The pyrite multiple sulfur isotope record of the 1.98 Ga Zaonega Formation: evidence for biogeochemical sulfur cycling in a semi-restricted basin


Abstract

The pyrite sulfur isotope record of the 1.98 Ga Zaonega Formation in the Onega Basin, NW Russia, has played a central role in understanding ocean-atmosphere composition and inferring worldwide fluctuations of the seawater sulfate reservoir during the pivotal times of the Paleoproterozoic Era. That, in turn, has led to a concept that Earth’s atmospheric oxygen levels underwent global-scale changes. Here we present a steady-state isotope mass-balance model to gain insight into the mechanisms governing the sulfur cycle and sulfate reservoir during deposition of the organic-rich Zaonega Formation. We demonstrate that coupling between high microbial sulfate reduction rates and effective sulfate removal by pyrite precipitation can lead to Rayleigh distillation of the basinal sulfate reservoir and development of high amplitude positive $\delta^{34}S$ excursions. This modelling approach illustrates that secular changes in
sedimentary pyrite isotope trends can be explained by processes that reflect local (basin-scale) fluctuations in sulfur cycling rather than global mechanisms.

**Keywords**: sulfur isotope fractionation, sulfur cycle, mass-balance model, Paleoproterozoic

### 1. Introduction

Biogeochemical sulfur cycling involves a multitude of processes that collectively influence the magnitude of sulfur isotope fractionation between different sulfur species and determine the final sulfur isotope signature captured in the rock record (Farquhar et al., 2010; Fike et al., 2015; Johnston, 2011). Sulfur isotope data have therefore proven useful for paleoenvironmental reconstructions and in obtaining important insight into the evolution of Earth’s surface redox environments (Canfield et al., 2010; Habicht et al., 2002; Sim et al., 2011). However, the complex relationships between microbial metabolisms and their immediate environments particularly within dynamic diagenetic settings can have a significant impact on sulfur cycling (Aller et al., 2010; Lin et al., 2016; Paiste et al., 2018). Consequently, disentangling the local from global signals in sulfur isotope records is not straightforward. Ideally, paleoenvironmental information is gained from concurrent isotope records of the initial sulfate reservoir and resulting sedimentary sulfide. Complicating this is the fact that sulfate minerals are often not preserved, hence reconstructions of past sulfur cycling commonly rely on sulfide mineral (mainly pyrite) records alone. To address this shortcoming, theoretical models have been used to track processes involved in the production and preservation of sedimentary pyrite (Berner, 1964; Donahue et al., 2008; Habicht et al., 2002; Johnston, 2011; Jørgensen, 1979; Zaback et al., 1993). However, simplifications in models reduce the complex depositional histories of rock successions to a few variables, significantly limiting the sensitivity and resolution of the model predictions when trying to reconstruct biogeochemical sulfur cycling processes.
Here we use the 1.98 Ga Zaonega Formation in the Onega Basin of NW Russia (Fig. 1) as a case study to investigate the mechanisms governing the sulfur cycle. The Formation was deposited in a magmatically active basin characterised by high organic carbon content in a mixed siliciclastic-carbonate depositional system that accumulated mostly below wave-base (Črne et al., 2014; Melezhik et al., 2015; Qu et al., 2012). In this study, four sets of drill cores (OPH, FAR-DEEP 12AB, FAR-DEEP 13A, OnZap; Fig. 1, A.1) recover nearly the entire Zaonega Formation as well as the lower part of the overlying Suisari Formation. Our new bulk multiple sulfur isotope (Δ$^{33}$S, δ$^{34}$S, Δ$^{36}$S) and major element data from 185 samples were integrated with previously published data from the OnZap cores (Paiste et al., 2018) to provide a nearly continuous sulfur isotope record of the Zaonega Formation. We show that the pyrite isotope record of the Zaonega Formation can be explained by processes bespoke to local (i.e. basin-scale) depositional settings without the need to invoke worldwide changes in ocean chemistry.

2. Geological context

The greenschist facies volcano-sedimentary succession of the Zaonega Formation forms the upper part of the supracrustal succession within the Onega Basin, located on the south-eastern part of the Archean Karelian craton in NW Russia (Melezhik et al., 1999). The Zaonega Formation represents a deep-water shelf-slope-basin setting characterised by syndepositional magmatism and volcanism. Although the exact paleobathymetry is unclear, the predominantly fine-grained textures and dearth of current-generated features imply depths below storm-wave base. The lower part of the Zaonega Formation is typified by organic-rich mudstones. The portion of mudstones decreases upward and dolostone beds become more common, implying a change towards carbonate-dominated depositional system in the upper part of the Formation (Črne et al., 2014). The organic-rich sedimentary rocks are interlayered with mafic lava flows and intersected by mafic intrusions emplaced into unlithified sediments as indicated by their
peperitic contacts. These igneous bodies induced hydrothermal circulation and oil-to-gas cracking of organic-matter in the Formations exceptionally $C_{\text{org}}$-rich sedimentary rocks (Črne et al., 2014; Melezhik et al., 1999; Qu et al., 2012). Following deposition of the Zaonega Formation, the basin was filled by thick sub-aqueously extruded basalts interlayered with rare thin mudstone beds of the Suisari Formation (Krupenik et al., 2011; Melezhik et al., 2015).

Whole-rock and mineral Sm-Nd and Pb-Pb isochrone ages from the Suisari Formation have been used to constrain the minimum depositional age for the Zaonega Formation at 1.98 Ga (Puchtel et al., 1999, 1998). Recent U-Pb zircon dates by Martin et al. (2015) imply that deposition of the Zaonega Formation was between 1982.0 ± 4.5 Ma (tuff in the lower Zaonega Formation) and 1967.6 ± 3.5 Ma (detrital grains in overlying Kondopoga Formation). However, the age constraints of the Zaonega Formation remain a matter of debate (Bekker et al., 2016). Until age relationships are more fully resolved, we adopt 1.98 Ga as the time of accumulation for the Zaonega Formation.

3. Materials and Methods

Samples for bulk pyrite sulfur isotope and major element analyses were taken from three cores in the Onega Basin (Fig. 1): Onega Parametric Hole (OPH, 119 samples), FAR-DEEP 12AB (49 samples) and 13A (17 samples). Data on these samples were combined with published bulk pyrite sulfur isotope and major element data for the OnZap cores (Paiste et al., 2018). A distinctive dolostone marker unit in the upper part of the Zaonega Formation (Črne et al., 2014; Melezhik et al., 2015; Paiste et al., 2018; Qu et al., 2012) is used to correlate the cores. The dolostone is characterised by mm- to 1-cm-thick discontinuous apatite layers at its base (Joosu et al., 2015) and striking black silica veins throughout that can be several meters thick and typically are concident with thin mudstone layers within the dolomite. Detailed descriptions of...
the OPH, FAR-DEEP and OnZap cores are available in Krupenik et al. (2011), Črne et al. (2014) and Paiste et al. (2018), respectively.

Major element composition of powdered samples was determined by means of X-ray fluorescence spectrometry (XRF) using a PANalytical Axios at 4 kW. Total sulfur (TS) and total organic carbon (TOC) from decarbonated residues were determined by sealed tube combustion using a Leco SC-444 analyser. Sulfur was extracted from powdered samples by a two-step sequential extraction method modified from Canfield et al. (1986) and isotope composition was measured on a Thermo Finnigan MAT 253 gas source mass spectrometer. The sulfur isotope data are reported using standard delta notation (δ), where: $\delta^{3x}S = 1000 \cdot \left(\frac{3x_{\text{sample}}}{3x_{\text{V-CDT}}} - 1\right)$, and $3x = 33$ or $34$ and $3x_{\text{V-CDT}}$ represents the international standard Vienna Canyon Diablo Troilite. We express the minor isotope values using the capital delta notation, $\Delta^{33}S = \delta^{33}S - 1000 \cdot [(1 + \delta^{34}S/1000)^{0.515} - 1]$. Sample reproducibility, as determined by replicate analyses of the in-house standard MSS-1, was generally better than 0.1‰ for $\delta^{34}S$ values, 0.015‰ for $\Delta^{33}S$ and 0.2‰ for $\Delta^{36}S$.

The isotope mass-balance model was developed using a steady-state model approach by Zaback et al. (1993) and modified to accommodate the multiple sulfur isotope system. The model comprises three sulfur reservoirs that include seawater sulfate ($SO_4^{2-}_{\text{SW}}$), pore water sulfate ($SO_4^{2-}_{\text{PW}}$) and microbially generated sulfide ($HS^-$) between which sulfur is transported and fractionated (Fig. 3). Model details are given in Supplementary material.

**4. Results**

### 4.1 Stratigraphic multiple sulfur isotope trends in the Zaonega Formation

Based on litho- and chemostratigraphic correlations, the studied cores provide a composite, nearly continuous sulfur isotope record of the entire Zaonega Formation and the lower part of the overlying Suisari Formation. The studied stratigraphic record has been subdivided into three
Members based on lithological features: Member A is characterised by siliciclastic mudstone (hereafter referred to as mudstone) and dolostone beds alternating with thin graded beds interpreted as turbidites; Member B is marked by exceptionally organic-rich (~5-65 wt.% TOC) mudstone and dolostone deposits (representing the Shunga Event; Kump, 2011); and Member C is represented by impure carbonate and mudstone beds (for more details see Fig. A.1).

The lower part of Member A has uniformly negative $\delta^{34}\text{S}$ and positive $\Delta^{33}\text{S}$ values, followed by an up-section stratigraphic trend towards $^{34}\text{S}$-enriched sulfides (from $\delta^{34}\text{S} \sim -15\%$ to $+15\%$) mirrored by a $\Delta^{33}\text{S}$ trend (from $-0.03\%$ to $-0.02\%$) (Fig. 2, A.1). This up-section increase in $\delta^{34}\text{S}$ and decrease in $\Delta^{33}\text{S}$ values continues throughout the lower part of Member B and is accompanied by concomitant increases up to 65 wt.% in TOC and up to 11 wt.% in total sulfur (TS). The upper part of Member B is dominated by sulfides with $\delta^{34}\text{S}$ of $\sim 18\%$ ($18.5 \pm 7.7\%$, $1\sigma$) and $\Delta^{33}\text{S}$ of $\sim 0.03\%$ ($-0.03\% \pm 0.03$, $1\sigma$) but also displays several positive $\delta^{34}\text{S}$ excursions reaching values as high as $+44\%$. Sedimentary pyrites reach their highest $\delta^{34}\text{S}$ and lowest $\Delta^{33}\text{S}$ values in the upper part of Member B whereas the overlying Member C shows an up-section decrease in $\delta^{34}\text{S}$ towards $\sim 3\%$ and more positive ($\sim 0\%$) $\Delta^{33}\text{S}$ at the top of the section. Thin sedimentary units in Member C occur between thick magmatic packages and are typified by generally low TOC and TS content, the only exception being a $\sim 20$ m thick mudstone interval (912–890 m) where TOC is up to 22 wt.% and TS is at 29 wt.% and $\delta^{34}\text{S}$ increases to $15\%$. The $\Delta^{36}\text{S}$ display a pattern similar to and consistent with that of $\delta^{34}\text{S}$. The $\Delta^{36}\text{S}$ values are $\sim 0.4\%$ in Member A, increase to $\sim 0.6\%$ in Member B and then turn back to $\sim 0.1\%$ in the upper part of Member C.

4.2 Exploring the sulfur isotope record of the Zaonega Formation

In order to test potential mechanisms behind the stratigraphic co-variances observed in the pyrite $\Delta^{33}\text{S}$-$\delta^{34}\text{S}$-$\Delta^{36}\text{S}$ record in the Zaonega Formation, an open-system steady-state isotope
mass-balance model (Zaback et al., 1993) was adapted to include the multiple S isotope system
(Fig. 3, Supplementary material). The open system assumption was justified by determining the
minimum number of pore volumes ($n_{\text{min}}$) of sulfate that was required to account for the
measured TS concentrations (Zaback et al., 1993) (Fig. 2). By considering the intrinsic sediment
properties (porosity and density) and ambient seawater sulfate (SWS) concentrations, $n_{\text{min}}$
compares the amount of sulfur trapped in the sediment as sedimentary sulfide and the amount
of sulfur which would have been present as sulfate in the initial porewater. If more sulfide is
trapped in the sediment than locked away in the initial porewater ($n_{\text{min}}>1$), then open system
conditions prevail, whereas if less sulfate is trapped as sedimentary sulfide than sulfate trapped
in the initial porewater ($n_{\text{min}}<1$), then open system conditions are less likely. Further, to explain
the unusually positive pyrite $\delta^{34}\text{S}$ values in Member B the range and evolution of the basin’s
sulfate levels were explored by considering potential Rayleigh distillation of the local SWS
reservoir (Fig. 3).

There is no direct constraint for SWS concentrations during accumulation of the Zaonega
Formation, however, a SWS concentration of at least 10 mM was recently estimated for the
conformably underlying ~2.0 Ga Tulomozero Formation (Blättler et al., 2018). This suggests
$n_{\text{min}}$ values >1. On average the $n_{\text{min}}$ values are ~7.0 in Member A, ~11.4 in Member B and ~2.2
in Member C, which indicate open-system conditions. Lower SWS concentrations (<10 mM)
would result in even higher $n_{\text{min}}$ values (Fig. 2, Table A.1).

The maximum isotope effect between seawater sulfate and microbially reduced sulfur is only
expressed when burial of reduced sulfur is very low (fraction of pyrite retained in sediments $f_s$
→ 0) and the net isotope fractionation ($^{34}\alpha_0$) approaches that of microbial sulfate reduction
($^{34}\alpha_{\text{MSR}}$) (Zaback et al., 1993; see modeling details and sensitivity analysis in Supplementary
material). In contrast, if all reduced sulfur formed by MSR is effectively captured as
sedimentary pyrite ($f_s \rightarrow 1$), $^{34}\alpha_{\text{MSR}}$ will only have a small effect on $^{34}\alpha_0$ and the precipitated
pyrite will have a similar composition to the initial sulfate. Microbial growth in the subsurface is energy limited and, therefore, sulfate reduction rates in sediments are typically slow (Hoehler and Jørgensen, 2013; Sim et al., 2011; Wing and Halevy, 2014) resulting in large biological fractionations (Aoyama et al., 2014; Pellerin et al., 2015). Based on that, fractionations of $^{34}\alpha_{MSR} = 0.945$, $^{33}\lambda_{MSR} = 0.514$ and $^{36}\lambda_{MSR} = 1.90$, were kept constant throughout the models (for further discussion see Supplementary material, Fig. A.3). Modelled trajectories for sulfide isotopic composition reflect the isotopic evolution of aqueous sulfide that is produced during net sulfate reduction. We assume that the produced aqueous sulfide is rapidly and irreversibly trapped as sedimentary pyrite (instantaneous product).

The lower limit for the starting seawater sulfate isotopic composition was derived from the Ca-sulfate evaporite deposits of the Tulomozero Formation, which record $\delta^{34}S$ of 6‰ and $\Delta^{33}S$ and $\Delta^{36}S$ of ~0‰ (Blättler et al., 2018). For the upper part of the Zaonega Formation, $\delta^{34}S$ of around 15‰ and $\Delta^{33}S$ of -0.05‰ has been estimated previously for SWS by Scott et al. (2014) based on the tight clustering of pyrite sulfur isotope data around those values. Following the approach of Scott et al. (2014) the latter estimate can be further refined by including the pyrite sulfur isotope data reported in this study for the upper part of the Zaonega Formation (our Member B). By doing so, the seawater sulfate isotopic composition inferred from pyrite data would have respective $\delta^{34}S$, $\Delta^{33}S$ and $\Delta^{33}S$ values of $17.9 \pm 7.8$‰ (1S), $-0.02 \pm 0.03$‰ (1S) and $0.04 \pm 0.23$‰ (1S). In the presented models we use $\delta^{34}S_{SWS}$ of 6‰, $\Delta^{33}S_{SWS}$ of -0.01‰ and $\Delta^{36}S_{SWS}$ of 0.01‰ values, since these are directly measured from the Tulomozero Formation. However, our data can also be satisfied with values of $\delta^{34}S$ of 18‰, $\Delta^{33}S$ of -0.02‰ and $\Delta^{36}S$ of 0.04‰ without significantly changing our interpretation (see model sensitivity analysis in Supplementary material, Fig. A.2).
5. Discussion

5.1 Interpreting the sulfur isotope record of the Zaonega Formation

5.1.1 Preservation of the sulfur isotope record

The organic matter in the Zaonega Formation experienced maturation at temperatures between 350–400 °C during greenschist metamorphism, thus reactions between organic compounds and sulfur-bearing fluids (possibly derived from the Ca-sulfate bearing underlying Tulomozero Formation) could have induced thermochemical sulfate reduction (TSR) and precipitation of late-stage pyrites that carry anomalous isotope signatures deviating from thermodynamic predictions ($\Delta^{33}S$ and $\Delta^{36}S \neq 0$; Amrani, 2014; Ono et al., 2006; Watanabe et al., 2009).

However, mass-independent fractionation effects ($\Delta^{36}S/\Delta^{33}S$ slope of $\sim$-1; Ono et al., 2006) typically attributed to TSR (Watanabe et al., 2009) are not evident in the pyrite multiple sulfur isotope data ($\Delta^{36}S/\Delta^{33}S$ slope of $\sim$-5) of the Zaonega Formation (Fig. 4; Paiste et al., 2018).

It is also possible that generation of acid volatile sulfides (AVS) at the expense of pyrite in Members A and B (Asael et al., 2013) was accompanied by isotope exchange between the different sulfide phases. Assuming that the occurrence of ubiquitous late-stage pyrite (e.g. vein pyrite, large pyrite crystals and aggregates; Paiste et al., 2018) reflects multiple stages of (re)crystallisation and/or that the presence of AVS reflects thermal degradation of pyrite (as suggested previously by Asael et al., 2013), several abiogenic mechanisms could have impacted the $\Delta^{33}S$, $\delta^{34}S$, and $\Delta^{36}S$ records, especially in Member B. However, the paired pyrite and AVS $\Delta^{33}S$ and $\delta^{34}S$ data display only small differences of a few ‰ indicating that either pyrite alteration was not accompanied by significant fractionations or the different AVS mineral phases (e.g. pyrrhotite, sphalerite) derived their sulfur from the same reservoir (Paiste et al., 2018). Also, pervasive re-equilibration of both pyrite and AVS appears unlikely because this would have smoothened the stratigraphic variability.
Interactions with magmatic intrusions and lava flows can also alter the sulfur isotope composition of the surrounding sedimentary country rocks. Indeed, the pyrite $\Delta^{33}S-\delta^{34}S$ profiles of magmatic bodies in Members A and B have the sulfur isotope signature of the country rock at the margins of the bodies and gradually shift, as expected for magmatic sulfur, towards 0‰, at the centres of magmatic bodies where sulfur concentrations are lowest <1 wt.% (Fig. 5). However, this alteration does not extend further into the sediment and is limited to the contact zones with the magmatic bodies. Thus, it is unlikely that magmatic fluids or sulfur leached from the magmatic bodies contributed any significant externally derived sulfur to the sedimentary rocks during diagenesis or metamorphism. The large-scale migrated hydrocarbon interval interpreted as seafloor asphalt spill in FAR-DEEP 12AB (156–136 m; Qu et al., 2012) is isotopically similar to its source rocks in the underlying strata suggesting that magmatically induced migration of hydrocarbons and fluidised sediments did not significantly alter early diagenetic pyrites that were being migrated with them (Fig. 2, Fig. A.1).

Although, we cannot conclusively dismiss contributions of pyrite generated by TSR or other late-stage processes, it is unlikely that any of these are the dominant mechanisms for fractionating sulfur isotopes in the Zaonega Formation rocks and the $\Delta^{33}S$, $\delta^{34}S$ and $\Delta^{36}S$ records likely reflect first-order stratigraphic changes in sulfur cycling in the depositional environment.

5.1.2 Member A

In order to reproduce the measured sulfur isotope data for Member A, we constructed a model that produced a set of predictions for sulfide $\Delta^{33}S-\delta^{34}S$ ($\Delta^{36}S-\delta^{34}S$) pairs that cover a spectrum of isotopic compositions between two opposing endmembers, where one is sulfide produced in open-system MSR ($f_s \rightarrow 0$) and the other being sulfide generated by quantitative reduction ($f_s \rightarrow 1$) of the same initial sulfate. If MSR alone was controlling sulfur isotope fractionations in Member A, the observed pyrite isotope data should converge on the modelled fractionation line.
Instead, the measured pyrite $\Delta^{33}\text{S}-\delta^{34}\text{S}$ and $\Delta^{36}\text{S}-\delta^{34}\text{S}$ data fall on a curved mixing line connecting the two sulfide endmembers (Fig. 6.1). Such $\Delta^{33}\text{S}-\delta^{34}\text{S}$-$\Delta^{36}\text{S}$ relationship suggests that other processes in addition to MSR (e.g. sedimentary, diagenetic) are contributing to the pyrite sulfur isotope variability.

The observed mixing signature can be explained by several processes. For example, it has been proposed that shoaling of anoxic/euxinic deep water could cut off sulfate supply into the sediments and lead to the formation of a separate generation of closed-system pyrite in addition to those that formed previously in open-system conditions (Shen et al., 2011). Under more energetic depositional conditions, episodic sediment reworking could also generate such mixing signatures even under an oxygenated water column by superimposing pyrites that formed at different stages of diagenesis (Aller et al., 2010). Another possibility is that due to fast deposition rates, some pyrite precipitates near the sediment-water interface, where sulfate and iron are not limiting, whereas other pyrite forms later in the burial history from an evolving pore water sulfate pool (Pasquier et al., 2017; Ries et al., 2009).

In Member A, $n_{\text{min}}$ values well above 1 in both the OPH and FAR-DEEP 12AB data imply an open system but strong correlations between Fe and S in the OPH data suggest high sulfidisation, whereas scattered Fe:S ratios in FAR-DEEP 12AB data suggest a lower degree of sulfidisation (Fig. 7A). Thus, redox conditions were varied across the basin but the sediment was open to sulfate transport. The high $n_{\text{min}}$ values (up to 27.9) can be attributed to rapid sulfate consumption within pore waters close to the sediment-water interface or alternatively, to low sedimentation rates in order to sustain prolonged connectivity between pore space and the overlying water column. However, the latter seems unlikely for Member A, as the occurrence of coarser-grained sediment-gravity flow and turbidity-current deposits in the lower part of the FAR-DEEP 12AB core argue for relatively rapid deposition. Although the correlative intervals between OPH and FAR-DEEP 12AB cores have ~8‰ difference in $\delta^{34}\text{S}$ values, --11‰ versus...
-19‰, respectively, this is explained readily by facies changes: OPH is characterized by mudstones and calcareous mudstones whereas FAR-DEEP 12AB is coarser-grained facies and these would have higher permeability and thus favour more open-system conditions as well as lower sulfidisation relative to the finer-grained OPH section.

While it is difficult to confidently determine from bulk samples if changes in sedimentation, diagenesis or both are responsible for the mixing of pyrites in Member A, it is likely that depositional style played an important role in the final S isotope composition of the sedimentary pyrites of the Zaonega Formation. In any case, the stratigraphically increasing $\delta^{34}$S and $\Delta^{36}$S and decreasing $\Delta^{33}$S trends infer a transition to lower connectivity between the SWS pool and sedimentary pore waters.

5.1.3 Member B

In the upper part of Member A and throughout Member B, pyrites with more positive $\delta^{34}$S$_{pyr}$ and $\Delta^{36}$S and negative $\Delta^{33}$S than the initial SWS ($\delta^{34}$S$_{sws}$ of 6‰, $\Delta^{33}$S$_{sws}$ of -0.01‰, and $\Delta^{36}$S$_{sws}$ of 0.01‰) can be explained by an evolving basinal sulfate pool as a result of increased pyrite burial (Fig. 3). The organic carbon content of >5 wt.% in the sedimentary rocks of the Zaonega Formation is significantly higher than is typical for marine sediments that accumulated under oxidizing conditions throughout the Phanerozoic (Lyons and Severmann, 2006). Such high organic carbon loading could support a large population of sulfate reducers within the sediment and increase the demand for sulfate (Habicht and Canfield, 1997). Accordingly, the consumption of sulfate via MSR could exceed its replenishment from the overlying water column and foster sulfate limitation in pore waters (Goldhaber and Kaplan, 1975; Jørgensen, 1979). This would result in small net fractionation, if the reduced sulfur was scavenged by reactive iron and effectively converted into pyrite. This is in agreement with the strong correlation of Fe:S ratios in Member B and $n_{\text{min}} >>1$ that suggest intense sulfate diffusion into
pore water, possibly at a very shallow redoxcline where sulfate and iron would have been readily available (Fig. 7).

Complicating the already complex depositional environment of the organic-rich Zaonega rocks, the episodic magmatic and volcanic activity would have influenced the configuration and connectivity of the basin and regulated nutrient fluxes to promote primary production (Fig. 3).

Lithological evidence suggests a shift towards predominantly carbonate precipitation in the upper part of the Zaonega Formation implying changes in the depositional conditions and possibly basin shallowing (Melezhik et al., 2015; Paiste et al., 2018). Hence, it is entirely feasible that semi-restriction or occasional closure of the Onega Basin occurred during deposition of the upper part of the Zaonega Formation.

Melezhik et al. (1999) have applied the TS/TOC paleosalinity proxy to suggest that the predominantly low TS/TOC ratios (<0.36) combined with elevated TS and TOC concentrations, and a positive correlation between the two parameters in the Zaonega Formation succession, is representative of sediment deposition in a swampy brackish water lagoon under non-euxinic conditions. Indeed, using the refined baseline values for the TS/TOC proxy from Wei and Algeo (2019) the <0.1 TS/TOC ratios determined for Member A are indicative of a freshwater environment, whereas varying freshwater to brackish and/or marine conditions characterize Member B (TS/TOC mostly between 0.1 and 0.5) and marine conditions typify Member C (TS/TOC >0.5) (Fig. 8). If taken at face value, the highly variable TS/TOC ratios in Member B could be attributed to a semi-restricted basin. However, we are cautious about using the TS/TOC proxy too liberally in any interpretations because, firstly, it has been calibrated for modern sediments and it is not clear how well it applies to metasedimentary rocks and, secondly, the Zaonega sediments were subject to much magmatic or hydrothermal activity and associated hydrocarbon generation and seepage. We do note, though, that the relatively high TS/TOC ratios in Member B imply that MSR was not sulfate-limited. In a semi-restricted
setting, the consumption of sulfate by MSR and increased pyrite retention in sediments would
cause distillation of the basinal sulfate reservoir and generate parallel increases in $\delta^{34}\text{S}_{\text{SWS}}$ and
$\delta^{34}\text{S}_{\text{pyr}}$ exhibiting Rayleigh behaviour of $^{33}\text{S}$, $^{34}\text{S}$ and $^{36}\text{S}$ as the residual sulfate becomes
enriched in $^{34}\text{S}$ (Fike et al., 2015; Fike and Grotzinger, 2010; Gomes and Hurtgen, 2013).

Assuming that a constant flux of sulfate entered the pore waters, whereas only a small fraction
of the sulfur was returned into the water column ($1 - f_s$), basinal sulfate levels would have
decreased gradually. According to the model for Member A, retention of half of the sulfate that
entered the sediments ($f_s = 0.5$) would correspond to a net fractionation of 0.974 for $^{34}\alpha_0$ paired
with $^{33}\lambda_0$ of 0.510 and $^{36}\lambda_0$ of 1.926. If we use these parameters to model the Rayleigh
distillation of the sulfate reservoir, the trajectory in which the basinal sulfate isotopic
composition ($\Delta^{33}\text{S}_{\text{SWS}}$, $\delta^{34}\text{S}_{\text{SWS}}$ and $\Delta^{36}\text{S}_{\text{SWS}}$) evolves is controlled by the overall isotope effect
of the sedimentary system. Previous work assumed that at sulfate concentrations <200 µM
(Habicht et al., 2002) microbial fractionation becomes suppressed; however, in natural
environments low respiration rates can lead to large fractionations even under extremely low
sulfate levels (<10 µM) (Crowe et al., 2014; Gomes and Hurtgen, 2013; Wing and Halevy,
2014). Thus, by using the same input parameters as in Member A, the model generates a set of
predictions for sedimentary pyrites in Member B that formed after a fraction of the initial sulfate
was removed from the system ($f_{\text{SWS}}$, Fig. 6.2).

By decreasing the size of the sulfate reservoir by 80% ($f_{\text{SWS}} = 0.2$), due to the basinal sulfate
being reduced and buried as pyrite, our model reproduces the most extreme $\delta^{34}\text{S}$ values of 44‰,
$\Delta^{33}\text{S}$ of -0.06‰ and $\Delta^{36}\text{S}$ of 0.6‰ found in the upper strata of Member B. There, where rapid
sulfate turnover is expected due to abundant organic matter (TOC up to 45 wt.%), the sediments
display relatively constant $f_s$ values (0.8–0.96), which is consistent with an increased sink for
tsulfide. Further, the positive sulfur isotope excursions where $\delta^{34}\text{S}$ evolves towards highly
positive values (>+30‰) occur over a few meters of strata. In the modern oceans with sulfate concentrations of 28 mM a multi-million-year residence time (>8 Myr) is estimated for marine sulfate (Berner, 2001; Canfield, 2004). Thus, even if the SWS reservoir during the Zaonega time was a fraction of the modern, it is unlikely that the punctuated Δ^{33}S-δ^{34}S (Δ^{36}S) excursions reflect global perturbations in the sulfur cycle, as it would require a mechanism capable of catalysing repeated expansions and contractions in the sulfate reservoir over a relatively short time (<<million years). However, such high frequency fluctuations in the size of the sulfate reservoir are consistent with a semi-restricted basin (e.g. the Baltic Sea; Döös et al., 2004), as sluggish water circulation could periodically cut off sulfate supply or rapid sulfate consumption could lower basinal sulfate concentrations faster than it was replenished (Fig. 3).

In the upper part of Member B (1130–1080 m interval) there are, though, a significant number of Δ^{33}S values more negative and Δ^{36}S more positive than predicted by the modelled pyrite field. These values cannot be reproduced even by accommodating almost the full range of fractionations associated with MSR (^{34}α_{\text{MSR}} 0.93–0.98; Aoyama et al., 2014; Johnston, 2011; Sim et al., 2011). The measured Δ^{33}S-δ^{34}S pairs that deviate from model predictions occur in the 1130–1080 m interval where the concomitant up-section decrease in TOC and TS and a wider span of f_s values (~0.6–0.96) suggest lower degrees of sulfate reduction and/or more open-system conditions. Generally low sulfate reduction rates and open-system conditions lead to large net fractionations between sulfate and sulfide but the highly positive δ^{34}S, Δ^{36}S and negative Δ^{33}S values within this interval are at odds with this assumption. However, the description of several generations of pyrites within the OnZap section by Paiste et al. (2018) imply that the occurrence of genetically distinct pyrites could account for the anomalous bulk pyrite S-isotope signatures in the 1130–1080 m interval. Most of these anomalous samples are from carbonate beds where multiple generations of pyrite co-occur, including large (>100 μm) disseminated euhedral to anhedral pyrite crystals, irregular aggregates of inclusion-rich pyrite
and fine-grained (≈10 μm) euhedral and typically octahedral pyrite. The large pyrite likely precipitated from evolved pore waters during late-stage diagenesis whereas the fine-grained pyrites are early-diagenetic precipitates. As in Member A, this can be tested by mixing of two sulfide endmembers, where one formed in open- and the other in closed-system conditions. Using this framework, our model satisfies more than 95% of the measured pyrite sulfur isotope compositions (Fig. 6.2).

5.1.4 Member C

In Member C the measured pyrite compositions can be explained by a general transition towards more open-system conditions, as indicated by the up-section shift in \( f_s \) values from around 0.9 to 0.6 (Fig. 6.3). Furthermore, reduced organic carbon load and lower rates of MSR would allow for a longer residence time of sulfate and subsequently diminish the Rayleigh effect on the basinal reservoir. Such a scenario is supported by \( f_{\text{min}} \) values that generally decrease in the upper part of Members B and C and are typically associated with lower TOC concentrations, which is consistent with lower rates of sulfate reduction (Fig. 2, 7B). These trends agree with the wide spread of Fe:S ratios indicating a low degree of sulfidisation (Fig. 7A). The occurrence of a mudstone interval in Member C (912–890 m) with very high TOC (up to 22 wt.%) and TS (up to 29 wt.%) concentrations and strong Fe:S correlation implicates episodes of more rapid sulfate consumption and increased pyrite burial. This interval is sandwiched between thick packages of mafic lava flows and displays extremely high \( n_{\text{min}} \) values, likely due to locally high geothermal gradients that induced hydrothermal fluid circulation and rapid sulfate consumption within pore waters. This is also in agreement with our model predictions, as in the 912–890 m interval the measured pyrite \( \Delta^{33}\text{S}-\delta^{34}\text{S} \) data converge on the modelled fractionation line where \( f_s \) values are close to 1 and the pyrite isotopic composition approaches that of the initial sulfate. However, these effects would be short lived and not persisting long enough to affect the basinal sulfate pool. Another possibility to explain the very high TS concentrations is generation of
secondary pyrite via reactions between sulfur-bearing magmatic fluids and iron in sediments. As documented above, addition of magmatic sulfur cannot be fully excluded but is unlikely since the studied magmatic bodies incorporate sulfur from the adjacent sediments rather than add magmatic sulfur to the diagenetic environment.

5.1.5 Implications for the global seawater sulfate reservoir

The main result of our modelling efforts is that in order to precipitate the abundant pyrite, explain the $n_{\text{min}}$ values $\gg 1$ and short-lived high amplitude $\delta^{34}S (>30\%_o)$ excursions, a sizeable basinal sulfate reservoir had to be maintained during deposition of the Zaonega Formation. We envisage that basinal sulfate levels were replenished via episodic inflow from an oceanic reservoir. In effect, the $\delta^{34}SSWS$ of 6‰, $\Delta^{33}SSWS$ of -0.01‰ and $\Delta^{36}SSWS$ of 0.01‰ (Blättler et al., 2018) used in our model could represent the lower limit for the sulfate composition of the global ocean during the Zaonega time. An upper estimate inferred in a similar way as in Scott et al. (2014) from pyrite sulfur isotope data suggests $\delta^{34}SSWS$ of 18‰, $\Delta^{33}SSWS$ of -0.02‰ and $\Delta^{36}SSWS$ of 0.04‰ during deposition of the upper Zaonega Formation (Member B). However, closure of the basin likely commenced (Melezhik et al., 2015) during deposition of the upper part of the Zaonega Formation and may have restricted water circulation with the ocean. Thus, even if pyrites in Member B capture the initial sulfate signal, it is not clear if it represents the oceanic or basinal sulfate pool. Nevertheless, the respective range of $\delta^{34}SSWS$, $\Delta^{33}SSWS$ and $\Delta^{36}SSWS$ values between 6–18‰, -0.01–-0.02‰ and 0.01–0.04‰ are in agreement with those reported in Crockford et al. (2019) for the time period between 2.0–1.9 Ga. However, the suggested range of $\delta^{34}SSWS$, $\Delta^{33}SSWS$ and $\Delta^{36}SSWS$ values are an indirect consequence of our modelling exercise and need further evaluation. Combining all of the above, the most circumspect use of the pyrite sulfur isotope data of the Zaonega Formation is to first understand the nature of the basinal sulfur cycle before considering those data as a proxy to estimate large-scale perturbations in the global SWS reservoir. We also note that isotope signatures ascribed
to biological and abiogenic processes could be difficult to distinguish in bulk samples and deeper insight on AVS formation and abiogenic reactions between sulfur-bearing fluids and organic matter could be obtained via petrographically constrained micro-scale analyses (e.g. SIMS investigation) of different sulfide minerals and pyrite generations.

Conclusions

The pyrite multiple sulfur isotope record of the Paleoproterozoic Zaonega Formation can be reproduced with a steady-state isotope mass-balance model by including an evolving basinal sulfate reservoir affected by Rayleigh distillation. While the rate of sulfate reduction versus transport largely controls sedimentary sulfur cycling in marine sediments, in a restricted basin the increased removal of sulfate by pyrite precipitation and/or changes in basin connectivity can generate secular changes in the quantity and composition of basinal sulfate. Given that the Zaonega Formation was deposited in a magmatically active and dynamic depositional setting, the entire pyrite isotope record and the mass dependent $\Delta^{33}S-\delta^{34}S-\Delta^{36}S$ relationships can be explained by variations in local sedimentological and biogeochemical conditions without the need for invoking global changes in ocean chemistry. This becomes even more obvious when realising that positive sulfur isotope excursions with high amplitude $\delta^{34}S$ values occur over only a few meters of strata in the Zaonega Formation, which would require repeated expansions and contractions in the seawater sulfate reservoir over unreasonably short time spans (i.e. likely much less than a million years). Our modelling exercise, albeit not capable of constraining unequivocally SWS concentrations at ~1.98 Ga, does demonstrate that a substantial sulfate reservoir was required in order to account for the abundant pyrite in the Zaonega Formation.

Acknowledgements

We are grateful to B. A. Wing for valuable advice and discussions of the data and model setup. We would like to thank G. Izon for assistance with laboratory procedures at the University of
St Andrews and T. H. Bui for help with sulfur isotope analyses at McGill University. We appreciate B. Killingsworth and an anonymous reviewer for helpful comments and L. Derry for editorial handling. The research is part of the Centre for Arctic Gas Hydrate, Environment and Climate and was supported by the Research Council of Norway through its Centres of Excellence funding scheme grant No. 223259. A. L. Z. acknowledges support from a Natural Environment Council Standard Grant NE/J023485/2. K. K and A. L. were supported by the Estonian Science Agency grant PRG447 and Estonian Center of Analytical Chemistry. K. P. was supported by the European Regional Development Fund and the programme Mobilitas Pluss grant MOBJD542.

References


**Figure captions**

**Figure 1.** Simplified geological map of the Onega Basin in Karelia, Russia and positions of drill cores (white circles). Inset map shows the distribution of Paleoproterozoic rocks (black) in Fennoscandia and the location of the Onega Basin (black square).
**Figure 2.** Composite stratigraphic $\delta^{34}$S and $\Delta^{33}$S, TS, TOC and calculated $n_{\text{min}}$ profiles for the Onega Parametric Hole (OPH), FAR-DEEP (FD) and OnZap (OZ) cores from the Zaonega and lower part of the Suisari Formations. The succession has been subdivided into three Members (A–C; for more details see Supplementary materials). Black and grey bars on core profiles show positions of sedimentary and magmatic intervals, respectively. Black (from sedimentary rocks) and grey (from magmatic rocks) dots represent data from this study, blue dots from Paiste et al. (2018) and yellow dots from Melezhik et al. (2012, 2015). The $n_{\text{min}}$ values were calculated at 28 mM (crimson dots), 10 mM (pink dots) and 2 mM (green dots) seawater sulfate concentrations [$\text{SO}_4^{2-}$]. Green arrows represent data points that fall outside of the plotted range of $n_{\text{min}}$ values.

**Figure 3.** Interpreted semirestricted depositional setting of the Zaonega Formation and inferred sulfur metabolisms including microbial sulfate reduction (A) and sulfide oxidation (B). White arrows illustrate sulfur cycling within the basin and the pathways involved in transport and isotopic fractionation of sulfur in the diagenetic environment. Organic matter (OM) is delivered into sediments via sinking particles of CO$_2$-fixing autotrophic biomass as well as via hydrocarbon seepage and methanotrophy. The steady-state S isotope mass-balance model (modified after Zaback et al., 1993) used to calculate the model fields in Fig. 6 is illustrated on the right; the boxes represent sulfur reservoirs (SW = seawater, PW = pore water and Py = pyrite) and white arrows indicate fluxes of sulfur ($\phi_i\delta^{33}\text{S}_i$) along different pathways, as described in the supplementary material.

**Figure 4.** A compilation of pyrite quadruple sulfur isotope data from the Zaonega and Suisari Formations. Grey circles represent Member A, black circles Member B and blue circles Member C. Dashed line represents an estimated slope of -5.14 for measured pyrite $\Delta^{33}$S-$\delta^{34}$S-$\Delta^{36}$S data ($R^2=0.54$).
Figure 5. A. Triple isotope plot of sulfide isotope data from magmatic bodies in the Zaonega Formation. Coloured dots represent paired $\Delta^{33}\text{S}-\delta^{34}\text{S}$ data from different magmatic bodies in the FAR-DEEP 12AB (FD12AB) and FAR-DEEP 13A (FD13A) cores. B. An example of $\delta^{34}\text{S}$ (left) and $\Delta^{33}\text{S}$ (right) profile through a gabbro in FAR-DEEP 12AB, depth 484–414 m. Numbers and black arrows denote locations of core pictures used to illustrate the gabbro within the contact zones and centres.

Figure 6. Measured and modelled pyrite $\delta^{34}\text{S}$ and $\Delta^{33}\text{S}$ data for 1) Member A; 2) Member B; 3) Member C and 4) all data. Grey curved lines display vectors for modelled pyrite $\Delta^{33}\text{S}-\delta^{34}\text{S}$ pairs that formed from sulfate with an isotope composition at the right end of the curve, yellow dotted curved lines represent mixing between two sulfide endmembers and black arrows the trajectory for sulfate isotope composition according to Rayleigh fractionation of the initial seawater sulfate (orange square) with $\delta^{34}\text{S}=6\%$ and $\Delta^{33}\text{S}=0\%$ (taken from Blättler et al., 2018).

Figure 7. A. Measured total sulfur (TS) and iron (TFe) concentrations. B. Calculated $n_{\text{min}}$ plotted against total organic carbon (TOC) concentrations from Leco analyses. Blue circles represent Member A, black circles Member B and grey circles Member C.

Figure 8. Measured total sulfur (TS) versus total organic carbon (TOC) concentrations from siliciclastic mudstones. Data has been filtered according to Wei and Algeo (2019) to include only samples that contain >1 wt.% TOC and lack significant carbonate component. The normal marine trend (0.36) of Berner and Raiswell (1983) is shown as a black dotted line and black solid lines represent threshold values determined for freshwater (<0.1) and marine (>0.5) environments from Wei and Algeo (2019). Blue, black and grey circles represent Member A, Member B and Member C, respectively.