

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

4 K. Paiste^{a,*}, A. Pellerin^b, A. L. Zerkle^c, K. Kirsimäe^d, A. R. Prave^c, A. E. Romashkin^e, A.
5 Lepland^{a,d,f}

6 ^aCAGE—Centre for Arctic Gas Hydrate, Environment and Climate, Department of
7 Geosciences, UiT The Arctic University of Norway, 9037 Tromsø, Norway.

8 ^bDepartment of Bioscience – Microbiology, Aarhus University, Ny Munkegade 116, 8000
9 Aarhus C, Denmark.

10 ^cSchool of Earth and Environmental Sciences and Centre for Exoplanet Science, University of
11 St Andrews, St Andrews, KY16 9AL Scotland/UK.

12 ^dDepartment of Geology, University of Tartu, 50411 Tartu, Estonia.

13 ^eInstitute of Geology, Karelian Science Centre, Pushkinskaya 11, 185610 Petrozavodsk, Russia.

14 ^fGeological Survey of Norway (NGU), 7491 Trondheim, Norway.

15
16 *Corresponding author: email kart.paiste@ut.ee

17 ¹Present address: Department of Geology, University of Tartu, 50411 Tartu, Estonia.

18 **Abstract**

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

29 sedimentary pyrite isotope trends can be explained by processes that reflect local (basin-scale)
30 fluctuations in sulfur cycling rather than global mechanisms.

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

32 **1. Introduction**

33 Biogeochemical sulfur cycling involves a multitude of processes that collectively influence the
34 magnitude of sulfur isotope fractionation between different sulfur species and determine the
35 final sulfur isotope signature captured in the rock record (Farquhar et al., 2010; Fike et al., 2015;
36 Johnston, 2011). Sulfur isotope data have therefore proven useful for paleoenvironmental
37 reconstructions and in obtaining important insight into the evolution of Earth's surface redox
38 environments (Canfield et al., 2010; Habicht et al., 2002; Sim et al., 2011). However, the
39 complex relationships between microbial metabolisms and their immediate environments
40 particularly within dynamic diagenetic settings can have a significant impact on sulfur cycling
41 (Aller et al., 2010; Lin et al., 2016; Paiste et al., 2018). Consequently, disentangling the local
42 from global signals in sulfur isotope records is not straightforward. Ideally, paleo-
43 environmental information is gained from concurrent isotope records of the initial sulfate
44 reservoir and resulting sedimentary sulfide. Complicating this is the fact that sulfate minerals
45 are often not preserved, hence reconstructions of past sulfur cycling commonly rely on sulfide
46 mineral (mainly pyrite) records alone. To address this shortcoming, theoretical models have
47 been used to track processes involved in the production and preservation of sedimentary pyrite
48 (Berner, 1964; Donahue et al., 2008; Habicht et al., 2002; Johnston, 2011; Jørgensen, 1979;
49 Zaback et al., 1993). However, simplifications in models reduce the complex depositional
50 histories of rock successions to a few variables, significantly limiting the sensitivity and
51 resolution of the model predictions when trying to reconstruct biogeochemical sulfur cycling
52 processes.

53 Here we use the 1.98 Ga Zaonega Formation in the Onega Basin of NW Russia (Fig. 1) as a
54 case study to investigate the mechanisms governing the sulfur cycle. The Formation was
55 deposited in a magmatically active basin characterised by high organic carbon content in a
56 mixed siliciclastic-carbonate depositional system that accumulated mostly below wave-base
57 (Črne et al., 2014; Melezhik et al., 2015; Qu et al., 2012). In this study, four sets of drill cores
58 (OPH, FAR-DEEP 12AB, FAR-DEEP 13A, OnZap; Fig. 1, A.1) recover nearly the entire
59 Zaonega Formation as well as the lower part of the overlying Suisari Formation. Our new bulk
60 multiple sulfur isotope ($\Delta^{33}\text{S}$, $\delta^{34}\text{S}$, $\Delta^{36}\text{S}$) and major element data from 185 samples were
61 integrated with previously published data from the OnZap cores (Paiste et al., 2018) to provide
62 a nearly continuous sulfur isotope record of the Zaonega Formation. We show that the pyrite
63 isotope record of the Zaonega Formation can be explained by processes bespoke to local (i.e.
64 basin-scale) depositional settings without the need to invoke worldwide changes in ocean
65 chemistry.

66 **2. Geological context**

67 The greenschist facies volcano-sedimentary succession of the Zaonega Formation forms the
68 upper part of the supracrustal succession within the Onega Basin, located on the south-eastern
69 part of the Archean Karelian craton in NW Russia (Melezhik et al., 1999). The Zaonega
70 Formation represents a deep-water shelf-slope-basin setting characterised by syndepositional
71 magmatism and volcanism. Although the exact paleobathymetry is unclear, the predominantly
72 fine-grained textures and dearth of current-generated features imply depths below storm-wave
73 base. The lower part of the Zaonega Formation is typified by organic-rich mudstones. The
74 portion of mudstones decreases upward and dolostone beds become more common, implying a
75 change towards carbonate-dominated depositional system in the upper part of the Formation
76 (Črne et al., 2014). The organic-rich sedimentary rocks are interlayered with mafic lava flows
77 and intersected by mafic intrusions emplaced into unlithified sediments as indicated by their

78 peperitic contacts. These igneous bodies induced hydrothermal circulation and oil-to-gas
79 cracking of organic-matter in the Formations exceptionally C_{org}-rich sedimentary rocks (Črne
80 et al., 2014; Melezhik et al., 1999; Qu et al., 2012). Following deposition of the Zaonega
81 Formation, the basin was filled by thick sub-aqueously extruded basalts interlayered with rare
82 thin mudstone beds of the Suisari Formation (Krupenik et al., 2011; Melezhik et al., 2015).

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

91 **3. Materials and Methods**

92 Samples for bulk pyrite sulfur isotope and major element analyses were taken from three cores
93 in the Onega Basin (Fig. 1): Onega Parametric Hole (OPH, 119 samples), FAR-DEEP 12AB
94 (49 samples) and 13A (17 samples). Data on these samples were combined with published bulk
95 pyrite sulfur isotope and major element data for the OnZap cores (Paiste et al., 2018). A
96 distinctive dolostone marker unit in the upper part of the Zaonega Formation (Črne et al., 2014;
97 Melezhik et al., 2015; Paiste et al., 2018; Qu et al., 2012) is used to correlate the cores. The
98 dolostone is characterised by mm- to 1-cm-thick discontinuous apatite layers at its base (Joosu
99 et al., 2015) and striking black silica veins throughout that can be several meters thick and
100 typically are coincident with thin mudstone layers within the dolomite. Detailed descriptions of

101 the OPH, FAR-DEEP and OnZap cores are available in Krupenik et al. (2011), Črne et al.
102 (2014) and Paiste et al. (2018), respectively.

103 Major element composition of powdered samples was determined by means of X-ray
104 fluorescence spectrometry (XRF) using a PANalytical Axios at 4 kW. Total sulfur (TS) and
105 total organic carbon (TOC) from decarbonated residues were determined by sealed tube
106 combustion using a Leco SC-444 analyser. Sulfur was extracted from powdered samples by a
107 two-step sequential extraction method modified from Canfield et al. (1986) and isotope
108 composition was measured on a Thermo Finnigan MAT 253 gas source mass spectrometer. The
109 sulfur isotope data are reported using standard delta notation (δ), where: $\delta^{3x}\text{S} = 1000 \cdot$
110 $(^{3x}\text{R}_{\text{sample}}/^{3x}\text{R}_{\text{V-CDT}} - 1)$, and $^{3x}\text{R} = ^{3x}\text{S}/^{32}\text{S}$, for $3x = 33$ or 34 and $^{3x}\text{R}_{\text{V-CDT}}$ represents the
111 international standard Vienna Canyon Diablo Troilite. We express the minor isotope values
112 using the capital delta notation, $\Delta^{33}\text{S} = \delta^{33}\text{S} - 1000 \cdot [(1 + \delta^{34}\text{S}/1000)^{0.515} - 1]$. Sample
113 reproducibility, as determined by replicate analyses of the in-house standard MSS-1, was
114 generally better than 0.1‰ for $\delta^{34}\text{S}$ values, 0.015‰ for $\Delta^{33}\text{S}$ and 0.2‰ for $\Delta^{36}\text{S}$.

115 The isotope mass-balance model was developed using a steady-state model approach by Zaback
116 et al. (1993) and modified to accommodate the multiple sulfur isotope system. The model
117 comprises three sulfur reservoirs that include seawater sulfate ($\text{SO}_4^{2-\text{sw}}$), pore water sulfate
118 ($\text{SO}_4^{2-\text{pw}}$) and microbially generated sulfide (HS^-) between which sulfur is transported and
119 fractionated (Fig. 3). Model details are given in Supplementary material.

120 **4. Results**

121 **4.1 Stratigraphic multiple sulfur isotope trends in the Zaonega Formation**

122 Based on litho- and chemostratigraphic correlations, the studied cores provide a composite,
123 nearly continuous sulfur isotope record of the entire Zaonega Formation and the lower part of
124 the overlying Suisari Formation. The studied stratigraphic record has been subdivided into three

125 Members based on lithological features: Member A is characterised by siliciclastic mudstone
126 (hereafter referred to as mudstone) and dolostone beds alternating with thin graded beds
127 interpreted as turbidites; Member B is marked by exceptionally organic-rich (~5-65 wt.% TOC)
128 mudstone and dolostone deposits (representing the Shunga Event; Kump, 2011); and Member
129 C is represented by impure carbonate and mudstone beds (for more details see Fig. A.1).

130 The lower part of Member A has uniformly negative $\delta^{34}\text{S}$ and positive $\Delta^{33}\text{S}$ values, followed
131 by an up-section stratigraphic trend towards ^{34}S -enriched sulfides (from $\delta^{34}\text{S}$ ~-15‰ to ~+15‰)
132 mirrored by a $\Delta^{33}\text{S}$ trend (from ~-0.03‰ to ~-0.02‰) (Fig. 2, A.1). This up-section increase in
133 $\delta^{34}\text{S}$ and decrease in $\Delta^{33}\text{S}$ values continues throughout the lower part of Member B and is
134 accompanied by concomitant increases up to 65 wt.% in TOC and up to 11 wt.% in total sulfur
135 (TS). The upper part of Member B is dominated by sulfides with $\delta^{34}\text{S}$ of ~18‰ ($18.5 \pm 7.7\%$,
136 1σ) and $\Delta^{33}\text{S}$ of ~-0.03‰ ($-0.03\% \pm 0.03$, 1σ) but also displays several positive $\delta^{34}\text{S}$ excursions
137 reaching values as high as +44‰. Sedimentary pyrites reach their highest $\delta^{34}\text{S}$ and lowest $\Delta^{33}\text{S}$
138 values in the upper part of Member B whereas the overlying Member C shows an up-section
139 decrease in $\delta^{34}\text{S}$ towards ~3‰ and more positive (~0‰) $\Delta^{33}\text{S}$ at the top of the section. Thin
140 sedimentary units in Member C occur between thick magmatic packages and are typified by
141 generally low TOC and TS content, the only exception being a ~20 m thick mudstone interval
142 (912–890 m) where TOC is up to 22 wt.%, TS is at 29 wt.% and $\delta^{34}\text{S}$ increases to 15‰. The
143 $\Delta^{36}\text{S}$ display a pattern similar to and consistent with that of $\delta^{34}\text{S}$. The $\Delta^{36}\text{S}$ values are ~-0.4‰
144 in Member A, increase to ~-0.6‰ in Member B and then turn back to ~-0.1‰ in the upper part
145 of Member C.

146 **4.2 Exploring the sulfur isotope record of the Zaonega Formation**

147 In order to test potential mechanisms behind the stratigraphic co-variances observed in the
148 pyrite $\Delta^{33}\text{S}$ - $\delta^{34}\text{S}$ - $\Delta^{36}\text{S}$ record in the Zaonega Formation, an open-system steady-state isotope

149 mass-balance model (Zaback et al., 1993) was adapted to include the multiple S isotope system
150 (Fig. 3, Supplementary material). The open system assumption was justified by determining the
151 minimum number of pore volumes (n_{\min}) of sulfate that was required to account for the
152 measured TS concentrations (Zaback et al., 1993)(Fig. 2). By considering the intrinsic sediment
153 properties (porosity and density) and ambient seawater sulfate (SWS) concentrations, n_{\min}
154 compares the amount of sulfur trapped in the sediment as sedimentary sulfide and the amount
155 of sulfur which would have been present as sulfate in the initial porewater. If more sulfide is
156 trapped in the sediment than locked away in the initial porewater ($n_{\min}>1$), then open system
157 conditions prevail, whereas if less sulfate is trapped as sedimentary sulfide than sulfate trapped
158 in the initial porewater ($n_{\min}<1$), then open system conditions are less likely. Further, to explain
159 the unusually positive pyrite $\delta^{34}\text{S}$ values in Member B the range and evolution of the basin's
160 sulfate levels were explored by considering potential Rayleigh distillation of the local SWS
161 reservoir (Fig. 3).

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

168 The maximum isotope effect between seawater sulfate and microbially reduced sulfur is only
169 expressed when burial of reduced sulfur is very low (fraction of pyrite retained in sediments f_s
170 $\rightarrow 0$) and the net isotope fractionation ($^{34}\alpha_0$) approaches that of microbial sulfate reduction
171 ($^{34}\alpha_{\text{MSR}}$) (Zaback et al., 1993; see modeling details and sensitivity analysis in Supplementary
172 material). In contrast, if all reduced sulfur formed by MSR is effectively captured as
173 sedimentary pyrite ($f_s \rightarrow 1$), $^{34}\alpha_{\text{MSR}}$ will only have a small effect on $^{34}\alpha_0$ and the precipitated

174 pyrite will have a similar composition to the initial sulfate. Microbial growth in the subsurface
175 is energy limited and, therefore, sulfate reduction rates in sediments are typically slow (Hoehler
176 and Jørgensen, 2013; Sim et al., 2011; Wing and Halevy, 2014) resulting in large biological
177 fractionations (Aoyama et al., 2014; Pellerin et al., 2015). Based on that, fractionations of
178 $^{34}\alpha_{\text{MSR}} = 0.945$, $^{33}\lambda_{\text{MSR}} = 0.514$ and $^{36}\lambda_{\text{MSR}} = 1.90$, were kept constant throughout the models
179 (for further discussion see Supplementary material, Fig. A.3). Modelled trajectories for sulfide
180 isotopic composition reflect the isotopic evolution of aqueous sulfide that is produced during
181 net sulfate reduction. We assume that the produced aqueous sulfide is rapidly and irreversibly
182 trapped as sedimentary pyrite (instantaneous product).

183 The lower limit for the starting seawater sulfate isotopic composition was derived from the Ca-
184 sulfate evaporite deposits of the Tulomozero Formation, which record $\delta^{34}\text{S}$ of 6‰ and $\Delta^{33}\text{S}$ and
185 $\Delta^{36}\text{S}$ of ~0‰ (Blättler et al., 2018). For the upper part of the Zaonega Formation, $\delta^{34}\text{S}$ of around
186 15‰ and $\Delta^{33}\text{S}$ of -0.05‰ has been estimated previously for SWS by Scott et al. (2014) based
187 on the tight clustering of pyrite sulfur isotope data around those values. Following the approach
188 of Scott et al. (2014) the latter estimate can be further refined by including the pyrite sulfur
189 isotope data reported in this study for the upper part of the Zaonega Formation (our Member
190 B). By doing so, the seawater sulfate isotopic composition inferred from pyrite data would have
191 respective $\delta^{34}\text{S}$, $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ values of $17.9 \pm 7.8\text{‰}$ (1S), $-0.02 \pm 0.03\text{‰}$ (1S) and $0.04 \pm$
192 0.23‰ (1S). In the presented models we use $\delta^{34}\text{S}_{\text{SWS}}$ of 6‰, $\Delta^{33}\text{S}_{\text{SWS}}$ of -0.01‰ and $\Delta^{36}\text{S}_{\text{SWS}}$
193 of 0.01‰ values, since these are directly measured from the Tulomozero Formation. However,
194 our data can also be satisfied with values of $\delta^{34}\text{S}$ of 18‰, $\Delta^{33}\text{S}$ of -0.02‰ and $\Delta^{36}\text{S}$ of 0.04‰
195 without significantly changing our interpretation (see model sensitivity analysis in
196 Supplementary material, Fig. A.2).

197 **5. Discussion**

198 **5.1 Interpreting the sulfur isotope record of the Zaonega Formation**

199 **5.1.1 Preservation of the sulfur isotope record**

200 The organic matter in the Zaonega Formation experienced maturation at temperatures between
201 350–400 °C during greenschist metamorphism, thus reactions between organic compounds and
202 sulfur-bearing fluids (possibly derived from the Ca-sulfate bearing underlying Tulomozero
203 Formation) could have induced thermochemical sulfate reduction (TSR) and precipitation of
204 late-stage pyrites that carry anomalous isotope signatures deviating from thermodynamic
205 predictions ($\Delta^{33}\text{S}$ and $\Delta^{36}\text{S} \neq 0$; Amrani, 2014; Ono et al., 2006; Watanabe et al., 2009).
206 However, mass-independent fractionation effects ($\Delta^{36}\text{S}/\Delta^{33}\text{S}$ slope of ~ -1 ; Ono et al., 2006)
207 typically attributed to TSR (Watanabe et al., 2009) are not evident in the pyrite multiple sulfur
208 isotope data ($\Delta^{36}\text{S}/\Delta^{33}\text{S}$ slope of ~ -5) of the Zaonega Formation (Fig. 4; Paiste et al., 2018).

209 It is also possible that generation of acid volatile sulfides (AVS) at the expense of pyrite in
210 Members A and B (Asael et al., 2013) was accompanied by isotope exchange between the
211 different sulfide phases. Assuming that the occurrence of ubiquitous late-stage pyrite (e.g. vein
212 pyrite, large pyrite crystals and aggregates; Paiste et al., 2018) reflects multiple stages of
213 (re)crystallisation and/or that the presence of AVS reflects thermal degradation of pyrite (as
214 suggested previously by Asael et al., 2013), several abiogenic mechanisms could have impacted
215 the $\Delta^{33}\text{S}$, $\delta^{34}\text{S}$, and $\Delta^{36}\text{S}$ records, especially in Member B. However, the paired pyrite and AVS
216 $\Delta^{33}\text{S}$ and $\delta^{34}\text{S}$ data display only small differences of a few ‰ indicating that either pyrite
217 alteration was not accompanied by significant fractionations or the different AVS mineral
218 phases (e.g. pyrrhotite, sphalerite) derived their sulfur from the same reservoir (Paiste et al.,
219 2018). Also, pervasive re-equilibration of both pyrite and AVS appears unlikely because this
220 would have smoothed the stratigraphic variability.

221 Interactions with magmatic intrusions and lava flows can also alter the sulfur isotope
222 composition of the surrounding sedimentary country rocks. Indeed, the pyrite $\Delta^{33}\text{S}$ - $\delta^{34}\text{S}$ profiles
223 of magmatic bodies in Members A and B have the sulfur isotope signature of the country rock
224 at the margins of the bodies and gradually shift, as expected for magmatic sulfur, towards 0‰,
225 at the centres of magmatic bodies where sulfur concentrations are lowest <1 wt.% (Fig. 5).
226 However, this alteration does not extend further into the sediment and is limited to the contact
227 zones with the magmatic bodies. Thus, it is unlikely that magmatic fluids or sulfur leached from
228 the magmatic bodies contributed any significant externally derived sulfur to the sedimentary
229 rocks during diagenesis or metamorphism. The large-scale migrated hydrocarbon interval
230 interpreted as seafloor asphalt spill in FAR-DEEP 12AB (156–136 m; Qu et al., 2012) is
231 isotopically similar to its source rocks in the underlying strata suggesting that magmatically
232 induced migration of hydrocarbons and fluidised sediments did not significantly alter early
233 diagenetic pyrites that were being migrated with them (Fig. 2, Fig. A.1).

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

238 **5.1.2 Member A**

239 In order to reproduce the measured sulfur isotope data for Member A, we constructed a model
240 that produced a set of predictions for sulfide $\Delta^{33}\text{S}$ - $\delta^{34}\text{S}$ ($\Delta^{36}\text{S}$ - $\delta^{34}\text{S}$) pairs that cover a spectrum
241 of isotopic compositions between two opposing endmembers, where one is sulfide produced in
242 open-system MSR ($f_s \rightarrow 0$) and the other being sulfide generated by quantitative reduction (f_s
243 $\rightarrow 1$) of the same initial sulfate. If MSR alone was controlling sulfur isotope fractionations in
244 Member A, the observed pyrite isotope data should converge on the modelled fractionation line.

245 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
246 connecting the two sulfide endmembers (Fig. 6.1). Such $\Delta^{33}\text{S}$ - $\delta^{34}\text{S}$ - $\Delta^{36}\text{S}$ relationship suggests
247 that other processes in addition to MSR (e.g. sedimentary, diagenetic) are contributing to the
248 pyrite sulfur isotope variability.

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

259 In Member A, n_{min} values well above 1 in both the OPH and FAR-DEEP 12AB data imply an
260 open system but strong correlations between Fe and S in the OPH data suggest high
261 sulfidation, whereas scattered Fe:S ratios in FAR-DEEP 12AB data suggest a lower degree of
262 sulfidation (Fig. 7A). Thus, redox conditions were varied across the basin but the sediment
263 was open to sulfate transport. The high n_{min} values (up to 27.9) can be attributed to rapid sulfate
264 consumption within pore waters close to the sediment-water interface or alternatively, to low
265 sedimentation rates in order to sustain prolonged connectivity between pore space and the
266 overlying water column. However, the latter seems unlikely for Member A, as the occurrence
267 of coarser-grained sediment-gravity flow and turbidity-current deposits in the lower part of the
268 FAR-DEEP 12AB core argue for relatively rapid deposition. Although the correlative intervals
269 between OPH and FAR-DEEP 12AB cores have ~8‰ difference in $\delta^{34}\text{S}$ values, ~11‰ versus

270 ~-19‰, respectively, this is explained readily by facies changes: OPH is characterized by
271 mudstones and calcareous mudstones whereas FAR-DEEP 12AB is coarser-grained facies and
272 these would have higher permeability and thus favour more open-system conditions as well as
273 lower sulfidation relative to the finer-grained OPH section.

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

280 **5.1.3 Member B**

281 In the upper part of Member A and throughout Member B, pyrites with more positive $\delta^{34}\text{S}_{\text{pyr}}$
282 and $\Delta^{36}\text{S}$ and negative $\Delta^{33}\text{S}$ than the initial SWS ($\delta^{34}\text{S}_{\text{SWS}}$ of 6‰, $\Delta^{33}\text{S}_{\text{SWS}}$ of -0.01‰, and
283 $\Delta^{36}\text{S}_{\text{SWS}}$ of 0.01‰) can be explained by an evolving basinal sulfate pool as a result of increased
284 pyrite burial (Fig. 3). The organic carbon content of >5 wt.% in the sedimentary rocks of the
285 Zaonega Formation is significantly higher than is typical for marine sediments that accumulated
286 under oxidizing conditions throughout the Phanerozoic (Lyons and Severmann, 2006). Such
287 high organic carbon loading could support a large population of sulfate reducers within the
288 sediment and increase the demand for sulfate (Habicht and Canfield, 1997). Accordingly, the
289 consumption of sulfate via MSR could exceed its replenishment from the overlying water
290 column and foster sulfate limitation in pore waters (Goldhaber and Kaplan, 1975; Jørgensen,
291 1979). This would result in small net fractionation, if the reduced sulfur was scavenged by
292 reactive iron and effectively converted into pyrite. This is in agreement with the strong
293 correlation of Fe:S ratios in Member B and $n_{\text{min}} \gg 1$ that suggest intense sulfate diffusion into

294 pore water, possibly at a very shallow redoxcline where sulfate and iron would have been
295 readily available (Fig. 7).

296 Complicating the already complex depositional environment of the organic-rich Zaonega rocks,
297 the episodic magmatic and volcanic activity would have influenced the configuration and
298 connectivity of the basin and regulated nutrient fluxes to promote primary production (Fig. 3).
299 Lithological evidence suggests a shift towards predominantly carbonate precipitation in the
300 upper part of the Zaonega Formation implying changes in the depositional conditions and
301 possibly basin shallowing (Melezhik et al., 2015; Paiste et al., 2018). Hence, it is entirely
302 feasible that semi-restriction or occasional closure of the Onega Basin occurred during
303 deposition of the upper part of the Zaonega Formation.

304 Melezhik et al. (1999) have applied the TS/TOC paleosalinity proxy to suggest that the
305 predominantly low TS/TOC ratios (<0.36) combined with elevated TS and TOC concentrations,
306 and a positive correlation between the two parameters in the Zaonega Formation succession, is
307 representative of sediment deposition in a swampy brackish water lagoon under non-euxinic
308 conditions. Indeed, using the refined baseline values for the TS/TOC proxy from Wei and Algeo
309 (2019) the <0.1 TS/TOC ratios determined for Member A are indicative of a freshwater
310 environment, whereas varying freshwater to brackish and/or marine conditions characterize
311 Member B (TS/TOC mostly between 0.1 and 0.5) and marine conditions typify Member C
312 (TS/TOC >0.5) (Fig. 8). If taken at face value, the highly variable TS/TOC ratios in Member B
313 could be attributed to a semi-restricted basin. However, we are cautious about using the
314 TS/TOC proxy too liberally in any interpretations because, firstly, it has been calibrated for
315 modern sediments and it is not clear how well it applies to metasedimentary rocks and,
316 secondly, the Zaonega sediments were subject to much magmatic or hydrothermal activity and
317 associated hydrocarbon generation and seepage. We do note, though, that the relatively high
318 TS/TOC ratios in Member B imply that MSR was not sulfate-limited. In a semi-restricted

319 setting, the consumption of sulfate by MSR and increased pyrite retention in sediments would
320 cause distillation of the basinal sulfate reservoir and generate parallel increases in $\delta^{34}\text{S}_{\text{SWS}}$ and
321 $\delta^{34}\text{S}_{\text{pyr}}$ exhibiting Rayleigh behaviour of ^{33}S , ^{34}S and ^{36}S as the residual sulfate becomes
322 enriched in ^{34}S (Fike et al., 2015; Fike and Grotzinger, 2010; Gomes and Hurtgen, 2013).

323 Assuming that a constant flux of sulfate entered the pore waters, whereas only a small fraction
324 of the sulfur was returned into the water column ($1 - f_s$), basinal sulfate levels would have
325 decreased gradually. According to the model for Member A, retention of half of the sulfate that
326 entered the sediments ($f_s = 0.5$) would correspond to a net fractionation of 0.974 for $^{34}\alpha_0$ paired
327 with $^{33}\lambda_0$ of 0.510 and $^{36}\lambda_0$ of 1.926. If we use these parameters to model the Rayleigh
328 distillation of the sulfate reservoir, the trajectory in which the basinal sulfate isotopic
329 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
330 of the sedimentary system. Previous work assumed that at sulfate concentrations $<200 \mu\text{M}$
331 (Habicht et al., 2002) microbial fractionation becomes suppressed; however, in natural
332 environments low respiration rates can lead to large fractionations even under extremely low
333 sulfate levels ($<10 \mu\text{M}$) (Crowe et al., 2014; Gomes and Hurtgen, 2013; Wing and Halevy,
334 2014). Thus, by using the same input parameters as in Member A, the model generates a set of
335 predictions for sedimentary pyrites in Member B that formed after a fraction of the initial sulfate
336 was removed from the system (f_{SWS} ; Fig. 6.2).

337 By decreasing the size of the sulfate reservoir by 80% ($f_{\text{SWS}} = 0.2$), due to the basinal sulfate
338 being reduced and buried as pyrite, our model reproduces the most extreme $\delta^{34}\text{S}$ values of 44‰,
339 $\Delta^{33}\text{S}$ of -0.06‰ and $\Delta^{36}\text{S}$ of 0.6‰ found in the upper strata of Member B. There, where rapid
340 sulfate turnover is expected due to abundant organic matter (TOC up to 45 wt.%), the sediments
341 display relatively constant f_s values (0.8–0.96), which is consistent with an increased sink for
342 sulfide. Further, the positive sulfur isotope excursions where $\delta^{34}\text{S}$ evolves towards highly

343 positive values ($>+30\%$) occur over a few meters of strata. In the modern oceans with sulfate
344 concentrations of 28 mM a multi-million-year residence time (>8 Myr) is estimated for marine
345 sulfate (Berner, 2001; Canfield, 2004). Thus, even if the SWS reservoir during the Zaonega
346 time was a fraction of the modern, it is unlikely that the punctuated $\Delta^{33}\text{S}-\delta^{34}\text{S}$ ($\Delta^{36}\text{S}$) excursions
347 reflect global perturbations in the sulfur cycle, as it would require a mechanism capable of
348 catalysing repeated expansions and contractions in the sulfate reservoir over a relatively short
349 time (\ll million years). However, such high frequency fluctuations in the size of the sulfate
350 reservoir are consistent with a semi-restricted basin (e.g. the Baltic Sea; Döös et al., 2004), as
351 sluggish water circulation could periodically cut off sulfate supply or rapid sulfate consumption
352 could lower basinal sulfate concentrations faster than it was replenished (Fig. 3).

353 In the upper part of Member B (1130–1080 m interval) there are, though, a significant number
354 of $\Delta^{33}\text{S}$ values more negative and $\Delta^{36}\text{S}$ more positive than predicted by the modelled pyrite
355 field. These values cannot be reproduced even by accommodating almost the full range of
356 fractionations associated with MSR ($^{34}\alpha_{\text{MSR}}$ 0.93–0.98; Aoyama et al., 2014; Johnston, 2011;
357 Sim et al., 2011). The measured $\Delta^{33}\text{S}-\delta^{34}\text{S}$ pairs that deviate from model predictions occur in
358 the 1130–1080 m interval where the concomitant up-section decrease in TOC and TS and a
359 wider span of f_s values (~ 0.6 – 0.96) suggest lower degrees of sulfate reduction and/or more
360 open-system conditions. Generally low sulfate reduction rates and open-system conditions lead
361 to large net fractionations between sulfate and sulfide but the highly positive $\delta^{34}\text{S}$, $\Delta^{36}\text{S}$ and
362 negative $\Delta^{33}\text{S}$ values within this interval are at odds with this assumption. However, the
363 description of several generations of pyrites within the OnZap section by Paiste et al. (2018)
364 imply that the occurrence of genetically distinct pyrites could account for the anomalous bulk
365 pyrite S-isotope signatures in the 1130–1080 m interval. Most of these anomalous samples are
366 from carbonate beds where multiple generations of pyrite co-occur, including large (>100 μm)
367 disseminated euhedral to anhedral pyrite crystals, irregular aggregates of inclusion-rich pyrite

368 and fine-grained (~10 μm) euhedral and typically octahedral pyrite. The large pyrite likely
369 precipitated from evolved pore waters during late-stage diagenesis whereas the fine-grained
370 pyrites are early-diagenetic precipitates. As in Member A, this can be tested by mixing of two
371 sulfide endmembers, where one formed in open- and the other in closed-system conditions.
372 Using this framework, our model satisfies more than 95% of the measured pyrite sulfur isotope
373 compositions (Fig. 6.2).

374 **5.1.4 Member C**

375 In Member C the measured pyrite compositions can be explained by a general transition towards
376 more open-system conditions, as indicated by the up-section shift in f_s values from around 0.9
377 to 0.6 (Fig. 6.3). Furthermore, reduced organic carbon load and lower rates of MSR would allow
378 for a longer residence time of sulfate and subsequently diminish the Rayleigh effect on the
379 basinal reservoir. Such a scenario is supported by n_{min} values that generally decrease in the
380 upper part of Members B and C and are typically associated with lower TOC concentrations,
381 which is consistent with lower rates of sulfate reduction (Fig.2, 7B). These trends agree with
382 the wide spread of Fe:S ratios indicating a low degree of sulfidisation (Fig. 7A). The occurrence
383 of a mudstone interval in Member C (912–890 m) with very high TOC (up to 22 wt.%) and TS
384 (up to 29 wt.%) concentrations and strong Fe:S correlation implies episodes of more rapid
385 sulfate consumption and increased pyrite burial. This interval is sandwiched between thick
386 packages of mafic lava flows and displays extremely high n_{min} values, likely due to locally high
387 geothermal gradients that induced hydrothermal fluid circulation and rapid sulfate consumption
388 within pore waters. This is also in agreement with our model predictions, as in the 912–890 m
389 interval the measured pyrite $\Delta^{33}\text{S}$ - $\delta^{34}\text{S}$ data converge on the modelled fractionation line where
390 f_s values are close to 1 and the pyrite isotopic composition approaches that of the initial sulfate.
391 However, these effects would be short lived and not persisting long enough to affect the basinal
392 sulfate pool. Another possibility to explain the very high TS concentrations is generation of

393 secondary pyrite via reactions between sulfur-bearing magmatic fluids and iron in sediments.
394 As documented above, addition of magmatic sulfur cannot be fully excluded but is unlikely
395 since the studied magmatic bodies incorporate sulfur from the adjacent sediments rather than
396 add magmatic sulfur to the diagenetic environment.

397 **5.1.5 Implications for the global seawater sulfate reservoir**

398 The main result of our modelling efforts is that in order to precipitate the abundant pyrite,
399 explain the n_{\min} values $\gg 1$ and short-lived high amplitude $\delta^{34}\text{S}$ ($>30\text{‰}$) excursions, a sizeable
400 basinal sulfate reservoir had to be maintained during deposition of the Zaonega Formation. We
401 envisage that basinal sulfate levels were replenished via episodic inflow from an oceanic
402 reservoir. In effect, the $\delta^{34}\text{S}_{\text{SWS}}$ of 6‰ , $\Delta^{33}\text{S}_{\text{SWS}}$ of -0.01‰ and $\Delta^{36}\text{S}_{\text{SWS}}$ of 0.01‰ (Blättler et
403 al., 2018) used in our model could represent the lower limit for the sulfate composition of the
404 global ocean during the Zaonega time. An upper estimate inferred in a similar way as in Scott
405 et al. (2014) from pyrite sulfur isotope data suggests $\delta^{34}\text{S}_{\text{SWS}}$ of 18‰ , $\Delta^{33}\text{S}_{\text{SWS}}$ of -0.02‰ and
406 $\Delta^{36}\text{S}_{\text{SWS}}$ of 0.04‰ during deposition of the upper Zaonega Formation (Member B). However,
407 closure of the basin likely commenced (Melezhik et al., 2015) during deposition of the upper
408 part of the Zaonega Formation and may have restricted water circulation with the ocean. Thus,
409 even if pyrites in Member B capture the initial sulfate signal, it is not clear if it represents the
410 oceanic or basinal sulfate pool. Nevertheless, the respective range of $\delta^{34}\text{S}_{\text{SWS}}$, $\Delta^{33}\text{S}_{\text{SWS}}$ and
411 $\Delta^{36}\text{S}_{\text{SWS}}$ values between $6\text{--}18\text{‰}$, $-0.01\text{--}0.02\text{‰}$ and $0.01\text{--}0.04\text{‰}$ are in agreement with those
412 reported in Crockford et al. (2019) for the time period between 2.0–1.9 Ga. However, the
413 suggested range of $\delta^{34}\text{S}_{\text{SWS}}$, $\Delta^{33}\text{S}_{\text{SWS}}$ and $\Delta^{36}\text{S}_{\text{SWS}}$ values are an indirect consequence of our
414 modelling exercise and need further evaluation. Combining all of the above, the most
415 circumspect use of the pyrite sulfur isotope data of the Zaonega Formation is to first understand
416 the nature of the basinal sulfur cycle before considering those data as a proxy to estimate large-
417 scale perturbations in the global SWS reservoir. We also note that isotope signatures ascribed

418 to biological and abiogenic processes could be difficult to distinguish in bulk samples and
419 deeper insight on AVS formation and abiogenic reactions between sulfur-bearing fluids and
420 organic matter could be obtained via petrographically constrained micro-scale analyses (e.g.
421 SIMS investigation) of different sulfide minerals and pyrite generations.

422 **Conclusions**

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

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619 **Figure captions**

620 **Figure 1.** Simplified geological map of the Onega Basin in Karelia, Russia and positions of
621 drill cores (white circles). Inset map shows the distribution of Paleoproterozoic rocks (black) in
622 Fennoscandia and the location of the Onega Basin (black square).

623 **Figure 2.** Composite stratigraphic $\delta^{34}\text{S}$ and $\Delta^{33}\text{S}$, TS, TOC and calculated n_{min} profiles for the
624 Onega Parametric Hole (OPH), FAR-DEEP (FD) and OnZap (OZ) cores from the Zaonega and
625 lower part of the Suisari Formations. The succession has been subdivided into three Members
626 (A–C; for more details see Supplementary materials). Black and grey bars on core profiles show
627 positions of sedimentary and magmatic intervals, respectively. Black (from sedimentary rocks)
628 and grey (from magmatic rocks) dots represent data from this study, blue dots from Paiste et al.
629 (2018) and yellow dots from Melezhik et al. (2012, 2015). The n_{min} values were calculated at
630 28 mM (crimson dots), 10 mM (pink dots) and 2 mM (green dots) seawater sulfate
631 concentrations $[\text{SO}_4^{2-}]$. Green arrows represent data points that fall outside of the plotted range
632 of n_{min} values.

633 **Figure 3.** Interpreted semirestricted depositional setting of the Zaonega Formation and inferred
634 sulfur metabolisms including microbial sulfate reduction (A) and sulfide oxidation (B). White
635 arrows illustrate sulfur cycling within the basin and the pathways involved in transport and
636 isotopic fractionation of sulfur in the diagenetic environment. Organic matter (OM) is delivered
637 into sediments via sinking particles of CO_2 -fixing autotrophic biomass as well as via
638 hydrocarbon seepage and methanotrophy. The steady-state S isotope mass-balance model
639 (modified after Zaback et al., 1993) used to calculate the model fields in Fig. 6 is illustrated on
640 the right; the boxes represent sulfur reservoirs (SW = seawater, PW = pore water and Py =
641 pyrite) and white arrows indicate fluxes of sulfur ($\phi_i\delta^{33}\text{S}_i$) along different pathways, as
642 described in the supplementary material.

643 **Figure 4.** A compilation of pyrite quadruple sulfur isotope data from the Zaonega and Suisari
644 Formations. Grey circles represent Member A, black circles Member B and blue circles
645 Member C. Dashed line represents an estimated slope of -5.14 for measured pyrite $\Delta^{33}\text{S}$ - $\delta^{34}\text{S}$ -
646 $\Delta^{36}\text{S}$ data ($R^2=0.54$).

647 **Figure 5.** A. Triple isotope plot of sulfide isotope data from magmatic bodies in the Zaonega
648 Formation. Coloured dots represent paired $\Delta^{33}\text{S}$ - $\delta^{34}\text{S}$ data from different magmatic bodies in
649 the FAR-DEEP 12AB (FD12AB) and FAR-DEEP 13A (FD13A) cores. B. An example of $\delta^{34}\text{S}$
650 (left) and $\Delta^{33}\text{S}$ (right) profile through a gabbro in FAR-DEEP 12AB, depth 484–414 m.
651 Numbers and black arrows denote locations of core pictures used to illustrate the gabbro within
652 the contact zones and centres.

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

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

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