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Stable Isotope Event Markers Near the Permo-Triassic Boundary in the Karavanke Mountains (Slovenia)

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Abstract

Stable isotope analyses of carbonates and organic matter from the Permo-Triassic boundary section in the Karavanke Mountains, Slovenia, indicate a further example of the "light carbon" event across the boundary. In this section the changes in carbon isotope values were a direct result of the culmination of the marine regression and associated events at the end of the Permian, which caused a drop in primary productivity, as well as related local environmental changes, with no evidence of any considerable diagenetic overprint.

over the world. One of the most remarkable anomalies is the worldwide negative shift of ¹³C of inorganic and organic carbon across the P/Tr boundary (MAGARITZ et al., 1992; WANG et al., 1994; WOLBACH et al., 1994; FAURE et al., 1995). A corresponding oxygen isotopic shift is more or less parallel, but less pronounced. Furthermore, significant shifts in sulphur (KAJIWARA et al., 1994) and strontium isotopes (KRAMM & WEDEPOHL, 1991) have also been recorded.

In this study we present the results of stable isotope analysis of the P/Tr boundary section in the Karavanke Mountains (Fig. 1), and discuss their implications with respect to a better understanding of the nature and causes of the P/Tr boundary events in this part of Western Palaeotethys.

1. INTRODUCTION

Permo-Triassic (P/Tr) boundary events, which took place approximately 250 Ma ago, led to the most extensive mass extinction in the history of life. A number of possible explanations for this profound break in the evolution of life have been proposed, such as volcanic activity, sea-level fluctuation, changes in sea-water chemistry, an extra-terrestrial impact event and various related factors (YOICHI, 1994). The most recently proposed cause of the mass extinction at the end of the Permian is a combination of these more or less co-occurring events operating in three phases (ERVIN, 1996). The first began with the marine regression during the Late Permian and resulted in the destruction of many marine basins, reduction in the habitat area of many organisms and increased climatic instability. The second phase involved the eruption of the Siberian Traps and further environmental degradation. The final phase may have started immediately prior to the boundary when the Late Permian regression ended and the earliest Triassic transgression begun. The global events outlined above coincide with isotope and elemental anomalies recorded in several P/Tr boundary sections all

2. GEOLOGICAL SETTING AND STRATIGRAPHY

In the southern Karavanke Mountains, the Middle Permian Val Gardena Formation of mostly fluvial origin, is overlain by a 270 m thick Upper Permian carbonate sequence, which was named the Karavanke Formation (BUSER, 1974). The boundary between the two formations is transitional and is characterized by thin sandy red dolomite layers alternating with the topmost Val Gardena shales and sandstones. The thickness of the transitional unit which grades upward into the Karavanke Formation is about 5 m (DOLENEC et al., 1981). The evaporitic sequence, up to 70 m thick, represents the basal unit of the Karavanke Formation composed of cellular dolomite, which alternates with rare black bituminous shales, and grey vuggy dolomites. The evaporitic sequence is overlain by a 200 m thick succession of fossiliferous biomicritic dolomites. The Upper Permian age of these beds is indicated by calcareous algal assemblages, as well as by foraminifera (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. It is followed by a red coloured partly terrigenous sequence predominantly composed of thin-bedded siltstones, mudstones and sandstones alternating with micritic dolomites, that contain no characteristic fossils. These earliest Triassic beds were deposited in an extremely shallow sea, which

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Fig. 1 Reconstruction of the supercontinent Pangea in the Late Permian after SUN et al. (1989). The point indicates the approximate position of the studied area in the Karavanki Mountains.

gradually became a wide, extensive mud flat (ASSERETO et al., 1973). Their thickness is about 25 m. In the investigated area these beds are mostly overlain by Lower Triassic dark grey and brown micritic and sparitic limestones intercalated with oolitic limestone, marls and shales.

3. MATERIALS AND METHODS

The boundary profile in the Karavanki Mountains was sampled at 10 m intervals, except in the vicinity of the lithostratigraphically defined P/Tr boundary where sampling intervals were reduced to 20 cm. The relative stratigraphic position of the samples and the analytical results are presented in Fig. 2. The isotopic measurements were carried out on un-dolomitized limestone and un-calcitized dolomite samples. 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-red. All samples were also evaluated by petrographic methods to assess their diagenetic history. Only unrecrystallized or insignificantly recrystallized samples were used for isotopic measurements. 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 ^{18}O and ^{13}C analysis were prepared by overnight digestion in >100% phosphoric acid at 50°C. CO_2 gas released during acid treatment was cryogenically cleaned and analyzed for O and C isotopic composition on a Varian MAT 250 mass spectrometer. Data were corrected for kinetic fractionation between phosphoric acid and carbonates using fractionation factors of 1.00925 for calcite and 1.01038 for dolomite (BEUKES et al., 1990).

The ^{18}O and ^{13}C values were normalized by assuming ^{18}O and ^{13}C values of -2.44‰ and +2.48‰ for IAEA-CO-1 standard on the PDB scale.

For preparation of the total organic carbon, powdered whole rock samples were treated with heated 3M hydrochloric acid at 50°C to react with the carbonates. Upon cessation of CO_2 evolution, excess acid was removed by repeated washing (three to four times) with doubly distilled water until a neutral pH was determined. After the final decanting of water, the carbonate free residues were oven-dried at 50°C. Organic carbon isotope ratios were measured in the carbonate-free residues in the Europa 20-20 Stable Isotope Analyser (Europa Scientific Ltd.) with the ANCA-NT preparation module for on-line combustion of bulk solid samples and chromatographic separation of the gases. Organic carbon isotope values were calibrated using the IAEA-CH-7 standard with a ^{13}C value of -31.8‰ on the PDB scale.

All bulk rock and carbonate-free residue samples were measured two or three times. The results are reported in the conventional delta notation as ‰ deviations from the PDB standard (CRAIG, 1957) for oxygen, carbonate and organic carbon. The analytical precision based on multiple analysis of internal laboratory standards was $\pm 0.02\text{‰}$ for ^{18}O , $\pm 0.01\text{‰}$ for $^{13}\text{C}_{\text{carb}}$, and $\pm 0.008\text{‰}$ for $^{13}\text{C}_{\text{org}}$, respectively. Overall analytical reproducibility of the isotopic data was $\pm 0.15\text{‰}$ for oxygen, $\pm 0.1\text{‰}$ for carbonate carbon and $\pm 0.095\text{‰}$ for organic carbon.

4. RESULTS AND DISCUSSION

The transition from Middle Permian to Upper Permian is characterized by a considerable enrichment of dolomite with ^{13}C (from -2.50 to +3.83‰) and ^{18}O (from -8.67 to -3.34‰) (DOLENEC et al., 1981), as well as by a drop in ^{13}C of total organic carbon (from -21.90 to -24.49‰). Positive ^{13}C and ^{18}O shifts in dolomite (Fig. 2) may reflect the transgression of the Palaeotethys Sea on the vast alluvial Middle Permian landscape. Documentation of this transgression exists not only in the south of Tethys, but also to the north in the Zechstein basin (ASSERETO et al., 1973). The general hypothesis, suggested to explain positive ^{13}C shifts of carbonate carbon, is that the expansion of shallow shelf areas increased the organic carbon burial rate and enriched the ocean in ^{13}C (COMPTON et al., 1990; FAURE et al., 1995). The corresponding oxygen isotope excursion is similar to that in ^{13}C , and also suggests a change from terrestrial to marine-evaporitic conditions. The ^{13}C of terrestrial plant remains in the Val Gardena Formation varies between -22.13 and -21.65‰ (DOLENEC, 1984). These values are up to 2.8‰ more positive than those of the evaporitic sequence. A negative shift at the Middle Permian-Upper Permian transition most likely suggests that the ratio of terrestrial to marine organic carbon changed.

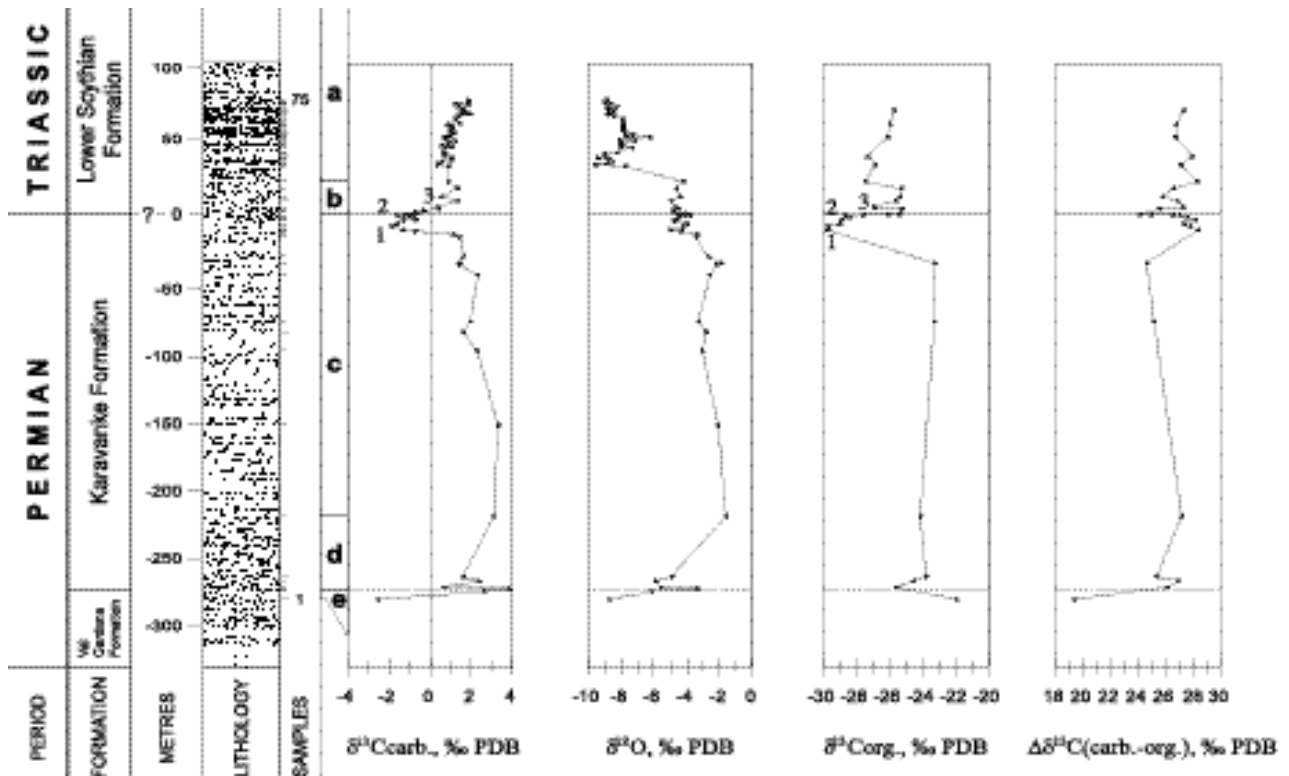


Fig. 2 Stable isotope composition of carbonates ($^{13}\text{C}_{\text{carb.}}$, ^{18}O), total organic carbon ($^{13}\text{C}_{\text{org.}}$) and carbon isotope fractionation between carbonate and total organic carbon ($^{13}\text{C}_{\text{carb.-org.}}$) across the Permo-Triassic boundary in the Karavanke Mountains. a) Dark grey and brown micritic and sparitic limestone intercalated with oolitic limestone, marls and shales; b) a red partly terrigenous sequence composed of siltstones, mudstones and sandstones alternating with micritic dolomites; c) light grey fossiliferous biomicritic dolomite; d) an evaporitic sequence composed of cellular dolomite intercalated with black bituminous shales and grey vuggy dolomites; e) a transitional unit composed of sandy red dolomite alternating with shales and sandstones; 1-3) carbonate and organic carbon anomalies.

The dolomites of the basal evaporitic sequence show a variation of $^{13}\text{C}_{\text{carb.}}$ in the range of +0.69 to +3.83‰, and of ^{18}O between -5.88 to -3.34‰. The oxygen isotopic composition of the evaporitic sequence is not as high as expected from recent evaporitic environments (TUCKER, 1990). The observed reduction in ^{18}O indicate an influx of fresh water into the evaporitic basin, less evaporation and/or a variety of different post-depositional processes, that may affect either oxygen or carbon or both stable isotopic records (BRAND & VEIZER, 1981; MAGARITZ & HOLSER, 1991). By selecting the least visibly weathered and recrystallized samples from the investigated sections we attempted to minimise the possible post-depositional effects. A weak positive correlation ($r = 0.40$) between ^{18}O and ^{13}C of the dolomite samples and a weak negative correlation ($r = -0.22$) between ^{18}O and ^{13}C of the limestone samples most probably suggests that the isotopically light meteoric water and dolomitizing fluids during diagenesis and burial to some extent reset the original whole rock oxygen and carbon isotopic composition. The low positive correlation ($r = 0.51$) between $^{13}\text{C}_{\text{carb.}}$ and $^{13}\text{C}_{\text{org.}}$ indicates that the whole rock isotopic composition was not modified by the oxidation of organic matter during diagenesis. Based on these observations, we tend to believe that the isotopic composition of the investigated Karavanke Mountain carbonate

rocks has not been seriously altered after their formation and that the primary palaeoceanographic signal was not completely overprinted.

The transition from Permian to Triassic is characterized by a prominent negative shift of carbonate ^{13}C as well as total organic carbon and a similar, but less pronounced ^{18}O decrease. The major drop of $^{13}\text{C}_{\text{carb.}}$ and $^{13}\text{C}_{\text{org.}}$, similar to that seen globally, begins approximately 15 m below the boundary. The $^{13}\text{C}_{\text{carb.}}$ curve reaches a minimum peak value of -1.86‰ about 8 m below the boundary and after that there is another minimum of -1.57‰ at the end of the Permian and a positive excursion of +0.55‰ in the lowermost Scythian, before settling to values which are 1 to 2‰ lower relative to those in the Upper Permian. The position of the negative $^{13}\text{C}_{\text{carb.}}$ peak anomaly may indicate that the P/Tr boundary in the Karavanke Mountains should be placed a little further downsection, since in the Carnic Alps a dramatic $^{13}\text{C}_{\text{carb.}}$ drop occurs right after the stratigraphic P/Tr boundary which is placed within the lowermost 0.5 m of the 4 m thick oolitic Tesserò Horizon or at its base (HOLSER et al., 1991). In the Karavanke Mountains this oolitic unit at the base of the Scythian was not recognized. The corresponding total organic carbon isotope curve is essentially parallel. The first (-29.89‰) and the second (-26.65‰) negative anomaly for $^{13}\text{C}_{\text{org.}}$ are coeval with the first two nega-

tive shifts observed for ^{13}C of carbonate carbon, while the third decrease of $^{13}\text{C}_{\text{org.}}$ (-26.92‰) occurs in the Triassic, 7 m below the third negative shift of $^{13}\text{C}_{\text{carb.}}$ values. During the Permian-Triassic transition the Karavanke Mountains constituted a semi-restricted marine basin, surrounded by vast areas of an extremely shallow epicontinental sea into which a considerable amount of terrigenous material was transported (DOLENEC et al., 1981).

The environmental stress conditions caused decreased bioproductivity in the upper water column and an associated decrease in dissolved carbonate (ZHENG et al., 1993). A drop of ^{13}C values in carbonate precipitates reflects this decrease. The incorporation of light carbon from eroded and oxidized organic matter into carbonates and photosynthetic marine organisms would also cause both to become isotopically lighter (WOLBACH et al., 1994). The variation between $^{13}\text{C}_{\text{carb.}}$ and $^{13}\text{C}_{\text{org.}}$ values, which can be used to evaluate major changes in the carbon cycle by removing the effect of changes in the ^{13}C of the surface water dissolved inorganic carbon reservoir (HOLLANDER et al., 1993), also indicates changes in bioproduction. For the P/Tr transition in the Karavanke Mountains the decreasing isotopic composition of total organic carbon of 6.5‰ (from -23.19 to -29.69‰) and increasing $^{13}\text{C}_{\text{carb.-org.}}$ of 3.78‰ (from 24.66 to 28.44‰) about 8 m below the boundary can be explained by a dramatic decrease in primary production. This breakdown in the photosynthesis/respiration cycle appears to coincide with events related to the accelerated fall in sea level and/or widespread volcanic activity in Siberia. These events began substantially before the end of the Permian and affected the carbon cycle long enough to cause a clear perturbation in both ^{13}C records. The ^{13}C shift of 3.5‰ (from -8.89 to -25.39‰) in total organic carbon toward higher values and the reduction in $^{13}\text{C}_{\text{carb.-org.}}$ by 4.1‰ (from 28.23 to 24.13‰) at the P/Tr boundary could be the consequence of a subsequent recovery period in the biological system before the sea gradually became a wide, extensive mud flat. This situation was changed after the sedimentation of the red terrigenous sequence, due to the earliest Triassic marine transgression which spread anoxic bottom water over the entire region of the Karavanke Mountains, and marked the end of the period of extreme variability in ^{13}C of both carbonate and organic carbon. During this phase deposition of the Lower Scythian dark grey and brown limestones began.

The variability of ^{18}O in the interval straddling the P/Tr boundary shows slightly different trends with respect to those of ^{13}C in carbonate and organic carbon, roughly indicating environmental changes from marine to desultory evaporitic conditions affected by an excessive input of terrigenous material, and by local freshening of waters, due to the influx of more or less isotopically modified meteoric waters into the sedimentary environment. A significant drop of ^{18}O from -4.19‰ to -9.51‰ approximately 25 m above the boundary is stratigraphically coincident with abrupt chan-

ges in the lithology, as well as carbonate mineralogy of the rocks. The Scythian limestones are considerably depleted in ^{18}O (from 3 to 8‰) relative to both the underlying lowermost Scythian dolomite and the Upper Permian dolomite of the Karavanke Formation. Such depletion cannot be interpreted only in terms of dolomite-calcite fractionation which is thought to be between +3 and +4‰ (DICKSON, 1990). It may also be caused by a change in the ^{18}O of seawater, a decrease of salinity, changes in the depositional environment, diagenetic processes and burial, or some combination of all of these factors. Due to the muddled oxygen isotopic pattern, it is difficult to give a definite explanation of the observed ^{18}O variations at the P/Tr transition. However, it is important to note that the ^{13}C signals of inorganic and organic carbon are independent of lithology and are preserved in both Scythian dolomite and limestone.

5. CONCLUSIONS

The results we have presented in this study indicate that the transition from the Permian to the Triassic in the Karavanke Mountains is characterized by a strongly negative complex pattern of carbonate and organic carbon anomalies, accompanied by changes in the ^{18}O values of the boundary carbonate rocks. These anomalies are supposed to record extremely adverse changes of the environment due to global events which marked the terminal Permian productivity crash and the P/Tr boundary. We suggest a causal connection between the global carbon isotopic anomalies and the marine regression at the end of the Permian, but the exact controls remain complex and enigmatic.

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