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The Permian-Triassic boundary in the Idrijca Valley (Western Slovenia) : isotopic fractionation between carbonate and organic carbon at the P/Tr transition

Permsko-triasna meja v dolini Idrijce (zahodna Slovenija): izotopska frakcionacija med karbonatnim in organskim ogljikom na prehodu iz perma v trias

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Abstract

The transition from Permian to Triassic is characterized by a well known prominent negative excursion of $\delta^{13}C_{carb.}$ and $\delta^{13}C_{org.}$ reflecting global perturbations in the carbon cycle, a dramatic increase in isotopic fractionation between carbonate and organic carbon ($\Delta\delta^{13}C_{carb.-org.}$) indicating a sudden break-down in primary productivity, and the drastic disappearance of typically Upper Permian marine fauna.

The surprising shift of 4.15 ‰ towards higher values in $\delta^{13}C_{org.}$ not reflected in the $\delta^{13}C_{carb.}$ pattern and a reduction of $\Delta\delta^{13}C_{carb.-org.}$ also by 4.15 ‰ 6 cm above the boundary may be most plausibly attributed to the unusual plankton blooms which could be the consequence of a subsequent recovery period in the biological system associated with an increase in oxidation conditions.

Kratka vsebina

Članek obravnava frakcionacijo ogljikovih izotopov na meji perm-trias v dolini Idrijce. Prehod iz perma v trias na raziskanem območju karakterizira negativna ogljikova anomalija, ki se odraža tako v karbonatih kot v organski snovi. Potek krivulje $\Delta\delta^{13}C_{carb.-org.}$, ki podaja frakcionacijo med karbonatnim in organskim ogljikom kaže, da je na permsko-triasni meji prišlo do nenadnega povečanje izotopske frakcionacije med obema vrstama ogljika. To je po našem mnenju posledica dramatičnega zmanjšanja primarne produkcije v takratnem morju, ki v raziskanem profilu tudi sovpada z drastičnim izginotjem tipične zgornjepermske faune. Hitra sprememba poteka frakcionacijske krivuje tik nad mejo je najverjeneje posledica ponovne vzpostavitve pogojev ugodnih za bohoten razvoj planktonskih organizmov, kar se odraža tudi v nenadnem zmanjšanju izotopske frakcionacije med karbonatnim in organskim ogljikom.

Introduction

Permo-Triassic (P/Tr) boundary events, which took place approximately 250 m.y. 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 global events outlined above coincide with isotopic and elemental anomalies recorded in several P/Tr boundary sections all over the world. One of the most remarkable anomalies is the world-wide negative shift of $\delta^{13}C$ 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 (Veizer, 1989; Kram & Wedepohl, 1991) have also been recorded.

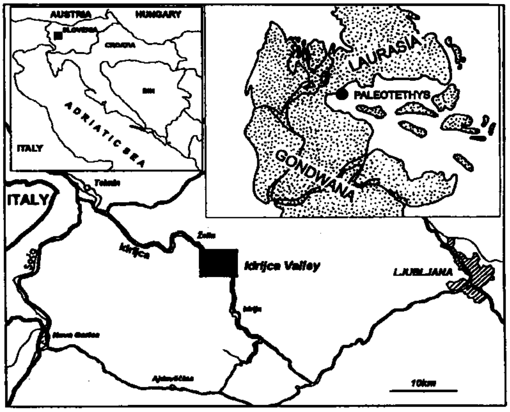

Fig. 1. Map showing the location of the studied region in Western Slovenia. Global paleogeography during the Permian-Triassic boundary interval is taken from Sun et al. (1989).

In this study we present the results of carbonate and organic carbon stable isotope analysis of the P/Tr boundary section in the Idrijca Valley, Western Slovenia (Fig. 1), and discuss their implications with respect to the nature and the causes of the boundary events at the end of the Permian in this part of the Western Tethys.

Geological setting and stratigraphy

In Western Slovenia, sedimentation proceeded concordantly across the P/Tr boundary. The Middle Permian Val Gardena Formation of mostly fluvial origin is overlain by an approximately 250 m thick dark grey and black well bedded abundantly fossiliferous shallow marine Upper Permian Žažar Formation. The uppermost unit of the Žažar Formation exposed in the Idrijca Valley is composed of 5 to 40 cm thick dark grey and black limestone layers interbedded with rare black shales. The total thickness of this unit is about 14 metres. Limestone microfacies are represented mostly by packstones and grainstones, partly wackestones very rich in microfossils; macrofossils, however, are very rare (Ramovš, 1986). The faunal composition displays gradual impoverishment of Upper Permian taxa moving upward towards the boundary and an abrupt disappearance at the boundary. The P/Tr boundary is sharp, not erosional and is represented by an up to 0.8 cm thick clayey marl layer (PTB layer) overlying the black algal packstone. The PTB layer which marks the Permo-Triassic boundary contains spherules, which most probably represent spherical prashynophite algal skeletons diagenetically infilled by magnetite (Hansen et al., 1999). The deposition of the PTB layer most probably took place during a period of maximum eustatic fall and regression. It is followed by a light grey well bedded Lower Scythian sparitic limestone. The total thickness of the basal Scythian unit exposed in this area is about 13 metres. Upward, the sparitic limestone is followed by a laminated dolomitic limestone alternating with grey stylolithic dolomites. According to present knowledge the basal Scythian unit contains some conical tube-like fragments of fossils. They may be characteristic of the lowermost lower Triassic.

Materials and methods

The boundary profile in the Idrijca Valley was systematically sampled at 20 cm intervals, except in the vicinity of the paleontologically defined P/Tr boundary where sampling intervals were reduced to 10, 5 and 2 cm. The isotopic measurements were carried out on un-dolomitized limestone samples. 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. Powdered rock samples for $\delta^{18}O$ and $\delta^{13}C$ 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 C isotopic composition on a Varian MAT-250 mass spectrometer. The $\delta^{13}C$ values were normalized by assuming $\delta^{13}C$ values of + 2.48 ‰ for the IAEA-CO-1 standard on the PDB scale.

For preparation of samples for the determination of total organic carbon, powdered whole rock samples were treated with heated 3M hydrochloric acid at 50 °C to react carbonates. Upon cessation of CO_2 evolution excess acid was removed by repeated washing (three to four times) with doubly distilled water until neutral. 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 an 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 the gases. Organic carbon isotope values were calibrated using the IAEA-CH-7 standard with a $\delta^{13}C$ value of - 31.8 ‰ on the PDB scale.

The analytical precision based on multiple analysis of internal laboratory standards was ± 0.01 ‰ for $\delta^{13}C_{carb.}$ and ± 0.008 ‰ for $\delta^{13}C_{org.}$, respectively. Overall analytical reproducibility of the isotopic data was ± 0.1 ‰ for carbonate carbon and ± 0.090 ‰ for organic carbon.

Results and discussion

The isotopic composition of organic and carbonate carbon exhibits synchronous shifts in an isotopic lighter direction only within a 50 cm thick interval, from the P/Tr boundary to - 50 cm downward (Fig. 2). These shifts imply a relatively rapid sequence of responses of the oceanic biota and

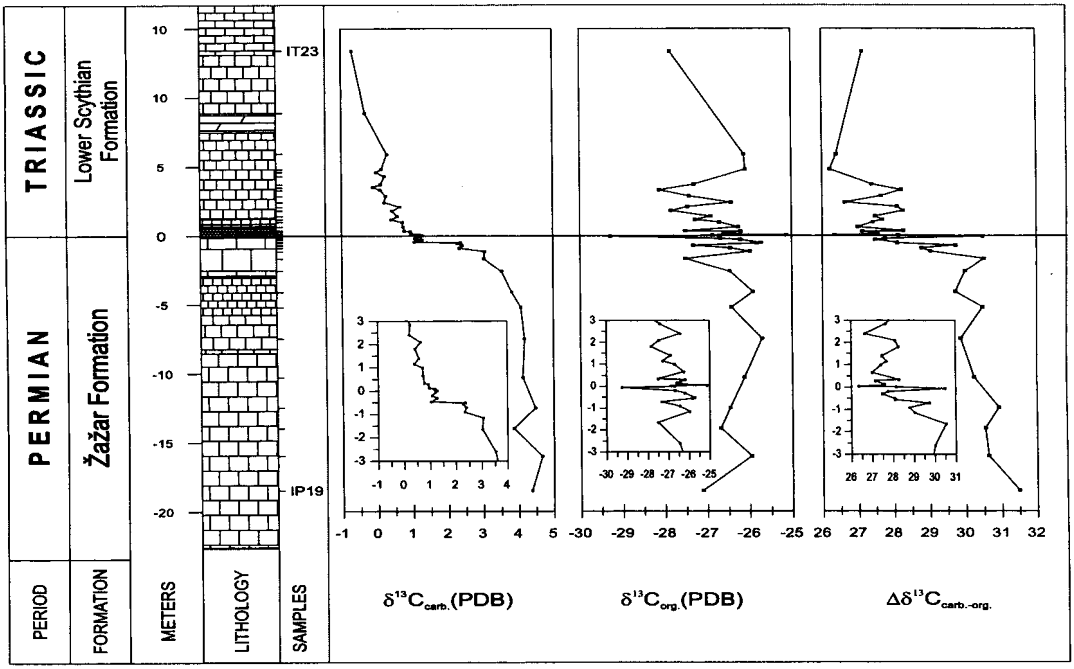

Fig. 2. Stable carbon isotope composition of limestone ($\delta^{13}C_{carb.}$), total organic carbon ($\delta^{13}C_{org.}$) and carbonate-organic carbon isotope fractionation ($\delta^{13}C_{carb.-org.}$) across the Permian-Triassic boundary in the Idrijca Valley section.

the global carbon cycle to the environmental stress imposed by the end Permian global events. Several questions are of interest: how does the isotopic composition of organic carbon in the P/Tr boundary sequence reflect the environmental stress on the marine biota, and what can the combined carbon isotopic composition of organic and carbonate carbon reveal about the sequence of global changes which affected the carbon cycle at the P/Tr transition?

To answer these questions, the $\Delta\delta^{13}C_{carb.-org}$ fractionation curve was constructed (Fig. 2). Hollander et al., (1993) have shown that the isotopic difference or carbon isotopic fractionation between carbonates and organic carbon $\Delta\delta^{13}C_{carb.-org.}$) can be used to evaluate major changes in the carbon cycle, removing the effect of changes in $\delta^{13}C$ of the dissolved inorganic carbon surface water reservoir. For the P/Tr transition in the Idrijca Valley section the decrease in isotopic composition of organic carbon by 3.51 ‰ (from - 26.21 to - 29.72 ‰) and increasing $\Delta\delta^{13}C_{carb.-org.}$ by 3.01 ‰ (from 27.49 to 30.50 ‰), as well as a decrease in $\delta^{13}C$ of carbonate carbon, can be explained by a decrease in primary production at the end of the Permian. This breakdown in the photosynthesis respiration cycle appears to coincide with a dramatic reduction of the accumulation rate (Dolenec et al., 1999) and an accelerated fall in sea level, also clearly indicated in the Karavanke Mountains (Dolenec et al., 1996; Hansen et al., 1999). A decrease in marine productivity appears to be consistent with the observed fossil record, which also suggests a drastic disappearance of Upper Permian marine fauna.

The surprising shift of 4.15 ‰ toward higher values in $\delta^{13}C_{org.}$ (from - 29.27 to - 25.12 ‰) and the reduction in $\Delta\delta^{13}C_{carb.-org.}$ also by 4.15 ‰ (from 30.50 to 26.35 ‰) 6 cm above the P/Tr boundary in contrast indicate: a subsequent recovery period in the biological system, a decrease in oceanic pCO_2, and an increase in surface water temperature or increase in influx of terrestrial isotopically heavier organic matter into the sedimentary basin. It appears that this positive organic carbon excursion occurred too suddenly to be explained as a result of any gradual processes. In fact, it is best interpreted as a result of unusual plankton blooms during the subsequent recovery period in the biological system, leading to a drastic reduction in the concentration of dissolved CO_2 in surface waters. The variability of $\Delta\delta^{13}C_{carb.-org.}$ during the remaining Scythian most probably suggests further fluctuations of primary productivity and insufficient recovery of higher consumers, as already mentioned by Kakuwa (1996).

A negative $\delta^{13}C$ excursion of inorganic and organic carbon isotopes and dramatic changes in the carbonate-organic carbon fractionation ($\Delta\delta^{13}C_{carb.-org.}$) across the P/Tr boundary indicate remarkable changes in the carbon cycle. Several possible explanations for these perturbations in the carbon cycle have been considered. They might have been caused by a combination of factors such as degradation and oxidation of organic matter (Magaritz & Holser, 1991; Faure et al., 1995), changes in biological productivity of the ocean surface (Magaritz et al., 1992; Kakuwa, 1996) or volcanic activity (Renne & Basu, 1991; Campbell et al., 1992). Veevers & Tewari (1995) suggested that volcanism along the Tethys margin together with that along the Panthalassan margin raised the background 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. The results presented here most probably indicate that the combination of degradation and oxidation of large amounts of organic matter due to global marine regression and/or regional epeirogenetic uplift (Faure et al., 1995) together with volcanic activity seem to be the factors most responsible for the observed carbon isotopic changes and the terminal Permian productivity crash.

Conclusions

Isotopic data based on $\delta^{13}C_{carb.}$, $\delta^{13}C_{org.}$ and $\Delta\delta^{13}C_{carb.-org.}$ values indicate well known perturbations in the carbon cycle and a dramatic decrease in primary productivity which is coincidental with an abrupt disappearance of Upper Permian marine fauna at the P/Tr boundary in the Idrijca Valley section.

A general and gradual decrease in $\delta^{13}C$ of carbonate and organic carbon across the

P/Tr boundary is consistent with an overall increase in atmospheric pCO_2 over a period of 10 m yr. (Faure et al., 1995) and seems to be related to the degradation and oxidation of a large amount of organic matter due to global marine regression.

A sharp negative $\delta^{13}_{Corg.}$ anomaly and the shape of δ^{13}_{Corg} and $\Delta\delta^{13}C_{carb.-org.}$ curves indicate a rapid interruption of these gradual process which could be attributed to the relatively short term events. These events accelerated the global changes in carbon cycling and caused a breakdown in the primary production. Disastrous environmental conditions, not yet explicitly understood, could be related to volcanic activity, most probably associated with the Siberian Traps volcanism which triggered these events with consequences not only for oceanic anoxia, but also for biological systems and for climatic changes. Decreasing $\delta^{13}C_{org}$ and increasing $\Delta\delta^{13}C_{carb.-org.}$ values at the P/Tr boundary are consistent with a sudden reduction in primary productivity, while the increasing $\delta^{13}C_{org.}$ and decreasing $\Delta\delta^{13}C_{carb.-org.}$ values 6 cm above the boundary indicate unusual plankton blooms which could be the consequence of the recovery period in the biological system associated with change to more oxidising conditions.

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