

1 Terrestrial sources as the primary delivery mechanism of
2 mercury to the oceans across the Toarcian Oceanic Anoxic
3 Event (Early Jurassic)

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34 **ABSTRACT**

35 This study evaluates the utility of sedimentary mercury (Hg) contents as a proxy for
36 fingerprinting ancient massive volcanism, which is often associated with biogeochemical
37 perturbations. Herein we present new Hg geochemical data from anoxic marine basins across the
38 Toarcian Oceanic Anoxic Event (T-OAE; ~183 Ma) as a test of the complex Hg cycle. The T-
39 OAE was likely initiated by the main eruptive phase of the Karoo-Ferrar large igneous province,
40 which caused a subsequent cascade of environmental perturbations and resulting mass extinction.
41 At present the leading interpretation of sedimentary Hg anomalies has been volcanogenic
42 outgassing as the primary source. Our study and compilation results suggest, however, that
43 Hg/TOC anomalies were restricted to shallow-water, and/or proximal environments, while deep-
44 water, more distal depositional settings document no significant Hg-related anomalies.
45 Furthermore, asynchronous stratigraphic deviations in Hg enrichments favor terrestrially sourced
46 materials and local redox variability, rather than direct volcanogenic emissions, as a primary
47 control mechanism. Additionally, Hg isotope signatures from our only study site documenting an
48 Hg anomaly are also consistent with a terrestrial Hg origin during the T-OAE. Therefore, our
49 results suggest that Hg anomalies in the geological record need to be re-evaluated as a “smoking
50 gun” proxy that only infers volcanogenic inputs.

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52 **Keywords:** Toarcian Oceanic Anoxic Event; carbon isotope excursion; Hg anomalies; Hg

53 isotopes; large igneous provinces; mass extinction

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65 **1. Introduction**

66 Mercury (Hg) enrichments have recently been identified as a novel proxy to track past
67 events of large-scale volcanism (e.g., Sanei et al., 2012). In the geologic record, the
68 emplacements of large igneous provinces (LIPs) are hypothesized as the lynchpin behind many
69 first- and second-order mass extinction events (e.g., Courtillot, 1999) and other episodes of
70 environmental perturbation. It is thought that volcanogenic outgassing during LIP emplacement
71 catalyzes a cascade of environmental and biogeochemical feedbacks, which have a dramatic
72 impact on the biosphere (e.g., Courtillot, 1999; Bond and Wignall, 2014; Bond and Grasby,
73 2017). One of the fundamental issues facing the correlation of sedimentological, geochemical,
74 and biological records is unequivocally linking the timing, magnitude, and effects of LIP
75 activity, because converging geochemical processes can often yield non-unique signals in the
76 sedimentary record.

77 Numerous studies have applied the Hg proxy to Phanerozoic extinctions and oceanic
78 anoxic events (OAEs) associated with documented or hypothesized LIP emplacements, and have
79 noted contemporaneous Hg concentration ([Hg]) anomalies and/or increases relative to total
80 organic carbon (Hg/TOC; e.g., Sanei et al., 2012, Percival et al., 2015; Thibodeau et al., 2016;
81 Grasby et al., 2017; Scaife et al., 2017; Wang et al., 2018; Fantasia et al., 2018; see SI for a list
82 of all ancient Phanerozoic Hg anomalies linked to volcanic activity). The strong affinity of Hg
83 with organic matter (e.g., Ravichandran, 2004) makes it necessary to report Hg/TOC values
84 when identifying Hg anomalies, a standard practice when documenting anthropogenic
85 enrichments in modern sediments (e.g., Fitzgerald et al., 2007). These studies have concluded
86 that LIP injections of CO₂, CH₄, or SO_x into the atmosphere caused the planet to warm and/or
87 cool, depending on the timescale, which then affected the biosphere through environmental and

88 biogeochemical feedbacks (e.g., Courtillot, 1999; Pálffy and Smith, 2000). These suggested
89 feedbacks may represent extinction mechanisms, so understanding the link between LIPs and
90 biological evolution remains critical to resolving the relationship between global environmental
91 change and life.

92 The Early Jurassic Toarcian OAE (T-OAE; ~183 Ma) is a well-documented, transient
93 climate event that was potentially triggered by the initial emplacement of the Karoo-Ferrar LIP,
94 and resulted in global-scale environmental change, culminating in marine mass extinction/s. The
95 T-OAE is characterized by a globally synchronous negative carbon isotope excursion (N-CIE)
96 that represents a major change in the carbon cycle (e.g., Hesselbo et al., 2000; Izumi et al., 2012;
97 Them et al., 2017a; c.f. Them et al., 2018). Other paleoenvironmental changes associated with
98 the T-OAE are an acceleration of the global hydrological cycle and rates of continental
99 weathering (e.g., Percival et al., 2016; Them et al., 2017b; Izumi et al., 2018), increased biomass
100 burning as a result of wildfires (e.g., Baker et al., 2017), carbonate platform demise (e.g., Trecalli
101 et al., 2012; Han et al., 2018), global oceanic deoxygenation (e.g., Them et al., 2018),
102 widespread pyrite burial due to expansion of euxinic (anoxic and sulfidic) conditions (e.g., Gill
103 et al., 2011), and a multi-phased marine mass extinction interval (e.g., Caruthers et al., 2013).

104 Constraining the timing and magnitude of the influence of the Karoo-Ferrar LIP (e.g.
105 Pálffy and Smith, 2000; Sell et al., 2014) is pivotal to our understanding of the effect of massive
106 volcanic eruptions on environmental changes and biological extinction/turnover during this time.
107 Previously published Pliensbachian-Toarcian Hg datasets show variable Hg enrichments (i.e.,
108 enrichment magnitudes and asynchronous stratigraphic enrichment variabilities) during the T-
109 OAE interval (e.g., Percival et al., 2015; Fantasia et al., 2018; Fig. 1); these are concurrent,
110 however, with lithological transitions (i.e., carbonates to organic matter-rich shales, mudstones to

111 clay-rich sandstones, or other similar changes). These Hg enrichments are directly linked to
112 volcanogenic Hg emissions associated with the Karoo-Ferrar LIP (e.g., Percival et al., 2015;
113 Fantasia et al., 2018), although other lines of evidence show increased LIP production and global
114 oceanic deoxygenation before the initiation of the classical defined T-OAE interval (e.g., Moulin
115 et al., 2017; Them et al., 2018).

116

117 **2. Mercury Cycle**

118 Today, Hg is emitted to the atmosphere from several sources including the oceans,
119 biomass burning, rock weathering, soil erosion, volcanism, and anthropogenic activities (Fig. 2).
120 Elemental Hg (Hg^0) is the dominant form of Hg in the atmosphere. The residence time of
121 atmospheric Hg^0 is 0.5 – 1 yr (e.g., Selin, 2009; Driscoll et al., 2013), which is less than the
122 mixing time of the hemispheres (ca. 1–1.5 yr), and therefore it can be globally transported
123 relatively rapidly (e.g., Schuster et al., 2002). Atmospheric Hg^0 is removed through two
124 pathways: [1] transformation to oxidized Hg(II) species, which are particle reactive and soluble,
125 and easily deposited through wet/dry deposition; and [2] direct uptake by vegetation and soils
126 followed by oxidation. Mercury enters the ocean primarily through direct atmospheric deposition
127 and terrestrial riverine runoff (e.g., Holmes et al., 2010; Amos et al., 2014). Mercury in major
128 rivers is particulate-bound, although it becomes decoupled from lithogenic materials after initial
129 deposition (e.g., Zhu et al., 2018); thus, normalizing Hg to lithogenic tracers (i.e., aluminum and
130 titanium; e.g., Scaife et al., 2017; many others) can be problematic. Approximately 25% of
131 riverine-derived Hg might reach the open ocean, with the majority being deposited in shallow
132 proximal locations such as estuaries and nearshore ocean margins (e.g., Amos et al., 2014).
133 Atmospheric Hg also contains more soluble Hg species (e.g., particulate bound Hg(II)), which

134 can be deposited and then re-volatilized to the atmosphere, similar to Hg(0). Importantly, these
135 processes can recycle initial Hg inputs several times through the environment (e.g., Driscoll et
136 al., 2013) before it ultimately enters the ocean where it is scavenged by organic-rich particles,
137 and sinks to the seabed (as reviewed by Fitzgerald and Lamborg, 2014). This results in an
138 average oceanic/atmospheric residence time – from source to ultimate sink – of ~3 thousand
139 years (e.g., Selin et al., 2008).

140 While volcanoes are the dominant input to the exogenic Hg cycle on geologic timescales,
141 the cycling of Hg through many intermediate reservoirs (Fig. 2) can make it difficult to identify
142 the primary source(s) of bulk sedimentary Hg (e.g., Driscoll et al., 2013). Enrichments alone
143 (i.e., Hg anomalies relative to pre-anomaly values) have proven to be a tenuous fingerprint for
144 the sources of Hg in the modern, thus several studies have used Hg isotopes. Mercury has seven
145 natural stable isotopes (^{196}Hg , ^{198}Hg , ^{199}Hg , ^{200}Hg , ^{201}Hg , ^{202}Hg , and ^{204}Hg), which can be
146 partitioned via mass-dependent (MDF, reported in $\delta^{202}\text{Hg}$) and/or mass-independent (MIF,
147 reported in $\Delta^{199}\text{Hg}$) fractionations during its cycling (e.g., Bergquist and Blum, 2007). To date,
148 large variations of Hg isotopic ratios (~10‰ for $\delta^{202}\text{Hg}$ and $\Delta^{199}\text{Hg}$ values) have been reported
149 for natural samples (e.g., Blum et al., 2014). Although $\delta^{202}\text{Hg}$ has been used as a source tracer in
150 many case studies, it needs to be cautioned that MDF is ubiquitous and occurs during all
151 biological reactions (e.g., reduction, methylation, demethylation), abiotic chemical reactions
152 (e.g., chemical reduction, photoreduction, oxidation), and physical processes (e.g., volatilization,
153 evaporation, adsorption, and dissolution), which may lead to ambiguous interpretations
154 (reviewed by Blum et al., 2014).

155 The addition of $\Delta^{199}\text{Hg}$ signatures greatly increases the usefulness of Hg isotopes because
156 they provide a unique fingerprint of specific pathways. It has been suggested that MDF and MIF

157 signatures can be combined to identify the Hg source(s) in the modern (e.g., Blum et al., 2014)
158 and in the ancient to varying effects (e.g., Thibodeau et al., 2016; Grasby et al., 2017; Gleason et
159 al., 2017; Yin et al., 2017). Plotting $\Delta^{199}\text{Hg}$ vs. $\delta^{202}\text{Hg}$ clusters data of unique process(es)
160 together (see Figure 1 in Blum et al., 2014). Although modern Hg isotope studies (e.g., Leticariu
161 et al., 2011; Das et al., 2013; Bessinger, 2015) show that there is an overlap in the isotope
162 composition of natural sources, the MIF signals could be useful in fingerprinting Hg sources (Fig.
163 2). On geologic timescales, it is suggested that Hg was emitted to the surface environment
164 through volcanic and potentially hydrothermal activities, and these sources have shown $\Delta^{199}\text{Hg}$
165 values close to zero (Fig. 2). $\Delta^{199}\text{Hg}$ anomalies have been predominately observed on Earth's
166 surface environment such as soils, sediments, and atmospheric and biological samples, and Hg
167 photoreactions are thought to play the foremost role in the generation of $\Delta^{199}\text{Hg}$ anomalies in
168 natural samples (e.g., Blum et al., 2014). It is these $\Delta^{199}\text{Hg}$ differences that may be useful to
169 distinguish between primary and secondary Hg sources.

170

171 **3. Study sites**

172 Here we investigate the dynamics of the Hg cycle across the T-OAE in two
173 independently constrained anoxic basins from northeastern Panthalassa and the European epeiric
174 seaway (Fig. 1). The first in Alberta, Canada, represents a transect in water depth from proximal
175 (East Tributary) to distal (drill cores 1-35-62-5W6 and 6-32-75-20W6) in the Fernie Formation
176 (Them et al., 2017a, b, 2018). The second represents a semi-restricted locality in the European
177 epeiric sea collected from Dotternhausen Quarry, South German Basin. These regions are ideal
178 localities for testing Hg anomalies, as they both have reducing redox conditions during the study
179 interval (Them et al., 2018). Constraining the local depositional conditions is important to

180 quantify Hg enrichments, as Hg is associated with TOC contents of the sediment and is also
181 redox sensitive (e.g., Ravichandran, 2004; Niessen et al., 2003), which represents the first
182 attempt to do this for the Pliensbachian-Toarcian interval. Additionally, the site with the highest
183 and only Hg/TOC anomaly (East Tributary) was chosen for isotopic analysis to potentially aid in
184 constraining Hg sources as it is the only site suggesting Hg source variability (e.g., Blum et al.,
185 2014; Thibodeau et al., 2016, Grasby et al., 2017; Wang et al., 2018). The sites where no
186 Hg/TOC anomalies were identified were not analyzed for Hg isotopic compositions, as they
187 suggest minimal change in the Hg cycle and confirm the null hypothesis (i.e., there is no change
188 in Hg/TOC across the T-OAE).

189

190 **4. Methods**

191 *4.1 Mercury Concentrations*

192 Splits of samples from previous studies of the Pliensbachian and Toarcian stages of the
193 Early Jurassic (e.g., Them et al., 2017a,b; Gill et al., 2011) were analyzed for Hg mercury
194 concentrations in the School of the Environment at Florida A&M University. Approximately 50-
195 100 mg of sample powder was added to a measuring boat and placed into a DMA-80 (Milestone
196 Inc, Shelton, CT) and heated in stages. Volatilized Hg was collected by gold amalgamation
197 before being measured via spectral analysis. All samples contained quantifiable mercury
198 concentrations. Data were calibrated using international reference standards (SRM Spinach
199 1570a, SRM Mussel 2976, BCR-60 Aquatic Plant, and TORT-2 SRM; see Supplementary
200 Information and SI Table 1 for values), which bracketed the full range of mercury concentrations
201 calculated in these geologic samples. TOC values for these samples were previously published
202 (e.g., Them et al., 2017a,b; Dickson et al., 2017). Mercury data collected by this technique

203 delivered the same values as the samples that were chosen for Hg isotopes and calculated using
204 different chemical processing and analytical instrumentation (see below).

205

206 *4.2 Mercury Isotopes ($\delta^{202}\text{Hg}$ and $\Delta^{199}\text{Hg}$)*

207 Splits of samples from the East Tributary section of Canada were analyzed for Hg
208 isotopes at the Laboratory of Advanced Environmental Analysis, Hong Kong Polytechnic
209 University. Approximately 0.5 g sample was digested in 5 mL of aqua regia (HCl:HNO₃ = 3:1,
210 v:v) using water bath (95 °C) for 1 hour. Mercury in the digest solutions were diluted to 0.2 to
211 0.5 ng mL⁻¹, and the acid concentrations were adjusted to 20% (v/v). Mercury and acid matrices
212 of the bracketing Hg standard (NIST SRM 3133) were matched to the sample solutions. Digests
213 of standard reference materials (MESS-1, ocean sediment) were prepared, and measured in the
214 same way as the samples. UM-Almadén secondary Hg standard solution containing 0.2, 0.5, and
215 1.0 ng mL⁻¹ of Hg in 20% (v/v) aqua regia was also measured. No statistical differences in Hg
216 isotopic compositions were observed for solutions with different Hg concentrations (see SI Table
217 1), and the results for UM-Almadén and MESS-1 agreed well with previous studies (e.g., Blum
218 et al., 2007; Blum and Bergquist, 2007; Donovan et al., 2013). Uncertainties in the data reported
219 in this study reflect the larger values of either the external precision of the replication of the UM-
220 Almadén or the measurement uncertainty of MESS-1. The Hg concentration and isotope data are
221 included in the SI data.

222 Mercury isotope ratios were measured by a Neptune Plus multi-collector inductively
223 coupled plasma mass spectrometry (MC-ICP-MS). The MC-ICP-MS was equipped with a gas-
224 liquid phase separator and an Apex-Q desolvation unit (Elemental Scientific Inc., USA) for Hg
225 and thallium (Tl) introduction, respectively. Briefly, SnCl₂ was continually pumped along with

226 Hg(II) sample solutions and allowed to mix prior to being introduced to a gas/liquid separator,
 227 producing gaseous elemental Hg(0). Using the gas/liquid separator, a relatively simple and dry
 228 sample stream contain just Ar and Hg(0) was added to the instrument, which minimized any
 229 possible matrix effect. It is possible that the wet digestion may cause incomplete reduction of
 230 Hg(II) by SnCl₂, which may cause Hg isotope fractionation. However, this is not the case for our
 231 samples. Hg concentrations of our samples were monitored using the ²⁰²Hg signals of MC-ICP-
 232 MS, and the total Hg estimated by ²⁰²Hg signals were 86 – 107% to that measured by the Hg
 233 analyser at the School of Environment at Florida A&M University (see above). Detailed methods
 234 for conducting the MC-ICP-MS analysis were described previously (Geng et al., 2018). The
 235 signals for ²⁰²Hg were <0.02 V for acid blanks. The sensitivities of ²⁰²Hg during Hg isotope
 236 analysis was 1.4 to 1.7 V per ng mL⁻¹ Hg. Mass dependent fractionation of Hg isotopes is
 237 expressed in δ²⁰²Hg notation in units of per mil (‰) referenced to the NIST-3133 Hg standard
 238 (analyzed before and after each sample):

$$239 \quad \delta^{202}\text{Hg} (\text{‰}) = [({}^{202}\text{Hg}/{}^{198}\text{Hg}_{\text{sample}})/({}^{202}\text{Hg}/{}^{198}\text{Hg}_{\text{standard}}) - 1] \times 1000 \quad (1)$$

240 Mass independent fractionation of Hg isotopes is reported in Δ notation (Δ^{xxx}Hg), which describe
 241 the difference between the measured δ^{xxx}Hg and the theoretically predicted δ^{xxx}Hg value using
 242 the following formula:

$$243 \quad \Delta^{\text{xxx}}\text{Hg} \approx \delta^{\text{xxx}}\text{Hg} - \delta^{202}\text{Hg} \times \beta \quad (2)$$

244 where β is equal to 0.2520 for ¹⁹⁹Hg, 0.5024 for ²⁰⁰Hg, and 0.7520 for ²⁰¹Hg (e.g., Blum and
 245 Bergquist, 2007).

246

247 **5. Results**

248 In northeastern Panthalassa, the most proximal shallow-water site (East Tributary section;

249 n = 36) shows an increase in [Hg] from 0.03 to 0.24 mg/kg (or ppm) and Hg/TOC of 0.02 to 0.05
250 ([mg/kg]/TOC), with the highest values coincident with the N-CIE interval (Fig. 3). During the
251 N-CIE, $\delta^{202}\text{Hg}$ and $\Delta^{199}\text{Hg}$ values (n = 8) become more negative (~ -0.5 to -1 ‰ and ~ -0.1 to -0.2
252 ‰, respectively; Fig. 3). The intermediate water depth site (core 1-35-62-20W5; n = 18), shows
253 an [Hg] increase at the base of the N-CIE from one sample, but lacks a corresponding Hg/TOC
254 anomaly due to simultaneous TOC enrichment (Fig. 3). The distal and deepest-water site (core 6-
255 32-78-5W6; n = 17) shows a decrease in [Hg] and Hg/TOC across the N-CIE (Fig. 3).

256 In the European epeiric sea Dotternhausen section (n = 29), a significant increase in [Hg]
257 from ~ 0.05 to 0.35 mg/kg occurred during the N-CIE, but again lacks a coincident Hg/TOC
258 anomaly as TOC is also enriched (Fig. 4). At this site there are higher Hg/TOC values below the
259 N-CIE, but these reflect extremely low and variable TOC contents (see SI Appendix) as there are
260 no corresponding Hg enrichments (Fig. 4).

261

262 **6. Discussion**

263 *6.1 Evaluating Volcanism as a Direct Driver of Toarcian N-CIE Hg Enrichments*

264 Mercury data from the Panthalassa transect show that only the most proximal location
265 (i.e., East Tributary) documents minor Hg enrichments (as compared to some values from
266 Europe) in both [Hg] and Hg/TOC during the N-CIE (Figs. 3, 5, and 6). As Hg/TOC values
267 increase during the N-CIE, there is a decrease in $\delta^{202}\text{Hg}$ and $\Delta^{199}\text{Hg}$ (~ -0.5 to -1 and ~ -0.1 to -0.2 ,
268 respectively), which suggests that the source(s) or geochemical process(es) controlling local Hg
269 deposition may have changed during the carbon isotope perturbation. As previously stated, there
270 are currently several known mechanisms controlling Hg cycling. These include: volcanism,
271 biomass burning, increased detrital inputs (rock weathering and soil loss), photoreactions, and/or

272 some combination of the above (Fig. 2). The isotope results from the N-CIE interval are
273 inconsistent with purely volcanic signatures which have $\Delta^{199}\text{Hg}$ near zero or more positive, and
274 therefore, are more suggestive of a trend toward terrestrial sources (e.g., soils, plants, and peat,
275 which have more negative $\Delta^{199}\text{Hg}$ values but slightly overlap; Fig. 2). Furthermore, the range of
276 $\delta^{202}\text{Hg}$ and $\Delta^{199}\text{Hg}$ values, along with the Hg/TOC anomaly, at this location is within the range
277 of modern and pre-anthropogenic marine sediments (e.g., Gehrke et al., 2009; Gleason et al.,
278 2017 and references within). As such, the Hg in our samples suggests the enrichment mechanism
279 is not sourced from direct volcanic emissions during the N-CIE. However, this result does not
280 rule out terrestrial cycling of previously deposited volcanogenic mercury. The recycling of
281 terrestrial Hg is likely related to climatic feedbacks associated with volcanism that could have
282 resulted in increased wildfires (e.g., Baker et al., 2017) and enhanced riverine loading of soil-
283 derived Hg through increased weathering (e.g., Percival et al., 2016; Them et al., 2017b; Izumi et
284 al., 2018). Additionally, at the East Tributary location, the T-OAE N-CIE interval is also
285 associated with the increased deposition of sand-sized grains (e.g., Them et al., 2017a) and
286 higher Al contents (e.g., Them et al., 2017b), which could be due to a local increase in detrital
287 input from an enhanced hydrological cycle (e.g., Izumi et al., 2018). These isotope data are also
288 similar in magnitude with previously published work for other Phanerozoic extinction events that
289 show minor $\Delta^{199}\text{Hg}$ perturbations (e.g., Grasby et al., 2017; Wang et al., 2018). It must be noted,
290 however, that the Hg isotope values of the multiple Hg sources overlap (Fig. 2); thus, caution is
291 needed when interpreting these data alone to identify specific source(s) as continental shelf to
292 nearshore environments likely record an amalgamation of these sources.

293 The Dotternhausen Quarry Hg/TOC data remain low during the T-OAE, with values only
294 significantly fluctuating below the N-CIE (Fig. 4). The one-point Hg and Hg/TOC increase in the

295 T-OAE interval is intriguing because it may represent an increase in volcanic activity. This
296 sample, however, is associated with elevated pyrite contents and is likely controlled by local Hg
297 cycling (see Supplemental Information). Notably, the fluctuating Hg/TOC values (0.05 to 0.17)
298 prior to the N-CIE are similar in magnitude to several previous studies that attribute such
299 fluctuations to volcanic activity (e.g., Percival et al., 2015; Scaife et al., 2017; Fantasia et al.,
300 2018; many others). There is no change in [Hg], however, and therefore we suggest that the
301 observed Hg/TOC values are driven by low and fluctuating TOC (<0.3%), which are also
302 associated with lithologic changes (organic matter-lean carbonate marls from 0 to 2 meters; Fig.
303 4). It is unlikely these Hg/TOC values are driven by local redox variability, as water column
304 redox conditions are predominantly reducing (anoxic) for the investigated intervals at this
305 location (e.g., Them et al., 2018; see Supplementary Information).

306 Diagenetic alteration of the primary Hg and TOC values could be a possible mechanism
307 to explain the lack of Hg enrichment at Dotternhausen; we suggest, however, that it would be
308 unlikely to have caused the observed Hg/TOC record. While the effects of diagenesis on Hg are
309 relatively unknown, it is probable that Hg and TOC would be affected similarly if Hg is truly
310 associated with organic matter, but could be incorporated in new mineral phases after dissolution
311 in pore fluids. If the Hg and TOC are decoupled, however, then loss of TOC through thermal
312 decomposition or other similar processes during burial may result in spurious Hg anomalies,
313 which is more likely in localities with highly variable TOC. This would be the case if Hg did not
314 also volatilize at temperatures resulting in thermal decomposition of organic matter. The reverse
315 is also true where loss of Hg through volatilization would result in a muted Hg/TOC signal if
316 there was no organic matter loss during burial and heating. Although possible, there is no
317 evidence to suggest that either of these scenarios resulted in the observed Hg/TOC values.

318 Alternatively, the observed increases in Hg during the N-CIE interval are potentially associated
319 with changes in the type of organic matter at this location (e.g., Schwark and Frimmel, 2004).
320 Changing organic matter sources (i.e., prokaryotic vs. eukaryotic, marine vs. terrestrial, etc.) and
321 the subsequent effect on Hg sequestration is not constrained for any ancient deposits, and
322 therefore moving forward will be an important parameter to constrain for the validity of the Hg
323 proxy, especially for events with large, widespread climatic and biological perturbations.

324 Comparable lithologic variability (low TOC to TOC-rich sediments) and ranges of
325 Hg/TOC values (0.14 to 0.4) to those observed at the Dotternhausen Quarry are also observed in
326 a mid-Pleistocene sediment core from the Mediterranean Sea. The Hg and Hg/TOC anomalies
327 are not linked to volcanic activity, but rather local redox variability and low TOC values
328 (~0.25%; e.g., Gehrke et al., 2009; see Fig. 4 and SI Figs. 1 and 2). This suggests that
329 fluctuations of this magnitude are non-unique in the geological record and can be driven by local
330 or regional Hg cycling.

331 All previously reported Toarcian N-CIE Hg/TOC anomalies occur in successions with
332 low and/or variable TOC contents (see Percival et al. (2015) and Fantasia et al. (2018) for these
333 values) and lithological variability (e.g., Percival et al., 2015; Fantasia et al., 2018; Fig. 5). Given
334 this, caution should be used when interpreting Hg data from low TOC settings (i.e., carbonates,
335 low-TOC siliciclastics, etc.) in the geological record (e.g., Grasby et al. (2016) set a lower limit
336 of 0.2%). This was suggested to minimize false positives, and generally this approaches the
337 lower limits of accuracy and precision for TOC measurements and therefore compromises
338 Hg/TOC values.

339 To better constrain the spatiotemporal record of Hg during the Toarcian N-CIE we have
340 compiled all published Toarcian N-CIE data (e.g., Percival et al., 2015, 2016; Fantasia et al.,

341 2018; this study; Figs. 1 and 5). This new compilation documents two observations: [1] there is a
342 clear proximity relationship to landmasses in sections with Hg anomalies (Fig. 6), and [2]
343 enrichments are asynchronous amongst these localities (Figs. 5 and 6). All of the locations
344 recording Hg enrichments (6 out of 7), highlighted in blue, are in close proximity to landmasses
345 (Mochras Borehole, Bornholm, Peniche, Arroyo Lapa, El Peñon, East Tributary; while Yorkshire
346 is the exception with no Hg/TOC anomaly; Figs. 1, 5, and 6). The deepest and more distal sites
347 have no Hg/TOC anomalies (0 out of 5; Sancerre core, Dotternhausen, Velebit core, and Alberta
348 cores). This suggests that proximity to land may control the Hg content of marine sediments
349 during the N-CIE, which is to be expected if the dominant source of Hg was terrestrial. This
350 seems to contradict the idea that the atmosphere was the dominant, direct source of Hg during
351 the N-CIE, which would be expected to deposit Hg more uniformly throughout the ocean as the
352 atmospheric residence time is close to the mixing time for the hemisphere of emission (Fig. 2).

353 The Hg deposited across a landscape directly from the atmosphere via volcanic eruptions
354 would also be expected to be redistributed/cycled during its transport within the intermediate
355 reservoirs (i.e., plants and soils; Fig. 2) before reaching estuarine and marine sediments.
356 Importantly, these reservoirs would have continued to host and cycle Hg long after its initial
357 deposition (e.g., Driscoll et al., 2013; Amos et al., 2013; Zhu et al., 2018; Fig. 2). The increase of
358 Hg from other terrestrial reservoirs (Fig. 2) could therefore mask any direct volcanic Hg signal.
359 Thus, the pattern of the N-CIE Hg enrichments suggests that the observed Hg anomalies most
360 likely reflect changes in regional riverine input. Furthermore, these enrichments would continue
361 well after the initial driver for climatic and environmental change ceased, potentially causing
362 heterogeneity in the timing of Hg burial and enrichment in the sedimentary record (Amos et al.,
363 2014; Fig. 5), an expected outcome of the propagation of some environmental signals to be

364 preserved in marine sedimentary record (e.g., Romans et al., 2016).

365 Increased Hg inputs from rivers (e.g., Amos et al., 2014; Rice et al., 2009) through rock-
366 weathering interactions, soil erosion, and/or biomass burning (e.g., Rice et al., 2009; Grasby et
367 al., 2017) would heterogeneously impact Hg inputs in nearshore environments (e.g., Zhu et al.,
368 2018). The idea of this process exerting an influence on the Toarcian record is supported by
369 evidence that global climates became both warmer and wetter, with increased continental
370 weathering, during the classical T-OAE interval (e.g., Dera and Donnadieu, 2012; Percival et al.,
371 2016; Them et al., 2017b, Izumi et al., 2018). Following this idea, local delivery of Hg through
372 rivers would most directly influence the observed Hg anomalies in proximal locations (e.g.,
373 Percival et al., 2015; Fantasia et al., 2018; this study). Furthermore, modern wildfires can
374 increase the supply of Hg to surface waters and the atmosphere (e.g., Burke et al., 2010). Recent
375 research suggests that a significant increase in sedimentary charcoal abundances is associated
376 with the latter half of the N-CIE interval, indicative of increased wildfires (e.g., Baker et al.,
377 2017), which could also enhance the input of Hg to the oceans on a local to regional scale (Fig.
378 2). Due to their unique accumulation pathways and preservation of Hg and TOC into sediments,
379 one would not necessarily expect to observe increases in charcoal abundances and Hg or
380 Hg/TOC at the same stratigraphic level. A similar relationship with wildfires was suggested for
381 proximal Hg anomalies at the Latest Permian extinction (e.g., Grasby et al., 2017). The increase
382 in Hg deposition from wildfire activity, the magnitude of which intensifies in a warming world
383 (e.g., Pechony and Shindell, 2010), needs to be considered as a probable Hg source during other
384 intervals of climatic upheaval.

385 The proximal locations that do record N-CIE Hg anomalies are not necessarily
386 inconsistent with the interpretation that LIP volcanism resulted in these enrichments, but there

387 are also asynchronous stratigraphic enrichments/depletions in Hg across the N-CIE interval (e.g.,
388 Percival et al., 2015; Fantasia et al., 2018; Fig. 5). It might be expected that an increase in
389 volcanic-derived Hg would result in synchronous stratigraphic Hg enrichments at each location;
390 the observation that Hg enrichments occur at different points in time (using correlations based on
391 carbon isotope stratigraphy and the estimated duration of the 300-500 kyr for the N-CIE interval;
392 e.g. Boulila et al. [2014] and Sell et al. [2014]) in specific locations suggests that local- and
393 regional-scale processes exert a control on the resulting stratigraphic record of Hg (Fig. 5). Thus,
394 the observed asynchronous stratigraphic Hg enrichments (or lack thereof) likely represent the
395 influence of the local/regional cycling of Hg rather than the direct input of Hg from volcanogenic
396 emissions with potential relationships to source-to-sink sedimentary dynamics (e.g., Romans et
397 al., 2016).

398 A striking observation is that there is no Hg/TOC anomaly during the N-CIE interval in
399 the proximal Yorkshire location even though there are small Hg increases (e.g., Percival et al.,
400 2015; Figs. 1, 5, and 6). The absence of a Hg/TOC increase at Yorkshire could be due to many
401 reasons: re-cycling and re-emissions of Hg prior to sedimentation, post-depositional release of
402 Hg due to local redox variability (e.g., Zhu et al., 2018), potential changes in organic matter
403 source affecting Hg bioaccumulation, or water column stratification as is observed at this
404 location (e.g., French et al., 2014). It may also be related to an early Toarcian sea level
405 transgression. Regardless, there will be local deviations to the model put forth to explain the
406 observed Hg/TOC anomalies during the N-CIE interval (Figs. 5 and 6), but it provides the most
407 parsimonious explanation to-date.

408 *6.2 Estimating the amount of mercury release across the T-OAE*

409 It is difficult to quantify the release of mercury from the emplacement of ancient LIPs as
410 there is no equivalent modern analog. A previous estimate by Percival et al. (2015) determined
411 that 150 megatons (Mt) of Hg was released by the K-F LIP based on its size and using the
412 modern Hg/SO₂ emission values from volcanoes. This estimation is much less than the ~3,800
413 Mt release of Hg estimated from the emplacement of the Siberian traps across the Permo/Triassic
414 boundary (e.g., Sanei et al., 2012). These calculations, however, are reasonable first attempts
415 given the number of unconstrained parameters from these ancient LIPs. It is also possible,
416 however, to quantify the increased fluxes of Hg to the ocean/atmosphere system from weathering
417 and wildfires using the modern mass balance (Fig. 2). For example, if global weathering rates
418 increased by approximately two-fold across the T-OAE (e.g., Them et al., 2017b) and global
419 wildfire activity increased by three-fold (c.f., Baker et al., 2017), an additional 210 Mt and 120
420 Mt of Hg, respectively, could be released above pre-perturbation steady state from these two
421 sources assuming a 300-kyr perturbation (see Them et al., 2017b and references within) and a
422 modern mass balance (see Fig. 2). Thus, the potential for increased fluxes should be considered
423 for Hg studies that are associated with other intervals of climatic perturbation and widespread
424 environmental destabilization.

425 *6.3 Mercury isotopes to fingerprint potential sources*

426 As noted above, Hg can be cycled through multiple reservoirs, many of which have
427 isotopic overlap, before it is eventually deposited in the sedimentary record (e.g., Blum et al.,
428 2014; Fig. 2). In near-modern marine sediments, the observed range of paired Hg/TOC and MDF
429 and MIF values (e.g., Blum et al., 2014; Gehrke et al., 2009; Gleason et al., 2017 and references
430 within) is similar to the range observed in the Toarcian record as well as other events in the
431 geologic record (e.g., Blum et al., 2014; Thibodeau et al., 2016; Yin et al., 2017; this study).

432 Notably, these ancient $\delta^{202}\text{Hg}$ and $\Delta^{199}\text{Hg}$ data also show less variation than those identified in a
433 modern coastal plain sediment core, where the observed variations were interpreted as a
434 combination of changes in sediment type, grain size, and/or Hg sources (e.g., Das et al., 2013).
435 Although coastal plain biogeochemical processes are not directly analogous to a purely marine
436 system, the potential control of grain size on Hg isotopes should remain ubiquitous in contrasting
437 depositional settings. Furthermore, it has recently been suggested that a negative MIF signal in
438 Mesoproterozoic black shales is indicative of photic zone euxinia (e.g., Zheng et al., 2018),
439 which highlights the need to constrain the local redox when interpreting Hg records. Therefore, it
440 is clear that challenges remain in the use of Hg isotopes to definitively pinpoint the overall global
441 changes in the source(s) of Hg to ancient marine sedimentary rocks if there are significant
442 lithological, grain size, and/or redox variations.

443 Despite these potential complications, compiled Hg isotope values from natural sources
444 of Hg do show negative $\Delta^{199}\text{Hg}$ values reflecting many terrestrial reservoirs (i.e., plants, soils,
445 rocks), and more positive $\Delta^{199}\text{Hg}$ values can be sourced from other terrestrial reservoirs (i.e.,
446 plants, soils, rocks) and volcanoes (e.g., Blum et al. (2014) and references within; Fig. 2). As
447 described earlier for the data from the Toarcian, the trends in Hg/TOC anomalies (Figs. 1, 5, and
448 6) also suggest enhanced terrestrial sourcing of Hg in T-OAE Hg cycle. Moreover, it may be
449 possible to more accurately interpret ancient Hg isotope records in geologic settings where local
450 changes in the sedimentary environment are minimal during the interval studied (e.g., Das et al.,
451 2013) as we have attempted to do so with the Toarcian Hg isotope data presented here from the
452 East Tributary section.

453

454 **7. Conclusions**

455 Our new data, when cast in the context of the existing Pliensbachian and Toarcian Hg
456 records, have major implications for the underlying mechanisms driving the Toarcian Hg
457 anomalies. Environmental destabilization during the early Toarcian was most likely driven by
458 multiple feedbacks associated with the emplacement of the Karoo-Ferrar LIP. Our compilation
459 of Hg anomalies along with previous evidence for environmental destabilization during the
460 Toarcian N-CIE suggests the following sequence of events: (1) Main phase emplacement of the
461 Karoo-Ferrar LIP and injection of an unknown quantity of Hg to atmosphere from LIP
462 emplacement; (2) Cycling and redistribution of this Hg in intermediate reservoirs (Fig. 2); (3)
463 Increases in the Hg flux to marine environments from continental weathering, soil erosion, and
464 wildfires; (4) Local changes in water column redox in some locations result in enhanced Hg
465 deposition; (5) LIP emplacement decreases or ceases (or Hg input from volcanism decreases
466 while volcanic activity continues) while enhanced Hg loading in proximal marine environments
467 continues for some time, and biogeochemical cycles and the climate are still perturbed. Events 2
468 – 4 may occur geologically simultaneously but potentially independently from one another.

469 The trends from the Pliensbachian-Toarcian Hg compilation illustrate the need to
470 generate similar records from other events in Earth's history. Warming, weathering, wildfires,
471 redox changes, and volcanism can all potentially affect sedimentary Hg enrichments and isotopic
472 signatures. Despite these complexities in the interpretation of the ancient Hg record, we suggest
473 that LIPs may have been the underlying driver of the observed environmental disturbances that
474 resulted in some Hg anomalies and mass extinctions. Volcanism or LIPs may have introduced
475 significant quantities of Hg to the ocean/atmosphere system, but there are many intermediate
476 steps in the cycling of Hg prior to ultimate burial in the sedimentary record, and other larger
477 reservoirs that respond to climatic perturbations may release Hg on similar timescales (Fig. 2).

478 Therefore, the role of these other mechanisms needs to be considered when interpreting ancient
479 Hg enrichments. To better identify these potential sources and feedbacks in the ancient Hg cycle
480 it is imperative to investigate Hg records from both proximal and distal as well as shallow- and
481 deep-water environments, and from multiple ocean basins with independent evidence for local
482 redox conditions, when possible. Further calibration of the Hg system in modern settings
483 (siliciclastic-dominated, carbonate-dominated, proximal vs distal, fluctuating redox, etc.) will
484 also sharpen our interpretations of the ancient Hg record.

485

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635

636

637 **Acknowledgements**

638 TRT would like to thank the FSU Arts and Sciences Postdoctoral Fellowship for ability to

639 conduct this project. The Alberta outcrop samples were collected under the following permits:
640 #YHTR-2014-16156, #13-058, #14-009, and #15-019. CHJ was supported by Cooperative
641 Agreement NA11SEC4810001 with NOAA's Education Partnership with Minority-Serving
642 Institutions. JDO acknowledges NSF grant OCE 1434785 and NASA Exobiology grant
643 NNX16AJ60G. RY was funded by the Chinese Academy of Sciences through the Hundred
644 Talent Plan. Manuscript preparation was performed at the National High Magnetic Field
645 Laboratory and the College of Charleston. The National High Magnetic Field Laboratory is
646 supported by National Science Foundation Cooperative Agreement No. DMR-1157490 and the
647 State of Florida. We would also like to thank editor Derek Vance and Michaël Hermoso and two
648 anonymous reviewers whose suggestions and comments helped to improve this manuscript.

649

650 **Competing Interests**

651 The authors declare no competing financial interests.

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654 **Figure Captions**

655 **Figure 1. Global paleogeography of the early Toarcian.** Dark grey represents landmasses,
656 light blue represents shallow seas, and dark blue represents open oceans. Of the 12 locations
657 analyzed across the T-OAE interval (Percival et al., 2015; Fantasia et al., 2018; this study), there
658 are only 6 that have Hg/TOC anomalies. Note that there are three locations within the Alberta
659 study site. This paleogeographic reconstruction was modified from previous versions (e.g., Them
660 et al., 2017a, 2018; Scotese, 2001).

661

662 **Figure 2. Modern Hg cycle and associated Hg-isotope composition of sources to marine**
663 **sediments.** Mercury is recycled in the environment multiple times before being ultimately
664 sequestered in marine sediments. Values in mass balance from Schuster et al. (2018) and
665 references therein. Note the units for Hg reservoirs (Gg Hg) and fluxes (Gg Hg yr⁻¹). Note that
666 $\delta^{202}\text{Hg}$ and $\Delta^{199}\text{Hg}$ values of various sources overlap with one another. Mercury isotope values
667 of sources from Blum et al. (2014) and references therein. In the ocean, the sinks of mercury are
668 organic matter and drawdown through sulfide production and preservation. Intermediate sinks
669 that can become sources on short timescales include soils, rocks, and vegetation.

670

671 **Figure 3. Mercury geochemistry of the Alberta sections that represent a basin transect.**
672 Lithostratigraphy, chemostratigraphy, and ammonite biostratigraphy from Them et al. (2017a,
673 2018). Tenuicostat. = Tenuicostatum, carb. = carbonate. East Tributary represents proximal
674 location; core 1-35-62-5W6 represents intermediate location; core 6-32-75-20W5 represents
675 distal location. The proximal East Tributary section is the only section from our Panthalassan
676 study sites that displays an anomaly in Hg/TOC values.

677

678 **Figure 4. Mercury geochemistry of the Dotternhausen section.** Lithostratigraphy, carbon-
679 isotope and TOC chemostratigraphy, and ammonite biostratigraphy from Dickson et al. (2017).
680 Note that the one-point Hg/TOC anomaly during the N-CIE interval is associated with elevated
681 pyrite contents (see discussion in Main Texas and Supplementary Information). Furthermore, the
682 gray circles in the Hg/TOC portion of this section were not interpreted to represent Hg anomalies
683 because their increases are caused by low TOC values.

684

685 **Figure 5. Compilation of sedimentary mercury geochemistry during the Pliensbachian and**
686 **Toarcian.** Lithostratigraphy, carbon-isotope (either organic or inorganic) and Hg/TOC
687 chemostratigraphy across the Pliensbachian-Toarcian interval from Europe, South America, and
688 North America. Blue text represents sites where an Hg/TOC anomaly occurred during the T-
689 OAE interval. Red text represents sites where an Hg/TOC anomaly did not occur during the T-
690 OAE interval.

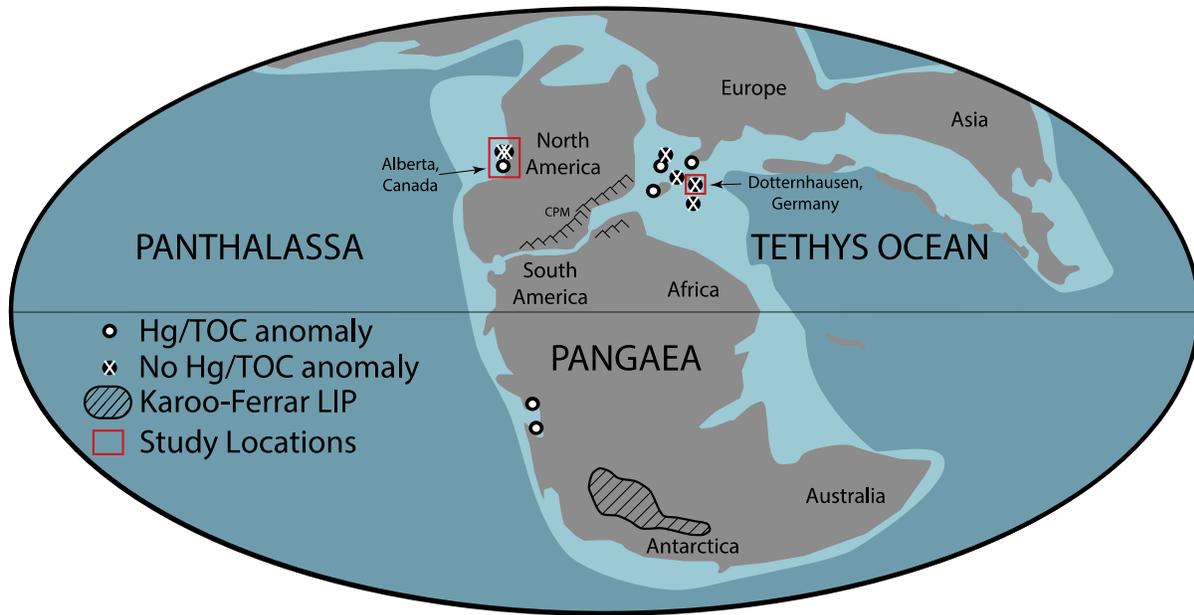
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692 **Figure 6. Idealized depositional settings of European, South American, and North**

693 **American locations during Pliensbachian and Toarcian.** (A) In the European epeiric sea,
694 multiple semi-restricted to severely restricted basins and emergent landmasses existed. Note that
695 this is not one continuous cross-section, thus it is not depicting the local restriction of the basins
696 as they are connected to other sub-basins (B) The two South American locations were directly
697 adjacent to the Laurentian continent and the basins were isolated due to volcanic terranes. (C)
698 The North American locations were located in an upwelling zone with strong connections to
699 Panthalassa. The bottom panels depict the study sites with respective max [Hg] and Hg/TOC
700 values during the T-OAE N-CIE interval, as well as their relative distance from any landmasses,
701 small or large. Note that small changes in the relative distance of any study area will not
702 significantly influence the observations. Blue text represents sites where an Hg/TOC anomaly
703 occurred during the T-OAE interval. Red text represents sites where an Hg/TOC anomaly did not
704 occur during the T-OAE interval. A north arrow is shown in each panel. Pan. = Panthalassa,
705 E.E.S. = European epeiric seaway.

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709 Figure 1.

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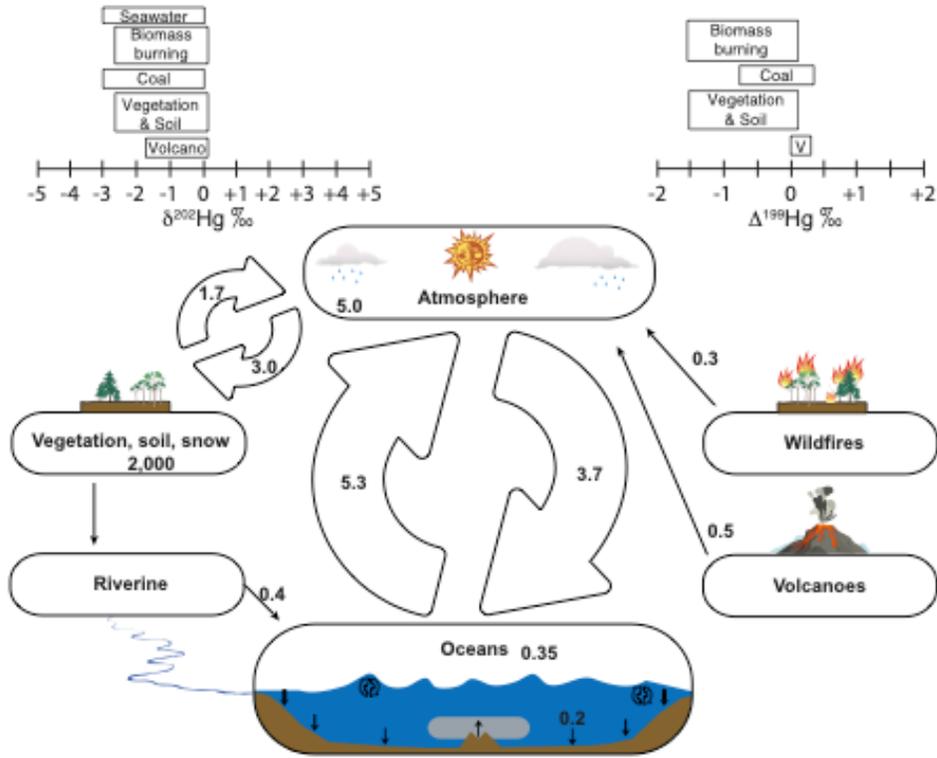
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721 Figure 2.

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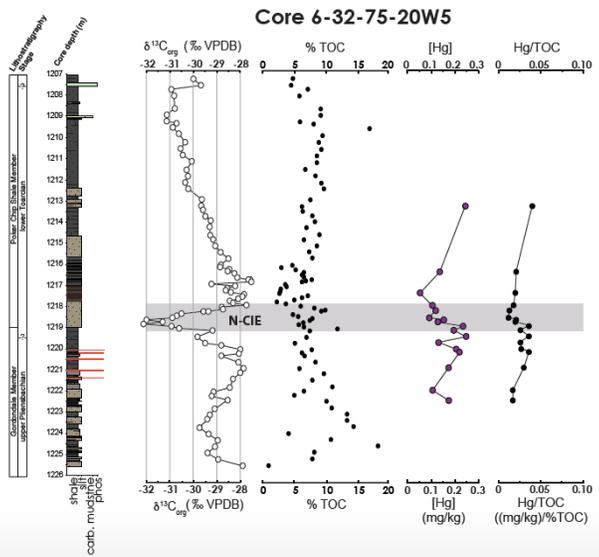
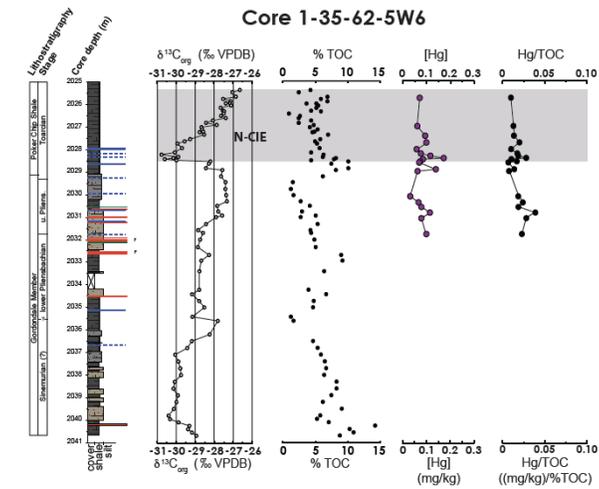
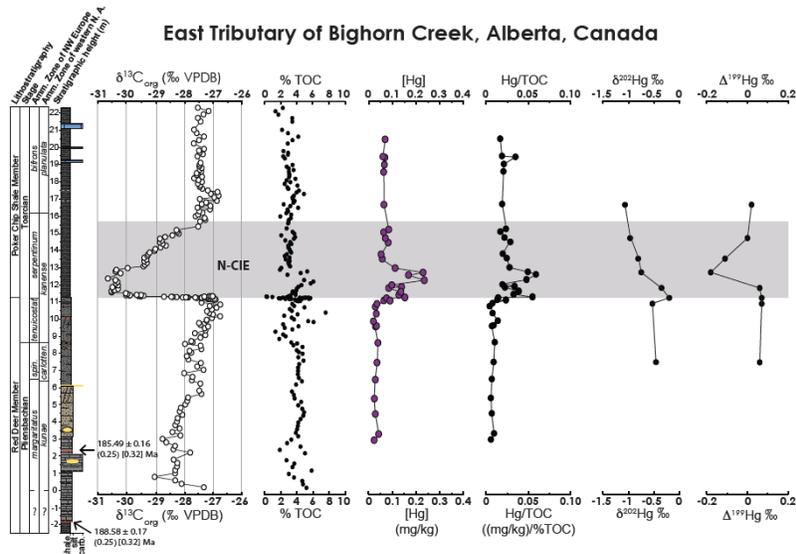
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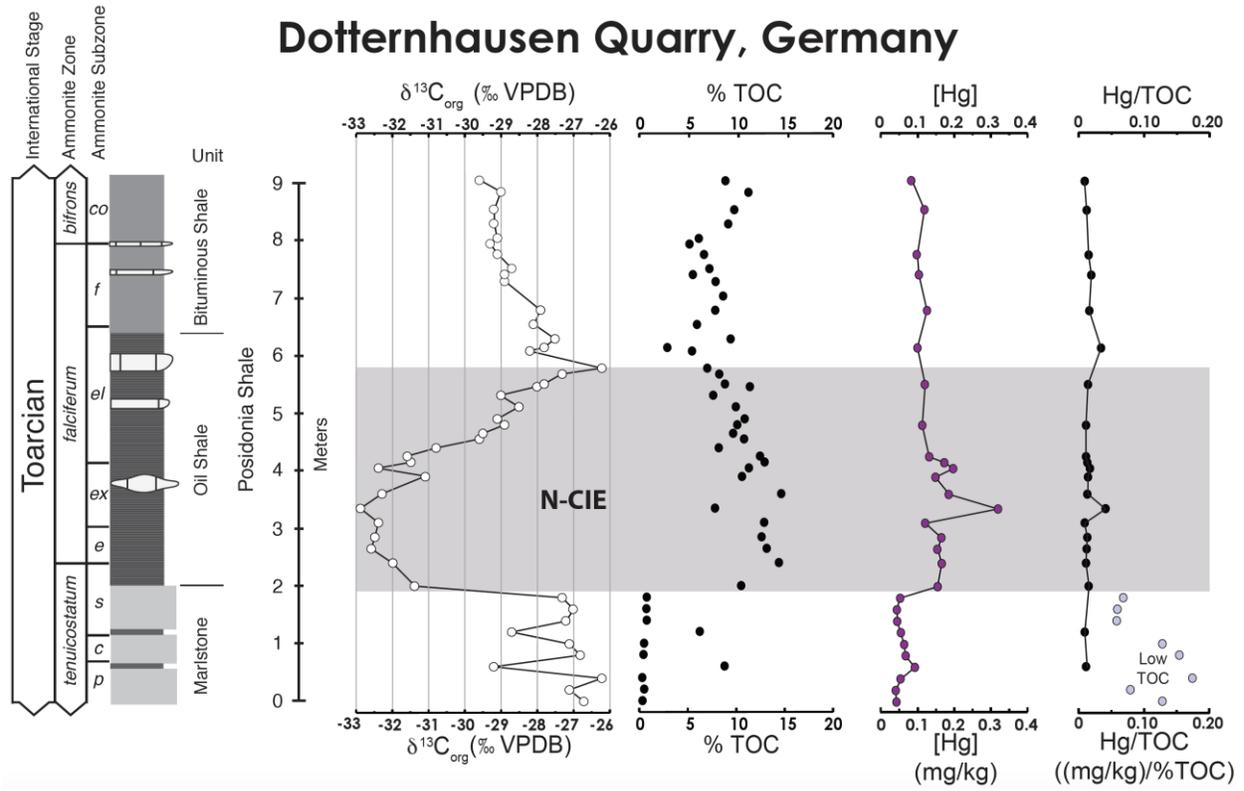
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735 Figure 3.



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737 Figure 4.

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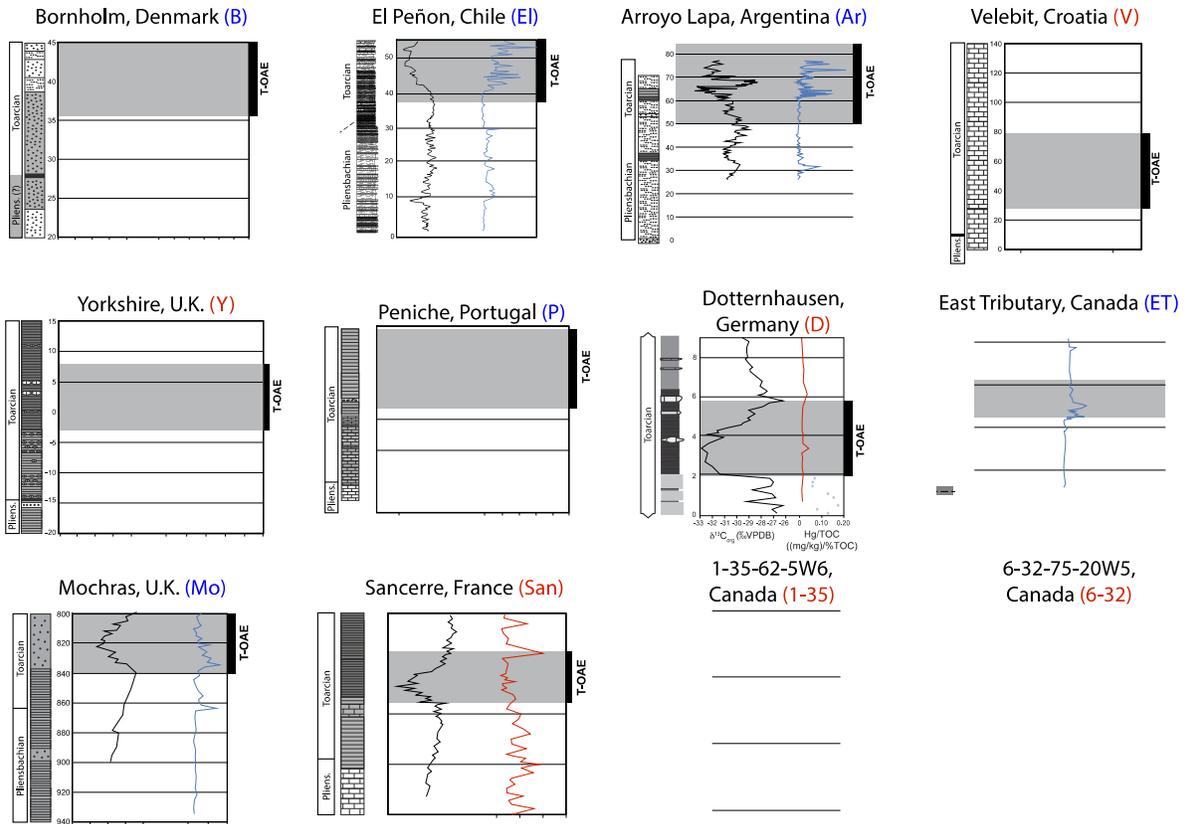
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750 Figure 5.

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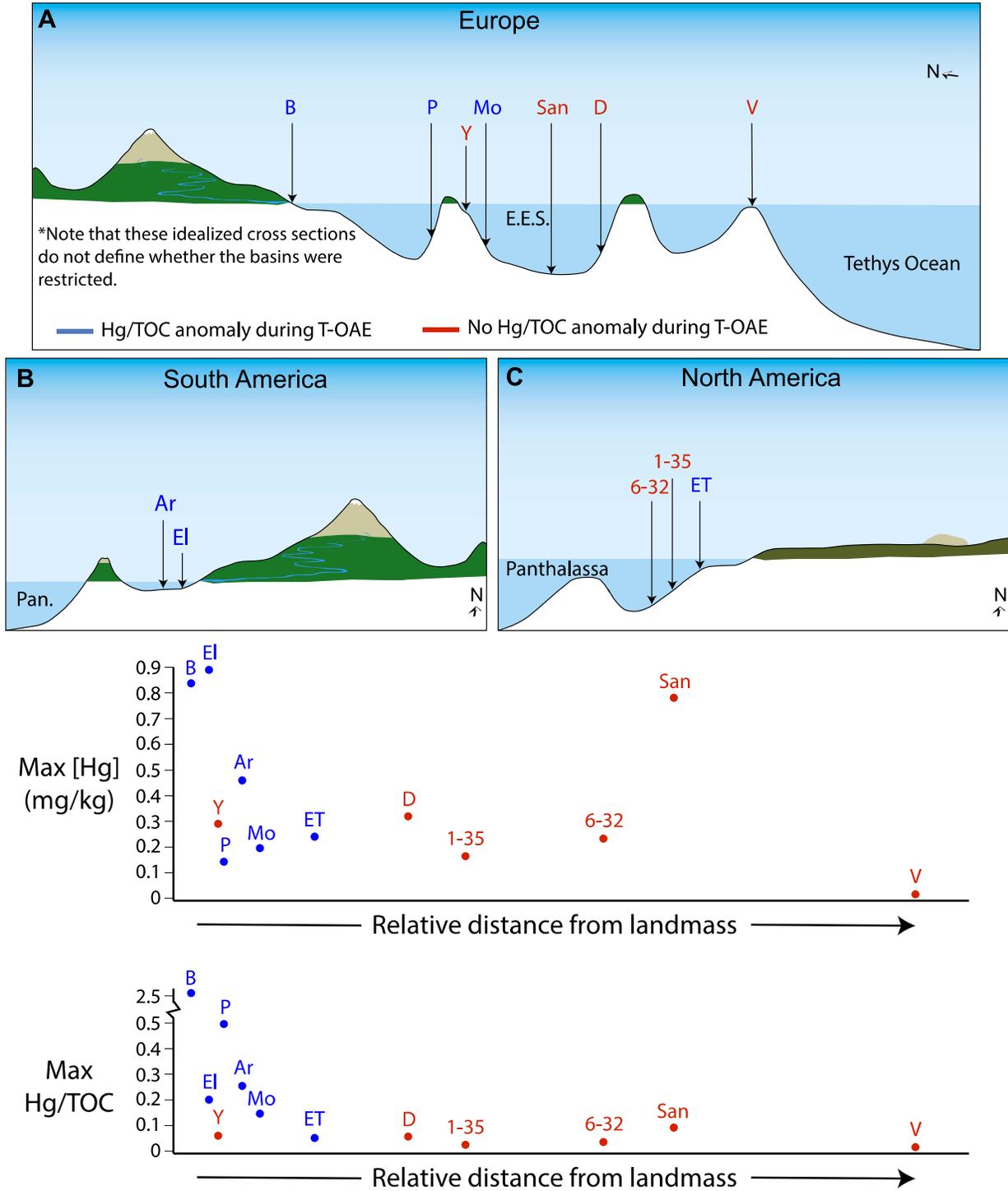
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762 Figure 6.