Identifying global vs. basinal controls on Paleoproterozoic organic carbon and sulfur isotope records

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Abstract

Paleoproterozoic sedimentary successions are important archives of the redox evolution of Earth's atmosphere and oceans. Efforts to unravel the dynamics of our planet's early oxygenation from this archive rely on various geochemical proxies, including stable carbon and sulfur isotopes. However, ancient metasedimentary rocks often experienced early- and late-stage (bio)geochemical processes making it difficult to discern primary environmental signals from bulk-rock $\delta^{13}C_{org}$ and $\delta^{34}S$ values. Such complexity in carbon and sulfur isotope systematics contributes to uncertainty about the redox structure of Paleoproterozoic oceans. A currently popular idea is that, following the Great Oxidation Event, global changes led to low-oxygen environments and temporally fluctuating ocean redox conditions that lasted until the Neoproterozoic. The volcano-sedimentary rocks of the Onega Basin have figured prominently in this concept, particularly the exceptionally organic-rich rocks of the 1.98 Ga Zaonega Formation. However, a growing body of evidence shows that local depositional processes acted to form the $\delta^{13}C_{org}$ and pyrite $\delta^{34}S$ records of the Zaonega Formation, thus calling for careful assessment of the global significance of these isotope records. Placing new and existing organic carbon and sulfur isotope data from the Zaonega Formation into the context of basin history and by comparing those results with key Paleoproterozoic successions of the Francevillian Basin (Gabon), the Pechenga Greenstone Belt (NW Russia) and the Animikie Basin (Canada), we show that the stratigraphic $\delta^{13}C_{org}$ and pyrite $\delta^{34}S$ trends can be explained by local perturbations in biogeochemical carbon and sulfur cycling without requiring global drivers. Despite their temporal disparity, we also demonstrate that individual successions share certain geological traits (e.g. magmatic and/or tectonic activity, hydrocarbon generation, basin restriction) suggesting that their pyrite $\delta^{34}S$ and $\delta^{13}C_{org}$ trends were governed by common underlying mechanisms (e.g. similar basinal evolution and biogeochemical feedbacks) and are not necessarily unique to certain time intervals. We further show that pyrites in these successions that are most likely to capture ambient seawater sulfate isotopic composition have consistent $\delta^{34}S$ values of 15–18‰, which hints at remarkable stability in the marine sulfur cycle over most of the Paleoproterozoic Era.

Keywords

Paleoproterozoic, Sulfur cycle, Carbon cycle, Ocean redox, Great Oxidation Event, Onega Basin

1. Introduction

The Neoarchean and Paleoproterozoic eras saw drastic perturbations in Earth system processes, spanning from the geodynamic, the emergence of continents and the initiation of supercontinent cycles (Reddy and Evans, 2009), to the climatic, as recorded by several episodes of global glaciations (Kopp et al., 2005; Young et al., 1998). In concert with those were major changes in Earth's surface environments: widespread accumulation of iron formations (Bekker et al., 2014; Cloud, 1973; Holland, 1978; Klein, 2005; Konhauser et al., 2002, 2017), disappearance of detrital pyrite and uraninite grains (Berkner and Marshall, 1965; Cloud, 1968; Holland, 2006), loss of mass-independent sulfur isotope fractionation (Farquhar et al., 2000; Guo et al., 2009; Luo et al., 2016), the large-magnitude positive $\delta^{13}C_{carb}$ excursion of the Lomagundi-Jatuli Event (LJE; Baker and Fallick, 1989; Karhu and Holland, 1996), accumulation of exceptionally organic-rich sediments of the Shunga Event (Melezhik et al., 1999; Kump, 2011; Strauss et al., 2013), and the appearance of phosphorous-rich sedimentary deposits (Lepland et al., 2013; Papineau, 2010).

These changes are thought to have occurred as a consequence of the build-up of atmospheric oxygen to above 0.001% present atmospheric levels at c. 2.4–2.3 Ga (Fig. 1; Bekker et al., 2004; Gumsley et al., 2017; Luo et al., 2016; but see also Ohmoto et al., 2014). Known as the Great Oxidation Event (GOE; Holland, 2006), this change towards oxidative surface conditions is postulated as having intensified continental weathering and prompted an increased riverine flux of sulfate, phosphate and metals into the global ocean (e.g. Konhauser et al., 2011). In turn, the increase in the availability of electron acceptors (e.g. O_2, NO_3^-, Fe^{3+}, Mn^{4+}, SO_4^{2-}) and macro/micro nutrients (e.g. PO_4^{3-}, Cu, Ni, Zn) is thought to have created the necessary conditions for establishment of new ecological niches exploited by microbes co-evolving with Earth's oxygenation (e.g. Zerkle et al., 2017). Various geochemical datasets though, including stable sulfur and carbon isotopes, imply that the oxygenation of Earth's atmosphere was dynamic and marked by spatiotemporal heterogeneities (Large et al., 2019; Luo et al., 2016; Ossa Ossa et al., 2018; Planavsky et al., 2018, 2012; Scott et al., 2014; Sheen et al., 2018). Nevertheless, what is agreed is that a substantial increase in seawater sulfate (SWS) concentrations to > 2.5 mM (Bekker et al., 2006; Reuschel et al., 2012b; Schröder et al., 2008) or even > 10 mM (Blättler et al., 2018) occurred during the c. 2.2–2.0 Ga LJE as a consequence of an oxygenated atmosphere-ocean system. The redox structure of Proterozoic oceans, however, remains debated with interpretations ranging from ocean deoxygenation and widespread euxinia at the end of the LJE (Luo et al., 2016; Ossa Ossa et al., 2018; Planavsky et al., 2012; Scott et al., 2014) to episodic deep-water oxygenation and spatiotemporal ocean redox variability that persisted until the late Neoproterozoic (Diamond et al., 2018; Planavsky et al., 2018; Sheen et al., 2018; Sperling et al., 2015, 2014).

Given that microbial sulfate reduction (MSR) coupled to oxidation of organic carbon exert great influence on the redox balance of Earth's surface environments (Fike et al., 2015; Jørgensen, 1979), concomitant changes in sedimentary records of global organic carbon and sulfur cycling can provide important insights to the redox state of past oceans (Canfield et al., 2013; Fike et al., 2015; Kump and Garrels, 1986). Biological processes preferentially utilise ^{12}C and ^{32}S isotopes over ^{13}C and ^{34}S, respectively, leaving the residual source pools enriched and the products depleted in the heavier isotopes. In low temperature environments the kinetic isotope fractionations imparted by microorganisms typically surpass the extent of abiotic isotope effects. These differences between biological and abiotic isotope effects can be used to trace carbon and sulfur fluxes through various reservoirs. Furthermore, biogeochemical sulfur cycling can produce small mass-dependent fractionations in the minor sulfur isotope ratios

($\Delta^{33}S$ and $\Delta^{36}S$) that can provide additional information about different processes governing sulfur cycling even when preserved $\delta^{34}S$ values overlap (Canfield et al., 2010; Johnston, 2011; Johnston et al., 2005; Seal, 2006; Zerkle et al., 2016, 2010). Therefore, coupled organic carbon ($\delta^{13}C_{org}$) and multiple sulfur isotope data ($\delta^{34}S$, $\Delta^{33}S$, $\Delta^{36}S$) can be used as indirect paleoenvironmental proxies for microbial processes and biogeochemical cycling during periods of significant change in Earth's surface environments. However, we recognise that stable isotope values can also be influenced by post-depositional geological processes (e.g. diagenesis, metamorphism) that can significantly affect the extent of fractionation between the oxidised and reduced species and, hence, the preservation of original isotope signatures within the rock record (Aller et al., 2010, 2008; Fike et al., 2015). Screening for pristine geochemical signals is especially important given the rarity of well-preserved Paleoproterozoic sedimentary basins.

Geochemical trends, including organic carbon and multiple sulfur isotopes and their global importance, from the c. 1.98 Ga Zaonega Formation in the Onega Basin of northwest Russia have figured prominently in investigations of the post-LJE time. Here we combine new and existing records of S-C systematics, from drill cores through the Zaonega Formation to assess ideas about the redox state of the Paleoproterozoic ocean following the LJE. We compare these records to other key Paleoproterozoic successions, the Francevillian Basin of Gabon, Pechenga Greenstone Belt of northwest Russia and Animikie Basin in Canada, to deconvolve local- from global-scale signals. These successions in particular have shaped ideas about the post-LJE world and their geochemical records and depositional models have helped refine understanding of this ciritical time period in Earth's history.

2. The Zaonega Formation in the Onega Basin

Situated in the eastern part of the Fennoscandian Shield in NW Russia, the Paleoproterozoic Onega Basin (Fig. 2) contains one of the most complete volcano-sedimentary successions that encompasses both the end of the LJE and the succeeding Shunga Event (Melezhik et al., 1999; Kump, 2011; Strauss et al., 2013); the former is mostly recorded by the carbonate rocks of the Tulomozero Formation and the latter by the organic-rich rocks of the Zaonega Formation (Melezhik and Hanski, 2013). Deposition during the LJE followed a phase of rifting associated with the opening of the Paleoproterozoic Kola Ocean and Svecofennian Sea (Lahtinen et al., 2008; Melezhik et al., 2015) and occurred in sabkha-coastal plain and shallow-marine peritidal carbonate platforms restricted by stromatolite reefs as represented by the Tulomozero Formation (Blättler et al., 2018; Melezhik et al., 2015; Melezhik and Hanski, 2013; Morozov et al., 2010). Continued basinal subsidence created a deep-water shelf-slope-basin during the deposition of the overlying Zaonega Formation (Črne et al., 2014; Melezhik et al., 2015), marked by organic-rich siliciclastic and carbonate rocks interlayered with numerous syn-depositional mafic lava flows and co-magmatic intrusions (Črne et al., 2013a, 2013b; Melezhik et al., 1999; Strauss et al., 2013). Subsequently, reduction in the rate of subsidence and sub-aqueous volcanism led to the filling of the basin by hundreds-of-meters of basalts of the Suisari Formation intercalated with thin organic-rich shale beds (Krupenik et al., 2011; Melezhik et al., 2015; Morozov et al., 2010) with final closure of the basin marked by deposition of turbiditic greywackes and siltstones, many containing pyrobitumen clasts (subaerial seeps), in the lacustrine settings of the Kondopoga Formation (Melezhik et al., 2015). The entire succession underwent greenschist facies metamorphism and deformation into a series of open folds cut by high-angle faults during the 1.89–1.79 Ga Svecofennian orogeny (Ojakangas et al., 2001; Stepanova et al., 2014).

The lower and upper parts of the Zaonega Formation consist of intercalated siliciclastic (dominating in the lower part) and carbonate (dominating in the upper part) rocks whereas the middle part contains massive organic-rich rocks (locally termed “shungite”) considered to be one of the world’s oldest petrified oilfields (Melezhik et al., 2013, 1999): total organic carbon (TOC) can reach up to 40 wt.% in shungite rock and as high as 90 wt.% in pyrobitumen-filled veins (Melezhik et al., 2013, 2004, 1999). Oil generation and hydrocarbon migration is attributed to syndepositional magmatism that promoted thermal maturation of the organic matter along the contacts of magmatic bodies (Črne et al., 2013a, 2013b; Qu et al., 2018, 2012). Organic-rich rocks in the middle part of the Zaonega succession have characteristic $\delta^{13}C_{org}$ values of < -30‰ (Kump, 2011; Lepland et al., 2014; Qu et al., 2018, 2012) and their presence and stratigraphic correlation is well documented in several outcrops and drill cores across the entire Onega Basin (Filippov and Yesipko, 2016; Galdobina, 1987; Melezhik et al., 2013).

The overwhelmingly fine-grained textures, dearth of large current-generated sedimentary structures, and rare emplacement of coarser-grained sediment-gravity flow and turbidity-current deposits indicate that deposition occurred predominantly in relatively low-energy environments (Črne et al., 2014, 2013a, 2013b; Galdobina, 1987; Melezhik et al., 2015). Although paleobathymetry is difficult to assess, depths must have remained consistently below storm-wave base during deposition of much of the Zaonega Formation.

2. 1 Age of the Zaonega Formation

Deposition of the Zaonega Formation in part coincided with the termination of the LJE, which is recorded in the conformably underlying Tulomozero Formation and the lowermost part of the Zaonega Formation (Melezhik et al., 2015; Morozov et al., 2010). This termination occurred at c. 2.06 Ga based on correlations of LJE-bearing rocks across Fennoscandia (Karhu, 1993; Karhu and Holland, 1996) and U-Pb radiometric ages on post-LJE bearing rocks: 2058 ± 2 Ma (Melezhik et al., 2007) and 2056.6 ± 0.8 Ma (Martin et al., 2015) for the Kolosjoki Sedimentary Formation in the Pechenga Greenstone Belt; 2055.5 ± 2.3 Ma for the Il'mozero Sedimentary Formation in the Imandra-Varzuga Greenstone Belt (Martin et al., 2013a, 2013b); and a 2050 ± 8 Ma age on felsic volcanites in the Peräphoja Belt, Finland (Perttunen and Vaasjoki, 2001). A younger age of the Zaonega Formation is provided by the emplacement ages of igneous rocks: 1919 ± 18 Ma (Priyatkina et al., 2014), 1956 ± 5 Ma (Stepanova et al., 2014) and 1961.6 ± 5.1 Ma (Martin et al., 2015) for dykes that cross-cut the Zaonega Formation; 1969 ± 18 Ma (Puchtel et al., 1998) and 1988 ± 34 Ma (Puchtel et al., 1999) on gabbro sills in the overlying Suisari Formation.

While the above ages bracket deposition of the Zaonega Formation between c. 2.06 and 1.98 Ga, its exact age remains unresolved. A carbonate whole rock Pb-Pb age of 2090 ± 70 Ma from the underlying Tulomozero Formation (Ovchinnikova et al., 2007) and a 2050 Ma Re-Os age on organic-rich siltstone from the Zaonega Formation (reported in a conference abstract by Hannah et al., 2008) indicate that deposition occurred essentially synchronous with the end of the LJE. More recently, Martin et al. (2015) reported single zircon ages of 1982.0 ± 4.5 Ma for a tuff in the lower Zaonega Formation and 1967.6 ± 3.5 Ma for a detrital zircon grain in the overlying Kondopoga Formation. These upper constraints are within error of zircon ages of 1976 ± 9 Ma (Puchtel et al., 1998) and 1975.3 ± 2.8 Ma (Martin et al., 2015) that have been determined for mafic magmatic rocks of the Jangozero Formation below the Tulomozero Formation, interpreted by Martin et al. (2015) as a lava flow. However, our recent field observations at the outcrop area near Hirvas (NW Russia), where the samples were collected for dating by both Puchtel et al. (1998) and Martin et al. (2015), indicate that this mafic body is a sill rather than a lava flow; hence, the ages derived from it cannot be used for defining the maximum depositional age of the Tulomozero and Zaonega formations.

In summary, i) the Zaonega Formation was deposited conformably over the Tulomozero Formation; ii) carbonates and calcareous mudstones in the lowermost part of the Zaonega Formation host the termination of the LJE ($\delta^{13}C_{carb}$ shift from c. 9‰ to 0‰; Melezhik et al.,

2015) that occurred across Fennoscandia at c. 2.06 Ga; iii) syndepositional magmatism—resulting co-magmatic sills with pepperite contacts and deposition of tuffs—place accumulation of the exceptionally organic-rich rocks in the middle part of the Zaonega Formation at c. 1.98 Ga, iv) an upper age limit of c. 1.98 Ga is further corroborated by the emplacement ages of the overlying Suisari Formation igneous and volcanic rocks. Taken together, and until more refined age constraints can be determined, we consider c. 1.98 Ga as the depositional age of the Zaonega Formation.

2. 2 New samples and data integrated with published data

In this study we integrate new $\delta^{13}C_{org}$ data on 117 samples from the drill core of the Onega Parametric Hole (OPH, 62.1559 N, 34.4073 E) with published geochemical data from OPH and other drill cores including FAR-DEEP 12AB, FAR-DEEP 13A, OnZap1, OnZap3, C-175 and C-5190 (Fig. 3, 4, 5). The OPH core was drilled between 2007–2009 in the southeastern part of the Onega Basin and intersects c. 3000 m of Paleoproterozoic rocks and 500 m of the Archean basement (Fig. 2; Krupenik et al., 2011; Morozov et al., 2010). Here we mainly focus on the 2115–525 m depth interval in the OPH core that comprises the Zaonega Formation and most of the sedimentary intervals of the overlying Suisari Formation. As part of the International Continental Drilling Program's Fennoscandian Arctic Russia-Drilling Early Earth Project (FAR-DEEP) in 2007, FAR-DEEP core 13A (240 m deep, 62.5891 N, 34.9273 E) was drilled near the village of Shunga and FAR-DEEP core 12AB (504 m deep, 62.4947 N, 35.2887 E) c. 25 km south-east from the village (Fig. 2). Both cores intersect the middle and upper part of the Zaonega Formation. Additional drilling was performed near the village of Shunga in 2012 when two 60 m long cores, OnZap1 (62.5870 N, 34.9310 E) and OnZap3 (62.5920 N, 34.9280 E), were recovered (Fig. 2). Together these two cores form a 102 m composite section that corresponds to the upper part of the Zaonega Formation. Detailed descriptions of the OPH, FAR-DEEP and OnZap cores are available in Krupenik et al. (2011), Črne et al. (2013a, 2013b) and Paiste et al. (2018), respectively. An additional Zaonega data set has been published from core C-175 (220 m thick interval; Scott et al., 2014) and core C-5190 (842 m thick interval; Melezhik et al., 2013; Scott et al., 2014); these are located 500 m to the northwest and c. 15 km south of the FAR-DEEP 12AB location, respectively (Fig. 2). Combined, these cores span the entire Zaonega Formation but the most detail is provided for the organic-rich intervals in the middle part of the Formation (Fig. 5).

3. Methods

The organic carbon (C_{org}) isotope composition of decarbonated residues was determined by flash combustion using an Elemental Analyser Continuous Flow Isotope Ratio Mass Spectrometer (EA-CF-IRMS: ThermoScientific Delta V Plus with Costech EA) at the NERC Life Sciences Mass Spectrometry Facility at the Scottish Universities Environmental Research Centre. The organic carbon isotope data are reported relative to the Vienna PeeDee Belemnite (V-PDB) standard using delta notation ($\delta^{13}C_{org} = 1000 \cdot (^{13}R_{organic\text{-}C}/^{13}R_{V\text{-}PDB} - 1)$, where ^{13}R is $^{13}C/^{12}C$). Sample reproducibility was determined by replicate analyses of the international standard USGS40 L-glutamic acid ($\delta^{13}C = -26.39 \pm 0.04‰$ V-PDB) which yielded $\delta^{13}C$ values of $-26.19 \pm 0.04‰$. The $\delta^{13}C$ values have been corrected for the 0.2‰ offset between the USGS40 measurements obtained during analysis and the accepted value for the standard. The sulfur isotopes reported from earlier studies are expressed as $\delta^{34}S = 1000 \cdot (^{34}R_{sample}/^{34}R_{V\text{-}CDT} - 1)$ and $\Delta^{33}S = \delta^{33}S - 1000 \cdot (1 + \delta^{34}S/1000)^{0.515} - 1)$. Details of chemical methods and isotope analyses are outlined in Scott et al. (2014) and Paiste et al. (2018, 2020).

4. Results for OPH core and basin-wide correlations

The OPH samples record $\delta^{13}C_{org}$ values ranging from -41.01‰ to -23.65‰ and define a stratigraphic profile marked by a prominent negative excursion ($\delta^{13}C_{org}$ values of <-30‰) in the 1226–1080 m interval and near invariant values below and above that excursion. Further, this negative $\delta^{13}C_{org}$ excursion is associated with a positive $\delta^{34}S$ excursion (Fig. 4). Examining all the available $\delta^{13}C_{org}$, $\delta^{34}S$ and $\Delta^{33}S$ core records for the OPH, FAR-DEEP and OnZap cores show that the middle and upper parts of the Zaonega Formation are typified by similar lithofacies, including a basin-wide dolomite marked by a prominent increase in P_2O_5 at the lower contact of that unit (Fig. 3). Further, in all those cores, the strongly ^{13}C-depleted biomass recording $\delta^{13}C_{org}$ values of <-30‰ occurs in a specific interval in the middle Zaonega Formation. Consequently, these independent criteria provide a firm basis for making correlations across the Onega Basin (Filippov and Yesipko, 2016; Melezhik et al., 2013) and dividing the Zaonega Formation into Members A, B and C (Fig. 5, Paiste et al., 2020). Direct correlation with cores C-175 and C-5190 studied by Scott et al. (2014) is hampered by the lack of lithological descriptions by those workers. However, given the stratigraphic consistency and uniqueness of the pronounced negative $\delta^{13}C_{org}$ excursion present in all other Zaonega cores, the occurrence of $\delta^{13}C_{org}$ values <-30‰ in the depth intervals from 184–16 m in C-5190 and 219–17 m in C-175 indicates their correlation with Member B and the depth interval between 296–

184 m in C-5190 with Zaonega Member A (Fig. 5). These correlations are in good agreement with those proposed between cores C-5190 and FAR-DEEP 12AB by Melezhik et al. (2013).

In detail, the Zaonega Formation houses a pronounced negative $\delta^{13}C_{org}$ excursion with values as low as -42‰ in Member B, whereas Members A and C are characterised by relatively invariant $\delta^{13}C_{org}$, -26.5 ± 2.4‰ (at 1SD level, here and elsewhere) and -29.7 ± 3.5‰, respectively. The sulfur isotope data show that Member A is marked by uniformly negative $\delta^{34}S$ (c. -11.9 ± 10.4‰) and positive $\Delta^{33}S$ (c. 0.02 ± 0.04‰) values that shift to positive $\delta^{34}S$ (17.8 ± 7.5‰) and mainly negative $\Delta^{33}S$ (-0.02‰ ± 0.03) values in Member B ($\Delta^{33}S$ data shown in Paiste et al., 2020). In Member B the values oscillate around a baseline of c. 18‰ in $\delta^{34}S$ and c. -0.02‰ in $\Delta^{33}S$ but several sharp positive excursions in $\delta^{34}S$, up to 44‰, and negative excursions in $\Delta^{33}S$, down to -0.12‰ occur. On average sulfides in Member C have $\delta^{34}S$ values of 15.5‰ ± 8.4 and $\Delta^{33}S$ of -0.01‰ ± 0.02 but record a negative trend to c. 3‰ in $\delta^{34}S$ and a positive trend to c. 0‰ in $\Delta^{33}S$ towards the top of the member. All these isotope shifts are accompanied by concomitant changes in TOC and TS abundances, that are relatively low in the lower part of Member A and in Member C but exhibit concentrations up to 65 wt.% TOC and 11 wt.% TS in Member B (Fig. 5).

5. Discussion

5. 1 Organic carbon and sulfur isotope records

5. 1. 1 Carbon fixation pathways and the $\delta^{13}C_{org}$ record

The most common organic matter source in marine sediments throughout Earth's history is the biomass of CO_2-fixing autotrophic organisms with $\delta^{13}C_{org}$ values between -10‰ to -30‰ (Preuß et al., 1989; Zerkle et al., 2005). This is corroborated by the relative consistency of $\delta^{13}C_{org}$ (-25 to -35‰) and $\delta^{13}C_{carb}$ (c. 0‰) records throughout Earth's history, reflecting the antiquity of autotrophic CO_2-fixing metabolisms and fairly uniform biomass burial and carbonate deposition through geologic time (Hayes, 1993; Hayes and Waldbauer, 2006; Marais, 2001; Schidlowski, 2001; Zerkle et al., 2005). However, natural environments may also host mixed biological communities, some of which can produce biomass significantly more depleted in ^{13}C such as those utilising CH_4 from either thermogenic ($\delta^{13}C_{CH4}$ from c. -20‰ to -50‰) or biogenic ($\delta^{13}C_{CH4}$ from c. -50‰ to -90‰) sources (Sackett, 1978; Schoell, 1983; Whiticar, 1999) and thereby result in sedimentary organic matter containing various $\delta^{13}C_{org}$ signals with values lower than -30‰.

Sequences with significant ^{13}C-depleted biomass ($\delta^{13}C_{org}$ < -30‰) are most notably documented in the 2.7–2.6 Ga Fortescue Formation (Hayes, 1983; Schidlowski, 2001), the c. 2.1 Ga Francevillian D Formation (Gauthier-Lafaye and Weber, 2003, 1989), and the c. 1.98 Ga Zaonega Formation (Kump, 2011; Melezhik et al., 1999). Such excursions have been explained variably as a global-scale negative isotope shift in the atmospheric CO_2 source via widespread exhumation and weathering of buried organic carbon (Kump, 2011), by increased methane oxidation (Yudovich et al., 1991) or as an increase of microbial methane cycling driving pervasive methanogenesis and subsequent methanotrophy (Bengston and Hayes, 1994; Hayes, 1983; Knoll and Canfield, 1998). However, basin-scale (or smaller) kerogen alteration and devolatilisation of ^{13}C-depleted hydrocarbons could equally provide a suite of carbon sources to sustain microbial communities, consequently lowering the bulk $\delta^{13}C_{org}$ of sedimentary organic matter (Qu et al., 2012). Another way to produce ^{13}C-depleted biomass is by enriching the local dissolved inorganic carbon (DIC) pool in ^{12}C by recycling of organic carbon in restricted and/or stratified environments. For example, organic matter with values as low as -45‰ $\delta^{13}C_{org}$ have been reported in a modern mountain lake and -34‰ $\delta^{13}C_{org}$ in a Norwegian fjord (Rau, 1978; van Breugel et al., 2005).

Metamorphism can also alter the isotope composition of primary organic matter but these isotope effects are generally small (< 3‰) and will typically shift the preserved $\delta^{13}C_{org}$ to more positive values (Clayton, 1991; Hayes, 1993; Lewan, 1983; Schidlowski, 2001). Significant negative shifts of residual graphite $\delta^{13}C_{org}$ are theoretically possible by oxidation of carbonaceous matter in prograde metamorphic conditions where >90% of carbon is removed by extreme CO_2 degassing at high temperatures (>500°C; Eiler et al., 1997). In addition, formation of abiogenic organic matter through deposition from carbonic fluids can yield low $\delta^{13}C_{org}$ values, but such processes facilitating deposition from fluids also occur at temperature and pressure regimes exceeding low grade, greenschist facies metamorphic conditions (Luque et al., 1998). Therefore, the $\delta^{13}C_{org}$ values preserved in organic matter in ancient sedimentary rocks of the Fortescue, Francevillian D and Zaonega Formations can be considered to carry primary signatures reflecting switching between different carbon sources and metabolic pathways that are induced by local and/or global processes. The principal way to discriminate between local and global mechanisms is to place stable isotope records into a depositional context.

5. 1. 2 Global and local processes governing the sulfur isotope system

On geological time scales, seawater sulfate (SWS) concentrations depend on the redox status of the atmosphere-ocean system and the relative fluxes of sulfur into and out of the oceans. Sulfur enters the oceans mainly via riverine input and is removed as oxidised (e.g. gypsum, anhydrite, barite, carbonate/phosphate associated sulfate) and reduced (e.g. pyrite, marcasite, pyrrhotite, sphalerite, chalcopyrite) minerals and organic sulfur (Raven et al., 2018, 2016). These sulfur carriers form as a result of microbial activity (e.g. microbial reduction, oxidation, and/or disproportionation of sulfur compounds) and abiogenic processing (e.g. evaporation, thermogenic sulfate reduction, photolysis), which generate distinct isotope effects (Berner, 1964; Berner and Raiswell, 1983; Canfield, 2001; Johnston et al., 2007, 2005; Seal, 2006; Sim et al., 2011). The difference between the sulfur isotope compositions of sulfate and sulfide minerals in sediments and their relative burial fluxes affect the isotopic compositions of both the SWS reservoir and the different sulfur sinks. Ideally, variations in the sulfur isotope composition of sedimentary sulfur species could, thus, be used as a proxy for past ocean chemistry.

Reconstructions of deep-time sulfur cycling are often limited to pyrite records because evaporite minerals, which more directly record SWS isotopic composition, are rarely preserved. Although pyrite is stable under a range of geological conditions, diagenetic or hydrothermal fluid flow or regional metamorphism can contribute to sulfur isotope variations in pyrite records (Craig, 1993; Meyer et al., 2017; Wagner and Boyce, 2006). Such late-stage overprinting of the primary pyrite $\delta^{34}S$ signals can be identified by proper petrographic and geochemical screening of samples (Cui et al., 2018; Fischer et al., 2014; Gregory et al., 2017; Large et al., 2014; Ono et al., 2009; Picard et al., 2018; Wagner and Boyce, 2006; Xiao et al., 2010). Therefore, relying solely on sedimentary pyrite records in paleoenvironmental reconstructions requires careful evaluation of mechanisms that affect its isotope composition at the time of deposition.

Strictly anaerobic MSR typically occurs within the shallow sediments where a combination of environmental factors (e.g. organic carbon concentrations, temperature, salinity, pH) can affect sulfate reduction rates, and sedimentary processes and characteristics such as sedimentation rate, porosity, permeability, and sediment reworking can limit sulfate transfer between pore space and the overlying water column (Aller et al., 2010, 2008; Bradley et al., 2016; Canfield et al., 2010; Farquhar et al., 2007; Fike et al., 2015; Ries et al., 2009; Sim et al., 2011). Generally, sedimentary pyrites with negative $\delta^{34}S$ and positive $\Delta^{33}S$ values are produced during steady-state conditions where microbial discrimination against ^{34}S is most expressed (Canfield et al., 2010; Rees et al., 1978; Seal, 2006). Conversely, if sulfate transport is limited, Rayleigh distillation effects attenuate biological fractionations and the $\Delta^{33}S$-$\delta^{34}S$ of pore-water sulfide will approximate the initial SWS isotope composition (Berner, 1964; Goldhaber and Kaplan, 1975; Johnston et al., 2007; Jørgensen, 1979; Zaback et al., 1993). In addition, the final composition of pyrite also depends on reactive iron availability and the fraction of sulfide that is reoxidised. Even in a closed system, ^{34}S-depleted pyrites will accumulate if only a fraction of pore-water sulfide is scavenged by reactive iron. Moreover, in sediments open to sulfate transport, sulfate limitation can develop as a result of high organic matter mineralisation rates by MSR when sulfate is rapidly consumed, reduced and effectively captured as sedimentary sulfide species (Aller et al., 2010; Berner, 1964; Canfield, 1991; Claypool, 2004; Fike et al., 2015; Goldhaber and Kaplan, 1975; Jørgensen, 1979; Zaback et al., 1993).

Physical reworking of sediments (e.g. storms, bioturbation) can disturb redox-stratified sediments and cause mixing between distinct sulfide pools that have undergone some degree of Rayleigh distillation. If formerly reduced sediments at some depth in the sedimentary column are placed into oxidising conditions, full or partial oxidation of pore-water sulfide by abiogenic or biogenic processes can impart additional fractionations of $< 5‰$ amplitude (Balci et al., 2007; Fry et al., 1988; Zerkle et al., 2009) leaving the residual sulfide enriched in ^{34}S. Further reactions between the modified sulfide and reduced iron can generate pyrites that preserve smaller sulfur isotope fractionations than predicted for MSR alone. Thus, shallow water environments, where sediment reworking is most intense, typically record pyrites with more positive and variable isotope signatures than their counterparts in deeper water settings. It has even been suggested that within such environments frequent disturbance of sediments and partial oxidation of sulfide can generate “superheavy pyrites” with $\delta^{34}S$ values that exceed those of ambient seawater sulfate (Ries et al., 2009). Overall, steadily accumulating pelagic shales are considered less likely to be affected by sedimentary reworking and more open to exchange with the overlying water, thus the sulfur isotope records therein are not as affected by limitations on sulfate diffusion (Fike et al., 2015; Pasquier et al., 2017; Ries et al., 2009).

However, this might not always be the case. For example, solid phase sulfur ($\Sigma S = FeS, FeS_2, S_0$) in the Amazon-Guianas inner shelf muds has unusually positive $\delta^{34}S$ signatures in areas episodically reworked by currents and/or wave action and negative $\delta^{34}S$ signatures where bioturbation occurs (Aller et al., 2010). If these sulfur phases were converted into pyrite and preserved in the rock record, it would be easy to misinterpret the nature of the processes that lead to such isotope signatures. We acknowledge that bioturbation had a limited effect on sedimentary iron and sulfur cycling prior to colonisation of the seafloor by benthic fauna in the early Phanerozoic (Canfield and Farquhar, 2009). Based on that, it is reasonable to assume that Precambrian nonbioturbated sediments would be more conductive to closed system sulfur cycling.

Another important aspect to be considered is the preservation of marine sedimentary records. Plate tectonics has effectively recycled Earth's crust and significantly reduced the likelihood of preserving deep-marine continental margins (Condie et al., 2017; Condie and Kröner, 2008; Hildebrand et al., 2018; Reddy and Evans, 2009). As the result, in Archean and Proterozoic successions the preservation of sedimentary successions is strongly biased towards marginal basins that may compromise the use of shales as representative archives of steady-state conditions (Woodcock, 2004).

Given difficulties that arise with variability of sulfate transport in early diagenetic systems and sedimentary facies, it has been suggested that pyrites that precipitate in euxinic conditions are more likely to indicate open-system sulfate reduction (Canfield et al., 2010; Lyons, 1997). This suggestion relies on the simple assumption that euxinia could indicate MSR within the water column, shifting the locus of pyrite formation from the sedimentary environment into the water column. Such pyrites should reflect stratigraphically consistent ^{34}S-depletions if sulfate is not limiting but approach SWS isotopic composition once sulfate limitation leads to smaller biological fractionations. Low apparent fractionation from seawater has, therefore, been used to argue for very low sulfate concentrations, since it has been assumed that biological discrimination against ^{34}S is supressed at sulfate concentrations <0.2 mM (Bradley et al., 2016; Habicht et al., 2002; Werne et al., 2003). This has given rise to the view that Proterozoic SWS concentrations were significantly lower than those of modern (28 mM) oceans (Canfield, 2001; Canfield and Raiswell, 1999; Habicht et al., 2002; Halevy et al., 2012; Havig et al., 2017; Kah et al., 2004; Lowenstein et al., 2003; Luo et al., 2015; Planavsky et al., 2012). However, this notion has been refuted by theoretical predictions (Wing and Halevy, 2014) and observations of >20‰ fractionations between sulfate and sulfide associated with MSR in settings with extremely low sulfate concentrations (<0.01 mM; Crowe et al., 2014).

In the modern oxygenated marine realm euxinic conditions are limited to isolated basins (e.g. the Black Sea), settings with restricted water circulation (fjords) or upwelling zones like Benguela, off-shore of Namibia (Meyer and Kump, 2008). In restricted basins, the sulfate reservoir can undergo Rayleigh distillation and evolve towards a more ^{34}S-enriched end-member if sulfide production and retention outpace sulfate supply (Fike et al., 2015; Gomes and Hurtgen, 2013; Gomes and Johnston, 2017; Johnston et al., 2008; Pufahl et al., 2010). These effects can be reversed, for example, if a more stable connection with a larger reservoir is restored or if sulfide sinks are decreased. Consequently, oscillations in basinal circulation and concomitant changes in sulfate levels would produce stratigraphic successions with opposing $\Delta^{33}S$ and $\delta^{34}S$ trends that are not directly reflective of changes in global ocean chemistry. Thus, unless it can be convincingly shown that euxinic conditions developed in open basins, such sulfur isotope records are likely to depict changes in the local environment, which may or may not track global trends.

Identifying unambiguously euxinic water column conditions and pyrite formation pathways in paleorecords is another concern. Geochemical proxies that explore the behaviour of iron in sedimentary environments (e.g. Fe/Al and Fe speciation proxy) have been used as indicators of paleoenvironmental redox conditions (e.g. Clarkson et al., 2014; Poulton and Canfield, 2005). The general premise is that enrichments of iron relative to the terrigeneous background and its prevalent partitioning to iron sulfide minerals in sedimentary rocks are compatible with euxinic waters (e.g. Raiswell et al., 1994; Raiswell and Canfield, 2012). While this concept can be applied in isolated basins such as the Black Sea, iron distribution patterns in modern open-marine high productivity settings like the Peruvian and Namibian shelf are often unrelated to water column chemistry and instead reflect the combined effects of local sedimentological and biogeochemical processes (Rico and Sheldon, 2019; Scholz, 2018; Scholz et al., 2019). Another aspect to consider is overprinting of the original proxy signatures, since iron is mobile under most diagenetic and metamorphic conditions and readily redistributed among different mineral phases (Clarkson et al., 2014; Slotznick et al., 2018). Consequently, connecting iron-based proxy signatures to water column chemistry and pyrite formation pathways is challenging and should be supported with additional lines of evidence (e.g. lithological observations, petrography, mineralogical and redox sensitive trace element analyses).

Even further, basins that are fully open to the ocean can also exhibit significant regional variability in sedimentary sulfide isotope compositions. For example, small fractionations between $\delta^{34}S$ of sulfate and sulfide are reported in the modern Benguela upwelling system along the Namibian coast where iron limitation and rapid oxidation of organic carbon promote episodic water column euxinia (Brüchert, 2004; Dale et al., 2009). Moreover, the distribution and development of sulfidic waters along the Namibian shelf relate to regional differences in the geochemical gradients and microbial communities, e.g. the sulfide-oxidising genera

Beggiatoa vs. *Thiomargarita* (Brüchert, 2004; Dale et al., 2009). Thus, even if it can be established that pyrites precipitated from euxinic waters, their δ^{34}S values might not directly relate to global seawater sulfate levels and isotopic composition. All in all, sedimentary pyrites can provide insights to ancient ocean conditions, but careful evaluation of the depositional environment, facies, microbial consortia, basinal configuration and late-stage diagenesis are necessary for any global conclusions to be drawn.

5.2 Organic carbon and sulfur isotopes tracking environmental changes in the Paleoproterozoic: Lessons from the Zaonega Formation

5. 2. 1 Hydrocarbon migration and alteration of the $\delta^{13}C_{org}$ record

Sedimentation of the Zaonega Formation was contemporaneous with magmatism (lava flows, sills with peperite contacts) that produced high heat gradients and hydrothermal circulation. This, in turn, induced thermal cracking of sedimentary organic matter, hydrocarbon generation, oil migration, and formation of ubiquitous pyrobitumen veining and impregnation of mudstones in the upper part of Member A and in Member B (Črne et al., 2013a, 2013b; Melezhik et al., 1999; Qu et al., 2018, 2012). Detailed geochemical investigations show that these Members have distinctive $\delta^{13}C_{org}$ values that can be pinpointed in the $\delta^{13}C_{org}$ values of organic matter in pyrobitumen veins and their sedimentary host rocks. This fingerprinting confirms that the migrating organic matter was locally sourced and that pyrobitumen impregnation and post-depositional alteration had only a limited (c. 4‰) effect on the preserved $\delta^{13}C_{org}$ stratigraphic record (Qu et al., 2012, 2018).

The relatively smooth stratigraphic $\delta^{13}C_{org}$ trend is, however, interrupted in the 156–136 m interval in the FAR-DEEP 12AB core by the presence of a massive C_{org}-rich rock (Qu et al., 2012). Its isotopic characteristics ($\delta^{13}C_{org}$ = -26‰, δ^{34}S = -18.7‰, and Δ^{33}S = 0.023‰) are distinct form adjacent under- and overlying sediments ($\delta^{13}C_{org}$ = c. -30‰, δ^{34}S = >10.6‰ δ^{34}S, and Δ^{33}S = <-0.015‰) but match those of the sedimentary units occurring more than 100 m lower in the Zaonega Formation ($\delta^{13}C_{org}$ = -26‰, δ^{34}S = -22.3‰ δ^{34}S, and Δ^{33}S = 0.026‰) (Fig. 4). Those relationships are readily reconcilable by recognising that this seemingly anomalous 20 m interval of massive rocks represents hydrocarbons and fluidised sediments, including pyrite, that migrated from Member A upward to the seafloor during accumulation of Member B. Thermal alteration and remobilisation of organic matter, however, cannot be offered as a mechanism to explain the c. 15‰ negative $\delta^{13}C_{org}$ excursion encompassed in Member B. While such processes can alter $\delta^{13}C_{org}$ values, as observed in pyrobitumen-rich veins and contact zones with magmatic bodies of Member A, the produced shifts are positive and rather small (a few per mil), inconsistent with Member B. Thus, the most straightforward explanation of the pronounced negative $\delta^{13}C_{org}$ excursion in Member B is a change in primary biomass.

5. 2. 2 Previous interpretations of the Zaonega Formation C_{org} and S records

Previous studies of the upper Zaonega Formation (e.g. Scott et al., 2014) inferred that Fe speciation data and $\delta^{34}S$ values (as low as -19‰) of pyrites in strata from Member A recorded conditions compatible with a sizeable sulfate reservoir but that ^{34}S-enriched pyrites ($\delta^{34}S$ up to +27‰) from strata corresponding to Member B precipitated from an euxinic water column and that this change coincided with a global drawdown in oxygen levels. They further suggested that the negative $\delta^{13}C_{org}$ shift that coincides with the ^{34}S-enriched sulfides expressed a biogeochemical response to deoxygenation and low sulfate levels, allowing methane flux and anaerobic oxidation of methane (AOM) in the water column. Selenium (Kipp et al., 2017), molybdenum (Asael et al., 2018) and multi-proxy (Ossa Ossa et al., 2018) studies of c. 2.1–2.0 Ga sedimentary rocks, including sections from the Zaonega Formation Member B, have also been used to argue for a global drawdown in oxygen levels at that time. However, instead of the progressive increase in pyrite $\delta^{34}S$ and decrease in $\Delta^{33}S$ values that would occur from a unidirectional, worldwide decrease in sulfate concentrations, the high resolution data show that Member B is marked by short-lived excursions around a baseline of c. 18‰ $\delta^{34}S$ and c. -0.02‰ $\Delta^{33}S$. Further, molybdnenum, uranium, rhenium and selenium enrichments and uranium isotope compositions (Kipp et al., 2020; Mänd et al., 2020; Partin et al., 2013; Sheen et al., 2018), as well as negative Ce anomalies in apatite (Joosu et al., 2015) and best preserved carbonate rocks (Kreitsmann et al., 2020) in the upper Zaonega Formation have been used to argue for prevailing oxygenated conditions after the LJE (Mänd et al., 2020). Support for a large oceanic oxidant pool during the Zaonega time was also found by a most recent selenium isotope study by Kipp et al. (2020). Lastly, the coinciding four-fold increase in TOC concentrations and the negative $\delta^{13}C_{org}$ excursion in Member B has been explained by a local bloom in methanotrophic organisms (Qu et al., 2012, 2018). Influence of methanotrophy on the basinal DIC pool can also be found from the relatively large up to 4‰ variations in $\delta^{13}C_{carb}$ values (as low as −6.3‰) in individual carbonate beds of Member B (Kreitsmann et al., 2019). In that Member B is characterised by syndepositional magmatism, hydrocarbon generation and seepage and changes in depositional conditions, it is not surprising that geochemical studies of the upper Zaonega Formation have produced contradictory interpretations.

An open-system steady-state modelling approach to the pyrite sulfur isotope record of the Zaonega Formation demonstrated that the positive $\delta^{34}S$ and opposing $\Delta^{33}S$ data in Member B can be explained by increased pyrite burial as a consequence of locally high sulfate reduction rates that ultimately led to diminished fractionation from seawater (Paiste et al., 2020). These results are consistent with the concomitant enrichments in TOC and TS seen in the upper part of Member A and lower to middle part of Member B (Fig. 5) and are suggestive of AOM coupled to MSR (Paiste et al., 2018; Qu et al., 2018, 2012). In contrast to previous work, these studies highlight the importance of local rather than global processes acting on the carbon and sulfur cycles in the Onega Basin. Considering the intraplate rift or active continental margin depositional setting (Črne et al., 2014; Melezhik et al., 2015) local control on sulfur and carbon cycling during deposition of the Zaonega Formation is feasible.

5. 2. 3 New interpretations of the previous C_{org} and sulfur records

In that syndepositional magmatic-volcanic activity generated hydrocarbon formation, it is likely that upward migrating methane produced from the organic matter of Member A fuelled sediment- or seafloor-housed methanotrophy during deposition of Member B. Thus, the coinciding four-fold increase in TOC, close association of strongly ^{13}C-depleted organic matter and ^{34}S-enriched sulfides within Member B suggest that a surge of carbon sources increased pore-water MSR fostering sulfate limitation and near quantitative uptake of sulfate. Alternatively, methanotrophy may have been established in an euxinic water column on the assumption that SWS levels were very low as previously suggested (Scott et al., 2014). In both of these scenarios, small fractionations from sulfate are expected and pyrites within Member B are most likely to have captured the SWS isotope composition, which was between 6–18‰ $\delta^{34}S_{SO4}$ and -0.05 – -0.02‰ $\Delta^{33}S_{SO4}$ based on modelling results (Scott et al., 2014; Paiste et al., 2020).

Besides helping to promote high primary productivity, active magmatism-volcanism would have modified basinal geography and influenced sedimentation patterns. Reshaping of the depositional setting and establishment of shallower conditions is implied by a higher frequency of thick dolostone beds in the upper part of the Zaonega Formation (Melezhik et al., 2015) and subsequent emplacement of the Suisari Formation lavas. Unstable redox conditions, as indicated by the large spatio-temporal variability in elemental proxies for the upper part of the Zaonega Formation (e.g. Asael et al., 2018; Kipp et al., 2017; Mänd et al., 2020; Paiste et al., 2018; Scott et al., 2014) also corroborates a semirestricted hydrographic regime because both well-oxygenated open basins and stably stratified restricted basins with anoxic/euxinic deep waters would, in contrast, record relatively constant redox conditions (Algeo and Li, 2020). Specific sediment biogeochemical conditions can, however, induce temporal and regional redox heterogeneity in continent-margin upwelling systems (Algeo and Li, 2020; Dale et al., 2009; Waldron and Probyn, 1991). Similar to modern upwelling zones, the occurrence of abundant phosphates (Lepland et al., 2014), high redox sensitive trace element concentrations as well as elevated uranium isotope ratios in the middle part of the Zaonega Formation point towards locally variable redox conditions in the backdrop of an oxygenated ocean (Mänd et al., 2020). On the other hand, Kreitsmann et al. (2020) has proposed that the preservation of prominent Eu_{SN} anomalies in the Zaonega Formation carbonates and positive and negative Eu_{SN} anomalies in apatites (Joosu et al., 2015) are suggestive of deposition in a semi-restricted rather than fully open-marine embayment, because otherwise the excess Eu would have been rapidly diluted. Taken together the large variability in elemental redox proxies for the upper part of the Zaonega Formation is best explained by sediment accumulation in a semi-confined embayment that had intermittent access to the open ocean. The modern Guaymas Basin in the Gulf of California is a representative example of a dynamic early rifting environment where seasonal upwelling, high heat gradients, hydrothermal fluid flow and syndepositional hydrocarbon generation induce regional redox heterogeneity (Chang et al., 2015; Curray, 1982; Scholz et al., 2019). Thus, instead of the common approach of using the Black Sea as a paleo-marine model system, the Guaymas Basin could serve as a closer analogue for deposition in the Onega Basin during the Zaonega time.

The combination of added carbon sources, shallowing and/or the establishment of a physical barrier within the basin could have led to sulfate limitation due to an increased pyrite sink. This would have allowed the basinal sulfate to undergo Rayleigh distillation and explain pyrites in Member B and lower part of Member C that exceed the oceanic SWS isotope composition. However, in order to maintain high rates of MSR over 150–200 meters of strata and sustain a baseline of c. 18‰ $\delta^{34}S$ and c. -0.02‰ $\Delta^{33}S$ of sedimentary sulfides, relatively constant sulfate concentrations had to be maintained. That MSR was not sulfate-limited is further implied by the relatively high but variable TS/TOC ratios that mostly fall between 0.1 and 0.5 in Member B (Melezhik et al., 1999; Paiste et al., 2020), even though organic matter mobilization, impregnation of the sediments with pyrobitumen and hydrocarbon spillage on the seafloor likely lowered TS/TOC ratios. In addition, the pronounced positive >30‰ $\delta^{34}S$ excursions in Member B that occur over a few m of strata are unlikely to reflect rapid fluctuations (in a range of << millions of years) in the size of the SWS reservoir, even if the residence time for sulfate in the Proterozoic ocean was shorter than in the modern (13 Ma; Berner, 2001). Therefore, it is likely that the Onega Basin was periodically cut off and/or sulfate consumption episodically exceeded supply from a larger reservoir. Another possibility is that a separate generation of late-stage pyrite—identified in intervals with >30‰ δ^{34}S values (Paiste et al., 2018)—could contribute ^{34}S-enriched sulfur to the bulk pyrite S isotope signature. Whether different pyrite morphologies in the Zaonega Formation carry distinct δ^{34}S signatures and to what extent this could affect the bulk pyrite δ^{34}S analysis is currently unknown and remains to be determined by future studies. In any case, it is doubtful that the anomalous >30‰ δ^{34}S values reflect abrupt fluctuations in the SWS reservoir. This renders previous interpretations suggesting water column methanotrophy in response to very low global SWS levels in Member B equivocal. Further doubts arise from the fact that such interpretations require a close association between the most positive δ^{34}S and negative $\delta^{13}C_{org}$ in the Zaonega Formation; instead what is observed is that intervals with δ^{34}S values >30‰ occur in the upper part of Member B where steadily increasing $\delta^{13}C_{org}$ values from -42‰ to -29‰ suggest increasing contributions of normal marine CO_2-fixing autotrophic biomass.

If the Zaonega Formation records global perturbations in the carbon and sulfur cycles, then the ^{13}C-depleted organic matter and ^{34}S-enriched pyrites in Member B represent the postulated global deoxygenation event; however, such conditions must have been short-lived as normal marine biomass and more open-system MSR resumed in Member C. Thus, instead of oscillating atmospheric oxygen levels, what is more likely is that changes in the basin dynamics and depositional environment affected both microbial and sedimentary processes, and it is these that were mutually responsible for generating the $\delta^{13}C_{org}$ and multiple sulfur isotope trends within the Onega Basin.

5. 3 Global vs local influence on the seawater sulfate levels and its isotope composition in the Paleoproterozoic

There is abundant evidence to suggest that seawater sulfate concentrations significantly increased during the GOE and the 2.2–2.1 Ga LJE (e.g. Guo et al., 2009; Reuschel et al., 2012b; Planavsky et al., 2012; Scott et al., 2014; Luo et al., 2015; Havig et al., 2017; Blättler et al., 2018). However, broadly similar chemostratigraphic trends with positive and upwards increasing δ^{34}S values characterize several post-LJE Paleoproterozoic sedimentary successions such as the Onega Basin (Kump et al., 2011; Scott et al., 2014), the Francevillian Basin (Kump et al., 2011; Canfield et al., 2013), the Pechenga Greenstone Belt (Reuschel et al., 2012a) and younger strata such as the Animikie Basin (Poulton et al., 2004, 2010) (Fig. 6). These trends have been proposed to reflect a contraction of the global seawater sulfate reservoir, redox stratified oceans and a return to more reducing surface environments (Canfield et al., 2013; Havig et al., 2017; Johnston et al., 2006; Ossa Ossa et al., 2018; Planavsky et al., 2012; Poulton et al., 2004; Scott et al., 2014). However, we and other workers have questioned the global nature of these preserved δ^{34}S records by demonstrating that sedimentary processes, facies changes and basinal restriction could equally govern sulfur cycling and isotope trends within these basins (Pufahl et al., 2010; Reuschel et al., 2012a). Evaluating the meaning of pyrite δ^{34}S records becomes even more important in light of recent time-series investigations of trace element composition of marine pyrite grains in black shales that have been used to infer that atmospheric oxygen levels remained persistently high until at least 1.8 Ga (Large et al., 2014, 2019; Mukherjee and Large, 2016).

5. 3. 1 Similar Paleoproterozoic organic carbon and sulfur isotope records - global vs local underlying mechanisms

Kump et al. (2011) argued that the distinct negative trend of $\delta^{13}C_{org}$ values in sedimentary successions of the upper part of both the Francevillian and Onega Basins signified a global and synchronous two-step shift towards strongly ^{13}C-depleted biomass at the end of the LJE. The compilation of Kump et al. (2011) used data from the FAR-DEEP 12AB core from the Onega Basin, compared it with data from the Francevillian reference stratigraphic column (Gauthier-Lafaye and Weber, 2003), and noted that the two $\delta^{13}C_{org}$ records exhibit similar trends, but are off-set by c. 7‰. However, ascribing outcrop and drill core material from the Francevillian Basin to specific stratigraphic intervals of the reference lithostratigraphic column has proven to be challenging. For example, the unit containing the most ^{13}C-depleted biomass ($\delta^{13}C_{org} < -45$‰) has been variably assigned to the Francevillian C (FC) Formation (Gauthier-Lafaye and Weber, 2003) or to the FD Formation (Canfield et al., 2013). The lack of robust stratigraphic correlation and disparate representations of the Francevillian reference lithostratigraphic column by different authors complicate direct comparisons with other basins.

Canfield et al. (2013) and Ossa-Ossa et al. (2018) have demonstrated that the first negative $\delta^{13}C_{org}$ shift (from c. -25‰ to -35‰) in the middle part of the Francevillian B Formation (FB1) coincides with a positive shift in pyrite δ^{34}S values (from c. -20‰ to 10‰, Fig. 6). The sulfur isotopes in the upper FB Formation (FB2) return to predominantly negative values ranging from -34‰ to 5‰. The overlying FC Formation exhibits more variable δ^{34}S values, with carbonate samples containing typically isotopically heavier pyrite (δ^{34}S from 12‰ to 59‰) than shales

(δ^{34}S from -4‰ to 16‰). According to Canfield et al. (2013), the FD Formation at the top of the Francevillian succession houses the second step of the negative $\delta^{13}C_{org}$ shift representing the most ^{13}C-depleted biomass ($\delta^{13}C_{org}$ values between -40‰ and -50‰) and pyrite δ^{34}S values typically ranging between -5‰ to 8‰ (with the exception of one 24‰ data point). By combining Francevillian $\delta^{13}C_{org}$ and δ^{34}S records, Ossa-Ossa et al. (2018) argued for negative coupling of the two isotope systems caused by shoaling of anoxic deep waters and sulfate limitation that was accompanied by two global episodes of ocean-atmosphere deoxygenation. While the opposing behaviour of the $\delta^{13}C_{org}$ and δ^{34}S trends during the first negative $\delta^{13}C_{org}$ shift in the FB Formation is evident, the available data do not support such co-variation during the second negative $\delta^{13}C_{org}$ shift in the upper FC and FD Formations. Notably, within the FC and FD Formations the most ^{13}C-depleted biomass does not typically associate with the highest δ^{34}S values. Using the interpretation of Scott et al. (2014) from the Zaonega Formation it was reasoned that low-sulfate conditions resulted in an overall increase in methane production by methanogens and a shift of methanotrophy into the water column, thus explaining the negative $\delta^{13}C_{org}$ shift and pyrites with highly positive δ^{34}S values (Ossa-Ossa et a., 2018). However, the decoupling of the δ^{34}S and $\delta^{13}C_{org}$ records in the upper part of the Francevillian succession does not favour such reasoning nor a pronounced contraction of the marine sulfate reservoir during the second negative $\delta^{13}C_{org}$ shift. Instead, these results suggest that the observed $\delta^{13}C_{org}$ and δ^{34}S trends can be produced by both local and global processes – their implication for large-scale changes in Earth's surface environments then rests mainly on comparisons with other basins of similar age (Ossa-Ossa et al., 2018).

Such comparisons, however, are fraught with difficulty in the Paleoproterozoic and verifying the global synchronicity of short-term (<10 Ma) geochemical trends is in most cases irresolvable by currently available geochronology methods due to precision and accuracy uncertainties. This is the case with the interpretation that a singular event encompassing large fluctuations in SWS concentrations was the underlying cause of the organic carbon and sulfur isotope records on two different cratons, as derived from the upper FC and FD Formations (Ossa Ossa et al., 2018) and the Zaonega Formation (Kump, 2011; Scott et al., 2014). The maximum age for most of the Francevillian succession is determined by a zircon ^{207}Pb/^{206}Pb age of 2191 ± 13 Ma derived from the N'goutou magmatic complex that intrudes the Francevillian FA, FB and possibly FC Formations (Sawaki et al., 2017; Weber et al., 2016), whereas the minimum age is defined as 2083 ± 6 Ma by zircon ages from a welded ignimbrite tuff in the FD Formation in the Lastrousville sub-basin (Horie et al., 2005). Current age constraints make the Zaonega Formation younger, at minimum c. 30 Ma (Hannah et al., 2008) and at maximum c. 100 Ma (Martin et al., 2015; Weber and Gauthier-Lafaye, 2013) and indicate that instead of a single global event, the geochemical conditions in the Francevillian and Onega Basins were not coeval. We suggest that a similar style of basinal evolution for the intracratonic Francevillian and the Onega Basins could be responsible for the similar $\delta^{13}C_{org}$ and $\delta^{34}S$ trends recorded at different time periods in these basins.

A recent review of the evolution of the c. 2.0 Ga Eburnean Orogeny (Weber et al., 2016) suggests that the depositional history of the Francevillian sedimentary basin is comparable to the Onega Basin, although the latter was magmatically more active. According to their interpretation the black shales of the FB Formation accumulated in confined and restricted environments during a period of tectonic instability and submarine volcanism. The overlying FC Formation, which has been thought to record the falling limb of the LJE, is characterised by widespread emersion and deposition of stromatolitic and evaporitic carbonates in very shallow environments, similar to the Tulomozero Formation of the Onega Basin. Moreover, the common occurrence of bitumen filled fractures in the lower part of the FC Formation has been related to syn-depositional hydrocarbon migration and seepage that likely invigorated methanotrophy and its contribution to the sedimentary biomass (Ossa-Ossa et al., 2018). In a larger tectonic framework the FA–FC Formations accumulated during a phase of basin opening, whereas the FD Formation represents sedimentation in a foreland basin towards the end of the Eburnean Orogeny (Weber et al., 2016). Pyrite precipitation within the FD Formation was interpreted to have occurred under euxinic conditions (Canfield et al., 2013) and the strongly ^{13}C-depleted biomass was related by Kump et al. (2011) to increased weathering of LJE organic carbon. However, this scenario was subsequently dismissed, since the negative $\delta^{13}C_{org}$ shift in the underlying FB Formation occurs during accumulation of isotopically heavy LJE carbonates (Ossa-Ossa et al., 2018). Instead, Ossa-Ossa et al. (2018) forwarded a scenario whereby increased methane cycling occurred in low-sulfate environments, similar to the interpretation of the FC Formation S and C_{org} isotope profiles. Even so, hydrocarbon migration and seepage are typically restricted to environments where high heat gradients are generated locally due to active magmatism and/or tectonic processes that can further impact depositional patterns and nutrient fluxes within confined areas. Given the similar history of basinal evolution, we suggest that the observed range of $\delta^{34}S$ and $\delta^{13}C_{org}$ in the Francevillian can therefore be explained by local processes without necessitating global oscillations in the sulfur and carbon cycles, as we have demonstrated for the Zaonega Formation.

In addition to the Onega and Francevillian Basins, pyrite sulfur isotope records from other Paleoproerozoic metasedimentary basins have also been subjects of debate about the meaning of the isotopic information and if the size and isotopic composition of the contemporaneous SWS reservoir can be estimated from bulk-rock pyrite $\delta^{34}S$ records alone. The organic-rich sediments of the Pilgujärvi Sedimentary Formation in the Pechenga Greenstone Belt record pyrites with positive $\delta^{34}S$ values up to 18.7‰ that accumulated in a tectonically active basin bound to an oceanic rift system (Melezhik and Sturt, 1994; Reuschel et al., 2012a). Until recently, the Zaonega and Pilgujärvi Sedimentary Formation were considered time equivalent; however, new age constraints suggest that the latter is significantly younger (1.92 Ga instead of 1.98 Ga; Martin et al., 2015). While some authors have linked ^{34}S-enriched pyrites in the Pilgujärvi Sedimentary Formation to global fluctuations in seawater sulfate levels (Planavsky et al., 2012; Having et al., 2017), Reuschel et al. (2012b) suggested that a combination of high sedimentation rates, increased organic carbon loading and highly reactive iron availability resulted in rapid pore water MSR and effective pyrite burial (Claypool, 2004). In such closed-system conditions, if all sulfate entering the pore waters was reduced and scavenged by reduced iron, the preserved sedimentary pyrites with the most positive $\delta^{34}S$ would have captured the sulfur isotope signature of the contemporaneous seawater (Johnston et al., 2006; Zaback et al., 1993). While this interpretation requires a more thorough assessment, it is intriguing that pyrites in the organic-rich Member B of the Zaonega Formation typically have very similar $\delta^{34}S$ values of c. 18‰.

Younger Paleoproterozoic successions such as the Gunflint and Rove Formations of the Animikie Basin have, likewise, been used to estimate a $\delta^{34}S$ signature of c. 17‰ for seawater sulfate at 1.84 Ga (Poulton et al., 2004, 2010). The Rove Formation was further interpreted to reflect low seawater sulfate concentrations under an oxygen-poor atmosphere. This conclusion was largely based on the assumption that water circulation between the ocean and the Animikie Basin was unrestricted and that the precipitated pyrites reflect relatively small fractionations from seawater sulfate. Pyrites in the Gunflint Formation with average $\delta^{34}S$ values of 8.4‰ ± 5.4‰ were interpreted to have formed within shallow sediments, while pyrites with $\delta^{34}S$ values of 17.2‰ ± 5.1‰ in the overlying Rove Formation were suggested to have precipitated from an euxinic water column. Taken together with other lines of evidence, the overall small fractionations between the estimated SWS composition and the positive $\delta^{34}S$ values were suggested to indicate SWS concentrations between 0.2 and 2.4 mM during accumulation of the Rove Formation (Poulton et al., 2004). However, a subsequent study of the time-equivalent

Michigamme Formation in the Baraga Group was used to argue that the Animikie Basin became increasingly isolated during its evolution and that the sulfur isotope profiles reflect basinal rather than global processes (Pufahl et al., 2010). Disseminated pyrites with average $\delta^{34}S$ values of 6.3 ± 1.0‰ throughout the Michigamme Formation were used to argue for freshening effects in the riverine delta areas that resulted in lateral gradients along the coast of the Animikie foreland. While this interpretation has been debated (Poulton et al., 2010; Fralick et al., 2011), further work in the Animikie Basin has strengthened the impression of important spatial and temporal variability in geochemical profiles across the area (Fralick et al., 2017; Poulton et al., 2010; Poulton and Canfield, 2011).

Expanding on their earlier work on the Rove Formation, Poulton et al. (2010) analysed several correlative core sections extending from the shallow- to deep-water settings of the Animikie Basin to further assess a redox stratified open-shelf environment with oxygenated surface, euxinic mid-depth and ferruginous deep waters. This change in iron proxy data across the Animikie shelf was accompanied by a negative shift in pyrite $\delta^{34}S$ from c. 17‰ in the shallow-shelf (Rove Formation) to 5.5 ± 3.6‰ in the correlative deeper-shelf (Virginia Formation). Following a similar reasoning as in Poulton et al. (2004), samples with an euxinic iron speciation signature were interpreted to capture the $\delta^{34}S$ signature of seawater sulfate, whereas those with ferruginous signatures were thought to reflect open-system MSR in sediments. Given these associations, a relatively small c. 15‰ fractionation between sulfate and sulfide was estimated and considered characteristic of a limited SWS reservoir that supressed biological sulfur cycling (Poulton et al., 2010). Enrichments of redox-sensitive metals and positive Cr isotope signatures of meteoric calcite cements in the Gunflint Formation have also been used to argue for oxygenated terrestrial conditions and an imbalance between the redox-state of the ocean and atmosphere, assuming the former remained reducing (Fralick et al., 2017). Conversely, a more recent multi-proxy study of the Stambaugh Formation that represents the deepest-water facies of the Animikie Basin has provided evidence for deep-water oxygenation at c. 1.85 Ga (Planavsky et al., 2018). The latter authors propose that variations in the geochemical signatures of the metasedimentary rocks of the Stambaugh Formation resemble those in the modern Baltic Sea, where local anoxia can develop due to fluctuations in basin connectivity with the larger ocean. While Poulton et al. (2010) and Fralick et al. (2011) argue against basin isolation, Planavsky et al. (2018) offer an alternative scenario in which periodic incursions of low oxygen, suboxic and oxic waters are responsible for the observed redox variability in the Animikie Basin. Although it is not clear if the 1.84 Ga Rove and 1.85 Ga

Stambaugh Formations are in part time-equivalent, they are considered time-transgressive on a regional scale (Planavsky et al., 2018), which has some interesting implications for the reported δ^{34}S data.

The bulk pyrite sulfur isotope data from the deep-water Stambaugh Formation range from −21.6 to +2.2‰ (average −6.3 ± 6.5‰) in δ^{34}S, as opposed to the dominantly positive shallow-shelf pyrites with δ^{34}S of around 17‰ in the Rove Formation. Additionally, the deeper-shelf pyrites of the Virginia Formation carry δ^{34}S signatures that fall between the more shore-proximal Rove Formation and most shore-distal Stambaugh Formation pyrites. Applying the modern analogy and the isotopic contrast between shallow- and deep-water settings (e.g. Fike et al., 2015; Pasquier et al., 2017) the discrepancy in δ^{34}S between Stambaugh, Virginia and Rove Formations could imply that facies differences are driving variability in the sulfur isotope records within the Animikie Basin. Moreover, if the δ^{34}S value of c. 17‰ from the Rove Formation represents a SWS signature as previously proposed, then a fractionation of c. 38‰ between sulfate and sulfide could be estimated. Such a c. 38‰ offset between pyrite and SWS is commonly observed in more recent sulfate-rich marine environments. This estimate supports the conclusion of Poulton et al. (2004) that sulfate concentrations within the Animikie Basin exceeded the 0.2 mM threshold generally required to induce large fractionations during MSR. We caution, however, that the upper limit for sulfate concentrations needs further evaluation, as the attenuated fractionation between sulfate and sulfide in the shallower environments is likely depositionally controlled, rather than directly reflective of global fluctuations in SWS concentrations.

Taken together, the sulfur isotope profiles of the Francevillian Basin, Onega Basin, Pechenga Greenstone Belt and the Animikie Basin record environmental changes within basins having complex sedimentation histories and variable environmental conditions all of which operated at disparate time intervals. Despite the influence of local factors on the pyrite records, it may be possible to estimate the δ^{34}S composition of ambient SWS by thoroughly screening for intervals where quantitative reduction of sulfate to sulfide and conversion into pyrite can be inferred. However, this screening requires a thorough understanding of the basinal evolution and local sedimentary and biological processes that can mutually influence the expression of stable isotope signatures in sedimentary minerals and organic matter. Thus, if typical δ^{34}S values of 15–18‰ in pyrites from the Zaonega, Pilgujärvi Sedimentary, and Rove Formations reflect an isotope composition similar to the initial SWS, it could imply that the global sulfate reservoir and its isotope composition was relatively stable throughout much of the

Paleoproterozoic. This stability, if confirmed, would suggest that the underlying mechanisms that govern pyrite formation and a sizeable SWS reservoir with stable δ^{34}S values may have been already established during or shortly after the initial rise in atmospheric oxygen levels, and have remained largely unchanged.

Conclusions

Exploiting the pyrite δ^{34}S and $\delta^{13}C_{org}$ records from recently drilled cores, bisecting the entire Zaonega Formation of the Onega Basin, we have undertaken a careful investigation of these proxies in the context of depositional history to constrain global and/or local influences on sulfur and carbon cycling as recorded in Paleoproterozoic rock records. Considering the emerging understanding of sulfur isotope effects associating with sedimentary and biological processes, the entire Zaonega Formation pyrite isotope record can be explained by local depositional changes and corresponding microbial feedbacks without the need to invoke large-scale fluctuations in ocean sulfate concentrations and isotope composition. Likewise, the negative $\delta^{13}C_{org}$ excursion encompassed in the organic-rich rocks of the middle Zaonega Formation can be explained by a blooming methanotrophic community responding to a surge of carbon sources to the local environment as a consequence of syn-depositional hydrocarbon seepage. In turn, this invigorated MSR causing a high demand for sulfate that overwhelmed its supply from an external pool. However, an influx of sulfate had to be maintained in order to account for the high pyrite burial and MSR rates throughout most of the Zaonega Formation, indicating that SWS levels were not in a state of decline as suggested by previous workers.

Further comparisons between the Zaonega Formation pyrite δ^{34}S and $\delta^{13}C_{org}$ records and the older Francevillian Formations in Gabon reveals that similar but temporally unrelated conditions marked these diachronous successions in which high primary productivity and dynamic basinal conditions governed the sulfur and organic carbon cycles subsequently producing broadly similar stable isotope records; they do not represent global perturbations in the ocean-atmosphere redox system and, in fact, this is a likely commonality between other Paleoproterozoic basins such as the Pechenga Greenstone Belt and Animikie Basin. However, screening for pyrites that infer small fractionations from the initial seawater sulfate has revealed consistent δ^{34}S values of 15–18‰ in the Zaonega, Pilgujärvi Sedimentary, and Rove Formations, which could indicate a relatively stable SWS reservoir throughout much of the Paleoproterozoic. All be it speculative, it highlights the importance of interpreting pyrite δ^{34}S and $\delta^{13}C_{org}$ records in a context of sedimentological evidence, facies changes and late-stage diagenesis underpinned by firm chronological constraints in each individual Paleoproterozoic succession.

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Figure captions

Figure 1. Key geobiological events and trends in Earth history; evolution of atmospheric oxygen modified from Lyons et al. (2014) and $\delta^{13}C_{carb}$ trend from Farquhar et al. (2014).

Figure 2. A. Simplified geological map of the Onega basin, NW Russia. Circles show locations of cores discussed in the text. B. World map showing the present distribution of Paleoproterozoic rocks, highlighting the locations of the Animikie Basin, Francevillian Basin, Onega Basin and Pechenga Greenstone Belt.

Figure 3. Lithological profiles for the dolostone marker unit and underlying P-rich mudstone used for correlating the OPH, OnZap 1 and 3, and FAR-DEEP 12AB cores across the Onega Basin, NW Russia. Photos show the dolostone-mudstone contact and the occurrence of mm- to cm-thick discontinuous layers of apatite at the base of the massive grey dolomite bed. Phosphate (expressed as P_2O_5) concentration logs displayed to the right of lithological profiles represent semi-quantitative determinations undertaken by XRF logging directly on cores (OnZap 1, 3 and

FAR-DEEP 12AB cores) whereas data for the OPH core are from bulk XRF quantitative determinations on extracted subsamples.

Figure 4. Lithostratigraphic profile and new $\delta^{13}C_{org}$ data from the OPH core and previously published sulfur isotope, total organic carbon (TOC) and total sulfur (TS) data for the OPH core (Paiste et al., 2020). These data are used to divide the OPH core into Members A, B and C (see text for details). Black bars at the side of the OPH lithological profile represent intervals of core recovery; interpolation of rock types in zones of no recovery are based on interpretations of downhole geophysical data (after Morozov et al., 2010).

Figure 5. Compilation of $\delta^{13}C_{org}$, $\delta^{34}S$, TS and TOC profiles for six cores from the Zaonega Formation. The three Members defined in the OPH core (Members A, B and C; see Fig. 4) can be identified in all the cores (data from Lepland et al., 2014; Melezhik et al., 2015; Qu et al., 2012; Scott et al., 2014; Strauss et al., 2013). Sedimentary and magmatic intervals are shown for the OPH, FAR-DEEP (FD) and OnZap core profiles but cores C-5190 and C-175 are left blank because, although C-S isotope data have been utilised from those cores (e.g. Scott et al., 2014), there are no lithological descriptions to accompany those data hence the exact distribution of sedimentary and magmatic bodies is not known.

Figure 6. Compilation of sulfide (grey) and sulfate (light blue) $\delta^{34}S$ data through time (modified after (Crockford et al., 2019; Fike et al., 2015; Havig et al., 2017) with expanded trends shown for stratigraphic pyrite $\delta^{34}S$ profiles from the Francevillian (Canfield et al., 2013; Ossa Ossa et al., 2018), Onega (Paiste et al., 2020, 2018; Scott et al., 2014), Pechenga (Reuschel et al., 2012a) and Animikie (Planavsky et al., 2018; Poulton et al., 2004) successions. Note that two different stratigraphic schemes have been proposed for the Francevillian reference column (Formations FB, FC and FD), one by Canfield et al., (2013) and the other by Ossa-Ossa et al., (2018), who use additional subdivisions of Formation FB (units 1a through 2b); both versions are shown.

Supplementary material

Supplementary Table 1. Organic carbon isotope data for the Onega Parametric drillhole (OPH).