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1 Paleoproterozoic oxygenated oceans following the Lomagundi-
2 Jatuli Event

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22

23 **The ~2220–2060 Ma Lomagundi-Jatuli Event (LJE) was the longest positive carbon isotope**
24 **excursion in Earth history and is traditionally interpreted to reflect increased organic**
25 **carbon burial and a transient rise in atmospheric O₂. However, it is widely held that O₂**
26 **levels collapsed for more than a billion years following the LJE. Here, we show that black**
27 **shales postdating the LJE from the ~2000 Ma Zaonega Formation (ZF) contain the highest**
28 **redox-sensitive trace metal concentrations reported in sediments deposited before the**
29 **Neoproterozoic. This unit also contains the most positive shale U isotope ($\delta^{238}\text{U}$) values**
30 **measured to date, providing novel evidence that there was a transition to modern-like**
31 **biogeochemical cycling during the Paleoproterozoic. Although these records do not**
32 **preclude a return to anoxia during the Paleoproterozoic, they uniquely suggest that the**
33 **oceans remained well-oxygenated millions of years after the termination of the LJE.**

34

35 The Paleoproterozoic era (2500–1600 Ma) witnessed the longest positive carbon ($\delta^{13}\text{C}_{\text{carb}}$)
36 isotope excursion in Earth's history, recorded in marine carbonates deposited worldwide
37 between ~2220–2060 Ma—the Lomagundi-Jatuli Event (LJE)^{1,2}. Marine carbonates are generally
38 characterized by $\delta^{13}\text{C}_{\text{carb}}$ values that vary between –5‰ to 5‰ for most of Earth's history,
39 whereas peak LJE $\delta^{13}\text{C}_{\text{carb}}$ values reach 10–15‰^{1,3,4}. There is ongoing debate regarding the
40 processes that led to the LJE. The standard and most commonly accepted interpretation invokes
41 increased burial of ¹³C-depleted organic carbon (C_{org}), leading to the ¹³C-enrichment of the
42 dissolved inorganic carbon pool and positive $\delta^{13}\text{C}_{\text{carb}}$ ^{3,4}. This acceleration in C_{org} burial may have
43 been the result of an increase in oxidative weathering and nutrient delivery to the oceans⁴. Using
44 a simple isotope mass balance, it has been estimated that between $5\text{--}9 \times 10^{20}$ mol of C_{org} was
45 buried over 100 Ma, corresponding to the release of O₂ equivalents representing 12–22 times the
46 present O₂ atmospheric pool. An ensemble of evidence points to atmospheric O₂ accumulation
47 during the LJE, including proxies indicating growth of the marine sulphate reservoir^{7–9}, elevated
48 concentrations of redox sensitive elements (RSE)^{10–13}, and evidence for locally oxic conditions^{4,15}.
49 However, others have argued that the 'standard' interpretation of the LJE is difficult to reconcile
50 with our understanding of the C and O cycles^{16–18}, and that there is a notable paucity of C_{org} -rich
51 deposits at this time¹⁹, the most basic tracer of enhanced organic carbon burial. Further, the
52 carbon isotope dynamics during and after the positive excursion are currently debated, and there

53 are multiple interpretations of the LJE positive $\delta^{13}\text{C}_{\text{carb}}$ values that do not invoke elevated rates of
54 organic carbon burial and oxygen release (ref 18). Therefore, additional constraints on carbon
55 and oxygen cycling are clearly needed to refine our view of this time interval.

56 In this work we present new redox tracer data from three correlative cores (OnZaP-1, 3 and
57 OPH) of the upper Zaonega Formation (ZF), a mudstone-dolostone succession deposited in the
58 aftermath of the LJE. We provide some of the most straightforward evidence for Proterozoic
59 surface oxygenation. In fact, current redox proxy records are most consistent with increasing
60 oxygenation in the aftermath of the LJ positive carbon isotope excursion—forcing a re-evaluation
61 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 tuff horizons within the lower ZF, the formation
64 was deposited at <1970 Ma, ~ 70 Myrs after the proposed termination of the LJE²⁸. 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 $\geq 8\text{‰}$ ²⁹, with
67 $\delta^{13}\text{C}_{\text{carb}}$ in preserved carbonate strata returning to normal marine values of $\sim 0\text{‰}$ further
68 upsection³⁰. In the OPH core, the studied section occurs after several hundred meters of
69 stratigraphy—including cumulatively ~ 210 meters of mudstone-dominated sediments—and
70 contains carbonates bearing a negative or normal marine (and therefore post-LJE) $\delta^{13}\text{C}_{\text{carb}}$ signal
71 (ref. 30). Assuming a reasonable range of deposition rates for the mudstones—e.g., $1\text{--}100$ m
72 Myr^{-1} (Sadler et al., 1999, GeoResearch Forum.)—the studied section of the ZF was deposited
73 millions of years after the termination of the LJE in the Onega Basin.

74 The section is rich in total organic carbon (TOC), with average values of 27.4 ± 18.5 wt.% in
75 mudstones of the OnZaP-1 and 3 cores (combined into the OnZaP section, see Methods), and
76 14.5 ± 9.9 wt.% in OPH mudstones (Figure 1). These values are roughly comparable to the most
77 organic-rich modern marine sediments (e.g., up to 21.3 wt.% on the Peru margin; Böning et al.,
78 2004, GCA). Molybdenum, uranium (U), and rhenium (Re) concentrations in Zaonega mudstones
79 are significantly elevated relative to other Proterozoic black shales^{11,13,26}, averaging 130 ± 142 μg
80 g^{-1} , 19 ± 15 $\mu\text{g g}^{-1}$, and 116 ± 84 ng g^{-1} , respectively, in OnZaP mudstones. In the OPH section, Mo

81 and U average $71 \pm 92 \mu\text{g g}^{-1}$ and $37 \pm 50 \mu\text{g g}^{-1}$, whereas overall maximum Mo, U, and Re
82 concentrations across both sites are $1009 \mu\text{g g}^{-1}$, $238 \mu\text{g g}^{-1}$, and 516ng g^{-1} , respectively. We
83 focus specifically on Mo, U, and Re enrichments, as these metals have previously provided robust
84 evidence for major shifts in Earth's redox state^{11,13,26}. In the OnZaP section, $\delta^{98/95}\text{Mo}$ is on average
85 $0.67 \pm 0.81\text{‰}$, with a maximum of $1.49 \pm 0.14\text{‰}$. Uranium isotope values in the OnZaP section
86 range from -0.03 to 0.79‰ , with an average of 0.47‰ . The maximum value is the most ^{238}U -
87 enriched shale value that has been reported to date (ref. 76, Yang et al., 2017, Precambrian Res.).

88 The primary source of these RSE to the oceans is the oxidative weathering of terrestrial RSE-
89 bearing minerals (e.g., pyrite, uraninite), and subsequent riverine transport as aqueous
90 oxyanions^{34,35}. Hydrothermal inputs, while not fully constrained at present, are not expected to
91 be a quantitatively significant source for any of these RSE^{26,35}. The most important sink for these
92 RSE is sequestration into marine sediments, which is influenced by the redox state of the
93 depositional setting^{34,36}. In oxic seawater, these RSE are present as recalcitrant species that tend
94 to accumulate in the water column^{35,37}, although Mo adsorbs to Mn(IV)-oxides under oxic
95 conditions and can then be released in pore waters following the reductive dissolution of Mn(IV)-
96 oxides in anoxic sediments³⁸. In anoxic environments, these RSE are progressively converted into
97 particle-reactive species resulting in efficient drawdown through authigenic sulphide
98 precipitation or adsorption to organic matter^{36,37}. With regards to Mo, it has been found that
99 most efficient Mo sequestration takes place under euxinic waters with $>11 \mu\text{M}$ of sulphide
100 (HS^-)³⁹. In a broad sense, the contrasting behaviour of these elements in oxic and anoxic
101 conditions ensures that the drawdown and marine reservoir sizes are governed by global ocean
102 redox—large reservoirs of these RSE develop in an oxic ocean, which leads to large local
103 sedimentary RSE enrichments under anoxic conditions^{13,26}.

104 The U and Mo isotope systems, similar to RSE enrichments, respond to the global marine
105 redox landscape. There is consensus that well-oxygenated oceans are characterized by heavy Mo
106 and U isotope values (ref. 71 and Andersen et al., 2017, Rev. Mineral. Geochem.). It is, however,
107 difficult to gauge when a sedimentary archive captures seawater U and Mo isotope values. For
108 instance, it is easiest to capture seawater Mo isotope values in shales deposited in isolated basins
109 with high HS^- levels (ref. 50), but euxinic marine basins often deviate from the seawater isotope
110 composition (ref. 71)— $\delta^{98/95}\text{Mo}$ in euxinic shales is therefore often interpreted as a minimum

111 estimate for seawater (ref. 15). Uranium isotope values in shales will be closest to seawater
112 values in oxic sediments and up to ~1‰ heavier than seawater in anoxic and high productivity
113 settings (Andersen et al., 2014, EPSL) (see SI for detailed discussion on Mo and U isotope values).
114 Using this framework, our data points to well-oxygenated oceans with high rates of primary
115 productivity during deposition of the Zaonega Formation.

116 **Marine RSE inventory**

117 Enrichments in RSE (in the rest of this manuscript, RSE refers specifically to Mo, U, and Re) in the
118 ZF far exceed anything known from pre-Neoproterozoic black shales (Figure 2). Similar values
119 are found only in the Phanerozoic, where they have been taken as evidence for an expanded
120 seawater RSE inventory, the direct result of pervasive ocean-atmosphere oxygenation^{11,13,26}. We
121 believe that the ZF, likewise, contains evidence of a large marine RSE inventory that strongly
122 suggests a relatively oxidized ocean-atmosphere system with a robust terrestrial oxic RSE
123 weathering flux, in which the drawdown of RSE was limited by the relative scarcity of anoxic
124 conditions on the seafloor. Further, U and Re enrichments—which, unlike Mo, are also drawn
125 down in ferruginous waters⁴⁸—suggest that this was an episode of thorough water column
126 oxygenation on continental shelves, rather than just a restriction of euxinic deposition, >1.4 Gyr
127 before terminal oceanic oxygenation during the Neoproterozoic⁴².

128 While low Mo in black shales could be explained by either a small marine Mo pool, basinal
129 restriction leading to localized Mo depletion³⁸, or inefficient Mo scavenging under low HS-
130 conditions³⁹, there are limited ways to explain elevated RSE concentrations in black shales of the
131 ZF (i.e., up to several hundreds of $\mu\text{g g}^{-1}$ of Mo throughout the >160 km-wide basin). One
132 possibility is anomalously low sedimentation rates, which have previously been invoked to
133 explain high TOC in U-rich black shales of the Miocene Monterey Formation, USA⁴⁷. Although low
134 sedimentation rates may have played a role in concentrating TOC and RSE in the ZF, the
135 magnitude of the RSE enrichment—consistent with Phanerozoic levels (Figure 2)—makes it
136 unlikely sedimentation rate alone could account for it. A more plausible explanation is that the ZF
137 was also a highly efficient RSE sink that had reliable access to a large oceanic RSE inventory^{38,43}
138 (see SI for additional discussion on factors controlling RSE accumulation).

139 The U isotope values provide an independent confirmation of highly oxygenated oceans—as
140 noted above they are the most positive shale $\delta^{238}\text{U}$ values reported to date (Figure 2), requiring
141 both heavy seawater $\delta^{238}\text{U}$ values (likely comparable to the modern value of $\sim -0.4\text{‰}$) and a
142 relatively full expression of the equilibrium $\sim 1.2\text{‰}$ fractionation during U reduction. Heavy
143 seawater values only develop when oxic U burial is a major U burial flux in well-oxygenated
144 oceans (Andersen, 2014). In addition, a significant positive U isotope fractionation ($>0.6\text{‰}$)
145 strongly suggests U reduction in the water column (Andersen, 2017, Rev. Mineral. Geochem.).
146 Uranium reduction rates appear to scale with sulphate (or iron) reduction rates (Barnes and
147 Cochran, 1993, GCA)—providing a link between amounts of organic matter loading in a marine
148 system and the isotope fractionation that occurs during U burial. For reference, there is limited
149 water column sulphate reduction in the modern Black Sea and Cariaco Basin because of low rates
150 of productivity and maximum sediment $\delta^{238}\text{U}$ values are $\sim 0.4\text{‰}$ and 0.2‰ , respectively
151 (Andersen, 2014, EPSL). Therefore, these strongly positive U isotope values, along with the RSE
152 enrichments, are most readily explained by invoking both globally well-oxygenated oceans and
153 markedly elevated rates of local primary productivity, the latter of which would tend to enhance
154 the expression of isotope effects associated with U 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.*¹⁹ 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, 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 rocks⁴⁹. Second, Scott *et al.*⁸
164 argued that highly ^{34}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.*²⁷ explained the same trends
166 through basin-specific processes involving quantitative uptake of sulphate. Third, Asael *et al.*¹⁴
167 inferred an $\sim 0.7\text{‰}$ seawater $\delta^{98/95}\text{Mo}$ value from two other cores in the upper ZF, identical to

168 the average in the OnZaP section. Mn-oxides, which form in oxic waters, preferentially scavenge
169 ^{95}Mo and drive seawater $\delta^{98/95}\text{Mo}$ to higher values. If one assumes a modern riverine input value
170 of $\sim 0.7\text{‰}$ for the Paleoproterozoic (ref. 71), a seawater value of $\sim 0.7\text{‰}$ suggests limited Mn-
171 oxide precipitation and, thus, little O_2 in the oceans. However, as outlined above, the
172 sequestration of Mo in sediments commonly imparts a negative $\delta^{98/95}\text{Mo}$ fractionation (ref. 71).
173 This highlights that the highest Mo isotope values of $\sim 1.4\text{‰}$ represent a minimum seawater
174 $\delta^{98/95}\text{Mo}$ estimate (see ref. 15 and SI) and that the Mo isotope data does not necessarily preclude
175 widespread oxic conditions.

176 **Implications of oxygenated oceans at ~ 2.0 Ga**

177 RSE-replete conditions during the deposition of the ZF have important implications for Earth's
178 global C and O cycles during the Paleoproterozoic. Tracking the evolution of Earth's redox history
179 is also critical for understanding early eukaryote evolution. The late rise to prevalence of
180 eukaryotes in the Neoproterozoic is thought to be linked to widespread anoxic and nutrient-poor
181 conditions that favoured prokaryotic metabolisms^{55,56}. Given the extent of ocean oxygenation and
182 nutrient abundance inferred from the ZF^{4,44}, conditions favourable to eukaryotic diversification
183 could have been present for much of the middle Paleoproterozoic. It is curious, then, that
184 molecular clock analyses and microfossil evidence of eukaryote origin tend to converge after
185 ~ 1900 Ma^{57,58}. In the simplest sense this discrepancy supports the central importance of a
186 unique endosymbiosis event for the emergence of eukaryotes, rather than removal or lessening
187 of an environmental barrier.

188 The ZF is part of a well-recognized overall trend towards elevated RSE concentrations at
189 ~ 2400 – 2000 Ma that has been linked to well-oxygenated oceanic–atmospheric conditions^{11–13}.
190 However, surprisingly our ZF data extend this trend past the termination of the LJE.
191 Furthermore, the extreme RSE enrichments hint that, instead of being in decline, atmospheric O_2
192 abundance could still have been high perhaps several tens of Myrs after the canonical end of the
193 LJE²⁸. In the modern, well-oxygenated world, the geologic O_2 response time is on the order of ~ 2
194 Myrs⁶⁰, whereas the residence times of Mo, U, and Re in the oceans are ~ 440 , ~ 400 , and ~ 780
195 kyrs, respectively^{35,40,41}. Therefore, if the LJE decline is linked to a decrease in O_2 production as

196 the result of diminishing C_{org} burial by the end of the LJE, then O_2 would be expected to be
197 significantly attenuated by this time. Instead, our observations provide evidence for the opposite.

198 Our observations provide empirical evidence for models (e.g., [ref. 18](#)) that decouple the
199 strongly positive carbonate carbon isotope values of the LJE from enhanced organic carbon
200 burial. Further, if highly oxidized conditions continued up to ~ 2.0 Ga—or, alternatively, if the
201 Paleoproterozoic experienced large fluctuations in O_2 conditions, the ZF being a zenith—it
202 follows that O_2 abundance was governed by more complex controls than a simple C_{org} burial mass
203 balance, as outlined in Bekker and Holland⁴. This highlights the importance of exploring
204 alternative mechanisms that could account for Paleoproterozoic O_2 accumulation and the need
205 for refined chemostratigraphic and geochronological studies focused on this key interval of
206 Earth's history.

207

208 **Methods**

209 **Materials**

210 The material for this study comes from drill cores in the Onega Basin that intersect the ZF—a
211 relatively well-preserved 1500 m-thick succession of organic-rich mudstones and carbonates,
212 interlayered and intersected with igneous units including lavas, tuffs, and sills (see SI for a
213 detailed geological setting)^{20,28,63,64}. The 60 m long cores OnZaP-1 and OnZaP-3 were drilled 500
214 m apart in Shunga village, close to drill core FAR-DEEP 13A^{27,65}. The 3500 m long OPH core was
215 drilled ~ 70 km to the south. Paiste *et al.*^{27,66} correlated the three cores based on C isotopes, trace
216 metal enrichments, P concentrations, and a distinct massive P-rich dolomite unit that occurs
217 throughout the Onega basin⁶⁷.

218 The lithology of this section is characterized by alternating dolomite to calcite-rich
219 carbonates and exceptionally organic-rich mudstones that are intersected by silica or
220 pyrobitumen veins (Figure 1). In the OnZaP section, the interval from the bottom of the core to
221 53 m depth is dominated by highly organic-rich mudstones with relatively few carbonate beds;
222 the 53–33 m interval is mostly dolostone and contains a distinctive dolomite unit; and the 33–1.7

223 m interval consists of grey mudstones and marly carbonate beds²⁷. Two sets of samples from the
224 OnZaP section were analyzed in this study. Set MSP0001 consists of 135 samples that were taken
225 at roughly 1 m intervals and is identical to that used in Paiste *et al.*²⁷. Set MSP0010 contains 79
226 samples that more specifically targeted RSE and organic-rich intervals. A set of 89 samples were
227 analyzed from the 1060–1230 m interval of the OPH core that is roughly equivalent to the OnZaP
228 section.

229

230 **Elemental concentrations**

231 Total organic carbon content of the MSP0001 and OPH samples were adapted from Paiste *et al.*²⁷
232 and were measured from powdered aliquots using a LECO SC-444 analyzer at the Geological
233 Survey of Norway (NGU), Trondheim, Norway. Detection limit was 0.1 wt.% and precision better
234 than 10%. For the MSP0010 set, TOC was measured at the Pôle Spectrométrie Océan, European
235 Institute for Marine Studies (IUEM), Brest, France. Dried and powdered samples were combusted
236 in ceramic beakers at 500 °C for 24h and loss of mass on ignition was determined. Repeat
237 measurements of 7 samples generally differed by <1 wt.%.

238 Major and trace element compositions of MSP0001 and OPH samples were determined at
239 Acme Labs, Bureau Veritas Commodities Canada Ltd. The samples were first pulverized and
240 combusted to remove organic carbon. For major elements, the sample was fused in LiBO₂ flux,
241 then digested, whereas minor elements were analyzed from full digests in HNO₃, HClO₄, and HF.
242 Measurements utilized inductively coupled plasma optical emission spectrometry (ICP-OES) or
243 mass spectrometry (ICP-MS). Average relative standard deviation was less than 5% for all
244 elements. MSP0010 element composition was determined at IUEM. Samples were pulverized in a
245 tungsten carbide crusher and an agate mill, then combusted at 500 °C for 24h to remove organic
246 carbon. Major element concentrations were measured on a Jobin Yvon Horiba Ultima 2 ICP-OES
247 after digestion overnight at 80 °C in concentrated HF and HNO₃ and neutralization with boric
248 acid to retain Si. For trace element concentrations, digestion was performed in a class 1000 clean
249 laboratory using distilled acids—samples mixed with concentrated HF and HNO₃ were heated to
250 80 °C overnight, then allowed to evaporate; this digestion was then repeated with concentrated
251 *aqua regia*, after which the sample was taken up in 6M HCl. Trace element concentrations were

252 measured on a Thermo Scientific Element 2 ICP-MS calibrated against commercial multi-element
253 standards and digested geostandards (e.g. BHVO-2) were

254 Samples with a ratio of $(\text{CaO}+\text{MgO})/(\text{SiO}_2+\text{Al}_2\text{O}_3) > 0.2$ —approximating >20 wt.% carbonate
255 content—were excluded when calculating Mo, U, and Re averages, since compilations of RSE in
256 black shales generally only include shale samples^{11,13,26}. An exception was made for samples with
257 >5 wt.% TOC, since such sediments would have played a role in trace metal cycling regardless of
258 their mineralogical composition.

259

260 **Mo isotopes**

261 Mo isotopes were measured from fully digested OnZaP MSP0010 samples that were purified via
262 column chromatography according to ref. 68. A ⁹⁷Mo–¹⁰⁰Mo double spike was employed⁶⁹ and the
263 isotopes were measured on a Thermo Scientific Neptune multi-collector ICP-MS at IFREMER,
264 Brest, France. Data is expressed relative to NIST SRM 3134 = 0.25‰⁷⁰. Detailed methodology is
265 provided in the SI.

266

267 **U Isotopes**

268 Sample for U isotopes were sequentially digested in a mixture of 3 mL HNO₃ and 1 mL HF at
269 100°C for 24 hours, then aqua regia at 95°C for 24 hours. Following each digestion step the
270 sample was evaporated to dryness. Sample residues were taken up in 5 mL of 3 M HNO₃ at 70°C.
271 All sample preparation was performed in a Pico-trace clean lab at the Yale Metal Geochemistry
272 Center. Uranium isotope values were measured on a Thermo Neptune Multi-collector ICP-MS
273 following the method in Wang et al., 2018 using the IRMM-3636 URANIUM 233/236 double
274 spike. Accuracy and precision were monitored with concentration matched USGS NOD-A1 and
275 CRM-112A. Error was less than 0.1‰.

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284 **Data availability**

285 The novel ZF geochemical data presented here are included in the supplementary files.

286 **Author contributions**

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

294 **Competing interests**

295 The authors declare no competing interests.

296 **References**

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299 **Figure captions**

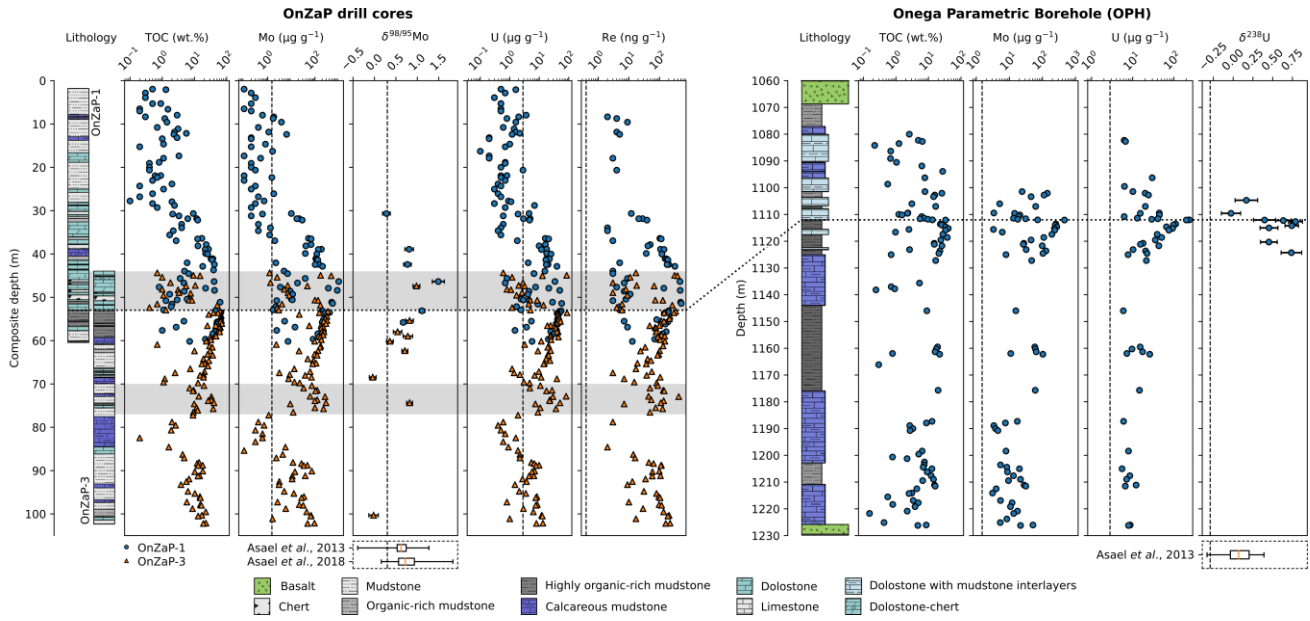
300 Figure 1: Lithology and geochemistry of the Zaonega Formation. Total organic carbon (TOC) and
301 redox sensitive metal (RSE) profiles, and Mo and U isotope ratios ($\delta^{98/95}\text{Mo}$ and $\delta^{238}\text{U}$) for the
302 OnZaP and OPH sections. Vertical dashed lines are average crustal values⁷¹⁻⁷³ and the dotted
303 horizontal line is the phosphorous-rich mudstone–dolostone contact used for intra-basinal
304 correlation (see Methods and SI). Boxplots below the Mo and U isotope plots represent the
305 distribution of previously published ZF data from lower in the succession^{14,68}. Gray horizontal
306 bands are partly silicified and calcified intervals due to fluid alteration²⁷. While these imply the
307 presence of secondary fluids that could have mobilized RSE, microscale RSE distribution
308 confirms the primary nature of the RSE enrichments (see SI).

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311 Figure 2: Secular trends in redox sensitive element concentrations from anoxic shales: Zaonega
312 Formation data plotted on compilations from literature. (a) Changes in $\delta^{13}\text{C}_{\text{carb}}$ ratio through
313 time, modified from Karhu⁷⁴. (b) Molybdenum concentrations from Robbins *et al.*⁷⁵. (c) Uranium
314 concentrations from Partin *et al.*¹¹. (d) Uranium isotope ratios from Wang *et al.*⁷⁶, Yang *et al.*
315 2017. (e) Rhenium concentrations from Sheen *et al.*¹³.

316 Figure 1:



317

318 Figure 2:

