environments in the same fashion as it does in siliciclastic sediments, provided that there is a reasonable amount of total Fe to source. Fe enrichment in carbonates can occur because of water column Fe precipitation or suspended load siliciclastic admixture. (Fe/Al ratios for carbonates were not measured due to interferences associated with high $[\text{Ca}^{2+}]$, a function of carbonate content.) Nonetheless, where FeT is high, as is the case with the EEP carbonates (FeT averages ~1.3 wt%), the potential for minor Fe mobilization and redistribution following deposition should not result in a spurious redox signal, and its association with carbonates suggests that it is reactive iron as opposed to silicate iron or iron delivered with detrital fluxes. With the discussion above and in noting that Fe in ancient carbonates usually stays close to original depositional values (Tucker and Wright, 1990), Fe speciation has been successfully applied in a variety of siliciclastic-poor settings (e.g. (Goldberg et al., 2005; Kendall et al., 2010; Marz et al., 2008)). However, although we argue that the Fe-speciation proxy should generally behave similarly in carbonate-rich and siliciclastic rocks (also see (Poulton and Canfield, 2005)), we do

not require the strict interpretation of carbonate iron data for the story forwarded here. We simply present iron data from a limited Cryogenian dataset against the backdrop of contemporaneous siliciclastic units from North America, which is discussed below.

Iron speciation data for the Vapol' and Yskemess formations are variable but suggest a highly reactive iron enrichment (and inferred bottom water anoxia), even though most of these rocks were deposited in no more than a few tens of meters of water. Calculated 95% confidence intervals for Fe_{Hr}/Fe_T in the Vapol' and Yskemess are $0.54^{0.04}_{1.21}$ and $0.48^{0.12}_{0.79}$, respectively (see also Fig. 2, 3). For the samples with elevated reactive iron contents, low sulfide contents (Fig. 2) result in low Fe_{py}/Fe_{Hr} ratios (~0.1), which, coupled with an Fe speciation signal that is Fe_{carb} dominated (Figure 3), points to anoxic ferruginous water column conditions (Poulton et al., 2004; Poulton and Canfield, 2011) for nearly 80% of the Cryogenian samples. As noted above, these data simply provide a complementary picture. Interestingly, however, and in support of using Fe methods on carbonates, correlative successions from other continents also feature low pyrite contents and signatures of anoxia. For example, by almost every metric, the EEP results are consistent with the shale-dominated Chuar Group in the Grand Canyon, USA (Johnston et al., 2010). There, a stratigraphically resolved data-set records persistent subsurface water column anoxia, in waters of similar depth, with only modest sulfide production corresponding to intervals of increased TOC burial. Given the dominant role of the atmosphere (and the O₂ reservoir) in disseminating oxygen into the surface mixed layer of the ocean, anoxia on the shelf likely reflects lower O₂, noting that local biogeochemistry can influence the DO load (Johnston et al., 2010).

4.2 Ediacaran records from the EEP

Geochemical data from the siliciclastic Ediacaran portion of the Kel'tminskya-1 drillhole (above 2779m) suggest a more fully oxygenated water column, as well as an increasing trend toward redox stability moving upward through the section. Total iron abundances for the Vychehda, Redkino and Kotlin formations are significantly higher than for the carbonate-rich Cryogenian section, as expected for a shale-dominated succession, with Fe and P concentrations similar to average Phanerozoic shale contents (~5 wt% and 0.07 wt %, respectively; Fig. 2) (Turekian and Wedepohl, 1961). The distribution of reactive iron phases from the EEP suggests a markedly more oxygenated depositional environment for the Ediacaran shales than for the underlying Cryogenian deposits. Ediacaran Fe_{Hr}/Fe_T values oscillate around a mean of $0.26^{0.13}_{0.36}$ (95% confidence interval), similar to that characteristic of modern oxic marine sediments (Fig. 2, 3) (Poulton and Canfield, 2011; Poulton and Raiswell, 2002).

Although suggesting more oxygenated conditions, in detail the chemical variability in the Vychehda Formation does allow (and may indicate; (Poulton and Canfield, 2011)) recurring intervals of less oxygenated bottom waters, which were replaced by more persistently oxygenated conditions by Redkino time. Along those lines, a closer look at the data reveals an important change *within* the Ediacaran portion of the succession. Notably, the Vychehda-Redkino sequence boundary separates distinct geochemical regimes (Fig. 2). Thus, we subdivide the Ediacaran stratigraphy into the earlier Ediacaran interval (~580 to 558 Ma) represented by the Vychehda Formation above 2779m and the upper Ediacaran interval (~558 to 542 Ma) recorded by the Redkino-Kotlin formations. As depicted in Figure 3, many of the reported geochemical metrics from the early and late Ediacaran successions scatter around similar average values, but early Ediacaran samples consistently show more variability. Our data, thus, present a

picture of a shelf environment that gradually evolved from one of significant redox heterogeneity in the Cryogenian, through a more oxygenated but still unstable redox regime in the early Ediacaran, to a stable, persistently oxygenated state in the late Ediacaran.

In the context of this interpretation, we can consider implications for local biogeochemical cycling. As posited earlier, atmospheric oxygen is one of a few levers on bottom water chemistry, acknowledging that heterotrophy following TOC loading and the ensuing benthic fluxes represent a significant local sink for oxidants (Johnston et al., 2010). To evaluate these contrasting mechanisms, we investigate the relationship between the carbon, phosphorus and iron budgets inferred from Kel'tminskaya-1 samples. The EEP shale is generally TOC lean (Fig. 2, 5), contains typical P contents, and low overall pyrite concentrations. The low observed pyrite contents suggest that dissimilatory sulfate reduction (Canfield, 2001) was not a prominent remineralization pathway in these settings. Without sulfate, this leaves oxygen, nitrate and iron oxides as potentially prominent electron acceptors. The ratio of TOC to reactive iron does not reveal a significant linkage (Fig. 5); however, the conversion of originally mixed valence Fe inputs to predominantly ferrous iron carbonate does require a reductive catalyst, which most naturally would be dissimilatory iron reduction (Fig. 5a). As an extension, the efficiency of P burial relative to organic C can provide important information about preferential P regeneration through remineralization reactions under different redox conditions (Algeo and Ingall, 2007; Ingall and Jahnke, 1994). This often results in a strong positive correlation between C and P, and high organic C:P under anoxic conditions (cf. (Jilbert et al., 2011; Kraal et al., 2010). For example, organic C:P in modern anoxic settings can exceed 300, but deposition under fully oxygenated modern conditions often drive organic C:P below 50 (Algeo and Ingall, 2007). In the case of the EEP, organic C:P ratios are consistently low,

approaching 1:1 for the Vychegda and ~2:1 for the Redkino and Kotlin formations (Fig. 5b). Low organic C:P ratios, coupled with low total organic C and the lack of an authigenic P enrichment above that of normal marine shale, is often interpreted as a result of a higher redox potential in the local environment, consistent with an oxygenated water column (Algeo and Ingall, 2007).

The distinction between early and late Ediacaran geochemistry can be investigated more quantitatively. To explore the robustness of this partitioning, we bootstrapped a Monte Carlo resampling ($n = 1000$) of the Vychegda – Redkino/Kotlin data sets ($n = 35$ and 44 , respectively). This approach clearly identifies differences in Fe/Al ratios and pyrite $\delta^{34}\text{S}$ values, with CIA values holding steady near a value of 0.70 (Fig. 6). Interestingly, the average FeHr/FeT value differs little between lower Ediacaran Vychegda shales and those of the overlying Redkino-Kotlin succession (Fig. 6a); however, the upper and lower Ediacaran successions differ in the distribution of FeHr/FeT values about the mean, indicating a marked *stabilization* of the redox environment by the late Ediacaran. Whereas the earlier Ediacaran samples record highly variable bottom water conditions, younger Ediacaran shales document a stable and persistently oxic seafloor. This up-section change in FeHr/FeT distribution does not necessarily require an increase in the dissolved oxygen content of seawater, although increasing oxygen provides a ready mechanism for increased redox stability. Fe/Al values also closely track this shift (Fig. 6), and in the absence of apparent change in other possible controls on FeT, these data point toward a broadly oxygenated environment throughout the entire interval of the Ediacaran Period sampled by the drillcore (cf. (Lyons and Severmann, 2006; Lyons et al., 2003; Severmann et al., 2008)). Similarly, more variability in Fe/Al ratios in the early Ediacaran, in part perhaps related to FeT, reflects a greater degree of redox instability, which is again succeeded by stable and

oxic-like Fe/Al ratios in the younger Ediacaran part of the succession. Finally, the CIA values of these two populations are similar (Fig. 5), and thus the chemical maturity of terrigenous clay inputs can also be taken as roughly constant, ruling out major change in the terrestrial weathering regime as a driver of the observed geochemical stabilization (Kennedy et al., 2006; Tosca et al., 2010). As clay minerals provide a critical template for the proficient burial of organic matter, it is important to place constraints on this vector. This is especially true considering that the inception of pedogenic clay formation was proposed as a spur for Ediacaran changes in organic burial and associated oxygen production (Kennedy et al., 2006). The absence of a change in the chemical composition of weathered material and sedimentation rate (as reflected by a persistent and similar depositional setting) indicates that there was no major change in provenance or composition of sediments entering the EEP basin.

Our data thus indicate that by the time that the main Vychegda sequence began to deposit, marine redox conditions had changed from persistent anoxia to a broadly oxygenated water column. This conclusion, of course, reflects oceanographic conditions in a single basin and does not preclude earlier oxygenation of water masses elsewhere. That noted, data from other continents similarly record a redox transition within the lower part of the Ediacaran Period (Canfield et al., 2007; Fike et al., 2006; Scott et al., 2008; Shen et al., 2008). Where the EEP data extend our understanding is their recording of redox *stabilization*, perhaps at ca. 560 Ma. Neither redox transition nor redox stabilization require that pO_2 reached modern levels in the Ediacaran – indeed, both data and models suggest that present day pO_2 was first reached only in the later Paleozoic Era (Bergman et al., 2004; Berner and Canfield, 1989; Dahl et al., 2010). Rather they suggest that, perhaps for the first time in Earth history, oxygen levels were sufficient to limit the spread of anoxia in shallow water settings.

353

354 **4.3 Insight from the sulfur cycle**

355 The sulfur cycle is sensitive to the oxygen content of the atmosphere, and as such, may
356 provide a test of proposed mid-Ediacaran transitions (cf. (Berner and Canfield, 1989; Claypool et
357 al., 1980; Garrels and Lerman, 1981)). We first look at the limited data from the Cryogenian
358 Vapok' and Yskemess formations. Here, $\delta^{34}\text{S}$ values are highly variable and range from above
359 estimates of contemporaneous seawater sulfate (Johnston et al., 2010) to almost -30‰. Scaling
360 loosely with TOC content (Fig. 7b), the 50‰ range certainly reflects primary microbial
361 contributions from sulfate reduction and may also indicate sulfur disproportionation reactions
362 (Canfield and Teske, 1996; Johnston et al., 2005), although mass-balance effects of local sulfate
363 limitation might also have been in play (Canfield, 2001; Hayes, 2001). Although the data
364 exhibit some scatter, in particular where TOC values are higher, $\delta^{34}\text{S}$ values are generally more
365 enriched, consistent with sulfate limitation within the sediments and, consequently, near-
366 quantitative reduction of pore-water sulfate.

367 The sulfur isotopic composition of pyrite from the Ediacaran portion of the EEP is also
368 quite variable. The $\delta^{34}\text{S}$ values of pyrite within the Vychegda Formation are, on average, more
369 depleted and variable than sulfides from the overlying Redkino and Kotlin formations (a mean
370 value of 2‰ as opposed to 12‰ for the late Ediacaran; Fig. 6d). Importantly, the Vychegda
371 Formation is also more pyrite-rich than overlying strata, averaging ~0.08 and ranging up to 0.3
372 wt% pyrite (the Redkino and Kotlin formations average ~0.02 wt%). If we presume a $\delta^{34}\text{S}$ of
373 seawater sulfate between 20‰ and 30‰, similar to estimates from early Ediacaran successions
374 in Oman, Namibia, South China and Australia (Fike et al., 2006; Halverson and Hurtgen, 2007;

Hurtgen et al., 2002; Hurtgen et al., 2006; McFadden et al., 2008), then the net fractionation associated with a consortium of microbial metabolisms only requires the influence of sulfate reduction. If the Ediacaran seafloor was moving toward a more oxygenated state, as suggested by iron speciation data, then an oxidative sulfur cycle was almost certainly present in the water column. Emerging tools, specifically the minor sulfur isotopes (Johnston, 2011), may provide a test of this interpretation and allow for the isotopic contributions of reductive and oxidative processes to be more uniquely constrained.

The overlying Redkino and Kotlin formations contain much less pyrite and preserve sulfur isotope compositions that cluster toward more enriched values. Although not as enriched as the super-heavy pyrites observed elsewhere (Ries et al., 2009), values are almost always positive ($> 0\text{‰}$). Limited data (Fike and Grotzinger, 2008; Fike et al., 2006; Kampschulte and Strauss, 2004) and a model treatment of that data (Halverson and Hurtgen, 2007) suggest an enrichment in the $\delta^{34}\text{S}$ of seawater sulfate toward the end of the Ediacaran, although more recent datasets suggest seawater sulfate remained near 20‰ at that time (Ries et al., 2009). The lack of consistency among these data is curious, as it points to either the infidelity of certain proxies, poor absolute correlation between continents, or – perhaps most likely – a heterogeneous seawater sulfate reservoir. Regardless of the reason, this variability makes the diagnosis of the Redkino and Kotlin sulfur cycle difficult. If sulfate was becoming more ^{34}S enriched at that time, then the net fractionation between sulfate and sulfide may not have changed significantly from that observed in the underlying Vychegda Formation. However, if sulfate remained largely invariant, these data suggest that the net fractionation decreased drastically. This later scenario could reflect an extreme deficiency in seawater sulfate concentrations (Habicht et al., 2002), but is more likely associated with simple sulfate limitation within the sediments. The latter

interpretation is consistent with other geochemical proxies in suggesting that, regionally, anoxia developed only within the sediment column.

4.4 Incorporating biological considerations

Geochemistry divides the Kel'tminskaya-1 record into three parts: a pre-Ediacaran (Cryogenian) portion recording the common occurrence of ferruginous water masses in shallow-water environments; a lower Ediacaran succession documenting more oxygenated, but still fluctuating bottom-water conditions on the shelf, and an upper Ediacaran interval that records a fully and persistently oxic water column. Fossils divide regional stratigraphy in much the same fashion (Fig. 1, 2): the Cryogenian rocks are characterized by a modest diversity of protists (Vorob'eva et al., 2009a), recording microscopic eukaryotes that could thrive at low pO_2 . In contrast, the upper Ediacaran (Redkino-Kotlin) succession contains macroscopic animals, as well as trace fossils (Fedonkin et al., 2007; Fedonkin and Waggoner, 1997). In between lie the diverse, large ornamented microfossil assemblage characteristic of lower Ediacaran successions worldwide (Vorob'eva et al., 2009a). Data on morphology, wall ultrastructure, size frequency distribution and preserved intracellular contents suggest that many of these distinctive microfossils represent egg and diapause cysts of early animals (Cohen et al., 2009; Sergeev et al., 2011; Yin et al., 2007). Modern animals produce resting stages when fertilized eggs have a high probability of landing where growth is difficult or impossible (Cohen et al., 2009); therefore, it makes physiological sense that the Ediacaran cysts should be abundant and diverse in basins where geochemical data indicate bottom water redox instability. Whether animal or something else, the abundance of these cysts in Vychegda Formation shale indicates that environmental

conditions were frequently inimical to growth. Few if any of these microfossils persist into beds marked by persistently oxic water column conditions. The hypothesis that the early Ediacaran seafloor was intermediate in redox character to its pre-Ediacaran and late Ediacaran counterparts is also consistent with the presence of moderately differentiated but essentially two-dimensional macrofossils in earlier Ediacaran shales from China (Yuan et al., 2011).

Diverse macroscopic animals first appear regionally in Redkino-aged deposits (Sokolov and Fedonkin, 1990; Sokolov and Iwanowski, 1990). Many of these appear to have a simple anatomy, and may largely represent bodyplans in which upper and lower epidermis enclose inert, mesoglea-like material (e.g., (Sperling and Vinther, 2010)). One body-fossil population, however, is widely regarded as the remains of a bilaterian animal. *Kimberella quadrata* was a roughly 2 cm long and at least 1 cm thick organism whose fossil impressions show a distinct anterior-posterior axis with a plane of symmetry running from front to back (Fedonkin et al., 2007). It is occasionally preserved at the end of a trace fossil that documents directional movement across the sediment surface and sometimes also occurs with anterior scratch marks similar to those made by the radulae of mollusks during feeding (Fedonkin et al., 2007). While the precise phylogenetic relationships of *Kimberella* remain open to question, it has a strong claim to status as a bilaterian animal and almost undoubtedly would have required more oxygen for physiological function than other commonly preserved Ediacaran macroorganisms. Independently of *Kimberella*, and consistent with the predictions of molecular clocks (Erwin et al., 2011), trace fossils in the Redkino succession indicate a modest diversity of bilaterian animals. Thus, in the EEP, geochemical evidence for stabilization of pervasively oxic conditions in shelf environments correlates with the appearance of animals with unprecedentedly high oxygen demand.

The statistical treatment presented in Figure 6 helps further explain why the Vychegda and Redkino/Kotlin intervals should be characterized by life cycles with resting stages and large, highly energetic animals, respectively. While neither succession displays Fe-speciation evidence for strong water mass anoxia, and while the mean value of FeHr/FeT is similar for the two intervals, the greater dispersal about the mean for Vychegda samples results in nearly half of all values falling within the ‘equivocal’ redox range; Redkino/Kotlin samples do not record such a FeHr enrichment. In a recent review, it has been postulated that these intermediate FeHr/FeT values (from 0.26-0.38 in FeHr/FeT) point toward “possible anoxia” (Poulton and Canfield, 2011). The term “dysoxia” is commonly frowned upon by geochemists because conditions of low (but measurable) DO are not demarcated by a reliable geochemical fence. Biologists, in contrast, pay close attention to dysoxic/hypoxic waters because their low oxygen contents (less than 1-2 ml/l) strictly limit animal size, locomotion and diversity (e.g., (Diaz and Rosenberg, 1995; Seibel and Drazen, 2007; Vaquer-Sunyer and Duarte, 2008)). Hypoxia during the deposition of the Vychegda Formation may have been sufficiently frequent to favor small animals able to survive episodic bottom water anoxia as well as other unfavorable conditions by forming resting cysts. The removal of this limitation, then, correlates with the first appearance of large, thick, highly motile animals.

In combination, then, geochemical and paleontological data from northwestern Russia are fully consistent with the hypothesis that evolving redox conditions exerted a strong influence on the timing of early animal evolution. What about contrasting ecological hypotheses? Few would dispute that ecology played an important role in animal diversification (Butterfield, 2007; Knoll, 1994), but what geochemical and paleontological features are uniquely predicted by this hypothesis? The ornamentation of large Ediacaran microfossils have been interpreted as a

defensive response to bilaterian predators (Peterson and Butterfield, 2005), but no bilaterian macrofossils have been found in Russian or other rocks that contain these ornamented microfossils, and as bilaterians begin to populate the fossil record, the microfossils largely disappear. Geochemically, ecological reorganization in a physiochemically stable ocean should be reflected in changes in biogeochemical cycling across the Vychegda-Redkino boundary (Butterfield, 2009; Logan et al., 1995). For instance, changes in the articulation of the biological pump (Butterfield, 2009) would carry direct consequences for carbon export, organic matter burial and preservation, and possibly even the type of organic compounds preserved in the sediments. As recorded on the EEP, however, neither TOC nor $\delta^{13}\text{C}_{\text{org}}$ values change significantly across this boundary; nor do pyrite contents or S:C ratios. The sulfur isotopic composition of pyrite does record mid-Ediacaran change (Fig. 2, 6, 7), and, like other proxies, records much less variability in the later Ediacaran. The more positive $\delta^{34}\text{S}$ values found for younger Ediacaran pyrites may simply be another consequence of redox evolution, as sulfate reduction increasingly became restricted to lower and lower horizons within the sediment column, which could have facilitated the net quantitative reduction of pore-water sulfate. The fossil record indicates that evolving animals drove ecological change, especially in the Cambrian, when diverse new bodyplans populated the oceans (Bengton and Morris, 1992); however, available data provide little support for Ediacaran ecological reorganization outside of the context of changing physiochemical conditions.

5.0 CONCLUSIONS

Geochemical reconstructions of Cryogenian and Ediacaran successions on the margin of the Eastern European Platform preserve a history of Earth surface evolution that can be related to similar reconstructions from other continents (Canfield et al., 2007; Johnston et al., 2010; McFadden et al., 2008; Shen et al., 2008), and, more importantly, extends our understanding of how atmospheric oxygen may have influenced the early diversification of metazoans. Previous geochemical models have qualitatively linked proposed increase in the dissolved oxygen content of the ocean with the appearance of macroscopic animals, and although tight constraints on absolute pO_2 remains elusive, data from the EEP suggests that the redox stabilization of the local marine depositional environment may be equally important. This does not preclude a role for changing pO_2 as a means of driving stabilization, although any such mid-Ediacaran change could have been quite modest. A better understanding of absolute pO_2 trajectory may be possible through high-resolution reconstructions of marine depositional environments with high TOC loading (for instance, the Ediacaran successions of the Wernecke and Mackenzie Mountains in the Yukon, Canada), which in contrast to the EEP, would provide a more prominent oxidant sink in the bottom waters and further insight into biogeochemical cycling.

In the Kel'tminskaya-1 drillhole, unconformities separate three paleontologically and geochemically defined packages, limiting inferences about the timing, rate, and mechanisms underlying these redox state transitions. That noted, the paleontological progression recorded in northern Russia characterizes Neoproterozoic successions observed globally. The oldest macroscopic animals occur in 565-579 Ma strata from Newfoundland (Narbonne, 2005), a deep-water succession that records a stably oxic seafloor (Canfield et al., 2007) predating Redkino deposition by up to 20 million years. Quite possibly, the fossiliferous Newfoundland rocks record a time interval missing on the EEP along the Vychegda-Redkino sequence boundary. It is

also possible, however, that redox stability was not imposed synchronously across the globe (Kah and Bartley, 2011). Indeed, protracted Ediacaran increases in pO_2 might have oxygenated basins regionally, one after another, with biological changes following suit as environmental conditions allowed. This hypothesis can be tested by integrated sequence stratigraphic, paleontological, geochemical, and geochronological analyses of Ediacaran successions.

By themselves, however, paleontological and geochemical data from the northeastern EEP support two first-order conclusions. First, as evidenced by a growing body of FeHr/FeT data, the oft-cited Neoproterozoic ‘oxygenation’ does not appear to be associated with the Shuram anomaly, as iron speciation data suggests an earlier arrival of this oxidizing capacity and cannot speak to the rate of change (gradual versus abrupt). Continued study of Cryogenian records will help to identify and describe the anatomy of this oxygenation, were a profound change in atmospheric chemistry to exist. Whatever the answer, the participation of oxygen in the atmospheric carbon cycle (as it interacts with critical greenhouse gasses, namely CO_2 and CH_4) suggests a relationship between Neoproterozoic pO_2 and low-latitude Cryogenian glaciations (Hoffman et al., 1998). Second, and most important for biological records, by about 580-560 Ma, redox stability came to define shallow marine seafloor environments, possibly (but not necessarily) reflecting a further increase in pO_2 . Our data thus most closely support the classic hypothesis that increasing atmospheric oxygen paved the way for the global expansion of bilaterian macrofossils, but underscores the role of redox *stability* in potentiating end-Proterozoic evolutionary events.

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Figure 1: A map of the Timan Ridge area showing the location of the Kel'tminskaya-1 drillhole on the northeastern margin of the Eastern European Platform (see arrow on the inset for the location on the Eastern European Platform). At right, a cartoon timeline of the characteristic fossils found in Cryogenian and Ediacaran rocks; protistan assemblages (Porter et al., 2003) are replaced by large ornamented microfossils, which gave way to complex animals (e.g. *Kimberella*).

Figure 2: Stratigraphic redox proxy variations for the Kel'tminskaya-1 drillhole. Note the break in vertical scale at the Vapoli'–Vycheгда sequence boundary. The age of deposition is based on lithological and biostratigraphic correlation to the White Sea and Ural Mountains successions. Note that the 635 Ma age relates to the strata underlying the hiatus in the lower Vycheгда, whereas the ~580 Ma age relates to that of the overlying ECAP-containing portion of the unit. All methods and additional data are described in the text and presented in the supplemental materials. The two leftmost chemostratigraphic frames are on a log scale. Vertical lines in the FeHr/FeT column are discussed in the text, with red circles with lines extending horizontally representing samples with FeHr/FeT > 0.6 and indicate anoxia. Where indicating anoxia, all samples are ferruginous. Carbon isotope axes for carbonate and organic carbon (far right panel) are offset by 31‰.

Figure 2

Figure 3: Two frames indicating the relationship between FeHr/FeT (a measure of anoxia) versus (a) top: a quantification of pyrite iron, $\text{Fe}_{\text{py}}/\text{FeHr}$ and (b) bottom: an alternative means of recording anoxia. A key to the symbols is listed under the figure, with all data coming from this work. In (a), regions of the plot characteristic of particular water column redox state and chemistry are noted. That is, $\text{FeHr/FeT} > 0.38$ is indicative of anoxia, whereas values below the modern average (0.26) are indicative of oxic conditions (Anderson and Raiswell, 2004; Poulton and Canfield, 2011; Poulton and Raiswell, 2002; Raiswell and Canfield, 1998). The hashed region, between these two values, carries a more equivocal meaning. For reference, the Phanerozoic average for shale is also listed (dashed line). In frame (b), the crustal average of Fe/Al is indicated. See text for further discussions, especially that of the Vapoh' and Yskemess formation carbonates.

Figure 4: A summary of Fe-speciation data for pre-Sturtian sediments from Russia (this work), North America (Johnston et al., 2010), East Greenland, and Australia (Canfield et al., 2008). Axes are the same as Figure 3a, as are distinctions in Fe_{py}/Fe_T.

Figure 5: An analysis of the covariance between different biogeochemical metrics. Here, we examine changes in TOC against (a) reactive iron to total iron ratios, and (b) versus total P content. Both figures are also contoured by lines representing different ratios between the abscissa and ordinate measures. These features are fully described in the text and both relate to oxygen content of the local environment.

Figure 6: A statistical resampling of key geochemical metrics from the Ediacaran of the EEP. Data sets were divided at the Vychegda-Redkino sequence boundary (Vychegda in blue, Redkino and Kotlin in red). Importantly, sampling of the Vychegda began at 2779 m, the bed at which distinctly Ediacaran acritarchs first appear (Vorob'eva et al., 2009a). **a)** A measure of overall water column redox, FeHr/FeT. **b)** The relationship between Fe and Al. **c)** The chemical index of alteration is described in the text. **d)** The isotopic composition of pyrite sulfur. In all cases, one thousand synthetic runs were performed (binned and recorded on ordinate axis). Ordinate axis scale changes from frame to frame.

Figure 7: Two plots examining the relationship between the sulfur isotopic composition of pyrite and (a) reactive to total iron ratio (FeHr/FeT) and (b) total organic carbon content, TOC. Symbols are described below the figure, and the data is discussed in the text.

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Highlights for *Late Ediacaran redox stability and metazoan evolution* by Johnston *et al.*

- 1) Redox stability, in addition to O₂, is critical for animal evolution.
- 2) We explain Ediacaran global asynchronicity in sedimentary proxy and animals records.
- 3) We revisit the importance of dysoxia for biological evolution.
- 4) The data reinforce that Ediacaran acritarchs are resting stages of early animals.