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Organic carbon isotope values from the Late Permian Seis/Siusi succession (Dolomites, Italy): Implications for palaeoenvironmental changes

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Abstract

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Key Words

carbon isotope stratigraphy microfossils organic matter from land plants P-T boundary Southern Alps The Permian-Triassic boundary is marked by a globally prominent negative carbon isotope excursion traceable in marine carbonates and organic matter. In the shallow marine carbonate succession at Seis/Siusi (Dolomites, Italy), the $\delta^{13}C_{carb}$ and $\delta^{13}C_{org}$ signatures follow the general Permian-Triassic boundary carbon isotope trend, but the $\delta^{13}C_{org}$ values are slightly less depleted in ^{13}C in two episodes representing restricted lagoonal environments and in the period around the Tesero Oolite Horizon. This isotopically less depleted organic matter in the lagoons is interpreted to be most likely caused by poor oxygen ventilation and/or slightly modified salinity which may have led to restricted bioproductivity and increased hence the relative amounts of continental-sourced organic matter. In addition, elevated riverine influx and supply of terrestrial organic matter, perhaps triggered by a wet period, might be the cause for the relatively less depleted ^{13}C in the organic matter around the Tesero Oolite Horizon and in overlying sediments.

Introduction

The Palaeozoic-Mesozoic transition is marked by the severest mass extinction in Earth history which took place in the latest Permian and affected both marine and continental biota (e.g., Schindewolf 1953; Sepkoski 1989; Raup 1991; Kozur 1998a, 1998b; Jin et al., 2000; Benton & Twitchett 2003; Erwin 2006; Peng & Shi 2009). This event was accompanied by major perturbations in the global carbon cycle marked by a prominent negative δ¹³C excursion across the Permian-Triassic boundary (PTB) (e.g., Chen et al. 1984; Holser & Magaritz 1987; Holser et al. 1989; Krull et al. 2000; Twitchett et al. 2001; Korte et al. 2004, 2010; Retallack et al. 2005; Algeo et al. 2007; Yin et al. 2007; Heydari et al. 2008), followed by distinct positive and negative fluctuations in the Early Triassic (e.g., Atudorei 1999; Tong et al. 2002, 2007; Payne et al. 2004; Korte et al. 2005; Galfetti et al. 2007; Horacek et al. 2007). Carbon isotope excursions, if global in scale, are usually traceable in carbonates and organic matter of marine and continental successions (ocean/atmosphere systems). This fact enables worldwide stratigraphic correlation of PTB successions (e.g., Cao et al. 2010; Korte & Kozur 2010; Richoz et al. 2010) as well as for several other stage boundaries, such as the Rhaetian–Hettangian (e.g., Hesselbo et al. 2002; Korte et al. 2009; Ruhl et al. 2009) or Cenomanian–Turonian (e.g., Jarvis et al. 2006; Sageman et al. 2006).

For the PTB, parallel trends in carbonate and organic matter $\delta^{13}C$ are reported for bulk organic matter and carbonate samples from some sections in the Alps and in Kashmir (e.g., Magaritz et al. 1992; Sephton et al. 2002; Algeo et al. 2007), but in other successions in Iran, Slovenia and China, deviating trends have been traced (e.g., Korte et al. 2004; Schwab & Spangenberg 2004; Zhang et al. 2006; Riccardi et al. 2007; Yin et al. 2007). Here we study the $\delta^{13}C_{carb}$ vs $\delta^{13}C_{org}$ variations



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in a shallow marine carbonate section in the European Southern Alps in order to investigate whether the fluctuations are parallel in shallow water successions or, if not, what the potential causes are for the variations.

Geological setting

The studied section is located about 1 km south of Seis (Siusi) village in South Tyrol (Dolomites, Italy), in a gorge (Seiser Klamm/Gola di Siusi) along the Weissenbach River (Rio Bianco) (Fig. 1). The section comprises the Bellerophon Limestone Formation overlain by the Werfen Formation (Fig. 2). The part of the latter Formation sampled in this study consists of the Tesero Oolite Horizon (TOH) and the lower part of the Mazzin Member. The sediments were deposited on a shallow marine, restricted inner shelf on a slightly eastwardstilted carbonate ramp (Bosellini & Hardie 1973; Noé 1987). The change from the limestone-dolomite cycles of the Bellerophon Formation to the oolites of the TOH is environmentally significant and also marks the traditional PTB (Leonardi 1967; Asserato et al. 1973). The base of the Triassic, however, is defined by the International Commission on Stratigraphy by the first appearance datum (FAD) of the conodont Hindeodus parvus (Kozur & Pjatakova, 1976). Conodonts are rare in the Southern Alps, but Hindeodus and Isaricella occur, enabling identification of the boundary in the Pufels and Tesero sections and in the Gartnerkofel core (Perri 1991; Schönlaub 1991; Farabegoli & Perri 1998; Nicora & Perri 1999; Korte & Kozur 2005; Farabegoli et al.

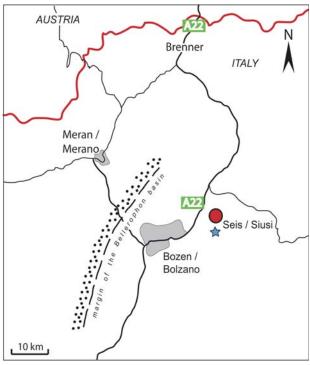


Figure 1. Sample locality in the Seiser Klamm (star) about 1 km south of Seis/Siusi (46 517° N, 11 568° E). Map modified after Brandner (1988) and Kraus et al. (2009).

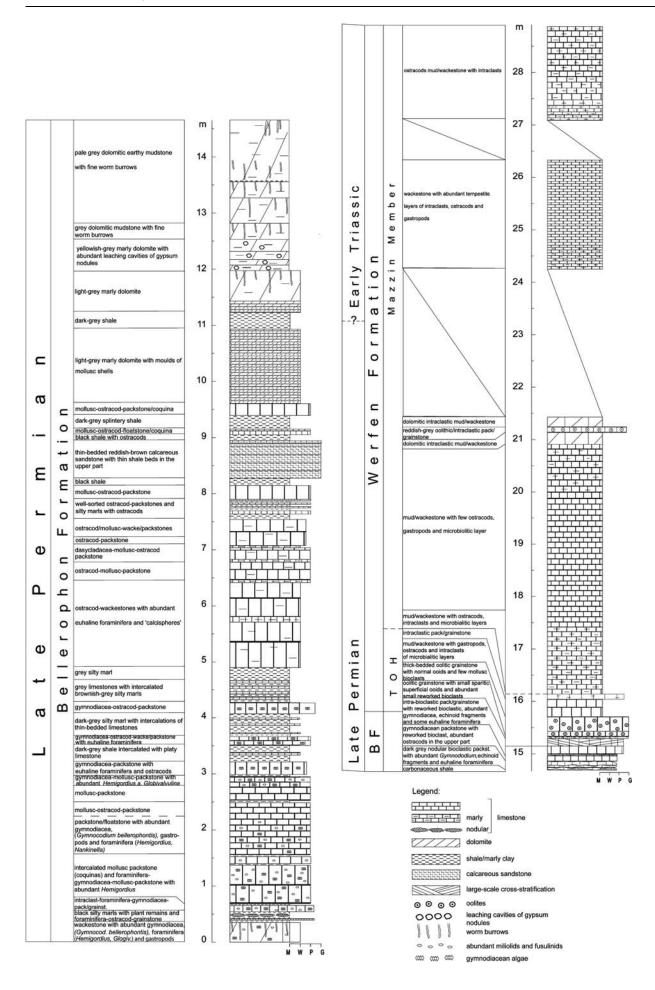
2007; Posenato 2009, 2010; Korte et al. 2010). No conodont distributions are published for the Seis section. Kraus et al. (2009) discussed the chemostratigraphic PTB by using the first δ^{13} C minimum (c.f., Korte & Kozur 2010) occurring 13 m above the base of the TOH. In this correlation there is a lack in δ^{13} C data between 6.4 m and 9.2 m (21.5 m and 24.3 m in Fig. 3). Horacek et al. (2010) subsequently published a higher resolution dataset with a carbon isotope minimum at about 8 to 8.5 m above the base of the TOH. We suggest, in agreement with Korte & Kozur (2010), that this chemostratigraphic marker may represent the PTB (Figs 2–3).

During the latest Permian low-latitude main extinction event in the Tethys, a ca. 1 % positive excursion (Kraus et al. 2009; Korte & Kozur 2010; Cao et al. 2010) or a "plateau" (Richoz et al. 2010) interrupts the negative trend. Kraus et al. (2009) used this chemostratigraphic marker, starting about 0.8 m above the base of the TOH in the Seis section (samples 53a; Fig. 2), to define the extinction event which is most probably somewhat above (Korte & Kozur 2010). This suggestion is in agreement with palaeontological results by Kozur (1994), but in contrast to sedimentological interpretations of the generation of the oolite or the interpretation of the disappearance of most biota which occurs at the base of the TOH in other western part of the Southern Alps PTB sections (Farabegoli et al. 2007; Posenato 2009). The biota, however, were affected at the base of the TOH, but fusulinids and Permian holothurian sclerites still occur in the lower Tesero Oolite Horizon (e.g., Broglio Loriga & Cassinis 1992; Kozur 1994; Cirilli et al. 1998; Cassinis et al. 2000; Gorjan et al. 2007). Fusulinids are not found anywhere in the world above the low-latitude main extinction event and, in addition, holothurian sclerites also disappear at or even below this event, but re-appear in the Anisian (Kozur 1994, 1998a, 1998b); both observations suggest that the main extinction event was higher in the TOH, but not at its base (Kozur 1994).

Methods

A total of 75 ca. 1.5 g powders were drilled from fresh surfaces of cleaned marly or micritic carbonate rocks. To avoid unwanted heating, a drill rotation of 200 rev/min was used for 5 seconds only. Approximately 100–400 microgram was filled into 10 ml exetainers, sealed with a septum cap. After flushing with He (6 min) and the addition of H₃PO₄, the resultant CO₂ was analysed for $\delta^{13}C_{carb}$ and $\delta^{18}O$ on a Thermo Finnigan Gasbench II linked online to a Thermo Finnigan Delta V mass spectrometer in the stable isotope laboratory of the Museum für Naturkunde in Berlin. The reproducibility of replicated standards was better than 0.1 ‰ (one standard deviation) for carbon- and oxygen-isotopes. The $\delta^{13}C$ and $\delta^{18}O$ values were calibrated against V-PDB and are reported in the standard ‰-notation (Table 1). Residual

Figure 2. Lithology and sample locations of the Seis/Siusi section.



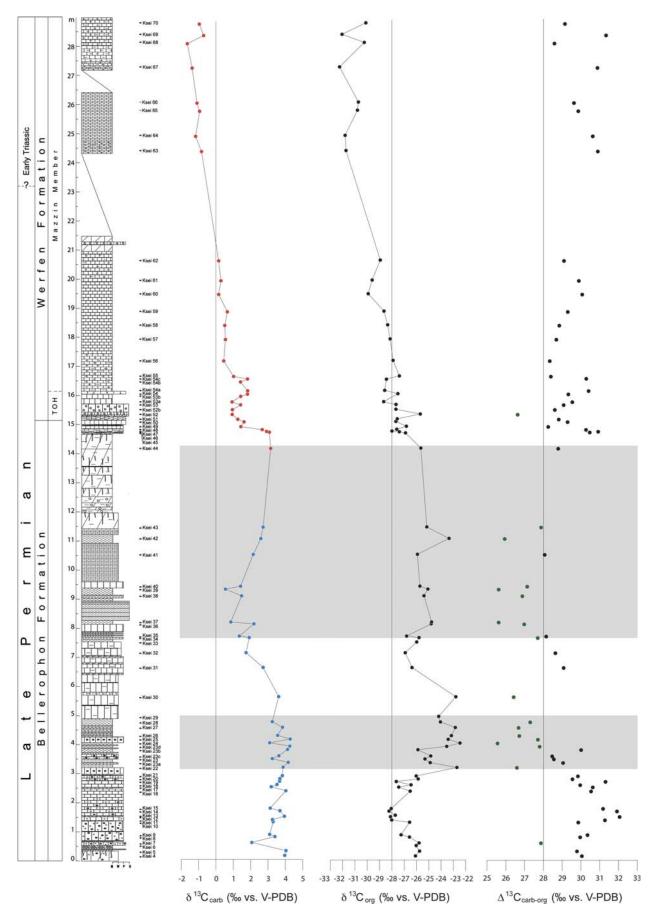


Figure 3. Carbon isotope values for bulk carbonates and organic matter and δ^{13} C of the Seis/Siusi section (the corrected scale deviates now slightly from Kraus et al. 2009).

Table 1. Stable isotope and TOC values of investigated samples.

Sample	$\delta^{13} \text{C}_{\text{carb}} \text{ vs.}$ V-PDB [‰]	0.8	TOC [%]	$\delta^{18}\text{O}$ vs. V-SMOW [‰]	Sample	$\delta^{13} C_{carb}$ vs. V-PDB [‰]	$\delta^{13} C_{org} \text{ vs.}$ V-PDB [‰]	TOC [%]	$\delta^{18}\text{O vs.}$ V-SMOW [‰]
Ksei 4	3.97	-26.08		23.07	Ksei 38	1.48	-25.39		25.76
Ksei 5	4.04	-25.75		25.02	Ksei 39	0.55	-25.07		25.58
Ksei 6		-26.02			Ksei 40	1.42	-25.72		26.59
Ksei 7	2.07	-25.79		23.35	Ksei 41	2.15	-25.92		29.51
Ksei 8	3.40	-26.57		23.93	Ksei 42	2.59	-23.35		26.75
Ksei 9	3.10	-27.25		22.79	Ksei 43	2.72	-25.16		25.69
Ksei 10	3.30	-26.56		23.03	Ksei 44		-25.64		
Ksei 11	3.26	-28.01		24.88	Ksei 45		-26.89		
Ksei 12	3.95	-28.11		25.28	Ksei 46		-27.39		
Ksei 13		-27.72			Ksei 47		-27.99		
Ksei 14	3.69	-28.23		24.88	Ksei 48		-27.60		
Ksei 15	3.13	-28.05		23.69	Ksei 49		-26.82		
Ksei 16	4.03	-26.51		22.64	Ksei 50		-27.67		
Ksei 17	3.19	-27.44		23.34	Ksei 51		-27.56		
Ksei 18	3.52	-26.44		25.49	Ksei 52		-25.69		
Ksei 19	3.67	-27.64		24.51	Ksei 52b		-27.67	0.09	
Ksei 20	3.69	-25.86		23.94	Ksei 53		-27.66		
Ksei 21	3.83	-26.02		26.44	Ksei 53a		-28.73	0.02	
Ksei 22	3.87	-22.71		24.68	Ksei 54		-27.51		
Ksei 23a	4.17	-24.88		25.85	Ksei 54a		-28.58	0.02	
Ksei 23	3.25	-25.31		24.24	Ksei 54c		-28.43	0.05	
Ksei 23c	3.63	-24.84		25.56	Ksei 55		-27.39		
Ksei 23b	4.13	-25.88		25.37	Ksei 56		-27.90		
Ksei 23d	4.26	-23.54		26.42	Ksei 57		-28.14		
Ksei 24	3.10	-22.46		24.98	Ksei 58		-28.34		
Ksei 25	4.28	-23.42		26.15	Ksei 59		-28.64		
Ksei 26	3.56	-23.16		25.25	Ksei 60		-29.92		
Ksei 27	3.84	-22.84		25.73	Ksei 61		-29.60		
Ksei 28	3.25	-24.05		26.27	Ksei 62		-28.94		
Ksei 29		-24.19			Ksei 63		-31.73	0.01	
Ksei 30	3.62	-22.80		25.09	Ksei 64		-31.80	0.08	
Ksei 31	2.72	-26.36		24.65	Ksei 65		-30.80	0.05	
Ksei 32	1.74	-26.91		25.47	Ksei 66		-30.72	0.03	
Ksei 33		-25.98			Ksei 67		-32.25	0.07	
Ksei 34	1.92	-25.79		24.78	Ksei 68		-30.24	0.05	
Ksei 35	1.35	-26.80		25.11	Ksei 69		-32.05	0.09	
Ksei 36	2.19	-24.80		25.86	Ksei 70		-30.11	0.04	
Ksei 37	0.86	-24.77		25.06					

sample powder was decarbonated using 2 M hydrochloric acid, followed by a repeated neutralisation treatment consisting of $\rm H_2O_{dest}$ rinse, centrifugation and decantation. The samples were dried at 40 °C for 48 hours. About 30 mg of each of these samples were packed into tin capsules and $\delta^{13}C_{org}$ and total organic carbon (TOC) was measured subsequently using a THERMO/Finnigan MAT V isotope ratio mass spectrometer, coupled to a THERMO Flash EA 1112 elemental analyzer via a THERMO/Finnigan Conflo III- interface in the stable isotope laboratory of the Museum für Naturkunde, Berlin (Table 1). Stable isotope ratios were expressed in the conventional delta notation relative to VPDB. The standard deviation for repeated measurements of lab standard material (peptone) was better than 0.15 ‰.

Results

The $\delta^{13}C_{carb}$ values (Fig. 3) from the Seis section, including data from Kraus et al. (2009), vary between + 3 and + 4 ‰ in the lower Bellerophon Formation (sample 4 to 30), decrease to + 1 to + 2 ‰ (sample 31 to 41) and return to \sim + 3 ‰ (sample 42 to 47) in the middle Bellerophon Formation. Above this level, $\delta^{13}C_{carb}$ values decrease subsequently, interrupted by a characteristic 1 ‰ positive excursion at 0.8 m above

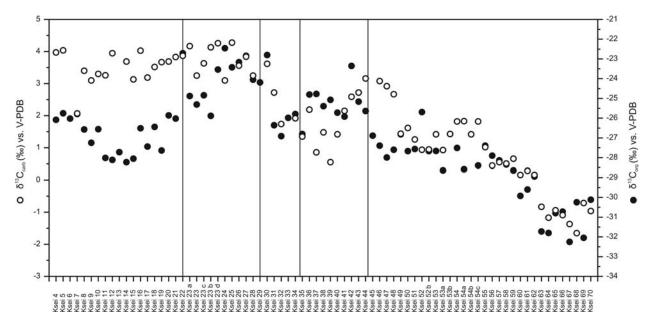


Figure 4. Comparison of $\delta^{13}C_{carb}$ and $\delta^{13}C_{org}$ trends of the Seis/Siusi section.

the base of the TOH (Kraus et al. 2009; Korte & Kozur 2010), to values of about +1.5 % in the lowermost Mazzin Member.

The organic matter carbon isotope values vary by about 10 % (Figs 3-4) from ~ -22 % to ~ -32 %. The values decrease from ~ -26 % to ~ -28 % between samples 4 and 14, increase gradually to ~ -22 % towards sample 24, decrease again to ~ -27 % at sample 32, then increase to ~ -23.5 % at sample 42, and finally decrease gradually to ~ -32 % towards the top of the sections.

The δ^{13} C signatures of carbonates and organic matter show in general similar, long-lasting negative trends across the PTB. It is further clear that the organic matter carbon isotopes, in comparison to the carbonate carbon isotopes, are less depleted in 13 C in the three parts of the section between samples 22 and 29, between samples 34 and 44 (grey shadows in Figure 3), and around the TOH (Figs 3, 4). The TOC concentrations of the carbonates from the Seis section, determined for 12 samples only, are low and range from 0.01 to 0.09 % (Table 1).

Discussion

Several hypotheses have been proposed to explain the initiation of the negative δ^{13} C excursion at the PTB. The most prominent are a global drop in sea-level (e.g., Holser & Magaritz 1987; Baud et al. 1989), a decrease in primary productivity (e.g., Magaritz 1989; Visscher et al. 1996), the release of methane from the seafloor, permafrost soils and/or heated coals (e.g., Erwin 1994; Krull & Retallack 2000), an oceanic overturn or an upwards rise of anoxic waters (e.g., Malkowski et al. 1989; Knoll et al. 1996; Kump et al. 2005; Riccardi et al. 2007) and burning or metamorphism of organics

by Siberian Trap sills and dykes when intruded into sediments (e.g., Payne & Kump 2007; Svensen et al. 2009; Korte et al. 2010). Many authors assume that a combination of various factors were presumably responsible (e.g., Berner 2002; Sephton et al. 2005; Corsetti et al. 2005; Retallack & Jahren 2008; Korte et al. 2010). Additional information about the causes of the PTB negative excursion can be interpreted from the carbon isotope trends at Seis.

The carbonate carbon isotope trend in the Seis section is similar to those of other Southern Alps sections (e.g., Magaritz et al. 1988; Holser et al. 1989; Oberhänsli et al. 1989; Korte & Kozur 2005; Horacek et al. 2007, 2010; Kraus et al. 2009; Korte et al. 2010) and to the general carbon isotope trend across the PTB as suggested by Korte & Kozur (2010). We therefore propose that deviations of the $\delta^{13}C_{\text{org}}$ record need extra explanation(s). The δ^{13} C trends of marine carbonates and organic matter should show the same trends because their carbon originates from the same source, the marine-dissolved carbon reservoir. It should be emphasized that the measured TOC values in the higher part of the Seis succession are very low and even slight secondary effects could have altered significantly the bulk rock $\delta^{13}C_{\text{org}}.$ The deviant isotope trends in organic carbon reported for the Bellerophon Formation (Fig. 3) are particularly prone to impregnation by migrating hydrocarbon fluids because of the high permeability of these limestones (Schwark, personal communication 2011). While a future organic geochemical characterisation of the Seis sections is a desirable, the carbon isotope signature of any migrated petroleum would be light, opposite to the observed deviations in the Bellerophon Formation (Fig. 3). It is therefore likely that the deviating trends are primary in origin.

Parallel trends of $\delta^{13}C_{carb}$ and $\delta^{13}C_{org}$ were reported for the Gartnerkofel core and the Misci (Seres) section

in the Southern Alps (Magaritz et al. 1992; Sephton et al. 2002), but both datasets do not allow precise observations because of their low resolution, especially above the top of the Bellerophon Limestone Formation. Opposing trends in carbon isotopes of carbonates and organics occur in the Idrijca Valley section in Western Slovenia (Schwab & Spangenberg 2004; see also Dolenec et al. 2001). Deviating $\delta^{13}C_{org}$ values with regard to carbonate carbon isotopes might be caused by heterogeneous sources of the organics (marine/terrestrial/bacterial) (see e.g., Deines 1980; Whiticar 1996). For instance, Permian wood shows heavier carbon isotope values than coeval marine organic matter (Faure et al. 1995; Foster et al. 1997; Korte et al. 2001). Changes in the amount of terrestrial organic matter in marine sediments probably impacted the negative carbon-isotope shift in Australian PTB successions (Morante 1996; Foster et al. 1997; Thomas et al. 2004). To complicate matters, ocean anoxia was widespread in the latest Permian oceans (e.g., Wignall & Hallam 1992; Kajiwara et al. 1994; Isozaki 1997; Algeo et al. 2008; Grasby & Beauchamp 2009) reaching even shallow water depths, as traced by green sulphur bacteria (= Chlorobiaceae) in the PTB Hovea-3 core from W-Australia (Grice et al. 2005). Chlorobiaceae are using H₂S and CO² in the photic zone for their anaerobic photosynthesis and do not discriminate as strongly against 13C as in the C³-pathway (Sirevag et al. 1977). The resulting biomass might therefore be heavier (although this is dependent on the δ^{13} C of the anoxic waters which can be already depleted in ¹³C) compared to marine organic matter that is produced coevally in oxygenated seawater (Summons & Powell 1986). The use of bulk $\delta^{13}C_{org}$ values for stratigraphic correlation purposes across the PTB might be therefore difficult (Riccardi et al. 2007).

The first two sedimentary units at the Seis section characterized by relative 13C-enriched (compared to δ¹³C_{carb}) organic carbon isotopes (grey shadows in Figure 3; samples 22 to 29 and 34 to 44; see also Figure 4) are interpreted to have been deposited in enclosed lagoons with low oxygen concentrations and/or reduced salinity, indicated by low diverse ostracod assemblages dominated by species of Cavellina and Sargentina. In these restricted palaeoenvironments, euhaline conditions would have likely occurred periodically, as indicted by a more diverse faunas with euhaline ostracods in sample 24. Diverse ostracod assemblages of large and thickshelled Paraparchitidae above sample 30 point to a typical high-energy environment (beach and foreshore area) and confirm microfacies interpretations of an open lagoon environment here. A second restricted lagoon environment commences above sample 33. Here, poorly oxygenated conditions and/or slightly modified salinity can be interpreted based again on a low diverse ostracod fauna. The water in this lagoon was mixed occasionally because slightly more diverse faunas (some euhaline species with few individuals) occur in samples 35 and 38 suggesting that normal marine conditions existed temporarily. All these observations suggest that low oxygen concentrations occurred during the two periods of restricted lagoonal conditions in the Late Permian Bellerophon Limestone Formation (grey shadow in Figure 3) at Seis. It is therefore possible that the $\delta^{13}C_{org}$ values might have been influenced occasionally by anoxic conditions (see above). However, an additional factor may have been more important in affecting carbon isotopic compositions. During the first restricted lagoonal period, enrichments in phytoclasts (coalified wood and other plant remains; Fig. 2) are indicative of a strongly enhanced influx of terrestrial organic matter and suggesting that this was the factor most responsible for the pronounced relative ¹³C-enriched organic carbon isotope signature in the lower grey shaded section of Figures 3 and 4 (heavier δ^{13} C of terrestrial versus marine-sourced organic matter; see above and δ^{13} C in Figure 3). A stronger influx of terrestrial organic matter in the second interval of restricted lagoonal facies cannot be confirmed by macroscopic investigations and here a geochemical characterization of the organic matter is desirable to verify this hypothesis.

The relative ¹³C enriched organic matter (compared to $\delta^{13}C_{carb}$) around the TOH in Seis (Fig. 4) is more difficult to evaluate because fossils are rare or absent and the origin of the TOH is still in discussion (see above). Information can be taken from organic geochemistry results from the Idrijca Valley section which was deposited more distally on the same carbonate ramp as the Southern Alps succession. A similar carbon isotope deviation has been reported here for practically the same stratigraphic level (Schwab & Spangenberg 2004). Relative ¹³C enriched organic matter occurs ca. 1 m below the top of the Žažar Formation, a stratigraphic level that is characterised by a gradual decrease in $\delta^{13}C_{\text{carb}}$. This period of deviating carbonate vs. organic δ^{13} C was developed under oxygenated conditions (Schwab & Spangenberg 2004) suggesting that the differing trends here were not caused by anoxia. In contrast, a contribution of organic matter from land plants is evident for the Idrijca Valley section (Schwab & Spangenberg 2004) and, in addition, also for the Misci (Seres) section in the Southern Alps (Sephton et al. 2001; Watson et al. 2005) and for the Rizvanuša and Brezimeniača successions in Croatia (Fio et al. 2010) at this time, thus supporting the suggestion that enhanced terrestrial influx around the TOH at Seis has produced the ¹³C-enriched organic matter.

Elevated influx of continental-sourced carbon around the TOH is consistent with other geological data. At this time an episode of elevated freshwater influx into the seas occurred, suggested to be the result of a pluvial event starting near the low-latitude marine event horizon (Kozur 1998a, 1998b; Krassilov & Karasev 2009; Korte & Kozur 2011; see also Sephton et al. 2005). This wet interval was probably not only restricted to the Southern Alps and Hungary, but does occur also in the Germanic Basin were hypersaline sabkha sediments are overlain by fluvial and fresh water lake deposits and in marginal development the water energy of rivers was

distinctly elevated. In addition, it has been shown that the water energy of discharging rivers in Australia (Michaelsen 2002), South Africa (Ward et al. 2000), Northern Alps (Kozur 1998a, 1998b) and Russia (Newell et al. 1999) was distinctly elevated, consistent with a global period of elevated rainfall. An exact stratigraphic correlation of the latter four areas with the Germanic Basin, however, is difficult.

Summary

In three parts of the Seis/Siusi section, represented by two restricted lagoons in the Bellerophon Limestone Formation and in the period around the Tesero Oolite Horizon, the $\delta^{13}C_{org}$ values are less depleted in ^{13}C (compared to coeval $\delta^{13}C_{carb}$) than in the remainder of the carbonate succession. These less depleted ^{13}C values are probably caused by the restricted nature of lagoons with a higher influx of terrestrial organic matter combined with low oxygen levels and occasionally anoxia effects and/or lower bioproductivity. Enhanced riverine influx around the Tesero Oolite Horizon (starting somewhat below its base and persisted somewhat upsection) might have supplied elevated terrestrial organic matter due to a wet phase (pluvial event).

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