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Mercury contents and isotope ratios from diverse depositional environments across the Triassic–Jurassic boundary

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- 1 Mercury contents and isotope ratios from diverse depositional environments
- 2 across the Triassic–Jurassic Boundary: Towards a more robust mercury proxy
- 3 for large igneous province magmatism
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24 ABSTRACT

25 Mercury is gaining prominence as a proxy for large igneous province (LIP) 26 volcanism in the sedimentary record. Despite temporal overlap between some mass 27 extinctions and LIPs, the precise timing of magmatism relative to major ecological and 28 environmental change is difficult to untangle, especially in marine settings. Changes in the 29 relative contents of Hg in sedimentary rocks through time, or 'Hg anomalies', can help 30 resolve the timing of LIP activity and marine extinctions. However, major questions remain 31 unanswered about the fidelity of Hg as a proxy for LIP magmatism. In particular, 32 depositional (e.g., redox) and post-depositional (e.g., oxidative weathering) processes can 33 affect Hg preservation in marine sediments. These factors pose challenges for confidently 34 using Hg as a fingerprint of volcanism. Here, we use the Hg anomaly at the Triassic-35 Jurassic boundary to explore the opportunities and challenges associated with two 36 approaches that may help build a more robust interpretation of the Hg proxy: (1) 37 measurements from sediments from diverse depositional environments, including 38 lithologies with low Hg and organic carbon content, and (2) the simultaneous use of Hg 39 stable isotope ratios. We present and compare Hg records from five geographically 40 disparate Upper Triassic-Lower Jurassic marine sections that represent nearshore, mid-41 shelf, deep-water, and carbonate platform settings. These sedimentary sections span the 42 emplacement of the Central Atlantic magmatic province (CAMP) and the associated end-43 Triassic extinction (ETE). Total organic carbon contents, carbonate contents, and Hg 44 contents and stable isotope compositions demonstrate the multiple ways in which different 45 depositional environments impact how Hg anomalies are expressed in ancient marine 46 sedimentary rocks. Although we observe an increase in Hg/TOC during the ETE in each 47 section, the pattern and duration of Hg enrichment differ notably between sections, and the 48 timing is not always coincident with CAMP activity, illustrating how the depositional filter 49 complicates the use of Hg/TOC ratios alone as a fingerprint of LIP magmatism. In 50 addition, Hg isotope measurements support a volcanic origin for Hg these 51 anomalies during the ETE, suggesting CAMP was the Hg source during the extinction 52 interval. These data support the use of Hg isotopes to help distinguish Hg loading that 53 results from LIP magmatism on a global scale and emphasize the importance of making Hg 54 proxy measurements from diverse depositional environments.

- 55
- 56

57 1. INTRODUCTION

58 The prevalence of mass extinctions coincident with large igneous province (LIP) 59 activity motivates a thorough understanding of the connections between magmatism and 60 global environmental change (e.g., Bond and Wignall, 2014). Extinctions may be caused or enhanced by the cascade of effects following the release of volcanic gases (e.g., S, CO₂) 61 62 in high quantities over geologically short periods of time. These gases perturb the Earth 63 system, potentially causing ocean acidification, ocean anoxia, and warming (or cooling), 64 all of which may be detrimental to metazoan life (e.g., Bond and Wignall, 2014). 65 Similarities between mass extinction-LIP emplacement intervals and modern 66 anthropogenic CO₂ emissions underscores their relevance today (e.g. Foster et al., 2018). 67 However, correlation between terrestrial sections (where LIPs often occur) and marine 68 sections (where many of the extinction records occur) is typically not straightforward, 69 motivating further work to better understand the relationship between LIP emplacements and related extinctions. Mercury preserved in sedimentary rocks may help link LIP magmatism with biotic and other environmental changes observed in the marine sedimentary record, because Hg can be measured in the same sedimentary records that preserve paleontological evidence (e.g., Grasby et al., 2016, 2019; Percival et al., 2015; Sanei et al., 2012; Scaife et al., 2017; Shen et al., 2019a, b; Thibodeau et al., 2016, amongst many other recent studies).

76 In the absence of anthropogenic perturbation, Hg is primarily introduced to the 77 atmosphere, ocean, and sedimentary record through volcanic inputs (e.g., Fitzgerald et al. 78 2014). In the geologic record, periods of high volcanic activity and associated increased 79 input to the Earth system may be reflected in sedimentary intervals with unusually high Hg 80 enrichments, termed 'Hg anomalies' (Sanei et al., 2012). Since Hg is often associated with 81 organic matter in sediments, recent literature has focused on identifying Hg anomalies 82 based on ratios to total organic carbon (TOC; reviewed by Grasby et al., 2019). The ease 83 of measuring Hg and TOC contents in sedimentary rocks has led to a rapid proliferation in 84 the application of this proxy across Phanerozoic LIP and mass extinction events.

85 As its application has grown, so too has the understanding of the complexity of 86 factors that can influence Hg contents and Hg/TOC ratios in sedimentary rocks. The 87 reliability of Hg contents as a proxy for LIP volcanism is significantly impacted by its host 88 phase, which is often organic matter but can also be clays or sulfur species (e.g., Shen et al 89 2019a,b). Redox conditions and diagenesis impact the formation and preservation of these 90 host phases and are all at least partially controlled by depositional environment. 91 Additionally, post-depositional fluid flow and weathering can redistribute Hg, altering 92 primary contents (Charbonnier et al., 2020). These multiple confounding factors may erase

the record of volcanic loading or generate Hg enrichments unrelated to volcanism (Shen et
al., 2019a), raising fundamental questions about whether increases in Hg content and/or
Hg/TOC ratios in sedimentary sections can be used as a simple and reliable fingerprint of
secular changes in volcanism.

97 The recognition of complexities is a vital step in the development of robust 98 geochemical proxies for past environmental change; an important next step is to explore 99 approaches and techniques that may provide for reliable interpretations despite the inherent 100 complexity (Elderfield, 2011). In this study, we explore two of the many possible directions 101 that may help develop a more robust Hg proxy. First, we ask whether measurements from 102 rock types that are low in Hg and TOC may help to broaden the applicability of the proxy, 103 as different depositional environments may differ in their deposition of sulfides, clays, and 104 TOC, and indirectly Hg contents. Mercury measurements are scarce in organic-poor 105 lithologies, in part because they are more difficult to measure and in part because prior 106 work has established thresholds of TOC content below which Hg/TOC ratios are regarded 107 as unreliable; however, this seems likely to be a product of ill-suited TOC methods and 108 difficulty interpreting low TOC samples, and we address both here. Second, and in tandem, 109 we evaluate how Hg isotopes may add vital but widely under-utilized information for 110 fingerprinting volcanism in the sedimentary record. Understanding how Hg isotope ratios 111 in sedimentary rocks are affected by local and regional cycling and depositional 112 environments remains incomplete yet critical to extracting the most from the 113 complementary information that they offer.

114 We address these two major questions by focusing on the Triassic–Jurassic 115 boundary (TJB), which is associated with one of the major Phanerozoic mass extinctions

116 and one of the iconic Hg anomalies that has enabled linking of the end-Triassic extinction 117 (ETE) with LIP activity associated with the Central Atlantic magmatic province, or 118 (CAMP) (Percival et al., 2017; Thibodeau et al., 2016). To this end, we present new records 119 of Hg content and isotopic compositions from diverse depositional settings across this time 120 interval. In the sections that follow, we begin with a review of the Hg proxy and its 121 complexities; we follow by introducing TJB sedimentary sections that are focus of our 122 study before presenting new records and discussing the implications of our data for use of 123 the Hg proxy.

124

125 **2. BACKGROUND**

126 **2.1 Hg as a proxy for LIP magmatism in the sedimentary record**

127 Volcanic emissions comprise ~75% of present-day natural Hg emissions, making 128 them the primary natural source of Hg to surficial reservoirs on Earth (Pyle and Mather, 129 2003). Mercury has an approximately 1 year residence time in the atmosphere, which 130 enables its global distribution and deposition (Schroeder and Munthe, 1998; Lindberg et 131 al., 2002; Douglas et al., 2008). From the atmosphere, Hg deposits into terrestrial and 132 marine environments where it can be cycled back to the atmosphere between terrestrial and 133 marine environments, with ultimately a major sink in marine sediments. Today, Hg has a 134 deep-ocean residence time of ca. 350 years, much shorter than the whole-ocean mixing 135 time (ca. 1000 years), and the surface ocean has an even shorter residence time (Gill and 136 Fitzgerald, 1988). As a result, periods of intense volcanism can increase the global 137 atmospheric Hg load and leave a systematic imprint on marine and terrestrial systems.

138 Once emitted, volcanogenic Hg can enter the marine system via atmospheric 139 deposition or terrestrial runoff, and in both cases Hg is thought to be transferred to marine 140 sediments mostly complexed with organic compounds and other particles (e.g., Kongchum 141 et al., 2011; Zhong et al., 2008). Thus, Hg contents in marine sediments are highly 142 dependent on the local organic load and/or dilution by non-Hg-bearing detrital sediments 143 (Grasby et al., 2013), and local effects may dominate the Hg signature in coastal marine 144 sediments. Although Hg is often associated with organic matter, in modern and ancient 145 sediments it can also be associated with sulfides (e.g., Huerta-Diaz and Morse, 1992; Shen 146 et al., 2019a; Shen et al., 2020) or clays (e.g., Them et al., 2019), depending on the redox 147 conditions during and immediately after deposition.

148 Due to the particle-reactive nature of Hg accumulation in sediments, Hg contents 149 are typically normalized to a host phase in order to identify changes in input to the 150 atmosphere-ocean system, such as that from volcanic loading. Given the predominant 151 associated of Hg with organic matter, total organic carbon (TOC) contents are widely used 152 for normalization to ensure that observations of high Hg contents are not simply a product 153 of high sedimentary TOC deposition in sediments. Observations of increases in Hg/TOC 154 in multiple stratigraphic sections are hypothesized to reflect globally increased 155 magmatism, and can help to relate the timing of magmatism with environmental and biotic 156 changes recorded in the same sections (e.g., Percival et al., 2017; Grasby et al., 2019).

Previous studies applying the Hg proxy have focused on sedimentary rocks with significant TOC content, which can easily be analyzed via thermal combustion methods. Previous work (recently reviewed by Grasby et al (2019)) exclueded Hg/TOC ratios from samples with <0.2% TOC. This threshold is presumably a holdover from analytical

161 methods that are unable to resolve lower TOC (e.g., Rock-eval pyrolysis); subsequent 162 studies have adopted this cutoff regardless of the TOC analysis method and its detection 163 limit. Many methods, such as those that use elemental analyzers, are capable of quantifying 164 low TOC contents and have been reported in other studies (e.g., Fujisaki et al., 2018; Galy 165 et al., 2007, 2008; Hilton et al., 2010; Scheingross et al., 2021) Here, we use a method that 166 can quantify low TOC samples and further describe its capabilities and limitations in the 167 supplement. Quantifying Hg/TOC ratios in low-TOC samples could open possibilities of 168 working in a wider range of lithologies across a wider range of depositional environments 169 than those available when restricted to samples with 0.2 wt.% TOC. Records from diverse 170 lithologies across the same period of time could help to avoid 'false positive' Hg anomalies 171 related to depositional artifacts. However, the challenge with this approach is not just 172 analytical; the meaning of Hg/TOC values in samples with very low TOC remains to be 173 fully understood.

174 2.2 H

2.2 Hg isotopes and the volcanic Hg proxy

175 Mercury isotopes can help identify the source of Hg in sediments and/or the pathway 176 of deposition (i.e., atmospheric versus runoff). In particular, isotopic information can 177 potentially identify anomalously high Hg contents originating from LIP magmatism 178 (Thibodeau and Bergquist, 2017; Bergquist 2017). Mercury has seven stable isotopes and 179 undergoes both mass dependent fractionation (MDF) and mass independent fractionation 180 (MIF). Mass dependent fractionation in Hg isotopes is typically reported using the 181 202 Hg/¹⁹⁸Hg ratio as δ^{202} Hg (where δ^{202} Hg (‰) = [(202 Hg/¹⁹⁸Hg)_{sample}/(202 Hg/¹⁹⁸Hg)_{standard} -182 1×1000). The NIST 3133 standard is widely used for Hg isotope measurement and is 183 adopted here (Blum and Bergquist, 2007). Mass independent fractionation is measured as 184 the difference between another measured δ value (e.g., δ^{199} Hg) and the MDF predicted 185 using the measured δ^{202} Hg value and the kinetic MDF law; this difference is typically 186 reported as Δ^{199} Hg for odd isotope MIF.

187 Gaseous elemental Hg emitted from volcanoes enters the atmosphere with no 188 measurable MIF (Δ^{199} Hg = 0‰; Fig. 1a) and with negative to zero MDF (δ^{202} Hg = -2‰ 189 to 0‰; e.g., Zambardi et al., 2009; Szponar et al., 2020; Si et al., 2020). After oxidation of 190 elemental Hg to more reactive and particle-reactive species, Hg can acquire odd MIF 191 mostly via photochemical reduction either in cloud droplets, surface waters, or on surfaces 192 in terrestrial settings (Thibodeau and Bergquist, 2017; Bergquist 2018). This results in 193 gaseous elemental Hg in the atmosphere having negative odd MIF compositions and 194 oxidized Hg species having positive odd MIF signatures (Blum et al., 2014). Because much 195 of the Hg accumulated in terrestrial soils is from uptake of gaseous elemental Hg by 196 vegetation (Zhou et al., 2021), terrestrial soils and surfaces typically preserve negative odd 197 MIF values (i.e., negative Δ^{199} Hg) and much more negative δ^{202} Hg or "negative MDF" in 198 biomass and soils due to the preferential uptake of the lighter Hg isotopes (Demers et al., 199 2013). Nearshore sediments that acquire Hg through terrestrial runoff thus typically exhibit 200 negative MIF and more negative MDF Hg isotope values (Demers et al., 2013; Zheng et 201 al., 2016; Thibodeau and Bergquist, 2017; see Fig. 1a). In contrast, settings further from the continent usually contain small odd-isotope excesses (i.e., positive Δ^{199} Hg and Δ^{201} Hg 202 203 values, or "positive MIF" and less negative δ^{202} Hg), which are from the deposition of 204 oxidized Hg species (Thibodeau and Bergquist, 2017; Bergquist and Blum, 2007; Sonke 205 2011).

206 Thibodeau et al. (2016) measured Hg isotopes in shallow marine sediments 207 spanning the Triassic–Jurassic boundary (TJB) and speculated that the absence of MIF 208 observed in these rocks during the end-Triassic extinction was due to increased volcanic 209 loading of Hg associated with the central Atlantic magmatic province (CAMP). Since then, 210 other studies have reported Hg isotope values associated with Hg anomalies during other 211 LIPs, including at the end–Permian (Grasby et al., 2017; Shen et al., 2019a,b; Wang et al., 212 2018), during the Toarcian ocean anoxic event (Them et al., 2019), across the Ordovician-213 Silurian boundary (Gong et al., 2017), and at the Cretaceous–Paleogene boundary (Sial et 214 al., 2016). Since volcanic Hg often initially exhibits negative MDF and MDF can be altered 215 by many other environmental processes, MDF is not as diagnostic as MIF in fingerprinting 216 magmatically sourced Hg. Here we focus our discussion on MIF signatures, which are 217 thought to be more useful for fingerprinting volcanic Hg.

218 **2.3** Complications in using the Hg proxy for LIP magmatism

219 Although Hg contents and isotopes are a promising proxy in many respects, a 220 growing number of studies are revealing that multiple, complex processes may influence 221 the preservation and magnitude of Hg and Hg/TOC anomalies. Release of Hg during LIP 222 activity may be influenced by magmatic style as well as non-volcanic sources such as fires 223 on land or release of sedimentary Hg by magmatic intrusions and emplacement (Grasby et 224 al., 2017). Periods of LIP activity were also likely characterized by both intrusive and 225 extrusive magmatism, and by eruptions that ranged from the subaerial to the submarine. It 226 is unclear how these different styles of eruption would have affected the release and 227 deposition of Hg and the resulting signals recorded in sedimentary records. It is possible 228 that subaerial, explosive volcanism may have led to more Hg in globally distributed

depositional environments, while submarine and effusive volcanism may not haveperturbed the global Hg cycle to the same extent (Percival et al., 2018).

231 Additional complexity in Hg records also results from depositional and diagenetic 232 processes (Percival et al., 2018; Charbonnier et al., 2020), including local redox 233 fluctuations (Shen et al., 2019a). Some apparent anomalies may be better explained by 234 local redox variability than by volcanic emissions of Hg (Them et al., 2019; Shen et al., 235 2019a), and the known association between Hg and sulfur in many sedimentary rocks 236 (Huerta-Diaz and Morse, 1992; Shen et al., 2020) and clays (Manceau et al., 2018; Shen et 237 al., 2019a, b) raises questions about whether TOC normalization alone accounts for the key 238 processes driving Hg enrichment or depletion in some environments (Sanei et al., 2012; 239 Shen et al., 2019a; Shen et al., 2020).

240 Given the complexity of Hg contents and Hg/TOC ratios in marine sediments, Hg 241 isotopes may offer key complementary information for fingerprinting LIP magmatism. 242 Despite a large number of studies measuring Hg contents and Hg/TOC ratios in a range of 243 depositional environments, there are few studies that utilize Hg isotopes to understand the 244 origin of Hg anomalies across depositional settings. A systematic investigation of Hg 245 isotopes in different depositional settings from the sedimentary record is important to 246 further understand the role of LIP magmatism (among other processes) in driving changes 247 in sedimentary Hg. Understanding such effects is particularly important because multiple 248 records of Hg, Hg/TOC, and Hg isotopes from the same time period are necessary to 249 demonstrate that perturbations to the Hg cycle are indeed global and not local (Percival et 250 al., 2017). Understanding site-dependent effects associated with depositional environment 251 may be critical to evaluating similarities and differences between sections. Here, we

explore how the depositional environment affects Hg contents and the Hg isotope signal across four different sections spanning the TJB, when a well-defined Hg anomaly has been previously identified and tied to LIP activity (Thibodeau et al., 2016; Percival et al., 2017).

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2.4 The Triassic–Jurassic Transition: A testbed for the Hg proxy

The CAMP (Marzoli et al., 1999) was a subaerial magmatic province emplaced over approximately one million years during the Late Triassic and Early Jurassic (Davies et al., 2017; Blackburn et al., 2013; Knight et al., 2004). Intrusive activity began ca. 100 kyrs before the dominant extrusive activity (Davies et al., 2017). Emplacement was likely characterized by 3–4 main pulses (Blackburn et al., 2013) of durations somewhere between 1–100 kyrs (Schaller et al., 2012; Berner and Beerling, 2007).

262 The end-Triassic extinction (ETE; 201.56 Ma) coincided with CAMP activity 263 (Marzoli et al., 2004; Schoene et al., 2010; Wotzlaw et al., 2014). The record of the ETE 264 is largely preserved in marine sediments, in which direct evidence of CAMP activity at 265 many localities is scarce. Thus, our understanding of the ETE and the TJB transition can 266 be greatly enhanced by the successful application of the Hg proxy, if Hg provides a 267 fingerprint of CAMP volcanism that can be related directly to the marine record of 268 extinction across multiple stratigraphic sections (Percival et al., 2017; Thibodeau et al., 269 2016). However, records of Hg contents from this time are different at each section that 270 has been measured to date. Mercury contents and Hg/TOC differ by orders of magnitude 271 from section to section, relative increases (i.e., anomaly severity) in each section are 272 different, and the relative timing of anomalies based on chemo- and biostratigraphy and 273 the extinction record are not consistent, raising questions about how increases in Hg or Hg/TOC can be directly interpreted as fingerprints of LIP volcanism (Kovács et al., 2020;
Lindström et al., 2019; Percival et al., 2017; Ruhl et al., 2020; Thibodeau et al., 2016).

In this study, we target five sedimentary sections that span the TJB and represent a range of depositional environments, from shallow through deep marine (here, we use the term "deep marine" to refer settings that are still on the continental margin but well below storm wave base in basinal settings). We also consider a carbonate platform. We report Hg contents, Hg/TOC ratios, and Hg isotopes from these localities and explore how differences and similarities in their Hg records may be tied to depositional setting and associated sedimentary processes.

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284 **3. OVERVIEW OF LOCALITIES**

285 We collected samples and measured Hg from five open marine sections (although 286 we note some debate exists for St. Audrie's Bay) spanning the Triassic–Jurassic boundary 287 from disparate paleogeographic locations (Fig. 1a) and from a range of depositional 288 settings with variable expected influences on the Hg proxy (Fig. 1b). We deliberately chose 289 depositional settings characterized by lithologies that have been widely used in applying 290 the sedimentary Hg proxy (specifically, rocks with substantial TOC) as well as those that 291 have been less well studied, including carbonate-dominated rocks with low TOC. In 292 working with low-TOC carbonates, our goal was to explore both analytical and interpretive 293 limits.

Most samples have a corresponding thin section for further lithologic comparison. Each locality has a well-characterized bio- and/or chemostratigraphic context; the position of the ETE and Triassic–Jurassic boundary are denoted in Figs. 2–7 and are based on

297 previous studies. We correlated each section and demarcated the end-Triassic extinction 298 based on the negative carbon isotope excursion seen in organic matter at each section (e.g., 299 Yager et al., 2017; their fig. 2). There is currently a lively debate regarding the source of 300 the organic carbon isotope excursion (e.g., Lindström et al. 2012), the ability to correlate 301 it between ocean basins (Fox et al., 2020), and its relationship to the ETE extinction. 302 However, given the presence of the initial carbon isotope excursion in Peru (Yager et al., 303 2017), Canada (Williford et al, 2007), Nevada (Guex et al., 2004; Ward et al., 2007), Japan 304 (Fujisaki et al., 2018), Argentina (Ruhl et al., 2020), and many European sections (e.g., 305 Lindström et al. 2012; Fox et al. 2020) and that in each of those sections it coincides with 306 the onset of the mass extinction, we think using a biostratigraphic and C isotope-based 307 correlation is reasonable. In any case, we note that different possible correlations, such as 308 those suggested by Lindström et al. (2019) and Zaffani et al. (2018), will not change our 309 conclusions.

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3.1 New York Canyon, Nevada, USA

311 The New York Canyon area of Nevada, USA includes a well-studied Panthalassic 312 record from the Triassic-Jurassic boundary (e.g., Taylor et al., 1983; Guex et al., 2004 and 313 references therein). The section is exposed on Ferguson Hill, which forms the northern 314 portion of Muller Canyon, is the auxiliary global stratigraphic section and point for the 315 period boundary (Bown et al., 2007; Morton and Hesselbo, 2008). The Gabbs Formation 316 and overlying Sunrise Formation comprise limestone, silty shale, and silty marl (Fig. 3), 317 with detailed biostratigraphy (the ammonite *Psiloceras spelae*; Guex et al., 2004) 318 indicating the Triassic–Jurassic boundary within the upper Gabbs Formation. Several 319 studies of the organic carbon (C) isotope signature ($\delta^{13}C_{org}$) at the Ferguson Hill section

320 (Bartolini et al., 2012; Guex et al., 2004; Ward et al., 2007; Corsetti et al., 2015) document 321 a negative excursion in $\delta^{13}C_{org}$ at the extinction horizon.

322 Upper Triassic rocks of the Gabbs Formation are interpreted to represent a robust 323 carbonate ramp (the Mount Hyatt Member), overlain by a finer-grained middle-shelf 324 deposit (the uppermost Muller Canyon Member). Lower Jurassic rocks first appear within 325 the Muller Canyon Member of the Gabbs Formation and persist into the increasingly thick 326 and resistant beds rich in limestone and chert, in the overlying Ferguson Hill Member of 327 the Sunrise Formation (Schoene et al., 2010), which are interpreted to represent a middle-328 ramp setting on a distally-steepened bioclastic habitat (Ritterbush et al., 2014; Taylor et 329 al., 1983). We interpret the rocks in this section as indicative of a local upward-shallowing 330 trend, which began in the Late Triassic and continued into the Early Jurassic (Sinemurian). 331 The paucity of inorganic carbonate and other benthic bioclastic content throughout the 332 Muller Canyon Member has been attributed to either a global drop in carbonate saturation 333 (but see Greene et al., 2012) or to a loss of carbonate producers during the extinction 334 interval (Kiessling et al., 2007; Ritterbush et al., 2014). Overall, the New York Canyon 335 area represents deposition along the mid to inner shelf (Fig. 3) (Ritterbush et al., 2014).

336 **3.2 St. Audrie's Bay, UK**

The St. Audrie's Bay section has been well studied for over 100 years (e.g., Richardson, 1911, 1906, 1905). The ammonite *Psiloceras spelae*, which denotes the base of the Jurassic (Guex et al., 2004, Guex et al., 2012), is absent in the section, so we rely on the presence of the aforementioned negative CIE and subsequent positive shift in δ^{13} C (e.g., Yager et al., 2017; Lindstrom et al., 2012) to place the Triassic–Jurassic boundary at ~15 m in the St. Audrie's Bay section (similar to Hesselbo et al., 2004; we note the possibility

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that this isotope excursion may also reflect a period of subaerial exposure as suggested by Fox et al., 2020, but argue that this would not fundamentally change our correlation).

345 The section at St. Audrie's Bay includes dramatic changes in depth, TOC (wt.%), 346 and calcium carbonate content (wt.%). Hesselbo et al. (2004) provided a thorough 347 summary of the depositional changes seen at the section, which we briefly summarize here 348 (we followed the stratigraphy from Hesselbo et al., 2004, for our sampling and use their 349 stratigraphic column in Fig. 4). The lowermost $\sim 2 \text{ m}$ comprise the Williton Member of the 350 Blue Anchor Formation, which consists primarily of mudstone, has marine trace fossils 351 and bivalves, and is interpreted as shallow marine (Hesselbo et al., 2004; Mayall, 1981). 352 Meters $\sim 2-12$ comprise the Westbury Formation, which consists of mudstone and siltstone 353 with carbonate concretions and phosphatic conglomerate (Hesselbo et al., 2004; 354 Richardson, 1911, 1906). The Westbury Formation is characterized by relatively low TOC 355 (although note scale difference for TOC between Figs 3-6), and carbonate is typically in 356 diagenetic concretionary horizons. The Westbury Formation is generally interpreted as 357 deeper and further offshore compared to the Williton Member, but the uppermost Westbury 358 Formation documents a shallowing (Hesselbo et al., 2004). The Cotham Member of the 359 Lilstock Formation overlies the Westbury Formation, comprises mudstones and 360 limestones, and is interpreted as a shoreface equivalent to the Westbury Formation 361 (Hesselbo et al., 2004). The Cotham Member contains an erosional surface, desiccation 362 cracks, and ooids, representing a substantial shallowing relative to the rest of the section, 363 subaerial exposure, and potentially non-marine conditions (Hesselbo et al., 2004 and 364 references therein). The negative CIE occurs in the Cotham Member, and thus this interval 365 likely represents the ETE. Although not found at St. Audrie's Bay, sections nearby contain 366 stromatolites in association with the negative excursion (Ibarra et al., 2016), and their 367 widespread occurrence suggests the absence of fauna and further supports the interpretation 368 of this interval as representing the ETE. The Langport Member of the Lilstock Formation 369 comprises limestone and mudstone and is interpreted as fully marine but relatively shallow 370 based on wave-generated ripples (Hallam, 1960; Richardson, 1911; Swift, 1995). Above, 371 the Blue Lias Formation comprises organic-rich shale and limestones that are likely a 372 product of diagenetic mobilization of carbonate (Hallam, 1964). Burrowing intensity varies 373 substantially in the Blue Lias Formation, and carbonate-rich beds typically reflect less 374 organic-rich, oxygenated settings while the more organic rich facies are interpreted to 375 reflect an anoxic sediment water interface (Hesselbo et al., 2004). Fossils and pyrite are 376 common and suggest marine but potentially euxinic conditions in the water column or 377 sediment water interface (Hesselbo et al., 2004; Wignall, 2001).

In summary, the shallowest portion of the St. Audrie's Bay section is during the ETE, while the remainder of the exposed Rhaetian and Hettangian are relatively deeper but with very different TOC and carbonate contents, likely due to differences in conditions at the sediment water interface and during early diagenesis.

382 **3.3** L

3.3 Lombardy Basin, Southern Alps, Italy

The Lombardy Basin (Southern Alps, Italy) is a rift-related basin developed during the Mesozoic. The Upper Triassic to Lower Jurassic succession (upper Norian to Sinemurian) comprises a mixed marly-carbonate to carbonate succession deposited on the western margin of Tethys (e.g., Jadoul et al., 2012; Zaffani et al., 2018). The lower portion of the Calcari di Zu Formation (i.e., Zu Limestones) is upper Norian–Rhaetian and contains common bivalves and foraminifera. Cycles of dark marls transition upwards into limestone

389 (Zu-1 Member; Fig. 5; Fig S1). These beds successively develop into centimeter-scale 390 carbonate beds interlayered with very thin, shale-rich intercalations (Zu-2 Member; Fig. 5; 391 Fig S1) (Galli et al., 2007; Zaffani et al., 2018). These cyclic packages comprise 392 bioturbated and fossiliferous wackestones and packstones, with patch reefs, sponges, and 393 foraminifers overlain by cyclic packages consisting of thick marl and micritic fossil-rich 394 limestones (Zu-3 Member; Fig. 5; Fig S1) containing benthic foraminifers, bivalves, 395 calcareous sponges, and corals (Galli et al., 2007; Zaffani et al., 2018). The Malanotte 396 Formation unconformably overlies the Calcari di Zu Formation and represents the 397 outermost and deepest portion of the carbonate ramp environment. It consists of thin-398 bedded micritic limestones and mudstones, with rare bioclasts at the base and abundant 399 reworked ooids in the upper part as it grades into the Albenza Formation (Galli et al., 2007). 400 The Albenza Formation represents a regional progradation of the Hettangian carbonate 401 platform, characterized by amalgamated beds of oolitic and bio-intraclastic grainstones, 402 which are locally dolomitized (Galli et al., 2007). This carbonate platform slowly drowned 403 during the Hettangian into an open subtidal shelf environment, represented by the Sedrina 404 Formation, which comprises mudstones-wackestones and thin marl intercalations, with 405 common black chert nodules, sponge spicules, brachiopods, pelagic bivalves, and rare 406 ammonites (Bersezio et al., 1997). The Sedrina Formation grades into the Sinemurian-407 Pliensbachian Calcare di Moltrasio Formation (i.e., Moltrasio Limestones; Fig. 5; Fig S1), 408 which is dominated by gray marl limestones and black cherts with slumps and calcarenitic 409 beds, representing a fully pelagic environment (Bersezio et al., 1997).

410 We sampled the Lombardy Basin succession at four sections that would allow us 411 to sample the mid-Rhaetian (Zu Limestone) through the mid-Hettangian (Moltrasio

412 Formation) and into the Sinemurian; no single section covers the entire Rhaetian-413 Hettangian. We sampled the Zu Limestone at the Brumano Section, which exposes ~ 200 414 m of stratigraphy that extends from the upper Norian (Zu-1 Member) to the mid-Rhaetian 415 (middle of Zu-3) (Zaffani et al., 2018). We sampled ~120 m of this section from Zu-2 (just 416 above the Norian–Rhaetian boundary) to the top of the Zu-3a sub-member at the top of the 417 section (Muttoni et al., 2010). We sampled the upper Zu Formation (sub-members 3b and 418 3c) up to the base of the Malanotte Formation at the Italcementi Quarry. The Triassic-419 Jurassic boundary is placed within the Zu-3c sub-member (Zaffani et al., 2018). There are 420 multiple sections at the Italcementi Quarry, and we sampled from the inactive quarry (~100 421 m total stratigraphy), corresponding to the same sites used by Zaffani et al. (2018). Only 422 the very base of the Malanotte Formation is exposed at the Italcimenti Quarry; we sampled 423 the remainder of this formation along the Valcava-Torre di Busi road (the ~30 m Malanotte 424 section from Galli et al., 2005). Finally, we sampled the upper portion of the Malanotte 425 Formation extending through the Albenza and Sedrina formations into the Moltrasio 426 Formation at Val Adrara (corresponding to the well-studied section described and studied 427 by Bachan et al., 2012; Galli et al., 2007; Van de Schootbrugge et al., 2008; Jost et al. 2017 428 and others). We sampled the lower ~350 m of the Val Adrara section. To generate a 429 composite stratigraphic section for the Lombardy Basin samples used in this study, we 430 correlated between sections based on formation boundaries, biostratigraphy, and 431 chemostratigraphy (δ^{13} C); a detailed correlation between these sections is available in the 432 supplementary information.

433 **3.4 Panormide platform, Sicily, Italy**

434 The Triassic and Lower Jurassic shallow water carbonates from Sicily are 435 dolostones and limestones that crop out in the Sicilian Maghrebian chain and in the 436 subsurface of the foreland areas of the Hyblean plateau and Sicily Channel (Antonelli et 437 al., 1988; Patacca et al., 1979). These rocks were deposited in a wide carbonate embayment 438 that was flanked by deep water basins in the southwestern branch of Tethys (Di Stefano et 439 al., 2015; Zarcone et al., 2010). During the Late Triassic, the carbonate platform edge was 440 a Dachstein-type reef complex dominated by hypercalcified coralline sponges that are now 441 well exposed in the Palermo and Madonie Mountains and in central-southern Sicily (Di 442 Stefano et al., 2015). The reef complex transitioned to an escarpment and to a deep water 443 basin, while the back reef zone was characterized by extensive lagoons. Westward, a 444 transition to evaporite facies (sabkha-type) characterized the innermost zone of the 445 carbonate platform (Lo Cicero, 1986). The shallow water carbonate sedimentation lasted 446 until the late Sinemurian–Pliensbachian, when the platform experienced a drowning. 447 In Sicily, the Triassic–Jurassic transition in peritidal settings has been documented 448 in a few areas from the Hyblean foreland and in the Sciacca area (Cacciatore et al., 2006;

449 Patacca et al., 1979). More recently, a well exposed and continuous peritidal succession 450 ~430 m thick, encompassing the Triassic–Jurassic boundary, was described in detail in 451 Northwestern Sicily (Mt Sparagio, San Vito Lo Capo Peninsula; Todaro et al., 2018, 2017). 452 In this section, the peritidal limestones are organized in shallowing upward cycles (1.5 m 453 thick on average) characterized by subtidal, intertidal and supratidal facies (D'Argenio, 454 1974; Strasser, 1991). Based on the fossil content in the subtidal facies, the Mt Sparagio 455 section is divided into three informal units: unit A records the common occurrence of very 456 large megalodontid shells (up to 30 cm in size), coral patch reefs, and benthic foraminifers

457 such as Triasina hantkeni Majzon, Auloconus permodiscoides (Oberhauser), Aulotortus 458 sinuosus (Weynschenk), Aulotuortus sp., Glomospirella sp., Trochammina sp., 459 Frondicularia sp., Nodosaria sp. (Todaro et al., 2017). Some horizons contain calcareous 460 algae, classified as Cayeuxia sp. and Orthonella sp. The presence of Triasina hantkeni 461 indicate this unit is Rhaetian in age. Unit B shows the same benthic foraminifera 462 assemblage as unit A, with differences in the macro benthic community, as corals disappear 463 and a change in the size of megalodontids is observed (Todaro et al., 2017, He et al., 2020). 464 The upper boundary of unit B is identified based on the last occurrence of the Rhaetian 465 benthic community and by the presence of an oolitic horizon. Above, there is a ~10 m thick 466 fossil-poor interval that contains only small calcispherae. Unit C consists of oligotypic 467 facies characterized by a bloom of the alga Thaumatoporella parvovesiculifera in 468 association with Aeolisaccus sp, and, higher up, by Siphovalvulina sp. This fossil 469 assemblage is considered typical of the Hettangian-Sinemurian interval (Barattolo and 470 Romano, 2005, Boudagher-Fadel and Bosence, 2007).

471 **3.5 Levanto, Peru**

472 The Levanto section in northern Peru spans the Upper Triassic and Lower Jurassic; 473 the ~105 m section is continuous for ca. four million years. The entirety of the outcrop 474 consists of the Aramachay Formation, which, at this location, comprises carbonate-rich 475 mudstones with abundant intercalated ash beds (Fig. 6). U-Pb dating of zircons of the ash 476 beds and ammonite biostratigraphy (Guex et al., 2012; Schaltegger et al., 2008; Schoene 477 et al., 2010; Wotzlaw et al., 2014) have constrained the durations of the Rhaetian and 478 Hettangian, and the chronology provides a valuable biostratigrahic and temporal 479 framework for geochemical work at the section. The section is well below storm wave base

480 and is characterized by little bioturbation, which we interpret as indicative of anoxic 481 conditions at the sediment water interface during deposition, persisting from the Rhaetian 482 through Hettangian. Previous work on carbon isotopes, TOC, and carbonate content (Yager 483 et al., 2017) record a typical Triassic-Jurassic boundary carbon isotope profile. Unlike 484 many Tethyan sections, Levanto is characterized by lower TOC during the Hettangian 485 relative to the Rhaetian. Carbonate content remains relatively high (~60%) through much 486 of the section but is variable, particularly at the top of the section, where carbonate is 487 concentrated in thick beds.

488 The first \sim 57 meters of the continuous section is characterized by alternating thin 489 and thick-bedded intervals, though this alternation has little influence on sedimentary 490 structures or lithology as observed in thin sections (Yager et al., 2017). At approximately 491 57 m, this alternation changes to meter-scale differences, and eventually (\sim 80 m) grades 492 into concretionary bedding and finally into meter-scale concretions (~85). Thin sections 493 contain carbonate-replaced radiolarians, rare foraminifera, sponge spicules, and low 494 contents of coarse detrital material (<5%). Pyrite is absent in the section, in stark contrast 495 to St. Audrie's Bay. In summary, the Levanto section records a relatively static depositional 496 environment spanning ca. four million years and has robust geochronological and 497 biostratigraphic constraints.

498

499 4. MATERIALS AND METHODS

500 **4.1 Sample processing**

501 Samples were collected from outcrop and then cut to remove weathered material,502 veins, and modern marine-derived debris (specifically from St. Audrie's Bay samples).

Portions of samples were crushed in a jaw crusher and pulverized either in a stainless steel
disk crusher (New York Canyon samples) at the University of Southern California, Los
Angeles, CA USA (USC), in a tungsten carbide ball mill at USC (St. Audrie's Bay
samples), or at Actlabs in Ontario, Canada (Levanto and Lombardy Basin samples). Long
term blank testing indicated none of the powdering processes resulted in Hg contamination.

508 4.2 Hg contents

509 For the St. Audrie's Bay, New York Canyon, and Levanto samples, total Hg was 510 measured using a Hydra IIc at The University of Toronto (Toronto, Canada), using similar 511 methods to those from Thibodeau et al. (2016). In the Hydra IIc, weighed sub-samples of 512 powdered rocks were combusted under O₂ flow at 350 ml/min, heated in a drying step to 513 300°C for 40 s, then decomposed for 300 s at 800°C. Following combustion, evolved gases 514 were carried through a heated (600°C) catalyst tube to remove possible interferences (e.g., 515 halogen compounds, sulfur oxides, nitrous oxides) and Hg was captured on a gold trap 516 while combustion gases were removed from the detection cell. The gold trap was heated 517 for 30 s at 600°C to release Hg, which was then carried to the detection cell where 518 absorbance from a mercury lamp is measured at 253.7 nm. For this study, instrumental 519 response was calibrated using the NIST 3133 Hg standard in a 0.25% L-cysteine solution. 520 Blank absorbance was <2% of typical sample signals and always <4%. NIST 3133 was 521 periodically combusted and analyzed alongside samples to determine precision, with 522 results within 5% of the nominal values. Samples measured more than once are reported 523 as averages, which typically have reproducibility better than 10%. External standards NIST 524 SRM 1944 and 1646a were combusted alongside samples to check measurement accuracy.

525 Errors on Hg content measurements are estimated to be 10% (2sd) based on reproducibility526 of samples and external standards.

527 Lombardy Basin and preliminary Panormide Domain samples were analyzed for 528 total Hg concentrations using an MA-3000 Direct Mercury Analyzer (Nippon Instruments 529 Corporation, Tokyo, Japan) thermal decomposition analyzer at USC. Similar to the Hydra 530 IIc, the MA-3000 combusts powdered samples, uses a catalyst to remove interferences, 531 traps Hg on a gold trap, and measures the amount of Hg after release from the trap by 532 absorbance at 253.7 nm. The MA-3000 allows for combusting multiple aliquots of a single 533 sample in order to accumulate enough Hg for analysis after release from the gold trap. This 534 approach is well suited to samples with low Hg contents, such as the rocks from the 535 Lombardy Basin. Total sample masses of up to 5 g were analyzed by combusting up to 20 536 \sim 250 mg sub-samples. Even with this approach, several samples contained too little Hg to 537 obtain robust results, because the detection limit of 1.5 ng could not be reached with a 538 reasonable number of combustions for some samples. Samples from the Lombardy basin 539 that were below the detection limit are noted in the supplementary dataset. No samples 540 from the Panormide domain in Sicily were above the detection limit, and results from this 541 section are not reported here. We consider these to represent the analytical limit of Hg 542 content measurement via the widely-used thermal decomposition method, though other 543 analytical methods might allow Hg quantification in such rocks.

544

4.3 Hg isotope measurements

545 Mercury isotope measurements followed the analytical methods from Thibodeau et 546 al. (2016). Briefly, Hg was extracted and purified from samples using the Hydra IIc without 547 the gold trap (with a longer decomposition time than that used for Hg concentration

548 measurements). Mercury was trapped by directly sparging the gas outflow with elemental 549 Hg into ~10% H₂SO₄ (v/v) and ~1% KMnO₄ (w/w), which oxidized the Hg0 gas to HgII. 550 To ensure removal of residual Hg in the furnace, after each sample combustion, 50 μ L of 551 Milli-Q was combusted and lines were heated with a heat gun to transfer any residual Hg 552 to the trap. NIST 3133 and 1646a were combusted and trapped as procedural standards and 553 blanks.

554 Procedural blanks were <0.02 ng/g, which is <1-2% of the sample Hg. Mercury 555 recovery was checked by neutralizing an aliquot of each solution with NH₂OH-HCl 556 immediately after vapor trapping and measuring its concentration using a Tekran 2600 cold 557 vapor atomic fluorescence spectrometer (Tekran instruments, Toronto, Canada). The ~10% 558 variation in sample recoveries reflects the uncertainty in concentration analyses and sample 559 heterogeneity. Mercury isotope analyses were conducted with a cold vapor multi-collector 560 inductively coupled mass spectrometer (Neptune Plus MC-ICP-MS, Thermo-Finnigan, 561 San Jose, CA, USA) at the University of Toronto. Sample solutions were neutralized with 562 NH₂OH-HCl and diluted to 1-2 ng/g with a matrix matched solution. Mercury was 563 introduced to the plasma as Hg0 after SnCl2 reduction and Hg0 vapor separation on a gas-564 liquid separator. A thallium internal standard and standard-sample bracketing with NIST 565 3133 were used to correct for instrumental mass bias, and an in-house Hg standard (J.T. 566 Baker Chemicals) was measured multiple times in each analytical session to determine 567 external reproducibility of the method. Signal concentrations and intensities of all 568 bracketing standards and samples matched within 10%. Isobaric interference from ²⁰⁴Pb 569 was monitored using ²⁰⁶Pb, but was always negligible (correction never altered the 570 calculated δ^{204} Hg). On-peak blank corrections were made on all Hg and Pb masses.

All samples and procedural standards were measured at least twice, and sample isotope values are reported as the mean of duplicate or triplicate measurements (Tables S2 and S3). Average values for procedural standards are reported and are consistent with previous values for these standards (Thibodeau et al., 2016). Sample errors are reported as either the 2σ (standard error mean) of sample replicates or the 2σ (standard deviation)

576 external reproducibility of the in-house J.T. Baker Hg standard, whichever is larger.

577 **4.4 TOC and TIC**

578 **TOC:** For samples from Levanto (Yager et al., 2017), St. Audrie's Bay, and New York 579 Canyon, sub-samples of powders (~1 g) were treated with 1M HCl at 70°C for four hours 580 to remove carbonate from the samples. Samples from the Italian sections (Brumano, 581 Valcava Torre di Busi, and Italcementi) were treated the same way, but with 1 hr 582 decarbonation times; our tests of decarbonation times indicate 1 hr heat treatments yield 583 the same results for δ^{13} C and TOC as up to 8 hr decarbonation times (unpublished data). 584 The samples then settled for 24 hours, the supernatant was decanted, and the decarbonated 585 powder was rinsed three times with repetitive settling and decanting before being dried 586 overnight at 50°C (after Galy et al., 2007). For dolomite-containing Val Adrara samples, 587 this decarbonation procedure failed to fully remove carbonate, a problem identified by 588 many unrealistically high δ^{13} C values for organic carbon (e.g., greater than -5%). 589 Additional sub-samples were treated with 3M HCl, agitated before heating (to expose all 590 sample to acid), and then heated at 70° C for 1 hour to ensure complete carbonate removal. 591 Acidified samples from Val Adrara were then centrifuged (2,000 RPM in an 8 inch 592 diameter centrifuge) for 2 minutes in lieu of letting samples settle. Reported results for 593 Italian samples are from this decarbonation procedure. We tested samples from New York 594 Canyon using both methods, and results were within the analytical uncertainty for both 595 TOC and $\delta^{13}C_{org}$ measurements, supporting either method as a viable means of TOC and 596 $\delta^{13}C_{org}$ measurement.

597 For all samples, TOC (wt.%) was determined on decarbonated powder using 598 Picarro cavity ring down spectroscopy (CRDS; G2131-I; Santa Clara, CA, USA) coupled 599 to a Picarro Liaison (A0301) and a Costech Elemental Combustion System (EA 4010, 600 Valencia, CA, USA). Picarro measurements of CO_2 concentrations were calibrated to 601 determine the percent of organic carbon in samples using the USGS 40 standard (L-602 glutamic acid) weighed at five different sample masses and run at the beginning and end 603 of each set of \sim 15 samples. Determination of the reported sample TOC took into account 604 the amount of carbonate lost during decarbonation (see further detail in supplemental 605 information and Fig. S2). Uncertainty was determined by replicate analysis of samples and 606 standards (typically ~2 replicates per sample; see Supplementary Table 1). Standard 607 deviation of replicates for measured %TOC was ± 0.08 on average, or approximately $\pm 3\%$ 608 of the measured value (1σ standard deviation). Because of potential errors introduced by 609 small amounts of sample loss during liquid decarbonation, including via solubilization of 610 organics (Galy et al., 2007), our conservative estimate of uncertainty is $\pm 10\%$ of the 611 measured value for reported TOC. We elaborate further on our methods for TOC 612 measurement in the supplement. Importantly, our methods do not have the same 0.2% TOC 613 detection limit reported in many previous studies (typically measured via Rock-eval) and 614 reviewed by Grasby et al. (2019), since we are able to calibrate the amount of organic 615 carbon in our samples well within a standard curve (see supplemental information).

616 **TIC:** Depending on the sample's carbonate content, 3–200 mg of sample was weighed into 617 10 mL glass Exetainer vials with rubber septa caps. Vials were evacuated and acidified 618 with 1 mL 30% H₃PO₄. Samples and standards were heated for 80 minutes in a water bath 619 at 70°C to ensure that C associated with all carbonate phases was released as CO₂. Samples 620 were then run on a Picarro CRDS coupled to an Automate preparation device, which 621 sparges the solution with N_2 gas to drive CO_2 into the analyzer. In-house carbonate 622 standards Optical calcite (OPT) and AR15 were run at different masses to calibrate total 623 inorganic carbon (TIC). Errors were calculated by replicate analyses of samples and 624 standards. Average error (1σ) for TIC measurements was ± 0.04 , or <1% of the measured 625 value. Our reported carbonate contents (wt.%) were calculated from measured TIC, 626 assuming all inorganic carbon in our samples is CaCO₃. No dolomite or other carbonate 627 phases were observed in thin sections of the NYC, SAB, and Levanto samples. Dolomite 628 is present in the Lombardy Basin samples, potentially introducing some uncertainty into 629 carbonate content values for this section. These independent TIC analyses also allow for 630 some constraint on the mass loss during decarbonation, which assist in understanding 631 potential error introduced to TOC measurements (see supplemental information).

632

633 **5. RESULTS**

We report Hg contents, TOC contents, carbonate contents, and Hg isotope compositions in the supplemental data set. We analyzed 193 samples for Hg contents and 18 samples for Hg isotopes from the Levanto section, 80 samples for Hg contents and 13 for Hg isotopes from St. Audrie's Bay, and 81 samples for Hg contents from New York Canyon, complementing the previously published 35 content and 35 isotope measurements from Thibodeau et al. (2016). The New York Canyon samples in this study are all stratigraphically above those previously published in Thibodeau et al. (2016). From the Lombardy Basin, we analyzed Hg contents in 24 samples from the Brumano section (11 yielding Hg above the detection limit), 57 from the Italcementi section (25 above the detection limit), 21 from Valcava Torre de Busi (18 above the detection limit), and 29 from Val Adrara (19 above the detection limit).

In Figs 3–6 we plot total Hg, TOC contents, Hg/TOC, δ^{202} Hg, and Δ^{199} Hg for each section with stratigraphy. In each figure, 'pre' denotes the pre-extinction interval (i.e., the available Rhaetian stratigraphy until the onset of the negative C isotope excursion), ETE is denoted (i.e., from the onset of the negative CIE to the TJB), and 'post' denotes postextinction (i.e., Hettangian and above, where available). Figure S3 contains selected cross plots of carbonate content, Hg, Hg/TOC, and TOC, with data separated by relative time intervals (pre-ETE, ETE, and post-ETE).

652 5.1 New York Canyon

653 In Fig. 3 and Fig. S3a-c we report data from Thibodeau et al. (2017) and additional 654 data from this study. Prior to the ETE, samples have average Hg contents of $\sim 12 \pm 4$ ppb 655 (n = 4; 1 s.d.). This value rises to ~50 ± 21 ppb (n = 14, 1 s.d.) during the ETE, and then 656 decreases to 11 ± 10 ppb (n = 100, 1 s.d.) during the Early Jurassic. Ratios of Hg/TOC have 657 average values of 48 ± 15 ppb/wt.% (n = 4; 1 s.d.) during the pre-extinction interval, rise 658 to an average of 244 ± 139 ppb/wt.% (n = 14; 1 s.d.) during the ETE, and decrease to an 659 average value of 92 ± 48 ppb/wt.% (n = 100; 1 s.d.) during the post-extinction interval. 660 Mercury isotope were originally reported and discussed in Thibodeau et al. (2017). The 661 δ^{202} Hg values during the Rhaetian and early Hettangian are between ~0% and -1.5%,

becoming progressively more negative upsection; Δ^{199} Hg values are near zero during the ETE and in the early Hettangian, but deviate from zero (in both negative and positive directions) during the Hettangian. The New York Canyon section is truncated in the Rhaetian, so it was not possible to measure additional samples from before the extinction from this studied section. Mercury and TOC contents are not correlated during the ETE but are correlated (r² = 0.50) in the Hettangian samples (Fig. S3b).

668 **5.2 St. Audrie's Bay**

669 Figures 4 and S3d-f report data from St. Audrie's Bay. During the Rhaetian, 670 average Hg contents are $\sim 29 \pm 15$ ppb (n = 38, 1 s.d.), during the ETE (correlated using the 671 negative CIE in organic C isotopes) average Hg contents are 19 ± 15 ppb (n = 13; 1 s.d.), 672 and during the Early Jurassic Hg contents are 42 ± 29 ppb (n = 29; 1 s.d.). Ratios of 673 Hg/TOC during the pre-extinction interval are on average 43 ± 27 ppb/wt.% TOC (n = 38; 674 1 s.d.), during the ETE are 102 ± 77 ppb/wt.% (n = 13; 1 s.d.), and during the Early Jurassic 675 are 18 ± 20 ppb/wt.%TOC (n = 29; 1 s.d.). Ratios of Hg/TOC rise to ~150 ppb/wt.% 676 coincident with the onset of the negative C isotope excursion (meter ~ 12) and then decrease 677 to an average of ~20 ppb/wt.% during the Hettangian. Mercury and TOC are correlated, 678 particularly during the ETE ($r^2 = 0.51$) and the Hettangian ($r^2 = 0.90$; Fig S3e). Percival et 679 al. (2017) also reported Hg data from St. Audrie's Bay, which are plotted in Fig. 4; their 680 TOC data are from Hesselbo et al. (2002). Mercury contents from Percival et al (2017) 681 match well with our data, and TOC data are similar in the two studies, but the interval 682 during the negative carbon isotope excursion differs slightly, resulting in a difference in 683 Hg/TOC ratios. This discrepancy could be due to heterogeneity in the section during

sampling or TOC methodological differences; the implications for this difference arediscussed in the figure caption.

Values of δ^{202} Hg at St. Audrie's Bay are similar throughout the measured section and range between -1.50% and -0.50%; Δ^{199} Hg values are negative during the Rhaetian (-0.20% to -0.40%), increase to about -0.10% during the ETE, and decrease again during

689 the Hettangian (-0.20% to -0.40%).

690 **5.3 Lombardy Basin**

The Lombardy Basin results are separated into the four respective sections (Fig. S1) and are reported in a composite section in Fig. 5. Considered together, the Lombardy sections exhibit low Hg contents (all <15 ppb, and contents greater than ~6 ppb found only in the Brumano section) and low TOC. Many samples contain so little Hg that the 1 ng detection limit would have required an estimated 10–20 separate combustions, implying a content well below 1 ppb (as noted above, we did not analyze samples with such little Hg). Marly samples contain slightly more Hg and sometimes elevated TOC.

698 At the Brumano section, samples have an average Hg content of 7 ± 4 ppm (n = 11, 699 1s.d.), TOC average of $0.2 \pm 0.1\%$ (n = 26; 1 s.d.), and Hg/TOC average of 25 ± 7 wt.% (n 700 = 10; 1 s.d.). The Brumano section, which is the deepest of the composite Italian sections, 701 deepens upwards, with less carbonate in samples from further up-section. Many carbonate-702 rich samples lower in the section were below the detection limit for Hg measurements. 703 Overall, the Brumano section Hg contents are low (below the detection limit to ~3 ppb) in 704 resistant, carbonate-rich beds and higher (between ~ 5 and 14 ppb) in marly, mudstone beds. 705 Samples from the Italcementi quarry section (Fig. S1) have average Hg contents of 706 4 ± 3 ppb (n = 25, 1 s.d.; not including 32 samples below detection limit), TOC contents

of 0.1 ± 0.04 wt.% (n = 22, 1 s.d.) and Hg/TOC ratios of 44 ± 26 (n = 22; 1 s.d.). The two high (>50) Hg samples ITZ62 and ITZ64 are from marly beds. Carbonate-rich beds exhibit somewhat lower Hg contents.

The Valcava Torre dei Busi section (Fig. S1) has average Hg contents of $\sim 2 \pm 1.5$ ppb (n = 18; 1 s.d.), TOC contents of 0.08 ± 0.16 wt.% (n = 27; 1 s.d.) and Hg/TOC values

712 of 44 \pm 25 ppb/wt.% (n = 16; 1 s.d.).

The Val Adrara section (Fig. S1) contains average Hg contents of 2.7 ± 1.4 ppb (n = 19; 1 s.d.), TOC concentrations of 0.03 ± 0.03 wt.% (n = 15; 1 s.d.) and Hg/TOC of 140 ± 119 ppb/wt.% (n = 15; 1 s.d.). Although the highest Hg/TOC values are found above the Triassic–Jurassic boundary from the Hettangian portion of the Val Adrara section, a less pronounced rise in Hg/TOC is synchronous with the TJ boundary.

718 **5.4 Levanto**

719 In Figs 6 and S3g-i we report data from the Levanto section. Mercury contents are 720 on average 33 ± 14 ppb during the Rhaetian pre-extinction interval, (n = 84; 1 s.d.), $37 \pm$ 721 24 ppb (n = 14; 1 s.d.) during the negative CIE and ETE Hg concentrations, and 36 ± 19 722 ppb following the ETE during the Hettangian (n = 96; 1 s.d.). Hg/TOC during the pre-723 extinction interval is 24 ± 25 ppb/wt.% (n = 84; 1 s.d.), during the ETE is 30 ± 29 ppb/wt.% 724 (n = 14; 1 s.d.), and following the ETE is $64 \pm 36 \text{ ppb/wt.}\%$ (n = 96; 1 s.d.). There is an 725 increase in Hg/TOC at ~57 meters, coincident with the negative CIE in organic carbon 726 isotopes (Yager et al., 2017). Mercury and Hg/TOC are negatively correlated with 727 carbonate (Fig S3h–i) during the ETE and Hettangian. Correlations between Hg and TOC 728 are weaker than for the St. Audrie's Bay and New York Canyon sections (Fig. S3g-i); 729 elevated Hg/TOC is expressed during the ETE and into the Hettangian. Values of δ^{202} Hg are between about -1.30% and -0.30% for the measured section, with a possible excursion from -0.3% to -1.5% during the late Rhaetian and ETE; Δ^{199} Hg is slightly positive during the Rhaetian (~0.1‰) and near zero without discernable MIF during the ETE and Hettangian (±0.05‰).

734 In the Rhaetian portion of the Levanto section, there is no discernible lithologic 735 control on Hg contents based on outcrop or thin section observations (i.e., neither high nor 736 low Hg contents appear to be related to specific lithologic composition). In contrast, during 737 the Hettangian, alternations in thick and thin bedded strata appear to impact Hg contents 738 and Hg/TOC. Samples high in Hg are compacted and contain less carbonate and slightly 739 higher TOC, while samples that are uncompacted and high in CARB contain less Hg and 740 lower Hg/TOC (Fig. S4). At ~57 m, carbonate content variability increases and samples 741 with lower carbonate contents are associated with higher Hg concentrations (Fig. S5). We 742 note proximity of samples to ash beds did not have any discernible effect on Hg contents, 743 and in fact the Rhaetian portion of the section includes more conspicuous ash beds than the 744 Hettangian, indicating ash bed presence does not control Hg contents in these samples.

745 **5.5 Consistent observations between sections**

Using organic C isotopes as a correlation tool, at all four sections Hg/TOC rises during the negative CIE and, by inference, during the contemporaneous ETE. At New York Canyon and St. Audrie's Bay, Hg/TOC decreases during the Early Jurassic after its peak associated with the CIE and ETE (Fig. 7). In contrast, at Levanto, Hg/TOC increases during the negative CIE and ETE and then increases further in the early Jurassic, remaining elevated for the remainder of the section (Fig. 7). In the Lombardy Basin, Hg/TOC is briefly elevated during the pre-ETE interval, decreases and then increases again during the ETE and negative isotope excursion, and then rises to the highest observed values during the early Hettangian (although these very high values from the Val Adrara section are associated with very low TOC). Thus, St. Audrie's Bay and New York Canyon both exhibit relatively well-defined Hg anomalies, while those at Levanto and in the Lombardy Basin appear more protracted and less clearly defined. Levanto and Lombardy also share somewhat enigmatic brief spikes in Hg/TOC in the late Rhaetian, prior to the ETE and C isotope excursion.

At St. Audrie's Bay, New York Canyon, and Levanto, each section also exhibits negligible or low MIF (near zero Δ^{199} Hg) during the ETE. New York Canyon and Levanto record a slightly negative shift in δ^{202} Hg during the Late Rhaetian and ETE, while low sampling resolution in Hg isotopes at St. Audrie's Bay may obscure any similar trend at this site. We were not able to measure Hg isotopes from the Lombardy sections.

765

766 6. DISCUSSION

All four sections contain elevated Hg/TOC during the ETE and negative CIE, when compared to pre-extinction values. During the same interval, MIF of Hg isotopes (Δ^{199} Hg) is near zero or shifts towards zero, suggesting an increase in Hg deposition derived from subaerial volcanism associated with CAMP activity during the ETE. Below, we detail the implications of elevated Hg/TOC and low MIF and discuss the caveats from our study and next steps for using and understanding the Hg proxy.

773

774 6.1 Mercury isotopes support a magmatically derived Hg signal at the ETE

775 At New York Canyon, Levanto, and St. Audrie's Bay, elevated Hg/TOC values 776 during the ETE coincide with Hg isotope signals that exhibit negligible MIF (Fig. 7), 777 consistent with a large increase in volcanic Hg that overwhelmed the surface reservoirs in 778 a way that resulted in minimal MIF producing photoreduction prior to deposition 779 (Thibodeau and Bergquist, 2017). Outside of the extinction interval, Hg isotopes are 780 consistent with normal Hg cycling through surface reservoirs, acquiring positive and 781 negative MIF (e.g., Bergquist and Blum, 2007; Blum et al., 2014; Thibodeau and 782 Bergquist, 2017 and references therein).

783 In more detail, deposition of Hg in many terrestrial systems is dominated by 784 gaseous elemental Hg via uptake by vegetation and subsequent litterfall that results in 785 terrestrial biomass and soils acquiring negative MIF and MDF. Thus, marine sediments 786 close to continents and dominated by terrestrial input often reflect this source of Hg. In 787 contrast, marine sediments farther from land that are dominated by atmospheric depositon 788 of HgII species have positive MIF and less negative MDF. Our results for MIF and MDF 789 outside of the ETE are consistent with varying mixtures of Hg sourced from the atmosphere 790 (positive MIF, less negative MDF) and Hg sourced from terrestrial runoff (negative MIF, 791 more negative MDF). The Hg MIF signatures are also consistent with the expectation for 792 the depositional environment of each section — with slightly positive MIF at the deeper 793 (Levanto) section, likely more influenced by atmospherically derived Hg, and more 794 negative MIF at the shallower sections (St. Audrie's Bay, New York Canyon), more 795 influenced by terrestrial sources (Figs. 3–4 and 6). The St. Audrie's Bay section, which is 796 shallow enough to have been exposed subaerially during the ETE, shows the most negative 797 MIF of any section studied here. In summary, when Hg/TOC ratios are relatively low
(typically before and after the ETE), each section bears a MIF composition consistent with
its major source of Hg input, with near-shore sections displaying terrestrial negative MIF
(which may also be related to fires and biomass burning as suggested by Grasby et al.,
2019; e.g., at St. Audrie's Bay) and more offshore sections having positive MIF values
reflected of atmospheric deposition of HgII species (positive MIF for offshore sections;
e.g., Levanto) (Figs 2 and 8).

804 In contrast, when Hg/TOC is elevated during ETE Hg/TOC anomalies, MIF values 805 approach zero, consistent with Hg input from unaltered volcanic sources (Thibodeau and 806 Bergquist, 2017). Importantly, the absence or decrease in the extent of MIF coincides with 807 the intervals of elevated Hg/TOC in each section. When the elevated Hg/TOC periods 808 cease, the two shallower sections also see a return to odd MIF values, although with 809 different timings. At St. Audrie's Bay, the Hg/TOC peak ends relatively abruptly, and 810 negative MIF returns in the first sample measured from the Hettangian. At New York 811 Canyon, there is a somewhat more gradual return to background Hg/TOC extending into 812 the earliest Hettangian, and the absence of MIF follows suit. The Levanto record is 813 different, and exhibits elevated and noisey Hg/TOC persisting throughout the Hettangian 814 and positive MIF does not reoccur after the ETE (discussed in more detail below). 815 Altogether, the disappearance of MIF is remarkably consistent across the three different 816 sections, suggesting that absence or decrease of MIF may be a general feature of TJB Hg 817 anomalies. This observation lends support to a global magmatic source for the Hg 818 anomalies at this time (consistent with the conclusions of Thibodeau et al., 2017).

Like the MIF signal, the Hg isotope MDF compositions largely reflect the depositional setting of each section. We observe negative MDF in all sections (Figs 3–4

821 and 6), but this signature is less pronounced at Levanto, which likely had less relative 822 terrestrial influence relative to St. Audrie's Bay and New York Canyon given its deeper 823 depositional setting and positive MIF values prior to the ETE. Closer proximity to the 824 continents results in more continental influence and more influence from biomass and soil, 825 resulting in more negative MDF compositions. At New York Canyon, there is a general 826 trend towards more negative δ^{202} Hg values coincident with upward shallowing through the section. The increasingly negative δ^{202} Hg values may reflect an increase in the relative 827 828 amount of continentally derived material versus atmospheric deposition. Unlike the MIF signal, we do not see systematic shifts in δ^{202} Hg values associated with the Hg/TOC 829 830 anomalies in any of the three sections studied here; this is not surprising given volcanic Hg 831 also has negative MDF that overlaps with terrestrial Hg and atmospheric HgII.

832

833 6.2 Comparison to Hg isotope records from other mass extinction and LIP intervals

834 Mercury isotope records are also available from other sedimentary sections 835 deposited during LIP activity (summarized in Fig. 8). Across these studies, as in the case 836 of the ETE, MIF signatures broadly reflect the depositional setting (e.g., as in Fig. 2). 837 However, the end-Triassic is distinct in that MIF is negligible or shifts towards zero during 838 the Hg/TOC anomaly, at least for the localities studied thus far, while similar systematic 839 shifts are not seen during other time periods. For example, there are several records of Hg 840 isotopes for the end–Permian mass extinction, with several deep-water sections (Buchanan 841 Lake, Sverdrup Basin, Canada; Daxiakou, Shangsi, Gujo-Hachiman) showing positive 842 MIF, and a platform carbonate section (Meishan, China) exhibiting negative MIF, 843 particularly during and after the increase in Hg/TOC (Grasby et al., 2017; Shen et al.,

2019b; Wang et al., 2018). However, changes in the MIF signature during the end–Permian
Hg/TOC anomaly are inconsistent. At Gujo-Hachiman, MIF decreases much as it does in
the end–Triassic sections, but there is little change in MIF of the other end–Permian
sections (Buchanan Lake, Xiakou) and a shift from positive to negative MIF is observed at
Meishan.

849 The limited Hg isotope data from other time intervals also present a mixed picture. 850 During the Toarcian Ocean Anoxic Event, data from a near-shore section suggest a shift 851 from slightly positive (0.06% to 0.07%) to negative MIF (less than -0.10%) during the 852 Hg anomaly and carbon isotope excursion (Them et al., 2019). At the Ordovician–Silurian 853 boundary, no significant change in the MIF signal was found during two apparent Hg/TOC 854 anomalies in deep water (Gong et al., 2017) or from S-rich shale sections (Shen et al., 855 2019a) in China (however, the potential of LIP emplacement at this interval is regarded as 856 circumstantial by some studies; e.g., Shen et al. 2019). Across the Cretaceous-Paleogene 857 transition, the MIF signature during Hg excursions range widely (Sial et al., 2016). In some 858 cases, the lack of consistent isotopic signatures associated with Hg/TOC anomalies might 859 indicate a non-volcanic origin of the anomaly. In other cases, such as during the end-860 Permian, volcanically derived Hg may have been subject to environmental transformation 861 after its release, imparting characteristic MIF depending on depositional setting (as 862 suggested by Thibodeau and Bergquist, 2017). At the end-Triassic, the rapid volcanic 863 release may have overloaded any MIF-inducing environmental processes prior to 864 deposition. If this interpretation is correct, the new data presented here show that this 865 overloading generated negligible MIF signature in sections across a wide range of depositional settings at the end–Triassic. Determining whether this feature is observed inall end–Triassic localities will require additional analyses.

868 The apparent contrast between the end–Triassic and end–Permian suggests that Hg 869 isotopes may not provide a "smoking gun" to distinguish whether apparent anomalies are 870 associated with LIP-derived Hg (Bergquist, 2017). Yet the differences in Hg behavior 871 between time intervals may also hold general clues about the fate of volatiles released by 872 different LIPs — an important question with implications for the environmental effects and 873 ultimately for the causes of mass extinction. Why the fate of volcanically released Hg might 874 have differed during the end-Permian versus the end-Triassic remains to be understood 875 but raises intriguing questions. For example, was the difference because of more rapid 876 volatile release during CAMP? Or did the Siberian trap emplacement release Hg from coal 877 beds and organic-rich sediments with MIF during the end-Permian? To date, the number 878 of studies reporting Hg isotope data from sedimentary rock records lags far behind those 879 presenting Hg contents and Hg/TOC ratios. Though Hg isotopes are much more 880 challenging to measure, they may offer unique insights that are simply missing from 881 concentration data alone. The consistency of the MIF patterns observed in this study at the 882 end-Triassic suggests that a concerted effort to add isotopic information may be important 883 to realizing the full scope of the Hg proxy.

884

885 6.3 Elevated volcanogenic Hg persists after CAMP magmatism in some Triassic886 Jurassic sections

887 The apparent ubiquity of elevated Hg/TOC during the ETE (Fig. 9; Percival et al.,
888 2017) suggests that elevated Hg may be a global signal during this interval of time,

889 presumably relating to CAMP volatile emissions. However, when viewing the Hg and 890 Hg/TOC 'anomalies' section by section, a number of complexities become apparent. The 891 Levanto section, which has a high-resolution chronology from ash bed U–Pb ages, seemed 892 a promising opportunity for testing the correspondence between CAMP timing (as 893 constrained by the U–Pb age dates) and increases in Hg and Hg/TOC contents. However, 894 Hg contents do not align with CAMP U–Pb ages in this section; instead elevated Hg begins 895 ca. 150 kyrs (ca. 201.5 Ma) after the oldest dated CAMP basalts (Fig. 10; 201.63 \pm 0.029 896 Ma; Davies et al., 2017). Meanwhile, the youngest U–Pb dated CAMP basalts are 201.1 \pm 897 0.071 Ma, but at the Levanto section elevated Hg persists until the top of the section at ca. 898 200.1 Ma. Similar elevated Hg/TOC also persists into the Early Jurassic in the Lombardy 899 sections (Fig. 9). These mismatches in timing between the Hg signal and CAMP activity 900 are a clear indication that increases in Hg contents and Hg/TOC are imperfect proxies for 901 magmatism in the sedimentary record, especially when looking to this proxy for temporal 902 correlation.

903 The effect of intrusive vs. extrusive magmatism on Hg release (e.g., Percival et al. 904 2017) does not on its own explain the timing discrepancy in the onset of the Hg anomaly 905 from Levanto. The earliest dated phases of CAMP activity were intrusive (Davies et al., 906 2017), possibly releasing less Hg than expected from extrusive volcanism. However, only 907 the first dated CAMP basalt is intrusive (red CAMP age in Fig. 10), and several ages for 908 CAMP extrusives also pre-date the increase in Hg/TOC seen at Levanto (Fig. 10), requiring 909 another explanation for the mismatch in timing at the onset of the Hg anomaly in this 910 section.

911 The long persistence of the anomaly at Levanto is also unexpected. Prolonged 912 supply of CAMP-related Hg, e.g., from the continents, could be one explanation. However, 913 if Levanto were receiving Hg from terrestrial runoff, or from atmospheric deposition, we 914 would expect to see a characteristic Hg isotope signal; instead, MIF remains near zero 915 throughout the higher and noiser high Hg/TOC interval. Another explanation would be that 916 CAMP activity lasted longer than suggested by currently available U/Pb dates; however, 917 similar non-MIF, high Hg/TOC samples do not persist into the Hettangian at the St. 918 Audrie's Bay or New York Canyon sections, so it seems unlikely that the long-lasting 919 signal at Levanto simply reflects more CAMP-derived atmospheric Hg deposition 920 extending into the Hettangian.

A more plausible explanation for the extended period of high Hg/TOC at Levanto and the Lombardy basin is that depositional and/or diagenetic processes in the local environments controlled Hg and TOC concentrations. These processes may also explain the delayed onset of the Hg anomaly at Levanto. In the section that follows, we consider these effects more deeply.

926

927 6.4 Depositional and diagenetic controls on Hg contents and Hg/TOC ratios in 928 sedimentary rocks

Recent studies have recognized and investigated the importance of the Hg host phase when applying Hg contents and Hg/TOC ratios as a proxy for LIP magmatism (Shen et al., 2019a, b, 2020; Keller et al., 2020; Kovács et al. 2020), as well as the role of weathering in altering depositional Hg contents (Charbonnier et al., 2020). We removed surficial, altered material from our samples and did not observe the kind of systematic

934 effects anticipated from weathering (Charbonnier et al., 2020), so we do not see weathering 935 as a likely control on the changes in Hg and Hg/TOC observed through the sections we 936 have studied. However, differences in depositional environment likely played an important 937 role. Since the depositional environment and diagenetic history control the presence of the 938 host phases of Hg, they ultimately control the Hg contents. We can therefore expect that 939 Hg concentrations of most if not all sedimentary sections will be primarily controlled by 940 depositional environment and in turn host phases of Hg, and secondarily controlled by 941 secular changes in the global surficial Hg pool.

942 6.4.1 Plausible host phases for Hg in relation to depositional environment of each section

943 Each section in this study exhibits a different depositional environment, and in 944 some cases these changed through time. The depositional and diagenetic histories of each 945 section and subsection impacted the TOC, S, clay, and carbonate contents, and thus 946 ultimately the Hg contents. While we lack detailed characterization of Hg associations in 947 each section, we can make some general observations based on Hg-TOC correlations and 948 independent information about each section, such as presence or absence of sulfide 949 minerals. In the New York Canyon section, the host phase for Hg in the post-extinction 950 interval is likely dominantly TOC (based on their close correlation). At St. Audrie's Bay, 951 Hg in likely hosted by TOC. In the Lombardy basin sections, TOC may be the dominant 952 host, although it seems likely that carbonate dilution plays a larger role in the measured Hg 953 contents than at other sections. The Levanto section Hg contents are negatively correlated 954 with carbonates, suggesting dilution may play a major role in determining the Hg contents 955 in these rocks. The host phase for Hg at the Levanto section may be clays, as TOC appears

to play a minor role (based on the low correlations) and there is no evidence abundant S(based on the absence of sulfide phases in thin sections).

958 6.4.2 Possible paleo-environmental controls on depositional effects

Depth and proximity to continental sources may influence Hg contents in the sedimentary record (e.g., Them et al., 2019; see their fig. 6). The rapid changes in depositional environment seen at shallow sections mean environmental parameters that can affect both Hg and TOC, as well with other rock materials including carbonate, may affect Hg concentrations and Hg/TOC ratios. We illustrate these changes in Fig. 11 and briefly discuss some below, in terms of their potential influence on the ETE Hg records studied here.

966 Carbonate deposition and diagenesis may have important effects on geochemical 967 proxies, especially in carbonate-rich rocks (typical of many marine sediments), (e.g., 968 Arvidson and Morse, 2014). Dilution occurs whereby increased carbonate content leads to 969 lower TOC and Hg contents. Mercury contents can be calculated on a carbonate-free-basis 970 to correct for dilution (see Fig S4–6), but this correction does not remove the high Hg and 971 Hg/TOC in the Hettangian at Levanto and Lombardy. Another important process in 972 carbonate rich rocks is the migration of carbonate during early diagenesis, possibly leaving 973 organic C and associated Hg behind. In the Hettangian and ETE portions of the Levanto 974 section, Hg is enriched in samples from thin beds with lower carbonate content and 975 depleted in carbonate-rich beds (Fig. SI 5), and carbonate and Hg contents are negatively 976 correlated (Fig. 7h). These patterns could be due to migration of carbonate and/or dilution, 977 but on its own, the bed-to-bed alternating enrichment and depletion does not explain the 978 overall relatively elevated Hg/TOC throughout this interval at Levanto. We note that at any

979 rate these aren't particularly elevated contents (e.g., see fig. 11 from Charbonnier et al.,980 2020).

981 Processes controlling organic C preservation are also expected to influence 982 Hg/TOC ratios. Organic C in marine sediments is subject to degradation that greatly 983 depends on water depth, local productivity, oxygen exposure time at the sediment water 984 interface, and sedimentary reworking (see also Charbonnier et al., 2020). Changes in depth 985 at St. Audrie's Bay may have contributed to the very low TOC (and potentially high 986 Hg/TOC) during the ETE at this section. Although there is no evidence for similar changes 987 in depth at Levanto that would have led to preferential TOC loss and the observed Hg/TOC 988 enrichment in the Hettangian, it is difficult to rule out all possible changes that could have 989 affected organic C preservation (e.g., Charbonnier et al., 2020).

Widespread anoxia and/or euxinia associated with the Triassic–Jurassic boundary
(Schootbrugge et al. 2008; Jost et al., 2017), like many other extinction events, may have
favored the deposition of sulfides and associated Hg enrichment (e.g., Bower et al., 2008;
Han et al., 2014; He et al., 2020). Large sedimentary pyrites are found in the Hettangian at
St. Audrie's Bay (Hesselbo et al., 2004; Wignall, 2001). Such an increase in anoxia would
likely affect sedimentary S deposition, and therefore may have also affected sedimentary
Hg deposition.

997 6.4.3 Interpretation of Hg/TOC ratios from low-TOC samples

The complexity of host phases and depositional effects on Hg content is magnified when interpreting Hg/TOC ratios in samples with particularly low TOC contents. While previous studies have regarded high Hg/TOC ratios in samples with TOC <0.2 wt.% as artifacts (see Section 2.1) or difficult to interpret, we instead suggest that they reflect an

1002 additional, and important, layer of complexity arising from the processes that sequester Hg 1003 and its associated elements in sediments. High Hg/TOC ratios associated with low 1004 TOC content are not artifacts per se, in that they do represent Hg enrichment relative to 1005 TOC. However, at low TOC values, small changes in TOC can lead to large changes in 1006 Hg/TOC despite little change in Hg contetns. The more relevant question is whether these 1007 represent the enrichment of Hg in association with TOC, or the increasing importance of 1008 Hg hosted in other phases — emphasizing the need to better understand Hg distribution in 1009 sedimentary rocks, especially in those with low TOC content (see also Shen et al., 2020). 1010 Recent studies have greatly expanded our understanding of the role of S sequestration in 1011 Hg 'anomalies' (Shen et al., 2019a; Shen et al., 2020), and demonstrated that sediments 1012 deposited in highly-reducing, highly sulfidic environments sequester Hg to an extent that 1013 obscures any global Hg signal (Shen et al., 2019a). Similar micro-scale study of carbonate-1014 rich, sulfide-poor lithologies such as those from Levanto and the Lombardy Basin could 1015 help illuminate the controls on Hg distribution in these low TOC rocks.

1016 6.4.4 Summary of depositional effects

1017 Mercury records in marine sedimentary rocks across the ETE, and at other 1018 extinction events, are likely affected by a combination of all the processes discussed above. 1019 Ocean anoxia and euxinia (from CO₂-induced global warming and increased nutrient 1020 runoff), increased Hg, and increased S are all possible direct and indirect consequences of 1021 CAMP, and elevated Hg and Hg/TOC may be affected by a combination of these effects. 1022 Further, changes in the carbonate system (e.g., Greene et al., 2012), global redox (e.g., 1023 Schootbrugge et al., 2013; Kasprak et al., 2015; Jost et al., 2017) or changes in delivery of 1024 clay (e.g., from increased weathering) are all downstream consequences of LIP magmatism that also could have impacted Hg delivery and/or preservation. Thus we expect a general connection between LIP activity and Hg, as observed consistently in our ETE sections, but the causes of that enrichment, and the timing of Hg anomalies, may be complex. Notably, the persistent Hg enrichment in the Hettangian that we see at both Levanto and Lombardy seems difficult to explain by one depositional effect alone, since the elevated Hg/TOC ratios are observed in carbonate-rich, low-TOC samples in Lombardy but the carbonate-1031 poor, higher TOC samples from the Hettangian at Levanto.

Better understanding of depositional effects, and distinguishing between them, may provide a more robust foundation for using Hg contents as a proxy for magmatism. What is clear is that the relatively poor correspondence between CAMP dates and the timing of the Hg/TOC anomaly at Levanto casts doubt the use of Hg contents from a single site to fingerprint the timing of discrete pulses of magmatism directly (cf. Percival et al., 2017), at least in the absence of independent constraints on sedimentary reworking of Hg.

1038

1039 **6.5 Next steps**

1040 Our examination of Hg in different depositional environments across the Triassic-1041 Jurassic boundary corroborates other recent studies noting the complexity in depositional 1042 and diagenetic controls on Hg concentrations and Hg/TOC ratios in sedimentary rocks 1043 (Faggetter et al., 2019; Percival et al., 2018; Shen et al., 2019a,b, 2020; Them et al., 2019; 1044 Charbonnier et al., 2020). At the same time, our results show that, despite the complexity, 1045 there may be a reliable signal of CAMP magmatism recorded by the combination of 1046 Hg/TOC and Hg isotopes across a range of depositional environments at the end–Triassic. 1047 When considered together, Hg isotopes and contents may provide valuable information

about LIP magmatism in sedimentary sections, but the numerous processes influencing Hg
contents and Hg/TOC ratios suggest caution is warranted when applying these
measurements alone, especially when using single-site records and when seeking to
identify detailed timing.

1052 Future studies of the Hg proxy in deep time should aim to investigate where in the 1053 rock Hg is found, specifically what minerals host Hg and what other elements it is 1054 associated with in each sample (e.g., organic C versus S; Shen et al., 2020). As suggested 1055 by Grasby et al. (2019), total S measurements may help elucidate the role of S sequestration 1056 in the Hg anomalies. Similarly, carefully relating Hg contents and Hg/TOC ratios to other 1057 geochemical records (e.g., of local anoxia), as well as investigating sequence stratigraphic 1058 changes within a record, provide opportunities for better informing interpretation of 1059 apparent Hg anomalies. Further understanding may come from exploring more Hg records 1060 when LIP magmatism is not expected. Finally, more connection to research on Hg in 1061 modern marine sediments could help to elucidate how Hg is delivered to and preserved in 1062 sedimentary environments.

1063

1064 7. CONCLUSIONS

We studied five sections spanning the Triassic–Jurassic boundary, and in the four sections with measurable Hg (excluding the carbonate platform of Mt. Sparagio (Sicily) which had Hg below the detection limit), Hg/TOC increases in association with the ETE and CAMP emplacement. At New York Canyon and St. Audrie's Bay, peaks in Hg/TOC are well defined and correspond well with the timing of the end–Triassic extinction as inferred from stratigraphic relationships and organic C isotopes. In contrast, at the Levanto

and Lombardy sections, Hg/TOC remains elevated for much longer, well into the
Hettangian. The well-constrained absolute chronology from Levanto shows that the longlasting elevated Hg/TOC persists well after the youngest U–Pb date of CAMP activity.
These results suggest abundant caution is needed when inferring the timing of mass
volcanism from Hg anomalies in sedimentary rocks, particularly from a single stratigraphic
section, and in the example studied here, even with the benefit of multiple sections.

1077 Mercury isotope signatures across the studied sections are consistent with the 1078 expected signatures based on each site's depositional environment. Shallow, nearshore sites have negative δ^{202} Hg and Δ^{199} Hg values, and the New York Canyon data are 1079 1080 consistent with existing interpretations of shallowing upwards at this locality. In the deeper 1081 basinal setting of Levanto, slightly positive MIF are indicative of an atmospheric and 1082 marine-influenced Hg source, but δ^{202} Hg values suggest some continental influence on 1083 MDF signatures. At each site, MIF is near or approaches zero during the ETE and CAMP 1084 magmatism, supporting the idea that a large source of volcanic Hg may have overwhelmed 1085 the surficial Hg cycle at the time, leading to a notable reduction in the Hg MIF signature 1086 recorded in sedimentary rocks. Differences between Hg isotope behavior during this time 1087 interval versus the end-Permian raise the intriguing possibility of whether Hg isotopes offer 1088 clues about volatile recycling associated with massive volcanism in the geologic past. 1089 Overall, our work suggests that, despite the complex processes that are increasingly 1090 recognized as influencing sedimentary Hg records, the Hg proxy can still be informative 1091 — but that it can be most reliably applied by studying sections that span diverse 1092 depositional environments and by including measurements of Hg isotope ratios as well as 1093 concentrations.

1094

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1111

1112 FIGURE CAPTIONS

Fig. 1. [A] [A] Late Triassic paleogeography with paleogeographic locations of studied
sections, adapted from Kuroda et al. (2010). 1: St. Audrie's Bay, UK; 2: New York Canyon,
Nevada; 3: Lombardy Basin, Italy; 4: Mt. Sparagio, Sicily, Italy; 5: Levanto, Peru. [B]
Relative depositional settings of study sites and expected Hg, TOC, and Hg isotope data at

each site based on relative depth and energy of environment. This is a simplified representation of how Hg enters the marine record, with particular attention to Hg isotopes and relative contributions based on proximity to the continent and depth, and these sites were thousands of kms apart during actual deposition. Based on Thibodeau and Bergquist (2016) and references therein.

1122

1123 Figure 2. Carbon isotope correlation of sections studied here. Mt. Sparagio data and 1124 stratigraphic column is from Todaro et al. (2018); Lombardy basin data is from Zaffani et 1125 al. (2018), Bachan et al. (2012), and this study; St. Audrie's Bay data is from this study 1126 and stratigraphic column is from Hesselbo et al. (2004); New York Canyon data is from 1127 Thibodeau et al. (2017) and this study; Levanto data is from Yager et al. (2017). Note that 1128 this correlation forms the basis for Fig. 9. Gray shape denotes the initial negative isotope 1129 excursion. Triassic–Jurassic boundary is placed at the first occurrence of P. spelae for the 1130 Levanto and New York Canyon sections and is based on Todaro et al. (2018), Zaffani et 1131 al. (2018), and Hesselbo et al. (2004) for the Mt. Sparagio, Lombardy basin, and St. 1132 Audrie's bay sections, respectively.

1133

Figure 3. Stratigraphic column from New York Canyon, Nevada (Corsetti et al. 2015) with δ^{13} Corg, Hg, TOC, Hg/TOC, δ^{202} Hg (MDF), and Δ^{199} Hg (MIF, vertical gray bar denotes no MIF) from this study and Thibodeau et al. (2016). Horizontal gray bar denotes ETE. Colored bar on Hg/TOC plot adapted from fig. 12 of Charbonnier et al. (2020), and provides relative guide for Hg/TOC anomalies.

1140 Figure 4. Stratigraphic column from St. Audrie's Bay, UK (Hesselbo et al. 2004) with 1141 δ^{13} Corg, Hg, TOC, Hg/TOC, δ^{202} Hg (MDF), and Δ^{199} Hg (MIF, vertical gray bar denotes 1142 no MIF) from this study. Horizontal gray bar denotes ETE. "Will" refers to Williton 1143 member; "Lils." Refers to Lilstock Fm. Horizontal gray bar denotes ETE. Mercury data 1144 from Percival et al. (2017) and Hg/TOC data (calculated from Hesselbo et al., 2002 and 1145 Percival et al., 2017) are also shown. Note that TOC data was measured using different 1146 methods. The discrepancies between both sections in TOC measurements, particularly in 1147 the Lilstock formation, result in a large discrepancy between Hg/TOC measurements. 1148 These may be due to TOC methodologies, heterogeneity in the section from bed to bed, or 1149 both. Colored bar in Hg/TOC plot as in Fig. 3.

1150

Figure 5. Composite stratigraphic heights from Italian sections (for lithologic logs for

1152 individual sections, see SI Fig. 2). Formation name and section name are displayed, with

1153 δ^{13} Corg, Hg, TOC and Hg/TOC. Zu = Calcari di Zu Formation; M = Malanotte Formation;

1154 Moltrasio = Calcare di Moltrasio Fm; stratigraphic logs are based on Galli et al. (2007),

1155 Jadoul et al. (2012), Zaffani et al. (2018), and this study. Horizontal gray bar denotes ETE.

1156 Colored bar in Hg/TOC plot as in Fig. 3.

1157

1158 **Fig. 6.** Stratigraphic column from Levanto, Peru (Yager et al., 2017) with δ^{13} Corg, Hg, 1159 TOC, CC, Hg/TOC, δ^{202} Hg (MDF), and Δ^{199} Hg (MIF; vertical gray bar denotes no MIF) 1160 from this study. Horizontal gray bar denotes ETE. Colored bar in Hg/TOC plot as in Fig. 1161 3.

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Fig. 7. Hg/TOC data and Hg isotope data (MIF) plotted with stratigraphy for St. Audrie's Bay, Levanto, and New York Canyon related based on organic C isotope correlation; horizontal gray bars indicate ETE. Stratigraphic column for New York Canyon is from Thibodeau et al. (2016); stratigraphic column from St. Audrie's Bay is from Hesselbo et al. (2004); stratigraphic column from Levanto is from Yager et al. (2017). Data from the lower portion of the New York Canyon section is from Thibodeau et al. (2016).

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1170 Fig. 8. Summary of Hg isotope data in this and previous studies.

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Fig. 9. Hg and Hg/TOC from this study with summary of anoxia/euxinia proxies. Gray bar denotes ETE based on the initial carbon isotope excursion in Fig. 2. Black boxes denote possible euxinia at those sections, which do not align with high Hg/TOC or Hg or at a single point in time. Mt. Sparagio is from $\delta^{34}S_{cas}$ data from He et al. (2020); Lombardy basin data is from δ^{238} U from Jost et al. (2017); St. Audrie's Bay data is from pyrite framboids reported in Hesselbo et al. (2004); New York Canyon data is from Larina et al. (unpublished data); Levanto data is from Yager et al. (unpublished data).

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- 1185 Fig. 11. Schematic displaying example ways LIP magmatism may impact the Hg cycle
- 1186 with respect to measured Hg contents and Hg/TOC.

1188 **REFERENCES**

- Antonelli, M., Franciosi, R., Pezzi, G., Querci, A., Ronco, G.P., Vezzani, F., 1988.
 Paleogeographic Evolution and structural setting of the northern side of the Sicily
 Channel. Mem. della Soc. Geol. Ital. 41, 141–157.
- 1192 Arvidson, R.S., Morse, J.W. 2014.
- 1193Bachan, A., Van De Schootbrugge, B., Fiebig, J., McRoberts, C.A., Ciarapica, G., Payne,1194J.L., 2012. Carbon cycle dynamics following the end-Triassic mass extinction:1195Constraints from paired $\delta^{13}C < inf > carb < /inf > and <math>\delta^{13}C < inf > org < /inf > records.$
- 1196 Geochemistry, Geophys. Geosystems. https://doi.org/10.1029/2012GC004150
- Barattolo, F., Romano, R., 2005. Shallow carbonate platform bioevents during the Upper
 Triassic-Lower Jurassic: An evolutive interpretation. Boll. della Soc. Geol. Ital. 124,
 123–142.
- Bartolini, A., Guex, J., Spangenberg, J.E., Schoene, B., Taylor, D.G., Schaltegger, U.,
 Atudorei, V., 2012. Disentangling the Hettangian carbon isotope record:
 Implications for the aftermath of the end-Triassic mass extinction. Geochemistry,
 Geophys. Geosystems 13, Q01007. https://doi.org/10.1029/2011GC003807
- Berner, R.A., Beerling, D.J., 2007. Volcanic degassing necessary to produce a CaCO3
 undersaturated ocean at the Triassic-Jurassic boundary. Paleogeogr. Paleoclimatol.
 Palaeoecol. 244 (1-4), 368-373.
- Bergquist, B.A., Blum, J.D., 2007. Mass-dependent and -independent fractionation of Hg
 isotopes by photoreduction in aquatic systems. Science (80-.). 318, 417–420.
 https://doi.org/10.1126/science.1148050
- Bergquist, B.A., 2017. Mercury, volcanism, and mass extinctions. Proc. Natl. Acad. Sci.
 U. S. A. 114 (33) 8675-8677.
- Bersezio, R., Jadoul, F., Chinaglia, N., 1997. Geological map of the Norian-Jurassic
 succession of the Southern Alps North of Bergamo. An explanatory note. Boll. Soc.
 Geol. It. 116, 363–378.
- Blackburn, T. J. et al. Zircon U-Pb geochronology links the end-Triassic extinction with
 the Central Atlantic magmatic province. Science 340, 941–945 (2013).
- Blum, J.D., and Bergquist, B.A., 2007, Reporting the variations in the natural isotopic
 composition of mercury, Anal Bioanal Chem, v. 388, p. 353-359, doi:
 10.1007/s00216-007-1236-9.
- Blum, J.D., Sherman, L.S., Johnson, M.W., 2014. Mercury Isotopes in Earth and
 Environmental Sciences. Annu. Rev. Earth Planet. Sci.
 https://doi.org/10.1146/annurev-earth-050212-124107
- Bond, D.P.G., Wignall, P.B., 2014. Large igneous provinces and mass extinctions: An
 update. Spec. Pap. Geol. Soc. Am. https://doi.org/10.1130/2014.2505(02)
- BouDagher-Fadel, M.K., Bosence, D.W.J., 2007. Early Jurassic benthic foraminiferal
 diversification and biozones in shallow-marine carbonates of western Tethys.
 Senckenbergiana lethaea 87, 1–39. <u>https://doi.org/10.1007/BF03043906</u>
- Bown, P., Morton, N., Lees, J., 2007. Newsletter: International Subcomission on Jurassic
 Stratigraphy v. 34, p. 1–72.
- Bower, J., Savage, K.S., Weinman, B., Barnett, M.O., Hamilton, W.P., Harper, W.F.,
 2008. Immobilization of mercury by pyrite (FeS2). Environ. Pollut. 156 (2), 504–
 514.

1233 Cacciatore, M.S., Di Stefano, P., Rettori, R., 2006, Carbonate platform-basin systems in 1234 Sicily around the Triassic/Jurassic boundary: new data from the Campofiorito area 1235 (Sicani Mountains, western Sicily). Quad. del Mus. Geol. Gemmellaro 9, 41–54. 1236 Charbonnier, G., Adatte, T., Fölmi, K. B., Suan, G., 2020. Effect of intense weathering and postdepositional degredation of organic matter on Hg/TOC proxy in organic-1237 1238 rich sediments and its implications for deep-time investigations. Geochem., 1239 Geophys., Geosyst. 21 doi: 10.1029/2019GC008707 1240 Corsetti, F. A., Ritterbush, K. A., Bottjer, D. J., Greene, S. E., Ibarra, Y., Yager, J. A., 1241 West, A. J., Berelson, W. M., Rosas, S., Becker, T. W., Levine, N. M., Loyd, S. J., 1242 Martindale, R. C., Petryshyn, V. A., Carroll, N. R., Petsios, E., Piazza, O., Pietsch, 1243 C., Stellmann, J. L., Thompson, J. R., Washington, K. A., Wilmeth, D. T., 2015, 1244 Investigating the Paleoecological Consequences of Supercontinent Breakup: Sponges Clean Up in the Early Jurassic. The Sedimentary Record 13:2. 1245 1246 D'Argenio, B., 1974. Le piattaforme carbonatiche Periadriatiche: una rassegna di 1247 problemi nel quadro geodinamico Mesozoico dell'area Mediterranea. Mem. della 1248 Soc. Geol. Ital. 13 (Suppl., 1–28. 1249 Davies, J.H.F.L., Marzoli, A., Bertrand, H., Youbi, N., Ernesto, M., Schaltegger, U., 2017. End-Triassic mass extinction started by intrusive CAMP activity. Nat. 1250 1251 Commun. https://doi.org/10.1038/ncomms15596 1252 Demers, J.D., Blum, J.D., Zak, D.R., 2013. Mercury isotopes in a forested ecosystem: 1253 implications for air-surface exchange dynamics and the global mercury cycle. Glob. 1254 Biogeochem. Cycles 27 (1), 222–238. Di Stefano, P., Favara, R., Luzio, D., Renda, P., Cacciatore, M.S., Calò, M., Napoli, G., 1255 1256 Parisi, L., Todaro, S., Zarcone, G., 2015. A regional-scale discontinuity in western 1257 Sicily revealed by a multidisciplinary approach: A new piece for understanding the 1258 geodynamic puzzle of the southern Mediterranean. Tectonics. 1259 https://doi.org/10.1002/2014TC003759 1260 Douglas, T.A., Sturm, M., Simpson, W.R., Blum, J.D., Alvarez-Aviles, L., Keeler, G.J., Perovich, D.K., Biswas, A., Johnson, K., 2008. Influence of snow and ice crystal 1261 formation and accumulation on mercury deposition to the arctic. Environ. Sci. 1262 1263 Technol. https://doi.org/10.1021/es070502d 1264 Elderfield, H., 2002. Foraminiferal Mg/Ca Paleothermometry: Expected Advances and 1265 Unexpected Consequences. Geochim. Cosmochim. Acta 66 Supplem, 213. 1266 Faggetter, L.E., Wignall, P.B., Pruss, S.B., Jones, D.S., Grasby, S., Widdowson, M., 1267 Newton, R.J., 2019. Mercury chemostratigraphy across the Cambrian Series 2 – 1268 Series 3 boundary: evidence for increased volcanic activity coincident with 1269 extinction? Chem. Geol. https://doi.org/10.1016/j.chemgeo.2019.02.006 1270 Fitzgerald et al 2014 (treatise) 1271 Foster G.L., Hull, P., Lunt, D.J., Zachos, J.C. 2018 Placing our current 'hyperthermal' in 1272 the context of rapid climate change in our geological past. Phil. Trans. R. Soc. A 1273 **376**: 20170086. http://dx.doi.org/10.1098/rsta.2017.0086 1274 Fox, C. P., Cui, X., Whiteside, J. H., Olsen, P.E., Summons, R.E., Grice, K. 2020. 1275 Molecular and isotopic evidence reveals end-Triassic carbon isotope excursion is not 1276 from massive exogenous light carbon. Prococeedings of the National Academey of 1277 Sciences. /doi/10.1073/pnas.1917661117 1278

- Galli, M.T., Jadoul, F., Bernasconi, S.M., Weissert, H., 2005. Anomalies in global carbon
 cycling and extinction at the Triassic/Jurassic boundary: evidence from a marine Cisotope record. Palaeogeogr. Palaeoclimatol. Palaeoecol. 216, 203–214.
- Galli, M.T., Jadoul, F., Bernasconi, S.M., Cirilli, S., Weissert, H., 2007. Stratigraphy and
 palaeoenvironmental analysis of the Triassic-Jurassic transition in the western
 Southern Alps (Northern Italy). Palaeogeogr. Palaeoclimatol. Palaeoecol.
 https://doi.org/10.1016/j.palaeo.2006.06.023
- Galy, V., Bouchez, J., France-Lanord, C., 2007. Determination of total organic carbon
 content and δ13C in carbonate-rich detrital sediments. Geostand. Geoanalytical Res.
 https://doi.org/10.1111/j.1751-908X.2007.00864.x
- Galy, V., Beyssac, O., France-Lanord, C., Eglinton, T. 2008. Recycling of graphite
 during Himalayan erosion: A geological stabilization of carbon in the crust. Science
 322: 943–945; doi 10.1126/science.1161408.
- Gill, G.A., Fitzgerald, W.F., 1988. Vertical mercury distributions in the oceans. Geochim.
 Cosmochim. Acta. https://doi.org/10.1016/0016-7037(88)90240-2
- Gong, Q., Wang, X., Zhao, L., Grasby, S.E., Chen, Z.Q., Zhang, L., Li, Y., Cao, L., Li,
 Z., 2017. Mercury spikes suggest volcanic driver of the Ordovician-Silurian mass
 extinction. Sci. Rep. https://doi.org/10.1038/s41598-017-05524-5
- Grasby, S.E., Beauchamp, B., Bond, D.P.G., Wignall, P.B., Sanei, H., 2016. Mercury
 anomalies associated with three extinction events (Capitanian Crisis, Latest Permian
 Extinction and the Smithian/Spathian Extinction) in NW Pangea. Geol. Mag.
 https://doi.org/10.1017/S0016756815000436
- Grasby, S.E., Sanei, H., Beauchamp, B., Chen, Z., 2013. Mercury deposition through the
 Permo-Triassic Biotic Crisis. Chem. Geol.
- 1303 https://doi.org/10.1016/j.chemgeo.2013.05.022
- Grasby, S.E., Shen, W., Yin, R., Gleason, J.D., Blum, J.D., Lepak, R.F., Hurley, J.P.,
 Beauchamp, B., 2017. Isotopic signatures of mercury contamination in latest
 Permian oceans. Geology. https://doi.org/10.1130/G38487.1
- Grasby, S.E., Them, T.R., Chen, Z., Yin, R., Ardakani, O.H., 2019. Mercury as a proxy
 for volcanic emissions in the geologic record. Earth-Science Rev.
 https://doi.org/10.1016/j.earscirev.2019.102880
- Greene, S.E., Martindale, R.C., Ritterbush, K.A., Bottjer, D.J., Corsetti, F.A., Berelson,
 W.M., 2012. Recognising ocean acidification in deep time: An evaluation of the
 evidence for acidification across the Triassic-Jurassic boundary. Earth-Science Rev.
 https://doi.org/10.1016/j.earscirev.2012.03.009
- Guex, J., Bartolini, A., Atudorei, V., Taylor, D., 2004. High-resolution ammonite and
 carbon isotope stratigraphy across the Triassic-Jurassic boundary at New York
 Canvon (Nevada). Earth Planet. Sci. Lett. https://doi.org/10.1016/j.epsl.2004.06.006
- Guex, J., Schoene, B., Bartolini, A., Spangenberg, J., Schaltegger, U., O'Dogherty, L.,
 Taylor, D., Bucher, H., Atudorei, V., 2012. Geochronological constraints on postextinction recovery of the ammonoids and carbon cycle perturbations during the Early Jurassic. Palaeogeogr. Palaeoclimatol. Palaeoecol.
- 1321 https://doi.org/10.1016/j.palaeo.2012.04.030
- Hallam, A., 1995. Oxygen-restricted facies of the basal jurassic of north west europe.
 Hist. Biol. https://doi.org/10.1080/10292389509380523
- 1324 Hallam, A., 1964. Origin of the Limestone-Shale Rhythm in the Blue Lias of England: A

1325 Composite Theory. J. Geol. https://doi.org/10.1086/626974 Hallam, A., 1960. The White Lias of the Devon coast. Proc. Geol. Assoc. 1326 1327 https://doi.org/10.1016/S0016-7878(60)80031-4 1328 Han, D.S., Orillano, M., Khodary, A., Duan, Y., Batchelor, B., Abdel-Wahab, A., 2014. 1329 Reactive iron sulfide (FeS)-supported ultrafiltration for removal of mercury (Hg(II)) 1330 from water. Water Res. 53, 310–321. 1331 He, T., Dal Corso, J., Newton, R.J., Wignall, P.B., Mills, B.J.W., Todaro, S., Di Stefano, 1332 P., Turner, E.C., Jamieson, R.A., Randazzo, V., Rigo, M., Jones, R.E., Dunhill, A. 1333 2020. An enormous sulfur isotope excursion indicates marine anoxia during the end-1334 Triassic mass extinction. Sciences advances. Vol. 6, no. 37, DOI: 1335 10.1126/sciadv.abb6704 1336 DOI: 10.1126/sciadv.abb6704 1337 Hesselbo, S.P., Robinson, S.A., Surlyk, F., 2004. Sea-level change and facies 1338 development across potential Triassic-Jurassic boundary horizons, SW Britain. J. 1339 Geol. Soc. London. https://doi.org/10.1144/0016-764903-033 1340 Hilton, R.G., Galy, A., Hovius, N., Horng, M.-J., Chen, H. 2010. The isotopic 1341 composition of particulate organic carbon in mountain rivers of Taiwan. 1342 Geochemica et Cosmochimica Acta 74: 3164–3181. doi: 10.1016/j.gca.2010.03.004. 1343 Huerta-Diaz, M.A., Morse, J.W., 1992. Pyritization of trace metals in anoxic marine 1344 sediments. Geochim. Cosmochim. Acta. https://doi.org/10.1016/0016-1345 7037(92)90353-K 1346 Ibarra, Y, Corsetti, F.A., Greene, S., and Bottjer, D. (2016) A microbial carbonate 1347 response in synchrony with the end-Triassic mass extinction across the SW UK, 1348 Scientific Reports (Nature Publishing Group) v. 6, 19808. 1349 http://doi.org/10.1038/srep19808. 1350 Jadoul, F., Galli, M.T., Muttoni, G., Rigo, M., Cirilli, S., 2012. The late Norian-1351 Hettangian stratigraphic and paleogeographic evolution of the Bergamasc Alps. GFT 1352 - Geol. F. TRIPS 4, 55. Jost, A. B., A. Bachan, B. van de Schootbrugge, K. V. Lau, K. L. Weaver, K. Maher, and 1353 1354 J. L. Payne (2017), Uranium isotope evidence for an expansion of marine anoxia 1355 during the end-Triassic extinction, Geochem. Geophys. Geosyst., 18, doi:10.1002/ 1356 2017GC006941. 1357 Kasprak, A. H., Sepúlveda, J., Price-Waldman, R., Williford, K. H., Schoepfer, S. D., 1358 Haggart, J. W., Whiteside, J. H. 2015, Episodic photic zone euxinia in the 1359 northeastern panthalassic ocean during the end-triassic extinction. Boulder: 1360 Geological Society of America, Inc. doi:10.1130/G36371.1 Keller, G., Mateo, P., Monkenbusch, J., Thibault, N., Punekar, J., Spangenberg, J.E., 1361 1362 Abramovich, S., Ashckenazi-Polivoda, S., Schoene, B., Eddy, M.P., Samperton, K. 1363 M., Khadri, S. F. R., Adatte, T. 2020. Global and Planetary Change. 194: 103312; 1364 doi: 10.1016/j.gloplacha.2020.103312 1365 Kiessling, W., Aberhan, M., Brenneis, B., Wagner, P.J., 2007. Extinction trajectories of 1366 benthic organisms across the Triassic-Jurassic boundary. Palaeogeogr. 1367 Palaeoclimatol. Palaeoecol. https://doi.org/10.1016/j.palaeo.2006.06.029 1368 Knight, K. B. et al. The Central Atlantic Magmatic Province at the Triassic–Jurassic 1369 boundary: paleomagnetic and 40Ar/39Ar evidence from Morocco for brief, episodic volcanism. Earth Plant. Sci. Lett. 228, 143-160 (2004). 1370

- Kongchum, M., Hudnall, W.H., DeLaune, R.D., 2011, Relationship between sediment clay minerals and total, v. 46, p. 534-539, doi: 10.1080/10934529.2011.551745.
 Kovács, E. B., Ruhl, M., Demény, A., Fórizs, I., Hegyi, I., Horváth-Kostka, Z. R., Móricz, F., Vallner, Z., Pálfy, J. 2020. Mercury anomalies and carbon isotope excursions in the western tethyan Csővár section support the link between CAMP volcanism and the end-Triassic extinction. Global and Planetary Change. 194; 103291. doi: 10.1016/j.gloplacha.2020.103291.
- 1378 Kuroda, J., Hori, R. S., Suzuki, K., Grocke, D. R., Ohkouchi, N., 2010. Marine osmium
 1379 isotope record across the Triassic-Jurassic boundary from a Pacific pelagic site.
 1380 Geology 38, p. 1095-1098, doi: 10.1130/G31223:1.
- Larina, L., Bottjer, D. J., Corsetti, F. A., Thibodeau, A. M., Berelson, W. M., West, A. J.,
 Yager, J. A. High-resolution record of environmental change in the lead-up to the
 end-Triassic mass extinction. *In review*.
- Lindberg, S.E., Brooks, S., Lin, C.J., Scott, K.J., Landis, M.S., Stevens, R.K., Goodsite,
 M., Richter, A., 2002. Dynamic oxidation of gaseous mercury in the arctic
 troposphere at polar sunrise. Environ. Sci. Technol.
 https://doi.org/10.1021/es0111941
- Lindström, S., van de Schootbrugge, B.,Dybkjaer, K., Pederson, K. G., Fiebig, J.,
 Nielsen, L. H., Richoz, S., 2012, No causal link between terrestrial ecosystem
 change and methane release during the end-Triassic mass extinction, Geology, v. 40,
 no. 6, p. 531-534, doi: 10.1130/G32928.1.
- Lindström et al., 2019, Volcanic mercury and mutagenesis in land plants during the end-Triassic
 mass extinction, Science Advances, 5:eaaw4018.Lo Cicero, G., 1986. Carbon and
 oxygen isotopic composition of Norian sediments. Panormide Carbonate Platform,
 Palermo. Rend Soc Geol It 9, 209–218.
- Manceau, A., Merkulova, M., Murdzek, M., Batanova, V., Baran, R., Glatzel, P., Saikia,
 B.K., Paktunc, D., Lefticariu, L., 2018. Chemical Forms of Mercury in Pyrite:
 Implications for Predicting Mercury Releases in Acid Mine Drainage Settings.
 Environ. Sci. Technol. https://doi.org/10.1021/acs.est.8b02027
- Marzoli, A., Bertrand, H., Knight, K.B., Cirilli, S., Buratti, N., Vérati, C., Nomade, S.,
 Renne, P.R., Youbi, N., Martini, R., Allenbach, K., Neuwerth, R., Rapaille, C.,
 Zaninetti, L., Bellieni, G., 2004. Synchrony of the Central Atlantic magmatic
 province and the Triassic-Jurassic boundary climatic and biotic crisis. Geology.
 https://doi.org/10.1130/G20652.1
- Marzoli, A., Renne, P.R., Piccirillo, E.M., Ernesto, M., Bellieni, G., De Min, A., 1999.
 Extensive 200-million-year-old continental flood basalts of the Central Atlantic
 Magmatic Province. Science (80-.). https://doi.org/10.1126/science.284.5414.616
- Mayall, M.J., 1981. The Late Triassic Blue Anchor Formation and the initial Rhaetian
 marine transgression in south-west Britain. Geol. Mag.
- 1410 https://doi.org/10.1017/S0016756800032246
- Morton, N., Hesselbo, S., Eds., 2008, Newsletter: International Subcommission on
 Jurassic Stratigraphy, v. 35, p. 1–76.
- Muttoni, G., Kent, D. V., Jadoul, F., Olsen, P.E., Rigo, M., Galli, M.T., Nicora, A., 2010.
 Rhaetian magneto-biostratigraphy from the Southern Alps (Italy): Constraints on
 Triassic chronology. Palaeogeogr. Palaeoclimatol. Palaeoecol.
- 1416 https://doi.org/10.1016/j.palaeo.2009.10.014
- 1417 Patacca, E., Scandone, P., Giunta, G., Liguori, V., 1979. Mesozoic paleo-tectonic

- 1418 evolution of the Ragusa zone (southeastern Sicily). Geol. Rom 18, 331–369. 1419 Percival, L.M.E., Jenkyns, H.C., Mather, T.A., Dickson, A.J., Batenburg, S.J., Ruhl, M., Hesselbo, S.P., Barclay, R., Jarvis, I., Robinson, S.A., Woelders, L., 2018. Does 1420 1421 large igneous province volcanism always perturb the mercury cycle? Comparing the 1422 records of Oceanic Anoxic Event 2 and the end-cretaceous to other Mesozoic 1423 events. Am. J. Sci. https://doi.org/10.2475/08.2018.01 1424 Percival, L.M.E., Ruhl, M., Hesselbo, S.P., Jenkyns, H.C., Mather, T.A., Whiteside, J.H., 1425 2017. Mercury evidence for pulsed volcanism during the end-Triassic mass 1426 extinction. Proc. Natl. Acad. Sci. U. S. A. https://doi.org/10.1073/pnas.1705378114 1427 Percival, L.M.E., Witt, M.L.I., Mather, T.A., Hermoso, M., Jenkyns, H.C., Hesselbo, 1428 S.P., Al-Suwaidi, A.H., Storm, M.S., Xu, W., Ruhl, M., 2015. Globally enhanced 1429 mercury deposition during the end-Pliensbachian extinction and Toarcian OAE: A 1430 link to the Karoo-Ferrar Large Igneous Province. Earth Planet. Sci. Lett. 1431 https://doi.org/10.1016/j.epsl.2015.06.064 1432 Pyle, D.M., Mather, T.A., 2003. The importance of volcanic emissions for the global 1433 atmospheric mercury cycle. Atmos. Environ. 1434 https://doi.org/10.1016/j.atmosenv.2003.07.011 Richardson, L., 1911. The rhætic and contiguous deposits of west, mid, & part of East 1435 Somerset. Q. J. Geol. Soc. London. https://doi.org/10.1144/GSL.JGS.1911.067.01-1436 1437 04.03 1438 Richardson, L., 1906. On the Rhætic and contiguous deposits of Devon and Dorset. Proc. 1439 Geol. Assoc. https://doi.org/10.1016/S0016-7878(06)80067-2 Richardson, L., 1905. The Rhætic and contiguous deposits of Glamorganshire. Q. J. Geol. 1440 1441 Soc. London. https://doi.org/10.1144/GSL.JGS.1905.061.01-04.20 1442 Ritterbush, K.A., Bottjer, D.J., Corsetti, F.A., Rosas, S., 2014. NEW EVIDENCE ON 1443 THE ROLE OF SILICEOUS SPONGES IN ECOLOGY AND SEDIMENTARY 1444 FACIES DEVELOPMENT IN EASTERN PANTHALASSA FOLLOWING THE 1445 TRIASSIC-JURASSIC MASS EXTINCTION. Palaios. 1446 https://doi.org/10.2110/palo.2013.121 1447 Ruhl, M., Kürschner, W.M., Krystyn, L., 2009. Triassic-Jurassic organic carbon isotope stratigraphy of key sections in the western Tethys realm (Austria). Earth Planet. Sci. 1448 Lett. https://doi.org/10.1016/j.epsl.2009.02.020 1449 1450 Ruhl, M., Hesselbo, S. P., Al-Suwaidi, A., Jenkyns, H. C., Damborenea, S. E., 1451 Manceñido, M. O., Storm, M., Mather, T. A., Riccardi, A. C. 2020. On the onset of 1452 Central Atlantic magmatic province (CAMP) volcanism and environmental and 1453 carbon-cycle change at the Triassic-Jurassic transition (Neuquén Basin, Argentina). 1454 Earth-Science Reviews 208: 103229. doi: 10.1016/j.earscirev.2020.103229. 1455 Sanei, H., Grasby, S.E., Beauchamp, B., 2012, Latest permian mercury anomalies. 1456 Geology. https://doi.org/10.1130/G32596.1 1457 Scaife, J.D., Ruhl, M., Dickson, A.J., Mather, T.A., Jenkyns, H.C., Percival, L.M.E., 1458 Hesselbo, S.P., Cartwright, J., Eldrett, J.S., Bergman, S.C., Minisini, D., 2017. 1459 Sedimentary Mercury Enrichments as a Marker for Submarine Large Igneous 1460 Province Volcanism? Evidence From the Mid-Cenomanian Event and Oceanic 1461 Anoxic Event 2 (Late Cretaceous). Geochemistry, Geophys. Geosystems. 1462 https://doi.org/10.1002/2017GC007153
- 1463 Schaltegger, U., Guex, J., Bartolini, A., Schoene, B., Ovtcharova, M., 2008. Precise U-Pb

- age constraints for end-Triassic mass extinction, its correlation to volcanism and
 Hettangian post-extinction recovery. Earth Planet. Sci. Lett.
- 1466 https://doi.org/10.1016/j.epsl.2007.11.031
- 1467 Schaller, M.F., Wright, J.D., Kent, D.V., Olsen, P.E., 2012. Rapid emplacment of the
- 1468 Central Atlantic Magmatic Province as net sink for CO2. Earth Planet. Sci. Lett.
- 1469 Scheingross, J. S., Repasch, M. N., Hovius, N., Sachse, D., Lupker, M., Fuchs, M.,
- 1470 Halevy, I., Gröcke, D. R., Golombek, N. Y., Haghipour, N., Eglinton, T. I., Orfeo, O.,
- Scleicher, A. M. 2021. The fate of fluvially-deposited organic carbon during transientfloodplain storage. Earth Planet. Sci. Lett. 561: 116822.
- Schoene, B., Guex, J., Bartolini, A., Schaltegger, U., Blackburn, T.J., 2010. Correlating
 the end-Triassic mass extinction and flood basalt volcanism at the 100 ka level.
 Geology. https://doi.org/10.1130/G30683.1
- van de Schootbrugge, B., Bachan, A., Suan, G., Richoz, S., Payne, J. L. 2013. Microbes,
 mud and methane: Cause and consequence of recurrent Early Jurassic anoxia
 following the end-Triassic mass extinction. Palaeontology, v. 56 p. 4, p. 685–709.
- 1478 Tonowing the end-massic mass extinction. Palaeontology, v. 56 p. 4, p. 683–709 1479 Schroeder, W.H., Munthe, J., 1998. Atmospheric mercury - An overview, in:
- 1480 Atmospheric Environment. https://doi.org/10.1016/S1352-2310(97)00293-8
- Shen, J., Algeo, T.J., Chen, J., Planavsky, N.J., Feng, Q., Yu, J., Liu, J., 2019a. Mercury
 in marine Ordovician/Silurian boundary sections of South China is sulfide-hosted
 and non-volcanic in origin. Earth Planet. Sci. Lett.
 https://doi.org/10.1016/j.epsl.2019.01.028
- Shen, J., Chen, J., Algeo, T.J., Yuan, S., Feng, Q., Yu, J., Zhou, L., O'Connell, B.,
 Planavsky, N.J., 2019b. Evidence for a prolonged Permian–Triassic extinction
 interval from global marine mercury records. Nat. Commun.
 https://doi.org/10.1038/s41467-019-09620-0
- 1489 Shen, J., Yu, J.X., Chen, J.B., Algeo, T.X., Xu, G.Z., Feng, Q.L., Shi, X., Planavsky,
 1490 N.J., Shu, W.C., Xie, S.C., 2019b. Mercury evidence of intense volcanic effects on
 1491 land during the Permian-Triassic transition. Geology 47, 1117–1121.
- 1492 Shen et al., 2020, Sedimentary host phases of mercury (Hg) and implications for use of Hg as a volcanic proxy, Earth and Planetary Science Letters, 543, 116333.
- 1494 Si, M., McLagan, D.S., Mazot, A., Szponar, N.S., Bergquist, B.A., Lei, Y.D., Mitchell,
- 1495 C.P., Wania, F. 2020. Measurement of atmospheric mercury over volcanic and
- fumarolic regions on the North Island of New Zealand, Earth and Space Chemistry, Vol.
 4 (12), DOI:10.1021/acsearthspacechem.0c00274.
- Sial, A.N., Chen, J., Lacerda, L.D., Frei, R., Tewari, V.C., Pandit, M.K., Gaucher, C.,
 Ferreira, V.P., Cirilli, S., Peralta, S., Korte, C., Barbosa, J.A., Pereira, N.S., 2016.
 Mercury enrichment and Hg isotopes in Cretaceous-Paleogene boundary
 successions: Links to volcanism and palaeoenvironmental impacts. Cretac. Res.
 https://doi.org/10.1016/j.cretres.2016.05.006
- Sonke, J.E., 2011. A global model of mass independent mercury stable isotope fractio nation. Geochim. Cosmochim. Acta 75 (16), 4577–4590.
- 1505 Szponar, N., McLagan, D., Kaplan, R.J., Mitchell, C.P.J., Wania, F., Steffen, A., Stupple,
- 1506 G.W., Monaci, F., Bergquist, B.A., 2020. Isotopic Characterization of Atmospheric
- Gaseous Elemental Mercury by Passive Air Sampling, Environmental Science andTechnology, 54, 17, 10533-10543.
- Strasser, A., 1991. Lagoonal-peritidal sequences in carbonate environments: autocyclic
 and allocyclic processes, in: Einsele, G., Ricken, W., Seilacher, A. (Eds.), Cycles

- and Events in Stratigraphy. Springer, Berlin, pp. 709–721.
- 1512 Swift, A., 1995. A review of the nature and outcrop of the 'White Lias' facies of the
 1513 Langport Member (Penarth Group: Upper Triassic) in Britain. Proc. Geol. Assoc.
 1514 https://doi.org/10.1016/S0016-7878(08)80236-2
- Taylor, D.G., Smith, P.L., Laws, R.A., Guex, J., 1983. The stratigraphy and biofacies
 trends of the Lower Mesozoic Gabbs and Sunrise formations, west-central Nevada.
 Can. J. Earth Sci. https://doi.org/10.1139/e83-149
- Them, T.R., Jagoe, C.H., Caruthers, A.H., Gill, B.C., Grasby, S.E., Gröcke, D.R., Yin,
 R., Owens, J.D., 2019. Terrestrial sources as the primary delivery mechanism of
 mercury to the oceans across the Toarcian Oceanic Anoxic Event (Early Jurassic).
 Earth Planet. Sci. Lett. https://doi.org/10.1016/j.epsl.2018.11.029
- Thibodeau, A.M., Bergquist, B.A., 2017. Do mercury isotopes record the signature of
 massive volcanism in marine sedimentary records? Geology.
 https://doi.org/10.1130/focus012017.1
- Thibodeau, A.M., Ritterbush, K., Yager, J.A., West, A.J., Ibarra, Y., Bottjer, D.J.,
 Berelson, W.M., Bergquist, B.A., Corsetti, F.A., 2016. Mercury anomalies and the
 timing of biotic recovery following the end-Triassic mass extinction. Nat. Commun.
 7. https://doi.org/10.1038/ncomms11147
- Todaro, S., Di Stefano, P., Zarcone, G., Randazzo, V., 2017. Facies stacking and
 extinctions across the Triassic–Jurassic boundary in a peritidal succession from
 western Sicily. Facies. https://doi.org/10.1007/s10347-017-0500-5
- Todaro, S., Rigo, M., Randazzo, V., Di Stefano, P., 2018. The end-Triassic mass
 extinction: A new correlation between extinction events and δ13C fluctuations from
 a Triassic-Jurassic peritidal succession in western Sicily. Sediment. Geol.
 https://doi.org/10.1016/j.sedgeo.2018.03.008
- Urbanek, A., 1993. Biotic crises in the history of upper silurian graptoloids: A
 palaeobiological model. Hist. Biol. https://doi.org/10.1080/10292389309380442
- 1538 Van De Schootbrugge, B., Payne, J.L., Tomasovych, A., Pross, J., Fiebig, J., Benbrahim,
 1539 M., Föllmi, K.B., Quan, T.M., 2008. Carbon cycle perturbation and stabilization in
 1540 the wake of the Triassic-Jurassic boundary mass-extinction event. Geochemistry,
 1541 Geophys. Geosystems. https://doi.org/10.1029/2007GC001914
- Wang, X., Cawood, P.A., Zhao, H., Zhao, L., Grasby, S.E., Chen, Z.Q., Wignall, P.B.,
 Lv, Z., Han, C., 2018. Mercury anomalies across the end Permian mass extinction in
 South China from shallow and deep water depositional environments. Earth Planet.
 Sci. Lett. https://doi.org/10.1016/j.epsl.2018.05.044
- Ward, P.D., Garrison, G.H., Williford, K.H., Kring, D.A., Goodwin, D., Beattie, M.J.,
 McRoberts, C.A., 2007. The organic carbon isotopic and paleontological record
 across the Triassic-Jurassic boundary at the candidate GSSP section at Ferguson
 Hill, Muller Canyon, Nevada, USA. Palaeogeogr. Palaeoclimatol. Palaeoecol.
 https://doi.org/10.1016/j.palaeo.2006.06.042
- Wignall, P.B., 2001. Sedimentology of the Triassic-Jurassic boundary beds in Pinhay Bay
 (Devon, SW England). Proc. Geol. Assoc. https://doi.org/10.1016/S00167878(01)80014-6
- Wotzlaw, J.F., Guex, J., Bartolini, A., Gallet, Y., Krystyn, L., McRoberts, C.A., Taylor,
 D., Schoene, B., Schaltegger, U., 2014. Towards accurate numerical calibration of
 the late triassic: Highprecision U-Pb geochronology constraints on the duration of

- 1557 the Rhaetian. Geology. https://doi.org/10.1130/G35612.1
- 1558 Yager, J.A., West, A.J., Corsetti, F.A., Berelson, W.M., Rollins, N.E., Rosas, S., Bottjer, D.J., 2017. Duration of and decoupling between carbon isotope excursions during 1559 1560 the end-Triassic mass extinction and Central Atlantic Magmatic Province 1561
 - emplacement. Earth Planet. Sci. Lett. 473. https://doi.org/10.1016/j.epsl.2017.05.031
- 1562 Zaffani, M., Jadoul, F., Rigo, M., 2018. A new Rhaetian δ 13 C org record: Carbon cycle 1563 disturbances, volcanism, End-Triassic mass Extinction (ETE). Earth-Science Rev. 1564 https://doi.org/10.1016/j.earscirev.2018.01.004
- 1565 Zambardi, T., Sonke, J.E., Toutain, J.P., Sortino, F., Shinohara, H., 2009. Mercury
- emissions and stable isotopic compositions at Vulcano Island (Italy). Earth Planet. 1566
- Sci. Lett. 277 (1), 236-243. 1567
- 1568 Zarcone, G., Petti, F.M., Cillari, A., Di Stefano, P., Guzzetta, D., Nicosia, U., 2010. A possible bridge between Adria and Africa: New palaeobiogeographic and 1569 1570 stratigraphic constraints on the Mesozoic palaeogeography of the Central 1571 Mediterranean area. Earth-Science Rev.
- 1572 https://doi.org/10.1016/j.earscirev.2010.09.005
- 1573 Zheng, W., Obrist, D., Weis, D., Bergquist, B.A., 2016. Mercury isotope compositions
- across North American forests. Glob. Biogeochem. Cycles 30 (10), 1475–1492. 1574
- 1575 Zhong Zhong, H.; Wang, W-X.. Effects of sediment composition on in- organic mercury 1576 partitioning, speciation and bioavailability in oxic surficial sediments. Environ. Poll. 2008, 151, 222-230. 1577
- 1578 Zhou, J. Obrist, D., Dastoor, A., Jiskra, M., Ryjkov, A., 2021. Vegetation uptake of 1579 mercury and impacts on global cycling. Nature Reviews, v. 2; p. 269-284; doi: 1580 10.1038/s43017-021-00146-y
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Figure 1











FIGURE 5



Levanto, Peru

Lombardy Basin, Italy (composite)



New York Canyon, Nevada





Mt. Sparagio, Sicily Hg ppb 6 8 10 12 14 16 0 2 4 m New York Canyon, Nevada, USA 1700 - Hg ppb
 40 60 80 100 120 0 20 St. Audrie's Bay, UK 600 -Levanto, Peru Hg ppb Hg ppb 100 150 m 50 280 25 20 40 60 80 100 120 Ó Jurassic 240 500 -Jurassic 50 ⁵² Jurassic 'n 200 20 Jurassic 160 Hores 400 80 ----15 --80 300-60 5 Triassic 40 0000 00000 10 0 200 -Triassic 4 40 -5 0 100 200 300 400 500 600 700 ⊖ Hg/TOC 0080° 5 Triassic 20 100 -0 0 0 50 100 150 200 250 300 300 400 500 ō 100 200 150 0 0 50 100 200 ⊖ Hg/TOC ⊖ Нg/ТОС ⊖ Hg/TOC

Lombardy Basin, Italy



