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1     **Environmental changes across the Triassic-Jurassic boundary and coeval**  
2     **volcanism inferred from elemental geochemistry and mineralogy in the**  
3     **Kendlbachgraben section (Northern Calcareous Alps, Austria)**

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15 **Environmental changes across the Triassic-Jurassic boundary and coeval**  
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18

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20

21 **Abstract**

22 The end-Triassic extinction (ETE), one of the five largest Phanerozoic mass extinctions,  
23 is associated with rapid and severe environmental change, but existing data permit alternative  
24 models of causation. Volcanism in the Central Atlantic Magmatic Province (CAMP) has been  
25 proposed as the main trigger, but direct evidence for this linkage is scarce. To help constrain  
26 scenarios for the ETE and other Triassic-Jurassic boundary (TJB) events, we obtained a  
27 temporally highly resolved, multidisciplinary dataset from the Kendlbachgraben section in the  
28 Northern Calcareous Alps in Austria. The section belongs to the same paleogeographic unit  
29 (Eiberg Basin) and share similar stratigraphy with the recently selected base Jurassic Global  
30 Stratotype Section and Point at Kuhjoch.

31 Micromineralogic study of the topmost bed of the Rhaetian Kössen Formation revealed  
32 pseudomorphs of altered, euhedral pyroxene and amphibole crystals. Their well-faceted  
33 morphology is consistent with their origin from distal mafic volcanic ash fallout. Spherical  
34 grains were also observed in the same bed, likely representing clay-altered volcanic glass.  
35 Clay minerals of this bed include low- to medium-charged smectite and Mg-vermiculite, both  
36 typical alteration products of mafic rocks. The same bed yielded a rare earth element pattern  
37 that differs from all other levels in an enrichment of heavy REEs, hinting at some minor  
38 contribution from mafic magmatic material. These features from a layer that was deposited

39 very near to the TJB are interpreted as direct evidence of CAMP volcanism, coeval or  
40 immediately preceding the ETE and the initial negative carbon isotope anomaly.

41 The kaolinite-dominated clay mineral spectrum of the overlying boundary mudstone  
42 records intensive weathering under hot and humid greenhouse conditions. Redox-sensitive  
43 minor and trace elements do not support the development of widespread anoxia in the studied  
44 section. Although pyrite is common in several layers, framboid size indicates formation  
45 within a reductive zone, below the sediment/water interface, rather than in an anoxic water  
46 column.

47 Our data provide a direct link between uppermost Triassic marine strata and CAMP-  
48 derived material. They support scenarios where CAMP volcanism induced climate and other  
49 environmental change, which in turn triggered the ETE and that is also reflected in the carbon  
50 isotope anomalies.

51

52

53 **Keywords:** Triassic-Jurassic boundary; end-Triassic extinction; Northern Calcareous Alps;  
54 micromineralogy; rare earth elements; redox-sensitive elements

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56

## 57 **1. Introduction**

58 The Triassic-Jurassic boundary (TJB) is preceded by one of the five largest Phanerozoic  
59 biotic crises, the end-Triassic extinction (ETE) (Alroy, 2008; Raup and Sepkoski, 1982),  
60 which in turn was associated with and likely triggered by rapid and severe environmental  
61 change (Hesselbo et al., 2007). The biotic change is manifest in a pronounced loss of global  
62 diversity (Sepkoski, 1981, 1993), major turnover in several marine and terrestrial groups  
63 (Carter and Hori, 2005; Flügel, 2002; Kiessling et al., 2007; McElwain and Punyasena, 2007;

64 Olsen et al., 1987) and ecologic reorganization (McElwain et al., 2007; McGhee et al., 2004).  
65 A major perturbation of the global carbon cycle likely reflects environmental disturbances and  
66 is recorded by carbon isotope anomalies in the TJB interval, documented at numerous  
67 localities worldwide (Galli et al., 2007; Guex et al., 2004; Hesselbo et al., 2002; Pálffy et al.,  
68 2001; Ruhl et al., 2009; Ward et al., 2001). Volcanism in the Central Atlantic Magmatic  
69 Province (CAMP) has been proposed to be synchronous with and therefore considered as the  
70 trigger for concomitant environmental and biotic change (Marzoli et al., 1999, 2004; Pálffy,  
71 2003). The ETE and TJB events have been in the focus of much recent research effort, yet  
72 several questions about the trajectory and causal chain of events remain open to debate  
73 (Hesselbo et al., 2007). Significantly, the key role of CAMP volcanism in triggering the  
74 extinction has been doubted (Whiteside et al., 2007) and alternative scenarios invoking a  
75 putative extraterrestrial impact event (Olsen et al., 2002), rapid sea level changes (Hallam and  
76 Wignall, 1999) or widespread marine anoxia (Hallam, 1995) have been proposed. Other  
77 possible proximate causes of the extinction include climate change, notably extreme  
78 greenhouse warming (McElwain et al., 1999; Schaller et al. 2011; Steinthorsdottir et al. 2011)  
79 and a marine biocalcification crisis (Hautmann, 2004; Hautmann et al., 2008). To further test  
80 these competing models of the TJB events, we obtained a temporally highly resolved,  
81 multidisciplinary dataset from the Kendlbachgraben section in Austria.

82       The Northern Calcareous Alps is a classical area of TJB studies and the section at  
83 Kendlbachgraben is the one with longest history of research (Golebiowski and Braunstein,  
84 1988; Hallam, 1990; Suess and Mojsisovics, 1868). The search for a Global Stratotype  
85 Section and Point (GSSP) for the system boundary generated much renewed interest in the  
86 TJB in general, and in the Austrian sections in particular. The newly selected base Jurassic  
87 GSSP at Kuhjoch (Hillebrandt et al., 2007) and the Kendlbachgraben section are both located  
88 within the Eiberg Basin (Fig. 1), now separated by 130 km, and share similar stratigraphies.

89 Thus our results reported herein have both regional and global relevance in constraining  
90 models for the ETE and TJB events.

91 The Kendlbachgraben section preserves a marine succession across the TJB which,  
92 together with the other well-correlated sections in the Eiberg Basin (Fig. 2), provide an  
93 excellent record of both the biotic turnover in various fossil groups and the significant  
94 changes in sedimentation (Golebiowski, 1990; Krystyn et al., 2005). The evolution of carbon  
95 isotope composition yielded a useful proxy record of environmental change (Ruhl et al.,  
96 2009).

97 Here we further explore the geochemistry and mineralogy of this section, in order to  
98 answer some of the remaining questions about the ETE and TJB events. Key issues addressed  
99 in this contribution concern climate change around the TJB in the source area of terrigenous  
100 sediment input, the redox conditions of local sedimentary environments, and detection of any  
101 volcanically-derived material in the section that might allow direct correlation with CAMP  
102 volcanic activity. Changes in humidity are inferred from major element chemistry reflecting  
103 detrital input, variations in clay mineralogy and enrichment in immature terrigenous  
104 components. Development of oxygen deficient conditions is tracked on the basis of redox-  
105 sensitive trace elements and distribution of pyrite. Clues of contemporaneous volcanism are  
106 sought in the rare earth elements (REE) abundance patterns and the micromineralogical  
107 spectrum.

108

## 109 **2. Geological setting**

110 The Kendlbachgraben section is located about 30 km southeast of Salzburg and 8 km  
111 southwest of Wolfgangsee in the Osterhorn Range in Salzkammergut, Austria. Access is via a  
112 forest road in the Zinkenbach valley. The studied section is exposed on the steep hillside  
113 immediately above the forest road (coordinates 47° 41' 21"N, 13° 21' 37"E), only ~300 m NW

114 from the point where the road crosses the gully which exposes the classical, long-known  
115 Kendlbachgraben section. The stratigraphic significance of this locality for the Triassic-  
116 Jurassic boundary was first recognized by Suess and Mojsisovics (1868). Modern studies  
117 focussed on palynostratigraphy (Morbey, 1975), changes in facies and macrofauna  
118 (Golebiowski and Braunstein 1988; Golebiowski 1990), and carbon isotope stratigraphy  
119 (Hallam and Goodfellow, 1990; Morante and Hallam, 1996; Ruhl et al., 2009).

120         The Kendlbachgraben section is located within the Eiberg Basin, an elongated, Late  
121 Triassic–Early Jurassic intraplateau basin on the shelf of the western Neotethys. Correlative,  
122 stratigraphically closely similar, and well studied sections elsewhere in the presently east-west  
123 trending, 200 km long and 20 km wide Eiberg Basin include the nearby Tiefengraben  
124 (Kürschner et al., 2007), the base Jurassic GSSP at Kuhjoch (Fig. 2) and its sister section at  
125 Hochalplgraben (Hillebrandt et al., 2007; Hillebrandt and Krystyn, 2009; Bonis et al., 2009).  
126 The Kendlbachgraben section is situated in the eastern segment of the Eiberg Basin,  
127 structurally within the Osterhorn syncline, which in turn belongs to the Stauffen-  
128 Höllengebirge nappe of the northern Tirolicum unit of the Northern Calcareous Alps (Linzer  
129 et al., 1995). The Kuhjoch GSSP locality is located in the western Eiberg basin, now  
130 preserved within the Karwendel syncline. Both sections are thought to represent proximal  
131 basin facies, sandwiched between the extensive Dachstein platform and its platform margin  
132 reefs (preserved as the “Oberrhätkalk”) (Krystyn et al., 2005).

133         At Kendlbachgraben, the base of the section is represented by the uppermost Triassic  
134 Eiberg Member of the Kössen Formation, a dark colored, pure limestone of bioclastic  
135 wackestone texture. Our XRD measurements reveal a 98–99% calcite content, and only the  
136 remaining 1–2% is of detrital and organic origin. The topmost Rhaetian conodont *Misikella*  
137 *posthernsteini* is reported from the highest limestone bed (Golebiowski and Braunstein,  
138 1988).

139           The transition at the formation boundary is represented by a 5 cm thick marlstone  
140 layer, overlain by 5 cm of brown claystone, yielding bivalves (e.g. *Cardinia*, *Chlamys*)  
141 (Golebiowski and Braunstein, 1988) and fish scales. The initial negative carbon isotope  
142 anomaly was detected at this level (Ruhl et al., 2009). The basal part of the overlying  
143 Kendlbach Formation is the ~2.5 m thick clay-rich boundary mudstone (“Grenzmergel” in the  
144 traditional terminology) which forms the basal part of the Tiefengraben Member. Early claims  
145 of a broad negative carbon isotope anomaly in this unit (Hallam and Goodfellow, 1990) were  
146 withdrawn on the basis of diagenetic overprint (Morante and Hallam, 1996). Higher upsection  
147 the Tiefengraben Member is composed of intercalated beds of marl and impure limestone, in  
148 turn overlain by the carbonate-dominated Breitenberg Member. Stable carbon isotope  
149 stratigraphy, in agreement with lithostratigraphy, permits good correlation with the GSSP  
150 section at Kuhjoch and suggests placement of the TJB in the middle of the Tiefengraben  
151 Member, where the main negative carbon isotope anomaly starts at ~3 m above the formation  
152 boundary (Ruhl et al., 2009).

153

### 154 **3. Material and methods**

155           A suite of 59 samples was collected from the section for whole rock major- and trace  
156 element analyses. The topmost layer of the Kössen Formation was sampled in duplicate  
157 (KBL-0 and KB-1) at different times and analyzed in different batches. Samples KB-2 and  
158 KB-3 originate from the first two layers immediately overlying the Kössen Formation,  
159 whereas 11 closely spaced samples represent the “Grenzmergel”, the boundary mudstone.  
160 One sample was taken from each of the 5 to 40 cm thick individual layers of the overlying 9.5  
161 m of alternating shale-marlstone and limestone lithologies of the Kendlbach Formation,  
162 except for the thickest (80 cm) marlstone interlayer which provided samples KB-31 and KB-  
163 32. From this part of the section, a total of 30 samples are from limestone beds (sample



164 numbers prefixed KBL), whereas 28 samples are from shale or marlstone (prefixed KB). A  
165 subset of selected samples was further subjected to mineralogical analyses.

166 Chemical analyses were carried out at the Acme Analytical Laboratories Ltd.,  
167 Vancouver, Canada. Total abundance of major oxides and several minor elements (Si, Al, Fe,  
168 Ca, Mg, Na, K, Mn, Ti, P, Cr) is reported on the basis of 0.2 g samples analyzed by  
169 inductively-coupled plasma optical emission spectrometry (ICP-OES) following a lithium-  
170 metaborate/tetraborate fusion and dilute nitric digestion. Loss on ignition (LOI) was  
171 determined by weight difference after ignition at 1000°C. Total carbon and sulphur analysis  
172 were done on a Leco instrument. Rare earth (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm,  
173 Yb, Lu) and refractory elements (Ba, Be, Co, Cs, Gd, Hf, Nb, Rb, Sc, Sn, Sr, Ta, Th, U, V,  
174 W, Y, Zr) were determined by inductively-coupled plasma mass spectrometry (ICP-MS)  
175 following lithium-metaborate/tetraborate fusion and nitric acid digestion of a 0.2 g sample  
176 (using the same decomposition as for major oxides). In addition, a separate 0.5 g split was  
177 digested in aqua-regia and analysed by ICP-MS to report the precious (Ag, Au, Cu) and base  
178 metals (As, Bi, Cd, Hg, Mo, Ni, Pb, Sb, Se, Tl, Zn).

179 From the analysed elements the following were under the detection limit (given in  
180 parentheses): Ag (0.1 ppm), Au (0.5 ppb), Hg (0.1 ppm), Se (0.5 ppm) and Tl (0.1 ppm).  
181 Concentrations of Be (1 ppm), Bi (0.1 ppm), Cd (0.1 ppm), Mn (100 ppm) and Sn (1 ppm)  
182 were near their detection limit.

183 REE were normalized to the C1 chondrite (Anders and Grevesse, 1989). The cerium  
184 anomaly was quantified using the following equation:  $Ce/Ce^* = Ce_N / (La_N \cdot Pr_N)^{0.5}$ , where  
185 subscript  $N$  indicates the C1 chondrite normalized value (Anders and Grevesse, 1989). To  
186 detect if any La enrichment occurred which may have caused an artefact in the Ce curve, we  
187 calculated the  $Pr/Pr^*$  ratios, where  $Pr/Pr^* = Pr_N / (0.5 \cdot Ce_N + 0.5 \cdot Nd_N)$  (Bau and Dulski, 1996).

188 Scanning electron microscopy (both energy-dispersive spectroscopy (EDS) and  
189 backscattered electron microscopy (BSE)) was carried out in polished sections from six  
190 limestone samples, using a JEOL JXA-8600 Superprobe electron microscope (15 kV, 15 nA)  
191 at the Institute of Mineralogy and Geology, University of Miskolc.

192 Micromineralogy studies focused on sample KB-1. After dissolving the carbonate with  
193 5 wt% acetic acid, the >45  $\mu\text{m}$  fraction was sieved and the grains were inspected and picked  
194 under a stereo-microscope. To investigate the altered pyroxenes, amphiboles and clay  
195 spherules of the sample, scanning electron microscopy and EDS measurements were done in  
196 two laboratories. Secondary electron (SE) images were captured on a Hitachi S-4800 electron  
197 microscope (20 kV, 10  $\mu\text{A}$ ) at BAY-NANO (Miskolc). EDS and BSE images were obtained  
198 at the Department of Metallurgy, University of Miskolc, using an AMRAY-1860 T6  
199 instrument (25 kV, 1–2 nA).

200 Whole rock mineral composition was determined and clay mineral investigations,  
201 including X-ray powder diffraction (XRD) measurements were done at the Institute of  
202 Mineralogy and Geology, University of Miskolc. The analyses were performed on a Bruker  
203 D8 Advance X-ray powder diffractometer (Bragg-Brentano geometry, Cu tube at 40kV and  
204 40mA,  $2^\circ$ – $65^\circ$  ( $2\theta$ ),  $0.04^\circ$  step scanning, 2 sec/step counting time, secondary graphite  
205 monocromator, fixed slit system of 0.6 mm primary-, 0.6 mm secondary- and 0.2 mm  
206 detector-slits, horizontal sample position, rotating sample holder), analyzed with EVA data  
207 handling program of the Bruker *DiffracPlus* evaluation software package, full profile fitting,  
208 and a semi-quantitative method. Mineral species were identified based on the PDF2 (2005)  
209 database, except for clay minerals. Semi-quantitative evaluation was performed only after the  
210 identification of clay minerals by diagnostic procedures (Zajzon et al., in press).

211

## 212 **4. Results**

## 213 **4.1. Major element geochemistry**

214 Changes in the ratio of terrigenous siliciclastic components are traceable through the  
215 analysis of Si, Al and CO<sub>3</sub> (Table 1). The two dominant detrital phases are quartz and clay  
216 minerals. The sum of SiO<sub>2</sub>+Al<sub>2</sub>O<sub>3</sub> is taken to represent the quantity of the siliciclastics,  
217 whereas the amount of clay minerals is tracked by Al<sub>2</sub>O<sub>3</sub>. Changes in the ratio of clay  
218 minerals and detrital quartz are thus reflected in the SiO<sub>2</sub> vs. Al<sub>2</sub>O<sub>3</sub> curve (Fig. 3).

219 Above the limestone beds of Kössen Formation, in the boundary mudstone, the detrital  
220 component increases abruptly and significantly, and reaches a maximum in sample KB-4.  
221 From here its amount gradually decreases upsection. The clay content is also highest in the  
222 boundary mudstone, and higher up quartz becomes more abundant among the detrital  
223 components.

224 The iron content is the lowest (0.07 wt% Fe<sub>2</sub>O<sub>3</sub>) in the pure limestones of the Kössen  
225 Formation. The other limestone interbeds higher in the section contain around 0.5 wt% Fe<sub>2</sub>O<sub>3</sub>.  
226 Much higher Fe content, typically between 3–4 wt%, is registered in the boundary mudstone  
227 (with peak values of 5.29 and 5.78 wt% in samples KB-4 and KB-8, respectively). The  
228 Jurassic marl interbeds usually contain 2–3 wt% Fe<sub>2</sub>O<sub>3</sub>.

229 The sulfur content in the section is low, except for the lower part of boundary  
230 mudstone and two other marl layers which contain more than 0.5 wt%. The sulfur content and  
231 partly also the iron in the samples is hosted by the pyrite and gypsum phases.

232

## 233 **4.2. Redox-sensitive minor and trace elements**

### 234 *4.2.1. Redox-sensitive elements*

235 The redox-sensitive elements such as Mo, Cd, V, U, Mn and other chalcophile  
236 elements (As, Sb, Sn and Cu) tend to concentrate in reducing environments in the form of  
237 sulphides or are absorbed in organic compounds (Berner, 1971; Calvert, 1976, Dolenc et al.,

238 2001). To filter out the dilution effect of the carbonate fraction on the signal, the measured  
239 values were normalized to Th, which is regarded as an element of the terrigenous component  
240 not controlled by the redox state of the depositional environment. Concentration of the redox-  
241 sensitive elements remain low throughout the section (Table 1, Fig. 4). Enrichment in these  
242 elements occurs only in the lowermost 10 cm of the boundary mudstone (samples KB-1, 2  
243 and 3).

244

#### 245 **4.2.2. U/Th ratio**

246 Although uranium and thorium are similar elements, their behavior is different in  
247 reducing and oxidative environments. Thorium is not sensitive to the redox conditions,  
248 whereas uranium is precipitated and concentrated only in reducing regimes. Oxidative bottom  
249 waters cause U to remain dissolved, hence the sediment would become depleted with respect  
250 to U. The PAAS („Post-Archean Australian Shale” standard, thought to represent the upper  
251 continental crust) has a U/Th value of 0.26 (McLennan, 1989), whereas that of the C1  
252 chondrite is 0.27 (Anders and Grevesse, 1989). Generally, a U/Th ratio > 0.5 is taken to signal  
253 anoxic environment (Adams and Weaver, 1958; Fisher and Wignall, 2001; Myers and  
254 Wignall, 1987). The U/Th ratio remains low in most of the studied section, except between  
255 the samples KBL-K2 and KB-3, where it increases up to 8.5. Significantly, most of the ~2 m  
256 thick boundary mudstone, except for its lowermost part, yielded consistently low U/Th  
257 values. High values return only in the upper part of the studied section, where the U/Th ratio  
258 in several limestone layers (KBL-25, 26, 28) exceeds 2.

259

#### 260 **4.2.3. Cerium anomaly**

261 Several studies demonstrated that the redox sensitivity of Ce is a useful indicator of  
262 paleoceanographic conditions (DeBaar et al., 1985, 1988; Elderfield, 1988; German et al.,

263 1995; Hu et al., 1988; Sholkovitz and Schneider, 1991; Schijf and DeBaar, 1995; Dolenc et  
264 al., 2001). The abundance of Ce of the carbonate phase in carbonate rocks directly reflects the  
265 Ce concentration of the seawater, which in turn is a good indicator of the redox state of the  
266 environment. Cerium enters the ocean in its soluble, trivalent state but under oxic bottom  
267 water conditions, Ce becomes relatively depleted, as its oxidized form, Ce(IV) is quickly  
268 precipitated from the water (Elderfield, 1988; Dolenc et al., 2001), causing a negative Ce  
269 anomaly in the REE pattern of the marine carbonates (Dolenc et al., 2001; Hu et al., 1988).  
270 However, under anoxic conditions, the behavior of Ce will be similar to other trivalent REE.  
271 Thus in the REE pattern of the carbonate phase no pronounced negative Ce anomaly will be  
272 visible, resulting a largely flat REE pattern (Dolenc et al., 2001). This can be represented  
273 with the Ce/Ce\* ratio.

274 In the studied section the Ce/Ce\* curve shows an opposite redox signal to the minor  
275 redox sensitive elements (Fig. 4). REE measurements could only be performed in the whole-  
276 rock samples, not in the separated carbonate fractions. In this case the terrigenous REE  
277 content is more dominant in the signal than the carbonate REE, which can be seen in the  
278 three-four times higher  $\sum$ REE of the marls, compared to the carbonates. The Ce-depletion is  
279 explained by the dissolution of Ce from the terrigenous component, and staying in the anoxic  
280 sea-water, causing an opposite pattern to that seen in the carbonate fraction.

281 The Ce/Ce\* is around 0.9 in the marls and 0.75 in the limestone beds. The difference  
282 between them is coming from the different terrigenous/carbonate ratio. The carbonate fraction  
283 contains a more depleted value, which suggests oxygenated bottom water in the section.  
284 Samples from the Kössen Formation yielded more depleted values (0.5) than the Kendlbach  
285 Formation limestones, which is explained by the higher carbonate content, and also reflects  
286 oxygenated water. The only samples which deviate from this trend are KB-1, 2 and 3. Even

287 though they have lower carbonate content than KBL-K3 and 2, they have more depleted  
288 Ce/Ce\* values (0.33–0.36).

289 To check if the Ce/Ce\* value is not an artifact of positive La enrichment, the Pr/Pr\*  
290 value was calculated (Bau and Dulski, 1996). The values do not show La enrichment.

291

### 292 **4.3. Rare earth elements (REE)**

293 The normalized REE patterns of most samples are remarkably similar to each other  
294 and resemble a presumed typical continental source rock (Table 3, Fig. 5). Three features of  
295 the REE patterns warrant further discussion: the occasional presence of a Ce-anomaly, HREE  
296 enrichment in two samples, and the systematically lower REE content of the limestone  
297 samples as compared with the marls. The majority of the observed anomalies are confined to  
298 the basal part of the section.

299 The two stratigraphically lowermost samples (KBL-K2 and KBL-K3) from the upper  
300 part of the Kössen Formation have the lowest amount of REE, but their overall pattern is  
301 similar to that of the others. These samples are from the purest limestone with the lowest  
302 amount of terrigenous material.

303 The next layer is the topmost limestone bed of the Kössen Formation (represented by  
304 duplicate samples KBL-0 and KB-1, yielding the same results), which shows a significant  
305 HREE enrichment.

306 Sample KB-2 was obtained from the 5 cm thick marl layer directly overlying the  
307 Kössen Limestone. The abundance of REE in this sample is comparable to most others and  
308 some HREE enrichment is also present here but less pronounced than in the underlying layer.

309 Sample KB-3 is from a brown, marly layer that contains scattered fish remains (scales  
310 and bone fragments). This is reflected in the high apatite content, determined by XRPD as 4  
311 wt%, and the high concentration of P<sub>2</sub>O<sub>5</sub>, determined by whole-rock chemistry as 2.72 wt%

312 (Tables 2, 3). The presence of apatite might explain the unusual abundance of REE in this  
313 sample, 1.5–3 times higher than in most of the other marl samples, making this sample the  
314 richest in REE in the entire studied section. However, there is no HREE enrichment in this  
315 sample, contrary to samples KB-1 and KB-2.

316 Starting from sample KB-4, the REE content and REE pattern of the samples are  
317 remarkably similar to each other. The only significant difference is that the marly samples  
318 contain approximately three times more REE than the limestones. This observation agrees  
319 well with the three-to-four times higher amount of detrital terrigenous material in the marls,  
320 as calculated from the carbonate content of the samples.

321

## 322 **4.4. Mineralogy**

### 323 ***4.4.1. Mineral phases from X-ray diffraction***

324 Mineral phases were identified in 22 samples from the section using X-ray powder  
325 diffraction (XRPD). Nine samples were further investigated for an in-depth characterization  
326 of their clay mineral content, the details of which are beyond the scope of this paper and are  
327 presented elsewhere (Zajzon et al., in press). The results are summarized here in Table 3 and  
328 Fig. 3.

329 The three main components of the samples are calcite, quartz and clay minerals,  
330 beside some less abundant phases such as pyrite, feldspar, apatite, aragonite, gypsum and  
331 dolomite. The purest limestone occurs in the Kössen Formation. In the overlying boundary  
332 mudstone, the carbonate content drops to 10 wt%. Quartz, clay minerals, feldspars and pyrite  
333 appear here as phases not encountered lower in the section. The highest clay mineral content,  
334 recorded in sample KB-8, is 45 wt%.

335 The occurrence of pyrite is characteristic for the boundary mudstone, although it is  
336 also found at other levels higher in the section. The FeO content of the samples correlates

337 well with the pyrite and goethite phases. The majority of the pyrite is framboidal, as revealed  
338 by SEM, indicative of bacterial origin (see below in 4.4.3.). The oxidation of pyrite led to  
339 formation of gypsum. The alteration may have occurred either in the outcrop or later, after  
340 sample collection. Sample KB-2 contains 4 wt% fluorapatite, which is bound to the unusually  
341 abundant fish remains (bones, teeth, scales) in this layer. Sample KB-3 contains 8.4 wt% of  
342 aragonite, which likely represents the original shell material of bivalves and foraminifera.

343 The feldspar phases present are albite, sanidine and microcline. The highest amount is  
344 registered in the middle to upper part of the boundary mudstone, reaching up to 16 wt%.  
345 Sanidine occurs only in the upper part of the boundary mudstone. Dolomite appears in only  
346 two samples, accompanied in both by sanidine.

347

#### 348 ***4.4.2. Clay mineralogy***

349 In the majority of samples, illite and kaolinite are registered as the main clay minerals  
350 with subordinate smectite, and their ratios were monitored to allow environmental and  
351 paleoclimatic inferences. Sample KB-1, however, shows a peculiar clay mineral composition  
352 very different from the other samples, because it is dominated by low- to medium-charged  
353 smectite and also contains vermiculite. These clay minerals commonly represent the alteration  
354 products of mafic and/or ultramafic rocks. Upsection, in the boundary mudstone, the clay  
355 mineral distribution is characterized by kaolinite  $\geq$  illite + muscovite  $\gg$  smectite. In the  
356 higher part of the section a distinctive change in the clay mineral pattern results in illite +  
357 muscovite  $\gg$  kaolinite  $\gg$  smectite ratios. For more detail, see Zajzon et al. (in press).

358

#### 359 ***4.4.3. Scanning electron microscopy (SEM) of pyrite***

360 Six polished samples (KB-1, KBL-K3, 1, 8, 15, 26) were selected for investigation by  
361 SEM. All of these samples contain a varying amount of pyrite, which is dominantly



362 framboidal. In some of the samples only goethite pseudomorphs were observed, but their  
363 shape clearly identifies them as alteration products from pyrite. In many instances the shell of  
364 a fossil or part of a microbial mat is recognizable as the locus of pyrite formation. Pyrite also  
365 frequently occurs together with apatite. Beside the framboidal form, euhedral pyrite is also  
366 common in the samples and both varieties may occur in distinct layers. The framboids are  
367 commonly large (0.1–0.2 mm in diameter), and form structures such as mats and spheres,  
368 indicative of their formation in the sediment rather than in the water column (Wignall and  
369 Newton, 1998; Wilkin et al., 1996). Barite was also found in some layers (e.g. sample KBL-  
370 26).

371

#### 372 **4.4.4. Micromineralogy of sample KB-1**

373 To follow up on the indication of a possible mafic detrital component suggested by  
374 REE data and clay mineralogy, sample KB-1 from the topmost layer of the Kössen Formation  
375 was subjected to heavy mineral separation and SEM/EDS examination. The grain size of this  
376 micritic limestone is very fine, not more than a few wt% is above 45  $\mu\text{m}$  of the insoluble part.  
377 Possible alteration products of volcanic material were indeed detected in this sample, in the  
378 form of goethite pseudomorphs after euhedral crystals of pyroxene and amphibole, and pale-  
379 green clay spherules that may represent altered glass (Fig. 6).

380 No fresh magmatic minerals were observed, only their alteration products. Goethite  
381 pseudomorphs are common, retaining the original shape of abundant pyroxene and  
382 subordinate amphibole crystals. These elongated grains are 0.1–0.2 mm in length, and the  
383 original crystal shape, the edges and facets are perfectly preserved (Fig. 6d–h). They are  
384 easily identifiable as three-dimensional grains in the acid insoluble residue. These  
385 pseudomorphs were also observed in the polished samples, where their recognition is more

386 difficult because the shape of their cross-section is less distinctive and often similar to  
387 pseudomorphs after pyrite crystals.

388 Pale green, opaque or slightly transparent grains are also present in the sample. Their  
389 shapes vary, some of them are perfectly spherical whereas others are subangular (Fig. 6a–c).  
390 Their composition, as revealed by EDS, is illite/aluminoceladonite. The shape, size and  
391 composition together suggest that these grains represent alteration products of volcanic  
392 material, the spheres and rounded particles are most suggestive of altered volcanic glass  
393 spherules.

394

## 395 **5. Discussion**

### 396 **5.1. Recorders of contemporaneous volcanism**

397 Causal relationship of the ETE and coeval carbon cycle perturbation with CAMP  
398 volcanism has been proposed by many authors (e.g. Marzoli et al. 1999, Pálffy 2003, Hesselbo  
399 et al. 2007). Support for this hypothesis is primarily provided by dating studies which have  
400 established with increasing precision and accuracy the synchrony between CAMP flood  
401 basalts (Marzoli et al., 1999, 2004; Nomade et al., 2007) and the Triassic-Jurassic boundary  
402 (Pálffy et al., 2000; Schaltegger et al., 2008; Schoene et al., 2010). However, direct  
403 stratigraphic evidence for CAMP-derived volcanic material in marine sections has been  
404 meager. Where CAMP flows or pyroclastics occur with marine sedimentary rocks e.g. in  
405 France and Morocco, precise biostratigraphic dating is hampered by a lack of age-diagnostic  
406 fossils (Olsen et al., 2003). Recent studies in terrestrial sections using palynostratigraphy  
407 (Cirilli et al., 2009) and conchostracan biostratigraphy (Kozur and Weems, 2010) demonstrate  
408 that CAMP volcanism began in the latest Triassic. Available circumstantial evidence for the  
409 onset of volcanism include the presence of potentially volcanically derived organic molecules,  
410 polycyclic aromatic hydrocarbons, from TJB sediments (van de Schootbrugge et al., 2009)

411 and increase in  $p\text{CO}_2$  detected both in pedogenic carbonates (Schaller et al., 2011) and by  
412 fossil leaf stomatal density (McElwain et al., 1999; Steinhorsdottir et al., 2011).

413 In the Kendlbachgraben section, both the pyroxene and amphibole pseudomorphs and  
414 the altered glass spherules found in the topmost Kössen Formation (sample KB-1) are  
415 interpreted as volcanic eruption products, most likely representing a distal record of CAMP  
416 eruptions. The size and the well preserved rounded original shape of the altered glass  
417 spherules suggest airborne origin and transportation. The pyroxene and amphibole crystals  
418 fall into the fine ash size range, capable of entering the upper atmosphere within the eruption  
419 plume. The well preserved crystal facets and edges rule out the possibility of even short  
420 terrestrial transportation that would have caused wear and damage of the grains. The presence  
421 of all these “exotic” grains in the pure micritic limestone are best explained as air-fall fine ash  
422 particles directly deposited in the marine sedimentary basin.

423 In agreement with the above interpretation, the clay mineral pattern of this layer is also  
424 quite different from the other samples. It contains dominantly low- to medium-charged  
425 smectite as well as Mg-dominated vermiculite. Typically, these clay minerals occur as  
426 alteration products of mafic and ultramafic rocks (Velde and Meunier, 2008; see also Zajzon  
427 et al., submitted).

428 A third line of evidence is provided by the REE distribution patterns. The same sample  
429 (KB-1) from the topmost layer of Kössen Formation differs from all other samples by a  
430 distinctive enrichment of heavy REE. Only the overlying layer (sample KB-2) shows a  
431 similar, albeit more subdued HREE enrichment. Such trace element signature, characterized  
432 by a V-shaped pattern, may be best interpreted as a mixed signal where the light REEs are  
433 derived from the sedimentary component and the enrichment in HREE is sourced from  
434 magmatic material. HREE enrichment is characteristic for mantle sources and is known to  
435 occur e.g. in N-MORB (Klein, 2003) and ultrabasic rocks (Bodinier and Godard, 2007),

436 where it is carried by mineral phases such as garnets, pyroxenes and amphiboles.

437 Pseudomorphs of the latter two minerals occur in the micromineralogical spectrum of the  
438 same sample.

439 The range of REE variation in CAMP extrusives have been reported in several studies  
440 and HREE enrichment is clearly documented by Marzoli et al. (2011) in the Preakness and  
441 Hook Mt. basalts in the Newark Basin, Sander basalt in the Culpeper basin, and the recurrent  
442 basalts in Morocco. The stratigraphic significance of this geochemical similarity to the late  
443 rather than early CAMP flows remains to be clarified.

444 To assess the feasibility of CAMP as a source of material preserved at  
445 Kendlbachgraben section, it is informative that paleogeographic reconstructions suggest an  
446 approximate distance of 2000–2500 km between northeastern CAMP eruptive centers and the  
447 marine Eiberg Basin in the western Tethys (Golonka, 2007). Volcanic particulates from  
448 eruption plumes are known to travel significant distances in downwind direction (Durant et  
449 al., 2010), as recently shown by widespread distribution of ash from the 2010 eruption of  
450 Eyjafjallajökull, clearly detected in the Alps, more than 2700 km from Iceland (Flentje et al.,  
451 2010). Climate modeling results suggest that the Eiberg basin was downwind of the CAMP at  
452 least seasonally during Pangean summers in the Triassic (Wang 2009). Therefore  
453 emplacement of CAMP-derived particles in sediments preserved at the Kendlbachgraben  
454 section appears plausible. The generally assumed quiet outpouring of flood basalts contradicts  
455 the here inferred explosive eruption, capable to produce a high eruption column necessary for  
456 long distance particle dispersal. We speculate that at least some of the CAMP volcanism may  
457 have been phreatomagmatic, where eruption fissures intersected lakes in the rift basin, thus  
458 resulting in unusually explosive eruptions. Because CAMP erupted in multiple pulses, further  
459 search for volcanic signatures, perhaps below the topmost Kössen Formation, is warranted to  
460 corroborate the evidence presented herein.

461

## 462 **5.2. Climate-driven changes in detrital input and clay mineralogy**

463 A first-order change in depositional regimes in the Kendlbachgraben section is  
464 manifest in the lithostratigraphic boundary between the intraplateform basinal carbonates of  
465 the Kössen Formation and clay-rich, fine silicilastics of the boundary mudstone of the  
466 Kendlbach Formation. The abrupt change from carbonate-dominated to siliciclastic-  
467 dominated sedimentation during the latest Rhaetian may be the stratigraphic expression of  
468 several factors. These include (i) a change in weathering regime, i.e. increased influx of  
469 terrigenous material and clay under hot and humid conditions, (ii) a biocalcification crisis that  
470 triggered a shutdown of the carbonate factory due to CO<sub>2</sub> saturation (Hautmann et al., 2008),  
471 (iii) loss of carbonate production due to eutrophication, (iv) rapid sea level rise manifested  
472 within a regression-transgression couplet (Hallam and Wignall, 1999), or (v) some  
473 combination of these factors.

474 Our major element and mineral phase distribution data allow quantification of these  
475 processes. The major drop in calcite content at the Kössen/Kendlbach formation boundary is  
476 clearly shown by XRD data (Table 3) and CaO and total C concentration (Table 1). The  
477 boundary mudstone has the highest ratio of clay minerals vs. other detrital components  
478 (mainly quartz), as expressed by the Si/Al ratio (Fig. 3) and XRD data (Table 3). Therefore,  
479 the initial increase of detrital components was accompanied by peak abundance of clay  
480 minerals, marking a significant climatic signal. Sudden climate change to hot and humid  
481 conditions leading to intensification of weathering may well explain the terrestrial influx. Co-  
482 occurrence of dolomite and feldspar in two samples in the boundary mudstone (KB-6 and 13)  
483 suggests further episodic increases in terrestrial input, whereby immature detrital components  
484 could reach the depocenter. The amount of the siliciclastic detritus decreases upsection,

485 reflecting either a decrease in humidity and/or transgression and increasing distance from  
486 terrigenous source areas.

487 Clay minerals are well-known indicators of climate. In the boundary mudstone the  
488 clay mineral composition is kaolinite  $\geq$  illite + muscovite  $\gg$  smectite > chlorite. The  
489 predominance of kaolinite is commonly interpreted to suggest humid climate and intensive  
490 terrigenous input. Similar data are known from other TJB sections. Ahlberg et al. (2003)  
491 report a kaolinite  $\approx$  illite  $\gg$  chlorite and smectite (I/S) clay pattern from Rhaetian-Hettangian  
492 terrestrial sedimentary successions, and kaolinite  $\approx$  illite > variable smectite  $\gg$  chlorite  
493 pattern from shallow marine deposits (Höganäs Formation) in southern Sweden. These  
494 authors concluded that the original detrital composition was better preserved in the shallow  
495 marine settings and infer warm, humid conditions and intense weathering. High amounts of  
496 kaolinite are also reported from the topmost Triassic *Triletes* beds in Germany, interpreted to  
497 reflect strongly leached soils that become enriched in aluminium (van de Schootbrugge et al.,  
498 2009). A pronounced increase in kaolinite also characterizes the TJB in sections of the Tatra  
499 Mts. (Slovakia), where a climatic driver was similarly invoked (Michalík et al., 2010).

500 Higher up in the Kendlbachgraben section, above the boundary mudstone, the clay  
501 mineral pattern changes to illite + muscovite  $\gg$  kaolinite  $\gg$  smectite, which corresponds to a  
502 less humid and less hot climate. Therefore our results suggest that the extreme greenhouse  
503 conditions around the TJB were initially forced by volcanic CO<sub>2</sub> degassing but had a limited  
504 temporal extent, which nevertheless coincided with the ETE and the onset of both the initial  
505 and main negative carbon anomalies.

506

### 507 **5.3. Changes in redox conditions**

508 Marine anoxia often accompanies greenhouse climate maxima due to reduced ocean  
509 circulation, and plays a role in extinction events. Specifically, oxygen-depleted facies across

510 the TJB were noted from northwest Europe (Hallam, 1995). Although no longer a favoured  
511 scenario, this possible cause is still often considered for the end-Triassic extinction (Hallam  
512 and Wignall, 1997). However, in sections in Britain, anoxic sediments were shown to occur  
513 only above the main end-Triassic extinction horizon and initial carbon isotope excursion  
514 (Wignall and Bond, 2008). Within our dataset, the occurrence of pyrite, distribution of redox-  
515 sensitive elements, and relative abundance of Ce among the other REE permit evaluation if  
516 dysoxic or anoxic conditions developed around the TJB in the Kendlbachgraben section.

517         Peak values of Fe and S within the boundary mudstone (see 4.1.) are tied to the  
518 occurrence of pyrite, as evidenced by XRD data (Table 3). SEM analyses reveal that  
519 framboidal pyrite of large size (up to 0.1–0.2 mm in diameter) is predominant, that suggests  
520 formation within the sediment under reducing conditions (Wignall et al., 2005), but it does  
521 not require the presence of anoxic bottom water.

522         Water column oxygenation is suggested by the redox-sensitive elements, whose  
523 concentration remains low throughout the section (Fig. 4). Enrichment of these elements is  
524 most pronounced in the lowermost 10 cm of the boundary mudstone (samples KB-1, 2 and 3),  
525 which are therefore permissive of reducing environment above the sediment/water interface.  
526 However, this observation contradicts the presence of benthic bivalves, but is compatible with  
527 the abundance of fish remains and phosphate in KB-3. A second interval with a somewhat  
528 elevated concentration of redox-sensitive elements is encountered near the top of the studied  
529 section, in the early Hettangian.

530         As an independent redox indicator, the U/Th ratio remains low in most of the studied  
531 section, except between the samples KBL-K2 and KB-3, where it goes up to as high as 8.5,  
532 possibly indicating oxygen-depleted conditions during deposition of the topmost Kössen  
533 Formation and the lowermost part of the boundary mudstone. This signal is comparable to

534 that obtained by McRoberts et al. (1997) from another section in western Austria.

535 Alternatively, the U/Th ratio at this level may also be influenced by volcanic input.

536 Interpretation of changes in Ce abundance in the section is not straightforward. As  
537 analyses were carried out on bulk samples, the Ce signal of marine carbonate is mixed with  
538 that of the detrital component. Higher carbonate content is correlated with negative shifts in  
539 Ce concentration, suggesting that the marine carbonate is depleted in Ce, which in turn points  
540 to oxidative water favoring precipitation of trivalent Ce. Anoxic bottom waters are not  
541 indicated by the Ce signal.

542 In summary, widespread anoxia near the TJB is not compatible with our data; oxygen-  
543 depleted bottom water may only characterized brief intervals during the earliest phase of  
544 boundary mudstone deposition, coinciding with the temperature maximum inferred from the  
545 clay mineral climate proxy. Several other sections in the Eiberg Basin contain the red  
546 Schattwald beds immediately below the TJB; this hematite-bearing unit is a regional  
547 stratigraphic indicator of oxidized facies (Krystyn et al. 2005).

548

## 549 **6. Conclusions**

550 Our study has focused on a Triassic-Jurassic boundary (TJB) section at  
551 Kendlbachgraben in the Northern Calcareous Alps, within the same intraplateau basin as the  
552 recently selected base Jurassic Global Stratotype Section and Point. The much debated  
553 causation of the end-Triassic mass extinction (ETE) and broadly synchronous major carbon  
554 isotope excursions instigated our research. In particular, the aim of our multi-approach study  
555 was to search for stratigraphic evidence in this marine section for distant volcanism of the  
556 Central Atlantic Magmatic Province (CAMP), widely regarded as a trigger of interrelated  
557 global climatic, environmental and biotic changes. The key findings of our study are the  
558 following:



559 1) The topmost bed of the otherwise pure micritic limestone of the Rhaetian Kössen  
560 Formation contains goethite pseudomorphs of euhedral pyroxene and amphibole crystals.  
561 Such grains in this depositional environment are thought to represent distal fallout of a  
562 volcanic ash cloud.

563 2) The same bed also yielded rounded or spherical grains of illite/aluminoceladonite  
564 composition, interpreted as alteration products of airborne volcanic glass particles. Additional  
565 clay minerals restricted to this bed are low- to medium-charged smectite and Mg-vermiculite,  
566 commonly formed by alteration of mafic volcanic material.

567 3) Another characteristic feature of this bed is its enrichment in heavy rare earth elements, a  
568 pattern noted from some mantle-derived mafic volcanics and documented from several flow  
569 units of the CAMP. This set of observed features is best explained by mafic volcanic material  
570 admixed to the carbonate from distal ash fallout, likely related to a CAMP eruption.

571 4) After the deposition of this layer, carbonate sedimentation of the Kössen Formation  
572 abruptly gave way to clay-rich, terrigenous sedimentation of the boundary mudstone and the  
573 overlying alternating mudstone, marl and marly limestone beds (topmost Rhaetian to lower  
574 Hettangian Tiefengraben Member of the Kendlbach Formation). Previous authors also noted  
575 the disappearance of Triassic ammonoid and conodont faunas and the onset of the initial  
576 carbon isotope excursion at this level. Thus this local facies change is best regarded as the  
577 record of far-reaching global changes immediately preceding the TJB, at the time of the ETE.

578 5) Elemental geochemistry and clay mineralogy helped quantify the increase in terrigenous  
579 and clay mineral input at the expense of carbonate production. The lowermost 2 m of the  
580 boundary mudstone is particularly rich in kaolinite, signifying a sudden change in weathering  
581 regime possibly related to transient extreme greenhouse climate in the hinterland.

582 6) Abundant framboidal pyrite is present in the TJB interval, but its size suggests formation  
583 within the sediment rather than in an anoxic water column. Redox-sensitive minor elements

584 and Ce also fail to support widespread oxygen-depleted conditions in the marine basin. Thus  
585 anoxia does not appear to play a fundamental role in the extinction.

586 In summary, independent geochemical, micromineralogical and clay mineralogical lines of  
587 evidence provide as yet the best direct link between end-Triassic volcanism and the marine  
588 stratigraphic record, where extinction and the carbon isotope anomaly are also present. The  
589 new data provide further support for a scenario where CAMP volcanism induced climate and  
590 other environmental change which in turn triggered the ETE and is also reflected in the TJB  
591 carbon isotope anomalies.

592

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602

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831  
832

833 **Figure captions**

834

835 Fig. 1. Location of Triassic-Jurassic boundary sections at Kendlbachgraben (subject of this  
836 study) and Kuhjoch (Global Stratotype Section and Point, GSSP) within the Eiberg  
837 basin, shown on a schematic tectonic map of the Northern Calcareous Alps (modified  
838 from Hillebrandt and Krystyn, 2009).

839 Fig. 2. Stratigraphic correlation of the Kendlbachgraben section with the basal Jurassic GSSP  
840 at Kuhjoch and the Tiefengraben sections (based on data in Hillebrandt et al., 2007;  
841 Kürschner et al., 2007; Ruhl et al., 2009). The simplified lithologic logs are drawn to  
842 the same scale; white denotes limestone and calcareous marl, dark grey denotes  
843 claystone and clayey marl, including the boundary mudstone. Reddish claystone of the  
844 Schattwals beds are marked by light grey. GSSP marks the officially agreed upon  
845 level of the Triassic-Jurassic boundary in the stratotype section. ICIE: Initial carbon  
846 isotope excursion. MCIE: Beginning of the main carbon isotope excursion. Lines with  
847 arrowhead mark the first and last occurrence datum of diagnostic taxa. *C. m.*:  
848 *Choristoceras marshi*; *C. t.*: *Cerebropollenites thiergartii*; *P. s.*: *Psiloceras spelae*; *P.*  
849 *t.*: *Psiloceras tilmanni*.

850 Fig. 3. Stratigraphy, mineral composition, and Si and Al elemental geochemistry of the  
851 Kendlbachgraben section. Sampled horizons are marked and labeled along the  
852 lithologic column. Horizontal bars show carbonate content and other mineral phases  
853 from XRD. Colors (and abbreviations) for mineral phases of the samples: blue (cal)–  
854 calcite, gray (Q)–quartz, brown (cl)–clay minerals, green (F)–feldspar, black (P)–  
855 pyrite, orange (a)–apatite, red (Ar)–aragonite, pink (D)–dolomite. The curve in the  
856 same panel shows changes in the carbonate content measured by XRD or from the  
857 chemical analyses (circles). Main changes in clay mineralogy are indicated. Panel to

858 the right shows the Si/Al ratio (on logarithmic scale). Solid markers denote marl  
859 samples, open markers denote limestone samples. ICIE: Initial carbon isotope  
860 excursion. MCIE: Beginning of the main carbon isotope excursion. Line with  
861 arrowhead marks the last occurrence datum of *Choristoceras marshi* (*C. m.*).

862 Fig. 4. Stratigraphy, and minor and trace elemental geochemistry of the Kendlbachgraben  
863 section. Sampled horizons are marked and labeled along the lithologic column. Panels  
864 to the right show Th-normalized values of redox-sensitive elements (note the  
865 combined scale: bld—below detection limit, logarithmic (0.001–1), normal (1–25),  
866 value shown >25), Ce content (in ppm, upper scale, black line), and Ce/Ce\* (lower  
867 scale, purple line). Solid markers denote marl samples, open markers denote limestone  
868 samples. ICIE: Initial carbon isotope excursion. MCIE: Beginning of the main carbon  
869 isotope excursion. Line with arrowhead marks the last occurrence datum of  
870 *Choristoceras marshi* (*C. m.*).

871 Fig. 5. Chondrite-normalized REE distribution patterns (spider diagrams) from the  
872 Kendlbachgraben section. Colored lines and larger markers denote samples explained  
873 in the text and named in the legend, grey lines refer to all other limestone samples,  
874 black lines refer to all other marl samples.

875 Fig. 6. SEM photomicrographs of assumed volcanically-derived mineral grains from sample  
876 KB-1 (latest Triassic, from top of Kössen Formation). a-c – illite-aluminoceladonite  
877 spherules, presumed altered volcanic glass droplets; d-f – goethite pseudomorphs after  
878 pyroxene crystals; g-h – goethite pseudomorphs after amphibole crystals.

879

880

881 **Tables**

882

883 Table 1. Data of major and trace element chemical analyses

884 Table 2. Data of REE chemical analyses

885 Table 3. Percent abundance of mineral phases from XRD analyses

886

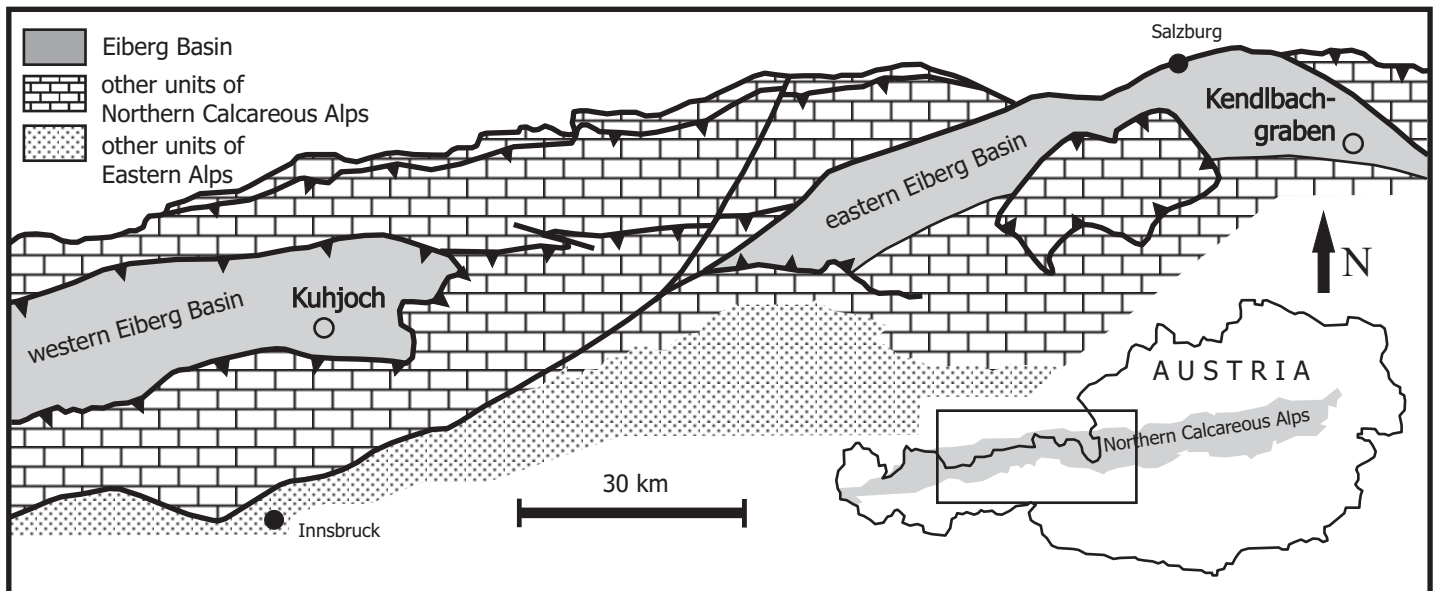
## \*Highlights

- New data from a classical Triassic-Jurassic boundary section, correlated with the GSSP
- First direct evidence for CAMP-derived material in a well-dated marine section
- Amphibole and pyroxene pseudomorphs and altered glass spherules from distal ash fall
- HREE enrichment and clay minerals also point to mantle-derived volcanic component
- Abundant kaolinite records change in weathering under extreme greenhouse climate

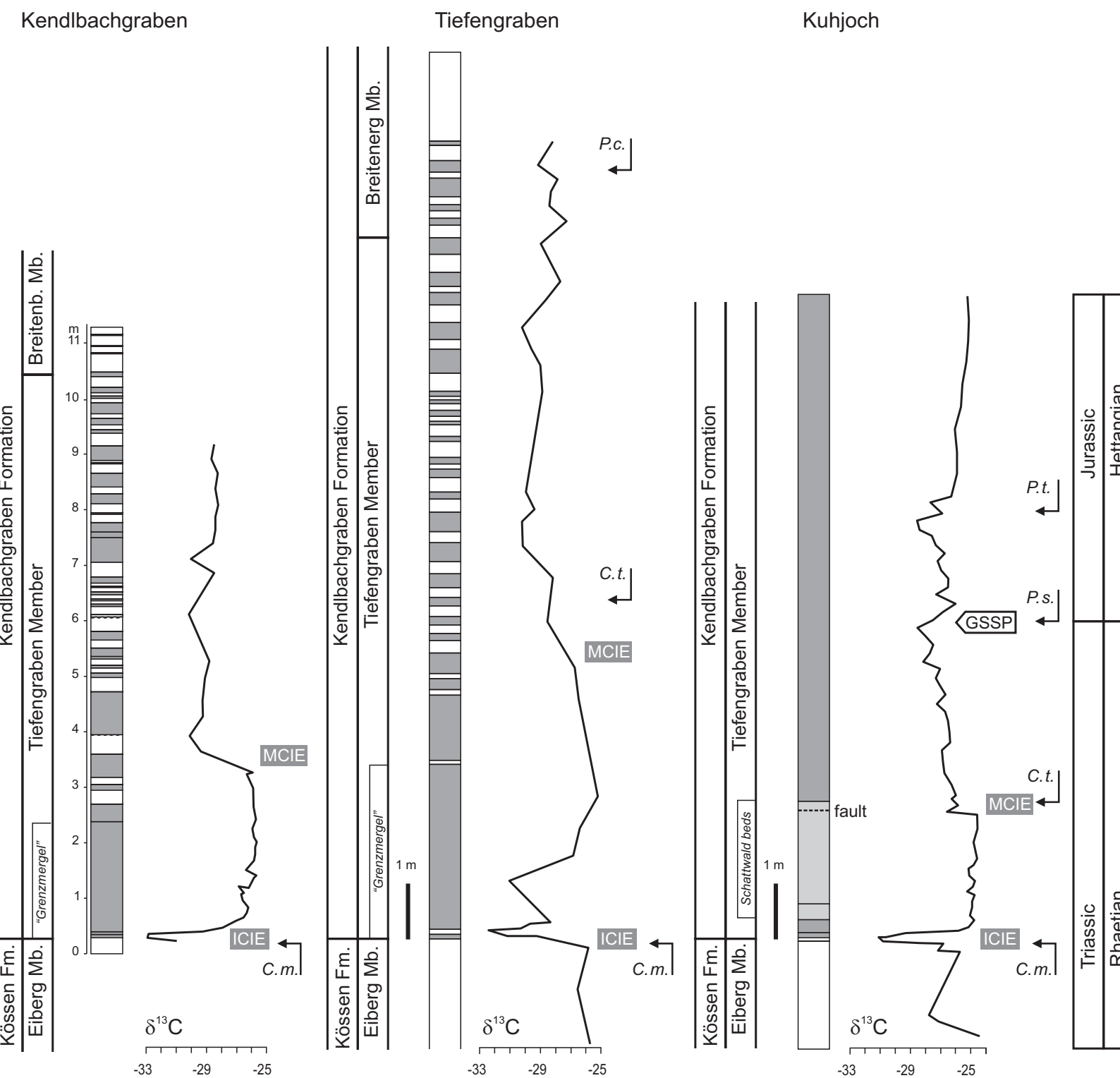


Figure 1

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**Figure 2**  
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**Figure 3**  
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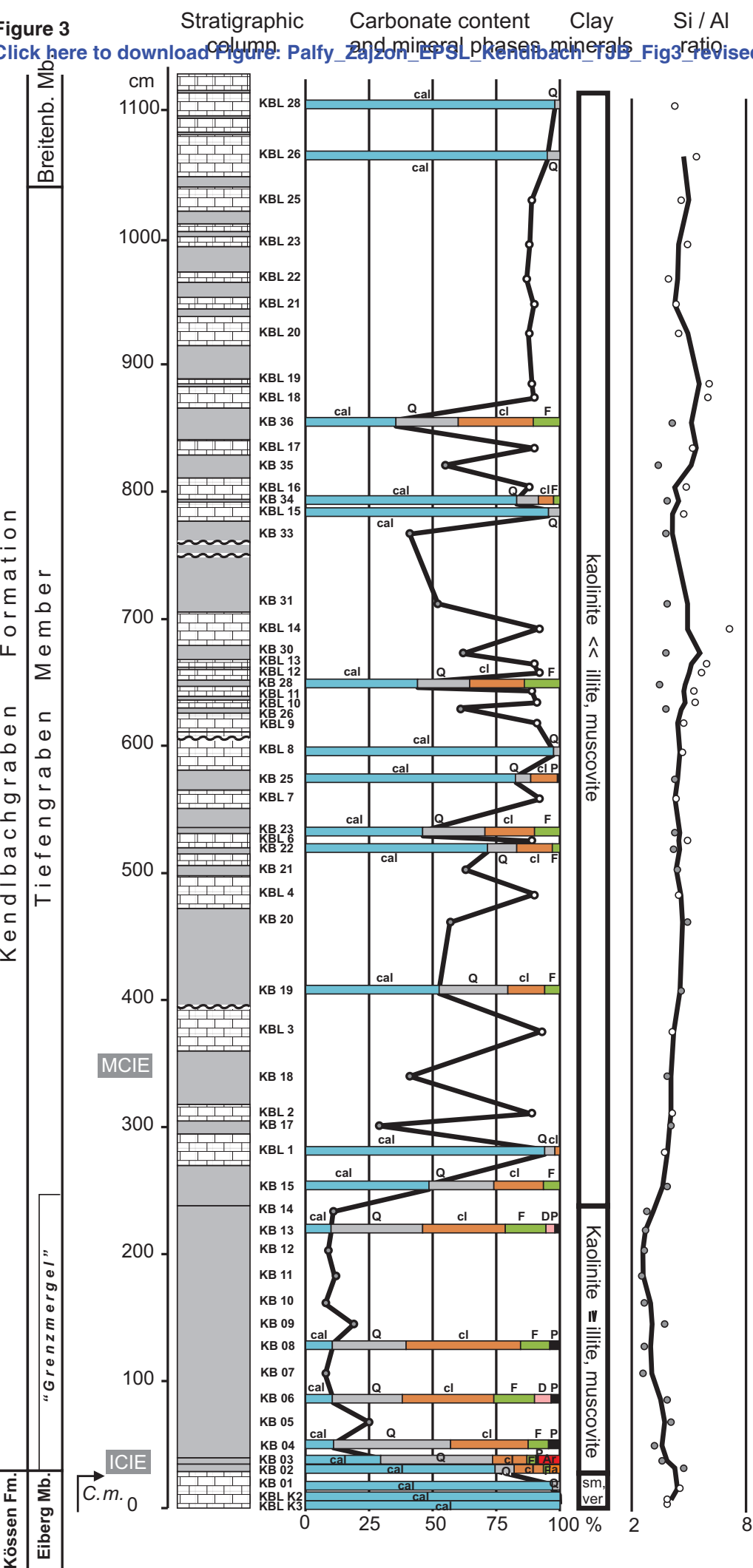


Figure 4

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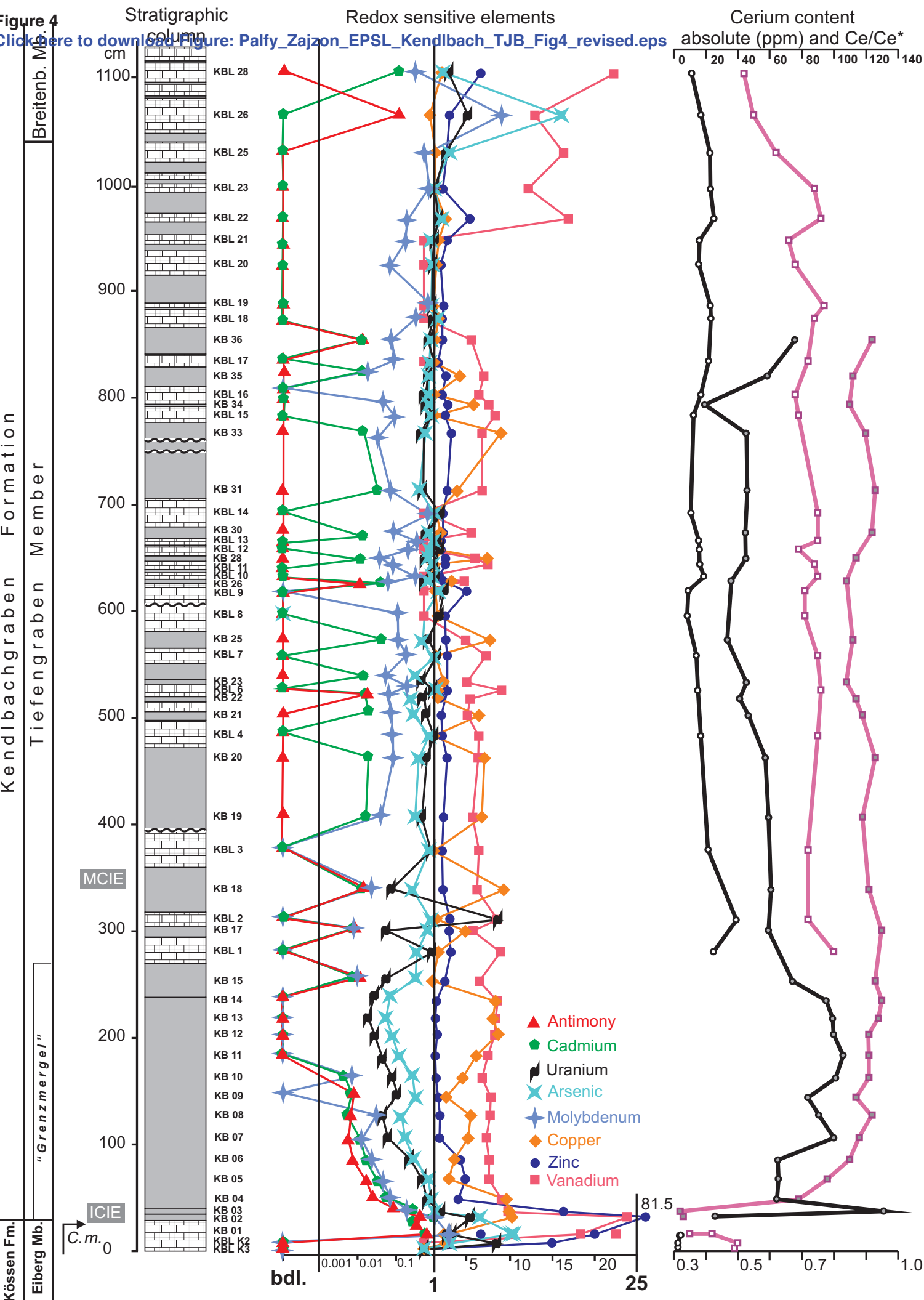
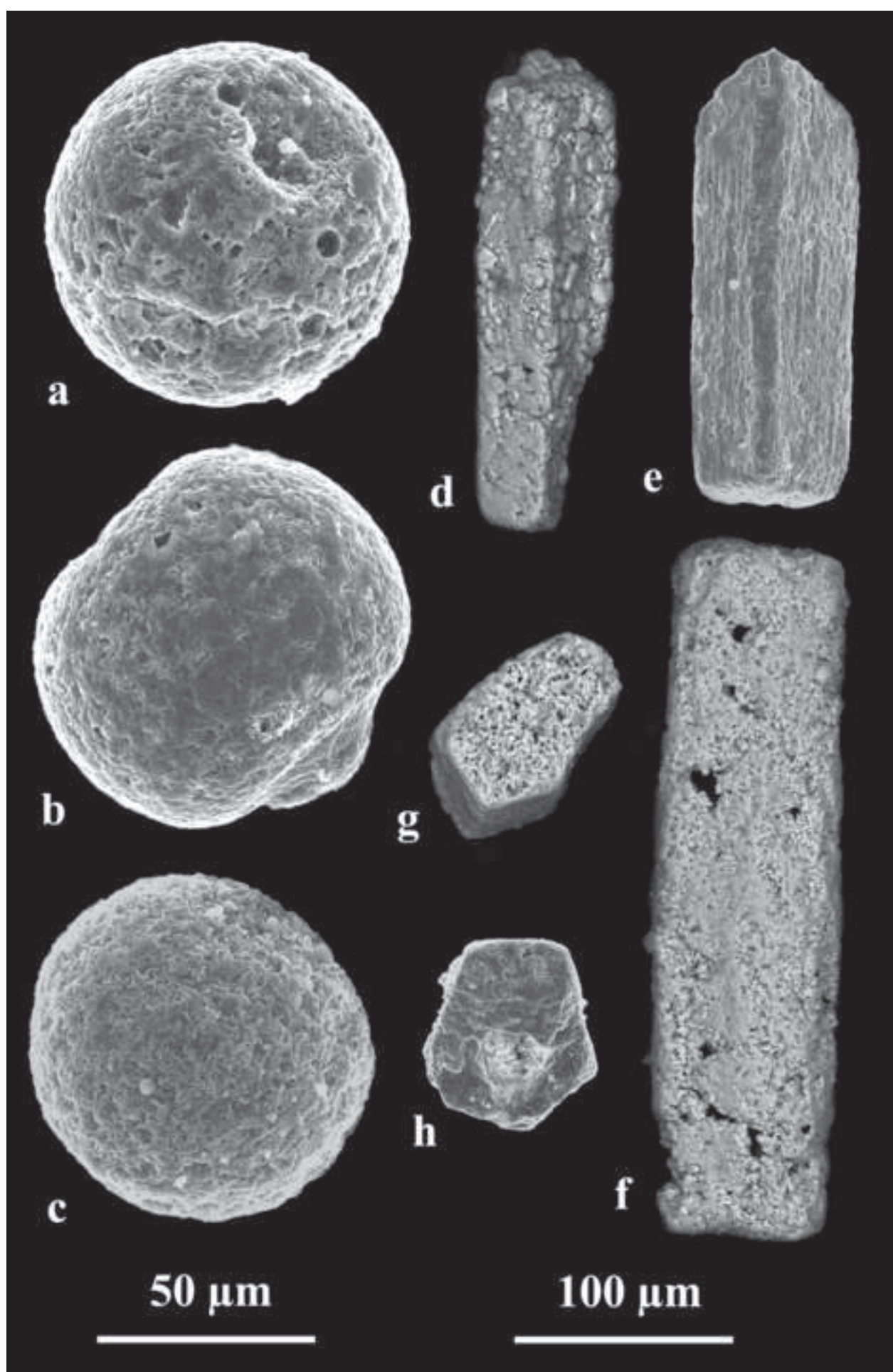




Figure 6  
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**Table 1**  
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Sample No.↓	C	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	S	CaO	Fe <sub>2</sub> O <sub>3</sub>	V	Cu	Zn	As	Mo	Cd	Sn	Sb	Th	U	LOI	Sum
	%	%	%	%	%	%	%	ppm	ppm	ppm	ppm	ppm	Ppm	ppm	ppm	ppm	ppm	%	%
det. limit→	0.02	0.01	0.01	0.001	0.02	0.01	0.04	8	0.1	1	0.5	0.1	0.1	1	0.1	0.2	0.1		
KBL-28	12.84	0.46	1.95	0.019	0.04	53.11	0.17	20	1.9	6	2.0	0.3	0.1	<1	<0.1	0.9	2.6	43.0	99.70
KBL-26	12.81	0.42	2.27	0.004	0.14	52.58	0.42	13	0.7	3	16.1	9.1	<0.1	<1	0.1	1.0	5.1	42.6	99.13
KBL-25	12.13	1.15	5.27	0.010	0.02	50.02	0.50	18	1.5	3	3.3	0.4	<0.1	<1	<0.1	1.1	2.8	41.5	99.54
KBL-23	11.79	1.32	6.53	0.037	0.22	49.16	0.62	22	2.2	4	2.2	1.0	<0.1	<1	<0.1	1.8	2.2	40.5	99.64
KBL-22	11.77	1.55	6.12	0.042	0.03	48.94	0.87	22	3.3	7	2.7	0.3	<0.1	<1	<0.1	1.3	2.2	41.1	100.02
KBL-21	11.98	1.23	5.33	0.014	0.03	50.43	0.50	<8	1.9	3	0.9	0.2	<0.1	<1	<0.1	1.1	1.3	41.7	100.27
KBL-20	11.93	1.37	6.16	0.032	<0.02	49.38	0.52	<8	2.2	3	1.5	0.1	<0.1	<1	<0.1	1.5	1.5	41.1	99.74
KBL-19	11.73	1.16	7.04	0.062	0.03	49.63	0.51	<8	1.4	3	1.1	0.6	<0.1	<1	<0.1	1.3	1.2	40.7	100.39
KBL-18	11.65	1.05	6.29	0.021	0.02	50.13	0.62	<8	2.4	3	2.2	0.4	<0.1	<1	<0.1	1.4	1.4	41.1	100.42
KB-36	7.16	7.00	28.72	0.050	0.20	29.49	2.88	41	9.3	16	6.0	0.5	0.1	1	0.1	7.4	3.5	28.4	99.96
KBL-17	11.67	1.25	6.51	0.012	0.04	50.13	0.51	<8	1.4	2	0.8	0.1	<0.1	<1	<0.1	1.2	1.4	41.2	100.88
KB-35	7.30	7.59	25.91	<0.001	0.10	31.00	2.21	49	9.6	18	3.9	0.1	0.1	1	<0.1	7.0	3.0	29.7	99.96
KBL-16	11.83	1.47	7.12	0.017	0.02	49.52	0.51	9	1.7	3	0.7	<0.1	<0.1	<1	<0.1	1.4	1.2	40.5	100.37
KB-34	10.14	3.20	12.39	<0.001	0.01	44.18	0.99	19	3.7	7	1.5	0.1	<0.1	1	<0.1	2.5	1.2	37.5	99.99
KBL-15	11.82	1.39	6.54	0.025	<0.02	49.88	0.41	10	1.5	3	1.0	0.1	<0.1	<1	<0.1	1.2	0.8	41.1	100.59
KB-33	5.73	9.27	35.42	0.040	0.01	23.01	3.04	49	12.4	23	2.9	0.2	0.1	2	<0.1	7.2	2.4	24.9	99.87
KB-31	7.03	7.59	29.24	0.020	0.45	28.95	2.21	45	9.1	18	2.4	0.4	0.2	1	<0.1	6.6	2.8	28.1	99.87
KBL-14	12.15	0.80	5.68	0.048	0.04	51.24	0.40	<8	1.3	2	1.1	0.5	<0.1	<1	<0.1	0.9	1.7	41.2	100.48
KB-30	8.59	5.83	22.10	0.020	0.01	34.64	2.26	37	8.9	15	3.7	0.5	0.1	1	<0.1	6.7	3.6	32.1	99.85
KBL-13	12.14	0.98	5.80	0.014	0.24	50.44	0.50	<8	1.4	2	1.1	0.3	<0.1	<1	<0.1	1.0	1.5	41.4	100.37
KBL-12	12.31	0.94	5.33	0.024	0.06	51.29	0.41	<8	1.7	2	0.6	0.2	<0.1	<1	<0.1	1.0	1.8	41.4	100.52
KB-28	6.17	9.06	31.37	0.030	0.01	25.38	3.02	52	13.4	22	4.2	0.3	0.1	2	<0.1	8.7	3.6	26.9	99.86
KBL-11	11.90	1.19	6.30	0.009	0.10	49.84	0.43	9	1.4	3	1.2	0.1	<0.1	<1	<0.1	1.2	1.3	41.1	100.11
KBL-10	12.14	1.00	5.35	0.019	0.05	50.77	0.50	<8	1.2	2	1.1	0.3	<0.1	<1	<0.1	1.1	1.4	41.4	100.20
KB-26	8.24	5.95	22.58	0.030	0.01	34.23	2.28	34	9.8	16	3.3	0.3	0.3	1	0.1	7.2	2.9	31.8	99.87
KBL-9	12.29	0.95	4.48	0.022	0.07	51.21	0.39	<8	0.8	3	1.0	<0.1	<0.1	<1	<0.1	0.6	1.4	41.7	99.91
KBL-8	12.51	0.75	3.51	0.031	0.03	51.78	0.33	<8	1.3	2	<0.5	0.1	<0.1	<1	<0.1	0.8	1.4	42.4	100.00
KB-25	10.05	3.65	15.47	<0.001	0.09	41.01	1.74	23	7.4	12	2.0	0.6	0.2	1	<0.1	4.7	3.2	35.7	99.86
KBL-7	11.89	1.12	4.85	0.009	0.14	51.32	0.38	8	1.5	3	1.0	0.2	<0.1	<1	<0.1	1.1	1.6	41.6	100.49
KB-23	8.38	5.25	22.52	0.020	0.01	35.45	2.05	31	8.3	13	1.8	0.3	0.1	1	<0.1	6.2	2.7	31.9	99.95
KBL-6	12.11	1.28	6.32	0.015	0.09	49.97	0.48	10	1.8	3	1.2	0.2	<0.1	<1	<0.1	1.1	1.1	40.6	99.98
KB-22	8.38	5.23	21.98	0.030	0.01	35.81	1.92	33	8.0	12	1.4	0.4	0.1	1	0.1	6.1	2.5	32.2	99.94
KB-21	8.13	5.11	22.61	0.030	0.01	35.50	2.09	30	8.8	12	1.5	0.4	0.1	1	<0.1	5.9	2.8	31.9	99.93
KBL-4	11.97	1.20	5.35	0.057	0.04	50.61	0.47	9	1.6	3	0.8	0.1	<0.1	<1	<0.1	1.4	1.6	41.1	100.13
KB-20	8.13	5.72	28.13	0.020	0.65	32.00	2.16	40	9.6	17	2.2	0.5	0.1	1	<0.1	6.3	3.1	28.8	99.87
KB-19	7.34	6.54	30.05	0.030	0.01	29.67	2.34	40	10.6	16	2.3	0.3	0.1	1	<0.1	7.0	2.9	28.1	99.95
KBL-3	12.01	1.17	4.87	<0.001	<0.02	51.94	0.46	9	1.6	3	0.8	<0.1	<0.1	<1	<0.1	1.4	1.1	41.4	100.80
KB-18	5.56	9.22	35.66	0.030	0.01	23.06	3.20	56	15.6	20	2.6	0.2	0.1	2	0.1	9.0	2.8	24.7	99.97
KBL-2	11.76	1.52	6.33	0.028	0.03	49.79	0.67	12	2.0	6	1.1	<0.1	<0.1	<1	<0.1	1.4	2.0	41.1	100.73
KB-17	3.95	10.88	44.26	0.050	0.02	16.27	4.00	70	17.3	36	4.8	0.1	0.1	2	0.1	12.2	2.8	19.9	99.95
KBL-1	11.39	2.15	8.00	0.015	0.03	47.87	0.81	17	3.2	6	0.9	<0.1	<0.1	<1	<0.1	1.9	1.7	40.1	100.29
reKB-15	4.15	11.00	42.46	0.070	0.03	17.39	3.87	69	11.3	28	5.2	0.1	0.2	2	0.1	9.2	3.8	20.5	99.96
KB-15	4.21	11.03	42.31	0.090	0.03	17.50	3.95	74	11.3	28	4.6	0.1	0.1	2	<0.1	11.4	4.0	20.4	99.94
KB-14	1.58	18.07	50.25	0.070	0.02	6.17	3.71	113	22.0	19	1.1	<0.1	<0.1	3	<0.1	13.1	2.1	14.8	99.85
KB-13	1.44	18.76	50.87	0.050	0.01	5.86	3.52	117	22.6	19	1.0	<0.1	<0.1	4	<0.1	14.2	2.0	14.2	99.97
KB-12	1.31	19.18	50.83	0.060	0.02	5.08	4.08	122	25.1	23	1.3	<0.1	<0.1	4	<0.1	14.7	2.7	14.0	99.96
KB-11	1.60	19.26	48.46	0.050	0.04	6.67	3.83	120	23.8	21	1.9	0.1	<0.1	4	<0.1	16.0	2.3	15.3	99.97
KB-10	1.13	19.09	51.44	0.070	0.03	4.50	4.29	116	23.8	24	3.9	0.1	0.1	4	<0.1	17.0	2.4	14.0	99.96
KB-9	2.67	13.78	51.16	0.080	0.01	10.44	3.27	98	16.7	21	3.8	<0.1	0.1	3	0.1	12.5	2.6	15.5	99.96
KB-8	0.97	19.33	52.18	0.060	0.52	3.75	5.78	124	23.1	30	1.9	0.4	0.1	4	0.1	16.0	3.1	12.8	99.84
KB-7	1.15	19.46	51.23	0.050	0.51	4.63	4.62	120	23.2	30	2.6	0.2	0.2	4	0.1	16.4	3.1	13.6	99.82
KB-6	3.34	12.33	47.70	0.060	0.45	12.12	3.49	88	15.6	49	3.0	0.3	0.2	3	0.1	11.5	2.3	17.3	99.83
KB-5	3.82	11.74	47.49	0.060	0.76	13.78	3.95	96	17.0	61	6.6	0.5	0.4	3	0.2	12.6	3.2	17.4	99.97
KB-4	3.04	15.88	51.30	0.060	0.67	7.31	5.29	138	29.3	61	12.9	1.0	0.7	4	0.4	15.2	5.2	15.1	99.94
KB-3	7.42	6.22	22.39	2.720	0.03	33.48	3.14	64	16.0	90	8.1	1.4	1.1	2	0.6	6.5	12.6	29.4	99.74

KB-2	12.81	1.48	7.05	1.190	0.04	46.42	2.78	30	13.4	106	8.5	1.6	1.4	<1	0.8	1.3	7.0	39.5	99.80
KB-1	12.81	0.58	2.62	0.030	<0.01	53.06	1.09	11	1.4	4	6.1	1.7	0.1	<1	0.2	0.6	1.6	41.7	99.87
KBL-0	12.62	0.37	2.50	0.040	0.03	52.90	1.36	9	1.2	8	4.2	1.2	0.2	<1	0.3	0.4	1.3	42.4	100.30
KBL-K2	12.92	0.15	0.58	0.008	0.02	55.23	0.07	<8	0.5	3	0.6	<0.1	<0.1	<1	<0.1	0.2	1.7	43.2	100.00
KBL-K3	13.06	0.09	0.35	0.018	0.02	56.23	0.07	<8	0.2	5	0.6	0.1	0.2	<1	<0.1	<0.2	2.0	43.2	100.52



**Table 2**  
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Sample No.↓	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
det. limit→	0.1	0.1	0.02	0.3	0.05	0.02	0.05	0.01	0.05	0.02	0.03	0.01	0.05	0.01
KBL-28	11.1	11.0	2.25	9.2	1.73	0.40	1.88	0.29	1.53	0.31	0.84	0.13	0.63	0.10
KBL-26	16.5	17.4	3.31	14.5	2.55	0.63	2.92	0.46	2.40	0.49	1.31	0.19	1.00	0.15
KBL-25	19.0	23.0	3.99	15.8	2.61	0.60	2.63	0.38	2.01	0.41	1.11	0.16	0.86	0.13
KBL-23	14.8	22.7	3.56	14.4	2.52	0.54	2.31	0.34	1.75	0.33	0.85	0.13	0.71	0.11
KBL-22	16.4	25.3	3.75	15.1	2.49	0.56	2.31	0.33	1.73	0.33	0.86	0.13	0.73	0.12
KBL-21	12.8	15.9	2.52	10.3	1.76	0.34	1.45	0.23	1.06	0.22	0.61	0.08	0.50	0.07
KBL-20	11.7	15.4	2.45	9.2	1.65	0.36	1.52	0.23	1.11	0.23	0.56	0.09	0.52	0.07
KBL-19	14.8	22.5	3.26	13.1	2.09	0.46	1.91	0.28	1.38	0.28	0.67	0.11	0.63	0.09
KBL-18	15.4	23.0	3.48	13.7	2.51	0.52	2.12	0.34	1.56	0.32	0.79	0.12	0.65	0.10
KB-36	36.2	76.0	10.66	42.1	7.88	1.65	6.30	1.09	4.72	0.87	2.46	0.33	1.98	0.29
KBL-17	15.1	21.4	3.23	12.3	2.27	0.45	1.90	0.27	1.34	0.28	0.66	0.10	0.59	0.09
KB-35	32.0	58.1	7.94	29.6	5.63	1.12	4.65	0.78	3.43	0.66	1.96	0.25	1.59	0.25
KBL-16	13.5	17.4	2.72	10.0	1.74	0.39	1.61	0.24	1.17	0.24	0.61	0.08	0.53	0.08
KB-34	11.4	19.3	2.54	10.0	1.61	0.36	1.48	0.25	1.08	0.23	0.66	0.08	0.51	0.08
KBL-15	9.8	12.6	1.88	6.9	1.34	0.28	1.24	0.17	0.83	0.17	0.46	0.07	0.41	0.06
KB-33	23.7	45.2	5.94	21.8	3.91	0.77	3.20	0.57	2.54	0.53	1.54	0.22	1.36	0.20
KB-31	23.9	46.5	5.94	22.3	4.19	0.83	3.26	0.62	2.72	0.56	1.57	0.22	1.34	0.21
KBL-14	7.6	10.4	1.43	5.2	1.00	0.21	0.96	0.15	0.79	0.15	0.44	0.07	0.39	0.06
KB-30	22.2	44.4	5.96	23.4	4.72	0.93	3.89	0.70	3.18	0.58	1.66	0.22	1.34	0.21
KBL-13	10.7	15.7	2.32	9.1	1.68	0.36	1.48	0.24	1.12	0.24	0.61	0.08	0.53	0.08
KBL-12	12.0	16.2	2.53	9.8	1.82	0.40	1.73	0.26	1.30	0.27	0.73	0.11	0.62	0.09
KB-28	24.8	44.8	5.99	22.3	4.28	0.85	3.65	0.66	3.12	0.64	1.86	0.26	1.59	0.23
KBL-11	11.0	16.8	2.59	9.8	1.85	0.37	1.61	0.24	1.23	0.25	0.63	0.09	0.54	0.08
KBL-10	12.2	18.6	2.79	10.7	2.01	0.44	1.90	0.29	1.42	0.28	0.70	0.11	0.59	0.09
KB-26	20.4	36.5	5.18	20.7	3.76	0.79	3.36	0.58	2.72	0.54	1.56	0.22	1.35	0.19
KBL-9	6.7	9.1	1.36	5.2	0.94	0.23	0.95	0.15	0.81	0.16	0.43	0.06	0.36	0.06
KBL-8	6.2	8.8	1.38	5.6	1.07	0.24	1.05	0.15	0.78	0.15	0.40	0.06	0.33	0.05
KB-25	18.0	33.4	4.68	18.3	3.54	0.77	3.18	0.56	2.62	0.50	1.36	0.18	1.18	0.18
KBL-7	9.4	13.7	1.97	7.7	1.48	0.32	1.35	0.21	1.08	0.22	0.58	0.08	0.52	0.08
KB-23	26.1	45.9	6.44	25.2	4.57	0.90	4.09	0.72	3.36	0.70	1.91	0.24	1.60	0.23
KBL-6	10.1	15.2	2.19	8.2	1.58	0.34	1.45	0.23	1.08	0.24	0.62	0.09	0.52	0.07
KB-22	22.3	40.7	5.48	20.9	3.87	0.83	3.47	0.62	2.91	0.59	1.64	0.23	1.40	0.21
KB-21	24.9	47.0	6.33	24.4	4.75	0.92	4.02	0.76	3.32	0.67	1.84	0.25	1.55	0.22
KBL-4	11.9	17.7	2.64	10.7	1.99	0.45	1.94	0.30	1.55	0.31	0.83	0.12	0.69	0.10
KB-20	27.9	57.5	7.64	30.0	5.59	1.15	4.70	0.83	3.84	0.75	2.05	0.27	1.81	0.27
KB-19	32.2	59.9	7.84	31.3	5.56	1.14	4.89	0.89	3.90	0.80	2.27	0.32	1.98	0.29
KBL-3	15.7	22.0	3.34	13.4	2.26	0.50	2.28	0.33	1.80	0.35	0.95	0.15	0.78	0.12
KB-18	32.0	61.5	7.99	29.9	5.59	1.08	4.67	0.84	3.78	0.79	2.27	0.32	1.93	0.30
KBL-2	27.2	38.0	5.68	22.1	4.04	0.87	4.02	0.62	3.26	0.66	1.84	0.25	1.44	0.22
KB-17	29.7	59.3	7.44	27.7	5.01	0.97	4.27	0.77	3.60	0.78	2.33	0.32	2.09	0.33
KBL-1	15.9	25.5	3.55	13.6	2.55	0.54	2.47	0.38	2.00	0.41	1.10	0.16	0.88	0.14
reKB-15	37.2	71.9	9.06	35.0	6.79	1.41	6.21	1.11	5.28	1.11	3.25	0.45	2.71	0.42
KB-15	38.9	74.9	9.42	35.8	6.69	1.44	6.17	1.16	5.61	1.14	3.43	0.45	2.91	0.44
KB-14	48.7	95.9	11.85	43.5	7.48	1.56	5.84	1.08	4.82	0.98	2.92	0.41	2.65	0.40
KB-13	49.8	98.0	12.37	46.1	7.85	1.63	6.47	1.17	5.00	1.07	3.10	0.46	2.68	0.42
KB-12	52.4	99.2	12.77	46.1	8.43	1.62	6.45	1.16	5.49	1.08	3.20	0.46	2.93	0.47
KB-11	55.2	106.3	14.00	51.3	9.02	1.91	7.47	1.31	5.84	1.19	3.32	0.48	3.00	0.46
KB-10	53.1	101.1	13.03	47.1	8.34	1.63	6.47	1.18	5.74	1.10	3.23	0.47	3.05	0.46
KB-9	46.1	83.9	11.21	43.3	8.21	1.70	7.23	1.33	6.01	1.20	3.54	0.49	3.09	0.49
KB-8	47.1	90.2	11.53	41.5	7.41	1.54	5.95	1.13	5.27	1.12	3.28	0.45	2.93	0.45
KB-7	53.7	99.4	13.41	49.4	8.22	1.56	5.96	1.11	5.30	1.03	2.91	0.44	2.82	0.44
KB-6	34.9	64.2	9.11	33.3	6.17	1.21	5.22	0.99	4.49	0.93	2.77	0.37	2.49	0.37
KB-5	39.6	65.6	10.07	37.8	6.72	1.36	5.67	1.06	5.14	1.01	2.97	0.41	2.58	0.42
KB-4	48.3	64.3	10.18	36.6	6.33	1.24	5.30	1.06	5.22	1.15	3.38	0.51	3.05	0.50
KB-3	241.5	131.9	38.32	146.2	21.73	5.50	26.25	4.51	22.97	5.22	14.60	1.74	9.17	1.31
KB-2	55.2	26.7	6.31	23.9	3.66	0.90	5.12	0.94	5.28	1.39	4.52	0.60	3.35	0.51

KB-1	7.6	4.3	0.74	2.7	0.44	0.11	0.53	0.11	0.64	0.21	0.81	0.13	0.91	0.17
KBL-0	7.7	3.2	0.58	2.2	0.38	0.09	0.47	0.08	0.54	0.18	0.69	0.13	0.84	0.16
KBL-K2	2.8	2.4	0.46	1.9	0.35	0.09	0.39	0.06	0.36	0.08	0.25	0.04	0.24	0.04
KBL-K3	3.0	2.5	0.48	1.9	0.34	0.09	0.38	0.07	0.38	0.09	0.26	0.04	0.24	0.05

