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Redox heterogeneity of subsurface waters in the Mesoproterozoic ocean

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ABSTRACT

A substantial body of evidence suggests that subsurface water masses in mid-Proterozoic marine basins were commonly anoxic, either euxinic (sulfidic) or ferruginous (free ferrous iron). To further document redox variations during this interval, a multiproxy geochemical and paleobiological investigation was conducted on the approximately 1000-m-thick Mesoproterozoic (Lower Riphean) Arlan Member of the Kaltasy Formation, central Russia. Iron speciation geochemistry, supported by organic geochemistry, redox-sensitive trace element abundances, and pyrite sulfur isotope values, indicates that basinal calcareous shales of the Arlan Member were deposited beneath an oxygenated water column, and consistent with this interpretation, eukaryotic microfossils are abundant in basinal facies. The Rhenium–Osmium (Re–Os) systematics of the Arlan shales yield depositional ages of 1414 ± 40 and 1427 ± 43 Ma for two horizons near the base of the succession, consistent with previously proposed correlations. The presence of free oxygen in a basinal environment adds an important end member to Proterozoic redox heterogeneity, requiring an explanation in light of previous data from time-equivalent basins. Very low total organic carbon contents in the Arlan Member are perhaps the key—oxic deep waters are more likely (under any level of atmospheric O_2) in oligotrophic systems with low export production. Documentation of a full range of redox heterogeneity in subsurface waters and the existence of local redox controls indicate that no single stratigraphic section or basin can adequately capture both the mean redox profile of Proterozoic oceans and its variance at any given point in time.

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INTRODUCTION

How the Earth's atmosphere and ocean transitioned from their early, essentially anoxic state to our familiar oxygen-rich world remains controversial. It is well documented that an oxygenation event at approximately 2400 Ma (Ma: million years) established a persistently oxic atmosphere and surface ocean, but deep ocean chemistry remains uncertain through the remainder of the Proterozoic Eon (Kah & Bartley, 2011; Lyons *et al.*, 2014). Geologists long posited that the widespread disappearance of banded iron formation at approximately 1800 Ma reflects oxygenation of the deep ocean (Holland, 1984); however, Canfield (1998) proposed that under relatively low atmospheric O_2, the deep ocean would remain anoxic and indeed become euxinic, reflecting increased rates of bacterial sulfate reduction at depth. The nature of subsurface ocean chemistry is critical to our understanding of Earth surface history and biological evolution.

Initial tests of the Canfield hypothesis were supportive: Iron geochemical studies of the McArthur and Roper basins (data from approximately 1730–1630 and 1500–1400 Ma, respectively) in northern Australia indicated that basinal euxinia existed beneath an oxic-mixed layer through an interval more than 300 Ma long (Shen *et al.*, 2002, 2003). Indeed, Poulton *et al.* (2004) argued that rocks of the Animikie Basin, Ontario, captured a global transition from ferruginous to sulfidic subsurface waters roughly 1800 million years ago. Subsequent organic geochemical research corroborated these findings, documenting biomarker molecules for green- and purple-sulfur bacteria in the 1640 Ma Barney Creek Formation of the McArthur Basin, a finding that requires euxinia within the photic zone (Brocks *et al.*, 2005). Studies of molybdenum isotopes, which track the percentage of seafloor bathed in euxinic waters, also pointed to more widespread sulfidic conditions than in the modern ocean (Arnold *et al.*, 2004; Kendall *et al.*, 2009).

Tracers based on the abundance and/or isotopic composition of Mo and other redox-sensitive trace metals (Partin *et al.*, 2013) are extremely useful in understanding how the mean state of the ocean has changed through time, but they do not address the question of variance among basins. Continuing studies of mid-Proterozoic sedimentary environments using local proxies (those that record conditions in the immediately overlying water column) have pointed to a more nuanced picture of sub-wave-base ocean chemistry, documenting both euxinic and ferruginous conditions within the same basin. Cores from both the Animikie (Poulton *et al.*, 2010) and McArthur basins (Planavsky *et al.*, 2011) demonstrate heterogeneity in deep ocean chemistry—S^{2-} and Fe^{2+} are mutually exclusive in space, but not in time. Similar features are also observed in more extensively studied Neoproterozoic successions, where it now appears that euxinia is the exception rather than the rule (Canfield *et al.*, 2008; Johnston *et al.*, 2010; Sperling *et al.*, 2013). Johnston *et al.* (2010) proposed a model for the development of euxinia, noting that oscillations between ferruginous and euxinic conditions in basinal strata track sedimentary total organic carbon contents, which suggests that euxinia is most likely to develop when organic carbon delivery exceeds the delivery of electron acceptors that outcompete sulfate (e.g., nitrate, ferric iron; Planavsky *et al.*, 2011; Sperling *et al.*, 2013). Adding to this emerging heterogeneity, data from mineral assemblages suggest that despite widespread anoxia in oxygen minimum zones, dysoxia (oxygen present but at low levels) apparently persisted in the deepest parts of at least some mid-Proterozoic oceans (Slack *et al.*, 2007, 2009).

Here, we report multiproxy sedimentary geochemical and paleobiological analyses of lower Mesoproterozoic strata recovered by the 203 Bedryazh drill core from the Volgo-Ural region, Russia (Fig. 1A), drilled about 5 km southwest from Bedryazh settlement (Google Map coordinates, decimal degrees latitude and longitude, 56.3430 N latitude, 55.5302 E longitude). To track water-column redox conditions, we integrate organic geochemical (biomarker) data, iron-based redox proxies, redox-sensitive trace elements, pyrite sulfur isotope values, and total organic carbon contents. As previous studies have suggested an empirical relationship between subsurface anoxia and the distribution of eukaryotic microfossils (Butterfield & Chandler, 1992; Javaux *et al.*, 2001; Shen *et al.*, 2003), we also document the composition of microfossils preserved in basinal Arlan shales. These data are then placed in the context of information from other basins to examine redox heterogeneity in Mesoproterozoic oceans.

GEOLOGIC BACKGROUND

Geology of the Ural Mountains and Volgo-Ural region

For many years, Russian geologists discussed Meso- and early Neoproterozoic stratigraphy in terms of a Riphean stratotype located in the Bashkirian meganticlinorium, a large structure on the western slope of the southern Ural Mountains (Keller & Chumakov, 1983; Chumakov & Semikhatov, 1981). In the southern Urals, the lower Mesoproterozoic (Lower Riphean) is represented by the Burzyan Group, traditionally divided into the Ai, Satka, and Bakal formations in ascending stratigraphic order (Fig. 1B). The age of Burzyan deposition is constrained by the approximately 1380 Ma Mashak volcanics in the overlying Middle Riphean Yurmata Group (Krasnobaev *et al.*, 2013a; Puchkov *et al.*, 2013) and approximately 1750 Ma basalts 200 m above the base of the Ai Formation (Puchkov *et al.*, 2012; Krasnobaev *et al.*, 2013b; Fig. 1B).

In the Volgo-Ural region to the west, subsurface Riphean stratigraphy is known from core and geophysical data. According to new geological and geophysical data, the correlative stratigraphy to the Burzyan Group in this region, the Kyrpy Group, is subdivided into the Sarapul, Prikamskii, and Or'ebash subgroups, and its base has not been penetrated by drilling (Kozlov *et al.*, 2009, 2011; Kozlov & Sergeeva, 2011). The Or'ebash subgroup is subdivided into the Kaltasy and Kabakovo Formations. The Or'ebash Subgroup previously included the Nadezhdino Formation as well (see Kah *et al.*, 2007, their fig. 2), but this formation was recently transferred to the overlying Serafimovka Group correlated with the Yurmata Group (Kozlov *et al.*, 2009; Kozlov & Sergeeva, 2011). The Kaltasy Formation, of interest here, is correlated with the Satka Formation in the Ural Mountains (Keller & Chumakov, 1983; Kah *et al.*, 2007; Kozlov *et al.*, 2009) and is subdivided into the conformable Sauzovo (not recognized in this core; Kozlov *et al.*, 2011), Arlan, and Ashit members. The formation ranges in thickness from 1230 to 3600 m. The Arlan Member (535–1216 m thick) is represented by carbonaceous shales (some of them fossiliferous) and subordinate siltstones, dolostones, limestones, and dolomitic marls.

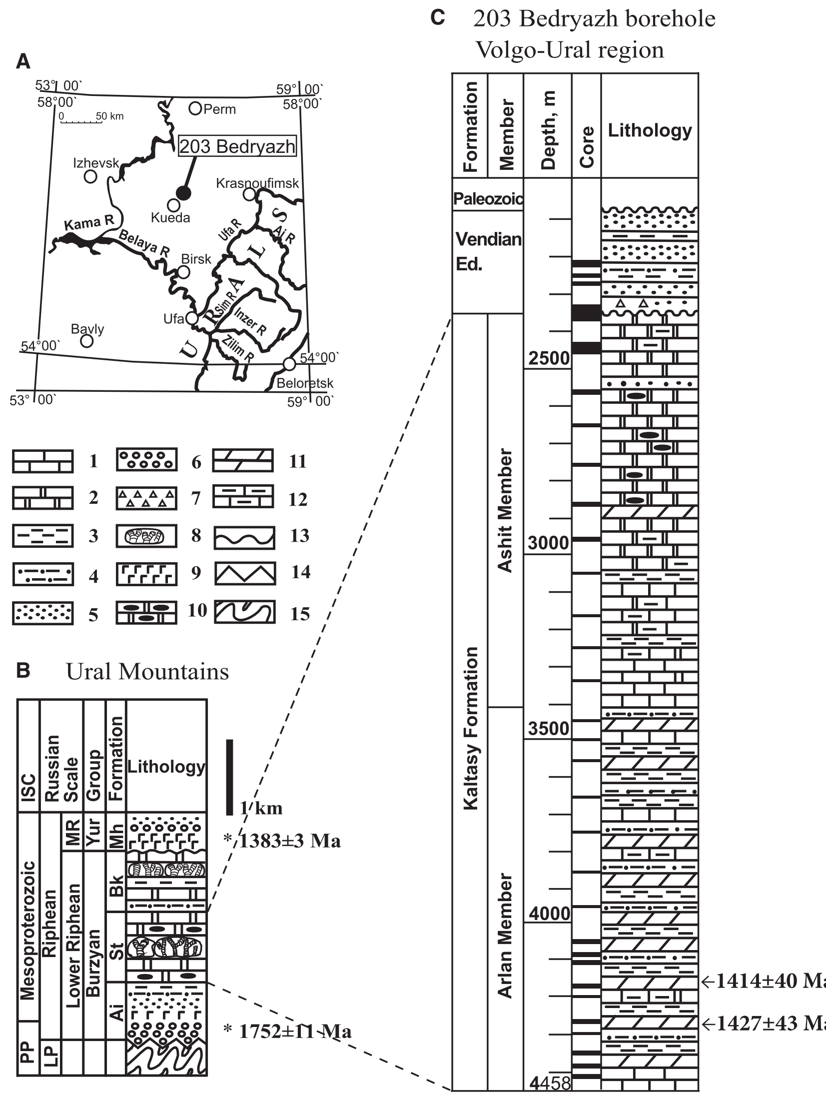

Fig. 1 (A) Map of the southern Ural Mountains and Volgo-Ural region showing the location of the 203 Bedryazh borehole (filled circle) and Riphean stratotypes in the southern Ural Mountains. (B) Generalized stratigraphic column of the Mesoproterozoic (Lower Riphean) deposits of the southern Ural Mountains (after Keller & Chumakov, 1983; Sergeev, 2006). Formation abbreviations: Ai, Ai; St, Satka; Bk, Bakal; Mh, Mashak. Other abbreviations: PP, Paleoproterozoic; LP, Lower Proterozoic; MR, Middle Riphean; Yur, Yurmanta Group; ISC, International Stratigraphic Chart. Asterisks mark geochronological constraints for the Lower Riphean (Puchkov *et al.*, 2012, 2013; Krasnobaev *et al.*, 2013a,b). Symbols denoting rock types are (1) limestone; (2) dolomite; (3) shale; (4) siltstone; (5) sandstone; (6) conglomerate; (7) tillite, tilloid; (8) bioherms with columnar stromatolites; (9) tuff, tuffaceous sandstone, and diabase; (10) dolomite with chert lenses; (11) marl; (12) clay dolomites; (13) hiatus, unconformity; (14) azimuthal discordance; and (15) basement gneiss. (C) Generalized stratigraphic column of the Mesoproterozoic (Lower Riphean) and Ediacaran (Vendian) deposits of the 203 Bedryazh borehole (after Kah *et al.*, 2007; Kozlov *et al.*, 2009). Borehole depth in meters is given to the center of the column, and available core is shown to right (dark lines). The most probable correlation of the Kaltasy Formation with the southern Ural Mountains Proterozoic succession is shown by dashed lines. New Re–Os age estimates from this core (this study) indicated by arrows. Abbreviation: Ed, Ediacaran.

Depositional environment of the Arlan Member in the 203 Bedryazh core

Redox profiles of paleobasins are most easily interpreted through transects of multiple stratigraphic sections in a sequence stratigraphic context (Shen *et al.*, 2003; Poulton *et al.*, 2010; Sperling *et al.*, 2013). A sequence stratigraphic framework for the Kyrpy Group has not been established, and core coverage across this basin was not available; consequently, interpretation of redox chemistry in relation to paleowater depth must be determined with respect to sedimentological indicators in the studied strata themselves. Such an approach has proven useful in many recent studies of Proterozoic sedimentary geochemistry (Johnston *et al.*, 2010, 2012; Wilson *et al.*, 2010; Cumming *et al.*, 2013).

In the 203 Bedryazh core, the Arlan Member consists almost entirely of parallel laminated dark shales with minor, commonly diagenetic micrite/dolomicrite. Petrography shows that clay-rich laminae predominate, with thin intercalations containing appreciable quartz silt. Fine sand grains of angular quartz occur in some laminae, commonly 'floating' in a finer matrix; these grains may have been transported into the basin by wind. No wave- or current-generated sedimentary structures are present, suggesting persistent deposition below storm wave base. Although some shallow environments may exhibit laminations and a lack of wave-generated sedimentary structures (for instance, isolated lagoons), such conditions only exist on relatively short stratigraphic scales. The complete uninterrupted absence of wave activity for over a kilometer of stratigraphic thickness strongly argues these sediments were deposited beneath wave base, and further, far enough below wave base that any sea-level oscillations did not bring the environment within the reach of storm waves. Consistent with this view, Kah *et al.* (2007) argue that the

203 Bedryazh drillcore penetrates some of deepest Arlan facies found in the entire basin.

A perennial question in pre-Mesozoic paleoceanography concerns the water depth of sediments deposited beneath storm wave base—these basinal strata are almost certainly not 'deep' in the oceanographic sense of an average ocean depth of 4 km. While the only hard constraint on these strata is that they were deposited in water depths persistently >150 m (as indicated by the lack of wave-generated sedimentary structures), such strata are generally considered more likely to fall into the depth range of several hundred meters rather than being significantly deeper. From a comparative sedimentological standpoint, the Arlan Member investigated here is comparable to 'basinal' strata recognized in stratigraphic studies of other Proterozoic basins, such as the Roper Group (Abbott & Sweet, 2000; Shen *et al.*, 2003) or Fifteenmile Group (Sperling *et al.*, 2013). That noted, the absolute lack of any wave-generated sedimentary structures clearly distinguishes the Arlan here from 'outer shelf' strata in those studies, which contain thin intercalated sandstones with sedimentological structures such as hummocky cross-stratification (Abbott & Sweet, 2000), indicative of shallower conditions than those from the Arlan. That is, to the extent that the Arlan depositional environment can be compared to those of shales sampled in previous studies of Mesoproterozoic redox conditions, Arlan deposits are likely to represent equally deep or deeper water conditions. Thus, while redox data from the Arlan succession cannot be interpreted in terms of the deep global ocean, they can be compared to equivalent environments in other basins and at other points in Earth history where the redox geochemistry has been explored.

MATERIALS AND METHODS

Re–Os geochemistry

For Re–Os geochronology, samples were collected from two intervals of the 203 Bedryazh drill core; (A) from 4197.97 to 4198.50 m and (B) from 4297.05 to 4297.40 m (arrows on Fig. 1C stratigraphic column). These intervals were analyzed following methodology in Selby & Creaser (2003), Cumming *et al.* (2013), and references therein. Briefly, samples were digested and equilibrated in $Cr^{VI}O_3$–H_2SO_4 together with a mixed tracer (spike) solution, and Re and Os were extracted and purified using solvent extraction, micro-distillation, anion column chromatography methods, and negative ion mass spectrometry. Isotopic measurements were performed using a ThermoElectron TRITON mass spectrometer. Full materials and methods and precision estimates for all geochemical analyses are located in Supporting Information.

Iron, carbon, sulfur, and major/minor element geochemistry

The core was sampled as closely as possible based on existing core coverage (Fig. 1C). Samples were first analyzed for iron speciation chemistry. Three pools of highly reactive iron (iron carbonate, iron oxides, and magnetite) were quantified using standard sequential-extraction protocols (Poulton & Canfield, 2005). Pyrite iron was determined using a hot chromous chloride extraction (CRS) and gravimetric quantification as Ag_2S (Canfield *et al.*, 1986). In addition to these four pools normally measured in studies of iron partitioning, a subset of samples (Table S2) were analyzed for other iron phases that could affect interpretation of iron speciation. Specifically, iron associated with acid-volatile sulfide (AVS) was quantified using the hot 6 N HCl + $SnCl_2$ extraction of Rice *et al.* (1993), and iron in poorly reactive silicates (Fe_{PRS}) was quantified with a 1-min boiling HCl extraction and calculated as the difference between that value and the sum of the sequentially extracted phases (Cumming *et al.*, 2013). Pyrite sulfur isotope values were determined on the silver sulfide from the CRS extraction via combustion in a Costech Elemental Analyzer linked to a Thermo Scientific Delta V mass spectrometer in continuous flow mode (measured as SO–SO_2). Major, minor, and trace elements (with the exception of Re and Os) were measured via ICP-AES at SGS Laboratories, Canada, following a standard four-acid digestion. Percent carbonate carbon was determined by mass loss following acid dissolution, and percent organic carbon was quantified by combusting acidified samples within a Carlo Erba NA 1500 Elemental Analyzer attached to a Thermo Scientific Delta V Advantage mass spectrometer.

Organic geochemistry and paleobiology

The Bedryazh-203 core was drilled with water-based fluids, not oil-based lubricants, and so was considered potentially suitable for an analysis of the lipid biomarkers associated with the rocks. For biomarker analysis and preparation, three samples (*b* on Fig. 3 stratigraphic column) from the core were selected. An organic geochemical preparation procedure (see Supporting Information) was used on these samples, beginning with a number of steps to remove external contamination, including removing the outside edges, followed by crushing using a cleaned puck mill, and extraction with a mixture of organic solvents in a high-pressure, high-temperature cell. Finally, the bitumen extract was analyzed using gas chromatography and mass spectrometry to identify lipid biomarkers.

Samples taken throughout the core were processed for microfossils using standard palynological methods (Sergeev *et al.*, 2011). Full materials, methods, and precision estimates for all analyses are given in Supporting Information.

RESULTS

Re–Os geochemistry

Elemental Re and Os abundances for horizon 4198 m range from 0.1 to 0.6 ppb, and 11.3 to 34.6 ppt, respectively, with $^{187}Re/^{188}Os$ and $^{187}Os/^{188}Os$ ratios between 42 and 109, and 1.204 and 2.795, respectively (Table S3). The samples from the 4297-m interval have Re abundances from 0.1 to 0.7 ppb and Os abundances from 10.3 to 32.8 ppt. Isotopic ratios for $^{187}Re/^{188}Os$ and $^{187}Os/^{188}Os$ range from 60 to 138 and from 1.558 to 3.652, respectively (Table S2). Regression of the isotopic composition data for the 4198-m interval yields a Model 1 age of 1414 ± 40 Ma [n = 6, mean square of weighted deviates (MSWD) = 0.35, initial $^{187}Os/^{188}Os$ (Os_i) = 0.20 ± 0.06; Fig. 2A]. The

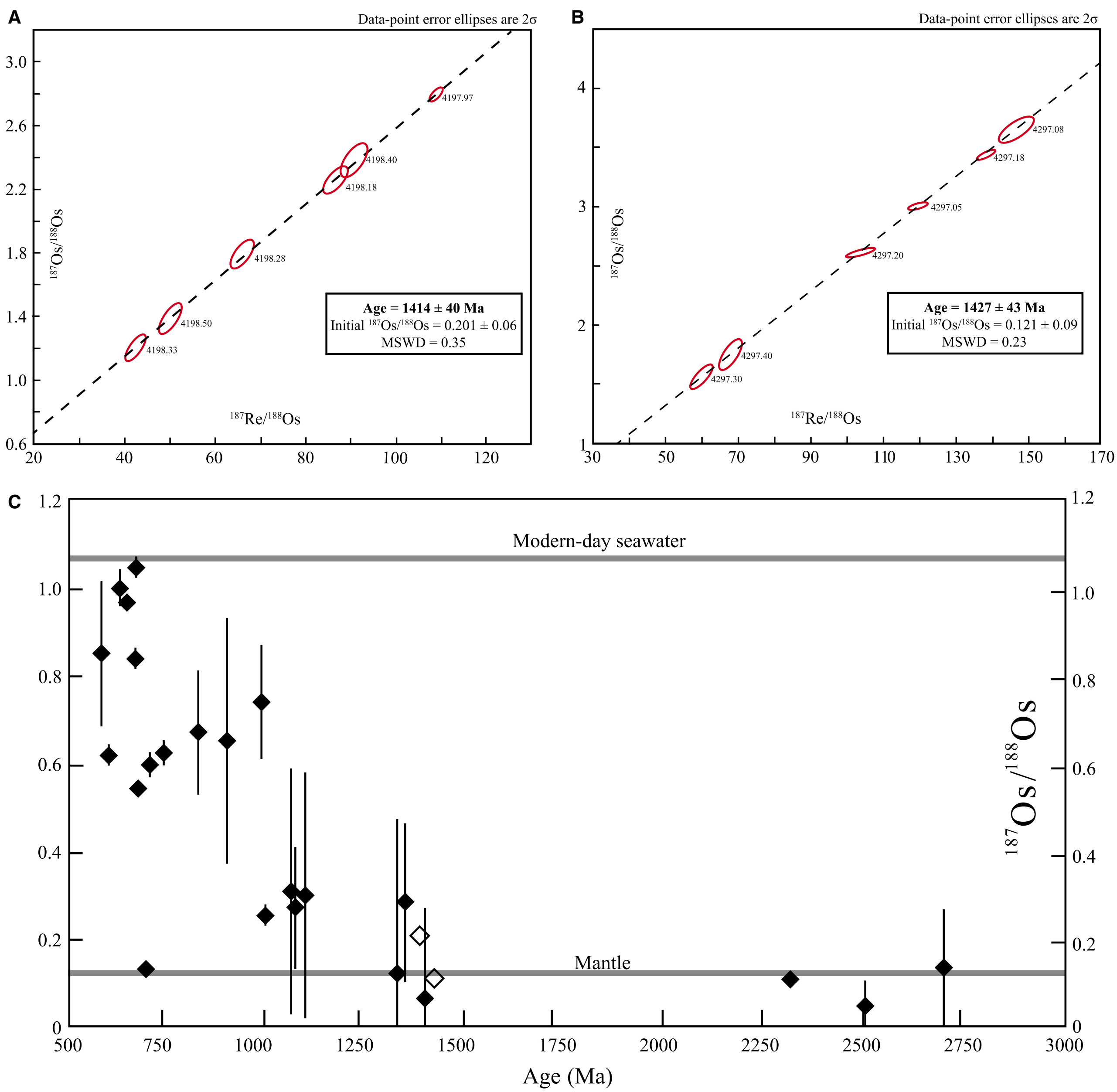

Fig. 2 Re–Os isochrons for the 203 Bedryazh shales. (A) Depth range 4197.97 to 4198.5 m. (B) Depth range 4297.05 to 4297.4 m. (C) Evolution of seawater $^{187}Os/^{188}Os$ values from the Archean through to the early Phanerozoic. Adapted from Van Acken *et al.* (2013) and updated with data from Geboy *et al.* (2013), Rooney *et al.* (2014), Strauss *et al.* (in press), and (A.D. Rooney, D. Selby, unpubl. data). Open symbols: this study. Mantle Os isotope composition of 0.13 is from Meisel *et al.* (2001). The modern-day seawater Os isotope composition of 1.06 and the modern-day continental weathering flux of 1.4 (not shown) is from Peucker-Ehrenbrink & Ravizza (2000). Uncertainties in initial $^{187}Os/^{188}Os$ values are 2 sigma, and uncertainties in ages are less than the size of the symbols.

Re–Os isotopic data for the 4297-m interval yield a Model 1 age of 1427 ± 43 Ma (*n* = 6, MSWD = 0.23, Os_i = 0.12 ± 0.09; Fig. 2B).

Redox-proxy geochemistry

Iron speciation chemistry focuses on the ratio of operationally defined 'highly reactive' iron pools (FeHR = iron in pyrite plus iron reactive to sulfide on early diagenetic timescales—namely iron carbonates and iron oxides, including magnetite) to total iron (FeT) in fine-grained siliciclastic sedimentary rocks. In these Arlan samples, reactive iron is dominated by iron carbonate (51%), followed by iron in pyrite (22.5%), iron oxide (13.5%), and magnetite (13%). FeHr/FeT is relatively constant throughout the Arlan Member (FeHr/FeT = 0.14 ± 0.04: Fig. 3). No significant acid-volatile sulfur was detected in the samples analyzed (Table S2 and Supporting Information). Iron in poorly reactive silicates (Fe_{PRS}) averaged 0.66 ± 0.25 wt% (Table S2 and Supporting Information) and the average Fe_{PRS}/FeT ratio of 0.20 ± 0.06 is not enriched compared with Modern or Phanerozoic normal shales (Poulton and Raiswell, 2002; Cumming *et al.*, 2013). Both total iron (3.26 ± 0.61 wt%) and total aluminum (7.36 ± 1.44 wt%) (Table S1) are less than average shale composition (4.72 and 8.00 wt%, respectively; Turekian & Wedepohl, 1961), with an average Fe/Al of 0.45 ± 0.06 (Fig. 3). Arlan shales are calcareous (24 ± 10%), perhaps leading to lower FeT and Al via dilution. Total organic carbon contents are low for basinal shales, averaging 0.11 ± 0.08 wt% (Fig. 3). Pyrite sulfur isotope values are moderately enriched (Fig. 3; $\delta^{34}S$ average = +13.2 ± 5.9‰). Redox-sensitive trace elements in Arlan samples are not enriched with respect to average shale (Turekian & Wedepohl, 1961; Gromet *et al.*, 1984). This holds if total abundances are considered or if abundances are normalized to biogeochemically-conservative elements such

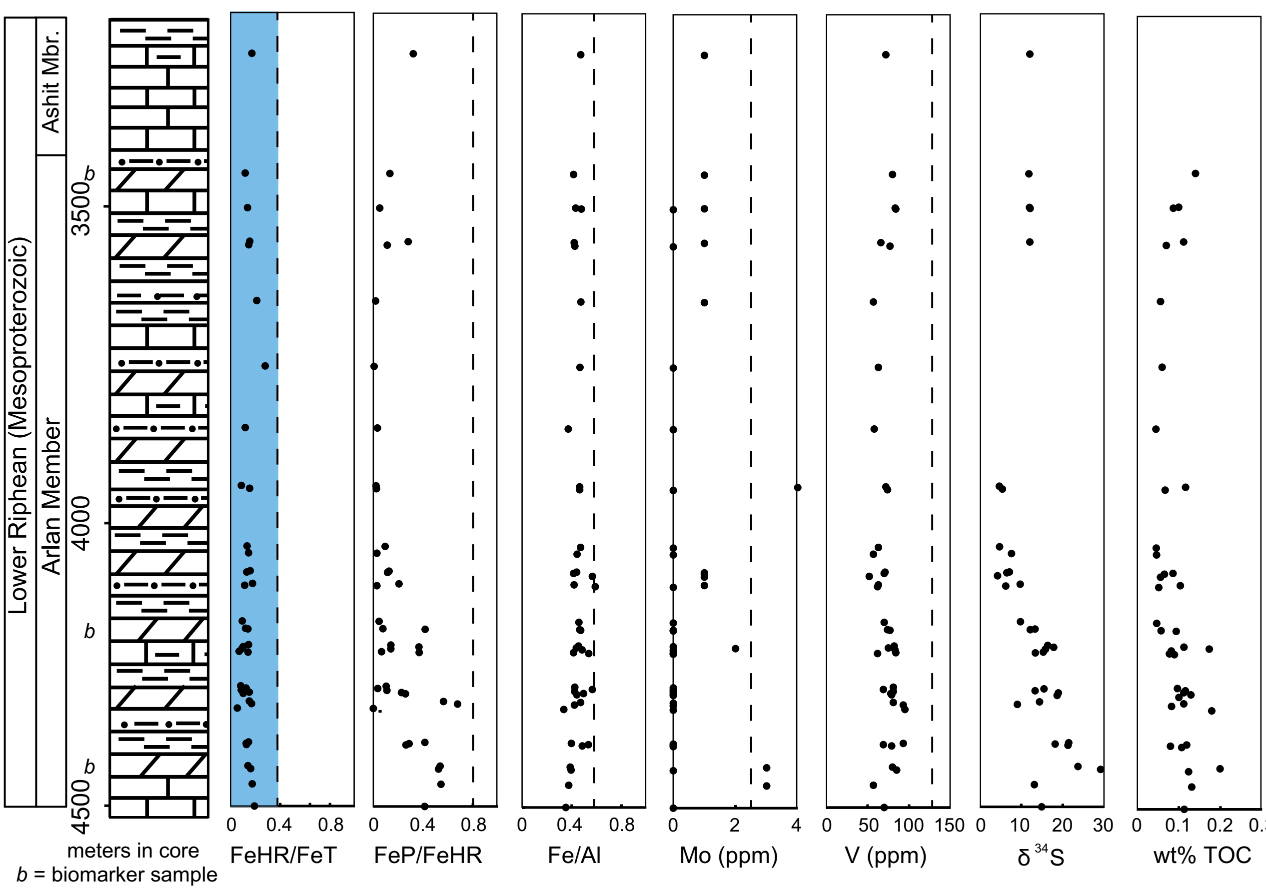

Fig. 3 Redox proxy data for the Arlan Member (Kaltasy Formation) in the 203 Bedryazh borehole. Stratigraphic column after Kah *et al.* (2007) and Kozlov *et al.* (2009); note that while much of the column is depicted as carbonate, direct measurements of samples investigated (Table S2) indicate they are mainly calcareous shales. Locations of biomarker samples indicated by *b*. Redox proxies from left to right are as follows: (1) Ratio of highly reactive (FeHR) to total iron (FeT); dashed line = 0.38. Blue-shaded area to left of 0.38 ratio indicates samples likely deposited under an oxygenated water column. (2) Ratio of iron in pyrite (FeP) to FeHR; dashed line = 0.8; (3) Ratio of total iron (FeT) to total aluminum (Al); dashed line = average shale value of 0.59 (average shale values from Turekian & Wedepohl, 1961); (4) Molybdenum in ppm; dashed line = average shale value of 2.6 ppm; (5) Vanadium in ppm; dashed line = average shale value of 130 ppm; (6) Pyrite sulfur isotope values measured relative to Vienna Cañon Diablo Troilite standard and reported in per mil (‰) notation; and (7) Total organic carbon contents reported in weight percent.

as aluminum. For example, molybdenum and vanadium contents are only approximately 20 and 60% those found in average shale, respectively (0.56 ± 0.98 and 76 ± 19 ppm) (Table S1).

Organic geochemistry

Organic geochemical data for analyzed samples are shown in Table 1. Two biomarker ratios for maturity, the 22S/(22S + 22R) ratio of the C_{31} hopane and the ratio of C_{27} 17α-trisnorhopane (Tm) to C_{27} 18α-trisnorhopane (Ts), are commonly used to evaluate the burial depth and maturity of sedimentary organic material by reflecting isomerizations in the compounds that reach a stable end point during hydrocarbon generation (Moldowan *et al.*, 1986; Peters *et al.*, 2005). The range in these proxies across the 203 Bedryazh samples is small, showing a uniformly mature organic content in these samples and suggesting that there has been no later input of less mature hydrocarbons to the lipid pool.

In basins where sedimentary organic matter is of appropriate maturity and does not show later contamination, hydrocarbon biomarkers can also provide a means of reconstructing paleoenvironmental conditions independent of lithology (Brocks & Summons, 2003; Peters *et al.*, 2005). The ratio of C_{26}/C_{25} tricyclic terpanes to C_{31}/C_{30} hopanes can be used to differentiate marine from lacustrine source rocks, as these compounds are produced in different ratios by micro-organisms from these environments (Peters *et al.*, 2005). Similarly, the ratios of C_{24}/C_{23} tricyclic terpanes and C_{22}/C_{21} tricyclic terpanes vary among depositional environments (Zumberge, 1987; Peters *et al.*, 2005). In the 203 Bedryazh core samples, these proxies are consistent with shale deposition in a marine setting (Table 1).

Redox-associated biomarker proxies indicate generally oxic conditions (Table 1). These include (i) low ratios of longer chain homohopanes—hopanes derived from polyfunctional C_{35} hopanoids present in bacteria, (ii) low concentrations of 28, 30 bisnorhopane, and (iii) absence of the biomarkers of the photosynthetic sulfur bacteria Chlorobi (Summons & Powell, 1986; Peters *et al.*, 2005).

Table 1 Organic geochemical (biomarker) ratios for investigated horizons in the 203 Bedryazh core

Biomarker Ratios	Samples B203-3452m	B203-4201.5m	B203-4390m
C_{31} S/(S+R) hopane	0.54	0.55	0.55
Ts/(Ts + Tm)	0.49	0.56	0.58
C_{26}/C_{25} tricyclic	0	0.82	0.3
$C_{31}R/C_{30}$ hopane	0.37	0.33	0.44
C_{24}/C_{23} tricyclic	0.43	0.38	0.31
C_{22}/C_{21} tricyclic	0	0.43	0.44
C_{31} hopane/(total hopane)	0.17	0.2	0.23
C_{32} hopane/(total hopane)	0.11	0.13	0.16
C_{33} hopane/(total hopane)	0.09	0.05	0.08
C_{34} hopane/(total hopane)	0.05	0.04	0.04
C_{35} hopane/(total hopane)	0.05	0.05	0.04
28,30—DNH/C_{30} hopane	0.09	0.09	0.17

Paleobiology

Microfossils occur throughout the sampled interval of the core. The Arlan Member assemblage is dominated by large (commonly >100 μm) spheroidal fossils, along with subordinate filaments (Fig. 4). Specifically, the assemblage comprises the remains of relatively large and morphologically complex forms including such taxa as *Leiosphaeridia, Synsphaeridium, Polytrichoides, Brevitrichoides, ?Chuaria, Siphonophycus, Oscillatoriopsis,* and others. These microfossils likely include the remains of both cyanobacteria and eukaryotic micro-organisms. The eukaryotic affinity of at least some of these forms is supported by evidence of the occupation of a spheroidal envelope by a single large cell (e.g., Fig. 4.10), thick walls, and/or ornamentation in the form of pleats (Fig. 4.4) and possible processes (Fig. 4.6). We thus interpret the Arlan assemblage as a cyanobacteria-rich microbiota, which contains a modest diversity of eukaryotes that lived in the surface waters in a basinal setting.

DISCUSSION

Re–Os ages and Os_i through time

Although the ages obtained are relatively imprecise (±3%) due to the limited range in $^{187}Re/^{188}Os$ and $^{187}Os/^{188}Os$, they are consistent with existing geochronological constraints for Lower Riphean strata from the southern Ural Mountain outcrop belt. Specifically, the ages of 1414 ± 40 and 1427 ± 43 Ma for the Lower Riphean in the Kyrpy Group are consistent with the bracketing ages on the Lower Riphean in the southern Urals from the approximately 1380 Ma Mashak volcanics and the approximately 1750 Ma Ai basalts (Puchkov *et al.*, 2012, 2013; Krasnobaev *et al.*, 2013a,b). Equally important, geochronology indicates that Arlan deposition was broadly synchronous with those of successions in Australia and North America that have been foci of previous investigations of mid-Proterozoic redox profiles.

Existing data from the Archean to the early Phanerozoic suggest that the seawater Os isotope composition evolved from mantle-like values being sourced predominantly from mantle-derived rocks via hydrothermal input to a crust-dominated (isotopically evolved units) weathering influx during the Mesoproterozoic (Fig. 2C). This transition has been interpreted as the onset of weathering of continental crust in a newly oxidized environment (Van Acken *et al.*, 2013 and references therein). Our new initial Os isotope data do not contradict this observation, but we note there is a paucity of data (<30 Os_i values for 3 Gy of Earth

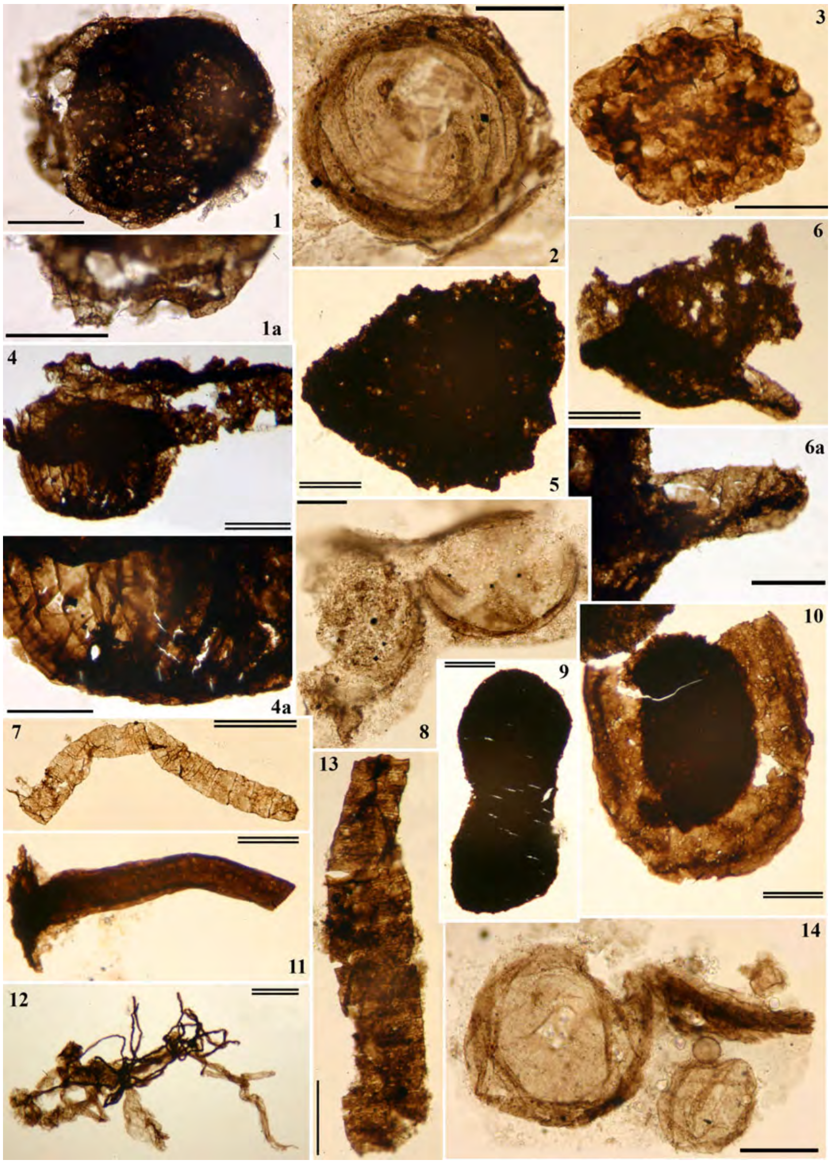

Fig. 4 Microfossils from the Arlan Member, 203 Bedryazh borehole. For all illustrated specimens, the sample number, its depth in meters in the 203 Bedryazh core (in parentheses), maceration slide number, and slide reference coordinates are provided. All specimens have been deposited to Paleontological Collection of the Geological Institute of Russian Academy of Sciences, collection No. 14005. For all figures, the single bar is 50 μm and the double bar is 100 μm. 1, 1a (fragment of 1), *Leiosphaeridia jacutica*, 30 (4285 m) – 1 – 1. 2, *Leiosphaeridia atava* with multiple folds, 40 (3565 m) – 3 – 7. 3, *Synsphaeridium* sp., 39 (3944.5 m) – 3 – 5. 4, 4a (fragment of 4), Leiosphaerid with multiple folds, 34 (4169.7 m) – 6 – 3. 5, Envelope with problematic spines or pseudospines, 31 (4267 m) – 1 – 3. 6, 6a (fragment of 6), Ellipsoid of *Brevitrichoides bashkiricus* above the slim, 34 (4169.7 m) – 6 – 1. 8, Paired envelopes of *Leiosphaeridia atava,* 40 (3565 m) – 2 – 7a. 7, *Oscillatoriopsis longa*, 39 (3944.5 m) – 3 – 2. 9, Paired envelopes of *Leiosphaeridia jacutica,* 34 (4169.7 m) –3 – 2. 10, ?*Chuaria circularis*, 32 (4201.5 m) – 1 – 1. 11, *Pseudodendron* aff. *P. anteridium*, 40 (3565 m) – 3 – 1. 12, *Siphonophycus kestron* and *S. solidum*, 31 (4267 m) – 3 – 4. 13, *Rugosoopsis* sp., 34 (4169.7 m) – 7 – 1. 14, *Leiosphaeridia tenuissima* and *L. minutissima,* 40 (3565 m) – 3 – 5.

history), of which some possess significant uncertainties (approximately $\leq \pm 0.3$ $^{187}Os/^{188}Os$ units). Thus, until more precise Os_i data are available, we advise caution when evaluating paleoenvironmental conditions using only Os isotopes.

Redox state of the Arlan Member, 203 Bedryazh core

The iron speciation proxy has been well calibrated in modern oxic and anoxic depositional settings: Sediments deposited beneath an oxic water column generally have a FeHR/FeT ratio <0.38 (Raiswell & Canfield, 1998), while sediments from anoxic basins are enriched in highly reactive iron (FeHR/FeT >0.38). The entire Arlan Member falls firmly within the range conventionally interpreted as 'oxic,' with only one sample falling above the modern oxic average of 0.26 (but, still below 0.38; Raiswell & Canfield, 1998; Fig. 3). As with any proxy, caveats exist. For example, certain sedimentological regimes, especially rapid sedimentation, can influence Fe-speciation data (Raiswell & Canfield, 1998; Lyons & Severmann, 2006; also Poulton & Canfield, 2011 and Farrell *et al.*, 2013, for discussion of caveats regarding iron-based redox proxies). In a basinal setting, turbidites might preserve evidence of rapid sediment emplacement, but no evidence for such conditions is preserved within the 203 Bedryazh core. As noted above, the Arlan Member is relatively calcareous; however, this is unlikely to dramatically affect our interpretation, for two specific reasons. Foremost, the modern calibration dataset covers the range of carbonate contents preserved in the Arlan Member (Raiswell & Canfield, 1998). Further, the primary effect of carbonate addition on iron speciation should be to add ferrous iron during diagenesis, and this would bias the Arlan samples toward an anoxic signal.

The small highly reactive iron pool in the Arlan sediments is dominated by iron carbonate (51%) and pyrite (22%). While significant enrichments in iron carbonate are normally associated with ferruginous conditions (Poulton & Canfield, 2011), it is emphasized that while iron carbonates do comprise the greatest percentage of highly reactive iron in the Arlan, the actual weight-percent quantities are quite low ($0.23 \pm 0.09\%$). For comparison, this is a factor of three less than ferruginous samples in the large compilation of Canfield *et al.* (2008; average Fe_{carb} of ferruginous samples = $0.69 \pm 0.76\%$). Given the low but present pyrite content of these rocks, the small weight-percent quantities of iron carbonate are most easily interpreted as the result of normal early diagenetic reactions in an anoxic sediment column: specifically, iron reduction results in alkalinity increase and the formation of iron carbonate, followed by low levels of sulfate reduction sufficient to form some pyrite but without the full sulfidization of all highly reactive iron phases. These typical early diagenetic reactions–leading to authigenic mineral formation–speak to pore water environments, and are fully consistent with an oxygenated water column.

It has recently been recognized in iron speciation studies that under anoxic and ferruginous water columns, authigenic iron-rich clays may precipitate (Cumming *et al.*, 2013). The exact conditions causing such precipitation are still unknown, but as the iron in these authigenic clays is not extracted by the sequential-extraction protocol employed here (Poulton & Canfield, 2005), such enrichments will be missed, and an anoxic water column might appear 'oxic'. The presence of iron-rich clays can be tested in two ways using bulk geochemical methods. First, iron in Fe_{PRS} will be extracted by a 1-min boiling HCl extraction, and so, significant Fe_{PRS} will indicate authigenic clay enrichment (Cumming *et al.*, 2013). The Arlan member shales investigated do not show significant Fe_{PRS} enrichments (Table S2 and Supporting Information). Second, total iron enrichments can be tested with the Fe/Al ratio (Lyons & Severmann, 2006). Aluminum is present primarily in the detrital phase, thus allowing the recognition of authigenic iron enrichment in *any* phase, while also serving to normalize dilution by carbonate. The Fe/Al values from the Arlan Member fall at or below values for average shale (Turekian & Wedepohl, 1961; Gromet *et al.*, 1984), implying no enrichment of total iron and, by extension, no anoxia.

While the other geochemical redox indicators investigated here do not provide strong independent evidence for water-column oxygen, they are consistent with such an interpretation. Put differently, there is no evidence for anoxia. Sulfur isotopes have commonly been used to probe paleoenvironmental conditions. Though Early Mesoproterozoic sulfate records are thin, published values for sulfate from the approximately 1400–1500 Ma Belt Supergroup, Montana, USA, show relatively large stratigraphic variation, with a mean $\delta^{34}S$ composition of $15.0 \pm 5.8‰$ (Gellatly & Lyons, 2005). In this context, the average pyrite sulfur isotope values in our Arlan samples ($\delta^{34}S = 13.2 \pm 5.9‰$) are essentially the same as sulfate values from coeval Belt rocks, implying that seawater sulfate was near-quantitatively reduced in the Arlan sediments. This points to limitation of the sulfate supply, most simply achieved when oxygen in overlying seawater drives the sulfate reduction zone into the sediment column. We note, however, that this isotopic pattern only demands a limited sulfate supply to the site of sulfate reduction; it could also be achieved under a ferruginous water column or through extremely high levels of sulfate reduction and depletion of a small basinal sulfate reservoir (Shen *et al.*, 2003). Given the modest pyrite contents in the Arlan shales, such increased rates and a large flux of sulfur through sulfate reduction are unlikely, especially given the presence of excess reactive Fe (siderite will become pyritized on diagenetic timescales).

Redox-sensitive trace elements, especially when interpreted in parallel, can give insight into water-column redox conditions (Tribovillard *et al.*, 2006). For example, Mo is efficiently scavenged from seawater only in the presence of sulfide, whereas V enrichment can occur under less strongly reducing conditions (Tribovillard *et al.*, 2006). When elemental abundances are analyzed from shales that have been independently determined to be anoxic, for instance with iron speciation data, these redox-sensitive trace elements can also provide insight into basinal hydrography and the global spread of reducing sinks (Algeo & Rowe, 2012; Reinhard *et al.*, 2013). Neither Mo nor V are enriched in the Arlan shales (Fig. 3). Interpreted in the traditional framework where water-column anoxia leads to trace metal enrichment, this would suggest an oxic or at least non-euxinic water column for these Arlan shales. It is particularly noted that in the absence of free sulfide, as indicated by the iron speciation data, there would be no mechanism to enrich Mo (Tribovillard *et al.*, 2006). Further, due to widespread reducing sinks, trace metal enrichments in anoxic sediments in the Proterozoic are generally muted (Reinhard *et al.*, 2013), potentially limiting their usefulness as local water-column redox proxies during this time (Scott & Lyons, 2012). Certainly, though, Arlan Member trace element data do not provide evidence for anoxia.

Further, organic geochemical data from selected Arlan samples reveal no evidence for anoxia. In contrast to coeval deposits of the MacArthur Basin, Australia (Brocks *et al.*, 2005), Arlan samples contain no detectable carotenoid biomarkers (isorenieratane, chlorobactane, and okenane) indicative of photic-zone euxinia. Although the absence of these biomarkers alone does not suggest an oxic depositional environment and is also consistent with a ferruginous condition, evidence for an oxygenated environment is supported by the low abundances of C_{31}–C_{35} homohopanes and 28, 30 bisnorhopane (Table 1; Peters *et al.*, 2005). As with any ancient rocks (and especially considering the low organic carbon contents of Arlan shales), the possibility of younger contamination exists (Rasmussen *et al.*, 2008). However, other lipid biomarker ratios measured for depositional environment and maturity suggest an autochthonous source for the organic compounds present. Further, any such contamination must have (i) simultaneously erased any primary evidence for anoxia (ii) while failing to add any signature of inconsistent maturity or different depositional environments, and thus, the redox signal from organic geochemistry is most parsimoniously regarded as syngenetic and recording an oxic water column.

The final piece of evidence regarding redox state comes from the eukaryotic microfossil record. As early as 1990, Vidal & Nystuen (1990) noted that in Proterozoic successions, basinal deposits generally lack the eukaryotic microfossils commonly found in younger successions. Butterfield & Chandler (1992) developed this theme further, stating that unambiguously eukaryotic fossils are absent from deep basinal facies in most Proterozoic successions. Javaux *et al.* (2001) tested this hypothesis in the approximately 1400–1500 Ma Roper Group, Australia, documenting the distribution of microfossils across a depth gradient recorded by multiple stacked sedimentary sequences. Indeed, in Roper successions, taxa interpreted as eukaryotic occur only or most abundantly in shore face to storm-dominated shelf deposits; microfossils likely to be eukaryotic are rare in basinal shales.

This paleoenvironmental distribution has commonly been interpreted in terms of Proterozoic redox conditions, either directly, with upward mixing anoxic (especially sulfidic) waters challenging eukaryotic organisms in open marine environments (Martin *et al.*, 2003; Johnston *et al.*, 2010), or indirectly, in terms of nutrient limitation of eukaryotic algae imposed by nitrogen and trace metal availability (Anbar & Knoll, 2002; Gilleaudeau & Kah, 2013; Stueeken, 2013). Whether ecological limitation of eukaryotes was direct, indirect, or both—and recognizing that other factors may well have been in play—the presence of eukaryotic microfossils in basinal shales associated with oxic bottom waters is consistent with hypotheses relating early protists to oxygen distribution.

In summary, iron geochemical data and the paleobiological record paint a consistent picture of life and environments and provide evidence from two independent data sources that Arlan shales recovered from the 203 Bedryazh borehole were deposited under an oxygenated water column. Redox-sensitive trace elements, pyrite sulfur isotope values, and biomarker data are consistent with an oxic water column. However, as discussed above, caveats exist—these qualifiers are shared with all other studies employing similar methods. Indeed, it is recognized that unlike the detection of euxinia in the ancient record, for which the iron, sulfur, trace element (particularly Mo), and organic geochemical records provide independent tests (Lyons *et al.*, 2009), there are few independent geochemical metrics distinguishing oxic from ferruginous conditions. As it is increasingly recognized that ferruginous water columns may have been the dominant anoxic state for long periods of Earth history (Poulton & Canfield, 2011), the development of independent tests to complement iron-based proxies would have high utility. Alternatively, as discussed here, geochemical data can be coupled with paleobiological observations to provide such an independent measure of oxic/anoxic conditions. In the case of the Arlan shale, these data together point toward subwave-base oxygenated conditions at approximately 1400 million years ago.

Mesoproterozoic redox heterogeneity in a global context

The Re–Os ages obtained here indicate that deposition of oxygenated basinal Arlan shales broadly overlapped temporally with euxinic and ferruginous conditions in the Roper (Shen *et al.*, 2003) and Belt (Planavsky *et al.*, 2011) basins. The almost inescapable conclusion is that just as oxygen concentrations in the modern ocean are heterogeneous (Helly & Levin, 2004), oxygen concentrations at depth in the Mesoproterozoic ocean were spatially variable as well. Surface waters in Proterozoic oceans were almost undeniably oxygenated after 2.4 Ga (Shen *et al.*, 2003; Canfield *et al.*, 2008; Sperling *et al.*, 2013), so the question rests with the nature of deeper water chemistry and the drivers underpinning observed spatial heterogeneity.

The oxygen content of subsurface marine waters is determined by the initial loading of O_2 into downwelling water masses, the ventilation time of deep waters, and the rate of organic carbon export from the surface-mixed layer (Sarmiento *et al.*, 1988). Even today, when surface waters are in equilibrium with an atmosphere containing 21% O_2, dysoxic to anoxic regions occur across large swaths of the Pacific, Indian, and eastern tropical to subtropical Atlantic oceans (Helly & Levin, 2004). Moreover, studies of current global warming show that as ocean temperatures rise, oxygen minimum zones are both shoaling and expanding laterally, driven by T-dependent changes in saturation and perhaps by increased stratification of surficial water masses (Keeling *et al.*, 2010; Gilly *et al.*, 2013). In a mid-Proterozoic ocean, with much lower atmospheric pO_2 and warm seawater temperatures (decreasing oxygen content, enhancing water-column stratification, and increasing rates of bacterial respiration; Gaidos & Knoll, 2012; Ulloa *et al.*, 2012), widespread oxygen depletion beneath surface waters might in fact be predicted. Given these controls, how does one account for oxic basinal water masses indicated by the Arlan shales?

Possibly, the oxygen minimum zone was simply at depths greater than those recorded by the Arlan deposits—in the modern ocean, the OMZ may lie hundreds of meters or more beneath the sea surface (Gilly *et al.*, 2013). Studies of other mid-Proterozoic basins, though, record oxygen depletions bathing the bottoms of shelf and platformal seas in environments similar to that of the Arlan. It is emphasized again that none of the Proterozoic basins being discussed represent true 'deep ocean,' but rather moderate depths beneath storm wave base. Thus, while the redox state of the truly deep ocean remains an open question (but see Slack *et al.*, 2007, 2009), the differences between the oxygenated Kyrpy Group, ferruginous Belt Supergroup, and euxinic Roper Group, whose basinal deposits represent broadly similar environments, requires explanation. Tectonics is unlikely to provide an answer, as the Lower Riphean basin of the Uralian region was either a shelf/platform setting much like those observed elsewhere or a rift basin (Puchkov, 2013), which would tend to enhance the prospect of restriction and subsurface anoxia.

Alternatively, Holland (2006) calculated that even at atmospheric oxygen levels of 10% of the modern, oxygenated conditions at depth are possible if organic carbon delivery is low. The redox data from the Mesoproterozoic Arlan Member are interpreted here as the geochemical manifestation of Holland's prediction, showing the persistence of oxic conditions in a region of low export production, recorded by the unusually low TOC in Arlan shales. We interpret the Arlan basin as oligotrophic with correspondingly low delivery rates of organic matter to subsurface water masses.

CONCLUSIONS

All redox proxies from the Arlan Member indicate that deposition occurred beneath an oxygenated water column. These data cannot inform the absolute concentration of O_2 either dissolved in seawater or present in the atmosphere; however, they do inform the mechanisms that controlled subsurface water chemistry in Mesoproterozoic oceans. It is worth emphasizing that these data are not interpreted as a mid-Proterozoic 'oxygenation event'—rather, they demonstrate that subsurface waters in at least one basin were oxygenated at a time when most basins appear to have sustained anoxic water masses at depth (Shen *et al.*, 2003; Planavsky *et al.*, 2011; Turner & Kamber, 2012; Gilleaudeau & Kah, 2013). Because there were local as well as global controls on marine redox profiles, no single stratigraphic section or basin can document both the mean state and the variance of the entire ocean at a given time point. In conjunction with global isotopic redox tracers, the evaluation of redox state in multiple sections/basins worldwide, analyzed in a statistical framework, will ultimately be needed to distinguish global signals from local heterogeneity. That said, previous data and the results reported here collectively paint an increasingly nuanced picture of mid-Proterozoic oceans that includes moderately oxic surface waters; underlying oxygen minimum zones that were weakly oxic, ferruginous, or euxinic, depending on organic carbon loading and, perhaps, nitrogen chemistry (Boyle *et al.*, 2013); and dysoxic water masses in the deep ocean (Slack *et al.*, 2007, 2009). Such geographic and bathymetric heterogeneity provides a necessary framework for interpreting phenomena that range from the 'boring billion' stasis in C-isotopic records (Buick *et al.*, 1995) to the persistence of low pO_2 in the Proterozoic atmosphere (Johnston *et al.*, 2009; Laakso & Schrag, 2014) and the early evolution of eukaryotic cells (Knoll *et al.*, 2006).

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CONFLICT OF INTEREST

The authors do not have any conflict of interests.

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SUPPORTING INFORMATION

Additional Supporting Information may be found in the online version of this article:

Appendix S1 Supplementary methods and results.

Table S1 Major-, minor- and trace-element data for samples from 203 Bedryazh borehole.

Table S2 Iron, carbon and sulfur geochemical measurements from the 203 Bedryazh borehole.

Table S3 Re and Os abundance and isotopic compositions from the 203 Bedryazh borehole- 4297 and 4198 m intervals.