

## Palaeoproterozoic oxygenated oceans following the Lomagundi-Jatuli Event

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### Abstract :

The oceans probably remained well-oxygenated for millions of years after the Palaeoproterozoic Lomagundi-Jatuli Event, according to high concentrations and isotope signatures of redox-sensitive metals in the 2-billion-year-old Zaonega Formation, Russia. The approximately 2,220-2,060 million years old Lomagundi-Jatuli Event was the longest positive carbon isotope excursion in Earth history and is traditionally interpreted to reflect an increased organic carbon burial and a transient rise in atmospheric O<sub>2</sub>. However, it is widely held that O<sub>2</sub> levels collapsed for more than a billion years after this. Here we show that black shales postdating the Lomagundi-Jatuli Event from the approximately 2,000 million years old Zaonega Formation contain the highest redox-sensitive trace metal concentrations reported in sediments deposited before the Neoproterozoic (maximum concentrations of Mo = 1,009  $\mu\text{g g}^{-1}$ , U = 238  $\mu\text{g g}^{-1}$  and Re = 516  $\text{ng g}^{-1}$ ). This unit also contains the most positive Precambrian shale U isotope values measured to date (maximum U-238/U-235 ratio of 0.79 parts per thousand), which provides novel evidence that there was a transition to modern-like biogeochemical cycling during the Palaeoproterozoic. Although these records do not preclude a return to anoxia during the Palaeoproterozoic, they uniquely suggest that the oceans remained well-oxygenated millions of years after the termination of the Lomagundi-Jatuli Event.

34 The Paleoproterozoic era (2500–1600 Ma) witnessed the longest positive carbon isotope  
35 ( $\delta^{13}\text{C}_{\text{carb}}$ ) excursion in Earth's history, recorded in marine carbonates deposited worldwide  
36 between ~2220–2060 Ma—the Lomagundi-Jatuli Event (LJE)<sup>1,2</sup>. Marine carbonates are generally  
37 characterized by  $\delta^{13}\text{C}_{\text{carb}}$  values that vary between -5‰ to 5‰ for most of Earth's history,  
38 whereas peak LJE  $\delta^{13}\text{C}_{\text{carb}}$  values reach 10–15‰<sup>1</sup>. There is ongoing debate regarding the  
39 processes that led to the LJE. The standard and most commonly accepted interpretation invokes  
40 increased burial of  $^{13}\text{C}$ -depleted organic carbon ( $\text{C}_{\text{org}}$ ), leading to the  $^{13}\text{C}$ -enrichment of the  
41 dissolved inorganic carbon pool and positive  $\delta^{13}\text{C}_{\text{carb}}$ <sup>1,3</sup>. This acceleration in  $\text{C}_{\text{org}}$  burial may have  
42 been the result of an increase in oxidative weathering and nutrient delivery to the oceans<sup>3</sup>. Using

43 a simple isotope mass balance, it has been estimated that between  $5\text{--}9\times 10^{20}$  mol of  $C_{\text{org}}$  was  
44 buried over 100 Ma, corresponding to the release of  $O_2$  equivalents representing 12–22 times the  
45 present  $O_2$  atmospheric pool. An ensemble of evidence points to atmospheric  $O_2$  accumulation  
46 during the LJE, including proxies indicating growth of the marine sulphate reservoir<sup>4–6</sup>, elevated  
47 concentrations of redox sensitive elements (RSE)<sup>7–10</sup>, and evidence for locally oxic conditions<sup>3,11</sup>.  
48 However, others have argued that the ‘standard’ interpretation of the LJE is difficult to reconcile  
49 with our understanding of the C and O cycles<sup>12,13</sup>, and that there is a notable paucity of  $C_{\text{org}}$ -rich  
50 deposits at this time<sup>14</sup>, the most basic tracer of enhanced organic carbon burial. Further, the  
51 carbon isotope dynamics during and after the positive excursion are currently debated, and there  
52 are multiple interpretations of the LJE positive  $\delta^{13}C_{\text{carb}}$  values that do not invoke elevated rates of  
53 organic carbon burial and oxygen release<sup>13,15</sup>. Therefore, additional constraints on carbon and  
54 oxygen cycling are clearly needed to refine our view of this time interval.

55 **The ‘standard’ interpretation suggests that oxygen release due to  $C_{\text{org}}$  burial must have**  
56 **significantly slowed down in the aftermath of the LJE. In order to test this,** we present new redox  
57 tracer data from two correlative sections (OnZaP and OPH sections; see Methods) of the upper  
58 Zaonega Formation (ZF), a **post-LJE** mudstone-dolostone succession. We provide some of the  
59 most straightforward evidence for Proterozoic surface oxygenation. In fact, current redox proxy  
60 records are most consistent with increasing oxygenation in the aftermath of the LJE—forcing a  
61 re-evaluation of our basic view of this turbulent interval of Earth’s history.

## 62 **Age and geochemical signatures of the Zaonega Formation**

63 According to the latest U-Pb age constraints on a tuff horizon within the lower ZF, the formation  
64 was deposited at  $\sim 1980$  Ma,  $\sim 80$  Myrs after the proposed termination of the LJE<sup>16</sup>. This age

65 model is consistent with  $\delta^{13}\text{C}_{\text{carb}}$  stratigraphy. In the Onega Basin,  $\delta^{13}\text{C}_{\text{carb}}$  values in the lowermost  
66 ZF and underlying Tulomozero Formation are characterized by typical LJE values of  $\geq 8\text{‰}$ <sup>17</sup>, with  
67  $\delta^{13}\text{C}_{\text{carb}}$  in preserved carbonate strata returning to normal marine values of  $\sim 0\text{‰}$  further  
68 upsection<sup>18</sup>. In the OPH core, the studied section occurs after several hundred meters of  
69 stratigraphy—including cumulatively  $\sim 210$  meters of mudstone-dominated sediments—and  
70 contains carbonates bearing a normal marine (and therefore post-LJE)  $\delta^{13}\text{C}_{\text{carb}}$  signal<sup>18</sup>. Assuming  
71 a reasonable range of deposition rates for the mudstones—e.g.,  $1\text{--}100\text{ m Myr}^{-1}$  (Ref. 19)—the  
72 studied section of the ZF was deposited millions of years after the termination of the LJE in the  
73 Onega Basin.

74 The section is rich in total organic carbon (TOC), with average values of  $27.4\pm 18.5\text{ wt.}\%$  in  
75 mudstones of the OnZaP section, and  $14.5\pm 9.9\text{ wt.}\%$  in OPH mudstones (Figure 1). These values  
76 are roughly comparable to the most organic-rich modern marine sediments (e.g., up to  $21.3\text{ wt.}\%$   
77 on the Peru margin<sup>20</sup>). We focus specifically on molybdenum (Mo), uranium (U), and rhenium  
78 (Re) enrichments, as these metals have previously provided robust evidence for major shifts in  
79 Earth's redox state<sup>8,10,21</sup>. In the Zaonega mudstones Mo, U, and Re are significantly elevated  
80 relative to other Proterozoic black shales<sup>8,10,21</sup>, averaging  $130\pm 142\text{ }\mu\text{g g}^{-1}$ ,  $19\pm 15\text{ }\mu\text{g g}^{-1}$ , and  
81  $116\pm 84\text{ ng g}^{-1}$ , respectively, in OnZaP mudstones. In the OPH section, Mo and U average  $71\pm 92\text{ }\mu\text{g g}^{-1}$   
82 and  $37\pm 50\text{ }\mu\text{g g}^{-1}$ , whereas overall maximum Mo, U, and Re concentrations across both sites  
83 are  $1009\text{ }\mu\text{g g}^{-1}$ ,  $238\text{ }\mu\text{g g}^{-1}$ , and  $516\text{ ng g}^{-1}$ , respectively. In the OnZaP section,  $\delta^{98/95}\text{Mo}$  is on  
84 average  $0.67\pm 0.81\text{‰}$ , with a maximum of  $1.49\pm 0.14\text{‰}$ . Uranium isotope values in the OnZaP  
85 section range from  $-0.03$  to  $0.79\text{‰}$ , with an average of  $0.47\text{‰}$ . The maximum value is the most  
86  $^{238}\text{U}$ -enriched shale measurement that has been reported to date<sup>22,23</sup>.

87 The primary source of these RSE (in the rest of this manuscript, RSE refers specifically to Mo,  
88 U, and Re) to the oceans is the oxidative weathering of terrestrial RSE-bearing minerals (e.g.,  
89 pyrite, uraninite), and subsequent riverine transport as aqueous oxyanions<sup>24,25</sup>. Hydrothermal  
90 inputs, while not fully constrained at present, are not expected to be a quantitatively significant  
91 source for any of these RSE<sup>21,25</sup>. The most important RSE sink is sequestration into marine  
92 sediments, which is influenced by the redox state of the depositional setting<sup>24,26</sup>. In oxic seawater,  
93 RSE are present as recalcitrant species that tend to accumulate in the water column<sup>25,27</sup>, although  
94 Mo adsorbs to Mn(IV)-oxides under oxic conditions and can then be released in pore waters  
95 following the reductive dissolution of Mn(IV)-oxides in anoxic sediments<sup>28</sup>. In anoxic  
96 environments, the RSE are progressively converted into particle-reactive species resulting in  
97 efficient drawdown through authigenic sulphide precipitation or adsorption to organic  
98 matter<sup>26,27</sup>. With regards to Mo, it has been found that most efficient Mo sequestration takes place  
99 under euxinic waters with >11  $\mu\text{M}$  of sulphide ( $\text{HS}^-$ )<sup>29</sup>. In a broad sense, the contrasting  
100 behaviour of these elements in oxic and anoxic conditions ensures that the drawdown and  
101 marine reservoir sizes are governed by global ocean redox—large RSE reservoirs develop in an  
102 oxic ocean, which leads to large local sedimentary RSE enrichments under anoxic conditions<sup>10,21</sup>.

103 The U and Mo isotope systems, similar to RSE enrichments, respond to the global marine  
104 redox landscape. There is consensus that well-oxygenated oceans are characterized by **high** Mo  
105 and U isotope values<sup>30,31</sup>. It is, however, difficult to gauge when a sedimentary archive captures  
106 seawater U and Mo isotope values. **For instance, seawater Mo isotope values are most likely to be**  
107 **captured in shales deposited in isolated basins with high  $\text{HS}^-$  levels<sup>32</sup>. However, non-quantitative**  
108 **reduction of Mo in euxinic marine basins results in negative fractionation and shale  $\delta^{98/95}\text{Mo}$**   
109 **values that are lower than seawater<sup>30</sup>, and therefore,  $\delta^{98/95}\text{Mo}$  in euxinic shales is often**

110 interpreted as a minimum estimate for seawater  $\delta^{98/95}\text{Mo}^{11}$ . Uranium isotope values in shales will  
111 be closest to seawater values in oxic sediments and up to  $\sim 1\%$  heavier than seawater in anoxic  
112 and high productivity settings<sup>31</sup> (see Supplementary Information for detailed discussion on Mo  
113 and U isotope values). Using this framework, our data points to well-oxygenated oceans with high  
114 rates of primary productivity during deposition of the Zaonega Formation.

## 115 **Marine RSE inventory**

116 RSE enrichments in the ZF far exceed anything known from pre-Neoproterozoic black shales  
117 (Figure 2). Similar values are found only in the Phanerozoic, where they have been taken as  
118 evidence for an expanded seawater RSE inventory, the direct result of pervasive ocean-  
119 atmosphere oxygenation<sup>8,10,21</sup>. We believe that the ZF, likewise, contains evidence of a large  
120 marine RSE inventory that strongly suggests a relatively oxidized ocean-atmosphere system with  
121 a robust terrestrial oxic RSE weathering flux, in which the drawdown of RSE was limited by the  
122 relative scarcity of anoxic conditions on the seafloor. Further, U and Re enrichments—which,  
123 unlike Mo, are also drawn down in ferruginous waters<sup>33</sup>—suggest that this was an episode of  
124 thorough water column oxygenation on continental shelves, rather than just a restriction of  
125 euxinic deposition,  $>1.4$  Gyr before terminal oceanic oxygenation during the Neoproterozoic<sup>34</sup>.

126 While low Mo in black shales could be explained by either a small marine Mo pool, basal  
127 restriction leading to localized Mo depletion<sup>28</sup>, or inefficient Mo scavenging under low  $\text{HS}^-$   
128 conditions<sup>29</sup>, there are limited ways to explain elevated RSE concentrations in black shales of the  
129 ZF (i.e., up to several hundreds of  $\mu\text{g g}^{-1}$  of Mo throughout the  $>160$  km-wide basin). One  
130 possibility is anomalously low sedimentation rates, which have previously been invoked to  
131 explain high TOC in U-rich black shales of the Miocene Monterey Formation, USA<sup>35</sup>. Although low

132 sedimentation rates may have played a role in concentrating TOC and RSE in the ZF, the  
133 magnitude of the RSE enrichment—consistent with Phanerozoic levels (Figure 2)—makes it  
134 unlikely sedimentation rate alone could account for it. A more plausible explanation is that the ZF  
135 was also a highly efficient RSE sink that had reliable access to a large oceanic RSE inventory<sup>28</sup>  
136 (see Supplementary Information for additional discussion on factors controlling RSE  
137 accumulation).

138       The U isotope values provide an independent confirmation of highly oxygenated oceans—as  
139 noted above they are the most positive shale  $\delta^{238}\text{U}$  values measured to date (Figure 2), requiring  
140 both **high** seawater  $\delta^{238}\text{U}$  values (likely comparable to the modern value of  $\sim -0.4\text{‰}$ ) and a **near**  
141 full expression of the equilibrium  $\sim 1.2\text{‰}$  fractionation during U reduction. **High** seawater values  
142 only develop when oxic U burial is a major U burial flux in well-oxygenated oceans<sup>36</sup>. In addition,  
143 a significant positive U isotope fractionation ( $\gg 0.6\text{‰}$ ) strongly suggests U reduction in the  
144 water column **instead of within the sediment pile**<sup>31</sup>. Uranium reduction rates appear to scale with  
145 sulphate (or iron) reduction rates<sup>37</sup>—providing a link between amounts of organic matter  
146 loading in a marine system and the isotope fractionation that occurs during U burial. For  
147 reference, there is limited water column sulphate reduction in the modern Black Sea and Cariaco  
148 Basin because of low rates of productivity and maximum sediment  $\delta^{238}\text{U}$  **is only  $\sim 0.8\text{‰}$  and**  
149  **$\sim 0.6\text{‰}$  higher than seawater**, respectively<sup>36</sup>. **In contrast, high productivity in the ZF is consistent**  
150 **with the anomalous organic carbon enrichments**. Therefore, the strongly positive U isotope  
151 values **in the ZF**, along with the RSE enrichments, are most readily explained by invoking both  
152 globally well-oxygenated oceans and markedly elevated rates of local primary productivity, the  
153 latter of which would tend to enhance the expression of isotope effects associated with U  
154 reduction.

## 155 **Conflicting views on oxygenation during ZF deposition**

156 Our interpretation that the ZF records well-oxygenated ocean conditions is ostensibly in conflict  
157 with previous interpretations derived from C, S, and Mo isotope records proposed to reflect  
158 global deoxygenation. However, much of this data can plausibly be explained through local rather  
159 than global processes. First, Kump *et al.*<sup>38</sup> postulated a post-LJE global negative  $\delta^{13}\text{C}$  excursion  
160 based on depleted  $\delta^{13}\text{C}$  in ZF carbonates. This was interpreted to result from the widespread  
161 oxidation of organic-rich shales, which would have favoured suppressed, rather than elevated,  $\text{O}_2$   
162 levels. However, negative  $\delta^{13}\text{C}$  in the ZF has subsequently been reinterpreted to reflect basin-  
163 wide methanotrophy and secondary overprinting of carbonate rocks<sup>39</sup>. Second, Scott *et al.*<sup>5</sup>  
164 argued that highly  $^{34}\text{S}$ -enriched pyrites in the upper ZF reflect a global collapse of the marine  
165 sulphate reservoir due to deoxygenation. In contrast, Paiste *et al.*<sup>40</sup> explained the same trends  
166 through basin-specific processes involving quantitative uptake of sulphate. Third, Asael *et al.*<sup>41,42</sup>  
167 inferred an  $\sim 0.7\text{‰}$  seawater  $\delta^{98/95}\text{Mo}$  value from two other cores in the upper ZF, identical to the  
168 average in the OnZaP section. Mn-oxides, which form in oxic waters, preferentially scavenge  $^{95}\text{Mo}$   
169 and drive seawater  $\delta^{98/95}\text{Mo}$  to higher values. If one assumes a modern riverine input value of  
170  $\sim 0.7\text{‰}$  for the Paleoproterozoic<sup>30</sup>, a seawater value of  $\sim 0.7\text{‰}$  suggests limited Mn-oxide  
171 precipitation and, thus, little  $\text{O}_2$  in the oceans. However, the sequestration of Mo in sediments  
172 commonly imparts a negative  $\delta^{98/95}\text{Mo}$  fractionation, **except in highly restricted euxinic basins**  
173 **where nearly all Mo is drawn down**<sup>30</sup>. This highlights that the highest Mo isotope values of  
174  $\sim 1.4\text{‰}$  represent a minimum seawater  $\delta^{98/95}\text{Mo}$  estimate (see Ref. 11 and Supplementary  
175 Information) and that the Mo isotope data does not necessarily preclude widespread oxic  
176 conditions.



## 177 Implications of oxygenated oceans at **approximately 2000 Ma**

178 RSE-replete conditions during the deposition of the ZF have important implications for Earth's  
179 global C and O cycles during the Paleoproterozoic. Tracking the evolution of Earth's redox history  
180 is also critical for understanding early eukaryote evolution. The late rise to prevalence of  
181 eukaryotes in the Neoproterozoic is thought to be linked to widespread anoxic and nutrient-poor  
182 conditions that favoured prokaryotic metabolisms<sup>43</sup>. Given the extent of ocean oxygenation and  
183 nutrient abundance inferred from the ZF<sup>3,44</sup>, conditions favourable to eukaryotic diversification  
184 could have been present for much of the middle Paleoproterozoic. It is curious, then, that  
185 molecular clock analyses and microfossil evidence of eukaryote origin tend to converge after  
186 ~1900 Ma<sup>45,46</sup>. In the simplest sense this discrepancy supports the central importance of a unique  
187 endosymbiosis event for the emergence of eukaryotes, rather than removal or lessening of an  
188 environmental barrier.

189 The ZF is part of a well-recognized overall trend towards elevated RSE concentrations at  
190 ~2400–2000 Ma that has been linked to well-oxygenated oceanic–atmospheric conditions<sup>8–10</sup>.  
191 Surprisingly, our ZF data extend this trend past the termination of the LJE. Furthermore, the  
192 extreme RSE enrichments hint that, instead of being in decline, atmospheric O<sub>2</sub> abundance could  
193 still have been high perhaps several tens of Myrs after the canonical end of the LJE<sup>16</sup>. In the  
194 modern, well-oxygenated world, the geologic O<sub>2</sub> response time is on the order of ~2 Myrs<sup>47</sup>,  
195 whereas the residence times of Mo, U, and Re in the oceans are ~440, ~400, and ~780 kyrs,  
196 respectively<sup>25,27</sup>. Therefore, if the LJE decline is linked to a decrease in O<sub>2</sub> production as the result  
197 of diminishing C<sub>org</sub> burial by the end of the LJE, then O<sub>2</sub> would be expected to be significantly  
198 attenuated by this time. Instead, our **data suggest** the opposite.

199 Our observations provide empirical evidence for models (e.g., Ref. 13) that decouple the  
200 strongly positive carbonate carbon isotope values of the LJE from enhanced organic carbon  
201 burial. Further, **given the likelihood that** highly oxidized conditions continued up to ~2.0 Ga, this  
202 highlights the importance of exploring alternative **interpretations of the carbon isotope record**  
203 and the need for refined chemostratigraphic and geochronological studies focused on this key  
204 interval of Earth's history.

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## 218 **Author contributions**

219 AL, KK, KOK, SVL, and KM conceived the study. KM, KP, TK, AER, KK, and AL conducted field  
220 studies and organized the sample acquisition. KP, TK, AER, KK, and AL provided the geological  
221 and sedimentary background. KP provided additional TOC data. KM, LJR, SVL, MT, PP, CTR, KL,  
222 AV, and KOK measured and interpreted the trace metal abundance data. MT, SVL, and KM  
223 analyzed and interpreted the Mo isotope data. NJP, LJR, and KM analyzed and interpreted the U  
224 isotope data. SVL, TK, PP and KK analyzed and interpreted *in-situ* trace metal abundance. KM  
225 wrote the manuscript with input from all of the co-authors.

## 226 **Competing interests**

227 The authors declare no competing interests.

## 228 **Figure captions**

229 Figure 1: Lithology and geochemistry of the Zaonega Formation. Total organic carbon (TOC) and  
230 redox sensitive metal (RSE) profiles (errors contained within symbols), and Mo and U isotope  
231 ratios ( $\delta^{98/95}\text{Mo}$  and  $\delta^{238}\text{U}$ , error bars are  $2\times\text{SE}$ ) are shown for the OnZaP and OPH sections.  
232 Vertical dashed lines are average crustal values<sup>30,31,48</sup> and the dotted horizontal line is the  
233 phosphorous-rich mudstone–dolostone contact used for intra-basinal correlation (see Methods



234 and Supplementary Information). Boxplots below the Mo and U isotope plots represent the  
235 distribution of previously published ZF data from lower in the succession (see Supplementary  
236 Information)<sup>41,42</sup>. Gray horizontal bands are partly silicified and calcified intervals due to fluid  
237 alteration<sup>40</sup>. While these imply the presence of secondary fluids that could have mobilized RSE,  
238 microscale RSE distribution confirms the primary nature of the RSE enrichments (see  
239 Supplementary Information).

240 Figure 2: Secular trends in redox sensitive element concentrations from anoxic shales. Zaonega  
241 Formation data (plus and circle symbols) are plotted on compilations from literature (X  
242 symbols). (a) Changes in  $\delta^{13}\text{C}_{\text{carb}}$  ratio through time, modified from Ref. 49. (b) Molybdenum  
243 concentrations from Ref. 50. (c) Uranium concentrations from Ref. 8. (d) Uranium isotope ratios  
244 from Refs. 22 and 23. (e) Rhenium concentrations from Ref. 10. Concentration errors are within  
245 symbols; for  $\delta^{238}\text{U}$  and age errors, refer to Fig. 1, Supplementary Information, and compilation  
246 data sources.

## 247 **Methods**

## 248 **Materials**

249 The material for this study comes from drill cores in the Onega Basin that intersect the ZF—a  
250 relatively well-preserved 1500 m-thick succession of organic-rich mudstones and carbonates,  
251 interlayered and intersected with igneous units including lavas, tuffs, and sills (see  
252 Supplementary Information for a detailed geological setting)<sup>51</sup>. The 60 m long cores OnZaP-1 and  
253 OnZaP-3 were drilled 500 m apart in the northeastern part of the Onega Basin near Shunga  
254 village, close to drill core FAR-DEEP 13A<sup>40</sup>. The OnZaP-1 and OnZaP-3 cores are partly

255 overlapping and combined provide a 102 m thick OnZaP section. The 3500 m long OPH core that  
256 intersects the entire supracrustal succession of the Onega Basin was drilled ~60 km to the south.  
257 Paiste *et al.*<sup>40,52</sup> correlated the upper ZF OnZaP and OPH sections based on C isotopes, trace metal  
258 enrichments, P concentrations, and a distinct massive P-rich dolomite unit that occurs  
259 throughout the Onega Basin.

260 The lithology of this section is characterized by alternating dolomite to calcite-rich  
261 carbonates and exceptionally organic-rich mudstones that are intersected by silica or  
262 pyrobitumen veins (Figure 1). In the OnZaP section, the interval from the bottom of the section to  
263 53 m depth is dominated by highly organic-rich mudstones with relatively few carbonate beds;  
264 the 53–33 m interval is mostly dolostone and contains a distinctive dolomite unit; and the 33–1.7  
265 m interval consists of grey mudstones and marly carbonate beds<sup>40</sup>. Two sets of samples from the  
266 OnZaP section were analyzed in this study. Set MSP0001 consists of 135 samples that were taken  
267 at roughly 1 m intervals and is identical to that used in Paiste *et al.*<sup>40</sup>. Set MSP0010 contains 79  
268 samples that more specifically targeted RSE and organic-rich intervals. A set of 89 samples were  
269 analyzed from the 1060–1230 m interval of the OPH core that is roughly equivalent to the OnZaP  
270 section.

## 271 **Elemental concentrations**

272 Total organic carbon content of the MSP0001 and OPH samples were adapted from Paiste *et al.*<sup>40</sup>  
273 and were measured from powdered aliquots using a LECO SC-444 analyzer at the Geological  
274 Survey of Norway (NGU), Trondheim, Norway. Detection limit was 0.1 wt.% and precision better  
275 than 10%. For the MSP0010 set, TOC was measured at the Pôle Spectrométrie Océan, European  
276 Institute for Marine Studies (IUEM), Brest, France. Dried and powdered samples were combusted

277 in ceramic beakers at 500 °C for 24h and loss of mass on ignition was determined. Repeat  
278 measurements of 7 samples generally differed by <1 wt.%.

279 Major and trace element compositions of MSP0001 samples were determined at Acme Labs,  
280 Bureau Veritas Commodities Canada Ltd. The samples were first pulverized and combusted to  
281 remove organic carbon. For major elements, the sample was fused in LiBO<sub>2</sub> flux, then digested,  
282 whereas minor elements were analyzed from full digests in HNO<sub>3</sub>, HClO<sub>4</sub>, and HF. Measurements  
283 utilized inductively coupled plasma optical emission spectrometry (ICP-OES) or mass  
284 spectrometry (ICP-MS). Average relative standard deviation was less than 5% for all elements.  
285 MSP0010 element composition was determined at IUEM. Samples were pulverized in a tungsten  
286 carbide crusher and an agate mill, then combusted at 500 °C for 24h to remove organic carbon.  
287 Major element concentrations were measured on a Jobin Yvon Horiba Ultima 2 ICP-OES after  
288 digestion overnight at 80 °C in concentrated HF and HNO<sub>3</sub> and neutralization with boric acid to  
289 retain Si. For trace element concentrations, digestion was performed in a class 1000 clean  
290 laboratory, using distilled acids—samples mixed with concentrated HF and HNO<sub>3</sub> were heated to  
291 80 °C overnight, then allowed to evaporate; this digestion was then repeated with concentrated  
292 *aqua regia*, after which the sample was taken up in 6M HCl. Trace element concentrations were  
293 measured on a Thermo Scientific Element 2 ICP-MS calibrated against commercial multi-element  
294 standards and digested geostandards (e.g., BHVO-2). OPH major and trace elements were  
295 measured on a Philips PW 1480 X-ray fluorescence spectrometer (XRF) equipped with a Rh X-ray  
296 tube at the Geological Survey of Norway. For major elements 0.6 g of ground and combusted  
297 (1000 °C) sample was fused into a bead in a CLAISSE FLUXER-BIS together with 4.2 g of Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub>.  
298 For trace elements 2.4 g of Hoechst wax was mixed with 9.6 g of sample in a Spex Mixer/Mill and  
299 pressed into a pellet using a Herzog pelletizing press. Major element detection limits were 0.01%

300 (P<sub>2</sub>O<sub>5</sub>, CaO), 0.5% (SiO<sub>2</sub>), 0.02% (Al<sub>2</sub>O<sub>3</sub>), or 0.02% (MgO) and precision (1σ) was typically ~2%.  
301 Detection limits for trace elements were ≤10 μg g<sup>-1</sup>.

302 Samples with a ratio of (CaO+MgO)/(SiO<sub>2</sub>+Al<sub>2</sub>O<sub>3</sub>) > 0.2—approximating >20 wt.% carbonate  
303 content—were excluded when calculating Mo, U, and Re averages, since compilations of RSE in  
304 black shales generally only include shale samples<sup>8,10,21</sup>. An exception was made for samples with  
305 >5 wt.% TOC, since such sediments would have played a role in trace metal cycling regardless of  
306 their mineralogical composition.

### 307 **Mo isotopes**

308 Mo isotopes were measured from fully digested OnZaP MSP0010 samples that were purified via  
309 column chromatography according to Ref. 41. A <sup>97</sup>Mo–<sup>100</sup>Mo double spike was employed<sup>53</sup> and the  
310 isotopes were measured on a Thermo Scientific Neptune multi-collector ICP-MS at IFREMER,  
311 Brest, France. Data is expressed relative to NIST SRM 3134 = 0.25‰<sup>54</sup>. Detailed methodology is  
312 provided in the Supplementary Information.

### 313 **U Isotopes**

314 Samples for U isotopes were sequentially digested in a mixture of 3 mL HNO<sub>3</sub> and 1 mL HF at  
315 100 °C for 24 hours, then aqua regia at 95 °C for 24 hours. Following each digestion step the  
316 sample was evaporated to dryness. Sample residues were taken up in 5 mL of 3M HNO<sub>3</sub> at 70 °C.  
317 All sample preparation was performed in a Pico-trace clean lab at the Yale Metal Geochemistry  
318 Center. Uranium isotope values were measured on a Thermo Neptune Multi-collector ICP-MS  
319 following the method in Ref. 22 using the IRMM-3636 233/236 U double spike. Accuracy and  
320 precision were monitored with concentration matched CRM112, CRM129a, and Ricca

321 geostandards. Error was less than 0.15‰. Detailed methodology is provided in the  
322 Supplementary Information.

### 323 **Data availability**

324 The novel ZF geochemical data presented here will be available in the PANGAEA data repository  
325 under the title “Trace metal concentrations and isotope compositions from the ~2.0 Ga black  
326 shales of the Zaonega Formation, NW-Russia (drill cores OnZaP, OPH)”<sup>55</sup>.

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