The Permian-Triassic boundary in the Karavanke Mountains (Slovenia): Stable isotope variations in the boundary carbonate rocks of the Košutnik Creek and Brsnina section

Permsko-triasna meja v Karavankah: variabilnost izotopske sestave v karbonatnih kamninah Košutnikovega potoka in Brsnine

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Abstract
The stable isotope composition of the Upper Permian and Lower Triassic beds at two locations (Košutnik Creek and Brsnina) in the southern Karavanke Mountains has been used to investigate δ13C and δ18O variations of the well exposed undisturbed marine carbonate sequence across the Permian-Triassic boundary. The lithostratigraphic boundary between the Lower Triassic-Scythian and underlying Upper Permian beds is transitional and no exact line can be drawn between them. The transition from Permian to Triassic is characterized by a major shift in carbonate carbon δ13C and δ18O from heavier to lighter values. The results suggest that the carbon isotope variability at the P/Tr boundary reflects global changes in the carbon cycle and/or climatic changes, probably controlled by the Upper Permian regression and further eustatic oscillations of the Tethys sea level and by tectonic. The corresponding δ18O variability should be regarded as indication of seawater oxygen isotopic composition, salinity and temperature changes, changes in carbonate mineralogy of the rocks, postdepositional alterations or some combinations of all the mentioned possibilities.

Kratka vsebina
sestave ogljika na meji P/Tr v raziskanih profilih odraža globalne spremembe v ogljikovem ciklusu, in klimatske spremembe, ki so najverjetneje posledica zgornje-permske regresije ter kasnejših spodnjetriassnih eustatičnih nihanj morske gladine. Variabilnost izotopske sestave kisika v meji sekvenci pa je po našem mnenju najverjetneje posledica različnih faktorjev, tako variabilnosti izotopske sestave kisika v takratni morski vodi, slabosti, temperature kot mineralne sestave kamnin in post sedimentacijskih sprememb.

Introduction

The Permian-Triassic (P/Tr) boundary events which took place approximately 250 Ma ago, led to one of the most extensive mass extinctions in the history of the life. Their causes are not yet well known. The most plausible current explanation for this extinction appears to evolve multiple elements such as volcanism-induced cooling, extraterrestrial impact and global anoxia (Erwin, 1994). It was already demonstrated that at the P/Tr boundary a reflection of worldwide collapse of terrestrial ecosystems with accompanying loss of standing biomass is indicated by unparalleled abundances of fungal remains (Binnikhuys & Visscher, 1994). Studies of several P/Tr boundary sections all over the world show that the transition from Permian to Triassic is characterized by a negative δ13C excursion of inorganic and organic carbon isotopes (Magaritz et al., 1986, 1992; Baud et al., 1989; Magaritz & Holser, 1991; Magaritz & Stemmerik, 1989; Erwin, 1993; Wang et al., 1994; Faure et al., 1995; Dolenc et al., 1981). A considerable enrichment of light carbon isotopes in marine carbonates and in organic matter is associated with many extinction related boundaries not only the P/Tr. The corresponding oxygen isotope anomaly is sometimes more or less parallel but usually less pronounced. Parallel behaviour of oxygen and carbon isotopes in marine carbonates may suggest some common driving mechanisms (Verhagen et al., 1990). It could be related to the dominance of meteoric water during the marine regression (Verhagen et al., 1990), oxidation of marine organic matter and accompanying kinetic oxygen isotope fractionation (Gruszczynski et al., 1989). According to Schrag et al. (1993) the oxygen isotopic composition of diagenetically unaltered bulk carbonates primarily reflects the temperature and/or isotopic composition of the seawater. Based on this assumption the major δ18O excursions thus could be related to global climatic changes, as well as changes in the isotopic composition of the ocean water.

The particular aims of this study have been to complete the previous investigations of the P/Tr boundary in the Karavanke Mountains (Dolenc et al., 1981) and to confirm the systematic changes during the Permian-Triassic transition.

Geological setting and stratigraphy

In the southern Karavanke Mountains, at Košutnik Creek and Brsnina (Fig. 1.) sedimentation continued concordantly across the P/Tr boundary. The biostratigraphic and litostratigraphic boundary between the Lower Triassic (Scythian) beds and the underlying Upper Permian beds is transitional and no exact line can be drawn between them (Fig. 2.). The Middle Permian Val Gardena Formation of mostly fluvial origin is overlain by a 270 m thick Upper Permian carbonate sequence that was
named the Karavanke Formation (Buser et al., 1986). The basal unit of this sequence is represented by an up to 70 m thick evaporitic facies composed of cellular dolomite (rauhwacke) which alternates with rare black bituminous shales and grey vuggy dolomites. In the lower part of the basal unit, only in the Košutnik Creek a 1.5 m thick sequence of well bedded black bituminous biomicritic limestone was found. According to Buser (1974; 1980) it contains tiny sulfur geodes, Bellerophon gastropods and numerous microfossils (Gymnocodium bellerophontis, Permocalculus fragilis, Velebitella triplicata, Mizzia velebitana and Glomospira sp.) that permitted to prove for the first time the Upper Permian age of the Karavanke Formation. The evaporitic sequence is overlain by a thick succession (up to 200 m) of fossiliferous biomicritic dolomites probably deposited in an open lagoon and shallow shelf environment. The Upper Permian age of these beds is indicated by calcareous algal assemblages (Mizzia cornuta, Permocalculus sp., Connecta sp.), as well as by very common small foraminifers which belong to Glomospira sp., Agathammina sp. and Hemigordius sp. (R a m o v s, 1986). About 70 to 80 m below the P/Tr boundary a porphyryte dyke of Middle Triassic age cuts the Upper Permian beds.

The P/Tr boundary is placed arbitrarily at the end of the sedimentation of the well bedded grey dolomictite. It is followed by a red coloured more or less terrigenous sequence predominantly composed of well bedded siltstones, mudstones and sandstones, alternating with micritic dolomites that contain no characteristic fossils. The sequence was deposited in a very shallow evaporitic part of the basin, into which abundant terrigenous material was transported. Its thickness is about 5 m in Košutnik Creek and 25 m at Brsnina. In the investigated area these beds are overlain mostly by dark grey and brown micritic and sparitic limestones intercalated with oolitic limestone, marls and shales.

Methods

The boundary profiles in the Košutnik Creek and at Brsnina were systematically sampled at 1 and 5 m intervals, except in the vicinity of the biostratigraphically and lithostratigraphically defined P/Tr boundary where sampling intervals were reduced to 20, 10 and 5 cm. The relative stratigraphic position of the samples and the analyti-
Fig. 2. Stratigraphic section of the Upper Permian and Scythian beds in the Karavanke Mountains, Tržič section (after Dolenc et al., 1981).
The Permian-Triassic boundary in the Karavanke Mountains

cal results can be seen in Fig. 2. The isotopic measurements were carried out on whole rock samples, carefully selected by using thin sections. The samples were ana-
yzed in the Jožef Stefan Institute, Ljubljana, Slovenia, following the modified pro-
cedure of (M c C r e a, 1950); carbonate samples were reacted overnight with 100 \% phosphoric acid at 50 °C. The CO₂ gas generated was isotopically analyzed using a Varian MAT 250 isotopic ratio-mass spectrometer. Therefore the data reflect a
weighted average of the isotopic composition of the entire carbonate components in the dolomite or limestone. All δ¹³C and δ¹⁸O values were reported in standard per mill (%o) notation relative to the PDB and SMOW standards. The analytical reproducibili-
ty of duplicate samples was always better than ±0.1 %o for both carbon and oxygen
isotope composition.

Results and discussion

After the Middle Permian period during which the predominantly elastic Val Gar-
dena Formation was deposited in continental environment gradual subsidence affect-
ed the extensive area of the Karavanke Mountains. The subsidence was followed by a
vast marine transgression of the Tethys Sea from the SE to the NW. A transgression is
consistent with conditions observed all over Europe during the late Permian. Documenta-
tions of a transgression exist not only in the Zechstein basin, but also to the
south in the Tethys (A s s e r e t o e t al., 1973). It was a time of climatic and geo-
graphic changes from continental to marine environment which are reflected in an
intertongued lithofacies. In the Lower part of the Upper Permian thin sandy
dolomite layers interfinger with the topmost Val Gardena shales and sandstones
(B u s e r, 1980). The thickness of this basal unit which grades upward into the evap-
oritic sequence of the Upper Permian is about 5 m. The carbonate rocks of the evap-
oritic sequence (Fig. 3) show the variation of δ¹³C mostly in the range between + 0.69
and + 3.63 %o (PDB) and δ¹⁸O between + 24.31 and + 26.93 %o (SMOW). Similar values
have been also found in the basal Upper Permian evaporitic unit of the southern
Karavanke Mountains at Tržič (D o l e n c et al., 1981). Outside this range is the
sandy dolomite of the basal unit which is distinctly depleted in ¹³C (δ¹³C = - 2.50 %o)
and ¹⁸O (δ¹⁸O = + 21.44 %o). This depletion is probably related to the precipitation from
low salinity solutions with a predominant component of meteoric water and/or post-
depositional isotopic alteration. The oxygen isotopic composition of the evaporitic
sequence is not as high as expected from the recent evaporitic environments. Modern
dolomites from the Arabian Gulf have a δ¹⁸O range mostly from + 30.4 to + 34.3 %o,
while those from the Baffin Bay are even slightly heavier with δ¹⁸O between + 34.5 to
+ 35.5 %o (T u c k e r, 1990). Such values are consistent with carbonate minerals for-
mation from hypersaline marine derived fluids (P e r k i n s et al., 1994). The observed
depletion of the evaporitic sequence in ¹⁸O suggests the influx of fresh water into the
evaporitic basin and extensive meteoric diagenesis which also lead to the
various distribution phenomena. Thus δ¹⁸O values are to be regarded as indicators of
seawater and pore fluids isotopic composition, as well as temperature and changes in
mineralogy. Studies of carbonate rocks have shown that the oxygen-isotope system is
more subject to exchange during diagenesis and burial metamorphism than the car-on isotope system (M a g a r i t z, 1975; 1983). By analysing the least visibly alter-
ted samples from the evaporitic sequence we attempt to minimise this effect. Thus we
can suppose that although the post depositional changes more or less altered the
original oxygen and carbon isotopic composition, the primary paleoceanographic signal was not completely overprinted. Parallel behaviour of the \( \delta^{13}C \) and \( \delta^{18}O \) curves and a relatively high correlation (\( r = 0.89 \)) between \( \delta^{13}C \) and \( \delta^{18}O \) suggest a transition from a terrestrial to shallow marine evaporitic conditions.

The transition from Middle Permian to Upper Permian is characterized by a considerable enrichment of carbonates with \( ^{13}C \) (from -2.50 to +3.83 \%) and \( ^{18}O \) (from +21.44 to +26.93 \%). Positive \( \delta^{13}C \) and \( \delta^{18}O \) excursions started when a transgressive sea flooded the vast alluvial Middle Permian landscape. The general hypothesis proposed to explain positive \( \delta^{13}C \) shifts is that during the marine transgression, the expansion of shallow shelf areas increased the organic carbon burial rate and enriched the ocean in \( ^{13}C \) (Magaritz & Stemberik, 1989; Compton et al., 1990; Faure et al., 1995). In terms of the corresponding isotopic changes, periods of high-sea level are reflected in enrichment of \( ^{13}C \) in carbonates (Hailam, 1992). According to the previous interpretation we suggest that a positive \( \delta^{13}C \) shift at Middle Permian–Upper Permian transition resulted from changes in the burial rate of organic carbon which began with the transgression of the Tethys Sea. The corresponding oxygen isotope excursion is similar to those in \( \delta^{13}C \) and also indicates changes from terrestrial to marine-evaporitic conditions.

Moving upward in the sections the sedimentary facies of the Upper Permian beds evolved from more or less restricted lagoon dolomites alternated with sabkha gypsum...
toward open lagoon-shallow shelf biomicrite dolomite, suggesting a transgressive trend of the Tethys Sea. The isotopic data show a slight enrichment in $^{13}$C and $^{18}$O of biomicrite dolomite relative to the rocks of the evaporitic unit with $^{13}$C and $^{18}$O values mostly in the range from +2.0 to +3.1 $\%_{o}$, and from +27.3 to +28.3 $\%_{o}$. Out of this range is the host rock of the porphyrite dyke enriched in light carbon $^{13}$C and oxygen $^{18}$O isotopes (up to -1.3 $\%_{o}$ for $^{13}$C and up to +17.8 $\%_{o}$ for $^{18}$O). However, the $^{13}$C and $^{18}$O alteration zones are only about 4 m thick.

Isotopic composition similar to those of the biomicrite dolomite has been also reported from the Upper Permian sections of the Carnic Alps (M a g a r i t z & H o l s e r, 1991), as well as from the Upper Permian beds at Tržič (D o l e n e c et al., 1981). The relatively high $^{13}$C values of these carbonate rocks can be related to the worldwide high storage of organic matter during the Late Paleozoic (M a g a r i t z & H o l s e r, 1991), while $^{18}$O values may reflect to some extent the temperature of the Tethys Sea water and/or dolomitizing solution.

The transition from Permian to Triassic is characterized by an abrupt shift of $^{13}$C and $^{18}$O toward lower values. In terms of amplitude, the depletion of $^{13}$C and $^{18}$O across the P/Tr boundary is of about 4 $\%_{o}$ for $^{13}$C and 7 $\%_{o}$ for $^{18}$O. A detailed sampling of the boundary interval in the Kostnàk Creek and at Brsnina shows that the $^{13}$C and $^{18}$O anomalies are not confined strictly to the lithostratigraphically and biostratigraphically proposed boundary. A major global drop of $^{13}$C and $^{18}$O begins about 30 m below the boundary. In Carnic Alps a decrease of $^{13}$C begins about 60 m (M a g a r i t z & H o l s e r, 1991), while in the Idrijca Valley the same shift of $^{13}$C starts only 5 m below the P/Tr boundary (D o l e n e c & R a m o v š, 1996). The $^{13}$C curve reaches the peak value of -1.86 $\%_{o}$ about 8 m below the boundary and after that

![Fig. 4. $^{13}$C and $^{18}$O data of the Brsnina section](image-url)
suffers a succession of additional drop at the end of the Permian and two in the lowermost Scythian, before settling to more normal values which are 1 to 2% lower relative to those in the Upper Permian (Fig. 4). If δ^13C values are to be regarded as indicators of changes in the oxidation and reduction system of carbon the shape of the carbon curve thus reflects at least two separate phases of subaerial oxidation of organic matter at the end of the Permian and two similar phases in the Lower Scythian. These phases may be related to the eustatic oscillations of the Tethys Sea level, as well as to the local fluxes of isotopically light organic derived carbon in a depositional environment which slightly disturbed the global carbon isotope signal. During marine regressions shelves were exposed to increased erosion and oxidation of organic carbon, producing a negative δ^13C shift (Tappan, 1968; Mackenzie & Piggot, 1981; Compton et al., 1990; Magaritz & Holser, 1991; Faure et al., 1995). The end Permian carbon isotopic perturbances in the investigated area span an interval of about 50 m, whereas in the Idrija Valley where limestone sedimentation proceeded concordantly across the P/Tr boundary the same shift of δ^13C happens over about 10 m of section (Dolenc & Ramovš, 1996). We suggest that the observed general decrease of δ^13C values at the P/Tr transition is probably associated with the global Late Permian marine regression which led to the destruction of terrestrial and marine ecosystems which related in a δ^13C depleted CO_2 flux into the atmosphere (Magaritz & Holser, 1991; Faure et al., 1995). This CO_2 then equilibrated with the ocean waters, ultimately resulting in a δ^13C enriched reservoir in ocean waters and therefore δ^13C depleted carbonates.

The variations in δ^18O across the P/Tr boundary show slightly different trends with respect to those in δ^13C. After a decrease from +27.55 to a minimum value of +25.22 % below the boundary, the variability of δ^18O in the interval straddling the P/Tr boundary is fairly uniform (between +25.30 and +26.05 %). A decrease of δ^18O in the topmost Permian is best explained by a change from marine to desultory evaporitic conditions affected by an excessive input of terrigenous material and by local freshening of waters due to the influxes of more or less isotopically modified continental waters into the sedimentary basin.

It is important to note that significant facies changes at the P/Tr boundary confirm the extensive regression and several second order transgressive-regressive cycles probably controlled by eustatic oscillations of the sea level and tectonic. The climatic conditions were presumably hot and arid to semi-arid and then changed to a somewhat more humid in the Lower Scythian (Asse r et al., 1973).

The end Permian regression was preceeded by a rapid early Triassic transgression which brought a shallow epicontinental sea over the entire region of the Karavanke Mountains. A shallow continental shelf extended during the time interval between the Upper Permian and the Anisian stage from Slovenia to the adjacent Alpine regions (Asse r et al., 1973; Bro gl io Lor ig a et al., 1979) and Dinarides (M ud renović, 1980; B us e r, 198? ). The sedimentation became more or less unified throughout the entire region. During this time micritic, sparitic and oolitic limestones, as well as marls and shales were formed. Carbon isotopic composition of this stratigraphic unit indicates a gradual enrichment in δ^13C. According to previous interpretations we speculate that this enrichment in the regional sense probably coincided with deposition of organic matter in shelf sediment during high sea level stand, and/or with slightly cooling events in the Lower Scythian.

It is interesting to note that the Scythian limestones are considerably depleted in δ^16O (from 3 to 8 %) relative to the Upper Permian as well as Lower Scythian dolomite.
of the boundary zone. Extrapolation of high temperature data yields values which indicate that dolomite which formed in isotopic equilibrium under sedimentary temperatures should be enriched in δ¹⁸O relative to calcite by 3 - 6 % (Sheppard & Schwartz, 1970). M. C. McKenzie (1981) showed that the enrichment of the naturally occurring dolomite in δ¹⁸O over sedimentary calcite is + 3.2 % at 35 °C. However, the oxygen isotopic composition of coexisting sedimentary dolomite-calcite occurrences was often found to be similar (Botz & v. der Borch, 1984). Our data show that the Scythian limestone are depleted in δ¹⁸O up to 4 % relative to the Scythian dolomite, and up to 8 % as compared to the Upper Permian dolomite. The isotopic composition of these limestones shows the variation of δ¹⁸O mostly in the range between + 20.57 and + 23.95 % and δ¹³C between + 0.34 and + 1.96 %. Similar depleted values have also been observed in Scythian and Upper Permian limestone of the Idrija Valley (Doleček & Ramovš, 1996). These values are also considerably depleted (up to 7 %) relative to the marine limestones of Recent age (Faura, 1977). Such depletion cannot be interpreted only in terms of seawater temperature. It may have also been caused by a change in δ¹⁸O of the seawater, decrease of salinity as well as by postdepositional alteration. Although there are several problems with regard to the interpretation of the differences in the isotopic composition between dolomites and limestones we suggest that the cause of the observed δ¹⁸O depletion in limestones could be related to changes in carbonate mineralogy, salinity and oxygen isotopic water composition, as well as to the diagenetic modifications.

The changes in carbonate mineralogy thus coincided with the drop in δ¹³C from values of around + 26.05 to + 22.45 %. Note that the corresponding δ¹³C signal is not changed and is preserved in both dolomite and limestone. After reaching the minimum value of + 20.57 % the δ¹³C curve returns to slightly more positive values of + 23.95 %, and then gradually decreases again. The shape of the δ¹³C curve thus probably indicates a slightly cooling trend - more humid conditions during the deposition of the grey limestone followed by a warmer period. A weak negative correlation between δ¹⁸O and δ¹³C (r = - 0.24 for 39 samples) in the Lower Scythian limestone suggests some different driving mechanisms which affected the isotopic composition of this unit.

Conclusions

The results we have presented in this study indicate that the transition from Permian to Triassic is characterized by a strong disturbance in the global carbon cycle accompanied by changes in δ¹³C values in the boundary carbonate rocks. The negative δ¹³C excursion is interpreted as reflecting an increased terminal Permian marine regression which resulted in a δ¹³C depleted CO₂ flux into the atmosphere. This CO₂ then equilibrated with the ocean waters, ultimately resulting in δ¹³C enriched carbonates. On the other hand the positive δ¹³C shift at the Middle Permian—Upper Permian transition is attributed to the Upper Permian marine transgression with corresponding enrichment of carbonates in δ¹³C. The shape of the carbon isotope curve reflects at least two separate phases of subaerial oxidation of organic matter at the end of the Permian and two similar phases in the Lower Scythian. These phases may be related to the eustatic oscillations of the Tethys sea level and/or local changes in the proportions of continental and marine contributions of organic matter into the sedimentary basin which slightly overprinted and masked the changes in global carbon isotope composition.
The much more muddled oxygen isotopic patterns indicates that the multiple influences on oxygen isotopic composition confuse the original paleoceanographic signal. Therefore it is difficult to give a definite explanation of the observed δ18O variations. However, the increases in δ18O at the Middle Permian–Upper Permian and decreases at the Permian-Triassic transition may have also reflected major changes of the sea level stand.

According to our speculative interpretation of existing data we also suppose a causal connection between the isotopic anomalies and a widespread regression during the terminal Permian, leading to destruction of terrestrial and marine ecosystems and to the suggested the end-Permian mass extinction.

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