

Organic carbon isotope variability across the P/Tr boundary in the Idrija Valley section (Slovenia): A high resolution study

Variabilnost izotopske sestave organskega ogljika na permsko - triasni meji v dolini Idrije: detajlna študija

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Cljučne besede: meja perm-trias, dolina Idrije, izotopska sestava organskega ogljika

Abstract

A systematic investigation of carbon isotopes in sedimentary organic carbon and microfacial analyses of the Idrija Valley section were carried out using very narrow sampling intervals. The high-resolution results demonstrate the following characteristics: 1) Permian/Triassic boundary marked by the PTB layer lies within a 15 cm thick Tesero oolite horizon, 2) Two large negative $\delta^{13}\text{C}$ sedimentary organic carbon anomalies exist, the first between 6 and 2 cm below and the second about the 4 cm above the PTB layer.

The first, and most probably worldwide, negative organic carbon isotope shift in the topmost Permian coincides with an abrupt disappearance of the Upper Permian fauna. The isotopic results suggest that the Permian/Triassic boundary events were very sudden (less than or equal to 67 kyr.), and are most probably related to an abrupt general decrease in the $\delta^{13}\text{C}$ value of ambient atmospheric CO_2 . The principal factors controlling $\delta^{13}\text{C}$ of atmospheric CO_2 were possibly related to volcanism together with degradation and oxidation of organic matter due to the terminal phase of the Upper Permian marine regression, rather than an instantaneous triggering event, such as an extraterrestrial body impact.

Kratka vsebina

S sistematskimi in nadrobnimi raziskavami izotopske sestave organskega ogljika in mikrofacialno analizo permsko - triasne mejne sekvence v dolini Idrije smo ugotovili, da poteka permsko - triasna meja, ki jo predstavlja PTB plast znotraj 15 cm debele, oolitne plasti (Tesero horizont). Krivulja izotopske sestave organskega ogljika kaže dve močni negativni anomaliji. Prva leži med 6 in 2 cm pod mejno PTB plastjo, druga pa je približno 4 cm nad njo.

Prva negativna anomalija za organski ogljik, ki je najverjetneje globalnega značaja, sovпада v z drastičnim izginotjem zgornjepermske favne. Rezultati časovno - izotopske analize kažejo, da so bili katastrofični dogodki na permsko - triasni meji relativno hitri in so trajali le okrog 67 tisoč let. Bolj verjetno so posledica nenadnega zmanjšanja $\delta^{13}\text{C}$ vrednosti atmosferskega CO_2 zaradi vulkanske dejavnosti v kombinaciji z oksidacijo in degradacijo organskih komponent v zaključni fazi zgornjepermske morske regresije, kot padca meteorita.

Introduction

Towards the end of the Permian, and specifically at the Permian - Triassic (P/Tr) boundary, the most severe mass extinction in the Earth's history took place (Raup & Sepkosky, 1986). This, one of the most remarkable mortality events in the history of life, probably lasted a million years, but reached its climax towards the very end of the Permian (Li et al., 1986). The final crisis thus may have been entirely restricted to the final one million years of the Permian (Wignall & Twitchett, 1996). Nowadays, P/Tr boundary sequences all over the world have been studied intensively because of interest in extinction events at the end of the Permian. Although several multidisciplinary

studies, including paleontology, sedimentology, geochemistry, paleogeography, magnetostratigraphy and volcanology have been made to analyse the extinction patterns and the causes of extinction, the mechanism which could have triggered the P/Tr boundary events and biotic crisis are not yet completely understood. The most plausible current explanation for this profound break in the evolution of life appears to involve volcanic activity induced global cooling (Renné et al., 1995), oceanic anoxia (Wignall & Hallam, 1992; Wignall & Twitchett, 1996) and the hypothesis of hypercapnia (Knoll et al., 1996).

The P/Tr extinction events coincide with isotopic and elemental anomalies recorded in several P/Tr boundary sections all over

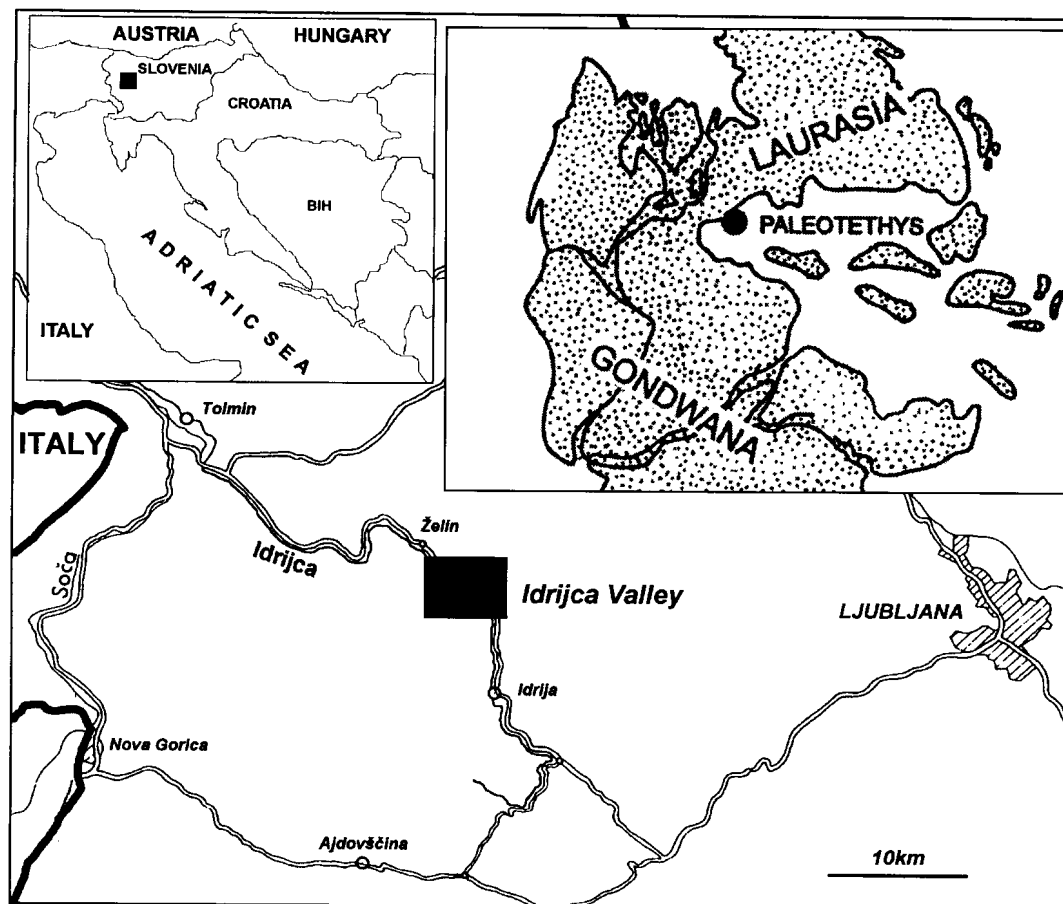


Fig. 1. Location of the studied P/Tr boundary profile in the Idrija Valley (Western Slovenia) (Dolenc et al., 1999).

Sl. 1. Lokacija raziskanega profila P/Tr meje v dolini Idrijce (Dolenc et al., 1999).

the world. One of the most remarkable anomalies is also the global negative shift of $\delta^{13}\text{C}$ of organic carbon, which in the Idrijca Valley coincides with the drastic disappearance of typically Upper Permian marine fauna (Dolenec T. et al., 1999; Dolenec T. & Lojen, 2000).

The object of this paper is to provide, by a high resolution study of organic carbon isotope variability across the P/Tr boundary in the Idrijca Valley, some additional information to further document the existence and importance of the world - wide negative $\delta^{13}\text{C}$ of organic carbon during the Permian - Triassic transition in the Western Tethys. The previously published works by Dolenec T. et al. (2001) on stable organic and inorganic carbon isotopes, together with preliminary studies on stable oxygen isotope variability at the P/Tr boundary in the Idrijca Valley section (Dolenec T. & Ramovš, 1996; 1998), served us the background against which the present geochemical study was carried out.

Geological setting and stratigraphy

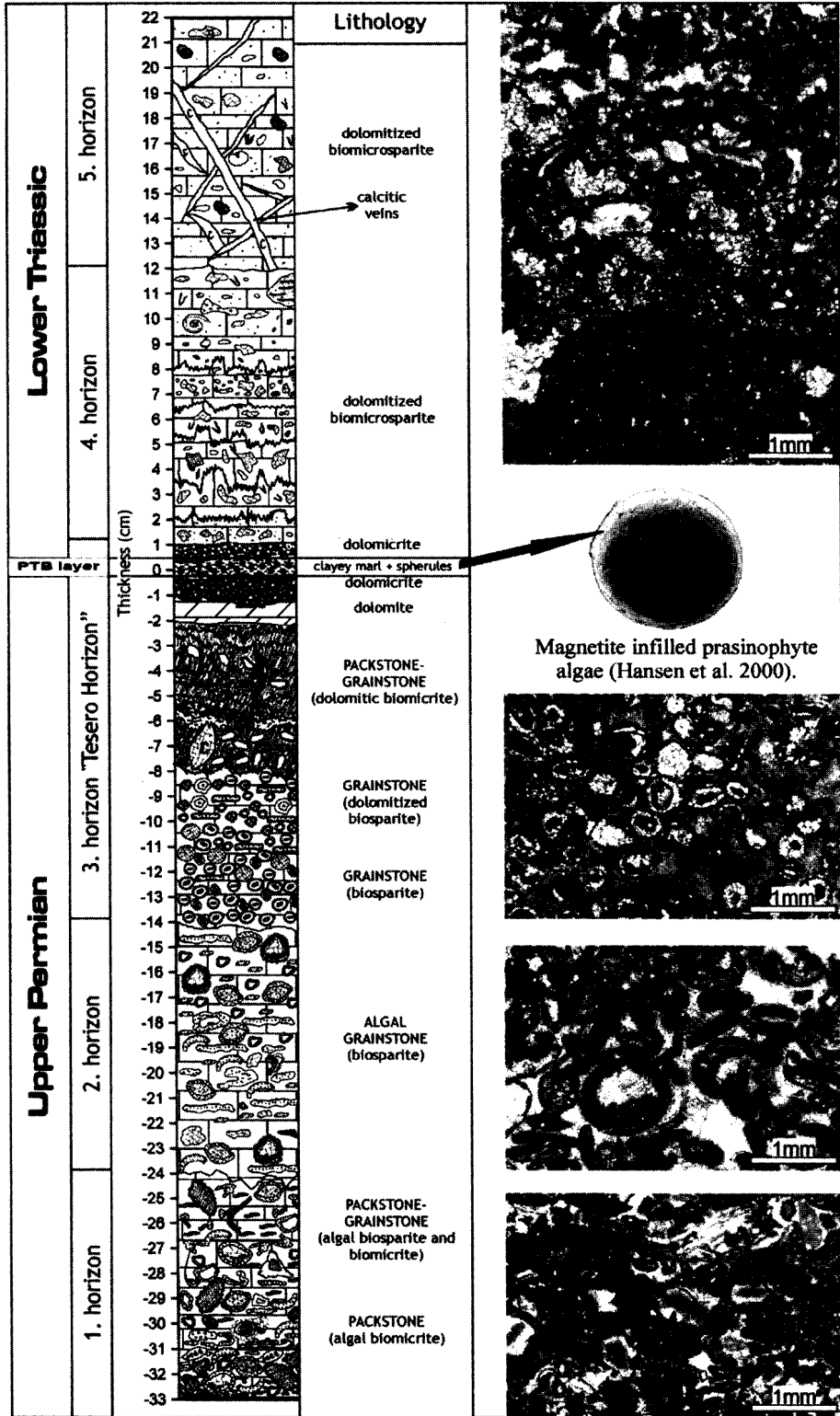
The geological setting and stratigraphy were discussed in more detail in some previous papers (Ramovš, 1986; Dolenec T. & Ramovš, 1998; Dolenec T. et al., 1999; Dolenec T. & Lojen 2000). For the present discussion it is important to note that in the boundary profile in the Idrijca Valley (Fig. 1 and 2) there is no evidence of a sedimentological or chronological break across the boundary. The Upper Permian black fossiliferous limestone (Žažar Formation - Ramovš, 1986) is overlain by a light grey, well bedded Lower Scythian sparitic limestone which alternates with laminated dolomitic and rare grey stylolitic dolomites. The total thickness of the P/Tr boundary sequence exposed in the Idrijca Valley is about 27 m. The boundary is represented by a thin, up to 0.8 cm thick clayey marl layer (Permian-Triassic Boundary - PTB layer) overlying the black Upper Permian algal packstone. The PTB layer shows a characteristic magnetic susceptibility pulse (Fig. 3) (Hansen et al., 1999, 2000) and considerable enrichment in most minor and trace elements (Dolenec,

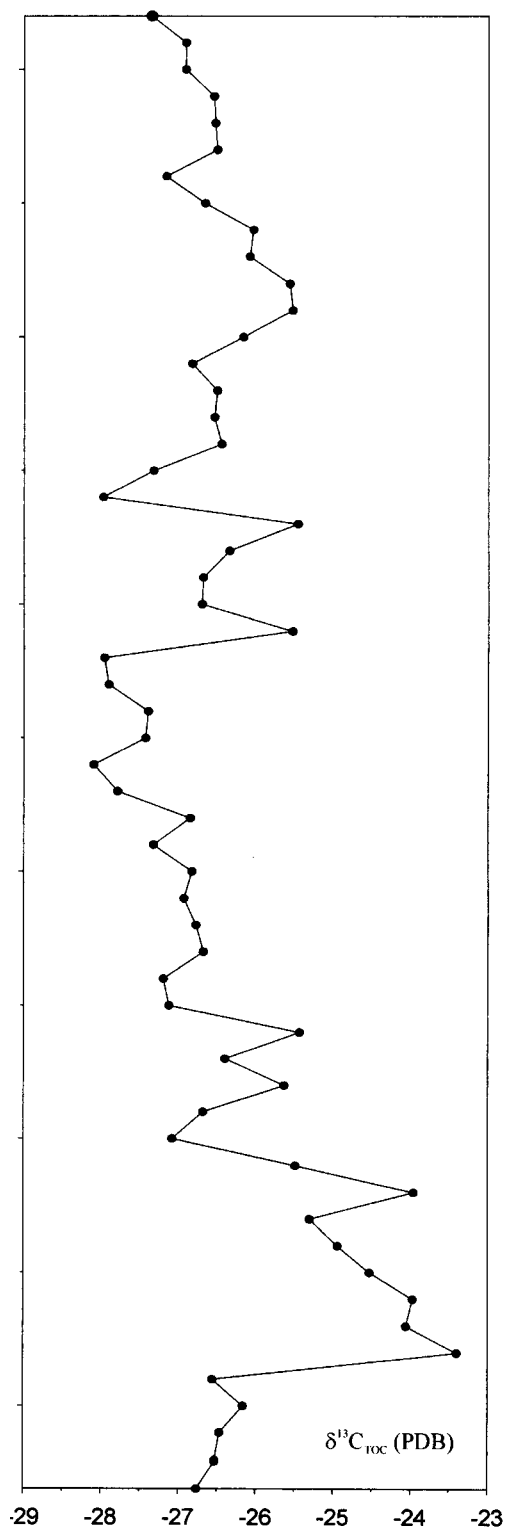
T. et al., 1999). It also contains spherules which most probably represent prasino-phyte algal skeletons, diagenetically infilled by magnetite (Hansen et al., 1999; 2000). A detailed study of the P/Tr boundary revealed that the PTB layer lies within an approximately 15 cm thick unit of oolitic grainstone, bioclastic grainstone and dolomicrite which most probably represents the well known Tesero Horizon (Dolenec M., 2000). Faunal assemblages (foraminifers, calcareous algae) at the base of this unit are consistent with an Upper Permian age for the lower part of the Tesero oolite. In contrast, the dolomicrite with rare ooids, which immediately overlies the PTB layer, contains conical tube like fossils (*Earlandia* sp.) and is of Lower Scythian age (Dolenec M., 2000). Another significant feature also observed by previous researchers (Ramovš, 1986; Dolenec T. et al., 1999) is the gradual impoverishment of the Upper Permian fauna towards the P/Tr boundary, and its abrupt disappearance at the boundary.

Materials and methods

The investigations were restricted to the P/Tr boundary itself. For this purpose continuous sampling on the centimetre scale was made of the topmost Upper Permian limestone from the P/Tr boundary down to 33 cm below (Fig. 2). Continuous samples of basal Scythian limestone were also collected up to 22 cm above the boundary. A total of 55 samples were taken. The sampling unit was 55 cm thick according to high resolution magneto-chronostratigraphy represents the time equivalent made by Hansen et al. (1999) of about 450 kyr. It should be noted that the previously discovered minimum peak of $\delta^{13}\text{C}_{\text{org}}$ values is within the interval from 30 cm below to 6 cm above the boundary (Dolenec T. et al., 1999).

All samples were evaluated by petrographic methods to assess their diagenetic history and microfacial characteristics. Samples for $\delta^{13}\text{C}_{\text{org}}$ analysis were obtained as a split of powder prepared from rock chips remaining after thin section preparation. For preparation of total organic carbon (TOC) for analysis, cleaned powdered limestone samples were treated with hy-





drochloric acid heated at 50° to react carbonates. Samples were then washed with distilled water until neutral and carbonate-free residues were oven dried at 50 °C. The measured TOC carbon ratio in the CO₂ produced by combustion was determined on a Europa 20 - 20 Stable Isotope Analyser with the ANCA - NT preparation module for on-line combustion of bulk solid samples and chromatographic separation of the gases at the Jožef Stefan Institute, Ljubljana. The results are reported in the standard $\delta^{13}C$ notation expressed in per mille (‰) relative to the PDB international standard. The analytical precision based on multiple analysis of an internal laboratory standard was ± 0.008 . The overall analytical reproducibility of the isotopic data for total organic carbon was ± 0.095 ‰.

Results

Lithology

The studied section together with organic carbon isotopic variations and high-resolution magnetostratigraphic data are shown in Fig 2. The analytical results are also tabulated in Table 1. From a microfacies point of view the investigated P/Tr boundary unit could be divided into 5 horizons:

1. horizon (from -33 to -24 cm below the P/Tr boundary)

Late diagenetic algal packstone containing densely packed fragments of *Gymnocodium bellerophontis*, echinoderms, ostracods and rare foraminifers

2. horizon (from -24 to -14 cm below the P/Tr boundary)

Biosparitic limestone - grainstone, very rich in fossils (*Gymnocodium bellerophontis* fragments, rare foraminifers, ostracods, mollusc and echinoderm debris). Some samples show evidence of stylolitization.

3. horizon (from -14 below to +1 cm above the P/Tr boundary)

This sedimentary sequence most probably represents the Tesero oolite horizon, a

Fig. 2. Stratigraphic section and organic carbon isotope variability of the Upper Permian and Lower Triassic beds in the Idrija Valley.

Sl. 2. Stratigrafski profil in variabilnost izotopske sestave organskega ogljika zgornjepermskih in spodnjetrijskih plasti v dolini Idrije.

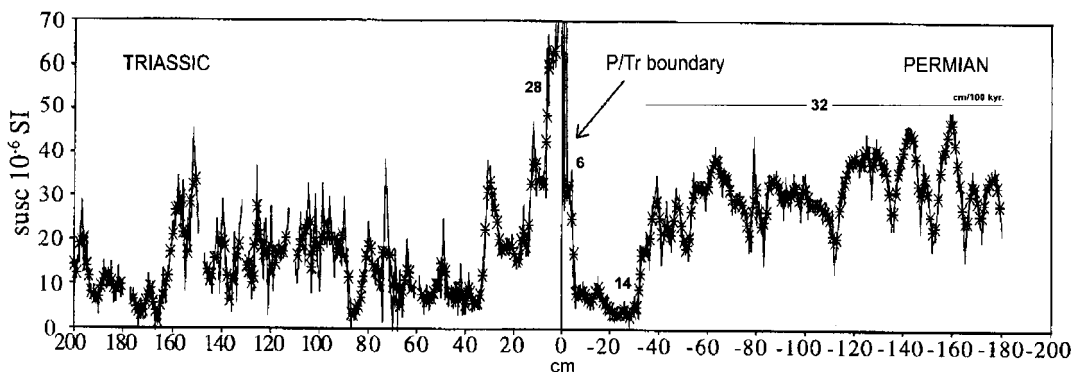


Fig. 3. Magnetic susceptibility of sediments from P/Tr boundary in Idrijca Valley section (po Hansenu et al., 2000).

Sl. 3. Magnetna susceptibilnost sedimentov P/Tr meje v dolini Idrijce (after Hansen et al., 2000).

thin up to 15 cm thick oolitic unit containing the PTB layer. This oolitic horizon was not recognised by previous researchers. The basal part of the Tesero Horizon (from -14 to -6 cm) is characterized by slightly dolomitized dark grey bioisparitic grainstone containing authigenic pyrite and detrital minerals (quartz, clay minerals and feldspars). Some ooids contain fragments of *Gymnocodium bellerophonis* that provided evidence of the Upper Permian age of the basal part of the Tesero Horizon. Bioisparite passes upwards (from -6 to -1 cm) into more dolomitized finely laminated biointramicrite, with numerous pyritic crystals. Dissolution of this part is common and different structures reinforced by stylolitization are developed. Petrographic analysis revealed that the stylolitic planes produced by pressure dissolution contain organic matter, clay minerals and opaque minerals. This sequence is capped (from -1 cm to the PTB layer) by a dark grey dolomitic packstone with no fossils. Lithostratigraphically the P/Tr boundary is represented by a sharp, yet not erosional contact. It consists of a 0.8 cm thick clayey PTB marl layer overlaid by unfossiliferous dolomicrite. It is followed (from the PTB layer to +1 cm above) by a dark grey dolomicrite. This dolomicrite, with no evidence of bioturbation, is taken as the top of the Tesero Horizon and is supposed to be of Lower Scythian age.

4. horizon (from +1 to +12 cm above the P/Tr boundary)

This is grey coloured bioisparite without any convincing evidence of bioturbation. The terigenous component is composed mostly of quartz, feldspars, muscovite, clay and opaque minerals. The limestone is scarce in fossils (ostracod debris), but in the uppermost part some conical tube-like forms appear. They most probably represent a dwarf microfauna of nodosariids - *Earlandia* sp. that is Triassic in age.

5. horizon (from +12 to +22 cm above the P/Tr boundary)

Consists of recrystallized and slightly dolomitized grey microisparitic wackstone containing detrital grains of quartz and clay mineral, as well as some conical tube-like fragments of *Earlandia* sp. and small amounts of pyrite framboids.

Isotopic data

The $\delta^{13}\text{C}$ profile of total organic carbon (TOC) shows distinct and characteristic values in five sedimentary horizons defined by the microfacies stratigraphy. In the first horizon the $\delta^{13}\text{C}_{\text{TOC}}$ values become rapidly heavier moving upward and reach -23.40 ‰ at -28 cm. After that there is a quite rapid change to more negative values at the top of the first horizon and at the base of the second horizon, before changing abruptly again to heavier values of -23.97 ‰ at -22 cm. Moving upward in the section TOC shows a gradual enrichment with the light carbon ^{12}C isotope. The decrease of $\delta^{13}\text{C}_{\text{TOC}}$, which begins 21 cm below the boundary, continues smoothly in the Tesero Horizon. The TOC

Table 1. Organic carbon Stable isotope composition of Upper Permian and Lower Triassic carbonate rocks in the Idrijca Valley.

Tabela 1. Izotopska sestava organskega ogljika v zgornjepermskih in spodnjetriasnih karbonatnih kamninah v dolini Idrijce.

Sample (cm)	$\delta^{13}\text{C}_{\text{org}}$ (PDB)	Sample (cm)	$\delta^{13}\text{C}_{\text{org}}$ (PDB)	Sample (cm)	$\delta^{13}\text{C}_{\text{org}}$ (PDB)	Sample (cm)	$\delta^{13}\text{C}_{\text{org}}$ (PDB)	Sample (cm)	$\delta^{13}\text{C}_{\text{org}}$ (PDB)
22	-27.35	11	-25.53	-1	-25.53	-12	-26.78	-23	-25.30
21	-26.91	10	-26.17	-2	-27.96	-13	-26.68	-24	-24.94
20	-26.91	9	-26.54	-3	-27.90	-14	-27.20	-25	-24.53
19	-26.55	8	-26.51	-4	-27.40	-15	-27.12	-26	-23.97
18	-26.53	7	-26.54	-5	-27.43	-16	-25.44	-27	-24.06
17	-26.51	6	-26.82	-6	-28.10	-17	-26.40	-28	-23.40
16	-27.17	5	-27.15	-7	-27.79	-18	-25.63	-29	-26.56
15	-26.66	4	-27.98	-8	-26.85	-19	-26.68	-30	-26.16
14	-26.04	3	-25.46	-9	-27.33	-20	-27.08	-31	-26.46
13	-26.09	2	-26.35	-10	-26.83	-21	-25.49	-32	-26.53
12	-25.57	1	-26.69	-11	-26.93	-22	-23.96	-33	-26.76

isotope values in this interval reach the first minimum of -28.10‰ at -6 cm and another of -27.96‰ at -2 cm below the boundary. These negative excursions of $\delta^{13}\text{C}$ most probably represent the most depleted ^{13}C total organic carbon of the entire section. They could be interpreted as the negative peak of $\delta^{13}\text{C}_{\text{TOC}}$ anomalies related to the well known global changes in the carbon cycle at the P/Tr boundary. After that there is an abrupt shift to a more enriched value of -25.53‰ 1 cm below the boundary. The TOC isotope data for the PTB layer show a depletion of $\delta^{13}\text{C}$, followed by a further enrichment of TOC at the top of the Tesero Horizon.

In the fourth horizon a shift of 1.23‰ towards higher values in $\delta^{13}\text{C}_{\text{TOC}}$ (-25.46‰) is followed by a decrease to almost the same level as that observed in the upper part of the Tesero Horizon (-27.97‰). The values then become rapidly heavier again and reach -25.57‰ in the topmost part of this horizon, before gradually decreasing to -27.35‰ in the upper part of the fifth horizon.

Discussion

The interpretation of the variations in $\delta^{13}\text{C}_{\text{TOC}}$ values given here rests on the important assumption that there are no carbon sources for the topmost Permian other than almost completely pure marine organic matter with only minor contributions from the terrestrial organic component, whereas the carbon sources for the Lower Triassic are supposed to be an admixture of marine and terrestrial organic matter.

This is supported by biomarkers characteristic of the terrestrial plants of the Lower Triassic in the same profile (Schwab et al., 2000). The $\delta^{13}\text{C}$ time series obtained from sedimentary organic matter exhibit high-frequency variations and long term decreasing and increasing trends. The high-frequency signals can be effectively explained by rapid changes in the $\delta^{13}\text{C}$ value of ambient atmospheric CO_2 and/or a relative increase in atmospheric pCO_2 (Fauré, 1995). A combined effect is also possible.

The high positive $\delta^{13}\text{C}_{\text{TOC}}$ values in the middle of the first horizon can be explained

by an increase in biogenic productivity, most probably due to enhanced oceanic nutrient levels at the end of the Permian, before the terminal productivity crash at the boundary occurred. According to *Darry et al.* (1994), any nutrient-driven productivity episodes should have been self-limiting on an approximately 10 kyr. time scale as the surface ocean supply of the Permian was drawn down.

The long term general decrease in sedimentary organic carbon values of about 4.65 ‰ (from -23.31 to -27.96 ‰) over a few hundred thousand years implies a relatively fast release of isotopically light carbon from a huge carbon reservoir that remains an enigma. Many regional processes can explain this gradual decrease in $\delta^{13}\text{C}_{\text{TOC}}$ values accompanied by a gradual impoverishment of Upper Permian fauna, including a decrease in surface productivity (*Kakuwa*, 1996), and degradation and oxidation of organic matter (*Magaritz & Holsen*, 1991; *Faure et al.*, 1995; *Renné et al.*, 1995). *Veevers and Tewari* (1995) suggested that volcanism along the Tethys margin raised the level of CO_2 in the atmosphere so that the spike of CO_2 from the end Permian Siberian Traps finally triggered the Permian-Triassic catastrophe. According to *Renné et al.* (1995) volcanogenic sulphate aerosols and the dynamic effect of the Siberian plume likely contributed to environmental extreme that led to the biota mass extinction.

The results for $\delta^{13}\text{C}_{\text{TOC}}$ presented clearly show that the first negative peak anomaly occurs in a narrow stratigraphic interval inside the Tesero Horizon (from -6 to -2 cm) and is not related to facies changes or breaks in sedimentation. With sedimentation rates of 6 cm/100 kyr. in the topmost Permian (*Hansen et al.*, 2000), for the 4 cm stratigraphic interval containing the negative peak anomaly this interval corresponds to a time period of 67 kyr. This peak anomaly is associated with a drastic disappearance of Upper Permian marine fauna. After that there is a sudden increase of $\delta^{13}\text{C}_{\text{TOC}}$ values followed by another spike-like perturbation in the Lower Scythian at +4 cm above the boundary. The positive or-

ganic carbon excursion at the P/Tr boundary was interpreted as a result of plankton

blooms during the subsequent short recovery period in the biological system (*Dolenc et al.*, 1999). Another sharp negative $\delta^{13}\text{C}_{\text{TOC}}$ anomaly just above the boundary most probably suggests a further collapse of surface productivity, which could be related to the major anoxic event at the beginning of the Triassic (*Wignall & Hallam*, 1992; 1993). However, the two sharp negative $\delta^{13}\text{C}_{\text{TOC}}$ anomalies in a distance of 10 cm (from -6 cm to +2 cm), which corresponds to approximately 115 kyr., most probably belong to well known perturbations in the global carbon cycle at the Permian-Triassic transition. Perturbations of $\delta^{13}\text{C}_{\text{TOC}}$ at the P/Tr boundary of the Idrijca Valley section are similar to the patterns of variations in $\delta^{13}\text{C}_{\text{carb}}$ across the P/Tr boundary of the Meishan section, South China (*Xu & Zheng*, 1993). These authors also found by high-resolution sampling two sharp $\delta^{13}\text{C}_{\text{carb}}$ P/Tr boundary anomalies spanning an interval of less than 20 cm.

If the P/Tr boundary is considered a catastrophic event, a short-time hiatus should be expected and is in fact a reasonable consequence of such a catastrophic event (*Xu & Zheng*, 1993). It should be noted that the organic carbon isotope variations across the P/Tr, as well as petrographic observations of the boundary sequence sample, show no evidence for a significant interruption in sedimentation.

This high resolution sampling in the Idrijca Valley allows a more refined interpretation. However, such high resolution results can be misinterpreted if they are compared with the results of previous studies of P/Tr boundary sequences all over the world based on widely-space sampling intervals. The results presented here indicate that the terminal P/Tr boundary mass extinction event most probably involved a number of more or less co-occurring events which triggered the end-Permian productivity crash and mass mortality. The extinction was not as sudden as the K/T event (*Alvarez et al.*, 1980; *Prinn & Fegley*, 1987), but was far faster than previously thought. Judging from the rate at which sediments accumulated in the Idrijca Valley (*Hansen et al.*, 1999) we estimate that the initial

and the final stage of the global $\delta^{13}\text{C}_{\text{TOC}}$ excursion associated with the end Permian extinction event span an approximately 4 cm thick interval (from -6 cm to -2 cm), which corresponds to 67 kyr. This time interval is of the same order of magnitude as the estimated duration between 10 kyr. and 100 kyr. of the $\delta^{13}\text{C}$ excursion observed in the Karoo Formation in S. Africa (MacLeod, 1997).

On the basis of estimated sedimentation rates for Italian sections in the Southern Alps, the end-Permian extinction could also have been very sudden (less than or equal to 25 kyr.), and the disappearance of most late Permian foraminifers was most likely coincident with a worldwide ecological stress event, identified by a global negative $\delta^{13}\text{C}$ anomaly that occurs in Italy near the base or within the time-transgressive Tesero Horizon (Rampino & Adler, 1998).

The variability of $\delta^{13}\text{C}_{\text{TOC}}$ during the remaining Scythian age most probably suggests that due to insufficient recovery of higher consumers, normal productivity was not completely re-established, as already mentioned by Kakuwa (1996) for the P/Tr transition of southwest Japan.

Conclusions

Detailed microfacial analysis and a high resolution sedimentary organic carbon isotopic study revealed two most probably global negative $\delta^{13}\text{C}_{\text{TOC}}$ anomalies that occur at the P/Tr boundary in the Idrija Valley section. They occupy a narrow stratigraphic interval of only 10 cm containing the P/Tr boundary. The first anomaly in the upper part of the 15 cm thick Tesero Horizon within a 4 cm interval and is coincidental with an abrupt disappearance of Upper Permian fauna. The negative $\delta^{13}\text{C}_{\text{TOC}}$ peak excursion was estimated to have occurred about 100 kyr. before the P/Tr boundary marked by a PTB clayey marl layer. The second negative $\delta^{13}\text{C}_{\text{TOC}}$ shift, which represents further evidence for breakdown in the photosynthesis-respiration cycle at the P/Tr transition, is estimated to have occurred in the early Scythian, 15 kyr. after sedimentation of the PTB layer.

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