GEOLOGIJA *43/1*, 103–107 (2000), Ljubljana 2000
https://doi.org/10.5474/geologija.2000.009

Ce anomaly at the Permian-Triassic boundary in the Idrijca Valley as evidence of changing redox conditions at the P/Tr transition in the western Tethys (Slovenia)

Ce anomalija na permsko-triasni meji v dolini Idrijce kot indikator sprememb redoks pogojev

Tadej DOLENEC[1,2] & Sonja LOJEN[2]
[1]Department of Geology, Faculty of Natural Sciences and Engineering, University of Ljubljana, Aškerčeva 12, 1000 Ljubljana, Slovenia.
[2]Department of Environmental Sciences, Jožef Stefan Institute, Jamova 39, Ljubljana, Slovenia.

Key words: Ce anomaly, oceanic anoxia, P/Tr boundary, Idrijca Valley
Ključne besede: Ce anomalija, oceanska anoksičnost, P/Tr meja, dolina Idrijce

Abstract

The shape of the Ce/Ce* curve suggests that oceanic anoxia was typical of the Upper Permian during sedimentation of the Žažar Formation, and that the transition to more oxygenated conditions occurred at the P/Tr boundary. An abrupt change of redox conditions at the P/Tr transition in this part of the Western Tethys coincides with the terminal phase of the Upper Permian marine regression, as well as with the drastic disappearance of typically marine fauna of algae, foraminifers and brachiopods.

Kratka vsebina

Potek krivulje za Ce/Ce* vrednosti kaže, da so v času sedimentacije žažarskega apnenca prevladovali redukcijski pogoji. Na prehodu iz perma v trias je prišlo do nenadne spremembe k bolj oksičnim pogojem, ki sovpada v tem delu zahodne Tetide z zaključno fazo zgornjepermske regresije morja in z drastičnim izginotjem tipične algne, foraminiferne in brahiopodne favne.

Introduction

Permian-Triassic boundary events led to the most extensive mass extinction in the history of life. The mechanism of the extinction has been much debated. 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 seawater chemistry, an extra-terrestrial impact event, and various related factors (Yoichi, 1994). More recently Wignall & Twichett (1996) suggested that oceanic anoxia at both low and high paleolatitudes in the Late Permian may have been responsible for the mass extinction at this time. According to the Knoll et al., (1996) hypothesis of hypercapnia, the Late Permian biological crisis was precipitated by a rapid overturn of the deep anoxic ocean, which introduced toxic concentrations of CO_2 and perhaps H_2S into the surficial environment.

In this study we used the Ce anomaly to evaluate the redox conditions under which the P/Tr boundary sequence in the Idrijca

Valley accumulated, and discuss the nature and causes of the drastic disappearance of typically Upper Permian marine fauna in this part of the Western Tethys.

Geological setting and stratigraphy

The geological setting and stratigraphy were discussed more extensively in some previous papers (R a m o v š, 1986; D o l e n e c & R a m o v š, 1996; D o l e n e c et al., 1999 b). For the present discussion it is important to note that in what is presently the Idrijca Vally sedimentation proceeded continuously across the P/Tr boundary. There is no evidence of a sedimentological or chronological break across the boundary. The total thickness of the Upper Permian and Lower Scythian beds exposed in the Idrijca Valley is about 27 metres. Although indications of shallowing are present over a broad region, sequential stratigraphic analysis of the Idrijca Valley section reveald no evidence of emergence or pronounced sea level change across the boundary. The P/Tr boundary is represented by a lithological marker bed - a thin, up to 0.8 cm thick, clayey marl layer (PTB) showing a characteristic magnetic susceptibility pulse and considerable enrichment in most major, minor and trace elements (D o l e n e c et al., 1999 b). The deposition of the PTB layer most probably took place during a period of maximum eustatic fall and regression, at approximately the same time as the sedimentation of the red coloured terrigenous P/Tr boundary sequence in the Karavanke Mountains began (D o l e n e c et al., 1999 a). Another significant feature is the gradual impoverishment of Upper Permian fauna moving towards the boundary and its abrupt disappearance at the boundary. Upper Permian taxa show an abrupt extinction in the topmost, up to 20 cm thick, black Upper Permian limestone bed underlying the PTB layer. It is overlain by a light gray, well bedded Lower Scythian sparitic limestone. Upward the sparitic limestone is followed by a laminated dolomitic limestone alternating with grey stylolitic dolomites. According to present knowledge, the basal Scythian unit contains some as yet unidentified conical tube-like fragments of fossils.

Materials and methods

The boundary profile in the Idrijca Valley (Fig. 1) 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 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 and paleontological characteristics.

Selected samples were analysed by inductively coupled plasma-mass spectrometry (ICP-MS) for REE (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb and Lu). Analytical blanks were run with the samples, and the reference limestone standard CCH-1 (Université de Liège, Belgium) as well as the sediment reference standard MAG-1 (US National Bureau of Standards) were used to check the analytical methods. Elemental analyses were carried out at Activation Laboratories, Ontario, Canada. Analytical precision and accuracy were better than ± 5 % for REE. This was indicated by the results of duplicate measurements for 3 samples and the MAG-1 standard.

Results and discussion

The chemistry of the rare earth elements (REE) makes them useful in geochemical studies on sedimentary rocks as a chemical tracer for redox and pH conditions of different geological environments (F l e e t, 1984). The REE in nature are commonly trivalent and exhibit very similar chemical properties. However, Ce and Eu may exhibit anomalies according to their unique oxidation/reduction geochemistry in aqueous solutions. Because the reduction of Eu^{3+} to Eu^{2+} does not seem to occurs within the ocean basin, except in hydrothermal systems (M i c h a r d et al., 1983), only the sensitivity of Ce to changing redox conditions was used in this study as an indicator of palaeocenographic redox conditions at the P/Tr transition in the Southern Alps in

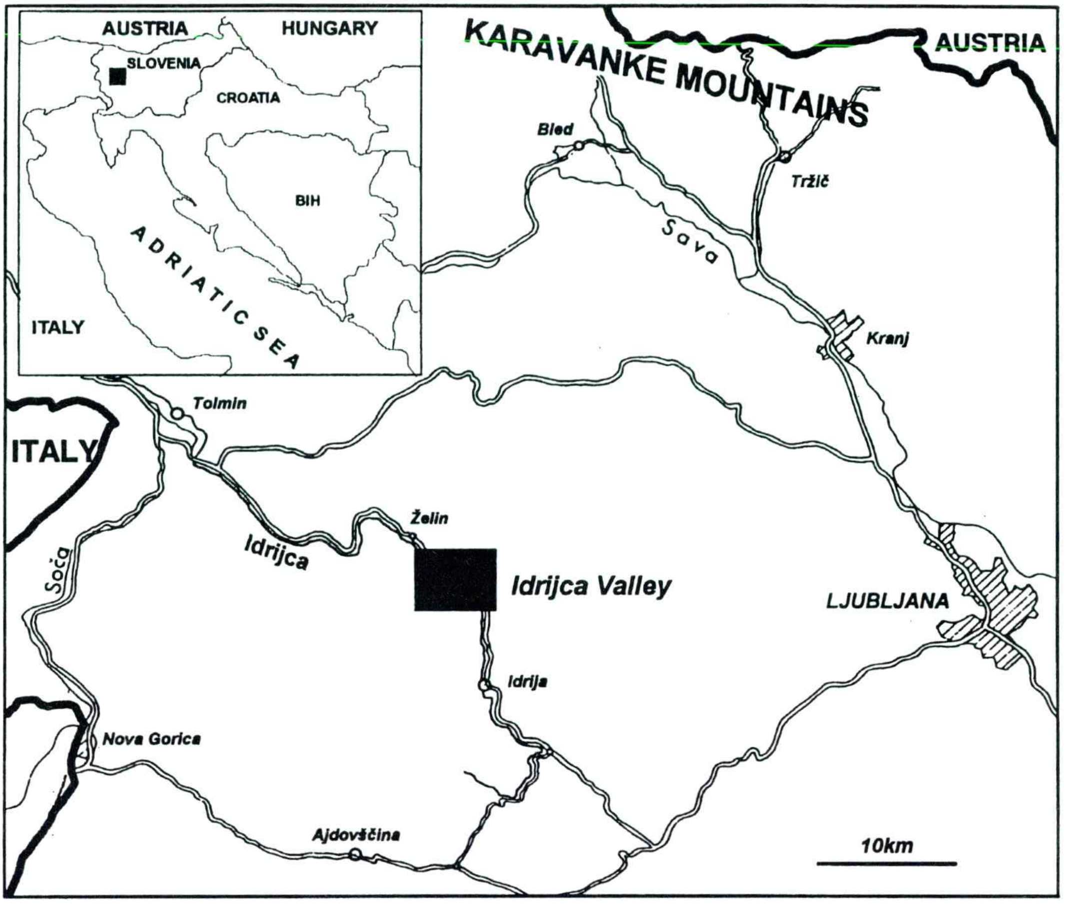

Fig. 1. Map showing the location of the studied region in the Idrijca Valley

Western Slovenia. The effect of the Ce oxidation-reduction reaction can be expressed by the Ce anomaly which is calculated using the following equation: $Ce/Ce^* = CeN/(LaN \cdot PrN)^{0.5}$ where subscript N indicates normalised value (Taylor & McLennan, 1985). Ce/Ce^* values > 1 indicate a positive Ce anomaly, while those of < 1 characterize a negative Ce anomaly.

Up to now only limited research efforts have been directed at understanding the relationship between the seawater chemistry of REE and their incorporation in marine carbonate phases. Parekh et al. (1977) observed a close similarity between REE distribution patterns in the calcite phase of marine limestones and normal seawater, which was interpreted as a direct coprecipitation of REE from seawater with no subsequent diagenetic redistribution. Wang et al. (1986) proposed that the REE are incorporated in marine carbonates chiefly by adsorption onto carbonate minerals and on Sc-Hf-and Ta-rich Fe-Mn oxyhydroxide-flocs as floating carbonates. Previous studies (Wang et al., 1986; Wright et al., 1987; Liu et al., 1988) have also suggested that depletion in the carbonate phase reflects Ce depletion in bottom waters and vice versa. If seawater is in a more reducing state, a larger fraction of Ce entering the ocean will remain trivalent and will behave like other trivalent REE, resulting in a more normal REE pattern in the overall carbonate phase with no negative Ce anomaly. Conversely, if seawater is in oxidizing conditions, a smaller fraction of Ce will be trivalent, therefore resulting in Ce depleted seawater. The depletion of trivalent Ce in oxidizing seawater will also be reflected in

Ce depleted REE patterns in marine carbonates (H u et al., 1988).

The positive Ce anomaly (Fig. 2) in the Upper Permian limestone reveals that the seawater was appreciably anoxic during the deposition of the Žažar Formation (Fig. 1). The transition from Permian to Triassic is characterized by an abrupt decrease of Ce/Ce* values which suggests an increase in oxidation conditions and ventilation in the topmost Permian and in the basal Triassic sea. This is also confirmed by geochemical data based on redox sensitive U concentrations and the Th/U ratio (D o l e n e c et al., 2000), as well as by the shape of the Mo concentrations curve (D o l e n e c et al., 1999 b) which also indicate the culmination of an anoxic event at about 50 cm below the boundary. The Ce/Ce* curve reaches its minimum values of 0.47 at the P/Tr boundary, and then afterwards sharply returns to higher values in the lowermost Triassic. The shape of the Ce/Ce* curve indicates that the redox environment in seawater drastically changed in the earliest Triassic, again resulting in oxygen deficient conditions and an absence of significant deep water circulation. This anoxic event may be the result of a rapid short-term transgression in the earliest Triassic which led to the spread of anoxic water on the epicontinental shelves, as well as to an abrupt dissapearance of Permian fauna in a mass extinction in the Alps of northern Italy, as proposed by W i g n a l l & H a l l a m, (1992). However, in the Idrijca Valley it is clear that the extinction occurred at the boundary close to the level of the maximum regression which is coincidental with the changes to oxic conditions. The anoxic conditions in the early Triassic were followed by oxic conditions for the remainder of the Lower Triassic.

The faunal composition displays a gradual impoverishment of Upper Permian taxa moving upward towards the boundary and an abrupt disappearance at the boundary. The causes of the mass extinction event at the observed P/Tr boundary in the Idrijca Valley are not attributed to major transgression of anoxic water in the earliest Triassic, but seem to be linked with a global sea-level minimun at the end of the Permian.

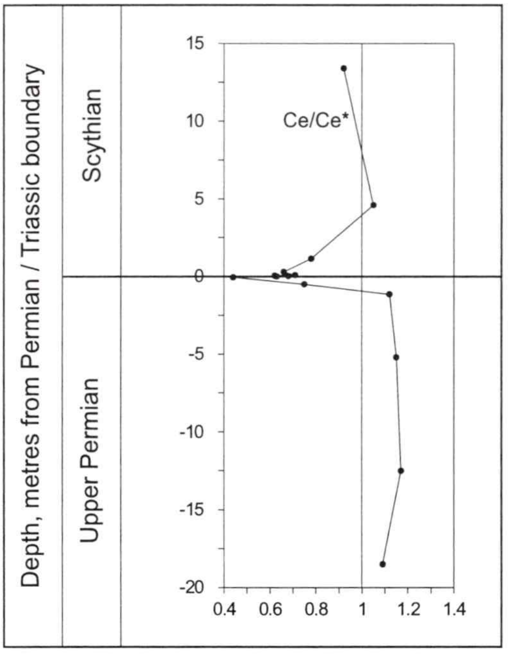

Fig. 2. The shape of the Ce/Ce* curve across the P/Tr boundary in the Idrijca Valley.

Conclusions

Our observations from the redox sensitive Ce anomaly suggest that seawater was appreciably anoxic during deposition of the Žažar Formation. The transition to more oxygenated conditions at the P/Tr transition, indicated by an abrupt shift of Ce/Ce* values to their minimum of 0.44, seems to be linked to a global sea-level minimum at the end of the Permian. The shape of the Ce/Ce* curve further indicates that the environmental redox conditions changed soon in the earliest Triassic, again the result of anoxic conditions. Although there is widespread disagreement about the causes of the end Permian mass-extinction, our data indicate that the Upper Permian fauna in the Idrijca Valley have been heavily stressed by the culmination of marine anoxia close to the boundary, and after that drastically reduced by the terminal phase of the end Permian marine regression.

Acknowledgements

This study was financially supported by the Ministry of Science and Technology, Republic of Slovenia, and Geoexp d.o. o. Tržič, Slovenia. To both these institutions we express our sincere thanks.

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