Discerning primary versus diagenetic signals in carbonate carbon and oxygen isotope records:

An example from the Permian-Triassic boundary of Iran

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25 **ABSTRACT**

26 Sedimentary successions across the Permian-Triassic boundary (PTB) are marked by a
27 prominent negative carbon isotope excursion. This excursion, found in both fossil (e.g., brachiopod)
28 and bulk carbonate at many sites around the world, is generally considered to be related to a global
29 carbon cycle perturbation. Oxygen isotopes also show a negative excursion across the PTB, but
30 because $\delta^{18}\text{O}$ is more prone to diagenetic overprint (especially in bulk carbonate), these data are
31 often not used in palaeoenvironmental analyses. In the present study, bulk-rock and brachiopod
32 $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$, as well as conodont $\delta^{18}\text{O}$, were analyzed in PTB successions at Kuh-e-Ali Bashi and
33 Zal (NW Iran) in order to evaluate diagenetic overprints on primary marine isotopic signals. The
34 results show that the use of paired C-O isotopes and Mn-Sr concentrations is not sufficient to
35 identify diagenetic alteration in bulk materials, because $\delta^{13}\text{C}$ - $\delta^{18}\text{O}$ covariation can be due to
36 environmental factors rather than diagenesis, and Sr/Ca and Mn/Ca ratios can vary as a function of
37 bulk-rock lithology. Comparison of $\delta^{13}\text{C}$ profiles shows that all bulk carbonate is altered to some
38 degree, although the general bulk-rock trend mimics that of the brachiopod data with a systematic
39 offset of $-1.2(\pm 0.4)\text{‰}$. This suggests that the first-order $\delta^{13}\text{C}$ trend in bulk carbonate is generally
40 robust but that the significance of small-scale carbon isotope fluctuations is uncertain, especially
41 when such fluctuations are linked to lithologic variation. The PTB interval, which is marked by a
42 low-carbonate 'Boundary Clay' in the study sections, may be especially prone to diagenetic
43 alteration, e.g., via late-stage dolomitization. Comparison of oxygen-isotope profiles for bulk rock
44 and well-preserved fossils (both brachiopods and conodonts) shows that the former are offset by $-$
45 $2.1(\pm 0.4)\text{‰}$. Diagenetic modeling suggests that these offsets were the product mainly of early
46 diagenesis at burial temperatures of $\sim 50\text{-}80^\circ\text{C}$ and water/rock ratios of <10 . Authigenic carbonates
47 precipitated during early diagenesis represent a potentially major sink for isotopically light carbon -
48 - at a global scale - that has received relatively little attention to date.

49

50 **1. Introduction**

51 Bulk-carbonate isotope data have been widely employed as a proxy for seawater chemistry,
52 climate, and marine productivity during the Proterozoic (Kaufman and Knoll, 1995; Knauth and
53 Kennedy, 2009; Knoll et al., 1986), Palaeozoic (Baud et al., 1989; Buggisch and Joachimski, 2006;
54 Holser and Magaritz, 1987; Marshall and Middleton, 1990; Saltzman, 2002), and Mesozoic
55 (Jenkyns and Clayton, 1986; Schlanger et al., 1987). Similarly to biogenic low-Mg calcite (e.g.,
56 brachiopods and belemnites), carbon isotope ratios of marine bulk carbonate have been assumed to
57 be a faithful proxy for the $\delta^{13}\text{C}$ of dissolved inorganic carbon (DIC) in palaeoseawater (Buggisch
58 and Joachimski, 2006; Holser and Magaritz, 1987; Payne et al., 2004), and C-isotopic excursions
59 are regarded as robust stratigraphic correlation markers (Hermann et al., 2010; Korte and Kozur,
60 2010; Kraus et al., 2009).

61 Palaeoclimatic studies utilizing oxygen isotope palaeothermometry generally prefer the use
62 of low-Mg carbonate shells, because they are thought to be less susceptible to diagenetic resetting
63 than other carbonate phases (Brand, 1989; Korte et al., 2005a, 2005b; Mii et al., 1999; van Geldern
64 et al., 2006; Veizer et al., 1999). On the other hand, bulk-carbonate oxygen isotope compositions
65 are usually rejected as a climate proxy owing to their susceptibility to diagenetic alteration. This
66 susceptibility is due to the large size of the oxygen reservoir in diagenetic fluids and the greater
67 isotope fractionation effects associated with oxygen (relative to carbon) (Brand and Veizer, 1981;
68 Marshall, 1992). Bulk-rock isotope records, however, can be generated with high temporal
69 resolution and do not depend on the availability of shelly fossils, which are often absent during
70 phases of severe environmental stress, such as mass extinction events. Thus, in many cases there are
71 distinct advantages to working with bulk-carbonate C and O isotope records.

72 Different opinions exist regarding the reliability of bulk-carbonate samples as a recorder of
73 primary palaeoseawater isotopic signals (see discussion in Brand et al., 2012a). It has been
74 suggested that abrupt stratigraphic shifts in bulk-carbonate $\delta^{13}\text{C}$ associated with lithological breaks
75 should be treated as possible evidence of stratigraphic gaps and/or diagenetic alteration of the host

76 rock (Algeo, 1996; Marshall, 1992). Carbonate sediments are complex recorders of isotopic
77 information because they consist of multiple components, each potentially having a different initial
78 C-O isotopic composition, and each responding in a unique manner to a series of diagenetic events
79 leading to final stabilization in the burial environment (Brand et al., 2012b; Jenkyns and Clayton,
80 1986). An improved understanding of how diagenesis affects the isotopic composition of carbonate
81 sediments is needed in order to better isolate the primary versus secondary components of bulk-rock
82 $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ signatures.

83 Various sedimentological, textural, and chemical indicators have been used to evaluate
84 diagenetic influences on bulk-carbonate isotope chemistry (Al-Aasm and Veizer, 1986; Brand and
85 Veizer, 1980; Melim et al., 2002). Textural changes, such as cementation and recrystallization
86 features, can give a general idea about the diagenetic history of a sample, but they are often
87 insufficient for detailed reconstructions, as too little is known about the timing and physical
88 conditions of their development (Melim et al., 2002; Munnecke et al., 1997). Chemical indicators of
89 diagenetic alteration, such as Sr and Mn concentrations, have been widely used (Banner and
90 Hanson, 1990; Brand and Veizer, 1980; Middelburg et al., 1987; Pingitore, 1978; Pingitore et al.,
91 1988). However, many carbonate units have experienced multiple diagenetic regimes and fluids
92 with spatially and temporally variable chemical properties, making accurate quantification of these
93 processes difficult.

94 We have undertaken a comparative fossil and bulk-rock geochemical investigation from
95 outcrop samples of two P-Tr boundary sections (Kuh-e-Ali Bashi and Zal) in NW Iran with the goal
96 of assessing bulk-carbonate carbon-oxygen isotopic records as a proxy for primary marine
97 carbonate isotopic composition. We analysed the C-O isotopic composition of brachiopods that
98 were well-preserved (as determined by micropetrographic and elemental analyses in Schobben et
99 al., 2014), in addition to making use of conodont O isotope data from earlier studies, as proxies for
100 primary marine carbonate isotopic compositions, and we compared these results with bulk-
101 carbonate $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$. We have then assessed the degree of diagenetic alteration of bulk

102 carbonate based on minor-element concentrations (i.e., Mn/Ca, Sr/Ca, and Mg/Ca). Our data
103 provide insight into the degree of secondary overprinting of the primary marine carbonate isotopic
104 signals of the study units. The implications of these results extend beyond the present study
105 sections, however, providing a new approach for analysis of diagenetic effects and recovery of
106 primary marine carbonate isotopic signals in bulk-carbonate samples of any age.

107

108 **2. Study locales**

109 The Kuh-e-Ali Bashi 1 (as defined by Teichert et al., 1973), at 38.940°N, 45.520°E, and Zal,
110 at 38.733°N, 45.580°E, sections of the Julfa region of NW Iran (Fig. 1A) are located on the north-
111 northeastern margin of the Northwestern Iranian Terrane, which belonged to the Cimmerian
112 microcontinents during the latest Permian (Fig. 1B). In this area, carbonate rock successions
113 spanning the P-Tr boundary interval consist of three major lithological units (in stratigraphic order):
114 the *Paratirolites* Limestone (which is the upper part of the Ali Bashi Formation), the ‘Boundary
115 Clay’ (Aras Member as defined by Ghaderi et al., 2014), and the ‘*Claraia* Beds’ (the latter two
116 forming the Elikah Formation).

117 The red nodular *Paratirolites* Limestone beds have CaCO₃ contents between 70 and 90 wt.
118 % (Ghaderi et al., 2014; Leda et al., 2014), classifying them as argillaceous limestone. The
119 limestone beds are separated by shale horizons with a thickness of not more than 10 cm and usually
120 less than 5 cm, and which become thinner towards the top of the *Paratirolites* Limestone. The
121 individual limestone nodules have a partly rounded surface and show a micritic matrix of generally
122 similar composition. The rare macrofossil assemblages comprise ammonites, nautiloids, rugose
123 corals, fish remains, and brachiopod shells. Microfossils are strikingly abundant in the insoluble
124 residue of acid digestions, yielding pectinoform and platform elements from conodonts and
125 actinopterygian teeth. Calcareous green algae and radiolarians have been identified from thin
126 sections (Leda et al., 2014). Other features of the *Paratirolites* Limestone are carbonate nodules

127 coated with Fe-Mn crusts, and Fe-Mn coatings of discontinuity surfaces accompanied by biogenic
128 encrustations (Leda et al., 2014; Mohtat Aghai et al., 2011; Fig. 2B). Besides micrite, the matrix
129 contains some minor sparry cement and in-situ crystallization (neomorphic spar). The nodular
130 limestones with hardground features and the pelagic fauna likely signify low rates of carbonate
131 accumulation in a deep-shelf environment (~100-200 m) (Leda et al., 2014).

132 The Boundary Clay, common in most of the Iranian P-Tr sections (Ghaderi et al., 2014;
133 Heydari et al., 2003; Leda et al., 2014; Taraz, 1971), overlies the *Paratirolites* Limestone, and its
134 base marks the end-Permian mass extinction (EPME) horizon (Kozur, 2007). The lithology can be
135 classified as red claystone and red/green marl. It reaches thicknesses of 1.2 m at Kuh-e-Ali Bashi
136 and 0.6 m at Zal, where it contains 18 and 35 wt. % CaCO_3 , respectively (Ghaderi et al., 2014).
137 Skeletal components are less abundant than in the *Paratirolites* Limestone but ostracod,
138 bellerophontid gastropod, and sponge remains occur frequently (Fig. 2E). The marine benthos
139 points to a continuation of fully marine conditions during deposition of this unit. The siliciclastic
140 matrix contains microcrystalline spar and micrite and is intersected by abundant anastomosing
141 stylolites.

142 In the overlying ‘*Claraia* Beds’, only the lower 5 to 10 m were studied here. The base of
143 this unit is slightly below the conodont-defined P-Tr boundary (Ghaderi et al., 2014; Kozur, 2007).
144 At Kuh-e-Ali Bashi, the lower part (1.10 m) of the ‘*Claraia* Beds’ is lithologically similar to the
145 pre-extinction *Paratirolites* Limestone, consisting of argillaceous nodular limestone with
146 intercalated marl beds. At Zal and above 1.10 m in the Kuh-e-Ali Bashi section, the ‘*Claraia* Beds’
147 consist of grey, thick-bedded, platy limestone. Leda et al. (2014) recognised that these limestones
148 exhibit a recrystallized texture, relating to microspar cementation and in-situ recrystallization (Fig.
149 2C). These lithologies were deposited in a low-energy environment and represent a continuation of
150 deep-water conditions from the Upper Permian (Leda et al., 2014).

151 The two sections have been well-studied with respect to their biostratigraphy and
152 sedimentology (Ghaderi et al., 2014; Korte and Kozur, 2005; Kozur, 2007; Leda et al., 2014;

153 Stepanov et al., 1969; Teichert et al., 1973). They both contain the Boundary Clay with the EPME
154 horizon at its base. These P-Tr boundary sections differ from coeval sites in Japan, China, and
155 Turkey, all of which show erosional truncation of end-Permian strata possibly caused by submarine
156 dissolution (Payne et al., 2007) or subaerial exposure (Collin et al., 2009).

157 Local diagenetic alteration, implied by lithological and facies changes, has been put forward
158 as an explanation for observed short-term $\delta^{13}\text{C}$ trends confined to the Boundary Clay of some
159 Iranian P-Tr sections (Heydari et al., 2001, 2003; Korte et al., 2004a, 2004b; Korte and Kozur,
160 2005). It has been suggested that calcareous clays, such as those found in the Boundary Clay, are
161 susceptible to post-depositional recrystallization that may alter their carbonate $\delta^{13}\text{C}$ composition
162 (Knauth and Kennedy, 2009).

163

164 **3. Methods**

165 Aliquots of the samples for isotope analysis were taken from fresh surfaces of carbonate
166 rocks, using a micro drill. Late-diagenetic cracks, veins, and stylolites were rejected to avoid major
167 contamination of the samples. Larger sample splits (one gram) for elemental analysis were taken by
168 trimming off altered parts of hand samples using a trim saw and crushing the residual with the aid
169 of a mechanical agate mill. The material sampled by micro-drill and by crushing of hand samples,
170 thus, consisted of a similar mixture of allochems, micrite, and early diagenetic cements, the relative
171 proportions of which could not be discerned through visual inspection. The generated aliquots of
172 such sampling procedures are commonly referred to as ‘micritic carbonate’ or ‘lithographic
173 limestone’ (cf. Brand et al. 2012a, 2012b) and will be referred to as either ‘bulk-rock’ or ‘whole-
174 rock’ samples in the following.

175 Stable isotope measurements were carried out using a Thermo Finnigan Gasbench II linked
176 online to a THERMO/Finnigan MAT V isotope ratio mass spectrometer in the stable isotope
177 laboratory of the Museum für Naturkunde in Berlin. After flushing the reaction vessels (12 ml

borosilicate glass capped with a rubber septum LABCO) with helium, approximately 30 μl of anhydrous phosphoric acid was injected through the septum into the sealed reaction vessel by using a disposable syringe. The sample was ready for isotope measurement after approximately 1.5 hours of reaction time at 72°C. Reference gas was pure CO_2 (99.995 %) from a cylinder calibrated against the IAEA reference materials (NBS 18, NBS 19). The accuracy of both $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ was determined against an in-house standard (Pfeil STD; Solenhofen Limestone) and the precision determined by repeated measurements was generally better than $\pm 0.1 \text{ ‰}$ (1σ). Oxygen and carbon isotopes are reported relative to Vienna Pee Dee Belemnite (VPDB) in standard delta notation.

One-gram splits of ground material were used for elemental analysis of the acid-soluble part (see the Supplementary Text, Supplementary Figure 1 and Supplementary Table 1 for additional discussion on the data generated by this procedure). Acid digestion was carried out using 20 ml 0.33 M acetic acid over 48 hours, with the solution constantly being agitated. The insoluble and soluble fractions were separated by filtration using a cellulose-nitrate membrane (0.45 μm) and were then dried and weighed. A part of the soluble fraction was dissolved with 0.2 M nitric acid in order to obtain a matrix-matched solution for analysis by Inductively Coupled Plasma - Optical Emission Spectrometry (ICP-OES) carried out at the University of Copenhagen (see Ullmann et al., 2013a for methodology). The Ca concentration of the solution was approximated; this allowed for a matrix match of the 0.2 M HNO_3 blank solution and multi-element reference solutions fabricated for a three-point calibration. The precision was monitored by international standards JDo-1 and JLS-1 yielding accuracies for Sr/Ca, Mn/Ca and Mg/Ca ratios with averages better than 5 % and reproducibility with biases less than 10% (2σ) (Table 1) (Imai et al., 1996). Calcite (CaCO_3) concentrations of the samples were determined by the weight loss-acid digestion method by using a 2M HCl solution (e.g., Siesser and Rogers, 1971). A small subset of the decalcified samples of the *Paratirolites* Limestone Member were analyzed for concentrations and carbon isotope compositions of the organic fraction with a THERMO/Finnigan MAT V isotope ratio mass spectrometer, coupled to a THERMO Flash EA 1112 elemental analyzer via a THERMO/Finnigan Conflo IV interface, in

the stable isotope laboratory of the Museum für Naturkunde, Berlin. Organic carbon isotope measurements were converted to the VPDB scale by reference to the IAEA standard CH3. Standard deviations for repeated isotope measurements of lab standard material (peptone) were generally better than ± 0.1 per mille (‰). The program R and the packages gridExtra, gTable and ggplot2 have been used for graphical plots and statistics (<http://cran.r-project.org/>).

4. Results

4.1. Isotope results

The $\delta^{13}\text{C}$ of carbonate rocks from Kuh-e-Ali Bashi and Zal (including data of Schobben et al., 2014) range from -2.8 to 3.5 ‰ and from -0.9 to 3.4 ‰, respectively (Fig. 3, Supplementary Tables 2 and 3). A general decline in bulk-carbonate $\delta^{13}\text{C}$ occurs upsection for samples from both localities, starting within the *Clarkina bachmanni* Zone. The pre-extinction brachiopod $\delta^{13}\text{C}$ values are slightly heavier but follow the general bulk-rock trend (Fig. 3). No articulated brachiopods are present in the post-extinction interval. The Kuh-e-Ali Bashi section is marked by two bulk-rock $\delta^{13}\text{C}$ minima of -1.4 and -0.7 ‰ at 1.70 m and 0.71 m below the EPME horizon, respectively. An inflection to even lower bulk-rock values marks the base of the Boundary Clay. However, this pattern is not observed at Zal, where bulk-rock $\delta^{13}\text{C}$ fluctuates around 1.5 ‰ in the correlative interval. Parallel bulk-rock $\delta^{13}\text{C}$ minima are observed at both sites within the *Hindeodus parvus* Zone. In this interval, the carbon isotope values average ca. -3.0 and -0.1 ‰ for Kuh-e-Ali Bashi and Zal, respectively, with a single sample in the latter section yielding a lower $\delta^{13}\text{C}$ value (-0.9 ‰ at $+2.0$ m). Post-extinction bulk-rock $\delta^{13}\text{C}$ of both sections remains more depleted than in pre-extinction strata, with values around -1 ‰. At Kuh-e-Ali Bashi, one additional negative $\delta^{13}\text{C}$ excursion (-1.4 ‰) occurs at 3.50 m above the EPME horizon.

The $\delta^{18}\text{O}$ of carbonate rocks from Kuh-e-Ali Bashi and Zal (including data of Schobben et al., 2014) range from -8.1 to -4.0 ‰ and from -8.3 to -3.0 ‰, respectively (Fig. 3, Supplementary

229 Tables 2 and 3). The bulk-rock oxygen isotope values from the lower *Paratirolites* Limestone of
 230 both sections are ca. -5.0‰ (Fig. 3). At the base of the Boundary Clay, bulk-rock $\delta^{18}\text{O}$ declines to
 231 ca. -7.0 to -8.0‰ and remains more depleted (ca. -7.0‰) upsection compared to pre-extinction
 232 strata. Calcite brachiopod shell $\delta^{18}\text{O}$, taken from Schobben et al. (2014), are heavier than coeval
 233 bulk-rock data (-4.0 and -3.0‰ VPDB). Conodont $\delta^{18}\text{O}$ is normally reported on the SMOW scale,
 234 but here we translate these data to the VPDB scale to simplify carbonate/apatite $\delta^{18}\text{O}$ comparisons.
 235 However, this comparison is not straightforward owing to the varying temperature dependence of
 236 equilibrium fractionations between water and solid phases (Wenzel et al., 2000). We used two
 237 different approaches for translating conodont $\delta^{18}\text{O}$ (also taken from Schobben et al., 2014) to the
 238 VPDB-scale: (1) by comparing the offset between pristine brachiopod and conodont oxygen isotope
 239 data, and (2) by back-calculating conodont $\delta^{18}\text{O}$ derived palaeotemperatures (as given in Schobben
 240 et al., 2014) using a carbonate-water fractionation equation from Kim and O'Neil (1997).
 241 Comparing the VPDB-translated conodont $\delta^{18}\text{O}$ derived from these two methods reveals a
 242 discrepancy of up to 0.5‰ (cf. Wenzel et al., 2000). This uncertainty is given as error bars on the
 243 VPDB scale in Figure 3. Pre-extinction conodont $\delta^{18}\text{O}$ ranges between equivalents of -4.0 and -3.0
 244 ‰ VPDB with an uncertainty of about 0.5‰ . Post-extinction conodont $\delta^{18}\text{O}$ values correspond to
 245 calcite values of ca. -5.0‰ VPDB (uncertainty $\sim 0.3\text{‰}$). and thus more depleted.

246 The total organic carbon (TOC) obtained from the *Paratirolites* Limestone unit ranges from
 247 0.01 to 0.02% , with organic carbon $\delta^{13}\text{C}$ values of -25.4 to -23.2‰ (VPDB).
 248

249 4.2. Elemental ratios

250 *Mn/Ca* – At Kuh-e-Ali Bashi, the *Paratirolites* Limestone has relatively stable Mn/Ca ratios
 251 averaging at about 1.8 mmol/mol ($1\sigma = 0.6$, $n = 25$) for the calcite fraction (Fig. 3, Supplementary
 252 Tables 2 and 3). A prominent peak of 11.9 mmol/mol occurs within the Boundary Clay followed by
 253 a steady decrease up-section, but Mn/Ca remains higher than average pre-extinction values (median

254 of 2.7 mmol/mol; $1\sigma = 0.6$, $n = 24$) up to a height of 2.35 m above the base of the EPME horizon.
255 The lowest values at Kuh-e-Ali Bashi are recorded for the upper part of the Elikah Formation,
256 yielding a median of 1.1 mmol/mol ($1\sigma = 0.4$, $n = 9$). At Zal, the *Paratirolites* Limestone is marked
257 by Mn/Ca ratios of 1.6 mmol/mol (median; $1\sigma = 0.1$, $n = 4$) (Fig. 3, Supplementary Tables 2 and 3).
258 Similar to Kuh-e-Ali Bashi, the Zal section displays a marked positive excursion with a Mn/Ca
259 maximum of 5.3 mmol/mol within the Boundary Clay (median = 2.6 mmol/mol; $1\sigma = 1.8$, $n = 10$).
260 Elevated Mn/Ca ratios between 1.1 and 3.3 mmol/mol occur within the interval up to 2.00 m above
261 the EPME horizon. The upper part of the Elikah Formation has Mn/Ca ratios of 0.6 to 0.7
262 mmol/mol ($n = 10$), and these are the lowest ratios within the section.

263 *Sr/Ca* – At Kuh-e-Ali Bashi, the Sr/Ca ratios are uniform throughout the *Paratirolites*
264 Limestone with a median of 0.6 mmol/mol ($1\sigma = 0$, $n = 25$) (Fig. 3, Supplementary Tables 2 and 3).
265 From the base of the Boundary Clay to 2.00 m above, the Sr/Ca ratios are marked by some small
266 fluctuations with a median value of 0.5 mmol/mol ($1\sigma = 0.1$, $n = 23$). The Sr/Ca ratios display an
267 increase up to 0.9 mmol/mol in the Elikah Formation, with a sharp positive excursion reaching 1.7
268 mmol/mol at 3.07 m above the EPME horizon. At Zal, the Sr/Ca ratios of the *Paratirolites*
269 Limestone yield a median of 0.7 mmol/mol ($1\sigma = 0.1$, $n = 4$) (Fig. 3, and Supplementary Tables 2
270 and 3) with a peak of 1.4 mmol/mol for the Boundary Clay. At 2.00 meters above the EPME
271 horizon, the Sr/Ca ratio displays large fluctuations with maxima of 2.3, 2.6, 3.1 and 3.5 mmol/mol.

272 *Mg/Ca* – The Mg/Ca values at Kuh-e-Ali Bashi and Zal are relatively stable throughout the
273 study interval with a median of 17.5 mmol/mol ($1\sigma = 4.9$, $n = 57$) and 21.4 mmol/mol ($1\sigma = 7.1$, n
274 = 17), respectively. Distinctly higher Mg/Ca ratios occur in the Boundary Clay, reaching 590 and
275 420 mmol/mol at Kuh-e-Ali Bashi and Zal, respectively (Figs. 3, Supplementary Tables 2 and 3).

276

277 **5. Screening for diagenesis**

278 *5.1. Recognition of diagenetic signals in carbonate $\delta^{13}C$ - $\delta^{18}O$ records*

279 Multiple methods have been developed for assessing diagenetic influences on carbonate
280 $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ records. Partial diagenetic alteration of marine carbonate sequences is likely to result
281 in covariation of carbon and oxygen isotope ratios of bulk carbonate (e.g., Brand and Veizer, 1981).
282 Bulk-rock $\delta^{13}\text{C}$ values are, therefore, often screened by quantifying their correlation with $\delta^{18}\text{O}$ using
283 Pearson's r correlation coefficients (e.g., Heydari et al., 2001). Our data show a highly significant
284 positive correlation between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ (p -value < 0.001 ; Table 2). This pattern is thought to be
285 diagnostic for lithification of carbonate rocks under the influence of meteoric water or in phreatic
286 lenses (Brand and Veizer, 1981). However, such an interpretation might be too simplistic because
287 our samples are positioned in a region of the $\delta^{13}\text{C}$ - $\delta^{18}\text{O}$ cross-plot (Fig. 4B) that is not typical for
288 carbonate rock lithified in contact with meteoric or phreatic water (cf. Knauth and Kennedy, 2009).
289 In addition, the overlying >100 m of Triassic sediments show no indications of subaerial exposure
290 (Horacek et al., 2007; Leda et al. 2014; Richoz et al., 2010). Both observations provide evidence
291 against the interpretation that meteoric diagenesis has altered the C-O isotope values of the study
292 successions. Correlations between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ do not necessarily represent secondary diagenetic
293 signals (Marshall, 1992; Ullmann and Korte, 2015). Severe environmental perturbations associated
294 with climate warming (hence more negative $\delta^{18}\text{O}$) and a concurrent negative $\delta^{13}\text{C}$ excursion are
295 known from the Paleocene-Eocene Thermal Maximum (PETM; Zachos et al., 2006) and the Early
296 Toarcian Oceanic Anoxic Event (T-OAE, Hermoso et al., 2012; Ullmann et al., 2014), and this is
297 probably also the case for the P-Tr boundary. The resulting unidirectional, environmentally
298 controlled signal on both isotope systems resembles meteoric diagenesis and makes any inferences
299 about sample preservation from a $\delta^{13}\text{C}$ - $\delta^{18}\text{O}$ cross-plot ambiguous.

300 Elemental data, especially Mn and Sr, are also widely utilized to identify diagenetic
301 alteration in bulk-rock samples (Brand et al., 2012a, 2012b; Denison et al., 1994). Manganese
302 usually becomes enriched during post-depositional dissolution and recrystallization of carbonate
303 (Brand and Veizer, 1980; Denison et al., 1994; Pingitore, 1978;), and strontium – modulated by its
304 variable initial concentration in primary carbonate phases (Korte and Hesselbo, 2011; Ullmann et

305 al., 2013b) – is lost due to dissolution and recrystallization of diagenetic calcite phases (Brand and
306 Veizer, 1980; Veizer et al., 1971). Rather than showing strong correlations with the C and O
307 isotopic proxies, Mn/Ca and Sr/Ca ratios follow smooth trends in the Kuh-e-Ali Bashi and Zal
308 sections where data density is sufficient (e.g., in the Boundary Clay interval; Fig. 3). Lithologically-
309 driven variation is evident at the transitions from nodular limestone (mainly the *Paratirolites*
310 Limestone) to clay (the Boundary Clay) and to platy limestone (mainly the ‘*Claraia* Beds’ Fig. 5).
311 The inference of strong lithologic control on Mn/Ca and Sr/Ca is further demonstrated by a
312 Kruskal-Wallis rank sum test suggesting significant differences between lithologies (p-value
313 <0.001). This coupling of Sr/Ca and Mn/Ca to lithology rather than to the isotopic trends (Figs. 4 C
314 and D) precludes an assessment of carbonate preservation based on these elemental ratios beyond
315 the choice of arbitrary threshold values, whose application would bias further discussion of the data.

316 Mg/Ca ratios in carbonate samples can help to distinguish between diagenetic endmembers
317 of low-Mg calcite and dolomite (e.g., Brand and Veizer, 1980). Several carbonate samples in the
318 Boundary Clay interval of Kuh-e-Ali Bashi and Zal show Mg enrichments beyond the limit of low-
319 Mg calcite, Mg enrichment being ten times greater than for the clastic fraction. The high Mg/Ca
320 content, together with the occurrence of rhombic crystals of dolomite in this interval, suggests a
321 localized process of dolomitization (Figs. 2D and 3; cf. Leda et al., 2014). A burial diagenetic
322 process that might be tied to a Mg-enriched diagenetic fluid is the transformation of smectite to
323 illite (McHargue and Price, 1982; Sternbach and Friedman, 1986). Samples enriched in Mg show a
324 tendency toward heavier carbon and oxygen isotope values than associated low-Mg calcite samples
325 (cf. Brand et al., 2012a,b). A similar relationship between dolomitization and more positive $\delta^{13}\text{C}$
326 values for time-equivalent beds in Meishan, China (Bed 27) has also been pointed out by Xie and
327 Wang (2011). From a bulk-rock perspective, Mg/Ca ratios are the only elemental proxy data in the
328 study sections that can be tied to a post-depositional effect on carbon and oxygen isotope ratios.

329 Besides textural and lithological examination (Al-Aasm and Veizer, 1986), preservation of
330 brachiopod shell calcite is often evaluated using Mn and Sr concentrations (Brand et al., 2012a;

331 Korte et al., 2005a, 2005b; Mii et al., 1999; van Geldern et al., 2006). Brachiopod samples from
332 Kuh-e-Ali Bashi show Mn/Ca ratios of 0.36 mmol/mol or lower, Sr/Ca ratios of 0.35 to 0.59
333 mmol/mol, and good preservation of shell microstructure (Schobben et al., 2014). The observed
334 Mn/Ca ratios are within the limits of those generally accepted as indicative of good brachiopod
335 shell preservation (Korte et al., 2003; Fig. 4A). Measured Sr/Ca ratios, however, are similar or
336 slightly lower than the lowest values observed in modern brachiopods (Brand et al., 2003), which
337 could be interpreted as a sign of diagenesis that generally causes Sr/Ca in biogenic calcite to
338 decrease (e.g. Al-Aasm and Veizer, 1986; Brand and Veizer, 1980; Ullmann and Korte, 2015).
339 However, the seawater Sr/Ca ratio, which exerts a first-order control on shell Sr/Ca, has changed
340 significantly through time and is predicted to have been low during times of ‘aragonite seas’
341 (Steuber and Veizer, 2002, Ullmann et al., 2013b). Average observed Permian brachiopod Sr/Ca
342 ratios are indeed lower than their modern counterparts (Steuber and Veizer, 2002), so that the
343 observed geochemical composition of the Kuh-e-Ali Bashi brachiopods is plausible for well-
344 preserved Permian brachiopods. Kuh-e-Ali Bashi brachiopod calcite is, therefore, interpreted to
345 reflect a near-primary marine signal (see also Schobben et al., 2014).

346

347 5.2. *Evaluation of primary and diagenetic influences on $\delta^{13}C$ profiles of Iranian PTB sections*

348 The bulk-carbonate carbon isotope curves do not deviate substantially from earlier records
349 for the same sections (e.g., Korte et al., 2004c; Korte and Kozur, 2005; Richoz et al., 2010; Fig. 6):
350 A negative trend through the Permian-Triassic boundary interval is clearly visible (e.g., Baud et al.,
351 1989; Hermann et al., 2010; Korte et al., 2004a; Korte and Kozur, 2010; Tong et al., 2007),
352 resembling the results from coeval deep-water PTB sections containing the Boundary Clay (Abadeh
353 and Meishan) and shallow-water sections that lack the Boundary Clay (e.g., Nhi Tao, Pufels, and
354 Gartnerkofel) (Korte and Kozur, 2010; Fig. 6).

Carbon isotope data reveal a relatively stable offset between brachiopods and bulk-rock samples ($\Delta^{13}\text{C}_{\text{bio-bulk}}$) of $\sim 1.2\text{‰}$ ($\pm 0.4\text{‰}$), based on comparison of the smoothed curves from Figure 7. The smoothed curves, which were generated using polynomial kernel regression, are necessary for data interpolation, as much of the brachiopod and whole-rock data do not come from matching stratigraphic levels. The uniformly positive $\Delta^{13}\text{C}_{\text{bio-bulk}}$ likely reflects pervasive weak alteration of bulk-rock $\delta^{13}\text{C}$ (cf. Brand et al., 2012b), as there is no evidence for a general primary ^{13}C -enrichment in brachiopods compared to other carbonate components (Wefer and Berger, 1991).

A source of ^{13}C -depleted carbon is oxidation of sedimentary organic matter. Aerobic respiration of organic carbon (OC) generates CO_2 that can lead to carbonate dissolution on a 1:1 molar basis, generating bicarbonate (HCO_3^-) that is markedly ^{13}C -depleted. Incorporation of such isotopically light carbon during precipitation of secondary carbonate phases causes a negative shift in bulk-rock $\delta^{13}\text{C}$. The amount of OC required to produce the observed $\Delta^{13}\text{C}_{\text{bio-bulk}}$ (Fig. 7) can be computed by the following equation:

$$\text{OC} = \left(\frac{\Delta^{13}\text{C}_{\text{bio-bulk}}}{\delta^{13}\text{C}_{\text{bulk}} - \delta^{13}\text{C}_{\text{HCO}_3} - \delta^{13}\text{C}_{\text{dia}}} \right) Fc \quad (1)$$

where $\delta^{13}\text{C}_{\text{HCO}_3}$ and $\delta^{13}\text{C}_{\text{dia}}$ stand for the carbon isotope composition of pore water bicarbonate and diagenetic carbonate precipitates, respectively. The fraction of carbon present in calcium carbonate is given as Fc ($= 0.12$, i.e., $12.0\text{ amu}/100.1\text{ amu}$). The isotopic composition of the diagenetic carbonate fraction depends, in turn, on $\delta^{13}\text{C}_{\text{HCO}_3}$ and temperature, and it can be calculated according to the relationship of Emrich et al. (1970). A $\delta^{13}\text{C}_{\text{HCO}_3}$ of -13.0‰ is reasonable, when considering measured $\delta^{13}\text{C}_{\text{org}}$ of -25.4 to -23.2‰ mixed with seawater bicarbonate having an average isotopic value of $\sim 0.0\text{‰}$ and following the stoichiometry of aerobic metabolism-driven carbonate dissolution. Following this approach, the observed $\Delta^{13}\text{C}_{\text{bio-bulk}}$ can be explained by authigenic carbonate incorporation from sediments with an initial OC value of $\sim 1.0\%$. This estimate is in good agreement with the inferred original sedimentary OC concentration (0.50 - 0.90%) of the study

379 samples, when applying the back-calculation procedure of Algeo et al. (2013) to the measured TOC
 380 concentrations (0.01-0.02 %). Following this procedure, TOC values are first converted to organic
 381 carbon accumulation rates (OCAR), based upon bulk accumulation rates (BAR). The nodular nature
 382 of this stratigraphic interval (the *Paratirolites* Limestone unit) has been attributed to a restricted
 383 sediment supply, and sedimentation rates (SR) would likely not have exceeded 0.5 cm kyr⁻¹ (Leda
 384 et al., 2013; Richoz et al., 2010). The OCAR can be derived from TOC, SR and the density (ρ) for
 385 bulk carbonate rock, per Equation 2, taken from Algeo et al. (2013):

$$386 \quad OCAR = TOC \times \rho \times SR \quad (2)$$

387 where, an average ρ of 2.5 g m⁻² yr⁻¹ has been used. Thermal loss of OC can be estimated from
 388 vitrinite reflectance values (R_0), which are ~0.65, for the NW Iranian localities. OC loss due to
 389 metamorphism is given by Equation 3, taken from Algeo et al. (2013):

$$390 \quad \log(OCAR / OCAR' = -0.283R_0 \quad (3)$$

391 where $OCAR'$ stands for the pre-metamorphosed OC content. Long exposure to oxygenated
 392 conditions, as a result of low SR, would have resulted in a (near total) aerobic degradation of the
 393 available sedimentary OC. Subsequent microbial sulfate reduction (MSR), an important contributor
 394 to sedimentary OC oxidation, likely had a minimal impact on the remaining OC, based on
 395 chromium-reducible sulfur concentrations (S_{pyr}) of 10 ppm (Schobben et al., 2015). Both loss of OC
 396 by MSR and oxic degradation can be quantified by successive application of Equations 4 and 5,
 397 respectively, as given in Algeo et al. (2013):

$$398 \quad OCAR'' = OCAR' + (0.75S_{pyr} BAR) \quad (4)$$

$$399 \quad OCAR''' = OCAR'' 10^{0.51(3.1 - BAR)} \quad (5)$$

400 Here, $OCAR''$ and $OCAR'''$ stand for the organic matter accumulation before MSR and oxic
 401 degradation, respectively. The original OC value of the sediment (before the start of early
 402 diagenesis) can be derived by dividing $OCAR'''$ with BAR. The back-calculated original OC values

403 of the study samples suggest that the process of OC oxidation and related carbonate dissolution can
404 account for the observed offset between brachiopod and whole-rock $\delta^{13}\text{C}$. Although this large
405 extrapolation ($> \times 10$) of measured TOC to obtain the original sedimentary OC values is connected
406 with a large uncertainty (see Algeo et al., 2013), the computed values are consistent with OC for
407 open-ocean carbonate platform sediments ($\sim 1.0\%$) based on modern observations (Emerson and
408 Hedges, 2003).

409

410 *5.3. Evaluation of primary and diagenetic influences on $\delta^{18}\text{O}$ profiles of Iranian PTB sections*

411 The oxygen isotopic composition of the phosphate in conodont apatite has proven valuable
412 for palaeoclimatic reconstructions of the latest Permian and Early Triassic (Joachimski et al., 2012;
413 Romano et al., 2013; Schobben et al., 2014; Sun et al., 2012). Our O-isotope record of Iranian
414 conodonts through the Permian-Triassic boundary interval is constructed from conodont platform
415 elements with colour alteration indices (CAI) between 1.0 and 1.5, indicating minor thermal
416 overprints (Schobben et al., 2014). This oxygen isotope record shows stable values throughout the
417 latest Permian, which is also the case for the latest Permian brachiopod O-isotope record (Fig. 3).
418 The general agreement between the conodont and brachiopod isotope records constitutes an
419 additional argument for good fossil preservation in the study sections. These fossil records can,
420 therefore, be taken as a baseline for assessing diagenetic alteration of the bulk-rock O-isotope
421 record (e.g., Brand et al., 2012a, 2012b). Brachiopods inform about the carbon and oxygen isotope
422 evolution of the latest Permian, before they disappear at the EPME horizon at the base of the
423 Boundary Clay (Fig. 3). For the remainder of the study succession, only conodont phosphate is
424 available for comparison with bulk-rock data.

425 Despite some uncertainty concerning the conodont $\delta^{18}\text{O}$ correction factor (see Section 4.1),
426 a significant offset (median: $2.1\text{‰} \pm 0.4\text{‰}$) exists between conodont/brachiopod and bulk-
427 carbonate $\delta^{18}\text{O}$ ($\Delta^{18}\text{O}_{\text{bio-bulk}}$) (Fig. 7). Thus, the bulk-rock $\delta^{18}\text{O}$ values almost certainly have been

shifted by diagenetic processes, with higher burial temperatures during recrystallization leading to reduced fluid-solid fractionation and, thus, more negative $\delta^{18}\text{O}$ values for secondary carbonate phases (cf. Algeo et al., 1992). The fraction of recrystallized carbonate rock that equilibrated with the diagenetic fluid ($F_{\text{CaCO}_3(\text{au})}$) would determine the final whole-rock $\delta^{18}\text{O}$ and is linked to burial temperature and the oxygen isotope composition of the diagenetic fluid via Equation 6:

$$F_{\text{CaCO}_3(\text{au})} = \frac{\Delta^{18}\text{O}_{\text{bio-bulk}}}{\delta^{18}\text{O}_{\text{bio}} - \delta^{18}\text{O}_{\text{dia}}} \quad (6)$$

where the $\delta^{18}\text{O}_{\text{bio}}$ and $\delta^{18}\text{O}_{\text{bulk}}$ is taken as the median of measured conodont/brachiopod (combined) and whole-rock oxygen isotope values, respectively. The oxygen isotope composition of the diagenetic carbonate ($\delta^{18}\text{O}_{\text{dia}}$), which depends on the isotope value of the pore water and the temperature at which secondary precipitation occurred, can be calculated using the fractionation relationship of Kim and O'Neil (1997). The study sites experienced maximum burial temperatures of 80 °C, based on low conodont CAI (1.0-1.5). The $\delta^{18}\text{O}_{\text{fluid}}$ was probably between that of contemporaneous seawater (ca. -1.0 ‰) and a pore fluid equilibrated with the calcitic sediment (-2.0 to -4.0 ‰). The observed $\Delta^{18}\text{O}_{\text{bio-bulk}}$ can be explained through an addition of authigenic carbonate ($F_{\text{CaCO}_3(\text{au})} = 0.2\text{-}0.3$; Fig. 8). This model implies diagenetic stabilization at low water/rock ratios (< 10), which is typical for carbonates that stabilize in contact only with marine/pore water-sourced fluid, in the marine phreatic environment under “closed system” diagenesis.

The vertical shifts in the bulk-rock $\delta^{18}\text{O}$ profiles of the two study sections match those of the brachiopod/conodont $\delta^{18}\text{O}$ profiles (Joachimski et al., 2012; Schobben et al., 2014). This is an additional strong argument that lithification and diagenetic stabilization of the whole-rock carbonate occurred in a closed system, resulting in a relatively uniform offset of the $\delta^{18}\text{O}$ values of secondary carbonate phases relative to those of well-preserved biogenic carbonates. The study sections, thus, exhibit partial retention of their primary marine carbon and oxygen isotope signals, preserving the

original pattern of stratigraphic variations in $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ despite negative offsets of up to several per mille due to diagenetic influences.

6. Discussion

6.1. Permian-Triassic carbonate $\delta^{13}\text{C}$ - $\delta^{18}\text{O}$ records

Uppermost Permian-Lower Triassic sections globally are characterized by large positive and negative excursions in carbonate $\delta^{13}\text{C}$. The interval bracketing the Permian-Triassic (P-Tr) boundary (251.902 ± 0.024 Ma; Burgess et al., 2014) is associated with a large negative $\delta^{13}\text{C}$ excursion that has been attributed to a global carbon cycle perturbation (for a review, see Korte and Kozur, 2010). A long-term (~ 0.5 - 1.0 Myr) negative carbonate carbon isotope trend started in the latest Permian and continued into the earliest Triassic, a feature characteristic of many P-Tr successions around the globe (e.g., Baud et al 1989; Hermann et al., 2010; Korte and Kozur, 2010; Korte et al., 2010; Tong et al., 2007; Fig. 6). This “first-order $\delta^{13}\text{C}$ trend” has been attributed to the effects of Siberian Traps volcanism (Sobolev et al., 2011) including the metamorphism of organic-rich sediments (Korte et al., 2010; Retallack and Krull, 2006; Svensen et al., 2009), as well as to the erosion of continental organic matter (Holser and Magaritz, 1987; Kraus et al., 2013; see also Sephton et al., 2005), and the reduction of marine primary productivity (Rampino and Caldeira, 2005). Superimposed fluctuations around the long-term carbon isotope trend have been reported (e.g., Algeo et al., 2007, 2008), and in the present study these short-term fluctuations are referred to as “second-order excursions” (Fig. 6). The latter have been employed to recognize short stratigraphic intervals including individual lithological horizons (e.g., Richoz et al., 2010). For example, a short-term (~ 2 - 20 kyr) negative $\delta^{13}\text{C}$ excursion coincident with the EPME horizon at Meishan (South China; Fig. 6) (Cao et al., 2009; Burgess et al., 2014) has been attributed to

475 massive CH₄ release from methane clathrate dissociation (Benton and Twitchett, 2003; Berner,
476 2002) or rapid expansion of methanogenic species (Rothman et al., 2014).

477 A bulk-carbonate oxygen isotope record from material of the Gartnerkofel core (Southern
478 Alps) has been interpreted to reflect a temperature rise of 5 °C across the P-Tr boundary (Holser et
479 al., 1989). An even more dramatic temperature rise (~10 °C) has been established based on bulk-
480 carbonate δ¹⁸O from another outcrop in the Southern Alps (Kearsey et al., 2009). However, both
481 these sites are marked by pervasive dolomitization, and the original whole-rock δ¹⁸O values have
482 likely been altered. In addition, stabilization of carbonate constituents might be stratigraphically and
483 spatially heterogeneous, tracking diagenetic and dolomitization processes (Brand et al., 2012b). The
484 oxygen isotope composition of phosphate locked in conodont apatite is considered to be more
485 resistant to diagenesis because of the highly impermeable nature of this biomineral (Joachimski et
486 al., 2009; Pucéat et al., 2004; Wenzel et al., 2000). A negative δ¹⁸O excursion in conodont apatite
487 slightly above the EPME horizon in South China and NW Iran has been attributed to a seawater
488 temperature increase of 7-10 °C (Joachimski et al., 2012; Schobben et al., 2014; Fig. 3).

489

490 *6.2. Sea level and the preservation potential of primary bulk-rock isotope compositions*

491 Our comparative analysis of bulk-rock and fossil isotope records combined with quantitative
492 modelling (see Sections 5.2-5.3) leads us to conclude that the first-order trends in the bulk-rock C-
493 and O-isotope profiles represent an environmental/climatic signal. We infer that a major
494 perturbation to the global carbon cycle recorded by the first-order negative δ¹³C trend across the
495 EPME coincided with global climatic and tropical seawater temperature warming, as recorded by a
496 parallel shift in δ¹⁸O profiles (cf. Holser et al., 1989). These primary signals can still be recognized
497 despite alteration of absolute C- and O-isotope values through subsequent diagenesis. Diagenesis
498 resulted in negative offsets from primary marine carbonate values in the whole-rock δ¹³C and δ¹⁸O
499 records as a result of the influences of elevated burial temperatures and (an)aerobic OC oxidation.

500 The degree of diagenetic alteration of the C- and O-isotope records appears to have been fairly
501 uniform throughout the study sections, possibly owing to limited lithologic variation and generally
502 similar burial conditions at the time of diagenesis. Conodont CAI values and modelling constraints
503 (see Section 5.3) suggest that diagenetic stabilization of carbonate occurred at relatively low burial
504 temperatures and, hence, shallow depths within the marine phreatic zone.

505 The study units show no evidence of alteration by meteoric waters. Platform carbonates that
506 recrystallize when exposed to meteoric (carbonate-undersaturated) waters show features of strong
507 dissolution, high water-rock ratios (“open system”), and low $\delta^{18}\text{O}$ compositions owing to the ^{18}O -
508 depleted nature of the meteoric fluid. The $\delta^{13}\text{C}$ compositions of secondary carbonates forming in
509 open diagenetic systems are typically variable but more depleted than the primary marine carbonate
510 owing to incorporation of ^{13}C -depleted carbon from oxidation of OC (Brand and Veizer, 1981;
511 Knauth and Kennedy, 2009; Marshall, 1992). The lack of evidence of meteoric influence in the
512 study units suggests that sea-level elevations remained high during their deposition. This inference
513 is consistent with the hypothesis of a global marine transgression during the latest Permian-Early
514 Triassic (for a review, see Hallam and Wignall, 1999). Although it has been proposed that the
515 boundary beds, especially on Chinese carbonate platforms, are marked by an erosional surface (Yin
516 et al., 2014) and show signs of subaerial exposure (Collin et al., 2009), the sedimentological
517 evidence is controversial and the supposed karstic surfaces have also been suggested to originate
518 from a submarine dissolution event (Payne et al., 2007). Furthermore, the present study sections as
519 well as other PTB carbonate successions globally (Fig. 4B) are marked by generally heavy carbon
520 isotope compositions despite variable and commonly light $\delta^{18}\text{O}$ values. This pattern is consistent
521 with marine phreatic diagenesis under high sea-level conditions, a scenario that offers strong
522 potential for preserving the original marine chemistry of both the bulk-carbonate sediment and
523 biogenic calcite components.

524

525 6.3. Significance of authigenic carbonate precipitation

526 Precipitation of ^{13}C -depleted secondary carbonate phases at a large scale can potentially
527 influence the global carbon cycle. Although carbonate dissolution related to CO_2 production
528 typically accompanies aerobic decay of organic matter in the shallow diagenetic environment (see
529 Section 5.2), subsequent decay reactions in the anoxic deeper sediment column lead to increased
530 pore water alkalinity and precipitation of authigenic carbonate phases. These processes include
531 microbial sulfate reduction (MSR) (Emerson and Hedges, 2003; Shen and Buick, 2004) and
532 anaerobic oxidation of methane (AOM) (Boetius et al., 2000; Hinrichs et al., 1999). Detection and
533 quantification of authigenic carbonate precipitation through Earth history might be of quantitative
534 importance for global carbon budgets, as suggested by Schrag et al. (2013).

535 Several considerations suggest that precipitation of authigenic carbonate during the PTB
536 crisis was considerable and possibly influenced the contemporaneous global carbon cycle. The
537 fraction of authigenic carbonate in the study samples is calculated at 20-30 % of the total rock
538 weight (Section 5.3), a value which lies at the upper range observed for modern carbonate deposits
539 (Schrag et al., 2013 and references therein). Sufficiently large-scale precipitation of isotopically
540 light authigenic carbonate in essence sequesters ^{13}C -depleted organic carbon (in oxidized form) in
541 the sediment, preventing it from diffusing back into the overlying water column and, thus,
542 contributing to an increase in the $\delta^{13}\text{C}$ of global dissolved inorganic carbon (DIC). A related
543 consideration is that widespread oceanic dysoxia/anoxia, as during the latest Permian-Early Triassic
544 (Wignall and Twitchett, 1996; Brennecke et al., 2011), decreases the total amount of aerobic
545 oxidation of OC in sediments globally and increases the amount of anaerobic oxidation, leading to a
546 general increase in pore water alkalinity and widespread precipitation of authigenic carbonates
547 (Schrag et al. 2013). This process should be accompanied by heavy $\delta^{13}\text{C}$ of seawater DIC owing to
548 increased sequestration of isotopically light carbon in authigenic carbonate phases. This diagenetic
549 C sink provides an alternative explanation for the enriched $\delta^{13}\text{C}$ in bulk carbonate sediments and
550 calcite biogens of the Late Permian (before the onset of the secular negative trend towards lighter

551 $\delta^{13}\text{C}$ values). These carbonates with enriched $\delta^{13}\text{C}$ are some of the heaviest values recorded for the
552 Phanerozoic (Veizer et al., 1999), a feature which has formerly been interpreted as the result of
553 elevated OC burial (e.g., Rothman et al., 2014). Incorporation of this diagenetic feature into our
554 current understanding of Permian-Triassic seawater chemistry evolution suggests the need for a
555 wide-ranging re-evaluation of bulk-rock carbonate isotope data.

556

557 *6.4. Second-order carbon isotope excursions: globally correlative signals or local diagenetic*
558 *effects?*

559 Second-order isotope excursions represent short-term deviations from the general first-order
560 trend towards lower $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ up-section, as shown in our case study of P-Tr boundary beds. In
561 the present study, second-order isotope excursions are confined to narrow stratigraphic intervals,
562 covered by only a few data points, and often associated with a certain lithology (Fig. 6). These
563 stratigraphically restricted isotope fluctuations contrast with the first-order isotope trends, which cut
564 across several different lithologies and, thus, are clearly not controlled by lithology.

565 Many PTB sections exhibit small-scale second-order fluctuations in bulk-carbonate $\delta^{13}\text{C}$
566 superimposed on the general negative trend (Cao et al., 2009; Korte et al., 2004a). At multiple PTB
567 sections, Heydari et al. (2001) attributed these features to meteoric diagenesis related to a subaerial
568 exposure surface, although $\delta^{13}\text{C}$ - $\delta^{18}\text{O}$ covariation patterns do not support this interpretation (cf. Fig.
569 4) and the evidence for subaerial exposure is weak (n.b., observed features in this section are more
570 likely due to submarine dissolution; Leda et al., 2014). At Nhi Tao, Vietnam, Algeo et al. (2008)
571 demonstrated that second-order $\delta^{13}\text{C}$ fluctuations were closely associated with framboidal pyrite
572 layers having strongly negative $\delta^{34}\text{S}_{\text{py}}$ values and, on this basis, inferred an origin through upward
573 chemocline excursions (cf. Kump et al., 2005).

574 In the present study sections, second-order $\delta^{13}\text{C}$ fluctuations, which are especially evident in
575 the Boundary Clay, are likely to have been the product of late-stage diagenesis. This inference is

576 based on the relationship of these features to variations in lithology and Mg/Ca ratios (Fig. 6). A
577 similar pattern is seen in the Meishan D section, in which high Mg/Ca is associated with second-
578 order positive $\delta^{13}\text{C}$ excursions within the clay-rich boundary interval (Fig. 6), and was attributed to
579 late-stage dolomitization by Xie and Wang (2011). These considerations suggest that second-order
580 $\delta^{13}\text{C}$ excursions frequently (although not always) have a diagenetic origin that precludes their use as
581 stratigraphic markers (e.g., Xie et al., 2007; Hermann et al., 2011).

582 Distinguishing an environmental from a diagenetic origin for second-order bulk-rock $\delta^{13}\text{C}$
583 and $\delta^{18}\text{O}$ excursions remains difficult. Patterns of covariation between carbonate C- and O-isotopes
584 and elemental data are not diagnostic of diagenesis, because environmental and biological
585 influences on calcite precipitation can mimic known diagenetic patterns (see Section 6.1).
586 Furthermore, if diagenetic artefacts are restricted to narrow stratigraphic intervals or specific
587 lithologies (as in the present study units), then the isotopic-elemental relationships indicative of
588 such an origin can be obscured when data for larger stratigraphic intervals are lumped together. A
589 robust approach to assessing the influence of local diagenesis on bulk-carbonate C- and O-isotopes
590 would entail fossil versus bulk-rock comparisons combined with elemental and TOC data at a
591 sufficiently high stratigraphic resolution to allow recognition of the diagenetic signals, as
592 demonstrated in the present study.

593

594 7. Conclusions

595 Fossils of brachiopods and conodonts that are well-preserved and minimally altered
596 diagenetically are favoured as proxies for primary marine isotopic compositions, although their
597 abundance and spatial distribution in many successions can be insufficient for construction of a
598 continuous isotopic profile. For this reason, the C- and, less often, O-isotopic compositions of bulk-
599 carbonate have been used in palaeoenvironmental studies, commonly with assessment of diagenetic
600 alteration through examination of elemental ratios (e.g., Mn/Ca, Sr/Ca). However, the application of

601 elemental screening to identify the extent of diagenetic alteration of calcite samples can lead to
602 uncertain results owing to environmental controls on these proxies. In this study, we have shown
603 that continuous isotopic profiles based on bulk-rock analyses can be tested for diagenetic influences
604 and preservation of a primary marine trend by comparison with limited C- and O-isotope data from
605 biogenic components. For carbonate successions, limited diagenetic alteration is most likely to be
606 encountered when post-depositional stabilization occurs in a marine phreatic environment, i.e.,
607 without exposure to meteoric fluids as a result of sea-level fall.

608 With regard to the present study sections, the first-order negative $\delta^{13}\text{C}$ excursion across the
609 P-Tr boundary at Kuh-e-Ali Bashi and Zal (as well as many sections globally) is a secular feature
610 that was caused by a major carbon cycle perturbation. However, small-scale secondary fluctuations
611 in $\delta^{13}\text{C}$, especially in the Boundary Clay, appear related to lithologic variation. This observation
612 suggests that such small-scale isotopic features should be interpreted with caution and only used for
613 palaeoenvironmental interpretation if they can be independently verified in multiple coeval
614 successions. The presence of substantial amounts of isotopically light carbon in the study sections
615 may be due to enhanced precipitation of authigenic carbonate, as evidenced by modelling of the
616 observed offsets in the C and O isotope signatures of different components in the carbonate rock.
617 This observation has implications for the global carbon cycle, suggesting that authigenic carbonates
618 may play an important role as a carbon sink.

619

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630

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953

954

955 **Figure and table captions**

956

957 **Fig. 1.** (A) Geographical location and (B) palaeogeographic setting of the Kuh-e-Ali Bashi and Zal
958 P-Tr boundary sections in the Julfa region of NW Iran (panel B is adapted from Stampfli and Borel
959 (2002; also Stampfli, pers. comm., 2011). Note that the colouring of the continents in the
960 palaeogeographic map is not indicative of climate zones and biomes.

961

962 **Fig. 2.** (A) Field photo of the Kuh-e-Ali Bashi section. (B-E) Photomicrographs of key lithological
963 and textural features (scale bars = 1 mm). (B) The nodular *Paratirolites* Limestone; note
964 hardground intraclasts ('subsolution clasts') with Fe–Mn crusts and biogenic encrustation on clast
965 rims. Ali Bashi 1, 0.75 m below the EPME horizon. (C) Platy limestone at the base of the *Claraia*
966 Beds showing evidence of recrystallization (e.g., sparry calcite spheres). Ali Bashi 1, 4.15 m above
967 the EPME horizon. (D) The Boundary Clay with abundant rhombic (high-magnesium?) crystals
968 floating in matrix, Ali Bashi 1, 0.40 m above the EPME horizon. (E) The Boundary Clay beds,
969 containing ostracods, sponge remains, and signs of bioturbation. Ali Bashi 1, 0.75 m above the
970 EPME horizon. B and C were adapted from Leda et al. (2014).

971

972 **Fig. 3.** $\delta^{13}\text{C}$, $\delta^{18}\text{O}$, Mn/Ca, Sr/Ca and Mg/Ca systematics of bulk-carbonate fraction and brachiopod
973 calcite (Schobben et al., 2014) for Kuh-e-Ali Bashi (A) and Zal (B). The conodont $\delta^{18}\text{O}$ data taken
974 from Schobben et al. (2014) were converted to the VPDB scale for comparison with carbonate $\delta^{18}\text{O}$.
975 The widths of the bars of the conodont $\delta^{18}\text{O}$ data represent the different values generated by two
976 different conversion methods (see Section 4.1). Bulk-rock mineralogy, CaCO_3 , and insoluble
977 residue (IR) are depicted as percentages of total rock. The most salient features of bulk-rock
978 composition are elemental enrichments within the Boundary Clay. In the bulk-rock $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$
979 profiles, red circles are used to show samples with elevated Mg/Ca ratios (i.e., values that are $>1\sigma$

above the mean). Conodont zones for Kuh-e-Ali Bashi (Kozur, 2007; Ghaderi et al., 2014) and Zal (Schobben et al. 2015) are: (1) *C. changxingensis*, (2) *C. bachmanni*, (3) *C. nodosa*, (4) *C. yini*, (5) *C. abadehensis*, (6) *C. hauschkei*, (7) *H. praeparvus*-*H. changxingensis*, (8) *M. ultima*-*S. ?mostleri*, (9) *H. parvus*, (10) *H. lobota*, (11) *I. staeschei*, and (12) *I. isarcica*.

Fig. 4. Cross-plots of (A) Sr/Ca vs Mn/Ca, (B) $\delta^{13}\text{C}_{\text{carb}}$ vs $\delta^{18}\text{O}_{\text{carb}}$, (C) Sr/Ca vs $\delta^{13}\text{C}_{\text{carb}}$, and (D) Mn/Ca vs $\delta^{13}\text{C}_{\text{carb}}$. Diamonds represent brachiopods and open circles represent bulk-rock samples. In A, data are from Kuh-e-Ali Bashi, Zal (white—this study; Schobben et al., 2014), Val Brutta and Sas de Putia (green—Brand et al., 2012b) and Meishan (blue—Korte et al., 2005a; Riccardi et al., 2006). The Mn/Ca threshold for well-preserved (<0.18 mmol/mol) versus altered (>0.18 mmol/mol) samples is from Denison et al. (1994) and Korte et al. (2003; 2005a). Note that most of the bulk-rock samples fall outside this range. In B, data are from (i) South China and Vietnam (blue), Meishan D (Cao et al., 2009; Korte et al., 2005a), Meishan B (Jin et al., 2000), Nhi Tao (Algeo et al., 2007), and Cili (Luo et al., 2010); (ii) southern Alps and Bükk mountains (green), Val Brutta (Brand et al., 2012b; Kearsley et al., 2009), Sas de Putia (Brand et al., 2012b; Korte and Kozur, 2005), Tesero (Korte and Kozur, 2005), Gartnerkofel (Holser et al., 1989), Bulla (Korte and Kozur, 2005), Gerrenavár (Korte and Kozur, 2005), Bálvány (Haas et al., 2006); and (iii) Iran (white), Kuh-e-Ali Bashi, Zal (this study; Korte and Kozur, 2005; Schobben et al., 2014), Abadeh (Korte et al., 2004a). Included is the range of Cenozoic carbon and oxygen isotope values from rocks that lithified under the influence of either marine or meteoric pore water (from Knauth and Kennedy, 2009). The arrows indicate directions of isotopic evolution associated with meteoric and deep burial diagenesis. The pattern observed in the study units is consistent with stabilization in the marine phreatic environment. In C and D, data are for the Kuh-e-Ali Bashi and Zal sections (this study).

Fig. 5. (A) Mn/Ca and (B) Sr/Ca as a function of lithology (red: Kuh-e-Ali Bashi; blue: Zal). In A, Mn/Ca ratios increase from platy limestone to nodular limestone, and, then, to the Boundary Clay.

1006 In B, Sr/Ca ratios are higher in platy limestone than in nodular limestone, with no consistent
 1007 pattern for the Boundary Clay. The yellow lines at the bottom represent average values for
 1008 brachiopod calcite; the ranges of Sr/Ca ratios observed in modern carbonate deposits (Bathurst,
 1009 1976) and diagenetic cements (solid—Banner, 1995; dotted—Ullmann and Korte, 2015) are shown
 1010 on the right side of B.. The black circles are outliers according to the convention of box-and-
 1011 whisker plots, i.e., values plotting at $>1.5\times$ the Interquartile Range (Q_3-Q_1).

1012

1013 **Fig. 6.** $\delta^{13}\text{C}_{\text{carb}}$ records for whole-rock samples from Kuh-e-Ali Bashi and Zal (this study—white
 1014 dots; Korte and Kozur, 2005—grey dots), Abadeh (Korte et al., 2004a), Meishan D (Cao et al.,
 1015 2009; Korte et al., 2005a), Meishan B (Jin et al., 2000), Gartnerkofel (Holser et al., 1989), and Nhi
 1016 Tao (Algeo et al., 2007, 2008). Note that the y-axis is scaled with regard to stratigraphic height and
 1017 relative time; absolute timescale on right for the interval between the EPME horizon and the top of
 1018 the *H. parvus* zone (based on Burgess et al., 2014). Biostratigraphy and EPME placement are based
 1019 on: Kuh-e-Ali Bashi and Zal (Ghaderi et al., 2014; Kozur, 2007), Meishan D and B (Jin et al., 2000;
 1020 Yuan et al., 2014). The stratigraphic subdivision of the Gartnerkofel section is taken from Korte and
 1021 Kozur (2010) and differs slightly from the original (Schönlaub, 1991). The FAD of *I. staeschei* is
 1022 not recognized in the sites considered here but is likely analogous to the FAD of *I. isarcica*. A
 1023 conodont biostratigraphy is not available for Nhi Tao, and correlations are therefore less certain for
 1024 this section. Red dots represent samples with significant Mg enrichment of the carbonate fraction.
 1025 The dark grey areas represent carbonate-bearing clay beds or volcanic ash layers, and the light grey
 1026 areas represent argillaceous limestone and limestone-clay alternations. Dotted vertical lines
 1027 represent the pre-extinction baseline value for bulk-rock $\delta^{13}\text{C}$.

1028

1029 **Fig. 7.** The offset between biogenic and bulk-rock C-O isotope compositions shown as smoothed
 1030 trends for Kuh-e-Ali Bashi (A) and Zal (B). The trend lines of bulk-rock $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ were
 1031 generated using a polynomial Kernel regression with a bandwidth equivalent to $1.5\times$ the distance of

the maximum sampling density. The legend for data points is the same as in Figure 3. The histograms show $\Delta^{13}\text{C}_{(\text{bio-bulk})}$, i.e., the difference in C-isotopic compositions of brachiopod and bulk-rock samples. (C) The offset and $\Delta^{18}\text{O}_{(\text{bio-bulk})}$ between conodont and brachiopod (bio) and whole-rock samples (bulk) are for the *Paratirolites* Limestone Member only. (D) The offset and $\Delta^{18}\text{O}_{(\text{bio-bulk})}$ between conodont and brachiopod (bio) and whole-rock samples (bulk) for the complete P-Tr boundary interval. Where the stratigraphic elevations of sample pairs differ, interpolated values were used in Δ calculation.

Fig. 8. Modelling results using parameters for the inferred underlying diagenetic mechanism and offsets between biogenic and bulk rock C-O isotope compositions (Fig. 7). A) Numerical solution for original sedimentary OC based on $\Delta^{13}\text{C}_{(\text{bio-bulk})}$ of 1.2 ‰ (median), based on a range of burial temperatures and $\delta^{13}\text{C}$ of the diagenetic fluid. B) Numerical solution for the fraction of authigenic carbonate required to explain an $\Delta^{18}\text{O}_{(\text{bio-bulk})}$ of 2.1 ‰ (median), based on a range of burial temperatures and $\delta^{18}\text{O}$ of the diagenetic fluid. C) Graphic representation of whole rock $\delta^{13}\text{C}$ under the influence of bicarbonate derived from aerobic OC degradation and the relation to the original sedimentary organic matter content. D) Graphic representation of whole-rock $\delta^{18}\text{O}$ as a factor of carbonate originally precipitated from seawater and the diagenetic fluid.

Table 1. Elemental ratios of the international certified standards JLS-1 and JDo-1 (published and measured; element ratios are taken from Imai et al., 1996).

Table 2. Results for linear model fit between different chemical proxies. The correlation is calculated using Pearson's correlation coefficient (r^2), n = degrees of freedom, p = significance. High Pearson r^2 values indicate a high correlation; low p -values indicate a statistically significant correlation. IR = insoluble residue after acid digestion of a carbonate sample.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Table 1

	Sr/Ca		Mn/Ca		Mg/Ca	
	(mmol/mol)	2 sd	(mmol/mol)	2 sd	(mmol/mol)	2 sd
JDo-1 (n=3)						
measured	0.21	0.04	0.14	0.02	750.11	21.04
published	0.22		0.15		761.21	
JLs-1 (n=23)						
measured	0.34	0.01	0.03	0.00	14.09	0.24
published	0.34		0.03		15.02	

Table 2

	x	y				
Section	(response)	(terms)	Coefficient	Pearson's r^2	p-value	n
Kuh-e-Ali Bashi	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$	0.44	0.73	2.20E-16	78
Zal	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$	0.51	0.34	5.64E-05	39
Kuh-e-Ali Bashi	Sr/Ca	Mn/Ca	-0.05	0.10	1.00E-02	58
Zal	Sr/Ca	Mn/Ca	-0.04	0.00	7.00E-01	33
Kuh-e-Ali Bashi	Sr/Ca	Mg/Ca	0.00	0.00	6.20E-01	58
Zal	Sr/Ca	Mg/Ca	0.00	0.00	7.80E-01	33
Kuh-e-Ali Bashi	Mn/Ca	$\delta^{13}\text{C}$	-0.18	0.02	2.93E-01	57
Zal	Mn/Ca	$\delta^{13}\text{C}$	0.27	0.08	9.95E-02	32
Kuh-e-Ali Bashi	Sr/Ca	$\delta^{13}\text{C}$	0.71	0.01	5.41E-01	57
Zal	Sr/Ca	$\delta^{13}\text{C}$	-0.55	0.11	5.77E-02	32
Kuh-e-Ali Bashi	Mn/Ca	IR	0.05	0.39	2.28E-07	55
Zal	Mn/Ca	IR	0.05	0.34	4.06E-04	31
Kuh-e-Ali Bashi	Sr/Ca	IR	-37.46	0.17	1.43E-03	55
Zal	Sr/Ca	IR	-2.87	0.02	4.59E-01	31

Graphical Abstract