

Multiple sulphur isotope records tracking basinal and global processes in the 1.98 Ga Zaonega Formation, NW Russia

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Abstract

The exceptionally organic-rich rocks of the 1.98 Ga Zaonega Formation deposited in the Onega Basin, NW Russia, have refined our understanding of Earth System evolution during the Paleoproterozoic rise in atmospheric oxygen. These rocks were formed in vent- or seep-influenced settings contemporaneous with voluminous mafic volcanism and contain strongly ¹³C-depleted organic matter. Here we report new isotopic ($\delta^{34}\text{S}$, $\Delta^{33}\text{S}$, $\Delta^{36}\text{S}$, $\delta^{13}\text{C}_{\text{org}}$) and mineralogical, major element, total sulphur and organic carbon data for the upper part of the Zaonega Formation, which was deposited shortly after the termination of the Lomagundi-Jatuli positive carbon isotope excursion. The data were collected on a recently obtained 102 m drill-core section and show a $\delta^{13}\text{C}_{\text{org}}$ shift from -38‰ to -25‰. Sedimentary sulphides have $\delta^{34}\text{S}$ values typically between +15‰ and +25‰ reflecting closed-system sulphur isotope behaviour

30 driven by high rates of microbial sulphate reduction, high sulphate demand, hydrothermal
31 activity and hydrocarbon seepage. Four intervals record $\delta^{34}\text{S}$ values that exceed +30‰. We
32 interpret these unusually ^{34}S -enriched sulphides to be a result of limited sulfate diffusion into
33 pore waters due to changes in sedimentation and/or periods of basinal restriction. Additionally,
34 there are four negative $\delta^{34}\text{S}$ and positive $\Delta^{33}\text{S}$ excursions that are interpreted to reflect changes
35 in the open/closed-system behaviour of sulphate reduction or availability of reactive iron. Our
36 findings highlight the influence of basinal processes in regulating sulphur isotope records and
37 the need for care before interpreting such signals as reflecting global conditions.

38 **Keywords:** Paleoproterozoic, Zaonega Formation, sulphur cycle, carbon cycle, Great
39 Oxidation Event

40 **1. Introduction**

41 The Paleoproterozoic represents a period in Earth's history, when a series of (bio)geological
42 events ultimately led to a change in the redox state of Earth's atmosphere-ocean system and the
43 rise of atmospheric oxygen at ca. 2.3 Ga during the Great Oxidation Event (GOE; Bekker et al.,
44 2004; Holland, 2006; Guo et al., 2009; Luo et al., 2016; Gumsley et al., 2017; but see also
45 Ohmoto et al., 2014). Following the GOE, the carbon cycle experienced unprecedented
46 perturbations, featuring the large-magnitude Lomagundi-Jatuli positive carbonate carbon
47 isotope excursion between 2.2 and 2.06 Ga (Karhu and Holland, 1996; Martin et al., 2013) and
48 the subsequent accumulation of organic-rich sediments during the ca. 2.0 Ga Shunga Event
49 (Melezhik et al., 1999, 2004; Strauss et al., 2013). It is postulated that these carbon cycle
50 perturbations were driven by intensified subaerial oxidative weathering, with concomitant
51 increases in riverine-derived nutrients, intensifying biological activity and facilitating the
52 growth of the marine sulphate reservoir (Bekker et al., 2006; Schröder et al., 2008; Reuschel et
53 al., 2012). Such inferences are supported by the presence of the oldest known globally
54 significant phosphorites associated with the Shunga Event (Bekker et al., 2003; Lepland et al.,
55 2013, 2014) and the oldest extensive evaporites of the ca. 2.0 Ga Tulomozero Formation, which
56 also archive the Lomagundi-Jatuli excursion in the Onega Basin of NW Russia (Morozov et al.,
57 2010; Krupenik et al., 2011; Blättler et al., 2018). Geochemical modelling of the evaporite
58 mineralogy and calcium isotope systematics of the latter indicate that, by ca. 2.0 Ga, the
59 concentration of seawater sulphate (SWS) was sufficiently high (>10 mM) to allow
60 precipitation of marine evaporite sequences with gypsum/anhydrite, halite and bittern salts
61 (Blättler et al., 2018). Such global-scale changes would seem to signify an irreversible trajectory

62 in Earth's redox state following the GOE. However, pyrite-derived sulphur isotope data
63 obtained from the organic-rich rocks of the 1.98 Ga Zaonega Formation and ca. 2.1 Ga
64 Francevillian Group have been used to argue for an environmental change and contraction of
65 the SWS reservoir (Scott et al., 2014; Ossa-Ossa et al., 2018). This conclusion was reached by
66 combining iron-speciation results with multiple-sulphur isotope data, interpreted to reflect
67 development of euxinic conditions on two different cratons with highly positive pyrite $\delta^{34}\text{S}$
68 values coupled to opposing $\Delta^{33}\text{S}$ - $\delta^{34}\text{S}$ behaviour suggesting low sulphate concentrations (Scott
69 et al., 2014; Ossa-Ossa et al., 2018).

70 To assess the significance of the carbon- and sulphur-isotope signals archived in the Zaonega
71 Formation against the backdrop of Earth System change, we have undertaken a multi-proxy
72 geochemical and petrographic study using recently obtained drill core material from the upper
73 part of the Formation (Fig.1). Samples were taken at approximately one metre intervals through
74 a 102-m thick section drilled in 2012 in the upper part of the Formation. Our multi-proxy dataset
75 extends the stratigraphic coverage of the isotopic profiles reported in previous studies to better
76 characterise the physical and chemical conditions under which biogeochemical carbon and
77 sulphur cycling occurred at ca. 2.0 Ga.

78 **2. Geological background**

79 The Zaonega Formation forms the upper part of the Paleoproterozoic succession of the Onega
80 Basin (Melezhik et al., 2013b) in the Karelia region of NW Russia (Fig. 1a). The succession
81 consists of mostly greenschist facies volcano-sedimentary rocks that lie unconformably on
82 Archean granites and gneisses. The entire succession was deformed into a series of open folds
83 cut by high-angle faults during the 1.89–1.79 Ga Svecofennian orogeny (Melezhik et al., 1999;
84 Ojakangas et al., 2001). The 1500 m thick Zaonega Formation occurs above the ^{13}C -enriched
85 shallow-marine carbonate rocks of the Tulomozero Formation and is overlain by basalts of the
86 Suisari Formation (Melezhik et al., 1999; Črne et al., 2013b). The proposed depositional model
87 for the Zaonega Formation suggests accumulation in a rift basin marked by contemporaneous
88 shallow-and deep-water mixed siliciclastic-carbonate deposition (Črne et al., 2014; Melezhik
89 et al., 2015).

90 The Zaonega Formation is younger than the Lomagundi-Jatuli event which terminated in
91 Fennoscandia at 2.06 Ga (Karhu and Holland, 1996; Melezhik et al., 1999, 2004) and is older
92 than a suite of cross-cutting dykes that yield ages of 1919 ± 18 Ma (Priyatkina et al., 2014),

93 1956 ± 5 Ma (Stepanova et al., 2014) and 1961.6 ± 5.1 Ma (Martin et al., 2015); it also predates
94 the gabbro sills in the overlying Suisari Formation dated at 1969 ± 18 Ma (Puchtel et al., 1998)
95 and 1988 ± 34 Ma (Puchtel et al., 1999). Hence the age of the Zaonega Formation has been
96 previously constrained to a time interval between 2.06 and 1.98 Ga. More recently, Martin et
97 al. (2015) place deposition between 1975.3 ± 2.8 Ma and 1967.6 ± 3.5 Ma, but these constraints
98 require additional assessment. In the absence of an agreed upon precise depositional age, we
99 adopt a 1.98 Ga estimate for the age of the Zaonega Formation.

100 The Zaonega Formation features well-preserved organic- and phosphorous-rich siliciclastic and
101 carbonate rocks with organic carbon contents reaching 40% in the mudstone units and up to
102 90% in pyrobitumen-filled veins (Melezhik et al., 1999, 2004, 2013a). Graded greywackes
103 interbedded with mudstones, dolostones and limestones have been interpreted as turbidity-
104 current deposits, punctuating background hemipelagic sedimentation. Deposition occurred
105 alongside syndepositional mafic magmatism in the form of mafic tuffs, lavas and gabbroic sills.
106 Peperitic contacts between the igneous and enclosing sedimentary rock indicate emplacement
107 into wet and unconsolidated sediments (Galdobina, 1987; Črne et al., 2013a, b; Melezhik et al.,
108 2015). Heat provided by this igneous activity triggered hydrothermal circulation and oil
109 generation as the organic-rich rocks passed through the oil window (Qu et al., 2012; Črne et al.,
110 2013a, b).

111 A comprehensive $\delta^{13}\text{C}_{\text{org}}$ dataset was previously obtained from FAR-DEEP cores 12AB and
112 13A that intersect 550 m of the Zaonega Formation. These data reveal a decline in $\delta^{13}\text{C}_{\text{org}}$ values
113 from -25‰ to -40‰ in the middle–upper Zaonega Formation prior to a return to values of -
114 25‰ (Kump et al., 2011; Qu et al., 2012; Lepland et al., 2014). Abundant sulphide minerals
115 associated with the organic-rich rocks have variable $\delta^{34}\text{S}$ values ranging from -19‰ to +27‰
116 (Shatsky, 1990, Scott et al., 2014), but generally become more ^{34}S -enriched up-section with
117 typical values of $\sim +15\%$ in $\delta^{34}\text{S}$ (Scott et al., 2014). Several contrasting explanations have been
118 proposed to explain these isotopic trends, including global-scale oxidation of organic matter
119 (Kump et al., 2011), seepage/spillage of locally generated hydrocarbons to the seafloor
120 triggering basinal methanotrophy (Qu et al., 2012), and a biogeochemical response to a global
121 collapse of the SWS reservoir (Scott et al., 2014). The first scenario is questionable since the
122 initial negative $\delta^{13}\text{C}_{\text{org}}$ excursion coincides with the Lomagundi-Jatuli positive excursion in
123 $\delta^{13}\text{C}_{\text{carb}}$ (Ossa-Ossa et al., 2018) and both excursions cannot be explained by a single, global
124 underlying cause. Even though hydrocarbon migration and seepage are considered as the main
125 factors in governing the negative $\delta^{13}\text{C}_{\text{org}}$ shift in the Zaonega Formation, Qu et al. (2012) related

126 this to a local bloom of methanotrophic organisms that induced high rates of pore water sulphate
127 reduction, while Scott et al. (2014) proposed that the negative co-variation of $\delta^{34}\text{S}$ and $\delta^{13}\text{C}_{\text{org}}$
128 values signalled water column methanotrophy and an overall increase in methane production
129 as a response to low sulphate concentrations. Considering such contrasting scenarios, the need
130 to discriminate between global, basinal and post-depositional controls becomes evident.

131 **2.1 Sulphur isotope systematics**

132 Geochemical and biological processes fractionate sulphur isotopes to different extents. The
133 largest known non-photochemical sulphur isotope fractionations are associated with reduction,
134 and to a lesser extent oxidation, reactions mediated by microbial communities (Johnston et al.,
135 2011). Microbial sulphate reduction (MSR) coupled to oxidation of organic matter is the
136 dominant pathway for anaerobic respiration in contemporary sediments. In Phanerozoic marine
137 environments with high SWS concentrations, precipitation and burial of sulphide minerals
138 (ultimately pyrite), mediated by MSR, is the main sink for sulphide. When sulphate
139 concentrations exceed 0.2 mM (Habicht et al., 2002; Bradley et al., 2016) the kinetic isotope
140 effect associated with MSR becomes pronounced, depleting the sulphate pool in ^{32}S via its
141 preferential incorporation into the sulphide product. Owing to MSR, modern seawater has a
142 $\delta^{34}\text{S}$ value of 21‰, and the sulphide product (and resulting pyrite sink) can be depleted in ^{34}S
143 (Rees et al., 1978; Seal, 2006; Canfield et al., 2010) by as much as 70‰ based on experimental
144 studies (Sim et al., 2011), although fractionations between 20‰ to 60‰ are common in nature
145 (Zaback et al., 1993). In sediments where sulphate demand exceeds sulphate supply, the sulphur
146 isotope composition of product sulphides will approach that of the sulphate (Goldhaber and
147 Kaplan, 1975; Jørgensen, 1979). The final $\delta^{34}\text{S}$ of sulphide that is preserved in the rock record
148 primarily as pyrite will also depend on multiple factors including iron availability and organic
149 carbon loading (Zaback et al., 1993; Aller et al., 2010; Fike et al., 2015). If the ambient sulphate
150 reservoir is limiting then ongoing MSR will deplete the residual sulphate in ^{32}S and generate
151 parallel increases in local $\delta^{34}\text{S}_{\text{SWS}}$ and $\delta^{34}\text{S}_{\text{pyr}}$, with similar effects registered in the minor
152 sulphur isotope ratios ($\delta^{33}\text{S}$ and $\delta^{36}\text{S}$; Johnston et al., 2008, 2007; Gomes and Hurtgen, 2013;
153 Fike et al., 2015). Further, S-based chemoautotrophic metabolisms also impart a small but
154 distinguishable $\delta^{34}\text{S}$ fractionation, expressed when sulphide and other reduced sulphur
155 compounds are oxidised to elemental sulphur and sulphate (Balci et al., 2007; Zerkle et al.,
156 2009, 2016). Additionally, microbial sulphur disproportionation (MSD) uses intermediate
157 redox state sulphur species to produce both sulphate and sulphide, causing additional $\delta^{34}\text{S}$

158 fractionations of up to 20‰ (Canfield and Thamdrup, 1994; Farquhar et al., 2003; Johnston et
159 al., 2005a).

160 All these various sulphur-utilising metabolisms have the capacity to produce overlapping $\delta^{34}\text{S}$
161 signatures, making it difficult to identify unambiguously specific metabolic pathways from $\delta^{34}\text{S}$
162 values preserved in the rock record. Furthermore, the extent of fractionation during MSR
163 depends on many factors such as cell-specific sulphate reduction rates, temperature, electron
164 donor availability, sulphate concentration, salinity and pH (Fike et al., 2015). Moreover, pure
165 culture experiments are rarely representative of natural environments where S-cycling consortia
166 often do not produce unique $\delta^{34}\text{S}$ isotope signatures (Detmers et al., 2001; Brüchert, 2004;
167 Johnston et al., 2011; Sim et al., 2011). Recent studies, however, have demonstrated that
168 biogeochemical sulphur cycling can cause mass-dependent fractionations that affect the
169 partitioning of sulphur's minor isotopes (Johnston et al., 2005a, 2011; Seal, 2006; Canfield et
170 al., 2010; Zerkle et al., 2016). These small differences are resolvable in the minor sulphur
171 isotopes ratios and can provide additional information even when $\delta^{34}\text{S}$ values overlap.

172 **3. Methods**

173 **3.1 Materials**

174 Samples were collected from two 60-m long cores that were drilled 500 m apart: OnZap1
175 (62.5870 N, 34.9310 E) and OnZap3 (62.5920 N, 34.9280 E) near the village of Shunga in
176 Karelia, NW Russia (Fig. 1). A third core, OnZap2, was drilled 70 m from OnZap1 and was
177 used for additional sedimentological and petrographic description. Between OnZap1 and
178 OnZap3 is the site of the 240-m long FAR-DEEP 13A core. A distinct dolomite-chert unit
179 occurs in each of the OnZap and FAR-DEEP cores (Črne et al., 2014), and its base is used as a
180 lithostratigraphic marker to enable correlations between cores. The overlapping OnZap cores,
181 therefore, provide a 102-m thick section of the upper Zaonega Formation, which we term the
182 OnZap section. Unless otherwise stated, all depths discussed hereafter refer to the composite
183 OnZap section (see the supplementary Tables for individual core depths and thicknesses).
184 Detailed lithological logging of the cores was performed prior to sampling. Sample locations
185 were carefully selected to minimise the effects of secondary overprints (e.g. large concretions,
186 veins, fractures). In total 134 samples were obtained at approximately 1 metre intervals through
187 cores OnZap1 and OnZap3 to produce our chemostratigraphic data set.

188 **3.2 Petrographical, mineralogical and major element analyses**

189 Petrographic characterisation of thin sections was performed by scanning electron microscope
190 (SEM) analysis using a ZEISS EVO MA15 SEM at the University of Tartu. The images were
191 captured in backscattered electron (BSE) mode. To complement the SEM imaging, chemical
192 characterisation by point analyses and elemental mapping of the samples were performed using
193 an Oxford AZTEC-MAX energy-dispersive spectrometer (EDS).

194 Major element composition was determined by Bureau Veritas Minerals, Vancouver, Canada
195 by inductively coupled plasma optical emission spectroscopy (ICP-OES). Powdered samples
196 were fused at 950 °C with lithium metaborate flux and the fusion beads were digested with a
197 combination of hydrofluoric and perchloric acids prior to analysis. Loss on ignition data were
198 obtained from heating samples in a furnace at 950 °C for 1 h. For all elements, average percent
199 relative standard deviation (average RSD%) was less than 5%. The mineralogical composition
200 of whole rock samples was determined on unoriented powdered samples using a Bruker D8
201 Advance X-ray diffractometer using Cu K α radiation and LynxEye positive sensitive detector
202 in 2–70° 2-Theta range at the University of Tartu. The obtained diffractograms were interpreted
203 and modelled with the Rietveld algorithm-based program Topaz. The content of crystalline
204 phases determined by XRD analysis were normalised to account for X-ray amorphous organic
205 carbon using the TOC abundance data determined from the same samples.

206 **3.3 Sulphur and carbon content**

207 The total carbon (TC), total organic carbon (TOC) and total sulphur (TS) abundances were
208 quantified using ~100 mg aliquots of powdered sample admitted to a LECO SC-444 analyser
209 at the Geological Survey of Norway. The TOC content was determined on acid-treated (10%
210 HCl vol/vol) residues. Detection limits for TS, TC and TOC were 0.02 wt.%, 0.06 wt.% and
211 0.1 wt.%, respectively. The relative precision was better than 2.5% for TC and 10% for TS and
212 TOC.

213 **3.4 Sulphur isotope analyses**

214 Powdered samples were subjected to a two-step sulphur extraction procedure (Canfield et al.,
215 1986). In this sequential extraction method, sulphur is liberated first as H₂S from acid volatile
216 sulphur (AVS; monosulphides such as pyrrhotite, sphalerite, mackinawite or greigite) via a 6
217 M HCl distillation, and pyrite is released via hot chromium(II) chloride distillation (CRS). To
218 prevent incorporation of elemental sulphur to the CRS fraction, we used chromium(II) chloride
219 solution adopted from Oduro et al. (2013). In addition to pyrite, the CRS solution may have

220 attacked marcasite, however our XRD analysis failed to detect this pyrite polymorph, rendering
221 any potential contribution negligible. The resulting H₂S was converted into Ag₂S by adding of
222 0.1 M AgNO₃. The precipitate was then cleaned using 1M NH₄(OH) and rinsed to neutrality
223 using ultra-pure (18 MΩ·cm) water (Oduro et al., 2013).

224 Sulphur isotope analyses were performed at McGill University. The Ag₂S samples were reacted
225 overnight with excess fluorine gas in nickel bombs at 250 °C to produce SF₆ that was first
226 purified cryogenically and then via gas chromatography. The sulphur isotope composition of
227 purified SF₆ was measured by dual-inlet gas-source mass spectrometry monitoring ion beams
228 at m/z of 127, 128, 129, and 131 using a Thermo Finnigan MAT 253 gas source mass
229 spectrometer. Sample reproducibility, as determined by replicate analyses of the in-house
230 standard MSS-1, was generally better than 0.1‰ for δ³⁴S values, 0.015‰ for Δ³³S and 0.2‰
231 for Δ³⁶S. Sulphur isotope ratios are reported in the standard delta notation as *per mil* deviations
232 from the international reference standard the Vienna-Canyon Diablo Troilite (V-CDT):

$$233 \delta^{3x}\text{S} = 1000 \cdot \left(\frac{{}^{3x}\text{R}_{\text{sample}}}{{}^{3x}\text{R}_{\text{V-CDT}}} - 1 \right),$$

234 where ${}^{3x}\text{R} = \frac{{}^{3x}\text{S}}{{}^{32}\text{S}}$, for 3x = 33, 34 or 36.

235 We express the minor isotope values in capital delta notation:

$$236 \Delta^{33}\text{S} = \delta^{33}\text{S} - 1000 \cdot \left[\left(1 + \frac{\delta^{34}\text{S}}{1000} \right)^{0.515} - 1 \right],$$

237 and

$$238 \Delta^{36}\text{S} = \delta^{36}\text{S} - 1000 \cdot \left[\left(1 + \frac{\delta^{34}\text{S}}{1000} \right)^{1.9} - 1 \right].$$

239 **3.5 Organic carbon isotope analyses**

240 Between 0.2 and 2 g aliquots of homogenised sample powders were reacted with 10% (vol/vol)
241 HCl at room temperature in centrifuge tubes for 24 hours. Acid treatment was repeated until no
242 further reaction was observed. The remaining residues were rinsed to neutrality using deionised
243 water and dried at 45 °C. Aliquots of dry decarbonated residue (0.2 mg) were then weighed into
244 tin capsules and the organic carbon isotope (δ¹³C_{org}) composition was determined by flash
245 combustion using an Elemental Analyser coupled to a Continuous Flow Isotope Ratio Mass
246 Spectrometer (ThermoScientific Delta V Plus with Costech EA) at the NERC Life Sciences
247 Mass Spectrometry Facility at the Scottish Universities Environmental Research Centre in East
248 Kilbride, Scotland.

249 The carbon isotope results are reported in standard delta notation as *per mil* deviation from the
250 Vienna-Pee Dee Belemnite (V-PDB) standard:

$$251 \delta^{13}\text{C} = 1000 \cdot ({}^{13}\text{R}_{\text{organic-C}}/{}^{13}\text{R}_{\text{V-PDB}} - 1).$$

252 Accuracy and precision was monitored via replicate analyses of the international standard USGS40
253 L-glutamic acid ($\delta^{13}\text{C} = -26.39 \pm 0.04\text{‰}$ V-PDB), which yielded an average $\delta^{13}\text{C}$ value of –
254 $26.19 \pm 0.04\text{‰}$. The $\delta^{13}\text{C}$ values have been corrected for the 0.2‰ offset between the measured
255 and expected values of USGS40 measurements.

256 **4. Results**

257 **4.1 Lithology and mineralogy**

258 Characteristic rock types and lithostratigraphic columns together with selected mineralogical
259 and geochemical parameters are presented in Figures 2 to 6. All mineralogical and geochemical
260 results are provided in Supplementary Tables 1 to 4. Correlation between OnZap cores was
261 made using the base of a massive dolomite interval that can be identified across the basin,
262 occurring at 53 m in OnZap1 and at 10.8 m in OnZap3 (Figs. 4–6). The cores recovered organic-
263 rich mudstone, dolostone and calcareous mudstone from the upper part of the Zaonega
264 Formation (Fig. 2). The upper part of OnZap1 provides an additional 25 m of stratigraphy with
265 respect to previous studies (Qu et al., 2012; Črne et al., 2013 a, b, 2014; Lepland et al., 2014;
266 Scott et al., 2014). Three units can be identified: Unit A, from 102–53 m depth, composed of
267 black organic-rich mudstones with a few carbonate beds; Unit B, from 53–33 m, consisting
268 predominantly of dolostone beds including the massive dolomite interval; and Unit C, from 33–
269 1.7 m, characterised by grey relatively organic-poor mudstone and marly carbonate beds (Figs.
270 2, 4).

271 **4.1.1 Unit A: organic-rich mudstones (102–53 m depths)**

272 Organic-rich mudstones display wispy, low-angle cross lamination and pass upward into
273 calcareous mudstones marked by clay partings. The former contain quartz comprising up to 72
274 wt.%, mica at ~17 wt.%, variable amounts of K-feldspar up to ~24.6 wt.% and minor amounts
275 of pyrite, calcite, talc and chlorite. The mica is predominantly a muscovite-type K-mica and a
276 phlogopite-type Fe/Mg-mica with Fe/(Mg + Fe) ratios in the range of 0.03–0.04, hereafter
277 referred to as Fe-poor Fe/Mg-mica. Pyrite abundances are relatively constant at 1–3 wt.% in
278 the lower part of Unit A but are elevated (maximum of 13.8 wt.%) in organic-rich mudstones

279 in its upper part. Dolomite is the main carbonate mineral, but calcite reaches ~10 wt.% in some
280 of the carbonate beds particularly along bed margins where it may co-occur with talc (also noted
281 by Črne et al., 2014, in the FAR-DEEP cores). A few carbonate beds in the upper part of Unit
282 A contain ~2 wt.% of an iron-rich dolomite to ankerite solid-solution phase, that can constitute
283 up to 12.8 wt.%. The calcareous mudstone at 86–77 m contains up to 15.2 wt.% talc and 29.3
284 wt.% calcite, but also has low abundances of other minerals.

285 Cross-cutting veins are ubiquitous. Those in mudstones are predominantly filled with
286 pyrobitumen, quartz and Fe-poor Fe/Mg-mica, whereas those in carbonate beds largely consist
287 of calcite (Figs. 2d, e). The interval at 77–70 m depth displays intense veining and silicification
288 at mudstone-dolostone contacts; here quartz can comprise up to 73.2 wt.% of the silicified
289 intervals. The mudstones in this interval are finely laminated and exhibit soft-sediment
290 deformation features that are cut by quartz veins (Fig. 2e).

291 Organic matter occurs as disseminated particles, pyrobitumen veins or as nodular aggregates (a
292 few hundred μm in diameter) in finely laminated mudstone and calcareous mudstone. An
293 organic-rich mudstone interval at 59–53 m depth has C_{org} contents of up to 65 wt.% and contains
294 a thin layer at 54 m depth of bedding-parallel nodules composed of pyrobitumen and varying
295 amounts of mica and pyrite. Its upper margin is marked by apatite nodules, layers and lenses.

296 **4.1.2 Unit B: dolomite unit (53–33 m depths)**

297 The dolostone interval defining the base of Unit B is cut by conspicuous black, massive chert
298 veins that can be up to several meters thick and form an often bed-parallel network associated
299 with thin mudstone interlayers. They contain relicts of the altered dolostone and their contacts
300 with the dolostone layers are marked by calcite, Fe-poor Fe/Mg-mica and talc. Smaller, mm- to
301 cm-scale veins are abundant and consist mainly of quartz, calcite, pyrobitumen and pyrite. The
302 central parts of the dolostone beds are massive, nearly pure, dolomite that lacks pervasive silica
303 veining and secondary calcite. The iron-rich dolomite to ankerite solid-solution phase is a
304 common subcomponent (~6 wt.%) of the dolostone beds and increases in content up section,
305 concomitant with a decrease in the frequency, extent and thickness of chert veining. In the upper
306 part of Unit B dark grey mudstone beds become more numerous and are composed of quartz
307 (~20 wt.%), mica (~40 wt.%; mainly muscovite-type K-mica but Fe-poor Fe/Mg-mica is also
308 present) organic matter and K-feldspar (~2 wt.%, maximum of 11.4 wt.%). Pyrite is most
309 abundant in the mudstones (~8 wt.%, maximum of 16.5 wt.%), but is also a common mineral
310 component in the carbonate beds.

311 **4.1.3 Unit C: relatively organic-poor rocks (33–1.7 m depths)**

312 Unit C is composed of alternating fine-grained mudstone, calcareous mudstone and carbonate
313 beds. The grey mudstones are finely parallel to ripple cross-laminated (Figs. 2a, c) and organic
314 matter is lower than in Units A and B, with typical TOC values of ~1 wt.% but can be as high
315 as 10 wt.%. Quartz and mica minerals comprise approximately ~35 wt.% and ~40 wt.%,
316 respectively. The latter are muscovite-type K-mica and a biotite-type Fe/Mg-mica with Fe
317 content ~20.8 wt.% (hereafter referred to as Fe-rich Fe/Mg-mica). Unlike the underlying units,
318 the content of K-feldspar, Fe-poor Fe/Mg-mica and calcite is low and talc is absent. In contrast,
319 plagioclase is more abundant reaching up to 13.2 wt.%. Overall, the content of disseminated
320 pyrite in Unit C is lower than in Units A and B (~1.6 wt.%), although large pyrite aggregates
321 and vein pyrite do occur. The iron-rich dolomite to ankerite solid-solution phase is a major
322 mineral component of the marly carbonate beds of Unit C and its content increases upwards in
323 the section reaching 38.5 wt.%. The marly carbonate beds vary from being massive with faint
324 lamination in their centres to cross laminated with mud drapes (Fig. 2b). Siderite, in association
325 with large anhedral pyrite, occurs in some of the marly carbonate beds and calcareous
326 mudstones in the uppermost part of Unit C. Petrographically the siderite-pyrite aggregates occur
327 as irregular to oval/lens-like masses of few hundred microns to few mm size. Siderite patches
328 are to different extent replaced by pyrite aggregates composed of euhedral crystallites.
329 Typically, the replacement of siderite aggregates starts at the contacts with the surrounding
330 mudstone and progresses inwards.

331 **4.1.4 Pyrite petrography**

332 Core inspection and petrographic analyses show that sulphide minerals are pervasive but are
333 typically concentrated within mudstone beds, with the highest abundances at the top of Unit A.
334 Pyrite is the main sulphide mineral, but minor pyrrhotite, sphalerite, and As-, Cu- and Ni-
335 bearing sulphides also occur. The minor sulphides are most abundant in Units A and B and
336 mostly absent in Unit C. Most pyrite occurs as fine-grained euhedral and typically octahedral
337 crystals ~10 µm in size (Figs. 3a, b, c). The central parts of individual pyrite crystals can be
338 either hollow or contain inclusions of quartz, mica and rarely Cu-sulphide minerals. These
339 minute pyrite crystals are concentrated in organic-rich layers within mudstones or carbonaceous
340 mudstones and many occur as ellipsoidal, densely packed 30–100 µm sized clusters (Fig. 3a,
341 b) encased within contorted mudstone layers.

342 Pyrite also occurs throughout the succession as large euhedral or anhedral disseminated crystals
343 or irregular aggregates (Fig. 3d). The latter is most abundant in Units A and B and is associated

344 with other metal sulphides, such as sphalerite. Solitary large pyrite crystals ($> 100 \mu\text{m}$) are
345 abundant in carbonate and calcareous mudstone beds but less so in mudstones. These large
346 pyrite crystals commonly contain numerous inclusions of quartz and dolomite. At 27 m in Unit
347 C, a dolostone bed contains large aggregates of pyrite that form clusters several cm in size with
348 dolomite inclusions that appear texturally co-genetic with calcite (Fig. 3d).

349 **4.2 Major element geochemistry**

350 Stratigraphic profiles of selected major elements are reported as oxides and shown in Figure 5.
351 Full datasets are in Supplementary Tables 1–4. The stratigraphic distribution of SiO_2 , Al_2O_3
352 and K_2O show close correspondence with the mineral abundances of quartz, mica and feldspar,
353 serving as a proxy for the respective mineral phases. The highest SiO_2 ($\sim 78 \text{ wt.}\%$) and the
354 lowest Al_2O_3 ($\sim 5 \text{ wt.}\%$), Fe_2O_3^* ($\sim 2 \text{ wt.}\%$; total Fe expressed as Fe_2O_3) and K_2O ($\sim 2 \text{ wt.}\%$)
355 abundances are observed in the lower part of Unit A and in the dolostone interval at the base of
356 Unit B (53–44 m). The SiO_2 content slightly decreases in the upper part of Unit B and in Unit
357 C, whereas Al_2O_3 ($\sim 14 \text{ wt.}\%$), Fe_2O_3^* ($\sim 9 \text{ wt.}\%$) and K_2O ($\sim 5 \text{ wt.}\%$) abundances increase.
358 Contents of TS and TOC vary from $0.02 \text{ wt.}\%$ to $10.9 \text{ wt.}\%$ and $0.12 \text{ wt.}\%$ to $65 \text{ wt.}\%$,
359 respectively. The highest TS and TOC abundances are observed in the upper parts of Units A
360 and B with TS averaging $\sim 2 \text{ wt.}\%$ (maximum of $10.9 \text{ wt.}\%$) and TOC averaging $\sim 13 \text{ wt.}\%$
361 (maximum of $65 \text{ wt.}\%$). In Unit C, TS content has average values of $\sim 1 \text{ wt.}\%$ (maximum of 4.3
362 $\text{wt.}\%$) and TOC $\sim 1 \text{ wt.}\%$ (maximum of $3.3 \text{ wt.}\%$). The depth profiles of TS and Fe_2O_3^*
363 abundances co-vary in Units A and B, but are decoupled in Unit C where iron concentrations
364 are the highest. This marked change in Fe_2O_3^* , TOC and TS contents in Unit C coincides with
365 an increase in Al_2O_3 , a change in the mica phase from Fe-poor to Fe-rich Fe/Mg mica,
366 increasingly more abundant Fe-rich carbonate phases, and a decrease in pyrite abundance.

367 **4.3 Carbon isotope composition of organic matter**

368 Organic carbon isotope ($\delta^{13}\text{C}_{\text{org}}$) values show an increase from -38.03‰ in Unit A to -24.51‰
369 in Unit C (Fig. 6). Unit B represents a transitional interval, with $\delta^{13}\text{C}_{\text{org}}$ values varying from -
370 38‰ to -29‰ . The same range of values and a similar shift in $\delta^{13}\text{C}_{\text{org}}$ was documented in FAR-
371 DEEP 13A core by Lepland et al. (2014). As described below, this shift in $\delta^{13}\text{C}_{\text{org}}$ values is
372 accompanied by a shift to more ^{34}S -enriched sulphides and lower TOC and TS concentrations.

373 **4.4 Sulphur isotope composition of sulphides**

374 Sulphur isotope data are shown in Figure 6 and the CRS and AVS data are reported in
375 Supplementary Table 1. The $\delta^{34}\text{S}$, $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ values of the pyrite sulphur (CRS) in the

376 OnZap section range from -0.8‰ to +43.6‰, -0.09‰ to 0.09‰ and -0.50‰ to 0.56‰,
377 respectively. Acid volatile sulphur (AVS) has $\delta^{34}\text{S}$ values from +15.3‰ to +34.8‰, $\Delta^{33}\text{S}$ values
378 from -0.07‰ to +0.03‰ and $\Delta^{36}\text{S}$ values from -0.37‰ to +0.68‰. The CRS $\delta^{34}\text{S}$ values in the
379 OnZap section are variable, with a slight trend towards heavier values in the upper part. Four
380 distinct excursions exhibiting highly positive $\delta^{34}\text{S}$ values ($> +30\text{‰}$) occur at 17.4 m, 27.8 m,
381 62.4 m and 80 m depths. Throughout the section the $\delta^{34}\text{S}$ and $\Delta^{33}\text{S}$ values show an anti-
382 correlation: where the former increases the latter shifts towards more negative values and *vice*
383 *versa*. Both $\Delta^{36}\text{S}$ and $\Delta^{33}\text{S}$ display small variations and correlate negatively, defining $\Delta^{36}\text{S}/\Delta^{33}\text{S}$
384 arrays with a change in the slope from Unit A to Unit C (Fig. 9). In Unit A the $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ array
385 has the slope of -8 whereas the difference between Units B and C is statistically insignificant
386 and the $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ array has a slope of -4. Although the $\Delta^{36}\text{S}-\Delta^{33}\text{S}$ relationships show significant
387 scatter, Unit A has a R^2 value of 0.75, whereas Units B and C show a weaker correlation, with
388 an R^2 value of 0.46.

389 5. Discussion

390 5.1 Influence of hydrothermal alteration on geochemical signals

391 The presence of lava flows and gabbroic sills with peperitic contacts demonstrate that the
392 Zaonega Formation was deposited in a magmatically active setting (Črne et al., 2013a,b;
393 Melezhik et al., 2015). This igneous activity triggered hydrothermal circulation, generating
394 hydrocarbons and other diagenetic fluids that permeated the sub-seafloor, altering primary
395 mineral assemblages and catalysing secondary mineral precipitation (Melezhik et al., 1999; Qu
396 et al., 2012; Črne et al., 2014). Thus, it is important to differentiate between depositional and/or
397 early diagenetic geochemical signals from those that formed later. For example, detailed
398 petrographic observations from the FAR-DEEP 12AB core revealed that hydrothermally
399 catalysed dedolomitisation reactions produced paragenetic mineral assemblages including
400 calcite, phlogopite and talc (Črne et al., 2014). This type of alteration is ubiquitous in Unit A
401 of the OnZap section, with enrichments of quartz and K-feldspar, as well elevated abundances
402 of secondary calcite and talc at lithological contacts. The FAR-DEEP 13A core, drilled ca. 300
403 m from the OnZap cores, contains a magmatic body at an equivalent stratigraphic level to Unit
404 A of the OnZap section, which had the potential to sustain localised hydrothermal circulation
405 (Črne et al., 2013a).

406 In contrast to Unit A, the upper part of Unit B and all of Unit C show less pronounced post-
407 depositional alteration, and thus are more likely to preserve the most pristine mineralogical and
408 geochemical signatures within the OnZap section. We hypothesise that the massive dolostone
409 body at the base of Unit B (53–44 m depth) acted as a stratigraphic seal, hindering the ascent
410 of hydrothermal fluids; an inference supported by a decrease in veining intensity, decreasing
411 quartz, calcite and K-feldspar abundances, and an increase in iron content of the Fe/Mg-micas
412 through Unit B and up into Unit C.

413 **5.2 Distribution of iron in mineral phases**

414 The conventional sequential iron extraction technique developed by Poulton and Canfield
415 (2005), commonly referred to as “Fe speciation”, is widely used to constrain depositional redox
416 conditions based on the quantity and distribution of highly reactive iron (e.g., Poulton and
417 Canfield, 2011). Because of the ubiquity of Fe-rich carbonate phases (dolomite to ankerite solid
418 solution and siderite) in our samples and their known recalcitrant nature (Raiswell et al., 1994,
419 2012; Poulton and Raiswell, 2002; Poulton and Canfield, 2011; Clarkson et al., 2014; Slotznick
420 et al., 2018), we used a combination of XRD and SEM-EDS analyses rather than the
421 conventional wet-chemical extraction scheme to assess Fe partitioning in the main Fe-bearing
422 carbonate (Fe_{Carb} = iron-rich dolomite to ankerite solid-solution phase and siderite), sulphide-
423 (Fe_{PY} = pyrite) and silicate-phase minerals (Fe_{SIL}). This procedure is preferable in that it exploits
424 the intrinsic physical properties of the minerals of interest and is thus not hindered by
425 incomplete dissolution. Previous work has demonstrated that pyrrhotite in the FAR-DEEP 13A
426 core is a product of pyrite alteration (Asael et al., 2013), hence we consider pyrrhotite as part
427 of the Fe_{PY} pool. Iron-oxides and iron-oxyhydroxides were below the XRD quantification limit
428 (<0.3 wt.%) in all the examined samples. We defined the silicate iron (Fe_{SIL}) pool as the sum
429 of Fe in phyllosilicates (K-mica, Fe/Mg-mica and chlorite), the only Fe-carrying silicate phases
430 identified in our samples.

431 Owing to the variable Fe contents of the varied mineral phases and types (e.g. micas and
432 carbonates), multiple measurements by SEM-EDS were made from several representative
433 samples from Units A, B and C. These data were then used to calculate the average iron content
434 of the individual phases. The average iron content of muscovite-type K-mica and chlorite was
435 found to be 3.2 and 1.6 wt.% Fe, respectively. Multiple SEM-EDS analyses demonstrated that
436 these values were constant throughout all examined samples, whereas the iron content of
437 Fe/Mg-mica phases was found to be variable, with low iron contents (1.4 wt.%) typifying Units
438 A and B and high iron (20.8 wt.%) contents dominating in Unit C. Iron-rich carbonate phases

439 in the dolomite to ankerite solid-solution series contained up to 10 wt.% iron and were confined
440 to the upper part of the OnZap section. Siderite, with a stoichiometric Fe abundance, is present
441 in few samples near the top of the section. Total XRD-derived iron (Fe_{T-XRD}) abundances were
442 calculated as the sum of Fe_{Carb} , Fe_{PY} and Fe_{SIL} . Generally, the calculated Fe_{T-XRD} and total Fe
443 (Fe_{T-OES}) determined by ICP-OES displayed a good fit ($R^2 = 0.92$); however, there are a few
444 samples where Fe_{T-XRD} diverged by more than 20% from the Fe_{T-OES} . This discrepancy is likely
445 due to the higher quantification limit (~0.3–0.5 wt.%) of XRD compared to ICP-OES.
446 Regardless, these typically iron-impoverished samples were excluded from iron distribution
447 assessments (Supplementary Fig. 1), as recommended by previous studies (Clarkson et al.,
448 2014). Although the XRD approach to Fe speciation is yet to be empirically calibrated, when
449 both XRD and conventional Fe speciation approaches have been tested elsewhere there is good
450 agreement between the two techniques (Raiswell et al., 2011), which, in the absence of full
451 calibration (e.g., Poulton and Canfield, 2005; Clarkson et al., 2014), provide confidence in our
452 approach.

453 **5.3 Redox constraints on deposition in the Onega Basin**

454 The XRD-defined Fe distribution data are illustrated in Figure 6 along with our $\delta^{13}C_{org}$ and $\delta^{34}S$
455 data. The raw data are given in Supplementary Table 3. Herein, the biogeochemically reactive
456 iron pool (Raiswell et al., 1994; Poulton and Raiswell, 2002; Poulton and Canfield, 2011;
457 Clarkson et al., 2014) is defined as $(Fe_{PY}+Fe_{Carb})/Fe_{T-XRD}$, whereas the proportion of pyrite in
458 the reactive iron pool is defined as $Fe_{PY}/(Fe_{PY}+Fe_{Carb})$. The ratios of $(Fe_{PY}+Fe_{Carb})/Fe_{T-XRD}$
459 greater than 0.5 and $Fe_{PY}/(Fe_{PY}+Fe_{Carb})$ of approximately unity in OnZap Units A and B, as well
460 as strong linear correlation between TS and Fe_{T-OES} (Fig. 7), show that pyrite is the main iron-
461 bearing phase in those strata. In Unit C, sulphur and iron concentrations show no correlation
462 (Fig. 7) and, $(Fe_{PY}+Fe_{Carb})/Fe_{T-XRD}$ and $Fe_{PY}/(Fe_{PY}+Fe_{Carb})$ ratios are lower, albeit variable (Fig.
463 6). Again, strengthening the applicability of our XRD approach, the XRD-derived data are in
464 good agreement with conventionally Fe speciation data from correlative parts of the upper
465 Zaonega Formation (Scott et al., 2014).

466 If these ratios were to reflect Fe distribution patterns in the original sediment, anoxic-euxinic
467 depositional environment would characterise Units A and B and variable redox conditions
468 including oxic episodes would characterize Unit C. It has been shown that physical disturbance
469 and non-steady state diagenesis of fine-grained sediments can produce highly reactive iron
470 enrichments, even beneath an oxygenated water-mass (Aller et al., 2010). Given the complex
471 depositional setting, featuring syn-depositional magmatism, turbidites and pervasively fluid-

472 influenced intervals (Unit A and lower Unit B), these data must be first treated with caution,
473 establishing the influence of post-depositional iron mobilisation before reaching any conclusion
474 concerning depositional redox.

475 Evidence for late-stage iron mobilisation is provided by the chemistry of the OnZap carbonate
476 phases. Iron concentrations in dolomite can reach 10%, whereas secondary calcite that formed
477 via dedolomitisation is essentially devoid of iron because of limited iron substitution and the
478 instability of $\text{CaFe}(\text{CO}_3)_2$ solid solution series at temperatures below 450 °C (Davidson, 1994).
479 There is, however, abundant evidence for sedimentary/early diagenetic pyrite. Petrographic
480 observations reveal that organic-rich lamina throughout Unit A and the mudstones from Units
481 B and C contain abundant disseminated fine-grained pyrite crystals ($>10\ \mu\text{m}$) and ellipsoidal
482 pyrite clusters (30–100 μm). Differential compaction of the organic-rich laminae around the
483 pyrite clusters/crystals (Fig. 3a, b), and the lack of cross-cutting sedimentary fabrics, or
484 association with quartz veins, attests to their formation early within the sediment prior to
485 compaction and silica alteration. Carbonate beds on the other hand contain large, inclusion-
486 laden, euhedral and anhedral pyrite crystals that clearly formed much later (Fig. 3d).
487 Consequently, the iron distribution patterns, particularly in Unit A and the lower part of Unit
488 B, were established within the diagenetic and metamorphic environments and cannot be used
489 for reliably inferring water column redox conditions.

490 Relative to Unit A and the lower part of Unit B, Unit C and the upper part of Unit B display
491 less evidence for post-depositional alteration. Significant part of iron in Unit C is housed in Fe-
492 rich carbonate minerals and the increase in $\text{Fe}_{\text{T-OES}}$ coincides with the transition from a Fe-poor
493 to a Fe-rich mica phase, reflecting less hydrothermal alteration relative to the underlying strata.
494 Accordingly, the lower and more variable $(\text{Fe}_{\text{PY}} + \text{Fe}_{\text{Carb}})/\text{Fe}_{\text{T-XRD}}$ and $\text{Fe}_{\text{PY}}/(\text{Fe}_{\text{PY}} + \text{Fe}_{\text{Carb}})$ ratios,
495 (Fig. 6), are a more reliable potential archive of depositional redox conditions, suggesting that
496 the upper Zaonega Formation was deposited in a highly dynamic setting.

497 Scott et al. (2014) used Fe-speciation data to conclude that the upper part of the Zaonega
498 Formation records a transition from oxic or ferruginous depositional conditions to euxinic
499 conditions. That conclusion was based on the assumption that a complete composite
500 stratigraphic succession of the upper Zaonega Formation was recovered by two cores: core C-
501 5190, ~25 km south of the OnZap cores (see Fig. 1), was inferred to capture the older strata and
502 core C-175, ~40 km south of the OnZap cores, the younger strata. Fe speciation data by those
503 workers indicate oxic or ferruginous conditions for core C-5190 and euxinic conditions for core

504 C-175. However, the inference that the cores represent a composite stratigraphy is questionable.
505 Many workers have documented a 150–200 m thick horizon containing strongly ^{13}C -depleted
506 organic matter ($\delta^{13}\text{C}_{\text{org}} < -30\text{‰}$) across the Onega Basin (Kump et al., 2011; Qu et al., 2012;
507 Strauss et al., 2013; Lepland et al., 2014; Melezhik et al., 2015; Krupenik et al., 2011). In fact,
508 Russian workers have considered it to be a basin-wide correlative marker (e.g., Filippov and
509 Yesipko, 2016). Both cores (C-5190 and C-175) contain ^{13}C -depleted organic matter ($\delta^{13}\text{C}_{\text{org}} <$
510 -30‰), implying that they broadly overlap and are correlative with OnZap Units A and B.
511 Adopting these chemostratigraphic constraints, the available Fe-speciation data are more
512 consistent with spatially variable redox conditions across the Onega Basin, rather than a secular
513 change in redox conditions (c.f., Scott et al., 2014). Until the relationship between cores C-5190
514 and C-175 is better known, especially within the wider stratigraphic context of the Zaonega
515 Formation, their utility for global correlations and environmental interpretations remains
516 limited.

517 In summary, post-depositional alteration most likely modified the iron inventory of Unit A and
518 lower part of Unit B of the OnZap section. Unit C, by contrast, is the least altered and preserves
519 a more primary mineral assemblage. Combining petrographic observations, with up-section
520 trends of decreasing TOC, TS and increasing $\text{Fe}_{\text{T-OES}}$ and Fe-rich dolomite-to-ankerite solid-
521 solution phase contents, as well as the appearance of siderite in Unit C, are consistent with a
522 change toward more variable redox conditions. Integrating our observations with the findings
523 of others indicates that the upper Zaonega Formation inherited its Fe inventory under spatially
524 and temporally variable depositional and diagenetic conditions, as would be expected in a
525 magmatically active and seep-influenced setting. In total, our data indicate that euxinia was not
526 as pervasive in the upper part of the Zaonega Formation as suggested previously (Scott et al.,
527 2014) and, in fact, conditions may have been episodically oxic.

528 **5.4 Biogeochemical sulphur cycling**

529 ***5.4.1 Hydrothermal influence on the Zaonega Formation sulphides***

530 Sulphide minerals in marine settings with active hydrothermal circulation can be produced by
531 several mechanisms and may have sulphur-isotope values that reflect contemporaneous but
532 unrelated processes (Aoyama et al., 2014; Eickmann et al., 2014). For example, modern
533 seawater sulphate is typically marked by positive $\delta^{34}\text{S}$ (+21.5‰) and $\Delta^{33}\text{S}$ (+0.04‰) values
534 (Ono et al., 2012; Johnston et al., 2014; Tostevin et al., 2014; Masterson et al., 2016), whereas
535 deep sourced hydrothermal fluids have values closer to primordial sulphur ($\delta^{33}\text{S} = \delta^{34}\text{S} = \delta^{36}\text{S}$

536 = 0‰; Ono et al., 2006, 2007, 2012). Furthermore, mass-dependent fractionations of up to 4‰
537 in $\delta^{34}\text{S}$ and 0.07‰ in $\Delta^{33}\text{S}$ can be imparted under certain oxygen fugacities and oxidation
538 reactions in magmatic and hydrothermal systems (Fiorentini et al., 2012; Ono et al., 2007;
539 Penniston-Dorland et al., 2012; Ripley et al., 2017). Thus, in a setting such as that in which the
540 Zaonega Formation was deposited, care must be taken when ascribing a pyrite sulphur isotope
541 value to a seawater sulphate source.

542 Several features of our sulphur isotope data, particularly the negative excursions, warrant
543 exploration. A prominent negative $\delta^{34}\text{S}$ excursion to $\sim 0\text{‰}$ within silicified mudstones at 77–
544 70 m depth is accompanied by distinctly positive $\Delta^{33}\text{S}$ values of $\sim +0.05\text{‰}$ (Fig. 6). Three
545 additional negative $\delta^{34}\text{S}$ excursions to values below $+5\text{‰}$ punctuate the OnZap section. These,
546 excursions occur at lithological boundaries between carbonate and mudstone beds at 86, 46 and
547 32 m depth. Of these, those at 85 m and 32 m also exhibit positive $>+0.05 \Delta^{33}\text{S}$ values. Pyrites
548 associated with these shifts have different origins and may reflect different processes in space
549 and time. Euhedral crystals associated with compacted sedimentary laminae, along with minute
550 octahedral pyrite crystals, were precipitated early in unconsolidated sediments. By contrast,
551 large inclusion-rich euhedral crystals that occur with minor sphalerite and pyrrhotite crystals,
552 particularly in Units A and B, suggest later post-depositional pyrite formation as noted also by
553 Asael et al. (2013). There are a variety of explanations for the observed negative S-isotope
554 excursions. For example, the addition of hydrothermally derived sulphur could account for the
555 observed $\delta^{34}\text{S}$ shift toward 0‰ but would not explain a positive shift in $\Delta^{33}\text{S}$ seen in the
556 silicified interval at 77–70 m. Alternatively, there may have been short-lived, more open-system
557 conditions that would have allowed the expression of larger microbially-induced S-isotope
558 fractionation. Otherwise, iron limitation could also have conceivably lowered $\delta^{34}\text{S}$ values by
559 limited sulphide sequestration to the initially produced, and presumably most ^{34}S -depleted,
560 sulphide.

561 We note that post-depositional isotope effects associated with pyrite remobilisation and AVS
562 formation depend on the temperature and oxidation state of the percolating fluid and hence is
563 difficult to constrain precisely (Wagner and Boyce, 2006). With few exceptions, the isotopic
564 composition of AVS is only separated from the CRS by a few per mil, thus the fluids interacting
565 with the Zaonega rocks were sufficiently reducing and were unlikely to have promoted large-
566 magnitude sulphur isotope fractionations during pyrite recrystallisation (Fig. 6). On the other
567 hand, it is possible that recrystallisation homogenised the sulphur isotope composition of the

568 early-formed small pyrite crystals and clusters masking the extreme variability of individual
569 crystals that are characteristic for modern seep environments (Lin et al., 2016).

570 Thermochemical sulphate reduction (TSR) could also serve as a mechanism for precipitating
571 secondary pyrites (Watanabe et al., 2009; Oduro et al., 2011). The Zaonega Formation is
572 underlain by the evaporite-bearing Tulomozero Formation (Reuschel et al., 2012; Blättler et al.,
573 2018). It is possible, therefore, that hydrothermal fluids could have leached sulphur from the
574 underlying evaporites, which could induce precipitation of late-stage pyrite upon reduction in
575 contact with the organic-rich strata of the Zaonega Formation. However, the Tulomozero Ca-
576 sulphate evaporites have $\delta^{34}\text{S}$ values ranging from +6 to +10‰ and $\Delta^{33}\text{S}$ values of ~0‰
577 (Reuschel et al., 2012; Blättler et al., 2018) which are not compatible with the combination of
578 S-isotope values encasing the negative excursions. Although progressive TSR could lead to ^{34}S
579 enrichments of sulphur-bearing fluids and Rayleigh distillation effects (Watanabe et al., 2009).
580 Oduro et al. (2011) demonstrated that TSR is associated with a mass-independent magnetic
581 isotope effect which influence odd-numbered isotope (^{33}S), generating $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ slopes that
582 deviate from thermodynamic predictions ($\Delta^{36}\text{S}/\Delta^{33}\text{S}$ slope of ~7; Ono et al., 2006). Thus, TSR
583 is not consistent with the $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ slope of ~-8 observed in Unit A which is more typical for
584 MSR (Johnston et al., 2005a, 2007).

585 Although the $\Delta^{36}\text{S}-\Delta^{33}\text{S}$ relationship is more scattered in Units B and C, these intervals are
586 relatively low in TOC, AVS is scarce and evidence for post-depositional alteration is infrequent,
587 rendering TSR unlikely. Furthermore, progressive TSR of ascending fluids would cause vertical
588 and lateral $\delta^{34}\text{S}$ and $\Delta^{33}\text{S}$ gradients, which are not observed in the OnZap pyrite record. We do
589 note that, while a magmatic sulphur source for explaining the four negative $\delta^{34}\text{S}$ and positive
590 $\Delta^{33}\text{S}$ excursions is unlikely, ambient seawater percolating in the sediments could have provided
591 a sulphur source, localising TSR for secondary pyrite formation. With the available data, we
592 cannot unequivocally preclude secondary processes, however, their effect appears to have been
593 limited. The four negative $\delta^{34}\text{S}$ shifts can most likely be explained by syndepositional and early
594 diagenetic processes such as changes in the openness of the pore water with respect to the
595 overlying water column or Fe availability. Further investigation by secondary ion mass-
596 spectrometry (SIMS) could test these competing hypotheses, and provide insight beyond the
597 bulk approach leveraged herein.

598 **5.4.2 Carbon and sulphur isotope records of microbial processes**

599 Given the preceding discussion, we interpret the sedimentary pyrites of the upper Zaonega
600 Formation as the product of sediment-hosted MSR, rather than direct precipitates from an
601 euxinic water column (e.g. Scott et al., 2014). Previous work (Qu et al., 2012; Lepland et al.,
602 2014) has shown that the Zaonega sediments were deposited in a magmatically active setting
603 with syndepositional hydrocarbon migration and venting. Such a nutrient replete environment
604 likely sustained microbial activity in the water column, at the seafloor and in the shallow sub-
605 surface, in turn creating sharp chemoclines and a complex seafloor ecosystem of sulphur
606 oxidisers and methanotrophic archaea. Evidence for migrating hydrocarbons is preserved as
607 numerous pyrobitumen veins and nodules that occur variably throughout the Zaonega
608 succession, including the OnZap section (e.g. nodules at 54 m depth). Comparisons of $\delta^{13}\text{C}_{\text{org}}$
609 in the host rock and cross-cutting pyrobitumen veins have demonstrated only minor differences
610 ($< 0.5\%$) in the FAR-DEEP 12AB core indicating a hydrocarbon source in adjacent organic-
611 rich sediments (e.g. Qu et al., 2012, 2018). Far-travelled hydrocarbon migration can be
612 precluded because there is no other known source of highly ^{13}C -depleted material in the Onega
613 Basin. Moreover, thermal cracking of organic matter will exclusively shift the preserved $\delta^{13}\text{C}_{\text{org}}$
614 to more positive values (Hayes, 1983; Lewan, 1983; Clayton, 1991; Schidlowski, 2001), the
615 opposite of what is seen. Thus, it appears likely that the highly ^{13}C -depleted organic matter in
616 Units A and Unit B contains a significant methanotrophic component.

617 As anaerobic methanotrophy coupled to sulphate reduction (anaerobic oxidation of methane;
618 AOM) proceeded, conditions in the diagenetic environment would have become increasingly
619 sulphidic, driving the redox interface closer to the sediment-water interface. A combination of
620 elevated methane and high biomass burial flux will have intensified pore-water sulphate
621 reduction rates, possibly exceeding diffusive replenishment from above (Goldhaber and
622 Kaplan, 1975; Jørgensen, 1979, 2004). Such a scenario would have resulted in the near
623 quantitative uptake of sulphate, muting the fractionation expressed between the initial sulphate
624 and product sulphide. Complete reduction of the available pore water sulphate pool would
625 produce sulphides with $\delta^{34}\text{S}$ values that approximate or even exceed those of the initial seawater
626 sulphate (Pasquier et al., 2017). During the Paleoproterozoic, MSR is thought to have been the
627 main sulphur utilising metabolism (Canfield and Teske, 1996; Johnston et al., 2005b, 2006,
628 2011). Pure culture studies of sulphate reducers have shown that, as MSR proceeds under
629 sulphate limiting conditions, the sulphate $\delta^{34}\text{S}$ values increase whereas the $\Delta^{33}\text{S}$ values decrease
630 relative to the starting sulphate (Johnston et al., 2005a). When plotted on a $\delta^{34}\text{S}$ vs $\Delta^{33}\text{S}$ three-

631 isotope plot, our sulphur isotope data mostly populate quadrant II (Fig. 8), which is indicative
632 of MSR (Johnston et al., 2005a, b, 2007; Sim et al., 2011). This, however, does not necessarily
633 exclude the presence of sulphur oxidisers, since sulphide oxidation results in much smaller
634 sulphur isotope fractionations than MSR and it is possible that the signal for sulphur oxidation
635 was not preserved and/or is masked within the sediments (Balci et al., 2007; Zerkle et al., 2009,
636 2016).

637 We propose that the inverse covariation between pyrite $\delta^{34}\text{S}$ and $\Delta^{33}\text{S}$ and the values that deviate
638 from that trend (i.e. positive $\delta^{34}\text{S}$ and $\Delta^{33}\text{S}$) observed in our data reflect an organic-rich seafloor
639 or shallow subsurface diagenetic environment where sulphate was readily available, but under
640 high demand, and rapidly consumed. Most of our $\delta^{34}\text{S}$ and $\Delta^{33}\text{S}$ values vary from +15‰ to
641 +25‰ and -0.05‰ to -0.02‰, respectively, with some slight variation ($\delta^{34}\text{S}$ $20.2 \pm 3.2\text{‰}$ and
642 $\Delta^{33}\text{S}$ $-0.03 \pm 0.01\text{‰}$, 1σ). Such isotopic stability in sedimentary sulphides requires an almost
643 constant sulphate flux with a uniform isotopic composition. Thus, the sulphate pool had to be
644 large enough to maintain high rates of sulphate reduction. Additionally, there is a clear
645 statistically significant ($p < 0.05$) negative correlation between $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ (Fig. 9): in Unit
646 A, $\Delta^{36}\text{S} = -7.66 * \Delta^{33}\text{S} - 0.08$, $R^2 = 0.75$; in Units B and C $\Delta^{36}\text{S} = -4.10 * \Delta^{33}\text{S} - 0.15$, $R^2 = 0.46$. These
647 small magnitude $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ values, and the observed co-variation between $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$,
648 approximate the theoretically predicted $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ ratio for mass-dependent low-temperature
649 processes (~ -7 ; Ono et al., 2006; Farquhar et al., 2007; Johnston et al., 2007). Moreover,
650 although the $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ array recorded in Unit A deviates slightly from the equilibrium
651 prediction, it is in the range of values measured for sulphate reduction in natural settings
652 (between -11 and -5; Johnston et al., 2007, 2008) and is thus consistent with MSR being the
653 dominant active sulphur-utilising metabolism in the lower part of the OnZap section. Given that
654 closed-system isotope effects may influence the relationship between $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$, whilst
655 generating large variability in $\delta^{34}\text{S}$ (Ono et al., 2006; Johnston et al., 2007), the up-section
656 increase in the $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ ratios (~ -4 in Units B and C) could relate to such effects.

657 ***5.4.3 Conditions during deposition of relatively organic-poor Unit C***

658 Unit C, the uppermost interval of the OnZap cores, represents a newly recovered and unstudied
659 part of the Zaonega Formation. This ca. 25-m-thick interval is marked by parallel-laminated to
660 ripple cross-laminated grey mudstones and dolostone beds that are less organic-rich than those
661 in underlying units. Unit C also lacks evidence for hydrocarbon generation or migration. There
662 is a slight trend towards more positive $\delta^{34}\text{S}$ values accompanied by a positive shift in $\delta^{13}\text{C}_{\text{org}}$
663 from -38‰ to -25‰ and a decrease in TOC and TS. We interpret this trend as indicating a

664 decreasing contribution from methanotrophic biomass in favour of more typical CO₂-fixing
665 autotrophic biomass contributing to the C-isotopic signatures of Unit C. As the hydrocarbon
666 flux decreased, sulphate reducing microbes capable of utilising both methane (AOM) and
667 organic carbon as electron donors (Joye et al., 2004), could have switched to solely organic
668 carbon. Despite changes in the microbial community, the TOC content in Unit C (≤ 3 wt.%) is
669 sufficiently high to have sustained sulphate reduction. A waning hydrocarbon flux would have
670 shifted the redox interface deeper into the sediments where the availability of labile organic
671 matter, iron concentrations and connectivity of pore waters to the overlying water column could
672 have influenced sulphate reduction rates and the extent of S isotope fractionation between
673 sulphate and sulphide (Zaback et al., 1993; Sim et al., 2011; Fike et al., 2015). The most variable
674 $\delta^{34}\text{S}$, $\Delta^{33}\text{S}$, $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ ratios and the highest ³⁴S-enrichments (outside Unit A) are found in Unit
675 C. These may represent Rayleigh-type effects either in the sediments or indicate episodes of at
676 least partial basinal isolation from the open ocean.

677 Most pyrites from the OnZap section exceed the lower estimate for SWS isotope composition
678 of $\delta^{34}\text{S} \sim +10\text{‰}$ and $\Delta^{33}\text{S} \sim 0\text{‰}$ derived from the underlying Ca-sulphate evaporites of the
679 Tulomozero Formation (Reuschel et al., 2012; Blättler et al., 2018). In ancient pyrite records,
680 sulphides with $\delta^{34}\text{S}$ values that exceed SWS are typically interpreted to reflect enhanced pyrite
681 burial or changes in the marine sulphate reservoir (Goldhaber and Kaplan, 1975; Johnston et
682 al., 2006, 2008; Gomes and Hurtgen, 2013; Fike et al., 2015). However, it has been highlighted
683 that the decoupling of pore water and seawater sulphate reservoirs via sedimentary and
684 diagenetic mechanisms can also produce highly ³⁴S-enriched pyrites approaching and, rarely,
685 even exceeding the seawater $\delta^{34}\text{S}$ value (Aller et al., 2010; Fike et al., 2015; Pasquier et al.,
686 2017). Within the tectonically active Onega Basin it is likely that a combination of changes in
687 microbial metabolic activity and sulphate mobility into the sediment pile resulted in the near
688 quantitative reduction of sulphate into sulphide.

689 The Onega Basin has experienced major variations in basinal configuration throughout its
690 history. Lower part of the underlying Tulomozero Formation with >800 m thick evaporate
691 succession revealed in Onega Parametric Hole captures one of such episodes in Onega Basin
692 history where a restricted marine embayment with sabkha/coastal plain was developed
693 (Krupeinik et al., 2011; Blättler et al., 2018). The exact palaeogeography of the Onega Basin
694 during Zaonega time is not known but it is possible that episodic volcanic activity could have
695 created barriers that impeded water mass exchange between the Onega Basin and the open
696 ocean. In such a setting, it is conceivable that constriction of the hydrographic connection

697 between the Onega Basin and the wider global ocean would result in a smaller sulphate reservoir
698 that would be more susceptible to sulphate drawdown and closed-system effects (e.g. Gomes,
699 2013; Fike et al., 2015). The occurrence of abundant Fe-rich dolomite to ankerite solid-solution
700 phase and siderite in Unit C might also imply a limited sulphate pool (Moore et al., 1992). Such
701 conditions would result in low pore water sulphide availability that would favour Fe²⁺
702 incorporation into carbonate phase(s). Speculatively, the four $\delta^{34}\text{S}$ positive excursions in the
703 OnZap section, rising from $\sim+20\text{‰}$ to $>+30\text{‰}$, followed by a return to $\sim+20\text{‰}$, could represent
704 such repeated expansions and contractions in the sulphate reservoir in pore waters and/or the
705 overlying seawater.

706 Thus, changes in microbial metabolic rates and communities, pore water connectivity and
707 basinal sulphate concentrations may all be imprinted into the Zaonega Formation C_{org}- and S-
708 isotope record. Previous workers have used the latter to argue for a postulated decrease in
709 atmospheric oxygen driving a decrease in global SWS concentrations (e.g. Scott et al., 2014).
710 Our new and more comprehensive geochemical dataset offers an alternative explanation, one
711 not dependent on equivocal assumptions about long-distance correlations and assumed
712 temporal equivalence. We argue that the relatively consistent pyrite $\delta^{34}\text{S}$ ($\sim 20\text{‰}$) and $\Delta^{33}\text{S}$ ($-$
713 0.03‰) values are best explained by a stable flux of sulphate into the sediments and rapid MSR.
714 These conditions would track fluctuations in basinal sulphate isotope composition and, thus,
715 the Zaonega sulphur isotope record is most parsimoniously explained as reflecting local (basin-
716 scale) conditions under closed-system behaviour rather than a global-scale phenomenon.

717 **7. Conclusions**

718 Detailed lithological, mineralogical and geochemical observations of the recently drilled 102-
719 m thick OnZap core encompassing the upper Zaonega Formation show that the organic-rich
720 mudstones and carbonate beds in the lower part of the section were deposited coevally with
721 mafic volcanism. This created a dynamic setting of high heat flux, hydrocarbon migration and
722 abundant nutrients that stimulated microbial activity within the sediments. In the lower Zaonega
723 Formation elevated TOC, TS, abundant sulphide minerals and ¹³C-depleted organic matter
724 ($\delta^{13}\text{C}_{\text{org}} < -30\text{‰}$) are all consistent with basin-wide methanotrophy and a high sulphate demand.
725 High rates of pore-water MSR fuelled quantitative conversion of sulphate to sulphide causing
726 pyrite to become increasingly enriched in ³⁴S and approach the $\delta^{34}\text{S}$ of the precursor sulphate.
727 In contrast, the finely laminated grey mudstone and marly dolostone beds in the uppermost part
728 of the Zaonega Formation record more variable redox conditions in a partially isolated/closed-

729 system basin setting. The decrease in TOC and TS abundances and less negative $\delta^{13}\text{C}_{\text{org}}$ at the
730 top of the section likely reflect changes in the microbial community, as methanotrophs were
731 superseded by CO₂-fixing autotrophs in response to a waning hydrocarbon flux. The excursion
732 towards $\delta^{34}\text{S}$ values that exceed +30‰ are best interpreted as recording changing basinal
733 conditions rather than changes in global seawater sulphate concentrations. Our findings
734 highlight the culmination of microbial and basin-specific processes (magmatic activity,
735 hydrocarbon seepage, sedimentary processes and basinal restriction), suggesting that these
736 local- to regional-scale processes dominated the sulphur isotope record of the Paleoproterozoic
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1058 **Figure captions**

1059 **Figure 1.** A. Simplified geological map of the Onega basin, NW Russia. Circles show locations
1060 of the OnZap 1 and 3 holes, FAR-DEEP holes 12AB, 13A, Onega Parametric Hole (OPH) and
1061 the C-175 and C-5190 holes. Inset map shows location of the Onega basin and occurrence of
1062 Paleoproterozoic rocks (black) across the eastern Fennoscandian Shield. B. Simplified
1063 geological map of the Zaonega Formation (after Melezhik et al., 2013a) near locations of OnZap
1064 1 and 3 holes and FAR-DEEP hole 13A.

1065 **Figure 2.** Representative images of the OnZap cores. A. Fine-grained laminated mudstone with
1066 pyrite concretions and layers (11.8 m depth). B. Laminated fine-grained dolostone (13.4 m
1067 depth). C. Finely parallel-laminated to ripple cross-laminated grey mudstone (19.38 m depth).
1068 D. Laminated organic-rich mudstone with soft-sediment deformation, quartz and pyrobitumen
1069 veining (63.4 m depth). E. Silicified organic-rich mudstone displaying deformation, intense
1070 veining and secondary pyrite (76.5 m depth). The width of all the images is 7 cm.

1071 **Figure 3.** Scanning Electron Microscopy (SEM) images of different textural types of pyrite. A.
1072 Organic-rich mudstone containing ellipsoidal clusters of fine pyrite crystals at 53.78 m depth;
1073 early diagenetic origin is indicated by the deflection of laminae around the clusters. B. Organic-
1074 rich mudstone with abundant fine pyrite crystals at 56.66 m depth. C. Close-up of fine-grained
1075 pyrite in image 3B containing inclusions of surrounding material in the central parts of the

1076 crystals. D. SEM EDS element composite map of large anhedral pyrite in a calcareous mudstone
1077 that appears texturally co-genetic with calcite at 26.8 m depth.

1078 **Figure 4.** Generalised lithostratigraphic profile of the OnZap section divided into Units A to C
1079 (see text for details) and XRD-derived distributions of select mineral phases. The two OnZap
1080 cores are correlated using the base of a dolomite-chert unit occurring at 53 m in OnZap1 and at
1081 10.8 m in OnZap3. Horizontal grey-shaded bars show intervals with evidence for secondary
1082 alteration. Grey and black data points denote samples from OnZap 1 and OnZap 3, respectively.

1083 **Figure 5.** Generalised lithostratigraphic profile of the OnZap section divided into Units A to C
1084 (see text for details) plotted alongside selected components (TOC; TS; Fe₂O₃; SiO₂; Al₂O₃ and
1085 K₂O). The two OnZap cores are correlated using the base of a dolomite-chert unit occurring at
1086 53 m in OnZap1 and at 10.8 m in OnZap3. Horizontal grey-shaded bars show intervals with
1087 evidence for secondary alteration. Grey and black data points denote samples from OnZap1 and
1088 OnZap3, respectively.

1089 **Figure 6.** Generalised lithostratigraphic profile of the OnZap section divided into Units A to C
1090 (see text for details) plotted alongside carbon and sulphur isotope data and XRD-derived iron
1091 distribution data. The two OnZap cores are correlated using the base of a dolomite-chert unit
1092 occurring at 53 m in OnZap1 and at 10.8 m in OnZap3. Horizontal grey-shaded areas show
1093 intervals with evidence for secondary alteration. Grey and black data points denote samples
1094 from OnZap 1 and OnZap 3, respectively, whereas blue dots represent AVS results. Errors for
1095 the $\delta^{13}\text{C}_{\text{org}}$ and $\delta^{34}\text{S}$ are encompassed within the data points whereas the grey-shaded envelope
1096 illustrates the 1σ estimates of the analytical uncertainty for the $\Delta^{33}\text{S}$ (0.015‰) and $\Delta^{36}\text{S}$ (0.2‰)
1097 data.

1098 **Figure 7.** Sulphur (TS) and iron (Fe_{T-OES}) concentrations for the entire OnZap section. Black
1099 circles are derived from Unit A, grey circles from Unit B and orange circles from Unit C. Errors
1100 are encompassed within each data point.

1101 **Figure 8.** Triple-isotope plot of the pyrite sulphur isotope data for the entire OnZap section.
1102 Black circles are derived from Unit A, grey circles from Unit B and orange circles from Unit
1103 C. Uncertainties in the $\Delta^{33}\text{S}$ values (0.015‰) are illustrated in grey, whereas the uncertainty in
1104 $\delta^{34}\text{S}$ values are encompassed within each data point.

1105 **Figure 9.** Quadruple-isotope plot of the pyrite sulphur isotope data for the entire OnZap section.
1106 Black circles are derived from Unit A and orange circles are from Units B and C. The dashed

1107 lines are regressions through the datasets derived from Unit A (-7.66; black) and Units B and
1108 C (-4.10; orange). The analytical uncertainties (1σ) in both $\Delta^{33}\text{S}$ (0.015‰) and $\Delta^{36}\text{S}$ (0.2‰) are
1109 illustrated in grey.

1110 **Supplementary table captions**

1111 **Supplementary table 1.** Sulphur and organic carbon isotope data for the OnZap1 and OnZap3
1112 drill cores from the upper Zaonega Formation, NW Russia.

1113 **Supplementary table 2.** Sulphur and carbon contents of the OnZap1 and OnZap3 drill cores
1114 from the upper Zaonega Formation, NW Russia. *Inorganic carbon (IC) abundances were
1115 calculated as the difference between TC and TOC.

1116 **Supplementary table 3.** Mineralogical composition of whole rock samples and iron
1117 distribution in different mineral phases for the OnZap1 and OnZap3 drill cores from the upper
1118 Zaonega Formation, Onega Basin, NW Russia.

1119 **Supplementary table 4.** Major element composition for the OnZap1 and 3 drill cores, from the
1120 upper Zaonega Formation, Onega Basin, NW Russia.

1121 **Supplementary figure**

1122 **Supplementary figure 1.** Comparison of the calculated $\text{Fe}_{\text{T-XRD}}$ and total Fe determined by
1123 ICP-OES ($\text{Fe}_{\text{T-OES}}$). The $\text{Fe}_{\text{T-OES}}$ and $\text{Fe}_{\text{T-XRD}}$ converge on a trend line with a slope of 1.1053
1124 and $R^2 = 0.92$.