The Permian Triassic Boundary in the Karavanke Mountains (Brsnina section, Slovenia): The Ratio of Th/U as a Possible Indicator of Changing Redox Conditions at the P/T Transition

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Abstract: The ratio Th/U calculated from geochemical data, together with the distribution of U in the P/T boundary sequence of the Brsnina section (Karavanke Mountains), was used to estimate redox conditions in the depositional environment. The data indicate a further example of an oxic event at the P/T transition, which is coincidental with the terminal phase of the Upper Permian marine regression.

Povzetek: Porazdelitev vsebnosti U in Th ter razmerje Th/U v permsko-triasni mejni sekvenci v profilu Brsnina v Karavankah kaže na spremembo oksidacijsko redukcijskih pogojev na prehodu iz perma v trias. Dobljeni rezultati potrjujejo kratkotrajno vzpostavitev oksidacijskih pogojev na P/T meji, ki sovpadajo z zaključno fazo zgornjepermske morske regresije.

Keywords: P/T boundary, Th/U ratio, oxic event, Brsnina section, Karavanke Mountains.
Ključne besede: P/T meja, razmerje Th/U, oksični dogodek, profil Brsnina, Karavanke.

Introduction

The period of time near the Permian-Triassic (P/T) boundary was marked by a number of anomalous events in the history of the Earth, including the mass mortality of nearly 90 % of all marine species, as well as a huge reduction in terrestrial vertebrates and plants (Sepkoski, 1986; Erwin, 1993; 1994). In addition to the biological record, a variety of drastically changing marine geochemical signals indicates prominent oceanographic and/or atmospheric perturbations. These geochemical anomalies reflect dramatic changes in seawater $\delta^{34}S$ (Claypool et al., 1980; Kaiwara et al., 1994; Newton et al., 2004) and $\delta^{13}C$ values (Baud et al., 1989; Magaritz et al., 1992; Wang et al., 1994; Kakuwa, 1996; Dolenec et al., 2001; Heydary et al., 2000, 2003; Krull et al., 2000; Mushashi et al., 2001; Krystyn et al., 2003; Sarkar et al., 2003), as well as in strontium isotopic composition (Veizer, 1989; Kramm and Wedepohl, 1991; Maritin and MacDougall, 1995).

A number of possible explanations for this profound break in the evolution of life at the

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transition from Palaeozoic to Mesozoic have been proposed, ranging from abrupt extraterrestrial phenomena (ZHANG AND XU, 1996; RETALLACK ET AL., 1998; BECKER AT AL., 2001; KAIHO ET AL., 2001) to prolonged climate deterioration due to volcanic contribution (Siberian traps) and /or methane released from high latitude clathrate deposits (ERWIN, 1993; KRULL ET AL., 2000, 2003; SARKAR ET AL., 2003), to changes in ocean stratification, circulation and cycling (WIGNALL AND TWITCHETT, 1996, 2002), to overturn of an anoxic ocean resulting in CO_2 poisoning (KNOLL ET AL., 1996), as well as to a reduction in shallow marine habitat resulting from the Late Permian sea level fall (HOLSER AND MAGARITZ, 1987).

Several authors (HALLAM, 1989; WIGNALL AND HALLAM, 1992; 1993; KAJIWARA ET AL., 1994; ISOZAKI, 1994; KNOLL ET AL., 1996; WIGNALL AND TWITCHETT, 2002) suggested that the extinction event was catastrophic and associated with a major anoxic event in the earliest Triassic. This anoxic event is supposed to 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 (HALLAM, 1989; WIGNALL AND HALLAM, 1992). Although some evidence suggests that anoxic conditions developed in the ocean during the P/T time, analyses of REE and Th/U ratio in the boundary sequence of the Idrijca Valley section (DOLENEC ET AL., 2000; 2001) indicate oxic conditions at the P/T boundary.

The purpose of this study is to examine the geochemical characteristic of Upper Permian and Lower Triassic sedimentary succession in the Brsnina section (Karavanke Mountains) and to evaluate the redox

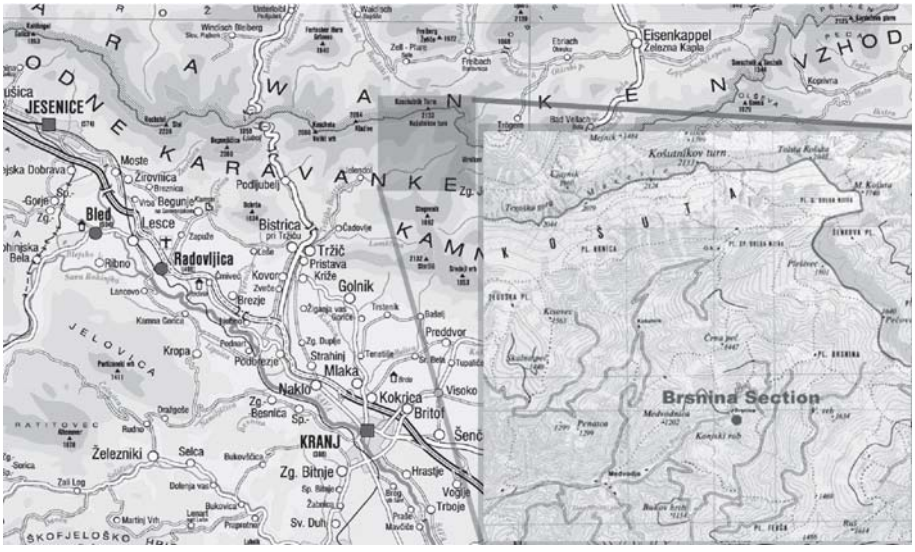

Figure 1. Geographic location of the studied P/T boundary profile in the Brsnina section (Karavanke Mountains, Slovenia).
Slika 1. Geografski položaj permsko-triasne mejne sekvence profila Brsnina v Karavankah, Slovenija.

conditions under which the P/T boundary sequence accumulated. In this study I used the U and Th distribution and Th/U ratio as an environmental redox indicator.

Geological setting and stratigraphy

In the Brsnina section (Fig. 1.) a continuous sedimentary succession straddles across the P/T boundary. The approximately 270 m thick Upper Permian evaporitic-dolomitic sequence (Fig. 2) referred to as the Karavanke Formation (Buser, 1974; Buser et al., 1986) is overlaid by up to a 30 m thick succession of red-coloured, partly terrigenous-evaporititc sequence composed predominantly of thin-bedded siltstones, mudstones and sandstones alternating with micritic dolomites, showing impressions of gypsum crystals (Dolenec M. et al., 2003). The lithostratigraphic boundary between the Upper Permian Karavanke Formation and the basal Triassic (Scythian) beds is placed at the end of the sedimentation of the well-bedded grey dolomite. The Late Permian age of these beds is indicated by calcareous algal assemblages, as well as by foraminifers (Ramovš, 1986). In the Brsnina section the P/T boundary is represented by a sharp, not erosional, contact that consists of a clay layer (PTB clay layer) with a maximum thickness of 1 cm. The PTB clay layer shows a characteristic magnetic susceptibility pulse (Hansen et al., 1999, 2000) and considerable enrichment in most minor and trace elements (Dolenec M., 2004). The deposition of the P/T boundary clay layer is supposed to be correlative with the sedimentation of the P/T boundary clayey marl layer (PTB layer)

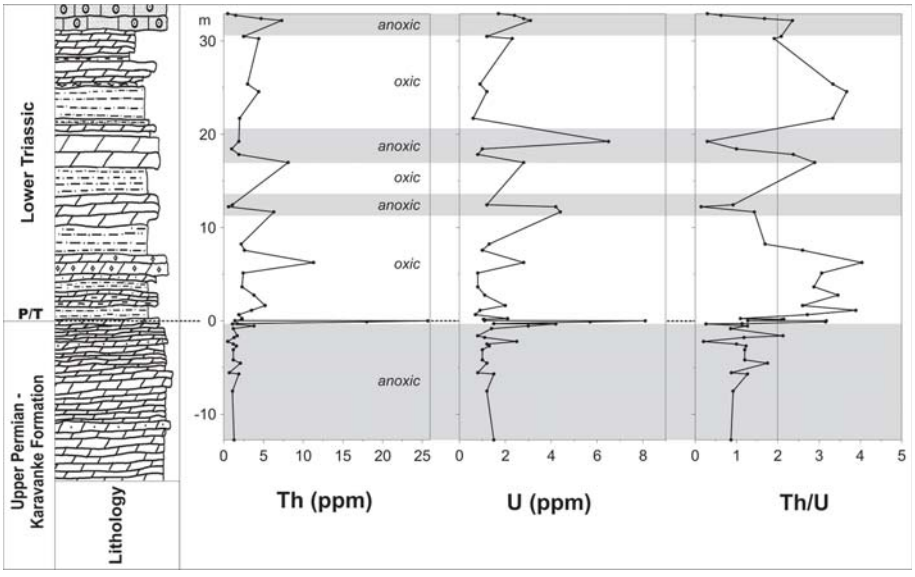

Figure 2. Lithology and depth profile of Th and U concentrations together with Th/U ratios across the Permo-Triassic boundary in the Brsnina section (Karavanke Mountains, Slovenia).
Slika 2. Litološki stolpec in vsebnost U in Th ter razmerje Th/U v permsko-triasni mejni sekvenci iz profila Brsnina (Karavanke, Slovenija).

in the Western Slovenia (Idrijca Valley section) and most probably indicates a period of maximum eustatic sea level fall and regression at the end of the Permian. In the investigated area of the Brsnina section the basal Triassic (Scythian) red coloured terrigenous-evaporitic sequence is overlaid by an approximately 200 m thickness of Lower Triassic dark grey and brown micritic and sparitic limestones and dolomites intercalated with oolitic limestone marls and shales.

MATERIAL AND METHODS

The boundary profile in the Brsnina section was systematically sampled on the decimetre and centimetre scale from the P/T boundary down to 13 m below. Continuous samples of basal Scytian partly terrigenous evaporitic sequence were also collected up to 30.5 m above the boundary. For the purpose of this study 17 samples of the Late Permian biomicritic dolomite and 29 samples of Scythian micritic dolomite, sandy dolomites and limestones, as well as a sample of the PTB clay were taken. The total thickness of the sampling unit was 43.5 m. The carbonate samples chosen for this study were evaluated by petrographic methods to assess their mineralogy and diagenetic history. The mineralogy of the carbonate samples was also determined by X-ray diffractometry. Samples were also analysed by inductively coupled plasma-mass spectrometry (ICP-MS) for Th and U, as well as for other trace elements including rare earth elements (REE) not discussed in this study. Analytical blanks run with the samples and the sediment reference standard MAG-1 (US National Bureau of Standards) were used to check the analytical methods. Elemental analyses were carried out at ACME - analytical laboratories, Vancouver, Canada. The analytical precision and accuracy were better than ± 5 % for both elements, as indicated by the results of duplicate measurements of 5 samples and the MAG - 1 standard.

RESULTS AND DISCUSSION

The depth profile of U and Th concentrations and the Th/U ratio across the P/T boundary, together with the relative stratigraphic position of the samples, are presented in Fig. 2. The major paleoenvironmental changes occur at the P/T boundary and are related to a short-term regression and/or sea level fluctuation as well as to terminal Permian global events. Similar transgressive-regressive events have also been recognised in the Scythian sequence of the Upper Austro-Alpine Units (KRAINER, 1993, and references therein). The geochemical composition of the boundary sequence reflects the geochemical characteristics of predominantly marine fractions in the topmost Permian beds, as well as of an increased amount of detritial fraction in the lowermost Triassic most probably introduced into the sedimentary environment via eolian transport.

The paleoenvironmental changes at the P/T boundary in the Brsnina section are also coincidental with redox changes. The dark grey coloured Upper Permian dolomite is laminated, and framboidal pyrite is commonly abundant. These characteristics could be interpreted as evidence of deposition under anoxic bottom waters, while the red coloured terrigenous and evaporitic sequence, which overlaid the

Upper Permian, dolomite indicates predominantly oxidising conditions across the P/T boundary. The return to anoxic conditions occurs in dark grey micritic limestone at the top of later sequence, which represents the basal unit of an approximately 200 m thick limestone-dolomitic sequence intercalated with oolitic limestones, marls and shales.

To evaluate independently the redox conditions under which the Upper Permian and Lower Triassic sediments of the Brsnina section accumulated, the ratio Th/U calculated from the data obtained by geochemical analyses was used (Dolenec M., 2004). The total U and Th contents in the Upper Permian dolomite range from 0.8 to 5.7 ppm and from 0.7 to 18 ppm respectively (Fig. 2). The highest concentrations of these elements (8.1 ppm for U and 25.7 ppm for Th) were measured in the PTB clay layer and could be attributed to the very high contents of clay minerals. In the red coloured terrigenous evaporitic sequence of the basal Triassic the U and Th concentrations vary between 0.6 and 6.5 and between 0.6 and 11.3 ppm. The total U and Th content of this sequence is much more variable than the U and Th concentrations of the Upper Permian dolomite. The concentration profiles across the P/T boundary display a general decrease of U towards the boundary, a peak anomaly at the boundary related to the P/T clay layer, and much more variable concentrations of U in the terrestrial evaporitic sequence than in the Upper Permian dolomite. The depth profile of Th content exhibits a slight increase in Th concentration from Upper Permian to Lower Triassic, the peak anomaly in the PTB clay layer, followed by a variable Th content in the Lower Triassic.

The marked enrichment anomalies of U and Th in the terrigenous evaporitic sequence can be attributed to the pronounced input of detrital fraction. Petrographic observations of sediments with elevated U and Th concentrations also show higher detrital fractions, mostly composed of quartz, feldspar, muscovite, clay and heavy minerals. According to my opinion, the observed detritial fraction is responsible for the loading of Si, Al and K and their complement of trace elements. This is confirmed by a very strong correlation between Si, Al and K with each other ($0.83 \leq r \leq 1.0$) and several trace elements, including Th. On the other hand, a slightly lower correlation ($0.49 \leq r \leq 0.67$) of U with Si, Al and K, as well as a positive correlation ($R=0.53$) of U with C_{org}, indicates that this metal may also be concentrated in organic matter (Dolenec M., 2004). The dark grey, basal micritic limestone overlaying the terrestrial evaporitic sequence exhibits U concentrations between 1.7 and 2.4 ppm and of Th between 0.5 and 1.5 ppm. The major factors controlling the distribution of U and Th in the investigated P/T boundary sequence appear to be the terrigenous detrital input, as well as the tendency of U and Th to fractionate because of 1) the precipitation of U from solution in a reducing environment and its possible bonding to the organic matter, and 2) the selective adsorption of Th in clay minerals, confirmed by a very strong correlation of Th with Al and K, also observed in the P/T boundary succession of the Idrijca Valley (Dolenec T. et al., 2001) and Masore section (Dolenec M., 2004).

Although the presence of a terrigenous component could mask the relationship between redox sensitive elements, such as U, and the prevailing environmental redox

conditions, I believe that the Th/U ratio was not affected in such a manner, that it would be impossible to evaluate the redox conditions across the P/T boundary. Anoxic sediments are generally much more U-rich than oxic ones. This enrichment is due mainly to reduction of soluble U^{6+} to U^{4+} (KLINKHAMMER AND PALMER, 1991). The shape of the U concentration curve indicates that oceanic anoxia was more or less typical of the Upper Permian during the sedimentation of the Karavanke Formation, and that a transition to more oxygenated conditions occurred at the P/T boundary. Two peak U concentration anomalies at 12 and 20 m above the boundary (Fig. 2) are related to dark grey sandy dolomite inside the red coloured terrigenous evaporitic sequence. Thorium is unaffected by redox conditions and remains in an insoluble state as Th^{4+}. The result is that anoxic sediments have a Th/U ratio below 2, oxic marine sediments have ratios between 2 and 7, and intensely oxidising terrestrial environments have ratios in excess of 7 (ADAMS AND WEAVER, 1985). The ratio of Th/U calculated from the data for the P/T boundary sequence of Brsnina section to be in the range between 0.2 and 2.1, as well as the shape of the Th/U curve, suggests that anoxic conditions prevailed during the deposition of the Karavanke Formation and that the transition to oxygenated conditions occurred at the P/T boundary. Inside the terrigenous evaporite sequence the Th/U ratios are generally higher than 2 suggesting the prevailing oxygenated conditions. This result is to be expected considering the nature of the depositional environment. However, a sharp swing to anoxic Th/U ratios at 12 and 20 m above the P/T boundary is related to the narrow intervals of a locally established anoxic facies inside the predominantly red series deposited in well-oxygenated conditions. Anoxic Th/U ratios (lower than 0.6) return abruptly in the black coloured micrites overlaying the terrigenous evaporitic sequence, indicating that the anoxic event started above the P/T boundary. This observation is also supported by an abrupt decrease in the boundary whole rock Mo, V and U content as well as by the shape of the Ce/Ce* curve of the Idrijca Valley section (DOLENEC T. ET AL., 2001) and the Masore section (DOLENEC M., 2004). This anoxic event may be the result of a rapid transgression in the earliest Triassic, which led to the spread of anoxic water on the epicontinental shelves (HALLAM, 1989; WIGNALL AND HALLAM, 1992).

CONCLUSIONS

Lithological characteristics and geochemical data based on redox sensitive U concentrations as well as the Th/U ratio suggest that anoxia prevails for most of the Karavanke Formation interval. In contrast the transition from the Permian to the Triassic is marked by a rapid development of predominantly oxic depositional conditions during the sedimentation of terrigenous evaporitic sequence. The shape of the Th/U curve indicates that redox condition changed abruptly in the earliest Triassic, approximately 32 m above the P/T boundary, again resulting in oxygen-deficient conditions. The oxic event at the P/T transition is coincidental with the terminal phase of the Upper Permian marine regression.

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