

28 marine sedimentary rocks, immediately following the end-Permian mass extinction. Here, we
29 present geochemical data primarily focused on microbialites. Our geochemical analysis
30 shows that U, V, Mo and REE (Ce anomaly) may be used as robust redox proxies so that the
31 microbialites record the chemistry of the ancient ambient sea water. Among the three trace
32 metals reputed to be reliable redox proxies, one (V) is correlated here to terrigenous supply,
33 the other two elements (U and Mo) do not show any significant authigenic enrichment,
34 thereby indicating that oxic conditions prevailed during the growth of microbialites. REE
35 profiles show a prominent negative Ce anomaly, also showing that the shallow marine waters
36 were oxic. Our geochemical data are consistent with the presence of some benthic
37 organisms (ostracods, scattered microgastropods, micro-brachiopods and foraminifers) in
38 shallow marine waters that survived the mass extinction event.

39

40 **Keywords**

41 Permian-Triassic mass extinction; microbialite; Rare Earth Elements; trace elements; shallow
42 marine water; oxygenation

43

44 **Introduction**

45 The rapid and profound changes in Earth-surface environments and biota across the
46 Permian-Triassic boundary (PTB) are well-known and relate to the end-Permian mass
47 extinction event. Over the past few years, these changes have become the subject of intense
48 study using multiproxy datasets published by many authors. These datasets include:
49 palaeontological information from many fossil groups (e.g., Erwin 2006; Brayard et al. 2009;
50 Brayard et al. 2011), stable isotopes, principally of carbon and sulphur (Algeo et al. 2007a;
51 Baud et al. 1989; Payne et al. 2004, Kajiwarra et al. 1994; Bottrell and Newton 2006; Meyer et
52 al. 2013), U/Th ratio (Wignall and Twitchett 2002; Algeo et al. 2007a), molecular biomarkers
53 (Xie et al. 2005; Grice et al. 2005; Fenton et al. 2007; Luo et al. 2013), pyrite framboids (e.g.
54 Wignall et al. 2005; Liao et al. 2010), Rare Earth Elements (REE; e.g., Ishiga et al. 1996;

55 Nan et al. 2002; Wright et al. 1987; Algeo et al. 2007b; Zaho et al. 2013) and modelling
56 (Hotinski et al. 2001; Kidder and Worsley 2004; Kiehl and Shields 2005; Kump et al. 2005;
57 Winguth & Winguth 2013). The more recent studies provide new insights into strong
58 palaeoceanographic changes during the end-Permian mass extinction and its aftermath; the
59 result of some of these studies is a growing opinion that oxygen levels declined in the ocean
60 at the end-Permian and during the Early Triassic. This was proposed as an extinction
61 mechanism and as a cause of the prolonged biotic recovery in the aftermath of the end-
62 Permian mass extinction (e.g., Wignall and Hallam 1992; Weidlich et al. 2003 and others).
63 The decrease of the oxygenation level in the oceans may have been caused by (1) the
64 ocean overturn and upwelling of anoxic waters (Schoepfer et al. 2013) invading shallow shelf
65 environments globally (Kakuwa and Matsumoto 2006; Knoll et al. 1996; Wignall and Hallam
66 1992), (2) the rising of the chemocline in the ocean and the spreading of the oxygen
67 minimum zone (OMZ) on the shelves (Algeo et al. 2007a) especially in the Palaeo-Tethys
68 Ocean which was mostly enclosed and restricted in circulation (e.g., Hotinski et al. 2001;
69 Kiehl and Shields 2005; Kidder and Worsley 2004), (3) a rapid transgression (Wignall and
70 Hallam 1992), (4) the expansion of the OMZ caused by an increase in nutrient flux to the
71 oceans coupled with an intense greenhouse effect (Algeo et al. 2011; Winguth and Winguth
72 2013). However, the datasets also show discrepancies, because recent studies suggest that
73 rather than a prolonged biotic recovery, the period in the aftermath of the end-Permian mass
74 extinction is contains examples of rapid recovery (e.g., Hautmann et al. 2011) and several
75 failed attempts of recovery (Brayard et al. 2011; Song et al. 2011). Other authors suggest
76 that the successive aborted recoveries relate to successive shifts back to ocean anoxia
77 (Grasby et al. 2013). However, although some data support development of prolonged
78 anoxia, especially in the deep ocean (e.g., Kato et al. 2002; Osen et al., 2013 Luo et al.,
79 2013), recent evidence suggests that anoxia was not a major characteristic of the shallow
80 ocean (Forel et al. 2009; Nielsen et al. 2010; Forel et al. 2013; Proemse et al. 2013) and that

81 the Early Triassic was characterised by a brief oxygenation event (Bond and Wignall 2010;
82 He et al. 2013).

83 Trace metals concentrations recorded in carbonate sediments are commonly used for
84 palaeoenvironmental reconstruction through examination of redox-sensitive elements that
85 may become enriched under low-oxygen or euxinic water conditions (e.g., Brumsack 2006;
86 Algeo and Maynard 2004; Tribovillard et al. 2006, 2012). In the same way, REE
87 concentrations in carbonates can be used to reconstruct the chemistry of ancient seawater
88 masses (Wright et al. 1987; Olivier and Boyet 2006; Webb and Kamber 2000).

89 Here, we assess the importance of past oxygen levels in the shallow marine shelves
90 and present geochemical data primarily derived from earliest Triassic microbialites that
91 developed immediately following the end-Permian mass extinction, relying on earlier studies
92 (Olivier and Boyet 2006; Webb and Kamber 2000) wherein the authors demonstrate that
93 microbialites can be used as proxies of the chemical and palaeoenvironmental characteristic
94 of seawater. Microbialites result largely from biologically induced carbonate precipitation
95 (Riding, 2000); Webb and Kamber (2000) and Olivier and Boyet (2006) demonstrated that
96 modern microbialites have shale-normalized REE patterns similar to those of modern sea
97 water and that the trace element and REE chemistry of the microbialites faithfully records
98 that of ancient ambient sea water. Moreover, some previous works (Banner et al. 1988)
99 demonstrated that relative REE abundance was not changed during extensive diagenesis
100 and REE mobilisation was only local in nature. Hence, ancient microbialites may retain their
101 original REE patterns and trace element concentration despite relatively intense subsequent
102 diagenesis (Kamber and Webb 2001; Olivier and Boyet 2006). In addition, Wang et al. (2005)
103 showed that distribution patterns of REE in microbialites of Sichuan measured in coarse
104 crystals of calcite or in adjacent micrite are similar. Also, comparison of C isotope values of
105 carbonate between microbialite branches and adjacent micritic sediment shows that there
106 are small but consistent variations (Mu et al. 2009).

107 In the present study, we demonstrate that the post-extinction microbialites
108 incorporated REE and trace metals in equilibrium with seawater and thus that microbialites
109 are valuable proxies for reconstructing ancient seawater chemistry. Our results suggest that
110 the analysed shallow shelf environments were fully oxygenated in the immediate aftermath of
111 the end-Permian extinction event. These results demonstrate the need for further high-
112 resolution work with the same proxies to induce a comprehensive understanding of the
113 nature of shallow shelf environments and of the palaeoceanographic changes during the
114 latest Permian - earliest Triassic biotic crisis.

115

116 **Geological setting of the study areas**

117 The major crisis occurring through the end-Permian and early Triassic time is demonstrated
118 by abrupt facies change associated with the End-Permian mass extinction. The carbonate
119 platforms show drastic facies change across the Permian-Triassic (PT) event with the
120 development of microbial carbonates, up to ten metres thick, especially in the low-
121 palaeolatitude shallow shelf environments. Microbialites have been described from a range
122 of sites in basal Triassic marine sedimentary rocks deposited in the immediate aftermath of
123 the end-Permian mass extinction (e.g., Erwin 2006; Wignall and Twitchett 2002. See
124 Kershaw et al. 2007 for the global palaeogeography with the location of the microbialite
125 deposits).

126 Microbialites are defined as microbially-mediated organo-sedimentary deposits
127 (Burne and Moore 1987). Their morphologies comprise stromatolites and thrombolites and
128 microbial processes are the main pathway of biologically induced carbonate precipitation.
129 Stromatolites are defined as benthic laminated organo-sedimentary deposits (Kalkowsky
130 1908; see Riding 2000 for a synthesis). Their morphologies are variable and include tabular,
131 domal, columnar, dendritic or undulated laminae. Thrombolites are defined as organo-
132 sedimentary deposits with a clotted macroscopic fabric, and are not laminated. Their
133 morphologies encompass digitate, equant, domal or tabular forms (see Kershaw et al. 2012

134 for details). Hybrid stromatolites (mixtures of microbial and inorganic components; Riding
135 2008) are also observed in some sites (Kershaw et al. 2012).

136 The microbialites studied here are marine and have a widespread association with
137 micritic sediments, indicating that they grew in relatively low-energy conditions. The micritic
138 sediment does not contain any microbialite fragments, indicating growth of the microbialites
139 in calm depositional environments. Uncommon coarse erosive bioclastic levels are observed
140 in the microbialites (pers. obs; Sichuan and Guizhou) and are related to occasional currents
141 in a normally calm depositional environment. Possible Hummocky Cross Stratifications were
142 also observed (Kershaw et al., 2010). These sedimentary structures are interpreted as more
143 or less distal tempestites. This is consistent with shallow shelf-seas, possibly below the
144 fairweather wave base and above or near the stormweather wave base, in the photic zone.
145 The post-extinction microbialites are never observed in deep shelf environments (Kershaw et
146 al. 2012). Thus, occurrence of the microbialites relates to large scale chemical-physical
147 changes in oceanic water but their significance as indicator of palaeoceanographic change is
148 still under discussion.

149 The sites selected for this study are located in western and eastern Palaeo-Tethys
150 and western Panthalassa (Fig. 1). In each site, microbialites occur directly on (Collin et al.
151 2009; Kershaw et al. 2012) or few tens of centimetres above (Baud et al. 2005; Hips and
152 Hass 2006; Forel et al. 2013) the PT event horizon.

153 In western Paleo-Tethys, two sites were used to provide data in two contrasting
154 bathymetries and sequence histories. In the Bükk Mountains of northern Hungary, a model
155 by Hips and Haas (2006) place planar and crinkled stromatolites in an outer ramp setting, in
156 a sequence of micritic carbonates. The conodont *Hindeodus parvus* (Kozur and Pjatakova
157 1976), which is recognised as the marker for the base of the Triassic (Yin et al. 1996, 2001),
158 was found just below the microbialites (Hass et al. 2007). The stromatolites are thus dated to
159 the early Triassic, Griesbachian, *H. parvus* zone. In contrast, in southern Turkey, shallow
160 shelf deposits in the Antalya Nappes contain a thick and complex sequence of stromatolites,

161 thrombolites and hybrid microbial-inorganic structures up to a total 15 m thick (Ricoz 2004;
162 Baud et al. 2005; Kershaw et al. 2011). The Conodont *Hindeodus praeparvus* (latest
163 Permian) is present just below the microbialites. *H. parvus* is present in the microbialite
164 deposits which are probably of the same age as in Bükk Mountains.

165 The remaining two sites selected for analysis are in the South China Block, as
166 follows. In Guizhou Province, the Great Bank of Guizhou (GBG) is an isolated shallow
167 carbonate platform in the Nanpanjiang Basin (Lehrmann 1999) on the southern South China
168 Block. From its palaeogeographic positioning it is interpreted as facing the Panthalassa
169 Ocean (Fig. 1) and may therefore be regarded as having a western Panthalassa position.
170 Immediately in the aftermath of the end-Permian mass extinction, a microbialite crust (up to
171 14 m thick) occurred in all the GBG, marking an abrupt change in the marine environmental
172 conditions. In the GBG, most of the microbialites are thrombolites, mainly clotted and
173 bedded, and sometimes with a digitate fabric. In the GBG, *H. parvus* occurs within the
174 microbialites, near the base of the sequence in some sections (Yang et al. 2011) or several
175 tens of centimetres above the base in other sections (Lehrmann et al. 2003). The fourth site
176 is in Sichuan Province, in the Huaying Mountains that lie on the northern side of the South
177 China Block; the PT sedimentary rocks contained therein were facing the Paleo-Tethys
178 Ocean during their deposition and represent the easternmost position of the Tethyan
179 microbialites in this study. In this area, the microbialite sequences are often thinner (from 2 to
180 4 m thick; e.g. in the Dongwan, Laolongdong or Baizhuyuan sections) and the microbialites
181 are thrombolites with varied morphologies (Ezaki et al. 2003, Kershaw et al. 2012). In
182 Sichuan, the first appearance of *H. parvus* occurs several tens of centimetres above the
183 microbialite base, suggesting that the base of microbialites is latest Permian in age (Ezaki et
184 al. 2003, Kershaw et al. 2012).

185 In summary, the four selected sites illustrate four different palaeogeographic aspects;
186 in all cases the microbialites illustrate a short period of growth (likely less than 200 kyr; Song
187 et al., 2013). Moreover, microbialites represent one of the carbonate facies well developed

188 immediately in the aftermath of the end-Permian mass extinction and during the beginning of
189 the prolonged Triassic biotic crisis. Microbialites are sediments appropriate for geochemical
190 analysis, as demonstrated in our literature review above. Although there are numerous works
191 on carbon isotope analysis, these deposits should receive a greater attention for
192 measurements of other geochemical proxies, such as REE and trace metals, the subject of
193 this study.

194

195 **Material and methods**

196 To test our methodology and as a first approach to illustrate the potential to record
197 palaeoceanographic chemical composition of microbialites, 27 samples were selected for
198 elemental analysis. The samples were chosen to illustrate different palaeogeographical
199 contexts and various microbialite morphologies (stromatolites, thrombolites with domal,
200 digitate or domal fabric) to analyse redox geochemical contents in the different settings
201 during microbial carbonate precipitation. The samples were collected in earliest Triassic
202 microbialites, restricted in age to the *H. parvus* zone, providing the best possible stratigraphic
203 resolution for the studied time interval, the best possible current correlation between coeval
204 microbialite sites (4 samples in Çürük Dag section, Turkey; 5 in Gerennavár section,
205 Hungary; 7 in Dongwan, Laolongdong and Baizhuyuan sections in Sichuan, China; 11 in
206 Dajiang, Dawen and Rungbao sections in Guizhou, China). Microbialites and adjacent
207 sediment were sampled from polished slabs and each sample was finely crushed. The
208 quality of the samples was assessed by microscopic petrographical observations, so that
209 calcite-filled fractures or highly altered parts of rocks were excluded from sampling. For each
210 sample, 50 mg of carbonate powder was dissolved in a mixture of concentrated HF-HNO₃.
211 REE and trace elements were measured using a Thermofischer 2X7 series ICPMS (iSTEP,
212 Paris 6 - Pierre and Marie Curie University – Institut de Physique du Globe de Paris).
213 Analytical quality was checked using the CAL S standard. Analytical precision is better than
214 5% for all measured elements. The results are presented in Tables 1 and 2.

215

216 **Results and interpretations**

217 *Trace elements as redox proxies*

218 Many trace elements show variations in oxidation state and solubility as a function of the
219 redox status of the depositional environment. Redox-sensitive trace metals tend to be soluble
220 under oxidizing conditions and less soluble under reducing conditions, resulting in authigenic
221 enrichments in oxygen-depleted sediments. Three trace metals among the most commonly
222 used as redox proxies are uranium (U), vanadium (V) and molybdenum (Mo); see syntheses
223 in Brumsack (2006), Tribovillard et al. (2006), and Algeo and Rowe (2012). U and V are
224 usually authigenically enriched in sediments deposited under suboxic to anoxic conditions
225 whereas Mo enrichment requires anoxic conditions and the presence of free sulphide ions
226 (i.e. euxinic conditions; see discussion in Tribovillard et al. 2006, 2012; Algeo and Rowe
227 2012; Chappaz et al. 2014). The results are presented in Table 1.

228 In the present case, V is well correlated to Al ($R_2 = 0.710$; Fig. 2), indicating a
229 terrigenous origin. U and Mo are poorly or not correlated to Al ($R^2 = 0.436$ and $R^2 = 0.050$,
230 respectively; Fig. 2). Concerning the Al vs. U relationship, the value of the determination
231 coefficient R^2 suggests (from a mathematical point of view) that both elements could be
232 correlated. However, the positive tendency drawn on Fig. 2A must be due to the two samples
233 with the highest U and Al contents. If these two points are excluded, R^2 value falls from 0.436
234 down to 0.106. Consequently, the main cluster of the sample cloud does not show any
235 tendency and the Al vs. U correlation appears to be artificial. U and Mo are also neither
236 correlated to other terrigenous proxies (Ti, Zr, Th). As the rocks studied here are limestones,
237 any authigenic enrichment may be masked by the very high content in carbonate. With such
238 high carbonate content (1) a correlation between Al and U or Mo could be also masked,
239 because Mo and U are present with very low concentrations, and (2) Al normalization
240 (classically used to avoid dilution effect by carbonate) might be biased, because very low Al
241 concentration causes element-to-Al ratios to be artificially high, limiting the use of

242 enrichment-factor calculation (see detailed discussion about Al normalization in Van der
243 Weijden 2002 and Tribovillard et al. 2006). However, in our samples, even if detrital
244 components (mainly clays) are present in small quantities (mean $\text{Al}_2\text{O}_3 = 1.15\%$; std. dev. =
245 0.86), their concentration is not negligible. Consequently, the calculation of enrichment
246 factors may be attempted. Enrichment factors (EF) are calculated with $X\text{-EF} = (X/\text{Al})_{\text{sample}} /$
247 $(X/\text{Al})_{\text{PAAS}}$ where X and Al represent the weight concentrations of element X and Al,
248 respectively, while PAAS stands for Post Archean Average Shale (Taylor and McLennan,
249 1985). If EF-X is larger than 1, then element X is enriched in the sample relative to its
250 average crustal abundance. Using such enrichment factors, patterns of authigenic U-Mo
251 covariation in marine environments provide insights regarding bottom water redox conditions
252 (Algeo and Tribovillard 2009; Tribovillard et al. 2012). In the present sample set, all samples
253 have low U and Mo enrichment factors (below 10 for all samples but one for U, and below 3
254 for all samples but 3 for Mo), indicating no or only barely detectable enrichment, but in no
255 way a significant enrichment. In addition, when above the value 1, the enrichment factors are
256 larger for U than for Mo. These results suggest that depositional conditions were oxic to
257 suboxic (see discussion in Algeo and Tribovillard 2009). It is thus meant that the water
258 column was oxygenated and that oxygen-poor, reducing, conditions developed only below
259 the sediment-water interface. The redox-cline depth may have fluctuated below the
260 sediment-water interface, sometimes being close to it (but still below it). In such a case, a
261 small authigenic U enrichment (between 5 and 10) may be detected as is the case for some
262 of the samples studied here. However it is emphasized that the redox-cline did not reach the
263 interface nor the base of the water column (otherwise marked U- and V-, or even Mo-
264 enrichment would have overprinted the sediment composition).

265 To avoid any doubt about potential biases due to Al-normalization, and hence
266 enrichment factors calculation, another process of the analytical results is examined. In our
267 samples (Table 1), U concentration is 0.44-1.91 ppm and Mo concentration is 0.007-0.84
268 ppm. Based on mean abundances in Earth's upper crust or average shale, a detrital U or Mo

269 concentration of 0.01-0.67 ppm and 0.00-0.34 ppm, respectively, can be expected, using the
270 equation: $X_{\text{detrital}} = Al_{\text{sample}} \times (X/Al)_{\text{PAAS}}$. Thence, we calculated the fraction of the element
271 concentration X_{excess} , which can be considered as resulting from authigenic enrichment, with
272 $X_{\text{excess}} = X_{\text{sample}} - X_{\text{detrital}}$. This calculation shows that Mo_{excess} is remarkably low and not
273 systematically observed (0.00-0.75 ppm; mean $Mo_{\text{excess}} = 0.15$ ppm). There is thus no
274 detectable authigenic enrichment in Mo. U_{excess} is somewhat higher and systematically
275 observed (0.25-1.73 ppm; mean $U_{\text{excess}} = 0.85$ ppm). However a ca.1 ppm-enrichment is not
276 sufficient to conclude to any marked authigenic enrichment in U.

277 To sum up, among the three trace metals reputed to be reliable redox proxies, one
278 (V) is clearly correlated to terrigenous supply, the other two elements (U and Mo) do not
279 show significant authigenic enrichment, thereby indicating that anoxic conditions can not be
280 detected in our dataset. When calculating trace-metal enrichment factors, a moderate
281 authigenic-U enrichment may be observed for some samples, with no co-eval V nor Mo
282 enrichment, which strongly suggests that both the sediment-water interface and the base of
283 the water column kept oxygenated, even for samples recording the possible shoaling of the
284 redox-cline within sediments.

285

286 *Rare Earth Elements*

287 REE concentration (table 2) and pattern (Fig. 3) provide a tool to assess palaeoceanographic
288 changes of the seawater chemistry (e.g., Webb and Kamber 2000; Shields and Webb 2004;
289 Wright et al. 1987; Négre et al. 2006). In the present case, the clastic content is low (mean
290 $Al_2O_3 = 1.15$ %; std. dev. = 0.86) and allowing the use of microbialites as a tracer of the
291 chemical signature of sea water during the time of microbialite growth. However, the REE
292 patterns are not flattened as should be the case if the terrigenous signal had blurred the REE
293 signature. Thus a consistent pattern of REE emerges from all four sites (Fig. 3). The REE
294 profiles show enrichment in the middle of the REE range, with a prominent, but variable,
295 negative Ce anomaly. The REE profiles show a reduction in both light and heavy REE (LREE

296 and HREE respectively; Fig. 3). Also significant is a strong positive Eu anomaly. In order to
297 test whether the negative Ce anomaly results from a Ce deficiency or a La relative
298 enrichment, we draw a Pr/Pr* vs. Ce/Ce* crossplot with $Pr/Pr^* = Pr_{SN} / (0.5 Ce_{SN} + 0.5 Nd_{SN})$,
299 where SN stands for "shale normalized", according to Bau and Dulski (1996). Samples with
300 an apparent negative Ce anomaly but with Pr/Pr* close to 1 have in fact a positive La
301 anomaly. The crossplot (Fig. 4) shows that, except for 2 (samples RUN77 and 78, stars), all
302 samples show a true negative Ce anomaly, corresponding to a depletion of the Ce
303 concentration in the studied samples.

304 Olivier and Boyet (2006) and Webb and Kamber (2000) demonstrated that
305 microbialites may be used as proxies of palaeo-seawater chemical characteristics. These
306 authors show that modern microbialites have shale-normalized REE patterns similar to those
307 of modern seawater and that the trace element and REE chemistry of the microbialites
308 faithfully records that of ancient ambient sea water. Cerium has been used as a tracer of
309 palaeoredox conditions in marine environments. Indeed, Ce is fractionated by co-
310 precipitation with metallic oxides or colloids under oxidizing conditions. This fractionation
311 produces a depletion of Ce in marine seawater and in the minerals, such as calcium
312 carbonate, which precipitate in equilibrium with seawater (as shown in modern microbialites
313 by Webb and Kamber 2000). Conversely, under local or basinal anoxic conditions, Ce
314 concentrations are enriched in sea-water and hence in carbonates. Here, the REE patterns
315 exhibit shapes typical of those recorded by carbonate sediments. The REE profiles show a
316 prominent negative Ce anomaly, except for three samples (PAJ 38, RUN 78 and B3). The Ce
317 anomaly varies both within and between sites, yet it is almost always negative (table 2), and
318 less than the critical value of $Ce/Ce^* = -0,1$ (Wright et al., 1987). For the two samples on
319 Figure 4 with a weakly pronounced Ce anomaly, only the sample RUN78 has a Ce/Ce* value
320 higher than -0.1 ($Ce/Ce^*_{RUN78} = 0.02$). This sample also shows a weak enrichment in V (Fig.
321 2) but also a lower carbonate content (Table 1) in comparison with other samples of our set.
322 So, the REE signature of this sample is difficult to interpret unequivocally. The same is true

323 for sample B3 but with a Ce/Ce* value lower than -0.1 ($Ce/Ce^*_{B3} = -0.18$). For sample
324 RUN77, which is at the limit on the Pr/Pr* vs. Ce/Ce* crossplot (Fig. 4), the Ce/Ce* value is
325 also at the limit value of -0.1 ($Ce/Ce^* = -0.1$). Sample RUN77 also shows a lower carbonate
326 content and a weak enrichment in Mo. No enrichment in V or U is observed. Thus no clear
327 interpretation can be deduced for this sample. Overall, for all our samples, the REE signature
328 shows that the shallow marine waters in all four sites were oxic.

329

330 **Discussion**

331 The view that the end-Permian mass extinction event was related to, and quite possibly
332 caused by, anoxia, was given by Wignall and Hallam (1992, 1993). Later, in the literature, the
333 role of anoxia has been reinforced (Wignall and Twittchet 2002). Successively, several
334 processes were invoked based on anoxia and stratification of the ocean water masses
335 (Kajiwara et al. 1994, Isozaki 1997), weak ocean circulation (Hotinski et al. 2001), euxinia
336 and presence of free H₂S in the ocean (Wignall et al. 1998; Grice et al. 2005; Riccardi et al.
337 2006; Wignall et al. 2010), the presence of a euxinic photic zone (Grice et al. 2005) or an
338 unstable chemocline overlying euxinic deep-water which periodically upwelled into the photic
339 zone on the shelves (Riccardi et al. 2006; Algeo et al. 2007a). Even decrease of the oxygen
340 content both in the atmosphere and ocean was mentioned (Weidlich et al. 2003). These
341 studies used various approaches and showed that anoxia, or even occasional euxinia, can
342 be admitted for basinal deposits. For the shelves, some works used the presence of pyrite
343 framboids, to suggest the occurrence of anoxia (e.g. Wignall et al. 2005; Liao et al. 2010).
344 However pyrite framboids may be abundant in sedimentary settings such as the one
345 described here, with oxygen-restricted conditions being present only below the sediment-
346 water interface (see discussions in Tribovillard et al., 2008; Bond and Wignall, 2010; Rickard,
347 2012). Moreover, the ostracod distribution suggests that shelf environments were well
348 oxygenated in several shelf localities around the Tethys or on the Panthalassa margin (Forel

349 et al. 2009, 2013). Finally, few studies have focused on shallow shelf environments (Dolenec
350 et al. 2001; Algeo et al. 2007a), where the role of anoxia is uncertain or occasional.

351 As noted earlier, immediately in the aftermath of the end-Permian mass extinction,
352 and during the beginning of the biotic crisis which has continued for several million years, the
353 well-developed Upper Permian bioclastic carbonate platforms are replaced by prokaryote-
354 dominated carbonated bioconstructions (microbialites) during the earliest Triassic (Kershaw et
355 al. 2012). These carbonate sequences provide high-resolution archives of shallow marine
356 environmental changes (Weidlich and Bernecker 2007). Trace-element abundances in
357 sedimentary deposits allow reconstruction of the physico-chemical conditions that prevailed
358 during the deposition of sediments or the precipitation of carbonates. More specifically, redox
359 sensitive trace metals (U, V, Mo), and their potential authigenic enrichment in the sediments,
360 are useful palaeoredox proxies (e.g., Algeo and Maynard 2004; Brumsack 2006; Tribovillard
361 et al. 2006; Algeo and Tribovillard 2009; Algeo and Rowe 2012; Tribovillard et al. 2012 for
362 detailed processes of enrichment). For example, in the case of U and V enrichment without
363 co-eval Mo enrichment, suboxic or anoxic depositional without free H₂S can be inferred.
364 Conversely, sediments exhibiting concurrent enrichments in U, V and Mo reflect euxinic
365 conditions at the sediment interface or higher up in the water column. Here, the studied rocks
366 do not record any enrichment in redox sensitive trace metals (U and Mo, Fig. 5; and V),
367 which indicates that shelf depositional conditions were neither durably suboxic, nor anoxic,
368 nor even euxinic during the microbialite growth. The REE patterns show also typical shapes
369 of oxygenated marine environments.

370 Finally, in our four sites, the post-extinction microbialites contain a very good record of
371 geochemical change, faithfully recording trace element and REE chemistry of the ancient
372 ambient sea water. Our results indicate that the marine shelf environments studied here were
373 oxic in the aftermath of the end-Permian mass extinction and at the beginning of the biotic
374 crisis, during the early Triassic (*H. parvus* conodont zone). Anoxia or euxinia occurred in the
375 deep ocean, as shown by several authors (e.g., Kajiwara et al. 1994; Ishiga et al. 1996;

376 Kakuwa 2008; Algeo et al. 2010); and in deep shelf environments (e.g., Grice et al. 2005;
377 Wignall et al. 2005). However, if upwelling of anoxic waters contributed to the biodiversity
378 crisis, as suggested by e.g., Algeo et al. (2007a), anoxic waters did not extend through the
379 entire water column, and in particular, they did not undergo large scale invasion of the
380 shallow shelf environment. Under these circumstances, the role of euxinia on the shallow
381 marine shelf represented by the localities studied here is discarded. Moreover, there are
382 numerous groups of oxygen-demanding benthic organisms in shallow marine fossil records
383 throughout the earliest Triassic microbialites in all the sites studied (Forel et al. 2013). Our
384 geochemical data are consistent with the presence of numerous groups of benthic organisms
385 in shallow marine waters throughout the boundary sequence that survived the mass
386 extinction event, and are therefore primary evidence that oxic conditions prevailed in shallow
387 marine waters. In particular, ostracod palaeobiology does not record any drop in oxygenation
388 in some sites, assuming Permo-Triassic ostracods had the same physiology as that of
389 modern ones (Forel et al., 2013). These results agree with the conclusions of Song et al.
390 (2013) who interpreted a pulse of anoxia linked with the mass extinction just before the
391 microbialites growth, which then occur in a re-oxygenated interval before a second pulse of
392 anoxia.

393 Thus, if anoxia contributed to, or even caused, the decrease of the biodiversity in the
394 deep ocean environment, our results dispute other research, referred to in this paper, which
395 interprets anoxia in shallow marine environments immediately in the aftermath of the end-
396 Permian mass extinction and during the beginning of the prolonged Triassic biotic crisis.
397 Thus interpretations of anoxia in these shallow marine sediments must be reconsidered, and
398 that a multi causal origin of the event may be envisioned.

399

400 **Conclusion**

401 Our geochemical investigations were conducted on four different geographic locations across
402 Tethys and western Panthalassa, in carbonate microbialites, which grew during the early

403 Triassic (*H. parvus* conodont zone) on shallow marine shelves in the aftermath of the end-
404 Permian extinction and during early Triassic, at the beginning of the biotic crisis. This work
405 shows that microbialites are valuable proxies for reconstructing ancient seawater chemistry.
406 Among the three trace metals reputed to be reliable redox proxies, in our samples, V is
407 correlated to terrigenous supply, but U and Mo do not show any authigenic enrichment,
408 demonstrating they do not indicate anoxia. The REE patterns of the studied samples exhibit
409 shapes typical of those recorded by carbonate precipitated in marine environments and show
410 a prominent negative Ce anomaly characteristic of precipitation of carbonate in an oxic
411 environment. In the present study, the post-extinction microbialites incorporated REE and
412 trace metals in equilibrium with seawater and we interpret our results to indicate that the
413 shallow shelf environments were fully oxygenated in the immediate aftermath of the end-
414 Permian extinction.

415

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780 **Figure captions**

781

782 **Fig. 1.** Palaeogeographic map of the Permian-Triassic boundary time interval (modified from
783 Golonka 2002) showing locations of the four sample sites in this study (1 - China, Guizhou; 2
784 - China, Sichuan; 3 - Hungary; 4 - Turkey).

785

786 **Fig. 2.** Crossplots illustrating the significant correlations linking Al to V, indicating that V trace
787 is strongly linked to the detrital supply. U and Mo are poorly correlated to Al ($R^2 = 0.436$ and
788 $R^2 = 0.050$, respectively).

789

790 **Fig. 3.** Shale-normalised REE patterns for microbialites from Turkey, Hungary and China
791 (Sichuan and Guizhou).

792

793 **Fig. 4.** Crossplot illustrating the relations between Cerium and Praseodymium anomalies.
794 The diagram is used to determine whether a Ce anomaly is due to a lack of Ce (true Ce
795 anomaly) or an excess of Lanthanum. Here all samples but three deviate from the $Pr/Pr^* = 1$
796 line, indicating a true Ce anomaly.

797

798 **Fig. 5.** Mo_{EF} versus U_{EF} for microbialites. solid lines show Mo/U molar ratio equal to the
799 seawater value (1xSW) and to fractions thereof (0.3xSW, 0.1xSW).

800

801 **Tables**

802

803 **Table 1.** The major elements and trace elements distributions of the microbialites. Major
804 elements contents are expressed in weight percents (wt %). $CaCO_3$ values are calculated
805 from the CaO content, as if Ca were only present in the form of carbonate. Trace elements
806 are expressed in ppm or $\mu g/g$, EF stands for enrichment factors, xs stands for "excess", that

807 is, the portion of the concentration in excess to what could be expected, basing on average
808 crustal concentrations (see text for explanations). CS/Do: China, Sichuan province, Dongwan
809 section; CS/B: China, Sichuan, Baizhuyuan section; CS/L: China, Sichuan, Laolongdong
810 section; CG/Daw: China, Guizhou province, Dawen section; CG/Daj: China, Guizhou
811 province, Dajiang section; CG/R: China, Guizhou province, Rungbao section; H/G: Hungary,
812 Gerennavar section; T/CD; Turkey, Çürük Dag section.

813

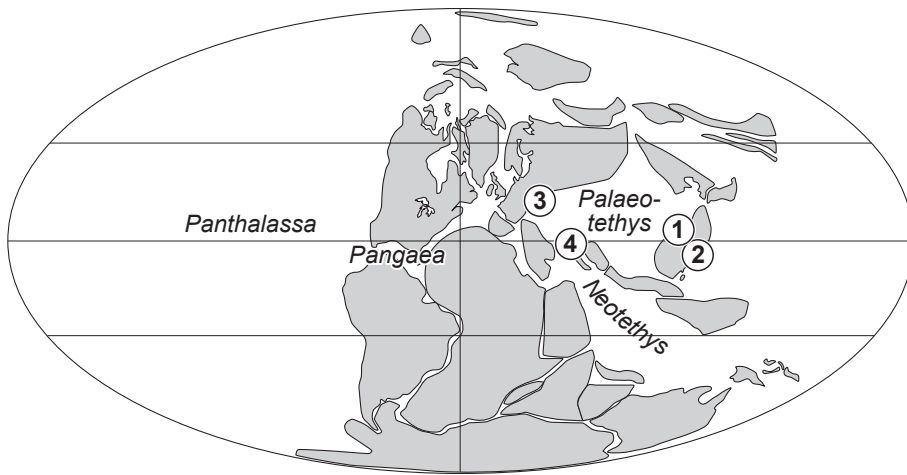
814 **Table 2.** REE distributions of the microbialites. REE are given as raw, non-normalized data.
815 CS/Do: China, Sichuan province, Dongwan section; CS/B: China, Sichuan, Baizhuyuan
816 section; CS/L: China, Sichuan, Laolongdong section; CG/Daw: China, Guizhou province,
817 Dawen section; CG/Daj: China, Guizhou province, Dajiang section; CG/R: China, Guizhou
818 province, Rungbao section; H/G: Hungary, Gerenovar section; T/CD; Turkey, Çürük Dag
819 section.

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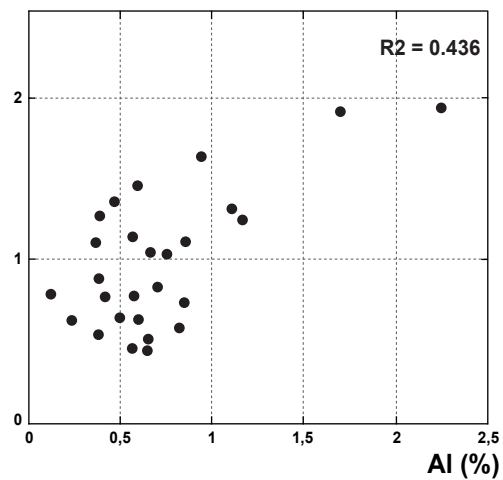
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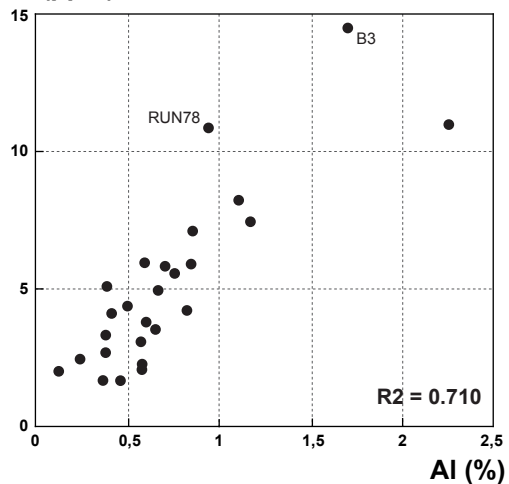
823



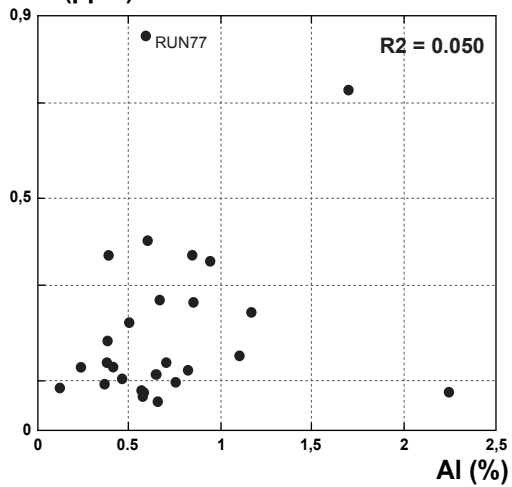
U (ppm)

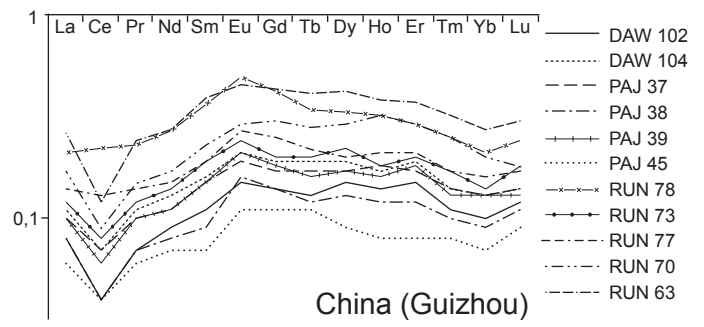
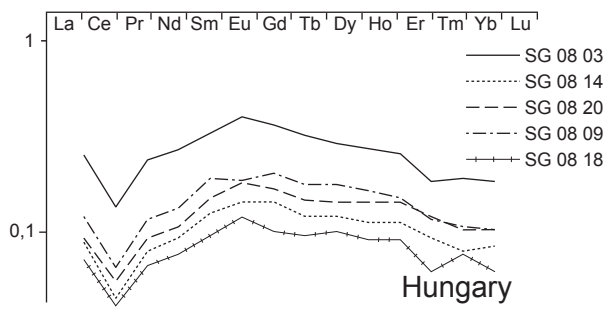
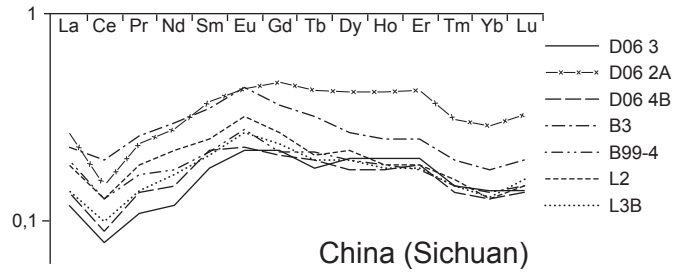
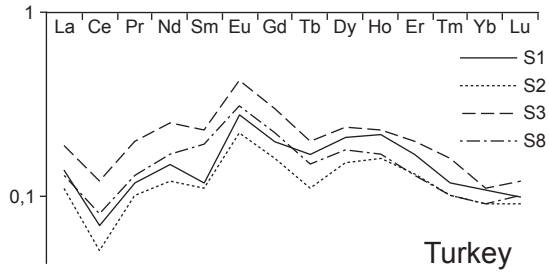


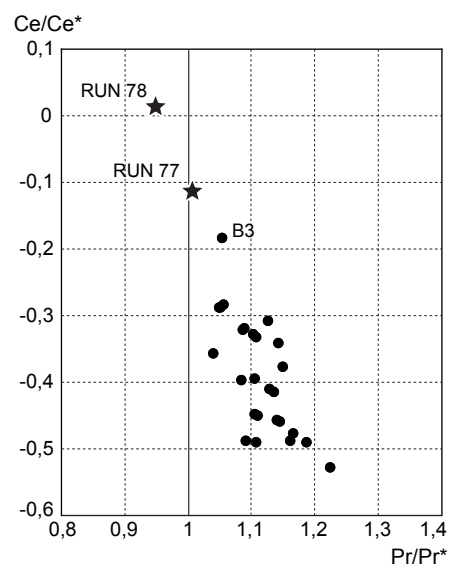
V (ppm)

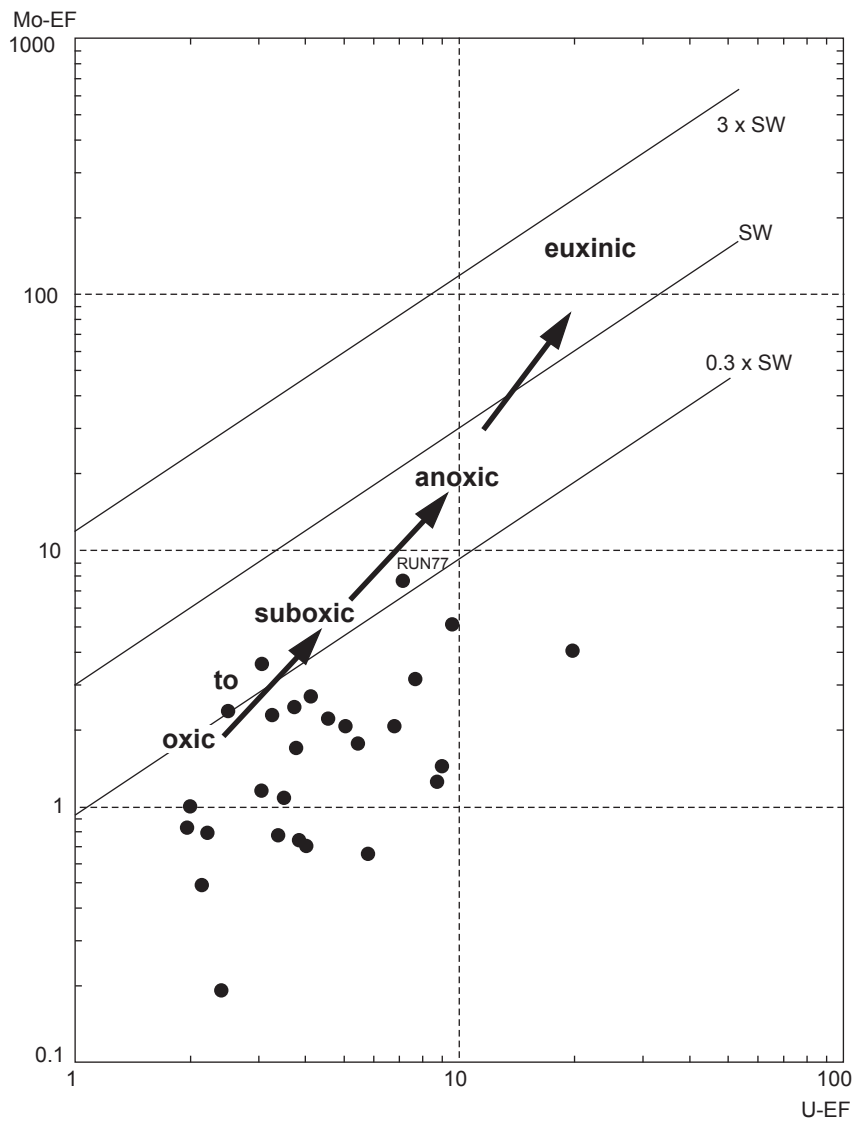


Mo (ppm)









Locations / sections	Samples	Al ₂ O ₃ (wt %)	Fe ₂ O ₃ (wt %)	MnO (wt %)	TiO ₂ (wt %)	K ₂ O (wt %)	MgO (wt %)	CaO (wt %)	CaCO ₃ (wt %)	Na ₂ O (wt %)	Th (ppm)	U (ppm)	V (ppm)	Cr (ppm)	Co (ppm)	Ni (ppm)	Cu (ppm)	Zn (ppm)	Sr (ppm)	Zr (ppm)	Mo (ppm)	Cd (ppm)	Sb (ppm)	Ba (ppm)	Al (wt %)	U-EF	Mo-EF	U xs (ppm)	Mo xs (ppm)
CS/Do	DO6 4B	1,13	0,08	0,17	0,01	0,07	2,96	48,87	81,45	0,02	0,55	0,63	3,82	7,79	1,29	8,54	6,76	13,43	552,60	5,52	0,41	0,08	0,098	21,75	0,60	3,0	3,6	0,4	0,3
	DO6 3	0,71	0,07	0,10	0,01	0,05	0,79	52,07	86,79	0,02	0,39	0,54	2,71	7,23	1,00	9,15	10,95	11,82	765,12	4,18	0,19	0,09	0,193	15,29	0,38	4,1	2,7	0,4	0,1
	DO6 2A	2,20	0,09	0,04	0,01	0,12	0,77	48,23	80,38	0,03	1,08	1,24	7,51	12,11	1,62	12,95	11,76	28,38	614,75	9,95	0,25	0,29	0,320	42,89	1,16	3,1	1,2	0,8	0,0
CS/B	B 3	3,20	0,15	0,06	0,03	0,18	6,36	35,39	58,98	0,05	1,91	1,91	14,65	24,91	3,15	33,95	24,88	21,40	478,22	27,85	0,73	0,25	0,577	55,96	1,70	3,2	2,3	1,3	0,4
	B 99-4	1,59	0,10	0,02	0,01	0,10	1,07	47,02	78,37	0,03	0,90	0,73	5,97	22,85	1,47	36,91	1421,99	41,29	968,09	10,61	0,37	5,80	0,550	37,93	0,84	2,5	2,4	0,4	0,2
CS/L	L 2	2,08	0,10	0,11	0,01	0,09	0,64	46,90	78,16	0,02	1,27	1,31	8,30	13,74	2,24	17,41	15,14	23,22	888,09	14,89	0,16	0,15	0,317	43,12	1,10	3,4	0,8	0,9	0,0
	L 3B	1,61	0,10	0,10	0,01	0,08	0,64	49,12	81,87	0,03	0,85	1,10	7,16	13,92	2,00	16,09	14,74	24,08	827,76	13,09	0,27	0,13	0,407	31,02	0,85	3,7	1,7	0,8	0,1
CG/Daw	DAW 104	0,72	0,07	0,07	0,01	0,03	0,54	53,64	89,39	0,01	0,23	1,27	5,11	7,31	1,19	9,54	8,84	10,30	524,19	6,62	0,37	0,07	0,133	17,65	0,38	9,5	5,2	1,1	0,3
	DAW 102	0,23	0,05	0,06	0,00	0,02	1,18	54,59	90,98	0,01	0,12	0,79	2,01	5,30	0,72	10,16	5,86	10,78	316,60	2,75	0,09	0,06	0,114	7,61	0,12	19,0	4,1	0,8	0,1
CG/Daj	PAJ 45	0,77	0,08	0,10	0,01	0,04	2,05	52,52	87,53	0,02	0,34	0,77	4,13	8,20	1,35	11,42	15,98	15,26	387,23	7,72	0,14	0,09	0,234	16,32	0,41	5,4	1,8	0,6	0,1
	PAJ 39	0,71	0,07	0,05	0,02	0,04	3,40	51,37	85,62	0,02	0,37	0,88	3,34	7,28	1,18	14,22	33,58	18,56	443,47	6,28	0,14	0,07	0,155	17,29	0,38	6,8	2,1	0,8	0,1
	PAJ 38	0,44	0,06	0,03	0,00	0,03	1,92	54,31	90,52	0,01	0,18	0,62	2,46	14,64	0,94	11,23	6,54	10,26	359,92	4,57	0,14	0,06	0,153	10,51	0,23	7,7	3,1	0,5	0,1
	PAJ 37	1,32	0,07	0,05	0,02	0,06	5,52	45,60	76,00	0,02	0,47	0,84	5,86	9,63	1,32	14,45	22,66	16,22	388,44	8,83	0,14	0,11	0,389	22,85	0,70	3,4	1,1	0,6	0,0
CG/R	RUN 78	1,77	0,12	0,98	0,02	0,07	5,92	41,52	69,20	0,06	1,11	1,63	10,96	14,86	7,47	18,62	25,10	53,94	470,89	15,34	0,36	0,16	0,327	44,12	0,94	5,0	2,1	1,3	0,2
	RUN 77	1,11	0,13	0,75	0,01	0,04	6,43	41,09	68,48	0,03	0,56	1,45	6,00	9,42	6,73	14,72	14,61	21,88	449,90	10,06	0,84	0,11	0,287	29,12	0,59	7,1	7,7	1,2	0,7
	RUN 73	0,94	0,07	0,06	0,01	0,04	1,83	50,48	84,13	0,02	0,41	0,64	4,39	8,45	1,12	9,79	9,62	23,08	373,08	6,77	0,23	0,09	0,175	19,27	0,50	3,7	2,5	0,5	0,1
	RUN 70	1,42	0,08	0,04	0,01	0,07	3,32	45,22	75,36	0,02	0,76	1,04	5,62	10,80	1,46	12,42	11,75	18,22	428,61	9,82	0,10	0,10	0,189	34,68	0,75	4,0	0,7	0,8	0,0
	RUN 63	1,25	0,08	0,03	0,01	0,06	4,08	44,06	73,44	0,02	0,76	1,04	4,99	9,70	1,33	13,33	16,53	15,75	427,65	8,37	0,28	0,09	0,178	32,16	0,66	4,5	2,3	0,8	0,2
H/G	SG 08 20	1,22	0,07	0,01	0,01	0,05	0,44	49,42	82,37	0,03	0,35	0,44	3,55	9,35	1,05	11,08	20,69	48,34	822,31	4,00	0,12	0,08	0,189	25,57	0,65	2,0	1,0	0,2	0,0
	SG 08 18	1,23	0,08	0,01	0,01	0,05	0,51	47,69	79,48	0,03	0,41	0,50	3,46	9,78	1,05	10,58	10,62	10,01	715,14	4,16	0,06	0,05	0,202	29,73	0,65	2,2	0,5	0,3	0,0
	SG 08 14	1,07	0,08	0,01	0,00	0,05	0,68	47,97	79,95	0,02	0,34	0,45	3,09	10,36	1,18	9,91	5,88	8,93	725,50	3,92	0,09	0,05	0,225	25,11	0,56	2,3	0,8	0,3	0,0
	SG 08 09	1,55	0,09	0,01	0,01	0,07	0,50	48,39	80,65	0,04	0,46	0,58	4,25	10,42	1,04	10,32	10,19	10,96	1147,77	4,49	0,13	0,07	0,353	34,76	0,82	2,0	0,8	0,3	0,0
	SG 08 03	4,24	0,08	0,02	0,02	0,16	0,64	38,50	64,16	0,09	1,43	1,93	11,09	22,42	1,49	16,07	8,39	24,67	1169,10	9,95	0,08	0,12	0,334	94,88	2,25	2,5	0,2	1,2	0,0
T/CD	S8	0,87	0,07	0,03	0,00	0,02	1,91	53,95	89,92	0,01	0,57	1,36	1,67	5,97	0,89	5,19	2,86	13,86	358,14	6,03	0,11	0,09	0,097	16,49	0,46	8,5	1,3	1,2	0,0
	S3	1,09	0,08	0,03	0,00	0,03	1,49	51,65	86,08	0,01	1,06	0,77	2,23	7,47	0,92	6,28	5,19	16,51	295,95	8,64	0,08	0,15	0,115	21,54	0,57	3,9	0,7	0,6	0,0
	S2	0,68	0,07	0,01	0,00	0,02	0,38	57,07	95,12	0,02	0,27	1,10	1,67	6,01	0,99	6,57	3,77	16,62	1874,50	5,29	0,10	0,14	0,095	14,72	0,36	8,7	1,5	1,0	0,0
	S1	1,08	0,07	0,01	0,00	0,03	0,40	55,91	93,18	0,02	0,51	1,14	2,06	6,96	1,13	6,45	2,06	14,72	1682,22	8,20	0,07	0,11	0,129	23,83	0,57	5,7	0,7	0,9	0,0

Locations / sections	Samples	La (ppm)	Ce (ppm)	Pr (ppm)	Nd (ppm)	Sm (ppm)	Eu (ppm)	Gd (ppm)	Tb (ppm)	Dy (ppm)	Ho (ppm)	Er (ppm)	Tm (ppm)	Yb (ppm)	Lu (ppm)	Ce/Ce*	Eu/Eu*	(La/Lu)N	(La/Sm)N	(Gd/Yb)N	Pr/Pr*
CS/Do	DO6 4B	5,16	7,183	1,220	5,153	1,246	0,253	0,995	0,153	0,853	0,180	0,536	0,057	0,377	0,062	-0,34	0,07	0,95	0,60	1,60	1,14
	DO6 3	4,76	6,347	0,971	4,160	1,016	0,240	1,008	0,139	0,937	0,200	0,564	0,060	0,382	0,059	-0,32	0,12	0,92	0,68	1,60	1,09
	DO6 2A	10,16	12,225	2,133	9,619	2,104	0,473	2,193	0,336	1,949	0,421	1,216	0,125	0,819	0,143	-0,39	0,04	0,81	0,70	1,62	1,10
CS/B	B 3	8,93	16,084	2,310	10,016	1,944	0,479	1,669	0,251	1,240	0,250	0,708	0,080	0,519	0,087	-0,18	0,25	1,16	0,67	1,95	1,05
	B 99-4	7,50	10,170	1,523	6,068	1,236	0,306	1,045	0,169	0,925	0,185	0,513	0,060	0,403	0,066	-0,31	0,27	1,29	0,88	1,57	1,12
CS/L	L 2	7,09	10,129	1,655	7,366	1,391	0,345	1,274	0,166	1,047	0,190	0,529	0,063	0,378	0,066	-0,32	0,22	1,22	0,74	2,04	1,09
	L 3B	5,35	8,114	1,272	5,801	1,192	0,294	1,128	0,154	0,951	0,178	0,517	0,062	0,379	0,070	-0,28	0,19	0,87	0,65	1,80	1,06
CG/Daw	DAW 104	4,09	5,820	0,974	4,315	0,914	0,232	0,869	0,145	0,869	0,164	0,532	0,055	0,374	0,060	-0,33	0,23	0,78	0,65	1,41	1,10
	DAW 102	3,09	3,366	0,636	2,989	0,621	0,163	0,660	0,104	0,679	0,142	0,418	0,043	0,292	0,053	-0,45	0,20	0,66	0,72	1,37	1,10
CG/Daj	PAJ 45	2,35	3,424	0,519	2,336	0,392	0,122	0,501	0,084	0,418	0,081	0,216	0,031	0,208	0,037	-0,29	0,30	0,72	0,87	1,46	1,05
	PAJ 39	3,92	4,672	0,849	3,798	0,855	0,224	0,856	0,121	0,802	0,154	0,500	0,052	0,354	0,056	-0,41	0,23	0,80	0,67	1,46	1,13
	PAJ 38	2,96	3,203	0,609	2,855	0,515	0,173	0,631	0,096	0,601	0,120	0,337	0,042	0,258	0,048	-0,45	0,43	0,70	0,83	1,48	1,11
	PAJ 37	3,79	5,233	0,859	3,729	0,849	0,201	0,813	0,128	0,782	0,174	0,496	0,057	0,370	0,059	-0,33	0,14	0,73	0,65	1,33	1,11
CG/R	RUN 78	7,93	17,751	2,052	9,076	1,987	0,530	1,960	0,265	1,552	0,312	0,825	0,099	0,590	0,106	0,02	0,27	0,85	0,58	2,01	0,95
	RUN 77	5,42	10,010	1,238	5,180	1,044	0,287	1,179	0,170	0,956	0,212	0,592	0,069	0,458	0,073	-0,11	0,22	0,85	0,75	1,56	1,01
	RUN 73	4,54	6,022	1,093	4,751	1,072	0,263	0,922	0,158	1,010	0,182	0,577	0,067	0,405	0,079	-0,38	0,25	0,65	0,61	1,38	1,15
	RUN 70	6,59	6,937	1,315	5,917	1,289	0,314	1,394	0,215	1,334	0,313	0,822	0,100	0,563	0,080	-0,46	0,10	0,94	0,74	1,50	1,14
	RUN 63	10,08	9,430	2,100	9,168	2,164	0,481	2,020	0,321	1,974	0,379	1,068	0,130	0,755	0,130	-0,53	0,08	0,88	0,68	1,62	1,22
H/G	SG 08 20	6,90	7,690	1,554	7,152	1,738	0,408	1,611	0,235	1,378	0,289	0,814	0,097	0,567	0,088	-0,46	0,15	0,89	0,58	1,72	1,14
	SG 08 18	5,01	5,810	1,044	4,587	0,995	0,249	0,902	0,143	0,892	0,166	0,487	0,045	0,382	0,048	-0,41	0,24	1,18	0,73	1,43	1,14
	SG 08 14	6,57	6,605	1,337	6,045	1,388	0,312	1,363	0,187	1,143	0,219	0,624	0,074	0,430	0,070	-0,49	0,07	1,07	0,69	1,92	1,16
	SG 08 09	9,31	9,943	2,051	9,300	2,203	0,419	2,027	0,287	1,752	0,339	0,887	0,092	0,585	0,086	-0,48	-0,07	1,23	0,61	2,10	1,16
	SG 08 03	20,94	21,484	4,486	19,916	4,130	0,994	3,833	0,555	3,012	0,594	1,586	0,155	1,127	0,164	-0,49	0,18	1,44	0,74	2,06	1,19
T/CD	S8	4,93	6,643	1,149	5,678	1,071	0,331	1,029	0,120	0,838	0,171	0,367	0,042	0,266	0,044	-0,36	0,48	1,28	0,67	2,34	1,04
	S3	7,40	9,509	1,777	8,550	1,260	0,465	1,389	0,157	1,135	0,225	0,559	0,066	0,312	0,050	-0,39	0,66	1,67	0,85	2,70	1,08
	S2	4,38	4,278	0,848	4,152	0,597	0,234	0,744	0,082	0,721	0,159	0,373	0,040	0,248	0,040	-0,49	0,65	1,24	1,06	1,82	1,09
	S1	5,25	5,215	1,058	5,132	0,659	0,300	0,945	0,130	0,988	0,222	0,496	0,049	0,307	0,041	-0,49	0,79	1,44	1,16	1,86	1,10