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UPPER CARBONIFEROUS TO LOWER TRIASSIC CARBON ISOTOPIC SIGNATURE IN CARBONATE ROCKS OF THE WESTERN TETHYS (SLOVENIA)

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Abstract: The carbon isotope composition of carbonate rocks spanning an approximately 1650 m thick interval ranging from Upper Carboniferous to Lower Triassic, together with pedogenic carbonate carbon and organic carbon isotope data of Middle Permian plant remains, were used to evaluate the carbon isotope evolution of the Late Paleozoic in the Western Tethys. The results indicate a "positive carbon isotope event" across the Carboniferous-Permian (C/P) boundary, a negative shift of $\delta^{13}C$ values at the end of the Lower Permian, a positive $\delta^{13}C$ excursion at the Middle Permian-Upper Permian transition and the well known worldwide perturbations of the carbon cycle at the end of the Permian marked by a prominent decrease of about 4 ‰ at the Permian-Triassic (P/Tr) boundary, followed by a gradual increase of $\delta^{13}C$ values from the Lower Scythian to the Anisian. It is suggested that the shape of the $\delta^{13}C$ curve records changes in the carbon cycle that reflecting variations in factors such as burial rate and oxidation of organic carbon due to sea-level oscillations, which could be slightly overprinted by local processes influencing carbon isotopic composition in particular sedimentary environments. However, the marked disturbances in the carbon cycle across the P/Tr boundary most probably resulted from a combination of factors such as an accelerated oxidation of organic carbon due to the terminal phase of the Upper Permian marine regression, in combination with volcanic activity and a possible expulsion of methane from stored hydrates, as well as from a crash in primary bioproductivity.

Key words: Western Tethys, Slovenia, Upper Carboniferous–Lower Triassic, Permian-Triassic boundary, $\delta^{13}C$ stratigraphy, carbon stable isotopes, carbonates.

Introduction

In the short-term, a high-resolution carbon isotope record at a frequency lower than the mixing time of the oceans (ca. 1000 yr.) is crucial when evaluating changes of marine productivity, while the interpretation at frequencies greater than the mixing time will reflect the transient partition between different water masses. The latter is the so-called "internal fractionation" within the marine reservoir of dissolved inorganic carbon (Corfield 1994). On timescales longer than this, any change in $\delta^{13}C$ of carbonate carbon reflects the fractionation of carbon isotopes between different carbon reservoirs (Berger & Vincent 1986; Shackleton 1987). This may be thought of as "external fractionation". Both internal and external fractionation of carbon isotopes may contribute to excursions in the $\delta^{13}C$ carbonate signal.

^{13}C enrichment in marine carbonates correlating with the increase of pCO_2 in the atmosphere has been interpreted as a consequence of an increase in organic carbon storage either on land (Shackleton 1987) or on newly flooded continental shelves (Magaritz & Stemmerik 1989; Faure et al. 1995). In contrast, slower burial or rapid oxidation of organic carbon will result in lower $\delta^{13}C$ values of marine carbonates due to release of ^{13}C depleted CO_2 to the atmosphere (Magaritz & Stemmerik 1989; Faure et al. 1995).

In this study the carbon isotope stratigraphy of selected stratigraphic sections from Western Slovenia — the Karavanke Mountains (Dolžanova soteska, Košutnik Creek and Brsnina), Julian Alps (Straža Hill), Sava Folds (Žirovski vrh, Sv. Valentin) and Idrija region — was used to examine their depositional environment and to provide further insights into the carbon isotopic evolution of the western part of the Tethys Ocean from the latest Carboniferous to the earliest Triassic (Fig. 1). The stratigraphic sections spanning an approximately 1650 m thick stratigraphic interval, ranged from Upper Carboniferous to Lower Triassic (Fig. 2). In addition, we also discuss the nature and the causes of the well known perturbations in the carbon cycle at the P/Tr boundary, which are more or less coincidental with the most severe extinction of marine and terrestrial organisms in the history of life (Erwin 1993; Wignall & Hallam 1996; Knoll et al. 1996; Musashi et al. 2001; Wignall & Twitchett 2002; Berner 2002 and references therein).

Some previously published works by Dolenec T. (1973), Dolenec T. & Ramovš (1996); Dolenec T. et al. (1981, 1998, 1999a,b,c; 2001) and Dolenec T. & Lojen (2000) on stable organic and inorganic carbon of the Permian and Triassic, together with preliminary studies on the carbon isotopic composition of plant remains from the Val Gardena Formation (Dolenec T. & Pezdič 1986) serve as the background against which the present geochemical study was carried out.

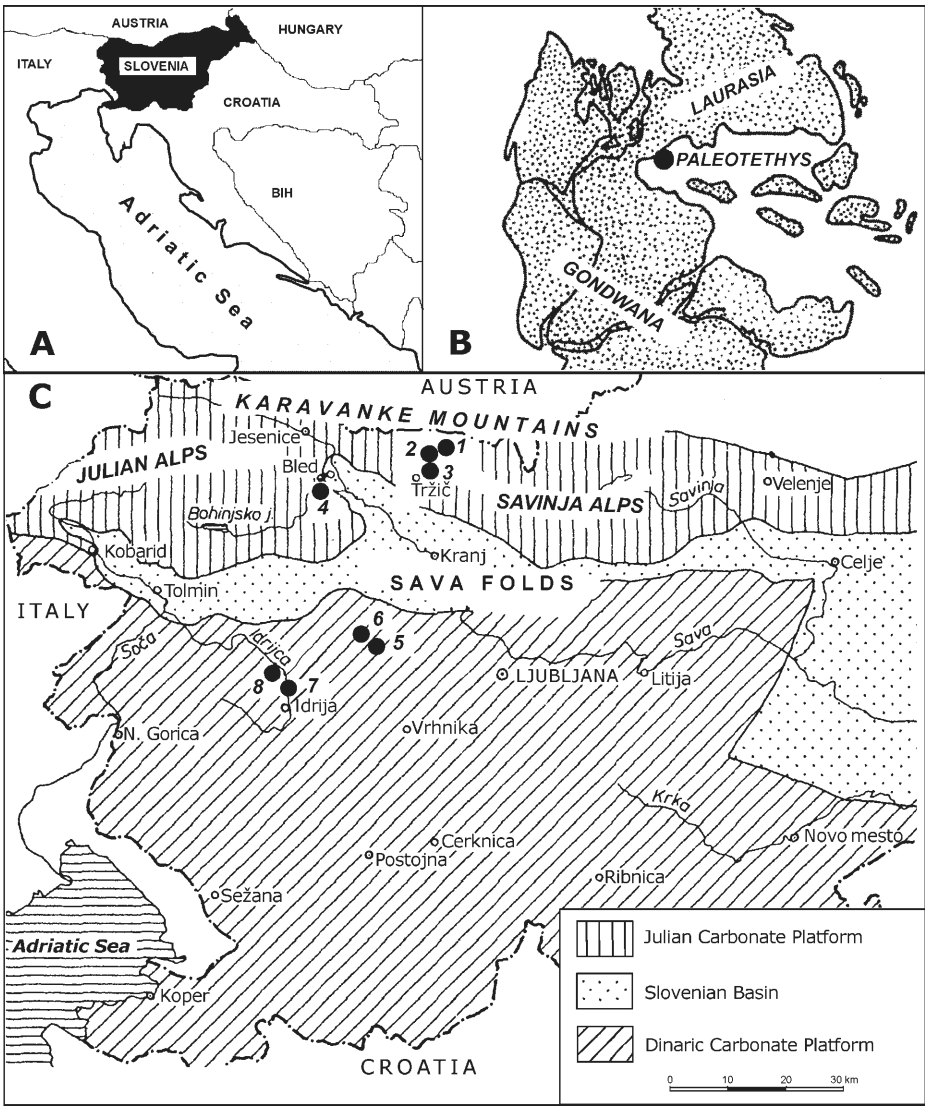

Fig. 1. **A** — Map showing the location of the studied sections in Slovenia. **B** — Global paleogeography during the P/Tr is taken from Sun et al. (1989) . **C** — The location of the investigated area is shown by a black point (1 Brsnina, 2 Košutnik Creek, 3 Dolžanova soteska, 4 Straža Hill, 5 Sv. Valentin, 6 Žirovski vrh, 7 Idrijca Valley, 8 Masore). The present extension of the ancient Julian and Dinaric Carbonate Platforms, together with the intermediate Slovenian Basin, is taken from Buser & Debeljak (1996).

Geological setting and stratigraphy

On the basis of a major tectonic event within the Permian (Saalian orogenetic phase), the late to post-Variscan sedimentary sequence of the Southern and Eastern Alps is divided into two evolutionary cycles (see Krainer 1993, and references therein). The sediments of the lower cycle (Late Carboniferous/Early Permian) were deposited in discrete, isolated intermontane basins, which were filled with different sediments and volcanic rocks. In the Southern Karavanke Mountains and in the Julian Alps the sequence of the first cycle is represented by deltaic, shallow marine to deep-marine clastic and carbonate sediments of the Late Carboniferous Auering Group (Ramovš 1976) and the Dolžanova Soteska Limestone Member (Buser & Forke 1995) ranging from Late Moscovian to Late Artinskian. The thickness of these sediments is up to 800 m (Fig. 2, section 3). The Dolžanova Soteska Limestone Member is introduced as a white, pale red to red limestone unit, named the Trogkofel Limestone in previous literature (Ramovš 1976). Conodont fauna together with fusulinids indicate an older age (Asselian) for these limestones than was previously thought (Buser & Forke 1995).

With a hiatus caused by block faulting (Saalian orogenetic phase), the Tarvis Breccia and Middle to Upper Permian sediments of the second cycle, which are more widely distributed and not restricted to discrete basins, conformably overlie Lower Permian sediments. The thickness of the Tarvis Breccia, which has been regarded as scarp-foot fan deposits and proximal debris-flows (Krainer 1993), varies in the Southern Karavanke Mountains from a few metres up to 150 metres (Buser & Cajhen 1978).

Freshwater calcite cements of the Tarvis Breccia indicate a subaerial exposure corresponding to a regressive event at the end of the first cycle, after the deposition of the Trogkofel For-

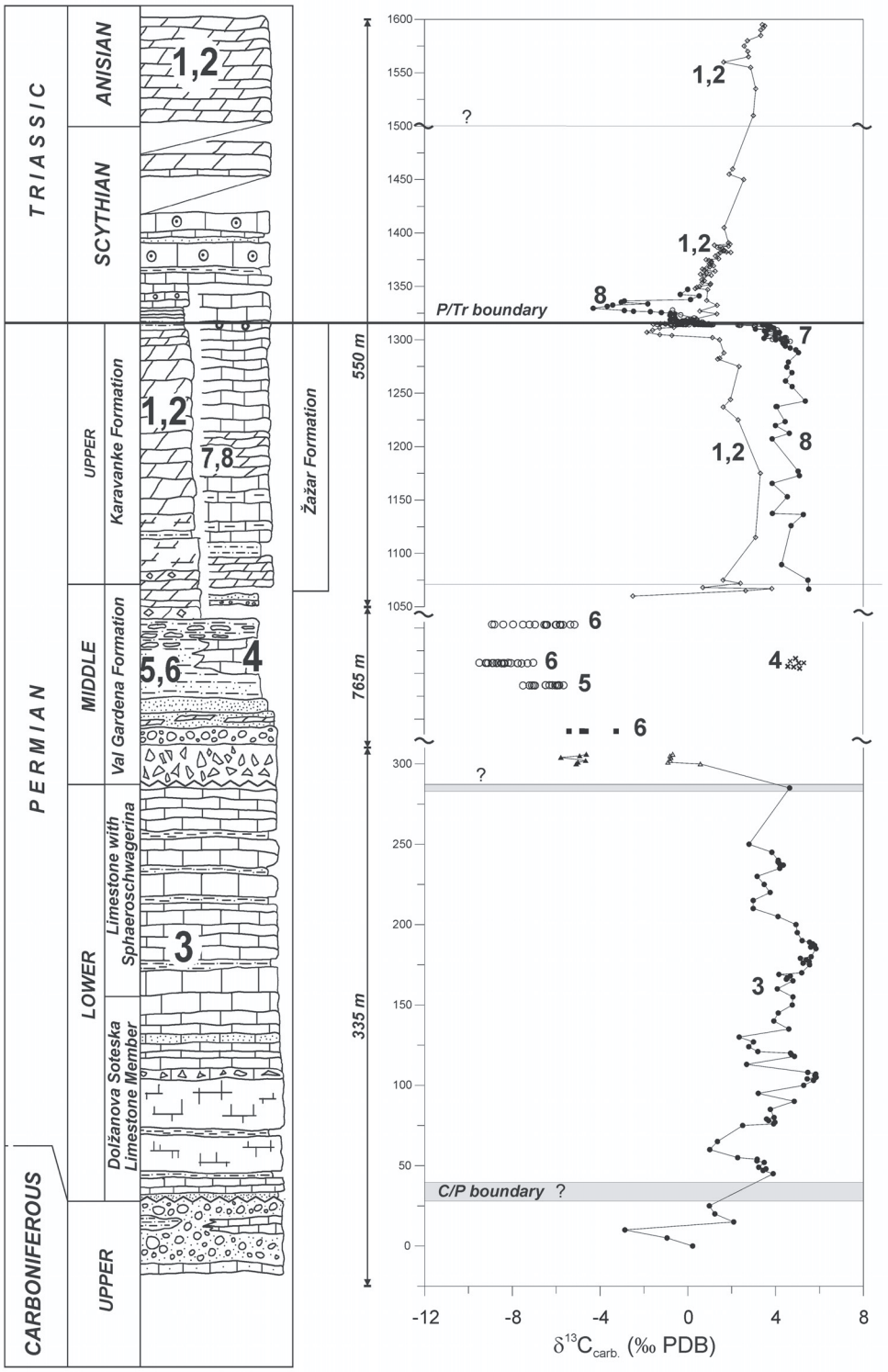

Fig. 2. Upper Carboniferous to Lower Triassic carbonate carbon isotopic record from the Southern Karavanke Mountains, Julian Alps, Sava Folds and Western Slovenia: **1, 2** — Upper Permian and Lower Triassic succession of the Southern Karavanke Mountains ◇ (Upper Permian Karavanke Formation, Lower Scythian and Anisian beds — Brsnina and Košutnik Creek section); **3** — Upper Carboniferous, Lower and Middle Permian sedimentary sequence (Dolžanova soteska section: Auering Group, Dolžanova Soteska Limestones, Tarvis Breccia Unit: △ — Dolžanova Soteska Limestone fragments, ▲ limestone cement); **4** — Middle Permian Neoschwagerina Limestone × (Straža Hill — Julian Alps); **5** — Middle Permian pedogenic carbonates — Val Gardena Formation (Sv. Valentin — Sava Folds); **6** — Middle Permian pedogenic carbonates ○ and playa lake dolomites ■ (Žirovski vrh — Sava Folds); **7** — Upper Permian Žažar Formation and Lower Scythian beds ○ (Idrijca Valley section — Western Slovenia); **8** — Upper Permian Žažar Formation and Lower Scythian beds ● (Masore section — Western Slovenia). Description of rock types see in the text.

mation (Buggisch & Flügel 1980). In the Karavanke Mountains the Tarvis Breccia is overlain by the up to 10 m thick basal conglomerates of the Val Gardena Formation, which is followed by prevalent sandstones, accompanied by conglomerates, siltstones and claystones. The Val Gardena Formation attains the greatest thickness (up to 600 m) in the Žirovski vrh area (Fig. 2, sections 5 and 6) which belongs to the western part of the Sava Folds (Omaljev 1967). The sediments are of fluvial, playa lake and shallow-marine origin (Buggisch 1978; Ori 1986) and were deposited in an arid and semiarid climate. Interbedded siltstones and claystones often contain pedogenic carbonate nodules and rare thin dolomite, as well as gypsum layers (Skaberne 1995). The gypsum layers are interpreted as being formed in playa lakes (Drovenik 1970). In the Julian Alps, near Lake Bled (Straža Hill), a shallow-water Neoschwagerina reef limestone (Fig. 2, section 4) — time-equivalent to the Val Gardena Formation — was deposited (Flügel et al. 1984).

In the Southern Karavanke Mountains the Middle Permian Val Gardena Formation is overlain by an up to 270 m thick Upper Permian evaporitic-dolomitic sequence (Fig. 2, sections 1 and 2) referred to as the Karavanke Formation (Buser 1974). The boundary between the two formations is transitional and characterized by thin sandy red dolomite layers alternating with the topmost Val Gardena shales and sandstones (Fig. 3, section 1), indicating a widespread and slowly progressive transgression of the Bellerophon Sea on the territory of the present Dinarides (Krainer 1993 and references therein). At this time the formation of the extensive Slovenian Carbonate Platform began in the area of the Southern Alps and the Dinarides (Buser 1996). The thickness of the transitional unit, which grades upward into the Karavanke Formation, is about 5 m (Dolenec T. et al. 1981). The basal unit of the Karavanke Formation is represented by an up to 70 m thick evaporitic sequence composed of cellular dolomite (rauhwacke), which alternates with rare black and slightly bituminous marls, and grey vuggy dolomites. Sulphate minerals are no longer present; they were entirely replaced by calcite. The evaporitic sequence is overlain by a 200 m thick succession of fossiliferous biomicritic dolomites (Buser 1974; Dolenec T. et al. 1999c). The Late Permian age of these beds is indicated by calcareous algal assemblages, as well as by foraminifers (Ramovš 1986). The lithostratigraphic boundary between the Upper Permian Karavanke Formation and the Lower Triassic (Scythian) beds is placed at the end of the sedimentation of the well-bedded grey dolomicrite (Dolenec T. et al. 1999c). It is followed by a red-coloured partly terrigeneous evaporitic sequence, predominantly composed of thin-bedded siltstones, mudstones and sandstones alternating with micritic dolomites, showing the impressions of gypsum crystals (Fig. 3, section 2). These dolomites contain no characteristic fossils and so could be any age within the P/Tr interval. The earliest Triassic beds represent a predominantly terrigenous sequence deposited in an extremely shallow sea, which gradually became a wide, extensive mud flat (Assereto et al. 1973), most probably indicating a short term regression or sea level fluctuation at the P/Tr boundary. Its thickness varies between 5 m in the Košutnik Creek section and 25 m in the Brsnina section. In the investigated area of the Southern Karavanke Mountains these beds are mostly overlain by an around 200 m thickness of Lower Triassic dark-grey and brown micritic and sparitic limestones and dolomites intercalated with oolitic limestone, marls and shales. Ooids were formed in intertidal channels and deltas (Dolenec T. et al. 1981). Episodically intercalated supratidal sediments and a clastic influx in the Lower Triassic sedimentary succession most probably indicate eustatic sea-level changes and tectonics (Assereto et al. 1973; Broglio-Loriga et al. 1983; Brandner et al. 1984). Anisian dolomite conformably overlies the Scythian beds (Fig. 2, sections 1 and 2; Fig. 3, section 1). Similar transgressive–regressive events have also been recognized in the Scythian sequence of the Upper Austro-Alpine units (Krainer 1993 and references therein). The thickness of the dolomite, which contains algal remains and foraminifers and which was only partly included in the present study, is over 200 m (Dolenec T. et al. 1981).

In Western and Central Slovenia the Val Gardena Formation is overlain by an approximately 250 m thick dark-grey to black bedded and fossiliferous shallow marine limestone (Fig. 2, sections 7 and 8; Fig. 4), the Žažar Formation (Ramovš 1958). The lower part of this limestone contains a rich brachiopod fauna, small bioherms and coral-patch reefs (Ramovš 1986). The faunal composition displays gradual impoverishment of the Upper Permian taxa moving upward towards the P/Tr boundary and an abrupt disappearance at the boundary level (Dolenec T. et al. 2001). Although indications of shallowing are present over a broad region, sequence stratigraphic analysis of the Idrijca Valley section revealed no evidence of emergence or pronounced sea-level changes across the boundary (Dolenec T. & Lojen 2000). The boundary is represented by a thin < 0.8 cm clayey marl layer (Permian-Triassic boundary — PTB layer) overlying black Upper Permian algal packstones. The PTB layer shows a characteristic magnetic susceptibility pulse (Hansen et al. 1999, 2000) and considerable enrichment in most minor and trace elements (Dolenec T. et al. 2001). It also contains spherules, which most probably represent prasinophyte 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 represents an equivalent to the well known Tesero Oolite Horizon (Dolenec M. 2000; Dolenec M. & Ogorelec 2001). 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 Horizon. In contrast, the dolomicrite with rare ooids, which immediately overlies the PTB layer, contains conical tube-like fossils, most probably of *Earlandia* sp., and is supposed to be of Early Scythian age (Dolenec M. 2000). The deposition of the P/Tr boundary layer most probably occurred during a period of maximum eustatic sea-level fall and regression, correlated with the sedimentation of red terrigeneous sediments across the P/Tr boundary in the Karavanke Mountains (Dolenec T. et al. 1998). A laminated dolomicritic limestone alternating with grey stylolitic dolomite overlies the Tesero Oolite Horizon. In the Masore section the stylolitic dolomite is covered by greyish-green and reddish

calcareous micaceous shale and sandstone, including lenses of oolitic limestone (Fig. 4, section 8). The thickness of the Lower Scythian dolomite is about 100 m.

Material and methods

A total of 380 carbonate samples and 10 samples of plant remains were collected in eight sections numbered 1–8 for isotopic analysis (Fig. 1 and 2). The carbonate carbon isotopic measurements were carried out on undolomitized limestone and uncalcitized dolomite samples, cellular dolomite, pedogenic carbonates, as well as on separated components of Tarvis Breccia calcite cement. The mineralogy of the carbonate phases was determined by X-ray diffractometry and by examination of thin sections by standard optical methods, including staining with Alizarin-reds. All samples were also evaluated by petrographic methods to assess their diagenetic history. Thin-section examination showed that the limestone and dolomite samples analysed are without crack-filling sparites and un-weathered, without evidence of meteoric-water diagenesis. By selecting the least visibly weathered and recrystallized samples from the investigated sections, we attempted to minimize possible post-depositional effects. A weak positive correlation (r = 0.40) between $\delta^{18}O$ and $\delta^{13}C$ of the dolomite samples and a weak negative correlation (r = –0.22) between $\delta^{18}O$ and $\delta^{13}C$ of the limestone samples of the Karavanke Formation (Dolenec T. et al. 1999c), as well as a lack of correlation between $\delta^{18}O$ and $\delta^{13}C$ values of the carbonate samples of the Žažar Formation (unpublished), most probably suggests that the isotopic composition of the investigated carbonate rocks has not been seriously altered after their formation and that the primary paleoceanographic signal is not appreciably overprinted.

Therefore, we suppose that the carbon isotope data can reflect the carbon isotopic composition of the original marine composition. Samples were obtained as a split of powder prepared from rock chips remaining after thin section preparation. In order to speed up the reaction time and to ensure complete reaction of carbonates, powdered rock samples for $\delta^{13}C$ analysis were prepared by overnight digestion in excess 100 ‰ phosphoric acid at 50 °C. CO_2 gas released during acid treatment was cryogenically cleaned and analysed for carbon isotopic composition on a Varian MAT 250 mass spectrometer. All whole rock and calcite cement samples were analysed in duplicate or triplicate. The results are reported in the conventional delta notation as ‰ deviation from the VPDB (Vienna PeeDee Bellemnitela americana) standard. The $\delta^{13}C$ values were normalized assuming $\delta^{13}C$ values of +2.48 ‰ for IAEA-CO-1 standard on the VPDB scale. The analytical precision, based on multiple analysis of an internal laboratory standard, was $\delta^{13}C$ ±0.01 ‰ (1σ). Overall analytical reproducibility of the carbonate carbon isotopic data was ±0.1 ‰.

Middle Permian plant remains from dark-grey and grey Val Gardena sandstones were selected from previously crushed samples by hand under a binocular microscope. The organic carbon plant remains were then powdered in an agate mortar and treated with 3 M hydrochloric acid at 50 °C to react the carbonates. Upon cessation of CO_2 evolution, excess acid was removed by repeated washing (three to four times) with doubly distilled water to neutral pH. After the final decantation of water, the carbonate-free residue, mostly composed of plant remains, was oven-dried at 50 °C. Organic carbon isotope ratios were measured in a Europa 20-20 Stable Isotope Analyser (Europa Scientific Ltd.) with an ANCA-NT preparation module for on-line combustion of bulk solid samples and chromatographic separation of gases. Organic carbon isotope values were calibrated using the IAEA-CH-7 standard with a $\delta^{13}C$ value of –31.8 ‰ on the VPDB scale. The results are reported in the conventional delta notation as ‰ deviation from the VPDB standard. The analytical precision for organic carbon based on multiple analysis of an internal laboratory standard was $\delta^{13}C$ ±0.01 ‰ (1σ). Overall analytical reproducibility of the organic carbon isotopic data was ±0.1 ‰.

Results

A schematic presentation of the carbon isotope stratigraphy together with the lithostratigraphic development of sedimentary rocks from the Upper Carboniferous to the Lower Triassic, is shown in Fig. 2. In Figs. 3 and 4 detailed sections and carbon isotope stratigraphy across the Middle Permian/Upper Permian boundary in the Karavanke Mountains and across the P/Tr boundary in the Karavanke Mountains and in Western Slovenia are also presented.

The shape of the $\delta^{13}C$ curve for the sedimentary sequences of the lower (Late Carboniferous/Early Permian) and upper cycle (Middle–Late Permian to Early Triassic) is characterized by a series of distinct carbon isotope changes (Fig. 2, section 3). There is a gradual positive $\delta^{13}C$ excursion from –2.9 to +3.9 ‰ at the transgressive C/P boundary in the Karavanke Mountains, followed by a moderately variable $\delta^{13}C$ signal in the Lower Permian sedimentary sequence containing some well developed clastic-carbonate cycles. The $\delta^{13}C$ values of the Lower Permian Dolžanova Soteska Limestone Member range from +1.2 to +5.8 ‰, with most of the values falling between +3.2 and +5.2 ‰. The most depleted $\delta^{13}C$ values were found in sandy limestone samples containing high amounts of detrital components.

At the Lower/Middle Permian transition in the Karavanke Mountains (Fig. 2, section 3) the negative excursion of $\delta^{13}C$ values is stratigraphically associated with the Tarvis Breccia Horizon. The carbon isotopic composition of the limestone cement of Tarvis Breccia from the Karavanke Mountains ranges between –5.8 and –4.7 ‰, while the $\delta^{13}C$ values of isotopically altered Dolžanova Soteska Limestone fragments cluster between –0.9 and +0.6 ‰ (Fig. 2, section 3).

The carbon isotopic composition of playa lake dolomite from the Val Gardena Formation falls between –3.3 and –5.7 ‰, while that of pedogenic carbonates clusters between –9.5 and –5.8 ‰ with an average value of –7.9 ‰ (Fig. 2, sections 5 and 6). These values are up to 14.7 ‰ lighter than time-equivalent Neoschwagerina limestone with $\delta^{13}C$ in the range from +4.8 to +5.2 ‰ (average +4.9 ‰) (Fig. 2, section 4). The $\delta^{13}C$ values of plant remains in the Val Gardena Formation from Žirovski vrh were found to be between –22.1 and –21.7 ‰ (Dolenec T. & Pezdič 1986). A slightly wider

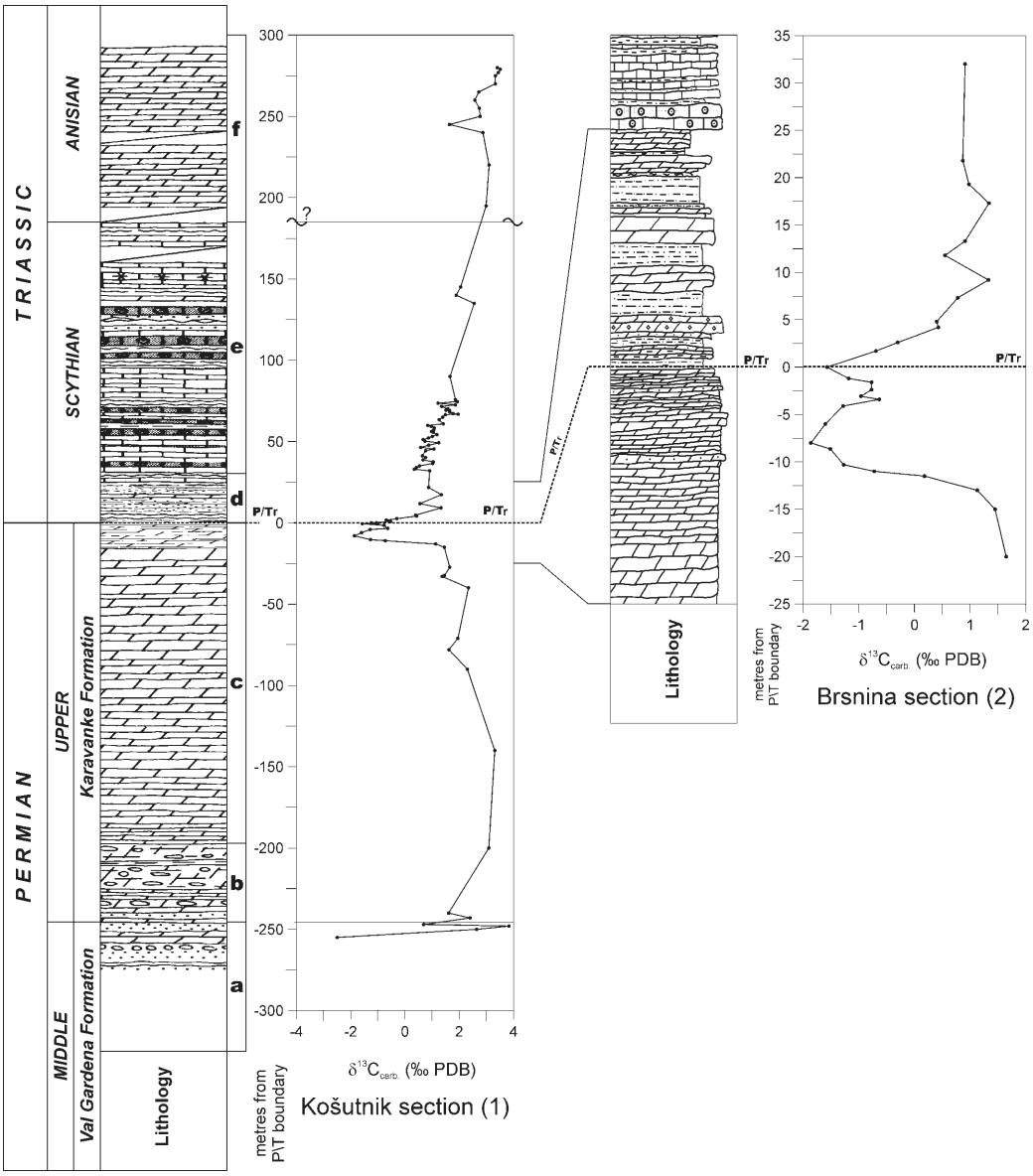

Fig. 3. Variations in lithology and carbonate carbon isotopic composition from Middle Permian to Anisian in Košutnik Creek section (1) and Brsnina Section (2). Detail from Fig. 2. **a** — transitional unit composed of sandy red dolomite alternating with shales and sandstones; **b** — an evaporitic sequence composed of cellular dolomite intercalates with black bituminous shales and grey vuggy dolomites; **c** — light-grey fossiliferous biomicritic dolomite; **d** — a red partly terrigeneous sequence composed of siltstones, mudstones and sandstones alternating with micritic dolomites showing impressions of gypsum crystals; **e** — dark-grey and brown micritic and sparitic limestone intercalated with oolitic limestone, marls and shales; **f** — grey dolomicrite and dolosparite. Legend to lithology see Fig. 4.

range of $\delta^{13}C$ values (from –23.4 to –21.3 ‰; average –22.8 ‰) was measured in additional samples during this study. Similar carbon isotopic composition values with $\delta^{13}C$ in the range between –23.8 and –21.2 ‰ were also reported for Permian coals and particulate organic matter from selected coalfields in South Africa (Faure et al. 1995).

The transition from Middle Permian to Upper Permian in the Karavanke Mountains is characterized by a positive $\delta^{13}C$ excursion from –2.5 to +3.8 ‰ observed at the base of the Karavanke Formation (Fig. 2, section 1 and Fig. 3, section 1). The dolomites of the basal evaporitic sequence show variation of $\delta^{13}C$ values mostly in the range between +0.7 and +3.8 ‰. In the overlying shallow-shelf biomicritic dolomite the $\delta^{13}C$ values range between +2.0 and 3.0 ‰. Slightly higher $\delta^{13}C$ values (+2.5 to +3.5 ‰) have been reported from the dolomitized Upper Permian Bellerophon Formation of the Carnic Alps (Magaritz & Holser 1991). In Western Slovenia the Upper Permian limestone of the Žažar Formation (Idrijca Valley and Masore section) exhibits variations of $\delta^{13}C$ values mostly in the range between +3.9 and +5.5 ‰ (Fig. 2, section 7, 8 and Fig. 4). These values are up to 2.5 ‰ higher than those of the Karavanke Formation.

The Permian to Triassic transition in the Karavanke Mountains is characterized by a prominent negative $\delta^{13}C$ shift of

about 4 ‰ (Fig. 2 and 3). A major drop of $\delta^{13}C$ values begins approximately 15 m below the lithologically proposed boundary. In the Carnic Alps the decrease of $\delta^{13}C$ begins about 60 m below (Magaritz & Holser 1991), while in Western Slovenia (Idrijca Valley and Masore section) the same shift of $\delta^{13}C$ values starts only 5 m below the P/Tr boundary (Dolenec T. & Ramovš 1996). In the Brsnina and Košutnik Creek section (Fig. 3) of the Karavanke Mountains the $\delta^{13}C$ curve reaches a first minimum peak value of –1.9 ‰ about 8 m below the boundary, a second minimum of –1.6 ‰ at the boundary itself, followed by a positive excursion of +0.6 ‰ in the basal Scythian, after which values are 1 to 2 ‰ lower than in the Upper Permian. The remaining Scythian and Lower Anisian carbonates are characterized by a general long-term gradual increase in $\delta^{13}C$ values by 2 ‰ (Fig. 2 and 3, section 1). $\delta^{13}C$ values of nearly 300 samples of Mesozoic limestones and dolomites from the same areas range mostly from –1.8 to +3.7 ‰ with an average of about +2 ‰ (Ogorelec et al. 1999). These values are distinctly lower than the $\delta^{13}C$ values of Permian carbonates.

The position of the negative $\delta^{13}C$ peak anomaly may indicate that the P/Tr boundary in the Karavanke Mountains does not correspond to the lithologically defined boundary and should be placed a little further down the section. This is because in the Carnic Alps a dramatic $\delta^{13}C$ drop occurs right after the stratigraphic P/Tr boundary which is placed within the lowermost 0.5 m of the 4 m thick Tesero Oolite Horizon (Holser et al. 1991). This horizon was not found in the investigated sections of the Karavanke Mountains. However, this interpretation is preliminary and has to await further detailed biostratigraphical studies.

Stable isotope data from the Idrijca Valley and Masore sections (Fig. 4) show an accelerating decrease of $\delta^{13}C$ values which begins about 5 m below the P/Tr boundary. This accel-

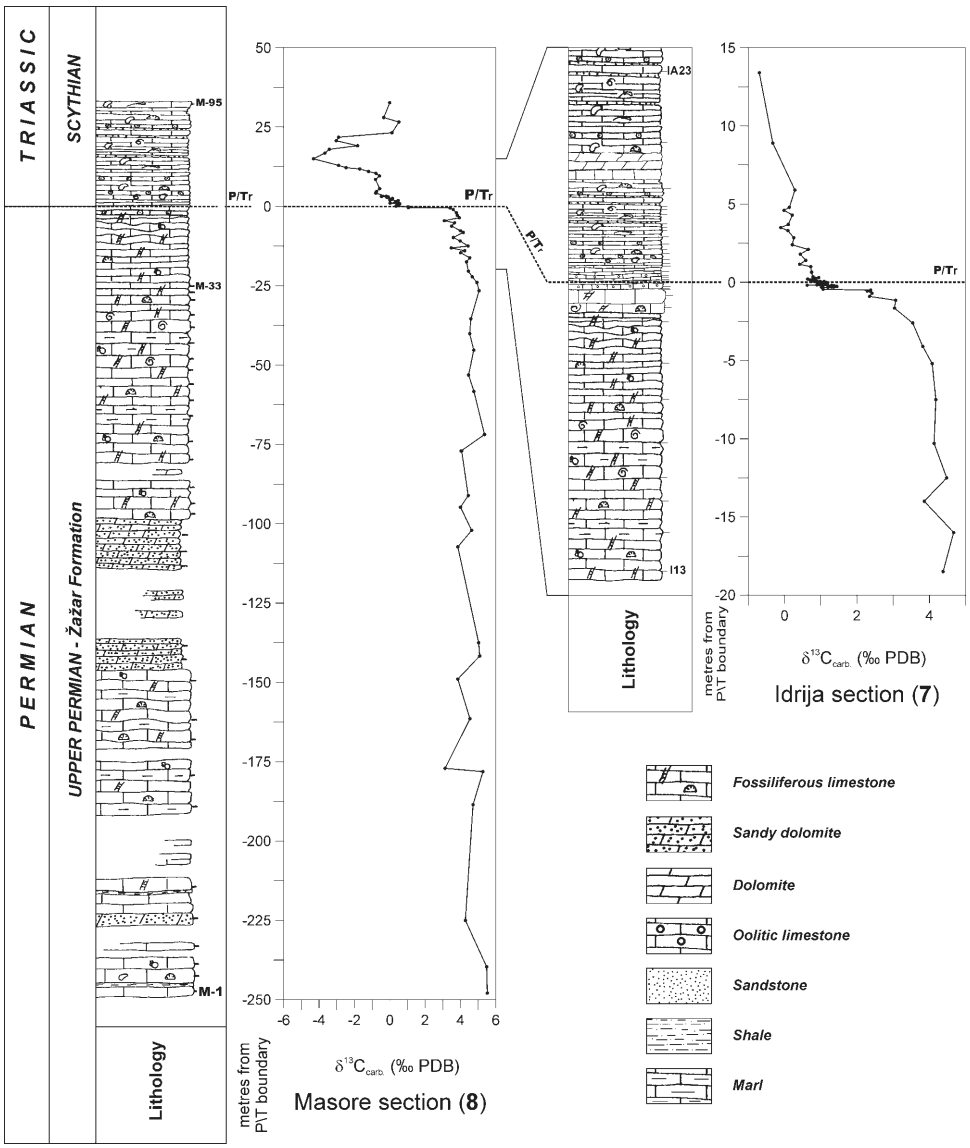

Fig. 4. Variation in lithology and carbonate carbon isotopic composition in the Upper Permian and Lower Scythian in the Masore section (8) and Idrija section (7). Detail from Fig. 2.

erating decrease of $\delta^{13}C$ values continues across the boundary into the Lower Scythian beds. In terms of amplitude the depletion of $\delta^{13}C$ values across the P/Tr boundary in both sections is about 4 ‰ (from +4.1 to –0.1 ‰ in the Idrijca Valley section and from +4.0 to –0.5 ‰ in the Masore section) and is similar to that found in the Karavanke Mountains. It is important to note that there is no evidence of a shift of $\delta^{13}C$ values back to their pre-excursion level. However, in the Masore section, where Lower Scythian beds are better exposed than in the Idrijca Valley section, two negative $\delta^{13}C$ peak anomalies of –4.3 and –3.7 ‰ (Fig. 4, section 8), similar to those reported from the Carnic Alps (Magaritz & Holser 1991) were found at 17 and 22 m above the boundary (Dolenec T. et al. 1999b). They are younger and unrelated to the P/Tr boundary events.

Discussion

The gradual positive $\delta^{13}C$ shift at the C/P boundary may reflect the transgressive trend of the Tethys Sea. The general hypothesis suggested to explain positive $\delta^{13}C$ shifts of carbonate carbon is that the expansion of shallow shelf areas increased the organic carbon burial rate and enriched the ocean water in ^{13}C (Magaritz & Stemmerik 1989).

The carbon $\delta^{13}C$ values of the Lower Permian Dolžanova Soteska Limestone Member are up to 3.8 ‰ higher relative to the Permian limestone average values (+2 ‰) proposed by Veizer et al. (1980). However, similarly high $\delta^{13}C$ values between +2 and +5 ‰ were also observed in Lower Permian limestones of the northern Yukon Teritory, while those of the basal Lower Permian limestones in the Sverdrup Basin in Canada range from +4 to +7 ‰ (Beauchamp et al. 1987) and are markedly heavier than known time-equivalent limestones elsewhere in the world (Keith & Weber 1964; Galimov et al. 1975; Veizer et al. 1980). Pronounced ^{13}C enrichments have also been observed in the Lower Permian of Tasmania (Rao & Green 1982). We suggest that the carbon isotopic composition of the Dolžanova Soteska Limestone Member could reflect a Lower Permian primary ^{13}C marine water enrichment. It can be explained as a result of increased organic carbon storage during this time. Extensive deposition of coal in the Upper Carboniferous and Lower–Middle Permian sediments has been regarded as an important site of organic carbon accumulation (Bluth & Kump 1991; Faure et al. 1995). The most reasonable explanation for the marked variations observed in the Lower Permian $\delta^{13}C$ record is a change in the burial fraction of organic carbon in marine sediments (Kump 1991), variable $C_{org}/C_{carb.}$ export ratio changes into the marine sedimentary carbon reservoir (Schidlowski 1987), as well as sea level fluctuations (Magaritz & Stemmerik 1989). The sharp, short-term $\delta^{13}C$ depleted spikes in this succession were most probably caused by pronounced local fluxes of isotopically light organic-derived carbon in the depositional environment during low sea level episodes due to oxidation of terrestrial sediments.

The negative $\delta^{13}C$ excursion across the Lower/Middle Permian transition observed in the Karavanke Mountains could be explained by a regression of the Tethys Sea due to Saalian movements. The observed $\delta^{13}C$ values of Tarvis Breccia undoubtedly indicate a subaerial exposure on the top of the lower cycle sedimentary sequence, which was also documented by Buggisch & Flügel (1980) for the Carnic Alps. During subaerial exposure decay of organic matter in soil zones at exposure surfaces generates larges volumes of ^{12}C enriched CO_2 with very low $\delta^{13}C$ values of about –2.5 ‰ (Heydari et al. 2001). Leaching of such isotopically light CO_2 dramatically lowers the $\delta^{13}C$ composition of percolating ground water, finally resulting in ^{13}C depletion of precipitating carbonate cement, as well as in decreasing the $\delta^{13}C$ of carbonate rock fragments, due to the effects of pronounced meteoric diagenesis (Pelechaty et al. 1996).

The carbon isotopic composition of pedogenic carbonates ($\delta^{13}C$ average value ~8 ‰) shows that they are enriched to about 15 ‰ relative to the carbon isotopic composition of the overlying flora ($\delta^{13}C$ average value ~23 ‰). Terrestrial plants in the Permian used only the C_3 photosynthetic pathway (Thomasson et al. 1986) and the $\delta^{13}C$ values of resultant organic matter fall around –27 ‰ (Quade et al. 1995). The mean $\delta^{13}C$ value of CO_2 from C_3 plants is also about –27 ‰ (Quade et al. 1995). These data indicate that the carbon isotopic composition of Permian C_3 plants is up to 4 ‰ more positive than the average value for C_3 plants. It has been demonstrated that increasing temperature, aridity, irradiation, a decreasing canopy effect and osmotic stress all increase the $\delta^{13}C$ value of C_3 plants (Faure et al. 1995).

It is generally accepted that the carbon isotopic composition of pedogenic carbonates is primarily determined by that of soil CO_2 which is a mixture of two components: atmospheric and plant derived CO_2 (Cerling et al. 1991). In modern soils, the effect of atmospheric CO_2 penetration and equilibrium isotope fractionation during mineral precipitation leads to soil carbonates with $\delta^{13}C$ values 15 ‰ heavier than those in the overlying flora (Cerling et al. 1989; Quade et al. 1989). According to the considerations outlined above, we suppose that pedogenic carbonates from the Val Gardena Formation precipitated mostly in isotopic equilibrium with Middle Permian soil CO_2.

The positive $\delta^{13}C$ excursion at the transition from Middle Permian to Upper Permian in the Karavanke Mountains most probably resulted from increases in the burial rate of organic carbon due to the marine transgression. This heavy carbon enrichment started together with transgression of the Tethys Sea on to the vast alluvial Middle Permian landscape and indicates changes from a terrestrial to a marine evaporitic environment (Dolenec T. et al. 1998). Documentation of this transgression exists not only to the south of the Tethys, but also to the north in the Zechstein Basin (Assereto et al. 1973).

The carbonate carbon isotopic composition of dolomites of the Karavanke Formation, which show up to 2.5 ‰ lower $\delta^{13}C$ values relative to the limestone of the Žažar Formation, could be attributed to biogenic carbon input from the surrounding land and/or deceleration in the rate of organic carbon burial in the sedimentary environment of the Karavanke Formation. Furthermore, according to some studies (Patterson & Walter 1994), evaporation can also result in lowering of seawater $\delta^{13}C$ composition and the $\delta^{13}C$ values of precipitating carbonates. The impressions of gypsum crystals in the

basal evaporitic succession and in the partly terrigenous, evaporitic P/Tr boundary sedimentary sequence suggest that evaporation in combination with a biogenic carbon input may be more a probable mechanism to explain the light carbon isotopic composition of the Karavanke Formation. On the contrary the limestone of the Žažar Formation acquired its carbon isotopic composition predominantly through isotopic equilibrium with Upper Permian atmospheric CO_2. It is interesting to note that the carbon isotopic composition of the Upper Permian limestone of the Žažar Formation below the P/Tr boundary is similar to that of the Lower Permian Dolžanova Soteska Limestone Member and Middle Permian Neoschwagerina limestone. Their $\delta^{13}C$ values are relatively high (mostly in the range between +2.5 ‰ and +5.5 ‰) and extremely stable (Fig. 2, sections 1–4, 7 and 8). We suppose that these values could be related to the worldwide high storage of organic matter during the Late Paleozoic. This interpretation is supported by deposition of vast amounts of coal and organic matter in sedimentary rocks from the Upper Carboniferous to the end of the Permian, when a global and abrupt break in coal formation and/or preservation occurred (Faure et al. 1995 and references therein).

In discussing the Permian-Triassic extinction events, several mechanisms for variations and dramatic perturbations in the $\delta^{13}C$ values of marine carbonates have been suggested, such as burial and erosion of organic carbon (Magaritz et al. 1992; Faure et al. 1995), variations of sea-level changes and salinity (Magaritz & Stemmerik 1989; Hallam & Wignall 1999), variability in primary production and a productivity crash (Wang et al. 1994; Kakuwa 1996; Wignall & Twitchett 1996), volcanic activity (Renné & Basu 1991; Wignall & Hallam 1993; Renné et al. 1995; Veevers & Tewari 1995), widespread anoxia (Wignall & Hallam 1992; Isozaki 1994; Wignall & Twitchett 2002), addition of ^{12}C-rich deep-water to the surface ocean (Heyerdary et al. 2000), large input of gas hydrate into the ocean-atmosphere system (Erwin 1993; Faure et al. 1995; Musashi et al. 2001), as well as an extraterrestrial impact event (Xu & Zheng 1993; Kaiho et al. 2001; Berner 2002).

The long term general decrease in the $\delta^{13}C$ values of marine carbonates, which starts several metres below the stratigraphic P/Tr boundary and is most probably associated with the increased terminal Permian marine regression, is considered to trace the release of a ^{13}C depleted CO_2 flux to the atmosphere due to oxidation of buried organic carbon and peat deposits, as well as the possible expulsion of oil and gas from the foreland basins along the peripheral margins of the entire supercontinent (Faure et al. 1995). Expulsion of such ^{13}C depleted CO_2 would have resulted in a decrease in atmospheric $\delta^{13}C$ values of up to a few per mil, ultimately resulting in ^{12}C enriched carbonates.

The sharp negative excursion of inorganic carbon $\delta^{13}C$ values at the boundary indicates a rapid interruption of these gradual processes and was most probably triggered by a major rapid volcanogenic input of isotopically light carbon released during the eruption of the Siberian flood basalts dated as contemporaneous with the P/Tr boundary (Renné & Basu 1991). Veevers & Tewari (1995) suggested that volcanism along the Tethys and Panthalasian 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. More recently Berner (2002) proposed that short-term changes in $\delta^{13}C$ at the P/Tr boundary are best explained by a combination of mass mortality from an impact or radiation blast together with methane release and CO_2 release. According to Berner (2002), the pressure wave most probably arising from a bolide impact could have triggered both the release of methane from stored hydrates and the initiation of Siberian volcanism.

The changes in the carbon cycle across the P/Tr boundary presented here are most likely related to end Permian volcanic activity, together with degradation and oxidation of organic matter due to the terminal phase of the Upper Permian marine regression. However, methane release from stored hydrates should also be taken into account. In the Karavanke Mountains the global $\delta^{13}C$ record across the boundary is supposed to be slightly perturbed due to local factors influencing the carbon isotopic composition of precipitating carbonates. However, in Western Slovenia the $\delta^{13}C$ paleoceanographic signal seems to be undisturbed and thus records a global decrease in the $\delta^{13}C$ values of surficial ocean water and carbonates, which coincides with the greatest extinction of marine and terrestrial organisms in the Phanerozoic.

Two negative excursions of the $\delta^{13}C$ values in the Lower Scythian of the Masore section are interpreted as reflecting two separate phases of subareal oxidation of organic matter, which could be related to stages in the lowering of the Tethys sea level and/or local fluxes of isotopically light organic-derived carbon in a depositional environment. The shape of the $\delta^{13}C$ curve for the Upper Scythian and Lower Anisian is most probably related to increased primary productivity of the ocean water and the sequestration of organic matter in sediments. Deposition of ^{12}C-rich organic matter in sediments results in an overall increase in $\delta^{13}C$ values of ambient seawater and therefore those of precipitating carbonates. Only exchanges between reduced and oxidized carbon reservoirs can explain such long term changes in carbonate $\delta^{13}C$ values (Schidlowski 1987; Hollander & McKenzie 1991).

Conclusions

Stable isotope analyses of carbonates from stratigraphic sequences in Western Slovenia ranging from Upper Carboniferous to Anisian revealed a marked enrichment in ^{13}C of Permian limestones relative to Mesosoic carbonates, thus revealing a further example of globally increased organic carbon storage during the Permian.

The pattern of carbonate carbon $\delta^{13}C$ values indicates a “positive carbon isotope event” across the C/P boundary, a “negative carbon isotope event” at the topmost Lower Permian, a positive shift of $\delta^{13}C$ values at the Middle Permian to Upper Permian transition and the well known global negative $\delta^{13}C$ anomaly at the P/Tr boundary, followed by a gradual increase of $\delta^{13}C$ carbonate carbon values toward Upper Scythian and Anisian. We propose that the positive $\delta^{13}C$ excursion at the C/P boundary and at the Middle to Upper Permian transition, as well as the gradual increase of $\delta^{13}C$ values from

Scythian to Anisian, could result from an enhanced organic carbon burial rate on continental shelves due to marine transgressions. This hypothesis is supported by the positive correlations observed between $\delta^{13}C$ changes and sea-level fluctuations in stratigraphic sections of the Karavanke Mountains. In contrast, the negative $\delta^{13}C$ shift at the topmost Lower Permian is well correlated with a subaerial exposure of these beds due to marine regression caused by the Saalian orogenic phase.

The $\delta^{13}C$ pattern for the Upper Permian seems to require a more detail explanation. We propose that the gradual decrease towards the P/Tr boundary was a result of increased erosion and oxidation of organic carbon during an enhanced Upper Permian marine regression and amalgation, as well as peripheral deformation of Pangea (Faure et al. 1995). The abrupt and relatively short-term negative $\delta^{13}C$ shift of about 4 ‰ at the P/Tr boundary most probably resulted from a combination of events which accelerated the changes in the global carbon cycle, such as erosion and oxidation of organic carbon, a release of methane from stored hydrates together with volcanic activity in the Siberian region, as well as along the Tethys and Panthalasia margins and a sudden reduction in primary productivity. These events accelerated the input of isotopically light CO_2 into the seawater–atmosphere system during the Permian-Triassic transition and caused further changes in the global carbon cycle. These changes are coincidental with the global environmental changes at the P/Tr boundary and the greatest mass extinction in the Phanerozoic.

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