

1 **Oxygenated conditions in the aftermath of the Lomagundi-Jatuli Event:**
2 **The carbon isotope and rare earth element signatures of the**
3 **Paleoproterozoic Zaonega Formation, Russia**

4 T. Kreitsmann^{1*}, A. Lepland^{1,2,3}, M. Bau⁴, A. Prave⁵, K. Paiste^{1,2}, K. Mänd^{1,6}, H. Sepp¹, T.
5 Martma⁷, A. E. Romashkin⁸, K. Kirsimäe¹

6 ¹Department of Geology, University of Tartu, 50411 Tartu, Estonia.

7 ²CAGE—Centre for Arctic Gas Hydrate, Environment and Climate, Department of
8 Geosciences, UiT The Arctic University of Norway, 9037 Tromsø, Norway.

9 ³Geological Survey of Norway (NGU), 7491 Trondheim, Norway.

10 ⁴Department of Physics and Earth Sciences, Jacobs University Bremen, Campus Ring 1,
11 28759 Bremen, Germany

12 ⁵School of Earth and Environmental Sciences, University of St Andrews, St Andrews, KY16
13 9AL Scotland.

14 ⁶Department of Earth & Atmospheric Sciences, University of Alberta, Edmonton, Alberta
15 T6G 2E3, Canada.

16 ⁷Department of Geology, Tallinn University of Technology, Ehitajate tee 5, 19086 Tallinn,
17 Estonia

18 ⁸Institute of Geology, Karelian Science Centre, Pushkinskaya 11, 185610 Petrozavodsk,
19 Russia.

20 *Corresponding author: email timmu.kreitsmann@ut.ee

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23

24 **Abstract**

25 The c. 2.0 Ga Zaonega Formation of the Onega Basin (NW Russia) has been central in efforts
26 to understand what led to the initial rise (Great Oxidation Event, GOE) and postulated fall in
27 free atmospheric oxygen and associated high-amplitude carbon cycle excursions, the
28 Lomagundi-Jatuli Event (LJE) and subsequent Shunga Event during Paleoproterozoic time.
29 The Formation accumulated shortly after the LJE and encompasses both the recovery in the
30 carbon cycle and hypothesised contraction of the oceanic oxidant pool. However, interpreting
31 the correct environmental context recorded by geochemical signatures in the Zaonega rocks is
32 difficult due to a complex depositional and diagenetic history. In order to robustly constrain
33 that history, we undertook a multiproxy study (mineralogy, petrography, carbon isotope and
34 rare earth element composition) of carbonate beds in the upper part of the Zaonega Formation
35 recovered in the 102-m composite section of the OnZap drill-cores. Our findings differentiate
36 primary environmental signatures from secondary overprinting and show that: (i) the best-
37 preserved carbonate beds define an upwards increasing $\delta^{13}\text{C}_{\text{carb}}$ trend from c. -5.4‰ to near
38 0‰; and that (ii) large intra-bed $\delta^{13}\text{C}_{\text{carb}}$ variations reflect varying contributions of
39 methanotrophic dissolved inorganic carbon (DIC) to the basinal DIC pool. Rare earth element
40 and yttrium (REY_{SN}) patterns confirm a marine origin of the carbonate beds whereas a
41 consistent positive Eu_{SN} anomaly suggests a strong high temperature hydrothermal input during
42 accumulation of the Zaonega Formation. Importantly, the presence of a negative Ce_{SN} anomaly
43 in the REY_{SN} pattern indicates an oxygenated atmosphere-ocean system shortly after the LJE
44 and indicates that models invoking a fall in oxygen at that time require reassessment.

45

46 **Keywords:** carbon isotopes, rare earth elements, Lomagundi-Jatuli Event, Ce anomaly,
47 Zaonega Formation

48 **1. Introduction**

49 Throughout most of Earth history the sedimentary carbonate carbon isotope record ($\delta^{13}\text{C}_{\text{carb}}$)
50 has been relatively stable at around 0‰, reflecting an overall balance between carbon pools
51 and sinks (Schidlowski, 2001). However, this trend is punctuated by several prominent
52 excursions, one of the largest being the Lomagundi-Jatuli Event (LJE) at 2.22 – 2.06 Ga
53 (Bekker and Holland, 2012; Karhu and Holland, 1996; Schidlowski et al., 1976). It followed
54 and partly overlapped the Great Oxidation Event (GOE) and is characterised by the formation
55 of ^{13}C -enriched carbonates with $\delta^{13}\text{C}_{\text{carb}}$ values reaching 15‰ (Bekker and Holland, 2012;
56 Karhu and Holland, 1996). In several Paleoproterozoic basins, such as the Onega and Pechenga
57 Basins in Fennoscandia and the Francevillian Basin in Gabon, the LJE-bearing carbonate rocks
58 are overlain by rocks highly enriched in organic matter (commonly >10% TOC; Asael et al.,
59 2013; Kump et al., 2011; Melezhik et al., 1999; Pr at et al., 2011; Strauss et al., 2013); this
60 remarkable burial of organic matter is known as the Shunga Event (SE; Strauss et al., 2013).

61 Both the LJE and SE are consequences of the dramatic changes in atmosphere-ocean
62 chemistry and oxygenation that marked the Paleoproterozoic (Bekker and Holland, 2012;
63 Holland, 2006; Kasting, 2001; Lyons et al., 2014). Different workers using datasets often
64 derived from the same carbonate and organic-rich rock successions have arrived at varying to
65 contradictory interpretations of the causal mechanisms that generated these perturbations of the
66 carbon cycle. For the SE, some workers interpret Fe-speciation, C-, Mo- and S-isotope and
67 trace element data as evidence that a global collapse in atmospheric oxygen occurred, leading
68 to contraction of seawater sulfate levels and a worldwide ocean anoxia (Asael et al., 2013,
69 2018; Bekker and Holland, 2012; Canfield et al., 2013; Partin et al., 2013; Ossa Ossa et al.,
70 2018; Planavsky et al., 2012; Scott et al., 2014). Others have put forward that weathering of
71 organic-rich rocks under an oxygenated atmosphere resulted in a flux of isotopically light
72 carbon into the world's oceans (Kump et al., 2011), with some workers pointing out that the

73 high concentration of redox-sensitive elements and elevated U isotope ratios in those rocks are
74 indicative of prolonged elevated O₂ levels throughout SE time (Mänd et al., 2020; Sheen et al.,
75 2018). Still others have used organic and carbonate carbon isotope and sulphur isotope signals
76 to infer that the isotope perturbations in key SE successions are due to basin-specific, not
77 global, conditions including diagenetic and hydrothermal overprinting and methanotrophy
78 (Črme et al., 2014; Kreitsmann et al., 2019; Paiste et al., 2018; Qu et al., 2012, 2018).

79 Central to many of these studies have been the rocks of the Paleoproterozoic Onega
80 Basin in NW Russia, specifically the Zaonega Formation recording the SE and the underlying
81 Tulomozero Formation recording the LJE (Fig. 1; Melezhik et al., 2015). Here we report new
82 stable carbon isotope, and rare earth element and yttrium (REY) data underpinned by detailed
83 petrographic and mineralogical characterisation of carbonate rocks in the upper Zaonega
84 Formation to study the paleoenvironmental and redox states of the atmosphere-ocean system
85 spanning this intriguing interval of Earth history. Contrary to several studies that have inferred
86 de-oxygenation in the upper Zaonega Formation, we find that carbonate rocks bearing post-
87 LJE $\delta^{13}\text{C}$ signatures contain Ce anomalies suggestive of continuing ocean-atmospheric
88 oxygenation.

89

90 **2. Geological background**

91 The Onega Basin consists of a volcanic and sedimentary succession formed between c. 2440 –
92 1890 Ma (Melezhik et al., 2015). The Zaonega Formation is in the upper part of that succession
93 and contains the type locality – the village of Shunga – of the SE. Its lower part consists of
94 rhythmically interbedded, fine-grained greywacke and mudstone and the upper part is organic-
95 rich mudstone, siltstone, calcareous mudstone and dolostone (Črme et al., 2013, 2014).
96 Contemporaneous with sedimentation was magmatic activity, as evidenced by lavas between

97 sedimentary packages and sills with peperite contacts (Črne et al., 2014; Qu et al., 2012). The
98 Zaonega Formation rests depositionally on the Tulomozero Formation which records the
99 positive $\delta^{13}\text{C}_{\text{carb}}$ excursion of the LJE (Brasier et al., 2011; Karhu, 1993) and is overlain by the
100 mafic and ultramafic lavas of the Suisari Formation. During the 1890 – 1790 Ma Svecofennian
101 orogeny, the succession experienced greenschist facies metamorphism (Melezhik et al., 1999).

102 Strongly positive $\delta^{13}\text{C}_{\text{carb}}$ values that typify the LJE occur in carbonate rocks in the
103 lower part of the Zaonega Formation (Melezhik et al., 2015) whereas the best-preserved $\delta^{13}\text{C}_{\text{carb}}$
104 values in the upper part of the Formation are at c. 0‰ (Črne et al., 2014; Kreitsmann et al.,
105 2019). This indicates that the Formation records the decline and termination of the LJE, which
106 in Fennoscandia occurred at 2.06 Ga (Karhu and Holland, 1996; Martin et al., 2013; Melezhik
107 et al., 2007) and provides a maximum age of deposition. The lower age limit is best constrained
108 by the 1988 ± 34 Ma age of a gabbro in the overlying Suisari Formation (Puchtel et al., 1999).
109 A U-Pb zircon age obtained by Martin et al. (2015) from a thin tuff bed (c. 5 cm thick)
110 interbedded with organic-rich mudstones in the lower to middle part of the Zaonega Formation
111 define a depositional age of 1982 ± 4.5 Ma.

112 The Zaonega Formation contains extremely organic-rich rocks (locally termed
113 shungite) with an average organic C content of c. 25% but reaching 98% in pyrobitumen veins
114 (Melezhik et al., 1999). $\delta^{13}\text{C}_{\text{org}}$ data define a profile in which values of c. -25‰ bracket an
115 excursion to as low as c. -40‰ in the middle and upper part of the Formation (Melezhik et al.,
116 1999; Paiste et al., 2018; Qu et al., 2012). Whether this accumulation of organic matter and the
117 associated $\delta^{13}\text{C}_{\text{org}}$ excursion were synchronous and global (Kump et al., 2011; Ossa Ossa et al.,
118 2018; Scott et al., 2014) or a consequence of temporally discrete basin-specific depositional
119 episodes (Lepland et al., 2014; Martin et al., 2015; Paiste et al., 2018; Qu et al., 2012, 2018)
120 remains debated.

121 **3. Material and Methods**

122 Samples were collected from dolostones and calcareous mudstones recovered in the OnZap1
123 (62.5870 N, 34.9310 E) and OnZap3 (62.5920 N, 34.9280 E) drill-cores from near the village
124 of Shunga, Karelia, NW Russia (Fig. 1); they define a 102-m-thick composite section through
125 the upper Zaonega Formation (for detailed information see Paiste et al., 2018). A total of 500
126 samples were taken for carbonate C and O isotope measurements by means of micro-drilling.
127 Internal parts of carbonate beds were sampled at 10 cm spacing whereas sampling density
128 increased to 2 to 5 cm approaching the bed contacts with the enclosing siliciclastic strata and
129 cross-cutting silica veins.

130 Carbonate O and C stable isotope compositions of the samples were analysed using a
131 Thermo Scientific Delta V Advance continuous flow isotope ratio mass spectrometer and a
132 GasBench II preparation line connected to a Delta V Advantage IRMS (Thermo Fisher
133 Scientific) at the University of Tartu and Tallinn University of Technology. The results of
134 carbonate mineral analyses are expressed in *per mil* deviation relative to the Vienna PeeDee
135 Belemnite (VPDB) scale for oxygen ($\delta^{18}\text{O}$) and carbon ($\delta^{13}\text{C}$). Long term reproducibility
136 exceeded $\pm 0.2\text{‰}$ (2σ) for $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values. The $\delta^{18}\text{O}$ values were corrected for the
137 phosphoric acid fractionation factor for calcite and dolomite (Rosenbaum and Sheppard, 1986)
138 in accordance with sample mineralogy.

139 Splits of micro-drilled samples were used for studying the mineralogical composition
140 by means of X-ray diffractometry (XRD) at the University of Tartu. Unoriented preparations
141 were scanned on a Bruker D8 Advance diffractometer using Cu $K\alpha$ radiation and LynxEye
142 positive sensitive detector in $2\text{--}70^\circ$ 2Θ range. Quantitative mineralogical composition was
143 modelled using the Rietveld algorithm-based software, Topaz. The relative error of

144 quantification is better than 10% for major phases (>5 wt.%) and better than 20% for minor
145 phases (<5 wt.%).

146 Thin sections and polished slabs of selected samples were studied using a ZEISS EVO
147 MA15 scanning electron microscope (SEM). Chemical characterisation (point analyses and
148 elemental mapping) was carried out with an Oxford AZTEC-MAX energy dispersive
149 spectroscopy detector (EDS) attached to the SEM at the University of Tartu.

150 Twenty-nine micro-drilled samples were chosen for major and trace element analyses
151 at Jacobs University Bremen. The samples were selected to span the entire OnZap section and
152 to include different carbonate mineralogies. For analyses, 0.1 g of sample was measured and
153 left to dry overnight at 105 °C. Dried samples were dissolved at high pressure at a temperature
154 of c. 165 °C in an acid mixture of suprapure concentrated 3 ml HCl, 1 ml HNO₃ and 1 ml HF
155 for 16 hours using a Picotrace digestion system. The acid-sample mixture was then evaporated
156 twice by adding 5 ml suprapure concentrated HCl followed by additional dissolving in 0.5 M
157 HNO₃. Major elements were measured with inductively coupled plasma optical emission
158 spectrometry (ICP-OES) and trace elements with inductively coupled plasma mass
159 spectrometry (ICP-MS). A dolomite standard reference material JDo-1 was used to monitor
160 analytical quality. The REY concentrations were normalised against Post Archean Australian
161 Shale (PAAS; Taylor and McLennan, 1985, except Dy from McLennan, 1989). The subscript
162 “SN” denotes shale normalised values. Elemental anomalies were calculated in a linear method
163 after Bau and Dulski, (1996) and Bolhar et al. (2004) and the bell-shape index (BSI) after
164 Tostevin et al., (2016; Eq. 6) using the following equations:

$$165 \quad (La/La^*)_{SN} = \frac{La_{SN}}{(3Pr_{SN} - 2Nd_{SN})} \quad (\text{Eq. 1})$$

$$166 \quad (Ce/Ce^*)_{SN} = \frac{Ce_{SN}}{(0.5La_{SN} + 0.5Pr_{SN})} \quad (\text{Eq. 2})$$

167
$$(Pr/Pr^*)_{SN} = \frac{Pr_{SN}}{(0.5Ce_{SN}+0.5Nd_{SN})} \quad (\text{Eq. 3})$$

168
$$(Gd/Gd^*)_{SN} = \frac{Gd_{SN}}{(2Tb_{SN}+Dy_{SN})} \quad (\text{Eq. 4})$$

169
$$(Eu/Eu^*)_{SN} = \frac{Eu_{SN}}{(0.67Sm_{SN}+0.33Tb_{SN})} \quad (\text{Eq. 5})$$

170
$$BSI = \frac{2*(Sm_{SN}+Gd_{SN}+Dy_{SN})/3}{(La_{SN}+Pr_{SN}+Nd_{SN})/3 + (Ho_{SN}+Er_{SN}+Tm_{SN}+Yb_{SN}+Lu_{SN})/5} \quad (\text{Eq. 6})$$

171

172 **4. Results**

173 **4.1. Mineralogy and petrography**

174 As defined in Paiste et al. (2018), we adopt the division of the OnZap section into three units:
 175 Unit A from depth 102 to 53 m is composed of black organic-rich mudstone, calcareous
 176 mudstone and dolostone; Unit B from depth 53 – 33 m consists of dolostone interlayered with
 177 organic-rich mudstone; and Unit C from 33 – 1.7 m depth is characterised by grey, organic-
 178 poor mudstone and marl (Fig. 2). In total, the OnZap section contains 11 carbonate-bearing
 179 intervals that have distinct geochemical patterns, mineralogy and petrography (Table 1).

180 Unit A has five carbonate intervals. A5 is dolomitic (dolomite content up to 89.5 wt.%),
 181 A2 and A3 are calcitic (up to 75.7 wt.%) and A1 and A4 have mixed carbonate mineralogy.
 182 Dolomite is characterised by fine-grained aggregates, 20 – 40 µm in size, of planar-s crystallites
 183 with minor Fe (Fig. 3A and B). In A5 dolospar is present as planar-s to nonplanar locally zoned
 184 crystallites 200 – 300 µm in size that have undergone dedolomitisation (Fig. 3C). Calcite occurs
 185 in three forms: (i) fine-grained (<100 µm in diameter) euhedral crystals (Fig. 3D); (ii)
 186 macroscopically visible poikilitic aggregates that have many inclusions of host-rock minerals
 187 (Fig. 3E); (iii) masses of anhedral calcite replacing dolomite (Fig. 3C, F). The calcareous

188 mudstones in Unit A contain significant amounts of micas, quartz, feldspar and talc (Fig. 2,
189 Supplementary Table 1).

190 In Unit B, there are three carbonate intervals. B1 is marked by massive dolospar beds
191 interlayered with organic-rich mudstones and is associated with secondary hydrothermal
192 silicification. The internal parts of the beds consist of relatively pure dolomite (up to 94.8 wt.%)
193 but calcite content increases towards bed margins to as high as 83.5 wt.% (Fig. 2, Table 1). B2
194 is a calcareous mudstone with calcite occurring in three forms: small (20 – 40 μm) subhedral
195 crystals with mica rims and some with quartz grain cores; large (>1 mm) calcite crystals as
196 early formed aggregates (laminae are compacted around the aggregates); or calcite aggregates
197 that cross-cut laminae and contain mica. Interestingly, some of the calcite is well-rounded
198 suggesting that it was reworked and transported as a sedimentary particle. B3 is also marked
199 by massive dolomite but with less secondary hydrothermal alteration. Dolomite textures in Unit
200 B vary from planar-e (Fig. 4A) and planar-s (Fig. 4B) to nonplanar crystals including, in rare
201 cases, void-filling dolomite crystals (Fig. 4C). Dolomite crystals are between 200 – 400 μm in
202 size, zoning is rare and Fe content does not vary as much as in the other units. Calcite in B1
203 and B3 intervals form large anhedral aggregates that replace and/or surround dolomite (Fig.
204 4D).

205 Three carbonate intervals occur in Unit C, all of which contain abundant Fe-rich
206 ankerite-dolomite solid-solution minerals (Fig. 5 and 6) characterised by planar-e to planar-s
207 zoned rhombohedral crystals (Fig. 5A, B and C) marked by varying Mg, Fe and, to lesser
208 extent, Mn concentrations (Fig. 5C). Calcite is rare and does not exceed 12 wt.%. C1 contains
209 secondary Fe-rich dolomite aggregates with crystals 20 – 40 μm in size. C3 has also siderite,
210 up to a concentration of 7.6 wt.% (Supplementary table 1). Siderite occurs as anhedral
211 aggregates, ~0.5 mm in size, commonly surrounded by pyrite, and many aggregates contain
212 inclusions of partially dissolved dolomite rhombs (Fig. 5D). Unlike Units A and B in which

213 carbonate cement is mostly calcite, Unit C is marked by an Fe-rich dolomitic cement and the
214 concentration of Fe increases upward from C1 to C3.

215 **4.2. Carbonate $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ isotopes**

216 Although carbonate $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values exhibit large variation (Fig. 2, Supplementary Table
217 1), the overall trend is one in which both increase upward through the Zaonega Formation and
218 then decline slightly in the uppermost strata. In most instances, higher $\delta^{13}\text{C}_{\text{carb}}$ values occur in
219 the interior parts of carbonate beds and decrease toward bed margins; in B1 and to some extent
220 in A4 and A5 this change is also accompanied by increasing calcite abundance. The exceptions
221 to this pattern are A1 and A2, where $\delta^{13}\text{C}_{\text{carb}}$ values increase towards the bed margins (Fig. 7),
222 and A3, where values remain relatively constant around $-10.2 \pm 1.0\text{‰}$.

223 In Unit A, $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{18}\text{O}$ values for dolomite-rich (calcite wt.% to total carbonate
224 wt.% ratio <0.2) samples range between -13.9‰ and -6.0‰ , and -13.8‰ and -11.2‰ ,
225 respectively (Fig. 8). For calcite-rich (calcite wt.% to total carbonate wt.% ratio >0.8) samples,
226 $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{18}\text{O}$ values are between -25.3‰ and -8.6‰ and -14.7‰ and -10.4‰ , respectively
227 (Fig. 8).

228 In Unit B, isotope values also show large variability but, in general, $\delta^{13}\text{C}_{\text{carb}}$ increases
229 from -12.8‰ to -1.0‰ in B1, decreases back to -16.4‰ in the calcareous mudstones of B2 and
230 then increases to near 0‰ in B3 (Fig 2). The $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{18}\text{O}$ values in dolomite-rich samples
231 are between -12.6‰ and -0.9‰ (outliers as low as -18.9‰), and -14.7‰ to -8.6‰ (outliers as
232 high as -5.2‰), respectively. In calcite-rich samples, $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{18}\text{O}$ values vary between -
233 16.4‰ and -6.3‰ , and -14.0‰ and -12.5‰ (one outlier at -10.6‰), respectively (Fig. 8).

234 The C1 interval exhibits variable $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{18}\text{O}$ values between -11.3‰ and $+0.8\text{‰}$,
235 and -11.1‰ and -5.8‰ , respectively. In C2, $\delta^{13}\text{C}_{\text{carb}}$ values decrease from -2.9‰ to -6.2‰ and
236 $\delta^{18}\text{O}$ values from -10.9‰ to -13.4‰ towards the top of C3 (Fig. 2).

237 4.3. Major and trace elements

238 Major and trace element concentrations are shown in Supplementary Table 2. In Unit A, Fe
239 content varies between 0.3 and 3.6 wt.%, in Unit B between 0.06 and 1.1 wt.% and in Unit C
240 between 4.8 and 6.1 wt.%. Manganese content shows a similar trend as Fe, with the lowest
241 concentrations in Unit B and the highest in Unit C: 0.05 to 0.13 wt.% and 0.32 to 0.68 wt.%,
242 respectively. In Unit A, Mn concentrations are between 0.09 and 0.3 wt.%.

243 Each unit has distinctive REY_{SN} patterns (Supplementary Table 3). In Unit A (n=13),
244 the total REE (Σ REE) concentrations range between 19.19 and 159.16 ppm (mean $46.79 \pm$
245 40.05 ppm). Y/Ho ratios are slightly above the chondritic ratio of 27 and range from 29.09 to
246 37.32 (mean 33.46 ± 2.63), whereas La_{SN} anomalies $[(La/La^*)_{SN}]$ are typically positive from
247 0.92 to 1.73 (mean 1.42 ± 0.29 , excluding two outliers -13.62 and 12.15). Further, there is a
248 positive Gd_{SN} anomaly $[(Gd/Gd^*)_{SN}: 1.08 - 1.3; \text{mean } 1.20 \pm 0.07]$ and light REE (LREE; La
249 to Nd) are depleted compared to heavy REE (HREE; Ho to Lu) as shown by Pr_{SN}/Yb_{SN} ratios
250 between 0.09 and 1.15 (mean 0.45 ± 0.31). In contrast, middle REE (MREE; Sm to Dy) are
251 enriched compared to LREE and HREE with BSI varying from 0.97 to 1.69 (mean 1.41 ± 0.22).
252 There is a strong positive Eu_{SN} anomaly $[(Eu/Eu^*)_{SN}: 1.17 - 3.21; \text{mean } 1.79 \pm 0.5]$. $(Ce/Ce^*)_{SN}$
253 values vary from 0.58 to 0.89 (mean 0.75 ± 0.1) with $(Pr/Pr^*)_{SN}$ ranging between 0.99 and 1.1
254 (mean 1.04 ± 0.04). Immobile trace elements Sc, Zr and Th show varying concentrations from
255 1.2 to 6.8 ppm, 2.05 to 39.04 ppm, and 0.09 to 2.84 ppm, respectively.

256 In Unit B (n=12), Σ REE values range from 4.44 to 41.17 ppm (mean 16.27 ± 11.51
257 ppm) and Y/Ho ratios are higher than in Units A and C (Y/Ho: 32.98 – 49.63; mean $39.01 \pm$
258 4.28). Unit B shows positive La_{SN} and Gd_{SN} anomalies between 1.16 and 1.70 (mean $1.41 \pm$
259 0.15) and 1.20 and 1.37 (mean 1.27 ± 0.05), respectively. LREE are depleted compared to
260 HREE with $(Pr/Yb)_{SN}$ ratios from 0.09 to 0.60 (mean 0.32 ± 0.14). Unit B does not show any

261 significant MREE enrichment and BSI values range between 0.92 – 1.22 (mean 1.04 ± 0.1).
262 Compared to other units there is a smaller but still positive Eu_{SN} anomaly, from 0.82 to 2.40
263 (mean 1.65 ± 0.52), $(Ce/Ce^*)_{SN}$ values show the largest negative anomaly, varying between
264 0.40 and 0.91 (mean 0.68 ± 0.13) and $(Pr/Pr^*)_{SN}$ varies between 0.99 – 1.36 (mean 1.11 ± 0.1).
265 Unit B also has the lowest Sc, Zr and Th concentrations: 0.27 – 2.16, 0.78 – 22.26, and 0.05 –
266 0.34 ppm, respectively.

267 Given that Unit C is dominated by shales, only four carbonate samples were chosen for
268 trace element analyses, and most of those showed a strong contribution from the siliciclastic
269 fraction as indicated by high Sc, Zr and Th concentrations with some samples having 12.45,
270 110.97, and 3.51 ppm, respectively. ΣREE ranges from 11.74 to 69.14 ppm (mean $33.35 \pm$
271 22.13 ppm), Y/Ho ratios are from 23.92 to 33.73 (mean 28.86 ± 3.53 , hence close to the
272 chondritic value), $(La/La^*)_{SN}$ varies between 0.88 and 1.38 (mean 1.07 ± 0.2), $(Gd/Gd^*)_{SN}$ is
273 between 1.09 and 1.18 (mean 1.13 ± 0.03) and there is a small LREE depletion with $(Pr/Yb)_{SN}$
274 varying between 0.41 and 0.88 (mean 0.69 ± 0.18). Unit C shows the highest MREE enrichment
275 with BSI from 1.18 to 2.03 (mean 1.57 ± 0.33) and positive Eu_{SN} anomalies with $(Eu/Eu^*)_{SN}$
276 ranging from 1.30 to 2.66 (mean 1.95 ± 0.5). Ce does not show anomalous behaviour:
277 $(Ce/Ce^*)_{SN}$ ranges between 0.93 and 1.02 (mean 0.98 ± 0.03) and $(Pr/Pr^*)_{SN}$ from 0.97 to 1.03
278 (mean 1.0 ± 0.03).

279 **4.4. Preservation of the $\delta^{13}C_{carb}$ signal**

280 The organic-rich siliciclastic-carbonate sediments of the Zaonega Formation were deposited in
281 a volcanically active basin and experienced complex post-depositional overprinting processes
282 resulting in a heterogeneous mineralogy (Črne et al., 2014; Kreitsmann et al., 2019; Melezhik
283 et al., 2015). Jacobsen and Kaufman (1999) have shown that carbon isotopes can be altered if
284 the water-rock ratio is very high such that carbon and oxygen isotope values will define an L-

285 shape declining curve. The C- and O-isotope ratios in OnZap section define such a curve (Fig.
286 9), implying that they experienced secondary alteration and that screening of the samples is
287 necessary in order to extract information about the depositional environment

288 The $\text{Mn}/\text{Sr}_{\text{carb}}$ ratio is commonly used to assess the effect of meteoric alteration in
289 marine carbonates (Brand and Veizer, 1980). For example, a $\text{Mn}/\text{Sr}_{\text{carb}}$ ratio <10 has previously
290 been used as a screening tool for Proterozoic rocks (Kaufman and Knoll, 1995; Melezhik et al.,
291 2015). However, Kreitsmann et al. (2019), in their study of rocks correlative to the OnZap
292 section in the OPH drill core, have shown that the $\text{Mn}/\text{Sr}_{\text{carb}}$ ratio <10 criterion is not always a
293 reliable indicator of better preserved samples and additional, thorough petrographic and
294 mineralogical characterisation are necessary. In the OPH core, as well as in the FAR-DEEP
295 12AB, 13A (Črne et al., 2014) and OnZap drill cores, calcitic margins (dedolomite) have
296 formed on carbonate beds with $\delta^{13}\text{C}_{\text{carb}}$ values as much as 15‰ lower than those in the better
297 preserved dolomite interiors. Yet, the $\text{Mn}/\text{Sr}_{\text{carb}}$ ratio is lower in the dedolomite than in the
298 original dolomite (Kreitsmann et al., 2019). Hence, in rocks with a mixed carbonate
299 mineralogy, the $\text{Mn}/\text{Sr}_{\text{carb}}$ ratio may not be a robust screening tool because calcite incorporates
300 Sr preferentially, whereas dolomite does so with Mn (Veizer, 1983). Furthermore, the $\text{Mn}/\text{Sr}_{\text{carb}}$
301 filter was developed for use in the context of freshwater alteration in Phanerozoic environments
302 (Brand and Veizer, 1980); chemistry of such environments in the lower- O_2 Proterozoic is likely
303 to have been markedly different. In the case of the OnZap samples, our analyses obtained
304 average $\text{Mn}/\text{Sr}_{\text{carb}}$ values of 9.02 ± 7.25 and 7.53 ± 4.4 for Units A and B, respectively, whereas
305 Unit C, containing mostly Fe-rich ankerite-dolomite with only minor calcite, has an $\text{Mn}/\text{Sr}_{\text{carb}}$
306 average of 53.91 ± 38.5 . While some of this contrast might result from varying degrees of
307 overprinting, it more likely that tracks a different depositional environment in Unit C leading
308 to different mineralogy compared to Units A and B.

309 Here we have, instead, opted for a combined mineralogical and oxygen isotope
310 approach for sample screening. In studies that have combined high-resolution geochemical and
311 isotope analyses with careful petrography and detailed mineralogy (e.g., Črne et al., 2014;
312 Kreitsmann et al., 2019), the emerging picture is that calcite in the upper Zaonega Formation
313 is largely a secondary carbonate phase, whereas dolomite is primary, except the calcareous
314 mudstone bed A2 which will be discussed separately. Further, there is mostly complete
315 resetting of isotopic signals at bed margins but bed interiors retain a better preserved, likely
316 original, carbon isotope signal. Consequently, we use a calcite to total carbonate ratio <0.05 as
317 a cut-off value to screen for the better-preserved samples with a primary carbon isotope signal
318 (Fig. 10). We combine this with a $\delta^{18}\text{O}$ -based screen using a $\delta^{18}\text{O}$ cut-off value $>-10.0\text{‰}$. On
319 the $\delta^{18}\text{O}$ and $\delta^{13}\text{C}_{\text{carb}}$ cross-plot (Fig. 9), there is no obvious correlation in samples having $\delta^{18}\text{O}$
320 values $>-10.0\text{‰}$, indicating that carbon isotopes in these samples carry a better-preserved
321 signal (Derry, 2010).

322 **4.5. Contamination in the carbonate REY_{SN} signal**

323 In order to use the carbonate REY_{SN} signal as a paleoenvironmental indicator, samples must
324 be screened to eliminate those with contamination from siliciclastic detritus, Fe-Mn oxides,
325 sulphides and phosphates (Bau, 1993; Kamber et al., 2014; Wang et al., 2018), all of which
326 carry considerably higher concentrations of REY compared to pure carbonates. The extent of
327 siliciclastic contamination is commonly monitored using the concentration of immobile trace
328 elements (e.g., Zr and Th; Bau, 1993; Bolhar and Van Kranendonk, 2007; Frimmel, 2009;
329 Kamber et al., 2014; Schier et al., 2018; Viehmann et al., 2015a, 2015b; Zhao and Zheng, 2017)
330 and by observing whether these elements correlate with typical seawater features such as
331 positive La_{SN} anomalies and supra-chondritic Y/Ho ratios (Schier et al., 2018; Viehmann et al.,
332 2015b, 2015a; Wang et al., 2018). Siderophile Ni and Cu can be monitored for contamination
333 by oxides and chalcophile Pb and Sc for contamination by sulphides (Fig. 11; Bolhar and Van

334 Kranendonk, 2007). X-ray diffraction can be used to monitor the contribution of phosphate to
335 the carbonate REY_{SN} pattern. Lastly, carbonate rocks typically have low REE concentrations;
336 thus, if contaminated, their Σ REE concentration would increase and in a binary plot of
337 immobile trace elements to Σ REE concentration show a positive correlation.

338 We used a Zr concentration of <4 ppm (as suggested by Frimmel, 2009) as the cut-off
339 value to screen carbonate samples for terrigenous contamination. For phosphate, our XRD data
340 show that apatite does not exceed 1.2 wt.% (usually <1 wt.%) in the screened samples (in fact,
341 the sample with the highest apatite abundance has the lowest Σ REE concentration;
342 Supplementary Table 3). Nine dolomite samples passed our screening: one sample each from
343 A5, B3 and C2 and six samples from B1 (Fig. 11; Supplementary Table 3). None of the
344 dedolomitised samples passed. These 9 samples retained their original REY signal and can be
345 used as reliable archives of paleoenvironmental proxies.

346

347 **5. Discussion**

348 The Zaonega Formation has figured prominently in recent efforts to better understand the
349 oxygenation state of the Paleoproterozoic Earth system but, as highlighted in the Introduction,
350 these efforts have come to contradicting conclusions: either global contraction of oxygen levels
351 (Asael et al., 2013, 2018; Kipp et al., 2017; Scott et al., 2014); elevated oxygen levels during
352 deposition of the Zaonega Formation (Mänd et al. 2020; Sheen et al., 2018) or fluctuating
353 basinal redox conditions (Paiste et al., 2018). Hence, views are divergent on the oxygenation
354 state of the Paleoproterozoic atmosphere-ocean system following the LJE. Below, we
355 summarise and discuss our C-isotope and REY data; the latter in particular provides an
356 independent proxy with the potential to resolve these divergent scenarios.

357 **5.1. Variations within individual intervals and stratigraphic $\delta^{13}\text{C}_{\text{carb}}$ trend in the**
358 **OnZap section**

359 Carbonate beds in intervals A1 and A2 have a distinctive reverse $\delta^{13}\text{C}_{\text{carb}}$ pattern compared to
360 other carbonate beds as the $\delta^{13}\text{C}_{\text{carb}}$ values become increasingly higher towards the margins of
361 the beds ($\delta^{13}\text{C}_{\text{carb}}$ values -15‰ in A2 and -10‰ in A1) compared to the interior parts that have
362 values as low as -25‰ (Fig. 7). As we and other workers (Črne et al., 2014; Kreitsmann et al.,
363 2019; Paiste et al., 2018) have documented through detailed bed-by-bed study of the Zaonega
364 rocks, bed margins are affected by secondary processes whereas bed interiors house the best-
365 preserved isotope signals. Thus, the $\delta^{13}\text{C}_{\text{carb}}$ values of -15‰ to -10‰ are observed at all bed
366 margins throughout Unit A and B, like those elsewhere, a consequence of hydrothermal
367 alteration. Accordingly, as per beds elsewhere, the isotopically lighter carbonates within bed
368 interiors in intervals A1 and A2 record a pre-alteration signal. The $\delta^{18}\text{O}$ values of intervals A1
369 and A2 are, in contrast, relatively uniform and do not exhibit a difference between the interiors
370 and margins, possibly reflecting a wholesale oxygen isotope resetting during the hydrothermal
371 alteration. Further, the upper strata of the Zaonega formation contain a record of ubiquitous
372 syndepositional methane cycling and methanotrophy (Qu et al., 2012, 2018). Thus, we suggest
373 that the low $\delta^{13}\text{C}_{\text{carb}}$ values in the interiors of carbonate intervals A1 and A2 evidence for early-
374 diagenetic methane derived carbonates formed *via* anaerobic oxidation of methane (AOM) in
375 an ancient seep system.

376 AOM derived carbonates are widely observed in modern hydrocarbon seeps but
377 examples can be also found in the Precambrian (Campbell, 2006). The ^{13}C -depleted carbon
378 source for the precipitation of authigenic seep carbonates is supplied by microbially mediated
379 anaerobic oxidation of hydrocarbons such as methane and oil (Boetius et al., 2000; Joye et al.,
380 2010), typically within shallow subsurface sediments. In these settings, hydrocarbons rising
381 through unconsolidated sediments are anaerobically oxidised at the lower boundary of the

382 sulfate reduction zone by microbial consortia of methanotrophic archaea and sulfate-reducing
383 bacteria (Boetius et al., 2000; Orphan et al., 2002; Whiticar, 1999). Anaerobic oxidation of
384 methane increases pore-water alkalinity and consequently causes the precipitation of
385 carbonates with ^{13}C -depleted signatures whose values depend on the origin of the methane.
386 Biogenic methane produced by methanogens is strongly depleted in ^{13}C and its $\delta^{13}\text{C}$ values
387 vary from -110 to -50‰, typically $-60 \pm 5\%$ (Sapart et al., 2012; Schoell, 1988). Thermogenic
388 methane typically has higher $\delta^{13}\text{C}$ values, from lower than -50‰ up to $-22 \pm 3\%$ in pyrogenic
389 methane (Sapart et al., 2012), that become increasingly heavier with increasing maturity of
390 organic matter (Whiticar, 1999).

391 Given hydrocarbon generation and circulation, triggered by magmatic activity during
392 accumulation of the middle and upper Zaonega succession (Qu et al., 2012), precipitation of
393 AOM-derived carbonates is expected to occur in a similar manner as that observed in the late
394 Paleocene Vøring Basin (Norwegian Sea; Svensen et al., 2003) or in the modern seeps of the
395 Guaymas Basin in the Gulf of California (Geilert et al., 2018; Simoneit et al., 1990) where
396 hydrothermal systems initiated by magmatic activity produce seep carbonates. Usually the
397 AOM-derived carbonates that consume microbial methane have $\delta^{13}\text{C}_{\text{carb}}$ values $< -30\%$
398 (Campbell, 2006); however, the isotope composition of the carbonate precipitating in the
399 system is a mixed signal strongly influenced by the relative balance between DIC derived from
400 AOM and seawater (Himmeler et al., 2010). Alternatively, variation in the source of methane,
401 i.e., microbial versus thermogenic origin can also produce methane-derived carbonates of
402 variable $\delta^{13}\text{C}$. Slightly higher $\delta^{13}\text{C}_{\text{carb}}$ values in the OnZap carbonate intervals A1 and A2
403 compared to common methane derived carbonates can, thus, be explained by mixing with the
404 seawater DIC pool and/or by thermogenic CH_4 being the dominant source. The AOM derived
405 origin of A1 and A2 carbonates is further evident by the presence of likely barite pseudomorphs
406 (Fig. 3H). Barite is a common precipitate at sulfate–methane interfaces in

407 methane/hydrocarbon seeps where ascending fluids from anoxic sediments containing methane
408 and Ba^{2+} (leached from K-minerals) interact with sulfate near the AOM zone (Castellini et al.,
409 2006; Griffith and Paytan, 2012).

410 Alternatively, the isotopically light interiors of intervals A1 and A2 could represent
411 carbonate concretions formed as a result of an alkalinity boost due to organoclastic sulfate
412 reduction in the diagenetic realm (Irwin et al., 1977). The carbon isotope values in diagenetic
413 carbonate concretions can be variable (from -43‰ to +13‰), with a significant overlap with
414 different organic matter mineralization reactions (e.g., sulfate reduction, methanogenesis and
415 thermal decarboxylation; Raiswell and Fisher, 2000). Given the abundance of biomass and its
416 $\delta^{13}\text{C}$ values around -35‰, it is possible that strongly ^{13}C -depleted porewater DIC generated
417 through mineralization of organic matter was responsible for the precipitation of these low-
418 $\delta^{13}\text{C}$ carbonates.

419 Moving upsection, the petrography of A3 calcareous mudstone resembles the A1 and
420 A2 intervals (e.g., calcite cement). However, the $\delta^{13}\text{C}_{\text{carb}}$ values of A3 are relatively stable (c.
421 $-10.2 \pm 1\%$) with similar values to the outer edges of A1 and A2 intervals that might reflect
422 the resetting of initial AOM signals as in A3. Likewise, varying dolomite/calcite ratios and
423 carbon isotopic signals of the calcareous mudstone interval A4 suggests that most of the
424 original signal has been overprinted by intensive dedolomitisation and/or recycling of organic
425 matter. Depending on the relative concentration of bicarbonate produced *via* microbial
426 oxidation of OM relative to the total amount of carbon in the system, organic diagenesis can
427 decrease or increase (e.g., through methanogenesis) the $\delta^{13}\text{C}_{\text{carb}}$ values of carbonate rocks
428 (Irwin et al., 1977; Mazzullo, 2000; Swart, 2015). In contrast, the purer and less organic-rich
429 dolostone intervals in the upper part of Unit A through Unit C must have been less influenced
430 by organic diagenesis than the organic-rich calcareous mudstones of Unit A. Like the
431 calcareous mudstone interval A4, dolostone intervals A5 and B1 did, however, experience

432 dedolomitisation at contacts between carbonate beds and mudstones, which resulted in lower
433 isotopic values on the margins compared to interiors of carbonate beds. Intra-bed $\delta^{13}\text{C}_{\text{carb}}$
434 variation (more than 5‰; Fig. 10) is probably due to the varying influence of methanotrophic
435 bicarbonate to the DIC pool of ambient seawater and/or organic diagenesis.

436 In the calcareous mudstone interval B2 the $\delta^{13}\text{C}_{\text{carb}}$ values vary between -16.4‰ and -
437 12.8‰; upsection, through intervals B3 and C1 values shift to +0.8‰. This excursion also
438 coincides with a transition from methanotrophy-contributed biomass ($\delta^{13}\text{C}_{\text{org}}$ values of -40 to -
439 35‰) to predominantly phototrophic biomass ($\delta^{13}\text{C}_{\text{org}}$ values of -25‰; Fig. 2; Paiste et al.,
440 2018). In addition, most of Unit C's Mn/Sr_{carb} ratios, REY_{SN} patterns, petrography and
441 mineralogy differs notably from the other units. Dolomite in Unit C rocks is typically zoned
442 and becomes increasingly more Fe-rich towards the top of the succession, as the carbonate
443 composition changes from dolomite to ankerite with siderite aggregates (Fig. 6). Petrography
444 and carbon isotopes suggest that dolomite in Unit C, except for the first two meters of C1, is
445 diagenetic and precipitated from Fe-rich anoxic pore-waters. There are no signs of significant
446 secondary alteration. In that regard our data agree with Paiste et al. (2018) who concluded that
447 the thick dolomite bed in Unit B acted as a stratigraphic seal that hindered further ascent of
448 dedolomitising hydrothermal fluids.

449 **5.2. The secular $\delta^{13}\text{C}_{\text{carb}}$ trend of the upper Zaonega Formation**

450 Screening of carbonate isotope data for the OnZap succession based on petrographical,
451 mineralogical and chemical criteria shows that, similar to the upper part of the Zaonega
452 Formation in FAR-DEEP 13A, 12AB and OPH drill-cores, the least-altered carbonate samples
453 are in the middle parts of carbonate beds (Črne et al., 2014; Melezhik et al., 2015, Kreitsmann
454 et al., 2019). None of the samples from Unit A passed the mineralogical and $\delta^{18}\text{O}$ screening.
455 The screened $\delta^{13}\text{C}_{\text{carb}}$ values in Unit B (n=29) vary from -5.4‰ to -0.9‰ and shift to more

456 positive values towards the top of Unit B (Fig. 10). The same $\delta^{13}\text{C}_{\text{carb}}$ trend continues in the
457 lower part of Unit C (n=8) with $\delta^{13}\text{C}_{\text{carb}}$ values increasing from -3.8‰ to 0.83‰, although most
458 of Unit C is represented by diagenetic carbonates.

459 Confirming what has been found in earlier studies (e.g., Črne et al., 2014; Melezhik et
460 al., 2015), this study reveals a negative excursion following the LJE in the upper Zaonega
461 Formation. The $\delta^{13}\text{C}_{\text{carb}}$ values as low as c. -20‰ in the middle and upper part of the Zaonega
462 Formation are now known to be due, in part, to diagenetic and hydrothermal processes (Črne
463 et al., 2014; Kreitsmann et al., 2019). Our screened samples for the upper Zaonega Formation,
464 which have values between -5.4‰ and +0.8‰, offer a better-preserved record of ocean
465 chemistry at the time of deposition. A similar transition in $\delta^{13}\text{C}_{\text{carb}}$ values in the lower part of
466 the upper Zaonega Formation in FAR-DEEP and OPH cores, i.e. from -6 to -2‰ and -6 to
467 0.5‰, respectively, has been described by other workers (Črne et al., 2014; Melezhik et al.,
468 2015; Kreitsmann et al., 2019). Such analogous behaviour of $\delta^{13}\text{C}_{\text{carb}}$ in correlative successions
469 at three different localities suggest a basin-wide nature of this trend. Nevertheless, variable
470 scattering of intra-bed $\delta^{13}\text{C}_{\text{carb}}$ values in the OnZap cores, and also in correlative intervals of
471 the OPH (Kreitsmann et al., 2019) and FAR-DEEP cores (Črne et al., 2014), suggests large
472 lateral/local isotopic variability of the DIC pool in the Onega Basin during accumulation of the
473 Zaonega Formation. We suggest that this variability reflects proximity of a particular area of
474 carbonate precipitation to active methane seeps and, hence, methane influence into the DIC
475 pool and carbonate $\delta^{13}\text{C}_{\text{carb}}$. This suggests that the negative excursion in the Onega Basin can
476 be related to basin-specific processes and cannot be used to infer the isotopic composition of
477 the global seawater DIC pool until similar negative excursions with the same extent are
478 identified in other post-LJE successions.

479

5.3. Paleoenvironment in the aftermath of the LJE in the Onega Basin

480
481 Abundances of the lanthanides and yttrium in sedimentary precipitates (e.g., cherts,
482 phosphates, carbonates) can be used as a proxy for ancient seawater compositions and redox
483 states (Alexander et al., 2008; Allwood et al., 2010; Bau and Alexander, 2006; Bellefroid et
484 al., 2019; Kamber et al., 2014; Kamber and Webb, 2001; Schier et al., 2018; Shields and Stille,
485 2001). In modern seawater, the REY signal is largely dominated by products of continental
486 weathering and dust. Input by hydrothermal activity at the ocean floor is insignificant in
487 modern systems but was more pronounced during the Archean, as evidenced by the widespread
488 positive Eu_{SN} anomalies in Archean chemical sediments (Alexander et al., 2009; Bau and
489 Dulski, 1996; Viehmann et al., 2015b).

490 REY speciation in seawater is influenced by two competing processes: stronger
491 complexation between dissolved ligands (e.g., CO_3^{2-}) and HREE as well as preferential
492 adsorption of LREE on settling particles (Elderfield, 1988), which result in progressive
493 enrichment of HREE compared to LREE and MREE in seawater REY_{SN} patterns. Seawater is
494 also characterised by positive La_{SN} , Gd_{SN} and possibly Lu_{SN} anomalies (Bau and Dulski, 1999;
495 Bolhar et al., 2004; Tostevin et al., 2016) and decoupling of Y and Ho due to preferential
496 adsorption of Ho on Fe-Mn-particles compared to Y (Bau et al., 1996; Nozaki et al., 1997). As
497 a consequence, the Y/Ho ratio becomes super-chondritic (>44) in open-marine settings,
498 whereas <44 are expected in restricted environments or those with freshwater and strong
499 hydrothermal influence (Bau et al., 1995; Bolhar and Van Kranendonk, 2007; Kamber and
500 Webb, 2001; Nozaki et al., 1997). Positive La_{SN} and Gd_{SN} anomalies, super-chondritic Y/Ho
501 ratios, LREE depletion compared to HREE and uniform REY_{SN} data in screened samples of
502 OnZap section (Fig. 12D; Supplementary Table 3) all suggest that samples from Unit B carry
503 the REY signature of ambient seawater. This also agrees with carbon isotopes that carry near-
504 normal marine $\delta^{13}C_{carb}$ values in Unit B.

505 A positive Eu_{SN} anomaly is present in all the screened samples, ranging between 1.24
506 and 2.26 (Fig. 12). Europium can be decoupled from other trivalent REE in high-temperature
507 hydrothermal fluids ($>250\text{ }^{\circ}\text{C}$) where Eu^{3+} is reduced to Eu^{2+} (Bau, 1991; Sverjensky, 1984).
508 The latter has a strong affinity to Cl^{-} complexation and more readily accumulates in solution,
509 whereas Eu^{+3} behaves similarly to other trivalent REE (Douville et al., 1999). As temperature
510 drops due to conductive cooling or mixing with ambient seawater, Eu^{2+} is re-oxidised, but the
511 excess Eu persists and is transferred to inorganic and biogenic precipitates such as sedimentary
512 and biogenic carbonates (e.g., Bau et al., 2010; Merschel and Bau, 2015). In very Ba-rich
513 samples positive Eu_{SN} anomalies can be analytical artefacts because of overlap of the masses
514 of BaO and Eu in ICP-MS analyses. However, in our samples there is no correlation between
515 measured Eu and Ba concentrations and at the low Ba/Eu ratios of these samples the correction
516 procedure for the isobaric BaO interference on Eu, which is based on experimentally
517 determined BaO yields in matrix-matched solutions, is not compromised. Noteworthy is that
518 the negative Ce_{SN} anomalies and well-preserved C isotopes of the screened samples eliminate
519 the possibility that the REY data reflect post-depositional overprinting.

520 While positive Eu_{SN} anomalies are common in Archean carbonates (Allwood et al.,
521 2010; Kamber and Webb, 2001; Schier et al., 2018), they are very rare in Proterozoic marine
522 carbonates (Bau and Alexander, 2006; Schier et al., 2018; Wang et al., 2018), suggesting a
523 diminishing influence of high-temperature hydrothermal input as a source of REY. This is
524 strongly supported by Nd isotope data for Precambrian marine chemical sediments such as
525 carbonates and banded iron-formations, that suggest a decreasing flux of hydrothermally-
526 sourced mantle Nd relative to continental Nd into seawater (e.g., Viehmann et al., 2015a; Schier
527 et al., 2018). If the selective Eu enrichment in Paleoproterozoic seawater was a global feature,
528 which is suggested by published data, the presence of prominent Eu_{SN} anomalies in the studied
529 samples implies that the Zaonega sediments were deposited in a semi-restricted basin, as in an

530 open-marine setting the excess Eu would be rapidly diluted. This interpretation agrees with the
531 geological context of the Zaonega Formation, which was marked by significant syndepositional
532 volcanic and hydrothermal activity (e.g., Črne et al., 2014) as well as basinal restriction during
533 its deposition suggested by Paiste et al. (2018; 2020).

534 The redox status of seawater during the formation of modern and ancient carbonates
535 has been widely assessed using Ce behaviour (Bellefroid et al., 2018; Elderfield and Greaves,
536 1982; Liu et al., 2019; Tostevin et al., 2016; Webb and Kamber, 2000; Wright et al., 1987). In
537 modern oxic seawater, dissolved Ce^{3+} is oxidised to more particle-reactive Ce^{4+} oxide on the
538 surface of Fe-Mn-(hydr)oxides and is removed from seawater by deposition of particulate and
539 colloidal material (Bau and Koschinsky, 2009). As a result, modern seawater shows a
540 distinctive negative Ce_{SN} -anomaly. However, a Ce_{SN} anomaly does not necessarily describe
541 the redox-conditions in the water column at the depositional site. Negative Ce_{SN} anomalies start
542 to develop during oxidative weathering and subsequent riverine transport (Byrne and Liu,
543 1998; Merschel et al., 2017), eventually producing Ce-depleted continental run-off and a
544 negative Ce_{SN} anomaly in seawater (Goldstein and Jacobsen, 1988). Further, a Ce_{SN} anomaly
545 suggested by comparing normalised Ce data to La and Pr can be ambiguous as an
546 environmental proxy, because it may be an artefact of the anomalous enrichment of La in
547 seawater (Bau and Dulski, 1996). Hence, any assessment needs to be based on comparison to
548 Pr_{SN} , Nd_{SN} and/or Sm_{SN} (eg., $(Pr/Pr^*)_{SN} > 1.05$), but must not consider La_{SN} (Fig. 13; Bau and
549 Dulski, 1996; Kamber and Webb, 2001). In that regard the screened samples from B1 show
550 negative Ce_{SN} anomalies with $(Pr/Pr^*)_{SN}$ ratios ranging between 1.06 – 1.36, whereas Units A
551 and C do not record true Ce_{SN} anomalies (Fig. 13). Our interpretation of the true negative Ce_{SN}
552 anomaly in the OnZap carbonate rocks is further strengthened by a persistently negative Ce_{SN}
553 anomaly of similar amplitude in diagenetic apatite from the organic-rich mudstone-dolostone
554 interval in the Shunga outcrop (Fig. 13; Joosu et al., 2015).

555 In the OnZap section, only screened samples from B1 can be considered reliable
556 archives of marine (and, by proxy, atmospheric) composition at the time of deposition, and
557 even then the setting was likely to have been semi-restricted rather than fully open-marine.
558 Hence, based on our REY, Ce and C-isotope data, what can be concluded about the marine
559 water-column in the Onega Basin during deposition of the B1 carbonate rocks is that the
560 oxidative power in the atmosphere-ocean system was strong enough to decouple Ce from other
561 trivalent REE, regardless of whether it occurred during continental weathering or in the marine
562 water-column. Other data, including those of previous workers who have carefully screened
563 their samples (e.g., Črne et al., 2014; Paiste et al., 2018; Kreitsmann et al., 2019), indicate that
564 C- and S-isotope signatures were influenced by basin-specific processes. Thus, our results
565 agree with Mänd et al. (2020) Paiste et al. (2018) and Sheen et al. (2018): namely, that the
566 rocks of the Zaonega Formation recorded varying redox conditions and at least episodically
567 elevated O₂ levels persisting after the LJE. Thus, models and hypotheses about Earth system
568 redox states that use the Zaonega Formation to infer a global collapse of oxygen levels at this
569 time are at best equivocal.

570

571 6. Conclusions

572 We presented new high resolution isotopic, trace element, mineralogic, and petrographic
573 characterisation of carbonate beds in a 102-m-thick section recovered in the OnZap drill-cores
574 through the c. 2.0 Ga the upper Zaonega Formation in the Onega Basin, Russia. Our data
575 indicate the following:

- 576 1) Carbonate beds of the upper Zaonega Formation have mixed carbonate mineralogy.
577 Most of the dolomite in units A and B is better preserved than calcite, although primary
578 calcite is present in Unit A. In Unit C, dolomite is closer to ankerite in composition.

- 579 2) Only the middle part of the OnZap section can be used to characterise the isotopic
580 composition of ambient seawater. The screened samples exhibit an upwards increasing
581 shift in $\delta^{13}\text{C}_{\text{carb}}$ values from -5.4‰ to 0.8‰.
- 582 3) Large intra-bed variability suggests a fluctuating influence of methane-derived carbon
583 on the basinal DIC pool.
- 584 4) Dolomite in Unit B carries the signal of ambient seawater as suggested by typical
585 seawater REY_{SN} patterns, super-chondritic Y/Ho ratios, LREE depletion compared to
586 HREE and positive La_{SN} and Gd_{SN} anomalies.
- 587 5) Negative Ce_{SN} anomalies in samples from B1 require enough oxidative power in the
588 atmosphere-ocean system to oxidise Ce(III) to Ce(IV) and decouple Ce from the other
589 trivalent REE.
- 590 6) Consistent positive Eu_{SN} anomalies highlight high-temperature hydrothermal input into
591 local seawater in the Onega Basin during Zaonega times.

592 In total, these findings contradict previous inferences that the Zaonega Formation
593 witnessed a global collapse of oxygen in the wake of the LJE – instead, we highlight that the
594 atmosphere-ocean system must have retained a significant degree of oxygenation following the
595 LJE.

596

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943

944 **Figure captions**

945 **Figure 1.** Simplified geological map of the Onega Basin in NW Russia (after Koistinen et al.,
946 2001). Drill-core locations are shown as red triangles. FAR-DEEP 13A and OnZap drill-cores
947 were drilled 500 m apart. OPH – Onega Parametric Hole.

948 **Figure 2.** Lithostratigraphic column of the OnZap section with quartz, dolomite, calcite and
949 mica abundances in wt.% and isotopic values of carbonate $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ (‰, VPDB). $\delta^{13}\text{C}_{\text{org}}$
950 (‰, VPDB) data are from Paiste et al. (2018). Dashed red boxes outline carbonate intervals
951 A1 to C3.

952 **Figure 3.** SEM images in back-scatter detector (BSD) mode characterising carbonate rocks in
953 Unit A. (A) Small (<100 μm) planar-s dolomite crystals with abundant talc and mica. Calcite
954 is replacing dolomite; A5, depth 74.54 m. (B) Pseudomorphic calcite replacing dolomite via
955 dedolomitisation; A5, depth 74.54 m. (C) Zoned dolomite crystals with cloudier cores and later
956 pore-filling and intracrystalline calcite formed via dedolomitisation; A5, depth 57.38 m. (D)
957 Calcite cement representing primary carbonate of methane derived origin. Note the abundance
958 of mica, quartz grains and the absence of talc and dolomite; A2, depth 97.19 m. (E) Probable
959 metamorphic calcite and large chlorite crystals that cross-cut the bedding. Calcite has a
960 poikilitic texture with quartz and pyrite inclusions; A4, depth 84.4 m. (F) Larger elongated
961 methane derived calcite crystals with quartz and dolomite inclusions; A1, depth 101.22 m. (G)
962 Possible conduits for fluid and hydrocarbon flow that are filled with massive organic matter
963 and surrounded by calcite; A2 depth 96.95 m. (H) Skeletal pyrite pseudomorphs after barite;
964 A2 depth 96.95 m. Cal – calcite, Dol – dolomite, Py – pyrite, OM – organic matter, Qz – quartz,
965 Sph – sphalerite.

966 **Figure 4.** SEM images in BSD mode characterising carbonate rocks in Unit B. (A) Large
967 planar-e dolomite crystals in an organic matrix; B1, depth 47.20 m. (B) Large planar-s dolomite

968 crystals with abundant small calcite inclusions; B1, depth 50.77 m. (C) Secondary calcite and
969 dolomite filling cavities. Slightly lighter areas in dolomite are more enriched in Fe compared
970 to darker areas; B1, depth 52.92 m. (D) Massive dedolomitisation on the margin of the
971 carbonate bed; B1, depth 52.92 m. Cal – calcite, Dol – dolomite, Py – pyrite, OM – organic
972 matter.

973 **Figure 5.** SEM images in BSD mode characterising carbonates in Unit C. (A) Small nonplanar
974 dolomite crystals with Fe-rich outer rims. Note larger secondary quartz-mica-dolomite
975 aggregates in which dolomite has varying concentrations of Fe; C1, depth 30.92 m. (B)
976 Moderately zoned dolomite crystals and secondary calcite with high porosity; C2, depth 29.28
977 m. (C) Small planar-e strongly zoned dolomite/ankerite crystals and a larger poikilitic calcite
978 aggregate; C2, depth 18.72 m. (D) Poikilitic siderite aggregates with abundant dissolution
979 marks (e.g., marked with red arrows). Note the well-rounded silt-sized quartz grains in the red
980 square; C3, depth 6.5 m. Cal – calcite, Dol – dolomite, Py – pyrite, Qz – quartz, Fsp – feldspar,
981 Sid – siderite.

982 **Figure 6.** Major element composition (Ca, Mg, Fe, Mn) in mol% of carbonate minerals from
983 the OnZap section measured with EDS. Siderite was found only in Unit C. Calcite and
984 dolomite-ankerite were found in all units; however, dolomite in Unit C was closer to ankerite
985 composition than dolomite from other units.

986 **Figure 7.** Carbonate $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ (‰, VPDB) and calcite abundance (wt.%) in the inferred
987 methane derived carbonate interval A2 with primary calcite. The interior of the calcareous
988 mudstone bed has lower $\delta^{13}\text{C}_{\text{carb}}$ values than the margins.

989 **Figure 8.** Box-plots with distribution of (A) $\delta^{13}\text{C}_{\text{carb}}$ (‰, VPDB) and (B) $\delta^{18}\text{O}$ (‰, VPDB)
990 values in the OnZap section grouped by carbonate mineralogy. Note the general trend of
991 increasing isotopic values from Unit A to C. Calcite-rich samples have systematically lower

992 isotopic values than dolomite-rich samples. Unit C is mostly dolomitic and hence all data are
993 grouped in one box. Calc – calcite wt.% to total carbonate wt.% >0.8; Mix – calcite wt.% to
994 total carbonate wt.% = 0.8 – 0.2; Dol – calcite wt.% to total carbonate wt.% <0.2.

995 **Figure 9.** Cross-plot of $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{18}\text{O}$ (‰, VPDB) values from the OnZap section grouped
996 by carbonate mineralogy. Note the L-shaped field, suggesting the complete resetting of the
997 carbon and oxygen isotopic signal in some samples.

998 **Figure 10.** Screened (calcite to total carbonate ratio <0.05 and $\delta^{18}\text{O}$ values >-10.0‰) $\delta^{13}\text{C}_{\text{carb}}$
999 and $\delta^{18}\text{O}$ values (‰, VPDB) are marked as black dots and samples that did not pass the
1000 screening are marked as light grey dots. Lithological symbols as on Figure 2.

1001 **Figure 11.** Element-total REE concentration plots of samples that passed screening for detrital
1002 REY contamination (i.e., Zr concentration <4 ppm). (A) Zr and (B) Th are used to evaluate
1003 siliciclastic, (C) Ni oxide and (D) Sc sulfide contamination. The absence of an obvious
1004 correlation between the element and total REE suggests no significant contamination.

1005 **Figure 12.** REY_{SN} patterns of Units A, B, C, and samples from all units (D) that passed
1006 screening (i.e., Zr <4 ppm). Unit A has a higher concentration of REY and shows MREE
1007 enrichment compared to LREE and HREE. Unit B has a coherent pattern but with varying REY
1008 concentration. Unit C is also enriched in MREE compared to other REE and does not show
1009 anomalous behaviour other than a positive Eu_{SN} anomaly. Samples from Unit A and C have a
1010 strong shale contamination and only one sample from each unit passed the screening.

1011 **Figure 13.** Plot of PAAS-normalised Ce/Ce* [Ce/(0.5La + 0.5Pr)_{SN}] vs Pr/Pr* [Pr/(0.5Ce +
1012 0.5Nd)_{SN}] for evaluating the Ce_{SN} anomaly (after Bau and Dulski, 1996) in screened OnZap
1013 samples and diagenetic apatite data from Joosu et al. (2015) taken from the Shunga village
1014 outcrop that corresponds to B1 in the OnZap section. (I) no anomalous behaviour; (IIa) positive
1015 La_{SN} anomaly, no Ce_{SN} anomaly; (IIb) negative La_{SN} anomaly, no Ce_{SN} anomaly; (IIIa) positive

1016 Ce_{SN} anomaly; (IIIb) real negative Ce_{SN} anomaly. All of the screened samples from Unit B
1017 display a negative Ce_{SN} anomaly, whereas the sample from Unit A plots in the positive La_{SN}
1018 anomaly field and that for Unit C shows no anomalous behaviour. Apatite REE data from the
1019 Shunga village displays similar but more varying patterns.

1020

1021 **Table captions**

1022 **Table 1.** Defined carbonate bed intervals with the average carbonate mineralogy and isotopic
1023 values. B.d. stands for below detection (<0.5 wt.%).

1024

1025 **Supplementary table captions**

1026 **Supplementary Table 1.** Mineralogical composition (wt.%), $\delta^{13}C_{carb}$ (‰, VPDB) and $\delta^{18}O$
1027 (‰, VPDB) values $\pm 0.2\text{‰}$ (2σ) of the OnZap section. Tr <0.5 wt.%.

1028 **Supplementary Table 2.** Major and trace element concentration in the OnZap section. Ca,
1029 Mg, Fe and Mn in wt.% and trace elements in ppm.

1030 **Supplementary Table 3.** REY systematics of the OnZap section. Samples that did not pass
1031 screening are in italics