

1 **Mercury chemostratigraphy across the Cambrian Series 2 – Series 3 boundary:**
2 **evidence for increased volcanic activity coincident with extinction?**

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5

6 **ABSTRACT**

7 Flood basalt volcanism represented by the Kalkarindji Province (Australia) is
8 temporally associated with a trilobite mass extinction at the Cambrian Series 2 –
9 Series 3 boundary, providing one of the oldest potential links between volcanism and
10 biotic crisis in the Phanerozoic. However, the relative timing of flood basalt volcanism
11 (Kalkarindji Province, Australia) and the trilobite extinctions, first recorded in North
12 America, is not known. Mercury (Hg) enrichment in the sedimentary record provides
13 a potential proxy for volcanism which may facilitate improved chronologies of
14 eruption and extinction. Here we report mercury records for three sections from mid-
15 shelf strata of the Great Basin (western USA) that straddle the Series 2 – Series 3
16 boundary. One section (Oak Springs Summit, NV) features a Hg enrichment at the
17 start of the extinction interval, but mercury anomalies are also present at lower
18 levels. These older anomalies may record either earlier phases of Kalkarindji
19 volcanism, eruptions in other locations, or may be the result of sedimentary and/or
20 diagenetic processes affecting the Hg record. In the Carrara Formation at Emigrant
21 Pass, CA, the precise extinction horizon is not well defined, but a carbon isotope
22 anomaly (the Redlichiiid-Olenellid Extinction Carbon isotope Event; ROECE)
23 provides a stratigraphic tie point to the Oak Springs Summit section. At Emigrant
24 Pass, Hg enrichments precede the ROECE interval and are absent in the inferred
25 extinction zone. The Pioche Formation at Ruin Wash, NV, lacks Hg enrichment at
26 the extinction horizon but contains older enrichments. The inconsistent Hg records
27 between the three sections demonstrate that factors controlling Hg accumulation and
28 preservation in marine sedimentary environments are not yet fully understood. The
29 effects of redox fluctuations may complicate one-to-one association of sedimentary
30 Hg enrichments and massive volcanism at the Cambrian Series 2 – Series 3
31 boundary and elsewhere in the geologic record.

32

33 **1. INTRODUCTION**

34 The temporal connection between large igneous province (LIP) eruptions and
35 Phanerozoic mass extinction events is well established, and the associated cause
36 and effect linkage compelling (e.g. Wignall, 2001, 2015; Courtillot and Renne, 2003;
37 Kravchinsky, 2012; Ernst & Youbi, 2017). Biotic change and carbon isotope
38 excursions are an established feature of the Cambrian, but their relationship to LIP
39 volcanism is poorly understood. In this context, the favoured candidate Cambrian LIP
40 is the Kalkarindji Province (including the Antrim lavas) of northern and western
41 Australia; this has been dated by a single zircon (Milliwindi dyke) to yield a U-Pb age
42 of 510.7 ± 0.6 Ma (Jourdan et al., 2014), demonstrating a close temporal relationship
43 to the previously reported $^{40}\text{Ar}/^{39}\text{Ar}$ date of 507.5 ± 1.6 Ma determined for its
44 extrusive portion (i.e. Antrim Lavas; Glass and Phillips, 2006). This LIP currently has
45 a surface exposure of c. 425 000 km² in northern and central Australia (Veevers,
46 2001), but was likely erupted over a much larger area; its scattered remnants could
47 indicate a possible original extent of >2 million km² (e.g. Glass and Phillips, 2006,
48 Jourdan et al., 2014). Accordingly, the province may thus be dimensionally
49 comparable with other significant Phanerozoic LIPs (e.g. Columbia River Basalts),
50 especially since it may also correlate with volcanics of similar age and/or
51 composition preserved in the Tarim Block in NW China and the North China Block (Li
52 et al., 1996; 2008), and the Sibumasu terrane preserved in current day Thailand and
53 Myanmar (Zhu et al., 2012; Cocks and Torsvik, 2013).

54 Dating of the Kalkarindji province indicates emplacement close to the
55 Cambrian Series 2 – Series 3 boundary (traditionally Lower – Middle), and thus
56 potentially contemporaneous with the extinction of the redlichiid and olenellid
57 trilobites (Palmer, 1998; Jourdan et al., 2014; Zhang et al., 2015). The extinction of
58 the olenellids has been well studied in detailed sections located in the western USA,
59 but locating the horizon that coincides with the Kalkarindji eruptions has hitherto
60 been difficult due to a lack of an eruption proxy within ancient marine sediments.
61 Temporal correlation between the Kalkarindji LIP emplacement and the Series 2 –
62 Series 3 boundary is based upon a U-Pb zircon date of 510.7 ± 0.6 Ma (Jourdan et
63 al., 2014), and the provisional age of the Series 2 – Series 3 boundary (~509 Ma,
64 Ogg et al., 2016). The association of this LIP with trilobite extinction at the Series 2 –
65 Series 3 boundary is therefore inferred on the basis of this temporal correlation
66 (Glass and Phillips, 2006; Hough et al., 2006; Jourdan et al., 2014).

67 Testing a causal link between the Kalkarindji and the Series 2 – Series 3
68 trilobite extinction requires improved correlations between the volcanic event(s) and
69 the trilobite extinction horizons. Recently, mercury (Hg) concentrations in the
70 sedimentary record have provided a proxy for both regional and global volcanic
71 activity (e.g. Schuster et al., 2002, albeit in ice-core, not sediments) and thus offers
72 the potential to correlate the interval of extinction with evidence for volcanism in the
73 same stratigraphic sections. The value of this technique has been demonstrated at
74 several key mass extinction and oceanic anoxic events including those at the
75 Ordovician–Silurian; latest Permian; Permian-Triassic; end-Triassic; early Jurassic
76 and end-Cretaceous events (Sanei et al., 2012; Sial et al., 2013; 2014; Percival et
77 al., 2015; Thibodeau et al., 2016; Font et al., 2016; Grasby et al., 2013; 2016;
78 Bergquist, 2017; Gong et al., 2017; Jones et al., 2017; Percival et al., 2018). Here
79 we present sedimentary Hg records for strata in which the trilobite extinction
80 horizons have been constrained and evaluate the potential of the Kalkarindji LIP to
81 produce this sedimentary geochemical record.

82 Volcanism represents a primary source of gaseous Hg^0 to Earth's surface;
83 unlike other volcanic trace metals, its long atmospheric residence time (0.5-2 years)
84 permits hemispheric circulation and establishes its potential as a tracer for volcanism
85 (Pyle and Mather, 2003; Percival et al., 2015, 2017). Atmospheric oxidation of Hg^0
86 by halogens, ozone and radicals forms reactive Hg^{2+} , a soluble ion which is
87 deposited during precipitation (wet deposition). Horowitz et al. (2017) found that,
88 during its residence in the troposphere, Hg is most effectively oxidised by bromine
89 (Br), forming atmospheric HgBr complexes. As the largest source of atmospheric Br
90 is organobromines - which are produced as a by-product of phytoplankton
91 photosynthesis - the most effective oxidation and wet deposition of Hg^{2+} occurs
92 above and, subsequently to, the marine realm (Horowitz et al., 2017). In modern
93 oceans ~49% of marine Hg deposition occurs in tropical oceans due to the greater
94 availability of productivity-driven organobromines and other oxidising radicals at
95 these latitudes (Horowitz et al., 2017). Once in the marine realm Hg^{2+} forms
96 complexes with clay minerals (Kongchum et al., 2011), organic matter (Benoit et al.,
97 2001), and, in anoxic/euxinic conditions, it can be scavenged from seawater by
98 sulphide complexes (Benoit et al., 1999). The effective oxidation of Hg^0 by marine-
99 derived organobromines and the complexing of Hg by organics and sulphides in the
100 oceans establishes marine sediments as an efficient sink of atmospheric Hg (Benoit

101 et al., 1999; Emili et al., 2011; Horowitz et al., 2017). Therefore, marine siliciclastic
102 and carbonate rocks can act as an important repository of Hg during times of
103 heightened environmental loading (Percival et al., 2015; Grasby et al., 2016). It is
104 also worth noting that once in the atmosphere particulate Hg can also be removed
105 via “dry deposition”, a portion of which may make its way into the terrestrial realm
106 (see Munthe et al., 2009 for discussion).

107 The Cambrian Period is marked by large oscillations of the inorganic carbon
108 isotope record which, at times, coincided with intensified extinction rates (Brasier et
109 al., 1994; Montañez et al., 2000; Zhu et al., 2006). At the Cambrian Series 2 – Series
110 3 boundary, a negative $\delta^{13}\text{C}$ excursion referred to as the Redlichiid – Olenellid
111 Extinction Carbon isotope Excursion (ROECE) has been documented from Laurentia
112 (Montañez, 2000; Faggetter et al., 2017), Gondwana (Schmid, 2017) and China (e.g.
113 Fan et al., 2011; Wang et al., 2011; Chang et al., 2017; Ren et al., 2017). This
114 coincides with major trilobite losses in both Gondwana and Laurentia (Montañez et
115 al., 2000; Zhu et al., 2004; 2006; Faggetter et al., 2017; Ren et al., 2017). The Series
116 2 – Series 3 boundary age (~509 Ma, Ogg et al., 2016) approximately coincides with
117 the 510.7 ± 0.6 Ma age of the Kalkarindji Province (Jourdan et al., 2014) but detailed
118 correlation is lacking. We attempt to resolve this issue by examining sedimentary Hg
119 concentrations in Cambrian Series 2 – Series 3 sections of the western USA. We
120 have analysed Hg concentrations and Hg/ total organic carbon content (TOC) from
121 two formations and three sections in the western Great Basin: Carrara Formation,
122 Emigrant Pass (Death Valley, CA) and the Pioche Formation at Oak Springs Summit
123 and Ruin Wash (Lincoln County, NV). These sections have an established
124 biostratigraphic framework, and also a record of trilobite extinction at Oak Springs
125 Summit and Ruin Wash (Webster et al., 2008; Moore and Lieberman, 2009).

126

127 **2. STUDY AREA**

128 Cambrian successions of the western Great Basin (USA) constitute the
129 primary field locations of this study. Following the breakup of the supercontinent
130 Rodinia in the late Neoproterozoic, a broad, equatorial clastic shelf developed on the
131 rapidly subsiding Laurentian margin (Prave, 1991; Howley et al., 2006). During
132 Cambrian Series 2, deposition in the Great Basin was on a broad shelf located on
133 the north-western margin of Laurentia (Fig. 1). Clastic deposition was waning and, by
134 Series 3, it had been replaced by carbonate production, resulting in the formation of

135 an extensive carbonate shelf (Fig. 1; Howley et al., 2006; Landing, 2012). We
136 present data from two formations spanning the Cambrian Series 2 – Series 3
137 boundary in the western Great Basin. The first section records the Carrara Formation
138 of Death Valley, exposed at Emigrant Pass, California (Fig. 2). The second section is
139 the Pioche Formation of eastern Nevada exposed at Oak Springs Summit (Fig. 3),
140 and a third section at Ruin Wash, also recording the Pioche Formation (Fig. 4). Oak
141 Springs Summit and Ruin Wash are close to each other (~20kms apart), whilst
142 Emigrant Pass is ~225km south-west of these two locations (Fig. 1). Both formations
143 comprise alternating siliciclastic- and limestone-dominated units (Merriam and
144 Palmer, 1964; Palmer and Halley, 1979; Faggetter et al., 2017). At Oak Springs
145 Summit and Ruin Wash, the Pioche Formation records the abrupt extinction of the
146 olenellid trilobites, making these two sections candidates for paired Hg-
147 biostratigraphic studies. At Emigrant Pass there is a paucity of trilobite fossils, but
148 $\delta^{13}\text{C}$ correlation, based on the record of the ROECE (e.g., Zhu et al., 2004), allows
149 an extinction interval to be inferred at the boundary between the *Olenellus* and
150 *Eokochaspis nodosa* biozones in the mid Pyramid Shale (Fig. 2; Faggetter et al.,
151 2017). As a further stratigraphic tie point between the two formations, the extinction
152 horizon within the Pioche Formation represents the top of the *Olenellus* biozone
153 (Palmer, 1998; Sundberg and McCollum, 2000).

154

155 3. METHODS

156 We analysed total Hg content in whole-rock powders from 93 samples taken
157 from the three Series 2 – Series 3 boundary sections in the western US (Figs. 2, 3,
158 4). The samples from Emigrant Pass and Oak Springs Summit were run at the
159 Geological Survey of Canada with a LECO® AMA254 mercury analyser (10%
160 precision, 5% relative standard deviation (RSD), Hall and Pelchat, 1997). Whole rock
161 powders from Ruin Wash, as well as a duplicate sample set from Oak Springs
162 Summit, were analysed at Amherst College (Massachusetts, USA) using a Teledyne
163 Leeman Labs Hydra IIc mercury analyser (RSD <10%). Duplicate samples returned
164 a correlation coefficient of 0.99, indicating a robust positive correlation between the
165 results from the two laboratories.

166 Whole-rock powders were decarbonated using hydrochloric acid, and their
167 carbonate content was calculated by mass loss following acid digestion. With the
168 exception of Ruin Wash samples, TOC was measured from insoluble residues at the

169 University of Leeds using a LECO® SC-144DR Dual Range carbon and sulphur
170 analyser. The carbon content of insoluble residues from Ruin Wash was measured
171 with a Costech ECS 4010 elemental analyser at Amherst College in order to
172 generate TOC measurements, with RSD <5%.

173 Inorganic carbon isotope values from the Carrara Formation at Emigrant Pass
174 and Pioche Formation, Oak Springs Summit are reproduced from Faggetter et al.
175 (2017), and new inorganic carbon isotope values from Ruin Wash are presented
176 here. Whole-rock powders were analysed at the GeoZentrum Nordbayern, FAU
177 Erlangen-Nuremberg, Germany, where carbon dioxide was prepared via reaction
178 with phosphoric acid at 70°C using a Gasbench II preparation system; carbon
179 isotope ratios were measured by a ThermoFisher Delta V plus mass spectrometer in
180 continuous flow mode. Isotope ratios are reported relative to the V-PDB standard,
181 with a reproducibility of $\pm 0.06\text{‰}$ for $\delta^{13}\text{C}$ and 0.05‰ for $\delta^{18}\text{O}$.

182 Inferred redox conditions (Figs. 2, 3, 4) are based upon pyrite framboid size
183 distribution as reported in Faggetter et al. (2017); samples were assessed using a
184 scanning electron microscope (FEI Quanta 650 FEG-ESEM) in backscatter mode
185 following Bond and Wignall (2010).

186

187 **4. RESULTS**

188 **4.1. TOC concentrations**

189 Throughout all three sections TOC content is generally very low and exhibits
190 correlation with facies (Fig. 5). The lowest TOC values (<0.15 wt% TOC) of all three
191 sections are found in marl facies that coincide with extremely low/carbonate free
192 intervals such as the C-Shale Member of the Pioche Formation (Fig. 5). In the
193 Pioche Formation, higher TOC values are preserved in limestone of the Combined
194 Metals Member, at Oak Springs Summit where levels reach 0.48 – 2.69 wt% within
195 an oncoidal limestone of the Combined Metals Member (Fig. 5). The majority of the
196 Carrara Formation is composed of marl with very low (<0.15 wt%) TOC content, the
197 exception being horizons within the Echo Shale and Gold Ace members where
198 values span the greatest range of all three sections (<0.15 – 5.17 wt% TOC) (Fig. 5).

199

200 **4.2. The ROECE and trilobite extinction**

201 The inorganic carbon isotope record from the Carrara Formation at Emigrant
202 Pass and the Pioche Formation at Oak Springs Summit are discussed in Faggetter

203 et al. (2017) in which a C isotope excursion of ~ -3.8 ‰ is interpreted to be the
204 ROECE. Within the Pioche Formation at Oak Springs Summit, the most negative
205 inorganic carbon isotope values coincide with the extinction horizon of the olenellid
206 trilobites. ROECE is also expected to occur at Ruin Wash (Palmer 1998; Faggetter
207 et al., 2017), but the extremely low carbonate content (below detection limits) in the
208 shale of the C-Shale Member at this location does not allow measurement of a
209 continuous inorganic carbon isotope curve. The ROECE is also observed within the
210 Pyramid Shale Member of the Carrara Formation, but unlike the Pioche Formation,
211 there is no trilobite fauna to delineate a clear extinction horizon at Emigrant Pass
212 (Fig. 2). An inferred extinction interval is therefore proposed at Emigrant Pass within
213 the Pyramid Shale Member (Fig. 2), based on the biostratigraphic boundary between
214 the *Olenellus* Zone and the *Eokochaspis nodosa* Zone (Fig. 2; see Palmer and
215 Halley, 1979; Faggetter et al, 2017).

216

217 **4.3. Hg concentrations, Hg/TOC ratios and extinction**

218 The Carrara and Pioche formations contain enrichments in Hg concentrations
219 (ppb) and excursions in Hg/TOC (ppb/wt% TOC) ratios (Figs. 2, 3, 4). Hg/TOC ratios
220 from samples with extremely low TOC of <0.01 wt% C are not considered robust
221 enough to record a primary Hg signal and are not plotted in figures but are included
222 in Table 1.

223

224 **4.3.1. Carrara Formation, Emigrant Pass**

225 The Carrara Formation at Emigrant Pass exhibits background Hg
226 concentrations of <50 ppb throughout the section (Fig. 2). High Hg and Hg/TOC
227 values are seen in samples with both high and low TOC wt% values (Fig. 6). A
228 number of prominent enrichments occur in the lowest 90 m, with the most enriched
229 sample containing 270 ppb Hg found in the basal Eagle Mountain Shale Member.
230 Smaller enrichments recorded by one or two data points each occur in the Echo
231 Shale, Gold Ace and Pyramid Shale members. Within the ROECE interval Hg values
232 are elevated at the beginning of the $\delta^{13}\text{C}$ excursion before concentrations return to
233 low levels for the remainder of the section.

234 The Hg/TOC enrichments in the Carrara Formation occur in two distinct
235 pulses where Hg and Hg/TOC peaks correlate; an initial, multi-peak enrichment in
236 the basal 30m of the Eagle Mountain Shale Member and another during early

237 ROECE at the base of the Pyramid Shale Member (Fig. 2). It is noteworthy that
238 across the inferred extinction horizon, there are no abrupt Hg or Hg/TOC peaks and
239 values remain stable in this interval.

240

241 4.3.2. Pioche Formation, Oak Springs Summit

242 Background Hg concentrations in the Pioche Formation at Oak Springs
243 Summit are <10 ppb (Fig. 3). Highest Hg values coincide with samples with low (<0.1
244 wt%) TOC (Figs. 5 and 6). A single elevated value (46 ppb Hg) occurs in the
245 Combined Metals Member, just below the base of the ROECE, and a smaller
246 enrichment (32 ppb Hg) coincides with the most negative ROECE value and the
247 olenellid extinction horizon at the base of the C-Shale Member. Finally, there is a
248 small increase in Hg concentration (17 ppb) at ~35m in the section, which, like the
249 other enrichments, correspond to three prominent Hg/TOC spikes at Oak Springs
250 Summit (Fig. 3).

251

252

253 4.3.3. Pioche Formation, Ruin Wash

254 High Hg and Hg/TOC values are recorded in samples with both high and low
255 TOC wt% values (Fig. 6) at Ruin Wash. The Hg values are highest (up to 500 ppb) at
256 the base of the measured section in the basal ~5m of the Combined Metals Member
257 (Fig. 4). Peaks are around an order of magnitude higher than the maximum values
258 seen at Oak Springs Summit. Above the level of elevated values at Ruin Wash, Hg
259 concentrations are consistently <5 ppb, and there is no increase at the olenellid
260 extinction horizon.

261

262 5. DISCUSSION

263 The three sections show an inconsistent correspondence between the
264 olenellid trilobite extinction, ROECE and sedimentary Hg enrichments (Fig. 7). We
265 review possible points for correlation between sections (e.g. ROECE interval and the
266 trilobite extinction) and discuss processes which may account for the variable Hg
267 signal.

268

269 5.1. ROECE, Hg and Hg/TOC correlation

270 To assess any correlation between the timing of Hg enrichment and ROECE,
271 we delineate the base of the excursion based on the following two criteria. Firstly, the
272 onset of ROECE should be present within the Pyramid Shale Member of the Carrara
273 Formation and the upper Combined Metals Member of the Pioche Formation; this is
274 based on an abrupt negative carbon isotope excursion within the *Olenellus* trilobite
275 biozone, immediately preceding the olenellid extinction (Montañez et al., 2000).
276 Secondly, given this stratigraphic constraint, we mark the onset of the excursion as
277 the stratigraphic base of the negative inflexion interpreted within these members, i.e.
278 ~60 m at Emigrant Pass and ~13 m at Oak Springs Summit. Between the Carrara
279 and Pioche formations, our data show no clear relationship between the onset of
280 ROECE and Hg or Hg/TOC enrichments. At Emigrant Pass an enrichment occurs
281 around 10 m above the base of ROECE and at Oak Springs Summit an enrichment
282 occurs ~1 m below the base of the excursion. It is clear from enrichments in the
283 Eagle Mountain Shale Member of the Carrara Formation and in the Combined
284 Metals Member of the Pioche Formation that the majority of Hg and Hg/TOC
285 excursions occur before the ROECE interval.

286

287 **5.2. Extinction, Hg and Hg/TOC**

288 In the Pioche Formation at Oak Springs Summit, a small Hg (32 ppb,
289 compared to a background of <5ppb for this section) and Hg/TOC excursion
290 corresponds closely with the extinction horizon and the top of the *Olenellus* biozone
291 (Fig. 7). However, the relationship between olenellid extinction and Hg or Hg/TOC
292 enrichment is inconsistent among the other studied sections (Figs. 3 and 7). There is
293 no enrichment coincident with the top of the *Olenellus* biozone at Emigrant Pass, nor
294 at the extinction horizon at Ruin Wash (Fig. 7).

295 The high levels of Hg enrichment are generally recorded low in the study
296 sections. In the Combined Metals Member at Ruin Wash, this is seen ~15 and ~10m
297 below the olenellid extinction level at Ruin Wash (Fig. 4), and even lower below this
298 level at Emigrant Pass (Fig. 2). Based on the lithostratigraphic correlation of Palmer
299 (1998), it is unlikely that the levels of Hg enrichment can be correlated with each
300 other (Fig. 7).

301 The inconsistency of the relationship between Hg, ROECE and extinction
302 across all three sections challenges the conventional use of Hg as a tracer for global
303 environmental Hg loading in this case. Previous Hg chemostratigraphic profiles

304 invoked to trace global LIP eruptions predict, and exhibit, synchronous Hg signals
305 across regional and global sites (e.g. Percival et al., 2017). The lack of a
306 reproducible Hg signal across our sections precludes a straightforward interpretation
307 of the Hg chemostratigraphy. Our data show that only at Emigrant Pass does the
308 base of ROECE coincide with Hg enrichment, but not the duration of the isotopic
309 excursion. There is no Hg enrichment across the extinction interval.

310 The observed heterogeneity of enrichments in Hg and Hg/TOC values could
311 be caused by several factors related to environmental and diagenetic processes. Our
312 data demonstrate that volcanic loading and binding to organic matter cannot be the
313 sole drivers of the Hg record in these strata. We therefore consider the possible roles
314 that redox variations and binding to clays (and possibly sulphides) may have played
315 in controlling Hg levels.

316

317 **5.3. Hg enrichments, redox variation and TOC**

318 Previous studies have exhibited limited correlation between redox conditions,
319 organic matter deposition and Hg drawdown (e.g. Grasby et al., 2013; Percival et al.,
320 2015). However, studies from the modern suggest the redox state of the sediment
321 and water column can play an important role in mobilising or re-mobilising Hg
322 species and enhancing or diminishing Hg exchange between the sediment and water
323 column (Mason et al., 2006; Emili et al., 2011). Mercury and methyl mercury (MeHg)
324 are scavenged in oxic conditions and sequestered in the sediments; however, the
325 upward migration of the redox boundary causes Hg and MeHg to be released into
326 the water column (Emili et al., 2011; Yin et al., 2017). Emili et al. (2011) modelled Hg
327 cycling between the sediment and water column under anoxic conditions and
328 showed a strong redox control on the mobility of Hg. They found that benthic Hg flux
329 from the sediment to water column is highest during anoxic conditions and is also
330 accentuated during sulfate reduction in euxinic conditions.

331 Assessment of redox states within the Carrara and Pioche formations found
332 intermittent and locally variable periods of dysoxia during the olenellid extinction
333 interval (Webster et al., 2008; Faggetter et al., 2017). Pyrite petrography shows
334 dominantly oxygenated conditions (i.e. no framboids, scarce pyrite crystals) at
335 Emigrant Pass (Fig. 2), variably oxygenated-dysoxic-euxinic conditions at Oak
336 Springs Summit close to the extinction horizon (Fig. 3) and, euxinic to oxygenated
337 conditions across the extinction horizon at Ruin Wash (Fig. 4) (Faggetter et al.

338 2017). These fluctuating redox conditions could have altered drawdown of Hg from
339 the water column to the sediments (Horowitz et al., 2017) during times of heightened
340 Hg loading. The euxinic pyrite framboid size data from two samples at the Ruin
341 Wash trilobite extinction level do not correspond with Hg enrichment. Thus, the
342 varying behaviour of Hg under different redox conditions could underlie the differing
343 relationship between Hg and extinction in the Pioche Formation.

344 It is important to note that previously published studies reporting Hg
345 sedimentary trends across multiple sections similarly reveal variable Hg and Hg/TOC
346 ranges between localities (e.g. Grasby et al., 2016; Jones et al., 2017). Such
347 discrepancies may be an inherent component of volcanically-derived deposition and
348 fixation in marine sediments. For instance, a variable record of Hg enrichment during
349 anoxia-related extinction is reported during the Toarcian (Early Jurassic) extinction
350 (Percival et al., 2015). This event coincides with the organic-rich shales of the Jet
351 Rock in northern England, but these sediments lack the Hg enrichment that
352 otherwise might be expected given contemporaneous eruption of the Karoo-Ferrar
353 flood basalt province. Percival et al. (2015) argue that efficient organo-Hg
354 scavenging in organic-rich euxinic settings may have caused over-printing of the
355 Hg/TOC anomaly by excess organic matter deposition. However, such a mechanism
356 is unlikely in our reported Cambrian examples because TOC values in the C-Shale
357 at Ruin Wash are low (<0.3 wt %; Fig. 5). The Carrara and Pioche formations are
358 similarly characterised by low TOC and a range of Hg concentrations and Hg/TOC
359 values; we interpret this signature as showing that even in organic-poor rocks it is
360 possible to record elevated Hg concentrations during times of heightened
361 environmental loading (Figs. 5 and 6), a conclusion drawn from other organic-lean
362 records (e.g. Font et al., 2016; Percival et al., 2017). At Oak Springs Summit Hg and
363 Hg/TOC excursions occur in samples containing low TOC (<0.15 wt% C), whilst at
364 Emigrant Pass and Ruin Wash enrichments occur across a range of wt% TOC
365 values (Fig. 6). The absence of a strong correlation between Hg and TOC (Fig. 5) at
366 all three sections therefore indicates that Hg enrichment is not a function of variable
367 TOC; we therefore posit that these anomalies are not solely a function of low TOC.

368

369 **5.4. Hg and mineralogy**

370 Hg accumulation may also be controlled in part by binding to phases other
371 than organic matter. The samples analysed here exhibit very low TOC (wt%) values

372 and commonly comprise marl facies. Because clay minerals can act as an efficient
373 Hg binding medium in the absence of a larger organic matter reservoir, the
374 sediment/rock composition at the time of Hg deposition may partially control Hg
375 concentration (Zhong and Wang, 2008; Kongchum et al., 2011). High surface area
376 reactivity for clay minerals make them effective regulators of Hg in aquatic sediments
377 and up to an order of magnitude higher Hg concentrations have been found in
378 secondary minerals such as clay versus primary minerals such as quartz and
379 feldspar (Tessier et al., 1982). Higher proportions of primary silicate minerals
380 therefore have the capability to “dilute” the amount of Hg binding during Hg loading
381 (Tessier et al., 1982), and a variation in sediment composition across our study
382 location could be a contributing factor to the observed inconsistent Hg records.

383

384 **5.5. Hg as an indicator of volcanism**

385 The pre-ROECE levels of Hg enrichment observed at Emigrant Pass and
386 Ruin Wash are enigmatic, and it is currently unclear if they record an unknown local
387 volcanic source, an early eruptive pulse of the Kalkarindji LIP, or are instead a
388 response to sedimentary/diagenetic redox variations. To resolve this uncertainty,
389 further work is required to determine how widespread these perturbations are, both
390 within Laurentia and globally.

391 Challenges to linking Hg excursions with LIP volcanism are not restricted to
392 our Cambrian successions. Percival et al. (2018) present a comprehensive
393 comparison of Hg records from the Mesozoic, focussing on the coincidence of LIP
394 emplacement and ocean anoxic events, and report variable (both in Hg and
395 Hg/TOC) concentrations across sections and lithologies and also contrasting
396 evidence of Hg enrichment during periods of LIP volcanism (e.g. an absence of a
397 broad global Hg excursion during Deccan volcanism contrasting with osmium-
398 isotope records). The apparent inconsistency between these proxies is likely due to
399 the various environments, lithologies and depositional processes.

400 Although the lack of consistent Hg records between the analysed sections
401 prevents arguing definitively for a link between Kalkarindji and the extinction event at
402 this stage, it remains likely that some of the recorded Hg excursions do record an
403 expression of these LIP eruptions for the following reasons:

- 404 • The Kalkarindji LIP lacks a robust body of radiometric dates, Accordingly,
405 additional dating efforts within the Kalkarindji province itself may also help

406 clarify its emplacement history, and whether initial volcanic pulses occurred
407 considerably earlier than current geochronological constraints suggest.
408 Current age dating does suggest that the onset of eruption may straddle, or
409 possibly predates the Series 2 – Series 3 boundary (Marshall et al., 2018),
410 thus raising the possibility that the Hg record from the Great Basin records
411 other volcanic eruptions. If this proves to be the case, then Hg anomalies may
412 be a useful marker for independently implicating specific volcanic events, but
413 offers limited resolution when attempting to discriminate between multiple
414 contemporaneous sources.

- 415 • Many LIPs, whilst erupted rapidly on a geological timescale, are iterative in
416 their eruptive behaviour and being characterised by short periods of very
417 intense activity (Chenet et al., 2008; Vye-Brown et al., 2013). For instance,
418 high-resolution geochronological studies have revealed that eruptions of other
419 large igneous provinces occur in a pulsed nature, particularly the Permo-
420 Triassic Siberian Traps (Burgess et al., 2017), the end-Triassic Central
421 Atlantic Magmatic Province (Davies et al., 2017) and the end-Cretaceous
422 Deccan Traps (Schoene et al., 2015). Given the evidence for pulsed LIP
423 emplacement throughout Earth history, it is plausible that multiple eruption
424 episodes characterise the emplacement of the Kalkarindji LIP.
- 425 • The broad-scale architecture of the province, as evidenced by the several
426 geochemically related sub-provinces (Glass and Phillips, 2006), may indicate
427 more than one eruptive focus during its eruptive lifetime.
- 428 • Marshall et al. (2016) report that many Kalkarindji flows were effectively
429 degassed: such near-complete degassing could have occurred either at the
430 vent source (Guilbaud et al., 2007) or during propagation across the evolving
431 lava fields. Importantly, degassing occurs either during fissure eruption and
432 associated fire-fountaining similar to that observed from Laki eruptions. Such
433 effusions can transport volcanogenic volatiles high into the troposphere, and
434 possibly into the stratosphere, since fire fountains, augmented by heat
435 released from nascent flows drive thermal uplift generating buoyant ash and
436 gas plumes (Thordarson and Self, 1998; Glaze et al., 2017). Accordingly,
437 volatiles may be lofted high into the atmosphere (Stothers et al., 1986;
438 Woods, 1993), and this available for distribution certainly at local and regional

439 scales or, under favourable conditions, more globally. In this context, it is
440 important to note that the Kalkarindji LIP was erupted near the equator (Fig. 1;
441 Cocks and Torsvik, 2013; Lawver et al., 2015) where the tropopause would
442 have been at a greater altitude thus mitigating against wider distribution, but
443 that atmospheric circulation patterns an equatorial location would have
444 otherwise aided in allowing aerosol distribution to both hemispheres

- 445 • In addition, Marshall et al., (2016) also argue for a fundamental change in
446 eruptive style; the main succession being typified by thick, inflated pahoehoe
447 flow and the overlying Blackfella Rockhole Member (BRM), which is instead
448 characterised by huge rubble-topped flows. This change in eruptive style,
449 together the occurrence of stromatolite reefs and aeolian(?) sand horizons
450 preserved within these upper eruptive units indicates that later eruptive
451 episodes occurred into a complex paleoenvironment affected by both
452 terrestrial and shallow marine conditions.

453

454 To summarise, the degree and timing of Hg release is likely to have varied
455 significantly during construction of the Kalkarindji LIP and, together with outlined
456 factors controlling lofting and circulation of volatiles, may thus help explain the
457 iterative and/or incomplete record of Hg here reported in the mid-Cambrian marine
458 sediments.

459

460

461 **6. CONCLUSION**

462 We report sedimentary Hg and Hg/TOC enrichments from both the Carrara
463 and Pioche formations of the western Great Basin, USA. These successions are
464 constrained within a biostratigraphic and chemostratigraphic framework to record the
465 Cambrian Series 2 – Series 3 boundary, and the extinction of the Laurentian
466 olenellid trilobites is observable within the Pioche Formation. The ROECE is present
467 at two of the three studied sections (Emigrant Pass, Carrara Formation and Oak
468 Springs Summit, Pioche Formation). In the Carrara Formation, the majority of Hg
469 enrichments predate ROECE, with a single enrichment occurring just above the base
470 of the excursion. At Oak Springs Summit ROECE is preceded by Hg enrichment.

471 Within the Pioche Formation at Oak Springs Summit the extinction horizon of
472 the olenellid trilobites is marked by positive Hg and Hg/TOC excursions; however, a

473 similar excursion is not apparent at the equivalent horizon from Ruin Wash. The
474 failure to locate Hg enrichment in the euxinic Ruin Wash section suggest that the
475 redox conditions were unfavourable. Our data supports the hypothesis that Hg and
476 Hg/TOC enrichments within the Carrara and Pioche formations are not solely derived
477 from enhanced TOC preservation, but that inconsistent Hg trends may have resulted
478 from variable environmental and diagenetic processes at the different sites. Given
479 the strong control anoxia exerts on Hg flux, speciation and accumulation in modern
480 settings, the role of redox states in deep time is clearly important when assessing the
481 record of Hg in rocks.

482 The timing, volume and palaeo-position of the Kalkarindji LIP makes it a key
483 candidate as the source of environmental Hg loading and subsequent enrichments in
484 the Carrara and Pioche formations. Thus, the Kalkarindji potentially contributed to
485 the Hg concentrations at the Cambrian Series 2 – Series 3 boundary, and that the
486 occurrence of precursor levels of Hg enrichment may point to hitherto unrecognised
487 phases of volcanism during construction of the Kalkarindji LIP, or else the possibility
488 of other, as yet, unknown major volcanic episodes.

489

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497

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763 Figure captions

- 764 1. Cambrian global palaeogeography at 510 million years ago showing
765 approximate palaeoposition of study sections, adapted from Lawver et al.
766 (2014). Architecture of Kalkarindji LIP taken from Marshall (2016) and aligned
767 to the palaeogeographic position of Australia at 510 Ma (green outline) as
768 depicted in Lawver et al. (2014).

- 769 2. Geochemical data from Emigrant Pass, Carrara Formation: TOC wt % C,
770 $\delta^{13}\text{C}_{\text{org}}$ (permil), Hg (ppb) and Hg/TOC (ppb/ wt % C). The position of the
771 *Olenellus - Eokochaspsis nodosa* biozone boundary is from Palmer and
772 Halley (1979) inferred redox conditions are based on framboid size
773 distribution data (Faggetter et al. 2017).
- 774 3. Geochemical data from Oak Springs Summit, Pioche Formation: TOC wt % C,
775 $\delta^{13}\text{C}_{\text{org}}$ (permil), Hg (ppb) and Hg/TOC (ppb/ wt % C). The position of the
776 *Olenellus - Eokochaspsis nodosa* biozone boundary is from Palmer (1998),
777 inferred redox conditions are based on framboid size distribution data from
778 Faggetter et al. (2017). See Fig. 2 for key.
- 779 4. Geochemical data from Ruin Wash, Pioche Formation: TOC wt % C, $\delta^{13}\text{C}_{\text{org}}$
780 (permil), Hg (ppb) and Hg/TOC (ppb/ wt % C). The position of the *Olenellus -*
781 *Eokochaspsis nodosa* biozone boundary is from Palmer (1998), inferred redox
782 conditions are based on framboid size distribution data from Faggetter et al.
783 (2017). See Fig. 2 for key.
- 784 5. Stratigraphic columns showing TOC wt % C through the Carrara and Pioche
785 formations. See Fig. 2 for key.
- 786 6. Cross plots of TOC wt % C vs. Hg (ppb) for the Carrara and Pioche
787 formations.
- 788 7. Summary of Hg (ppb) and Hg/TOC (ppb/ wt % C) from the Carrara and
789 Pioche formations. The position of the *Olenellus - Eokochaspsis nodosa*
790 biozone boundary is from Palmer (1998), inferred redox conditions are based
791 on framboid size distribution data from Faggetter et al. (2017). The yellow
792 highlight correlates the Gold Ace Member of the Carrara Formation with the
793 Combined Metals Member of the Pioche, after Palmer (1998). See Fig. 2 for
794 key.

795

796 Table 1. Table containing stratigraphic and geochemical data. Rows coloured in grey
797 indicate samples excluded due to low TOC (< 0.01 wt% TOC). Rows coloured in
798 orange indicate the extinction horizon at Oak Springs Summit and Ruin Wash.

799

800

801

510 Ma

60° N

30° N

0°

30° S

60° S



Laurentia

Siberia

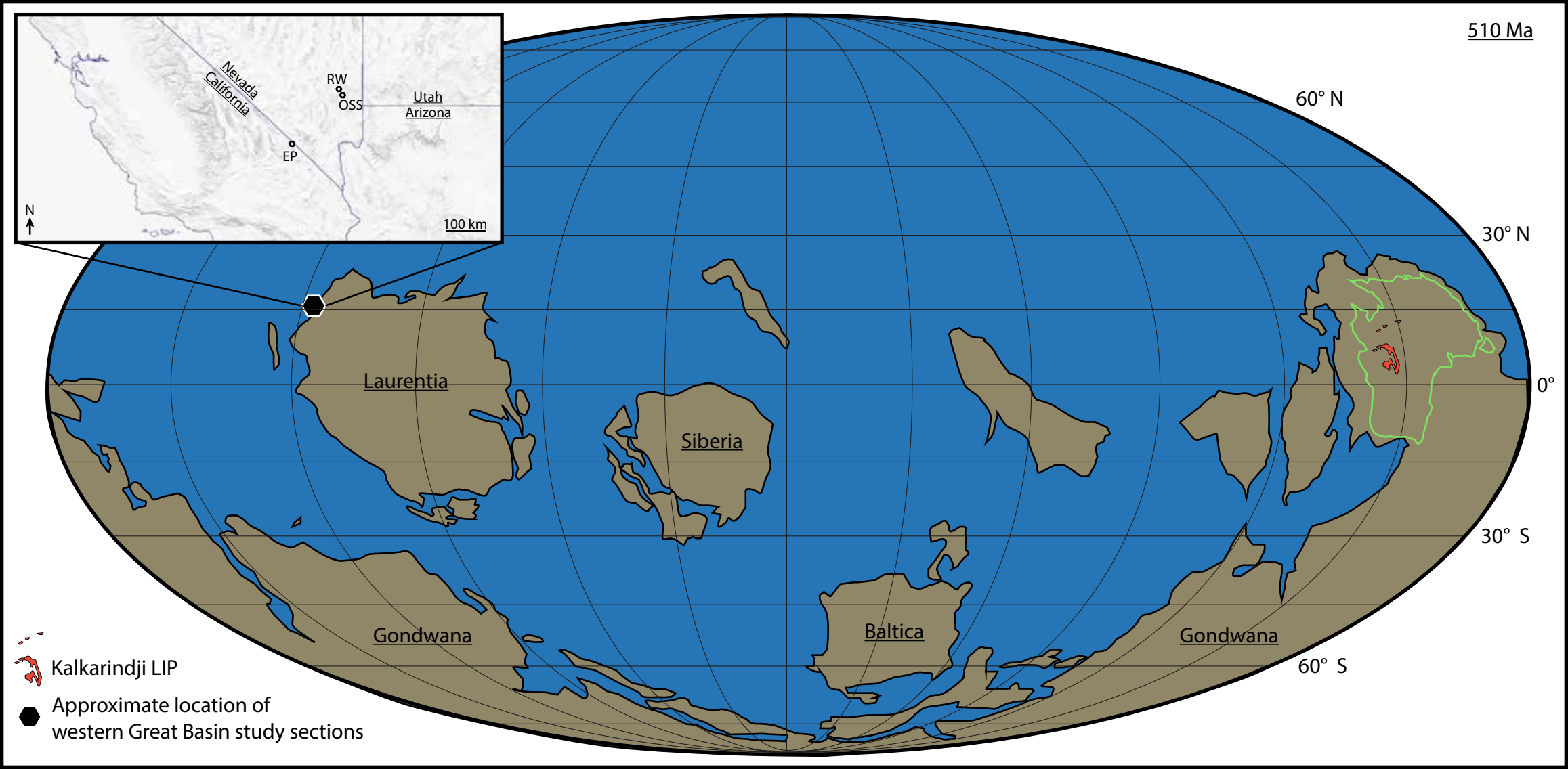
Baltica

Gondwana

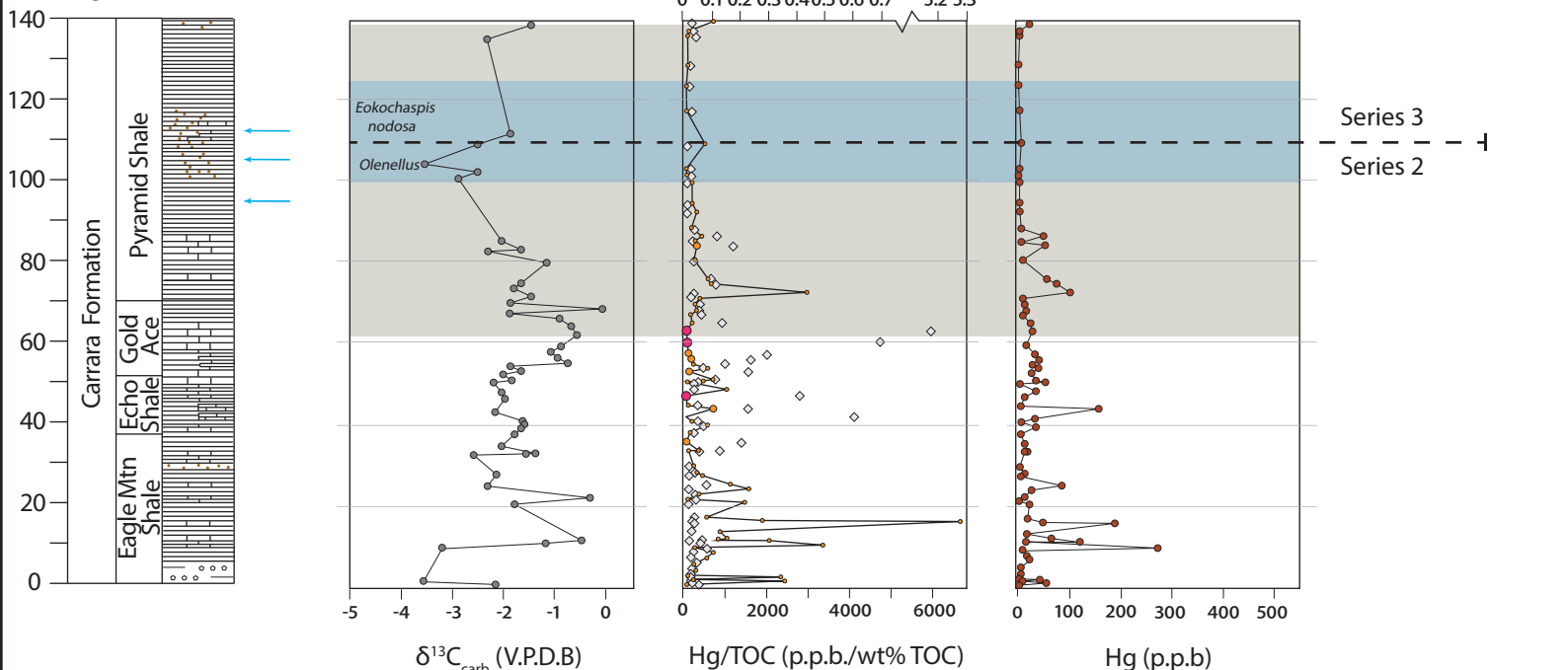
Gondwana

Kalkarindji LIP

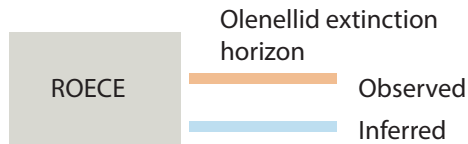
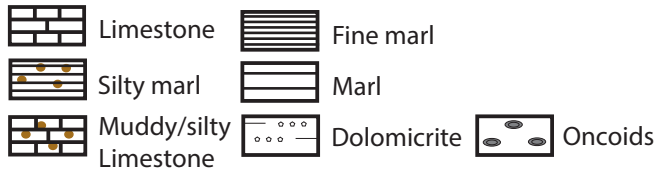
Approximate location of western Great Basin study sections



Emigrant Pass, CA.



KEY



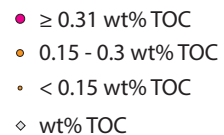
Inferred redox

← Dysoxic

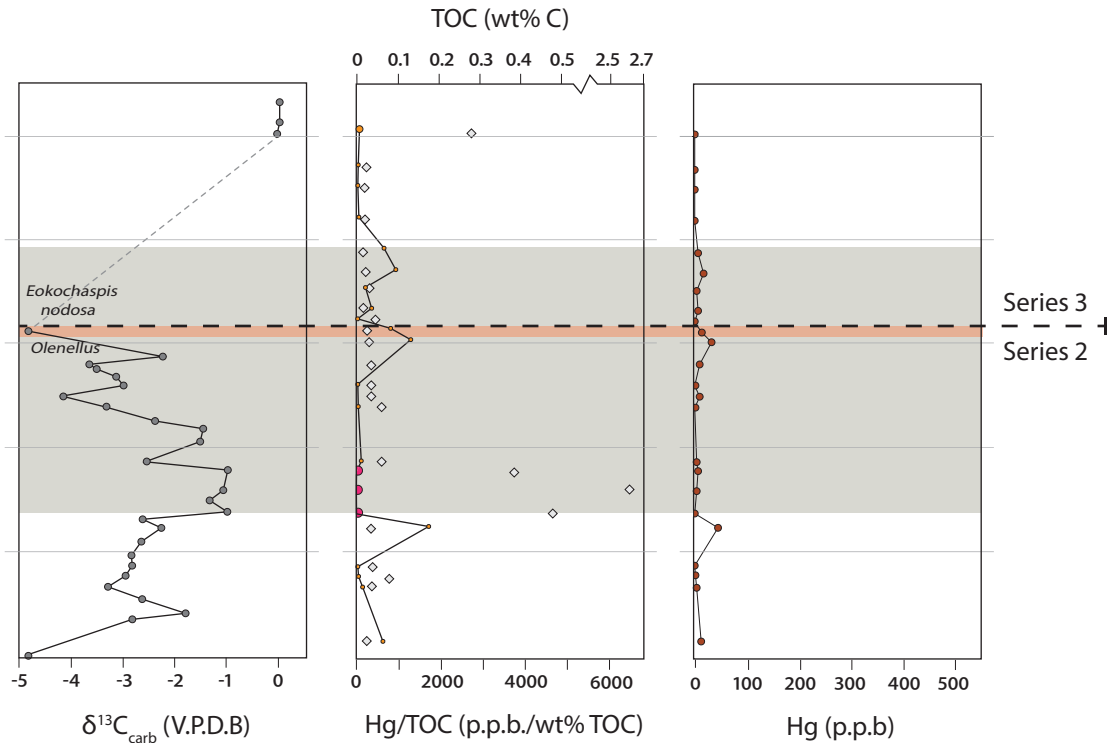
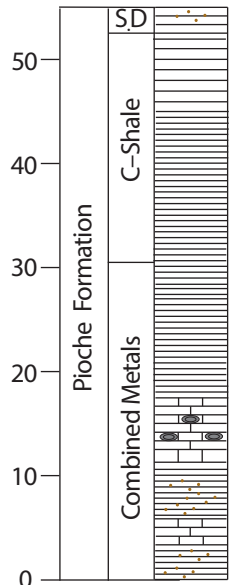
← Euxinic

← Oxic

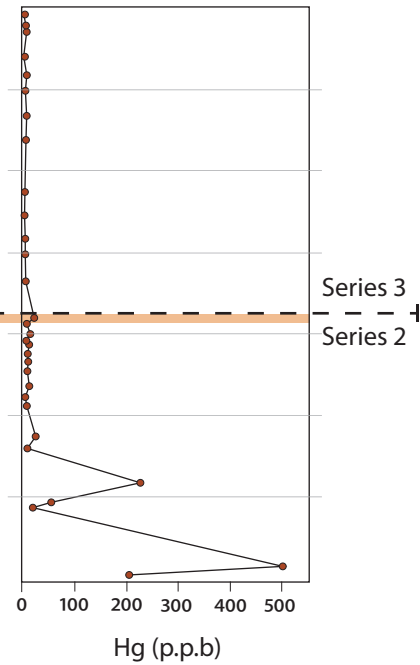
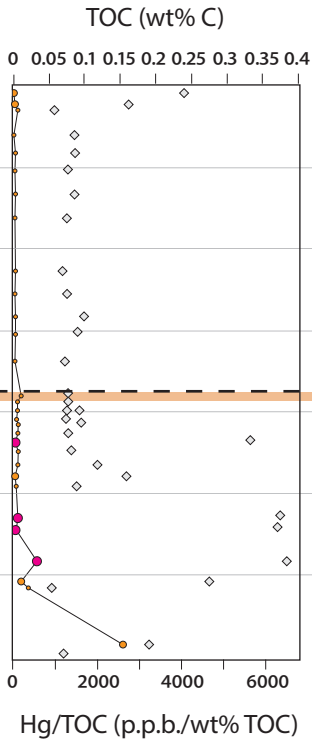
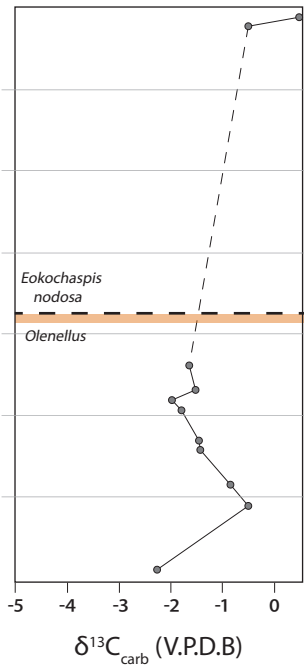
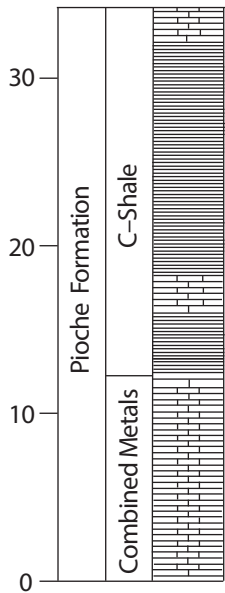
Hg/TOC



Oak Springs Summit, NV.



Ruin Wash, NV.



Emigrant Pass, CA.

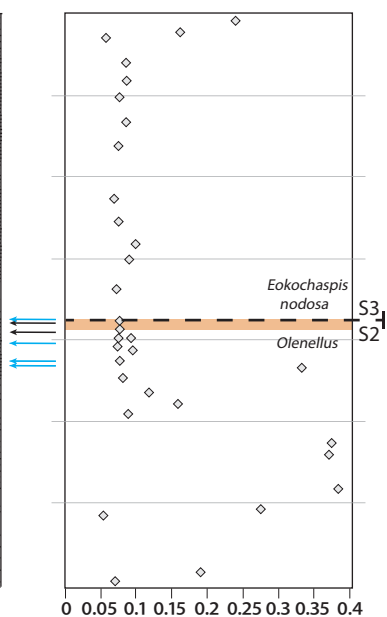
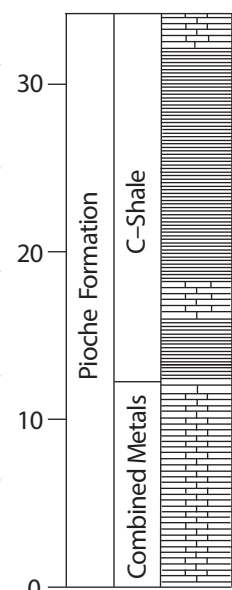
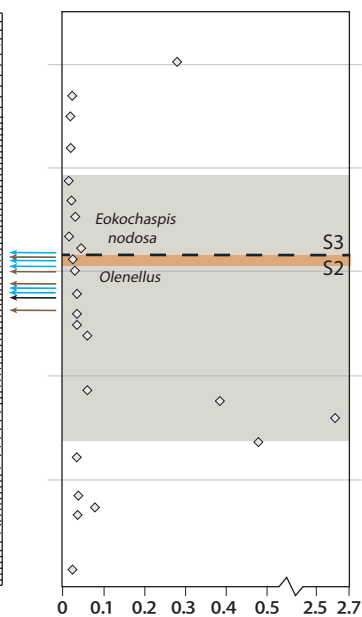
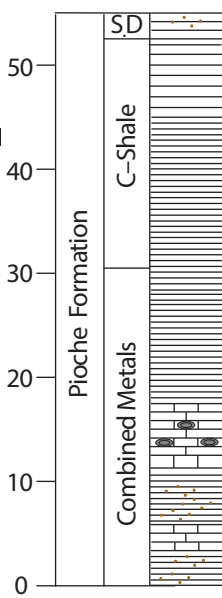
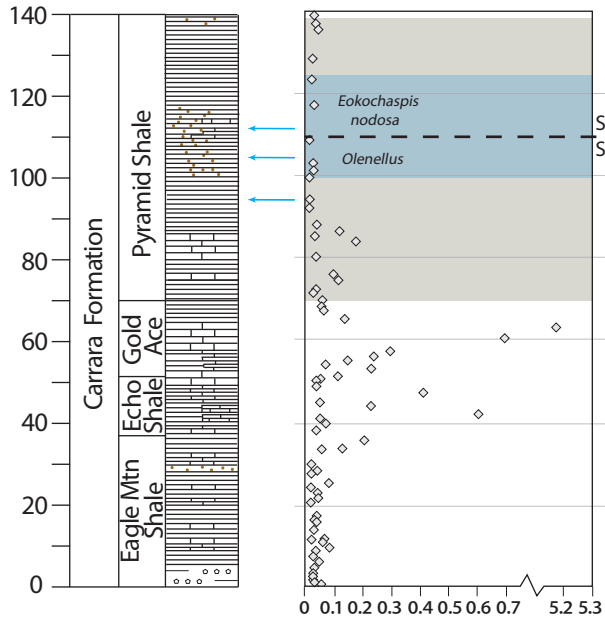
TOC (wt% C)

Oak Springs Summit, NV.

TOC (wt% C)

Ruin Wash, NV.

TOC (wt% C)



Ruin Wash, NV.

