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Geochemical changes at the Permian–Triassic transition in Southern Alps and adjacent area: a review

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Abstract

Compilation of the recent literature from the Southern Alps and adjacent area confirms the geochemical variations of unusual amplitudes during the Permian-Triassic boundary interval (PTBI). A great attention has been given to the negative $\delta^{13}C$ anomaly within the Tesero Member close to the Permian-Triassic boundary. Very detailed geochemical works have been done on the scientific Gartnerkofel core (Gk-1) and on the Slovenian sections. Major minor and rare earth elements (REE) data are reported and show a marked enrichment in alkaline metals and REE of some levels of the boundary interval. But recent studies show that the low Iridium anomalies and the Osmium and Helium isotopes anomalies lack the characteristics of a large extraterrestrial impact.

Keywords: boundary, isotope, Carbon, Sulfur, REE, Gartnerkofel, impact.

Introduction

During the last 30 years, late Permian to early Triassic marine carbonates of the Western end of the Tethys (N Italy Slovenia and adjacent Austria) have been intensively investigated in term of chemostratigraphy and geochemistry.

Carbon isotope stratigraphy and accessory geochemistry works

The first main geochemical investigations on the boundary were presented during the field conference on Permian and Permian-Triassic boundary in the South-Alpine segment of the western Tethys that was held from 6 to 12 July 1986 in Brescia (N Italy). The pioneers were R. Brandner and his research group who gave the first Carbon isotopic curve ($\delta^{13}Ccc$) for the Permian-Triassic transition (Brandner et al. 1986) and Oddone and Vannucci (1986, 1988) who presented the geochemistry of REE and PGE of the Permian-Triassic transition units. During the Fieldtrip a team composed by W.T. Holser M. Magaritz and the author (A.B.) sampled the Idrijca section in Slovenia and the Auronzo and Tesero sections in Southern Alps (Italy). Results on Carbon isotope ($\delta^{13}Ccc$) stratigraphy were published with J. Bär in "Nature" (Magaritz et al. 1988) from the Tesero and Auronzo sections and the first complete data set of Carbon isotope studies of the Permian-Triassic of the Tethys from the Southern Alps to China were published one year later (Baud et al. 1989).

The detailed work of Broglio Loriga (1986) on the Permian-Triassic stratigraphy of the Dolomite helped us greatly. Also the same year a comparison in terms of C isotope values ($\delta^{13}Ccc$) of the Permian-Triassic transition between Greenland and Southern Alps was presented by Oberhänsli et al. (1989).

But slightly earlier according to Holser et al. (1991b) in their introduction to the Gartnekofel volume the first geochemical sampling for Carbon isotope has been done in 1982 at the Repwand outcrop and published three years later (Holser and

Magaritz 1985). This paper focuses on the high C isotope values (δ^{13}Ccc) of the Upper Permian Bellerophon Formation.

Noe and Burggisch (1994) in their work on late Permian and earliest Triassic sequence stratigraphy made some comparisons on δ^{13}Ccc isotope curves between three published sections and their own data on Valles section. Buggisch et al. (1994) presented some geochemical results on the Upper Permian Bellerophon Formation as do Buggisch (1974) twenty years earlier: changes in salinity are reflected by decreasing Sr and increasing Na, Fe, Mn and dolomite contents. Ceretta and Cimmino (1998) studied the petrography and associated geochemistry of the "Serie de Seres" in Val Badia.

Data on δ^{13}Ccc from the Montan section reported by van de Schootbrugge (1997) display a regular negative shift of moderate amplitude.

In their analysis of the Carbon isotope curve (δ^{13}Ccc) of the Werfen Formation from Bulla and Uomo sections Horacek et al. (2000) indicate a strong positive anomaly in the lower Olenekian Campil Member.

Korte and Kozur (in press) worked on the Permian-Triassic transition Carbon isotope curve (δ^{13}Ccc) from Sass de Putia Bulla and Tesero sections with similar results as reported in earlier works.

The Gartnerkofel core (Gk-1)

It is also in 1986 that the first scientific core crossing the Lower Triassic Werfen Formation down to the Upper Permian Bellerophon the Gartnerkofel core (Gk-1) has been achieved under the Leadership of H.P. Schönlaub and W.T. Holser. The three main objectives were the calibration of the δ^{13}Ccc and δ^{13}Corg curves the study of REE and Ir contents and the analysis of anoxia. The first results have been published by these two authors in 1988 and some unique geochemical results by Holser et al. (1989). But most of the data were provided in a special volume of the "Abhandlungen der Geologisches Bundesanstalt" edited by Holser and Schönlaub (1991) and containing 18 contributions with 8 concerning geochemical analysis (Attrep et al. 1991; Holser et al. 1991, 1991a, 1991b; Klein et al. 1991; Kralik et al. 1991; Magaritz and Holzer 1991; Pak et al. 1991; Stattegger et al. 1991). In the synthesis chapter, Holser et al. (1991) concluded that the Carbon isotope curve (δ^{13}Ccc) reflect a very complex and extensive shift away from the dominant organic deposition of earlier Permo-Carboniferous time. Close to the boundary, the minima of δ^{13}Ccc are associated with narrow zones of early diagenetic pyrite and weak anomalies of Ir and other trace metals. Very low ratios of Ir to Co, Cr, Ni and Au in these peaks compared to chondrites and to the K/T boundary anomaly, indicate that the P/Tr boundary metals represent stratabound mineralization rather than a bolide impact.

Wolbach et al. (1994) gave some complements on the δ^{13}Corg analysis. Later Holser (1997) discussed again the Gk-1 Carbon isotope curve (δ^{13}Ccc) and proposed to decompose the negative shift into two components: the decrease of productivity (transient shift) and the burial decrease (long term shift).

Some other investigations on this core are the following:

- One consists of estimating the tempo of the observed geochemical changes. Rampino et al. (2000, 2002) assessed an interval less than 40'000 years for the sharp negative global carbon-isotope shift.

- Another was the use of ^{3}He for the possible detection of an extraterrestrial event. Farley et al. (1999) founded a great amount of terrestrial He arising from high U sediment content and swamping possible extraterrestrial ^{3}He component.

From 1991 until now the Gartnerkofel core is a reference for the Permian-Triassic transition Carbon isotope curve.

Organic Carbon analysis

Analysis by Sephton et al. (1999, 2001) of organic rich marls from the uppermost layers of the Bellerophon Formation at Val Badia (latest Permian Northern Italy) indicates that the dominant source of organic matter is decomposed land plants debris and that the Kerogens are of type III; they found polysaccharides and the possible source is the organic constituents of microbes and fungi. Schwab and Spangenberg (2004) founded evidence for alga and bacterial organisms.

According to Wignall and Twitchett (1996, p. 47), the organic matter of the overlying Mazzin Member micrite contains well-preserved Kerogens of type II typical of oxygen poor deposition.

Sephton et al. (2002) analyzed the Carbon isotopic composition of the alkane (δ^{13}Calk) and compared it with Carbon isotopic composition of the carbonate (δ^{13}Ccc) in the Val Badia Permian-Triassic transition.

They concluded of a syn-chronous disturbance of the atmospheric and marine chemistry.

Carbon isotope and geochemistry in Slovenia

New results on geochemical change at the PTBI in Slovenia have been published by the Dolenec research group from Ljubljana (Dolenec et al. 1997, 1998a, 1998b, 1999a, 1999b). These studies of different Slovenian sections show negative shifts in both Corg and Ccc isotope values. In addition these authors also found a depleted Cerium anomaly at the Permian-Triassic transition interpreted as an increase of oxidation conditions and ventilation in the uppermost Permian and in the basal Triassic (Dolenec et al. 1997). Dolenec et al. (2001) gave information also on major minor and REE variations at the PTBI of the Idrijca section with the highest concentration of the elements at the boundary clay layer. According to chalcophile elements enrichment as the higher concentration of Mo V and U in the upper Permian Zazar limestones they concluded that oceanic anoxia was typical for the upper Permian. Changes to oxygenated conditions occur at the transition and, according to their Ce/Ce curve, the redox environmental conditions changed again in the earliest Triassic with oxygen deficient conditions (Dolenec et al. 2003).

Hansen et al. (2000) illustrated organic carbon isotope curve from 2 Slovenian sections: Idrijca and Karawanke.

Dolenec et al. (2004) analyzed carbonate and total organic carbon stable isotope from the Upper Permian and Lower Triassic succession in the Masore section in western Slovenia and founded a high storage of organic matter during the Upper Permian and a pronounced changes in the carbon cycle across the Permian-Triassic boundary.

Schwab and Spangenberg (2004) analyzed the organic matter and the δ^{13}Corg in the uppermost Permian and in the basal Triassic of the Idrijca section and founded evidence for a diverse community of algal and bacterial organisms.

Redox and Sulfur isotopes studies

The Th/U ratio is an indicator experimented by Wignall and Twitchett 1996 on samples from eight sections of the S Alps. This ratio was calculated to estimate the redox conditions based on Th/U ratio obtained by γRay Spectrometer measurements. Their data indicate that anoxia prevailed during the deposition of the Mazzin Member (Early Griesbachian).

The first Sulfur isotope studies have been done on evaporite (sulfate) later on pyrite (sulfite) and more recently on carbonate associated sulfate (CAS).

Southern Alps Permian and Triassic Sulfur isotopes from sulfates received attention as early as 1978 and 1981 by Pak (in Pak and Holser 1991) by Cortecci et al. (1981) and by Holser and Magaritz (1985). In a tectonic melange of the Northern Calcareous Alps S and Sr stable isotopes were investigated by Spötl and Pak (1996) in not precisely dated Permian and Triassic evaporites.

From the Gartnerkofel core syngenetic pyrite Pak and Holser (1991) published eleven Sulfur isotopes values between -21 and -27 .

Dolenec and Vokal (2003) illustrated a Sulfur isotope curve showing high variability from syngenetic pyrite of the Permian-Triassic transition of the Idrijca section (W Slovenia)

Newton et al. (2004) indicate that sulfur isotopic analyses of carbonate associated sulfate (CAS) across a Permo-Triassic boundary Siusi section show a positive isotopic excursion interpreted to have resulted from prolonged oceanic anoxia.

Impact or extraterrestrial collision

Iridium anomaly was the subject of 15 years of discussion. The measured Iridium concentrations are at least an order of magnitude lower than the Iridium spike at the K/T boundary but similar to Iridium concentrations described at other major boundaries as shown by Holser et al. (1991) from the Gartnerkofel-1 core measurements.

The use of ^{3}He for the possible detection of an extraterrestrial event has been applied by Farley et al. (1999) who founded a great amount of terrestrial He from the Gartnerkofel-1 core arising from high U sediment content and swamping possible extraterrestrial ^{3}He component.

Microspherules were reported from the Gartnerkofel-1 core (Holser et al. 1991) close to the boundary and from the Idrijca and Tesero sections (Hansen et al. 2000). Some authors interpreted it as possible indicator of an extraterrestrial event but for Hansen et al. (2000) it consist of Magnetite infilled prasinophyte algae.

Following a renewing of the impact theory by Becker et al. (2004), Koeberl et al. (2004) published

a short paper based on Osmium and Helium isotopes analysis indicating that there is no evidence for a Permian-Triassic boundary extraterrestrial chemical component neither in the Val Badia section nor in the Gartnerkofel core.

Tempo of geological changes

In order to estimate the duration of the paleoenvironmental and geochemical changes Bowring et al. (1998) provided U/Pb zircon dates from interbedded volcanic ash beds in S China marine PTB sections. According to their result the Changhsingian duration (latest stage of the Permian) is about 2 My the main pulse of latest Permian extinction occurred in less than 1 Ma and the abrupt shift of δ^{13}Ccc at Meishan section lasted less than 165'000 years.

Based on time-series analyses of the Gartnerkofel-1 core a duration of less than 40'000 years for this δ^{13}Ccc shift is given by Rampino et al. (2000, 2002).

High resolution U/Pb data on the PTBI at Meishan have been published by Ludwig et al. (1999) and by Metcalfe et al. (2001). For these authors the Changhsingian duration between 4 an 6 Ma is at least two time of the previous value published by Bowring et al. (1998). Recalibration is also presented by Bowring and Schmitz (2003) and by Mundil et al. (2001, 2004). In his last paper Mundil et al. (2004) are giving a 252.6 My for the main extinction pulse and about 4My for the Changhsingian duration. Perturbation and the "abrupt" shift of δ^{13}Ccc lasted more than 2My in the Shangsi section (China) that is 50 time more than the 40Ky given by Rampino et al. (2000) for the same shift in the Gartnerkofel-1 core.

Conclusions

The amplitude of the geochemical perturbations confirms that the PTBI was a time of major global changes. The tempo of some of these perturbations is still controversial.

Main advances in geochemical studies on the PTBI have been done in the Southern Alps and concern shallow shelf and adjacent continental deposits. To be underlined is that the Southern Alps and adjacent area have been the starting point for the Carbon isotope studies and for the sulfur isotopic analyses of carbonate associated sulfate (CAS) within the Permian-Triassic Boundary interval. The precise correlations and biochrono-logical data due to Broglio-Loriga and collaborators (1986, 1992) open the way for these pioneer geochemical works.

Due to the willpower of W.T. Holser and H.P. Schönlaub, the Gartnerkofel core (Gk-1) greatly contributed to the success of geochemical studies. The rare Earth analysis confirms the absence of extraterrestrial components during the Permian-Triassic transition.

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Riassunto

[Cambiamenti geochimici al passaggio Permiano-Triassico nelle Alpi meridionali e nelle aree limitrofe: una revisione]

Durante gli ultimi trent'anni i carbonati marini del Permiano Superiore e del Triassico Inferiore della Tetide occidentale (Italia settentrionale, Slovenia, Austria) sono stati oggetto di intensi studi chemiostratigrafici e geochimici.

L'analisi dei dati della letteratura riguardanti le Alpi Meridionali e le aree adiacenti conferma le variazioni geochimiche di inusuale ampiezza avvenute durante l'intervallo al passaggio Permiano-Triassico (PTBI). Grande importanza è stata data all'anomalia negativa del $\delta^{13}C$ presente nel Membro di Tesero in prossimità del passaggio Permiano-Triassico. Studi geochimici molto dettagliati sono stati effettuati sul carotaggio scientifico Gartnerkofel (Gk-1) e su sezioni stratigrafiche slovene. Sono stati identificati elementi in tracce e terre rare (REE) che mostrano un marcato arricchimento in metalli alcalini e REE di alcuni livelli dell'intervallo studiato. Studi recenti mostrano, tuttavia, che le anomalie negative in Iridio e le anomalie degli isotopi di Osmio ed Elio sono privi delle caratteristiche di un importante impatto extraterrestre.

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