The Permian-Triassic Boundary in the Carnic Alps of Austria (Gartnerkofel Region)  
Editors: W.T. Holser & H.P. Schönlaub


The Permian-Triassic of the Gartnerkofel-1 Core  
(Carnic Alps, Austria):  
Synthesis and Conclusions

By WILLIAM T. HOLSER, HANS PETER SCHÖNLAUB, KLAUS BOECKELMANN & MORDECKAI MAGARITZ*)

With 13 Text-Figures

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Zusammenfassung

In der 331 m tiefen Forschungsbohrung Gartnerkofel-1, Karnische Alpen, Österreich, wurde das Geschehen an der Perm/Trias-Grenze eingehend untersucht.

Der obere 100 m mächtige Abschnitt der Bellerophon Formation des Oberperms (Dzhulfa/Dorasham-Stufe) wird konkordant und lückenlos von 174 m mächtigen Äquivalenten der Werfen Formation der basalen Trias überlagert. Nach Conodonten erweist sich der Griesbach-Anteil dieses Profilab schnittes als außergewöhnlich und sehr komplex. Ökologische Ereignisse, die sich an der Perm/Trias-Grenze über rund 3 Millionen Jahre hinweg in der Bio- und Hydrosphäre ereignet haben und in einem auffallenden Gegensatz zur Zeit davor stehen.

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In den beiden δ¹³C-Minima-Zonen treten zudem frühdiagenetischer Pyrit und erhöhte Iridium- und andere Spurenelementgehalte auf. Die niedrigen Verhältnisse von Iridium zu Kobalt, Chrom, Nickel und Gold im Vergleich zu Chondriten und zu den Verhältnissen an der Kreide/Tertiär-Grenze (K/T) machen wahrscheinlich, daß diese Mineralisationen eher schichtgebunden und sedimentärer Natur sind und nicht von einem Impakt eines extraterrestrischen Boliden stammen.


Zum Schluß diskutieren wir anhand unserer neuen geochemischen Daten ausführlich den Zusammenhang zwischen Massensterben und Regression des Meeresspiegels an der Perm/Trias-Grenze.

Abstract

Events at the P/Tr boundary were investigated in the 331-m core Gartnerkofel-1, Carnic Alps of Austria. 100 m of the upper Bellerophon Formation of Dzhulfian/Dorashamian age are succeeded conformably by 174 m of Triassic Werfen Formation, in which conodont zonation verifies a thick Griesbachian section.

The carbon isotope profile drops smoothly and with increasing steepness across the boundary to a series of minima in the lower 40 m of the Werfen Formation before returning to nominal levels in the upper Werfen; these data reflect a very complex and extensive (=3 Ma) shift away from the dominant organic deposition characteristic of Permo-Carboniferous time.

The lower and upper minima of δ¹³C 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. Rather the P/Tr “event” may have been spread out over several million years during which extinctions were paralleled by the deterioration of organic carbon deposition consequent on sea level regression.

The traditional linkage of extinction to sea-level regression is re-examined in the context of the new geochemical data.

1. Introduction

This paper summarizes the results of an international group of 19 scientists from 5 countries who studied the Permian-Triassic boundary beds in a cross-disciplinary comprehensive project in the Carnic Alps of Southern Austria. Previous studies had indicated that in this part of the Southern Alps complete sections across the boundary are well preserved and accessible. They are located near the western end of the Tethys Sea of that time (Text-Fig. 1), on a carbonate ramp gently dipping to the southeast, but about 150 km east of the shoreline exposed in the Dolomites of Northern Italy (Text-Fig. 2). The area is very close to segments of the Periadiatric Fault Zone in the Gail Valley of Austria, immediately in the north. This prominent fault separates the predominantly marine Upper Paleozoic and Mesozoic sediments of the Southern Alps from clastic terrigenous Permian and lowermost Triassic deposits of the Central Alps of Austria.

Our objective in the current debate on mass-extinction in Earth’s history has been to completely charac-
2. The Permian-Triassic Event(s)

The Permian-Triassic (P/Tr) boundary is associated with the largest extinction event in Phanerzoic time (D.M. RAUP & J.J. SEPKOSKI, 1982, and others). It also witnessed changes in the environment (W.T. HOLSER &
The high concentrations at the K/T boundary (L.W. AL... Silurian boundary (C.J. ORTH et al., 1986; C.J. ORTH, with other extinction events (M. MAGARITZ, 1989): the

$^{13}{\text{C}}$ has also been observed in connection with other extinction events (M. MAGARITZ, 1987) notably indicated by a large drop in $^{87}{\text{Sr}}/^{86}{\text{Sr}}$. Similar to those in the Late Eocene (P.E. PLAYFORD et al., 1984; C.J. ORTH, 1988, 1989; C.J. ORTH et al., 1988), but analysis of these same sections in other laboratories have failed to find concentrations of more than 100 ppT Ir (F. ASARO et al., 1982; D.L. CLARK et al., 1986; L. ZHOU, 1987; D.BOCLET et al., 1988). Similarly low levels of Ir were found in P/Tr sections in Soviet Armenia (A.S. ALEKSEEV et al., 1983) and in the Dolomite Alps (M. ODDONE & R. VANUCCI, 1988; R. BRANDNER, 1988).

Iridium anomalies associated with the P/Tr boundary have been controversial. Notable Ir anomalies have been reported at exposures of the P/Tr boundary in China (Y. SUN et al., 1984; D.-Y. XÍ et al., 1985; C. CHAI et al., 1986), but analysis of these same sections in other laboratories have failed to find concentrations of more than 100 ppT Ir (F. ASARO et al., 1982; D.L. CLARK et al., 1986; L. ZHOU, 1987; D.BOCLET et al., 1988). The Upper Permian Bellerophon Formation is conformably overlain by the 300 m thick alternation of dolostones, marls and limestones of the fossiliferous Werfen Formation. It contains varying amounts of quartz, mica and other clastic detritus and represents subtidal to supratidal environments with transgressive and regressive sedimentary features. In our study area 6 of 9 lithostratigraphic units and subunits recognized in the Dolomites, are developed. The basal member, named Tesero Horizon, spans the Permian-Triassic boundary, and consequently, its initial recognition in the Gartnerkofel area by our group was of great importance for the aim of our study.

4. Litho- and Biostratigraphy

The core Gartnerkofel-1 started in the Muschelkalk Conglomerate (Lower Anisian), entered the Werfen Formation (Scythian) at 57 m, the Bellerophon Formation (Dzhulian/Dorashamian) at 231 m, and bottomed in the same formation at 331 m. Oolites in the lowermost 6 m of the Werfen Formation (224.50–231.04 m) correlate with the 4 m thick Tesero Horizon in the outcrop section and with the Tesero Horizon in the Italian Dolo­mites (C. BROGLIO LORIGA et al., 1988), where the P/Tr boundary, as defined by the last occurrences of Perm­ian fusulinids and molluscs, lies within the basal part of this horizon. In both core Gartnerkofel-1 and the nearby outcrop on the Reppwand cliffs, conodonts were abundantly recovered from the Tesero Horizon and the overlying equivalents of the Mazzin Member and Selis Member. They confirm a very thick and complete representation of lowermost Triassic sediments at this locality (H.P. SCHÖNLAUB, this volume).

The bulk of the cored section is fine-grained dolomite, with occasional mm-to cm-thick interbeds of dolomitic marls or shale. More than 400 thin sections taken from the core and the outcrop section were studied for textural microfacies (K. BOECKELMANN, this volume) and micropaleontology (C. JENNY-DESHUSSER, this volume). Based on this four lithostratigraphic units are recognized in the core.

Unit 1 (depth range from 330 to 231.04 m in the core, and the section below the Tesero Horizon in the outcrop) comprises the middle and upper part of the Bellerophon Formation. Originally it represented a homogenous, bioturbated biomicrite. The characteristic feature of some beds is a Stromatactis-like fenestral fabric, otherwise the dolomitized mud-and wacke-

3. Geological Background

In the Southern Alps Late Paleozoic sediments unconformably overlie the Variscan basement. These rocks are deeply eroded and show greenschist facies metamorphism in the Dolomites but are unmetamorphosed or only anchimetamorphic in the Carnic Alps. Nevertheless, due to strong Variscan tectonics during the Westphalian Stage of the Upper Carboniferous this underlying unit shows a complex deformatonal style including folds, nappes and tectonic slices. Alpine tec­tonics affected both the basement and its cover.

In the Carnic Alps the Late Paleozoic cover comprises clastic and calcareous shallow marine sedi­ments of the Auerberg Formation in the youngest Car­boniferous followed by various Lower Permian shelf and shelf-edge deposits known as Pseudoschwagerina and Trogkofel Limestones. They indicate differentially subsiding platform areas and outer shelf environments characterized by transgressive-regressive sedimentary cycles that lasted from the Westphalian to the Artins­kian Stage of the Lower Permian.

Upper Permian sediments of the Carnic Alps rest disconformably on the above mentioned Lower Perm­ian and its equivalents in the Dolomites, or farther west on phyllices of the Variscan basement. They clearly indi­cate a transgressive regime starting with the red beds of the Gröden Formation in the Middle (?) Per­mian followed by the Bellerophon Formation in the Late Permian. This latter formation, between 160 and 170 m thick in the Carnic Alps, comprises several lithofacies which suggest depositional environments from coastal sabkhas to restricted lagoon, open lagoon and shallow shelf settings with decreasing terrigenous or coastal influence. Most sediments of this time represent a low­energy environment of a marginal Tethyan basin.

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Text-Fig. 4.
Lithology and fauna of the P/Tr boundary section (Tesero Horizon) in the Gartnerkofel-1 core (K. BOECKELMANN, this volume).
stones indicate a low-energy environment. Foraminifera of the Hemigordius-Globivalvulina Association are prevalent, but less abundant and diversified than at other localities (e.g., Tesero, Dierico; see C. Jenny-Deshusses, this volume). The microfacies of this unit shows the normal marine environment of a shallow inner shelf, without influence of terrigenous clastics. Some beds are very fossiliferous and strongly bioturbated.

Farther west in the Carnic Alps and the Dolomites evaporitic facies are common in the Bellerophon Formation, but at Naßfeld evaporitic conditions are only evident as Rauhwacke near its base and below the bottom of the section cored in Gartnerkofel-1 (W. Buggisch, 1974; W. T. Holser & M. Magaritz, 1985; S. Noé, 1987).

Unit 2 (depth range from 231.04 to 224.50 m in the core, and the lowermost 4 m of the Werfen Formation in the Reppwand outcrop) is here referred to the Tesero Horizon. This unit conformably overlies the uppermost beds of the Bellerophon Formation. It consists of fine-to medium-grained dolomite which according to thin section analysis originally comprised oolitic and bioclastic grainstones with increasing incidence upward of intraclasts, ostracods, Earlandia (foraminifera),
the worm tube *Spirorbis* and conodonts. The Tesero Horizon represents a shallow and restricted environment, being transitional in its setting from the low-energy biomicrites of Unit 1 to the ostracod-rich carbonates and high-energy tempestites of the following Unit 3. The sedimentary and paleontological features of the Tesero Horizon are illustrated in Text-Fig. 4 (K. BOECKELMANN, this volume).

Conodonts from the lowermost 0.50 m of the Tesero Horizon are identified as *Hindeodus cf. lalidentatus*, *H. minutus*, *H. parvus* and *H. n.sp.*. The first two taxa are restricted to this lowermost part of the Tesero Horizon, while the others range higher up in the section. We correlate this lowermost association with the lower part of the Otoceras woodwardi Zone of the ammonoid-based subdivision of the Triassic, which by most paleontologists has been regarded as the base of the Griesbachian Stage of the early Triassic (E.T. TOZER, 1980). Consequently, the stratigraphic boundary between the Permian and the Triassic is placed within this lowermost half meter of the Tesero Horizon or at its base. Ranges of conodont species in the core and outcrop sections are illustrated in Text-Fig. 4 (H.P. SCHÖNLAUB, this volume).

Unit 3 (depth range from 224.50 to 95 or 82 m in the core, and from 4 to 59.70 m of the Werfen Formation of the Reppwand outcrop section) includes undifferentiated Mazzin and Seis Members. The lower part is a strongly bioturbated, ostracod-rich microparite, with coquina-bearing tempestites, oolitic horizons, grain-and-packstones becoming more common upward. Fossils are micro gastropods, foraminifers, bivalves, worm tubes and conodonts. All lithologies are – except for a few samples with relic calcite – completely dolomitized-making it difficult to identify any fossil remains.

Conodonts of Unit 3 are characterized by *Hindeodus parvus* ranging in the core from 187.20 to 224.97 m and in the outcrop section possibly up to 43.40 m of the Werfen Formation; partly time equivalent are *Hindeodus n.sp.*, *Hindeodus turgidus* and *Isarcicella isarcica*. These latter two species, however, have a restricted range within the upper range of *Hindeodus parvus*. The only occurrence of *Hindeodus turgidus* is in sample no. 64, 32.70 m above the base of the Werfen Formation in the outcrop section; it is followed by the distinctly recognizable worldwide index conodont *Isarcicella isarcica*, first occurring in the succeeding sample 65, 34.20 m above the base of the Tesero Horizon. In the outcrop this species ranges upward to 42.40 m; the last occurrence in the core lies between 184.50 and 185.00 m. In both sections *Isarcicella isarcica* is followed by abundant occurrences of the multielement *Ellisonia aequabilis*. This taxon characterizes both the upper part of the Mazzin Member and the lower part of the Seis Member in the Dolomites (U. STAESCHE, 1964).

Unit 4 (depth ranges from 95 [or 82] to 57 m in the core and on the Kammleiten above the measured outcrop section) represents the Campil Member of the Werfen Formation. In the core the boundary between the Seis and the Campil Member is transitional. Color gradually changes from grey to red, fossil content decreases and clastic interlayers become more abundant. The lithology comprises dolomitite and siliciclastic beds with intercalated mollusc shell layers. Most rocks are altered to dolomite of varying grain size.

In the Gartnerkofel-1 core, and in the outcrop as well, part of the Campil Member and the overlying Val Badia and Cencenighe Members were eroded in the Anisian. They are reworked in the disconformably overlying Muschelkalk Conglomerate.

The facies development in the early Scythian is characterized by a regressive trend starting in the uppermost Permian and ending in Campil time. A regressive event of even smaller magnitude occurs at the P/Tr boundary and is documented in the Tesero Horizon. At the top of the Campil Member sea-level again rose giving way to subtidal conditions that characterized the Val Badia Member farther to the west.

5. Mineralogy

The mineralogy of the GK core is dominantly micritic to microparitic dolomite (K. BOECKELMANN & M. MAGARITZ, this volume), with 1 to 2 mol. percent excess CaCO$_3$ (M. KRALIK, this volume). X-ray diffraction studies indicate that the dolomite is usually accompanied by up to 3 % calcite containing up to 15 % excess MgCO$_3$ (M. KRALIK, this volume); at outcrops elsewhere in the region the limestone section is only partly dolomitized. Preservation of relict fossils, petrographic texture, and trends of trace element (Na, Fe, Mn) and strontium isotope content point to an early diagenetic origin of this main dolomite component (K. BOECKELMANN & M. MAGARITZ, this volume; M. KRALIK, this volume). Coarse rhombic dolomite, particularly associated with stylolites, mordic porosity and fenestral fabric, is probably crystallized in a late diagenetic stage.

The dominant clastic components are quartz, illite/muscovite and chlorite (A. FENNINGER, this volume). The measured crystallinity of the mica indicates only very low grade diagenesis (<180°C) (J.-M. SCHRAMM, this volume).

The pyrite is in part frambooidal, as characteristic of early diagenetic deposition, and in part microcubic (W. T. HOLSER, this volume). Oxidation of pyrite to goethite and hematite apparently occurred in two stages, leading to overprints of the natural remanent magnetization by both Cretaceous normal and Recent field directions (W. ZEISSL & H. J. MAURITSCHE, this volume).

6. Chemical Trends

Through the Permian/Triassic Boundary

6.1. Carbon isotopes

The most striking general feature of the chemistry of the P/Tr boundary is a dramatic drop in δ13C of carbonate. This is a general phenomenon, which has been documented worldwide (W. T. HOLSER et al., 1986) and recently verified all along the shores of Tethys (A. BAUD et al., 1989). The carbon isotope profile in Gartnerkofel-1 provides new detail concerning the drop in δ13C, as shown in Text-Fig. 6 (M. MAGARITZ & W. T. HOLSER, this volume). The differences among segments of this profile suggest further (local) subdivisions of the stratigraphic section: Unit 1A is the lower part of the Bellerophon Formation intersected by the core from
the bottom to 294 m, and has $^{13}$C-enriched values ($\delta^{13}$C = $+3.0\pm0.3\%$). Unit 1B is the upper part of the Bellerophon Formation, where $\delta^{13}$C values drop gradually from $+2.8\%$ to $+1.5\%$ at 231 m. In Unit 2, the Tesero Horizon of the Werfen Formation, which includes the P/Tr boundary, $\delta^{13}$C continues to drop, through a value of 0.0% at 224.7 m. This segment has the same values of $\delta^{13}$C and thickness as at the Tesero Horizon at Tesero, Italy (C. Broglio Loriga et al., 1988; M. Magaritz et al., 1988), 140 km to the west. Unit 3A is an interval of low $\delta^{13}$C in the lower part of the Mazzin Member of the Werfen Formation, extending to 175 m and including three minima, which will be discussed below. Unit 3B (mostly Seis member) and 4 (Campil Member) comprise the upper part of the Werfen Formation that was intersected by GK-1 to 57 m, with a constant $\delta^{13}$C = $+1.3\pm0.2\%$.

This general trend of $\delta^{13}$C across the P/Tr boundary is placed in a long-term general context in Text-Fig. 7, which integrates the trend of $\delta^{13}$C in the Upper Permian, averaged from many profiles throughout the Tethyan belt (A. Baud et al., 1989) with the cross-boundary profile of GK-1 (Text-Fig. 6), which is suggested to represent the section best documented at present by a

<table>
<thead>
<tr>
<th>Depth (m)</th>
<th>Sample</th>
<th>Age</th>
<th>Unit</th>
<th>$\gamma$-ray</th>
<th>$\delta^{13}$C (% vs PDB)</th>
<th>$\delta^{18}$O (% vs PDB)</th>
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<tr>
<td>0-100</td>
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Text-Fig. 6. Oxygen and carbon isotopes in GK-1. $\delta^{13}$C continues the downward trend initiated earlier in the Late Permian (see Fig. 7), accelerates smoothly to minima in the lowermost Triassic, and returns to a constant value in the overlying part of the Lower Triassic. These variations represent major shifts in crustal carbon reservoirs from organic carbon ($\delta^{13}$C to the right) to carbonate ($\delta^{13}$C to the left), with consequent shifts from oxygen to carbon in the atmosphere/ocean reservoirs. The mean shift of $\delta^{18}$O to lower values in the Lower Triassic may represent in part an increase in surface temperature owing to the increase in atmospheric carbon dioxide. After W. T. Holser et al. (1989).
thick densely sampled section under close biostratigraphic control (H.-P. SCHÖNLAUB, this volume and Text-Fig. 8). Other sections may not be as complete: Comparison of Text-Fig. 4 with other profiles to the west at Tesero and Auronzo (M. MAGARITZ et al., 1988) indicates that the segment of Unit 1B corresponds to a sharp drop in δ13C that occurred within a few tens of cm in the Italy sections. The multiple minima taken in Text-Fig. 7 from Text-Fig. 6 have not yet been duplicated at other sections in Tethys, possibly owing to less dense sampling of Griesbachian sections that are more condensed or less complete.

The lesson of Text-Fig. 7 is a smooth but accelerating decrease in δ13C that begins considerably before the P/Tr boundary and moves quickly but smoothly through the boundary, and an extended interval of complexity before re-establishment of uniformly lower δ13C in the post-Middle Griesbachian Lower Triassic. The interval of drop and complex change extends for perhaps 3 Ma, as indicated in Text-Fig. 7.
6.2. Oxygen Isotopes

δ18O values also show some consistent variations in certain intervals (Text-Fig. 6). In Unit 1A the values of δ18O show a bimodal distribution, centered at δ18O = -0.5 and -3.0‰, and the less negative values continue in the lower part of Unit 1B. More negative values of δ18O about -3.5‰ occur in the upper part of Unit 1B, and persist through Units 2 (δ18O = -4.5±0.5‰) and Units 3 and 4 (δ18O = -4.2±0.8‰), consistently, despite the substantial variations of δ13C that characterize those intervals (Text-Fig. 6). The consistent nature of the variations of δ18O speaks for a mainly primary record of δ18O in this core section.

Relative to the oceanic water isotope ratio, which is presumed to be a non-glacial ratio of about -1.5‰ throughout the section, the variations of δ18O would therefore be mainly owing to shifts of sea water temperature and/or salinity. It is not possible to separate unequivocally the effects of temperature and salinity changes. As a tentative approach we suggest that the oscillations of δ18O in Unit 1A are the result of cyclic evaporitic events, such as have been recognized further west in this basin (A. BOSCELLI & L.A. HARDIE, 1973). The following record in Units 1B through 4, which does not exhibit these cyclic variations, may be due to a rise in temperature. The shift from δ18O = -3‰ in the presumed lower salinity limits of Unit 1A to δ18O = -4.5‰ in Unit 2 (and perhaps less negative values in the overlying units) translates to a temperature rise of about 6°C. Of course part of this shift of δ18O may still be due to undetermined differences in salinity, or diagenesis, in the two sections.

6.3. Trace Element Trends

The wide sweep of carbon isotope shifts near the P/Tr boundary is mirrored in a general shift of sedimentation (K. BOECKELMANN, this volume, as reviewed above) and in the chemical composition of sediments. The analytical data of P. KLEIN (this volume) and M. ATTREP et al. (this volume) were treated with discrimination statistics by K. STATTEGGER (this volume), resulting in a clear progression of trace-element chemistry. This shift is illustrated in Text-Fig. 8, which shows for the acid-soluble fraction a decrease of one canonical variable to the Mazzin Member (Unit 3A), followed by an increase of a second canonical variable through the Campil part of the section. In terms of elements, this means a decrease of δ13C, V and S, and an increase of K, followed by an increase of P, Zn and Fe and decrease of Ni and Ba. The shifts of these complex chemical attributes indicate a critical change in the chemistry of sedimentation centered on Unit 3A and the end of the carbon isotope minimum interval. Similar shifts are shown by the INAA data (M. ATTREP et al., this volume; K. STATTEGGER, this volume, Text-Fig. 9) but with less definition. Obviously this analysis is only directly applicable to this particular section of the Permian-Triassic.

Some geochemical measures of detrital provenance are constant, with no trend along the whole length of the core: Th/Al = 0.161±0.028×10^-3 (n = 76), and Ga/Sc = 1.70±0.36 (n = 25) (M. ATTREP et al., this volume). The latter ratio (J.A. WINCHESTER & P.A. FLOYD, 1977), and minor olivine and augite in heavy-mineral concentrates in Unit 3 (A. FENNINGER, this volume) suggest some input of fresh basic volcanic material, such as may have been derived from the Permian-Scythian Haselgebirge of the Northern Calcareous Alps (E. KIRCHNER, 1980).

7. Details of Chemical Shifts

Across the Permian/Triassic Boundary

7.1. Carbon Isotopes

Detailed profiles of selected stable isotope and chemical variations for the interval 235-175 m, crossing the P/Tr boundary, are displayed in Text-Fig. 10. This interval, from the upper part of Unit 1B through Unit 3A, has complex variations of carbon isotopes and chemistry.

The smooth decrease of δ13C, which starts in Unit 1B, continues through Unit 2 at an accelerating rate, reaching 0.3‰/m. This sharp drop in δ13C signals the beginning of a zone of low δ13C values that includes three minima at 220 (-1.5‰), 193 (-0.6‰), and 186 m (-0.9‰), until a more stable regime of δ13C (at about +1.3±0.2‰) is re-established above 173 m (Text-Fig. 6) (M. MAGARITZ & W.T. HOLSER, this volume).
Fig. 10. Details of geochemistry in GK-1, from 235 to 175 m, across the P/Tr boundary (near the base of the Tesero Horizon).

Squares represent dolomite, triangles represent shale or marl, and samples of the two iridium maxima are shown as solid symbols.

A) Carbon isotope profile (M. Magaritz & W.T. Holser, this volume). Note the steep but smooth decline of $\delta^{13}\text{C}$ across the P/Tr boundary, and the subsequent three minima in the lowermost Triassic.

B) Total sulfur (P. Klein, this volume) and total iron (M. Attrep et al., this volume) contained in pyrite or its oxidation products.

C) Ce'/La* (M. Attrep et al., this volume) normalized to the North American Shale Composite. Note the shift from low to high ratio (oxidizing to reducing conditions) near the upper boundary of the Tesero Horizon.

D) Ir (M. Attrep et al., this volume) normalized by Al to the shaly component - the distribution of the shaly component is shown by high gamma-ray counts on the downhole log at the left (R. Schmoller, this volume). Two Ir peaks at many times background level are seen at the Tesero-Werfen contact as $\delta^{13}\text{C}$ passes through zero, and at about 40 m higher where $\delta^{13}\text{C}$ drops to its upper minimum. After W.T. Holser et al. (1988).
7.2. Pyrite

This $^{13}$C-depleted zone is also characterized by chemical changes. The initial (decreasing $\delta^{13}$C) segments of the first and third carbon-isotope minima have high concentrations of pyrite, over 500 $\mu$mol/g (P. Klein, this volume), as shown by dashed lines in Text-Fig. 10B. Total Fe (M. Attrep et al., this volume), shown by solid lines in Text-Fig. 10, is nearly matched (in $\mu$mol/g) by $S_2$ in these two pyritic intervals. Pyrite has wavy lamellar bedding, seen in polished section to consist of globular masses 20 to 100 $\mu$m in diameter (W.T. Holser, this volume), similar to early diagenetic "framboidal" pyrite common in modern marine muds and in stratiform sulfide deposits such as the Kupferschiefer, Meggen and Rammelsberg (W.G. Love & G.C. Amstutz, 1966; J. Ostwald & B.M. England, 1979). Microprobe analyses indicate a nearly constant content of 1000 ppm Co in all pyrite, but no detectable As at a sensitivity of 500 ppm (W.T. Holser, this volume). Globular pyrite is widely regarded as a product of very early diagenesis. Strongly negative isotope ratios of the sulfide, $\delta^{34}$S = -18 to -27 $\%$o (E. Pak & W.T. Holser, this volume), are consistent with a primary origin by biologically mediated reduction in the sediment, rather than by hydrothermal solution. Each of the stratigraphically distinct sulfide concentrations in Text-Fig. 8B has a negative, uniform but distinct isotope ratio: for example near 185 m $\delta^{34}$S = -19.3±0.2 $\%$o and at 221–222 m $\delta^{34}$S = -25.7±1.1 $\%$o. These data indicate that the pyrite is syngenetic-diagenetic, and that each bed was deposited in its own distinct reducing environment.

7.3. Iridium

Iridium also shows two peaks (M. Attrep et al., this volume; normalized to Al in Text-Fig. 10) substantially above background. The earliest, of 165 ppT Ir (Ir/Al = $4.15 \times 10^{-9}$), at the top of Unit 2 (224.5 m) occurs while $\delta^{13}$C is still declining sharply towards its first minimum,
7.4. Other Trace Elements

These anomalies of $\delta^{13}C$, pyrite and Ir are accompanied by concentrations of V, Cr, Ni and Co, as well as As, Sb, U and Rare Earth elements (REE) (M. ATTREP et al., this volume). In detail the relations are complex. All those elements show concentrations substantially above background in Unit 3 (the Tesero Horizon), just below the lower anomaly of $\delta^{13}C$, pyrite and Ir, in an interval (231–225 m) where a lack of sulfide and the presence of oolites suggests oxidizing rather than reducing conditions in the sediment. At the upper anomaly of $\delta^{13}C$, pyrite and Ir, the trace elements V, Ni, As, Sb and to a lesser extent Co (but not Cr, U or REE) are also concentrated, but in the reducing interval itself (M. ATTREP et al., this volume). A separation between Ir above and metals below, as in the lower anomaly, had previously been described from the K/T boundary (K.H. HANSEN et al., 1988).

Statistical treatment (see K. STATTEGGER, this volume) of the acid-soluble chemistry (P. KLEIN, this volume) of Unit 3A also showed significant positive correlations of P with V, Ni and total S. The concentration of Ir and related metals by precipitation at oxidation/reduction boundaries has been modelled for the K/T boundary by B. SCHMITZ (1985). Such concentrations are analogous to the occurrence of platinum group elements in the Late Permian Kupferschiefer of northwestern Europe, where Ir and other PGE are concentrated in black shale and thucolite overlying oxidized sandstone (H. KUCHA, 1981, 1982).

7.5. Relation of Iridium to Other Trace Metals

The content of iridium and its relation to other trace metals have been prominent factors in evaluating an extraterrestrial component in K/T boundary clays. M.A. NAZAROV et al. (1988) have summarized all available data for these elements, and demonstrated that the most intense anomalies at the K/T boundary worldwide are the platinum group elements (including Ir), Ni, Cr, V, Zn and Co. Our data for the P/Tr allow comparisons for some of these elements with those at the K/T boundary. A log plot of Co vs. Ir (Text-Fig. 11) shows P/Tr samples (including both our data from Austria and
two analyses from China: D.L. CLARK et al., 1986) at significantly lower Ir than:

1) mean CI chondrite (J.T. WASSON, 1985),
2) chondritic spherules from the deep sea (A. BONTE et al., 1987),
3) chondritic spherules from the Tunguska event (R. GANAPATHY, 1983) and
4) peak spikes at the K/T boundary (J. SMIT & J. HERTOGEN, 1980; F.T. KYTE et al., 1980).

As indicated in Text-Fig. 11, the ratios of Co/Ir in both background and in the nominal peaks of the GK-1 profile are more like those found in deep-sea muds (J.H. CROCKET & H.Y. Kuo, 1979) and manganese nodules (Ir: R.C. HARRISS et al., 1968; Co: V.E. McKELVEY, 1986). Cr vs. Ir (Text-Fig. 12) shows a similar relation, as does the more limited data for Ni vs. Ir.

Three samples from our upper Ir high were also analyzed by RNAA for Au (M. ATTREP et al., this volume), giving Au/Ir = 16, 30 and 56 (wt). This is more like the ratios found in mid-ocean ridge basalts (J.H. CROCKET, 1981) or kimberlites (summarized by D.K. PAUL et al., 1979) than in chondrites (J.T. WASSON, 1985), K/T boundary clays (summarized in M.A. NAZAROV et al., 1988: Au/Ir = 0.26:0.04) or manganese nodules (R.C. HARRISS et al., 1968).

7.6 Rare Earth Elements

Text-Fig. 10C displays the variation of Ce*+La* (normalized to the North American Shale Composite: L.P. GROMET et al., 1984) through the critical boundary interval (M. ATTREP et al., this volume). The most notable feature is the minimum of this ratio, about 0.5, in the oxidized but metal-bearing interval just below the lower anomaly of \( \delta^{13}C \) and Ir. This low ratio of Ce*+/La* is characteristic of a generally oxidized state of sea water (J. WRIGHT et al., 1987) and suggests that the REE and perhaps some of the metals concentrated in this zone, were derived from sea water. Immediately above this zone, where Ir and pyrite are concentrated in a reducing zone, Ce*+/La* rises as expected to a high value of about 1.0. However, the low of Ce*+/La* is mainly owing to an increase of La/Al; and the ratio of heavy to light REE (Yb/La and Lu/La) is also high in this interval (M. ATTREP et al., this volume). The probable interplay of detrital compositions with sea-water diagenesis makes the interpretation of the REE data somewhat ambiguous in this local occurrence.

8. A Model for Chemical Changes Across the P/Tr Boundary

The wide variety of mechanisms that have been proposed as the cause of the P/Tr extinctions have been reviewed recently by W.D. MAXWELL (1988), including sea-level regressions, fluctuations in oceanic salinity, temperature changes, trace-element poisoning, and of course bolide impacts. Our approach to the problem is to go directly to the geological and chemical evidence, and suggest a model that fits these lines of evidence as well as possible. Taking into consideration the evidence developed in this study, as well as related earlier studies (A. BAUD et al., 1989; W.T. HOLSER & M. MAGARITZ, 1987; W.T. HOLSER et al., 1988; M. MAGARITZ, 1989; M. MAGARITZ et al., 1988) we suggest the following model for changes that occurred in the environment across the P/Tr boundary. The argument may be followed in the outline of Text-Fig. 13.

The closing stages of the Permian were characterized by one of the strongest regressions of the sea in the entire Phanerozoic (W.T. HOLSER & M. MAGARITZ, 1987), which may explain why part of the boundary beds is missing in most of the marine sections around the world. However, the thickness of the section in GK-1 yielding Hindeodus parvus (Text-Fig. 5) suggests that the Nassfeld area was favourably situated (on the broad inner shelf) to accumulate a rather complete representation of Early Griesbachian time. The entire sequence of chemical anomalies, starting with the drop in \( \delta^{13}C \) and ending with the upper anomaly of \( \delta^{13}C \), pyrite and metals, with a thickness of about 90 m, may have extended over 3 Ma or more (Text-Figs. 5, 7). Thus the chemistry of GK-1 provides a very detailed record that substantially constrains geochemical models.

The carbon isotope record indicates that a major shift in the carbon cycle was initiated early in the Dorasamian Stage of the Permian, based on evidence in sections across Tethys (Text-Fig. 7; A. BAUD et al., 1989). The drop in \( \delta^{13}C \) that began in GK-1 at least 50 m below the P/Tr boundary (Text-Fig. 6) indicates a net oxidation of the world reservoirs of organic carbon, as sea level dropped and exposed paralic and shallow shelves to erosion and oxidation. The \( \delta^{13}C \) profile in GK-1 (Text-Fig. 5) confirms an acceleration in the net rate of organic carbon oxidation as the boundary is approached that was previously seen at Tesero, Italy (M. MAGARITZ et al., 1988). At both Tesero (C. BROGLIO LORIGA et al., 1988) and in GK-1 (Text-Fig. 4) the occurrence of oolites suggests that the sea had withdrawn to nearly expose these parts of the Tethys shelf.

In response to this proposal (W.T. HOLSER et al., 1989) R.A. BERNER (1989) suggested that alternatively the net loss of organic carbon could be attributed to increasing aridity at the end of the Permian, which inhibited the deposition of organic carbon on the continents. BERNER concludes his note by observing that "it is not clear what brought about this climate change". We have previously remarked a close correspondence between the Late Permian fall of \( \delta^{13}C \) and the retreat of the sea (W.T. HOLSER & M. MAGARITZ, 1987) and would still prefer this as a proximate cause of organic carbon decrease that is observed rather than inferred. It may be that the emersion of the continents was also responsible for changes of atmospheric circulation that caused increased aridity – climate change, exposure to erosion, and reduction of shallow water habitats all may have worked together to decrease the standing stocks of organic carbon and \( \delta^{13}C \).

A sharp change to anoxic conditions is evident at the top of Unit 2 by the appearance of pyrite and high S/C. The inception of anoxia, as \( \delta^{13}C \) was dropping through zero for the first time, was marked by concentrations of Ir and other metals, and the maximum of the anoxic zone corresponds to the initial minimum in the profile of \( \delta^{13}C \). A similar sequence is repeated during a minimum of \( \delta^{13}C \) at the top of Unit 3A (185.6 m), with a second concentration of iridium, metals and sulfide. The two anomalies differ in detail. But both the minima

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in $\delta^{13}C$ and the accompanying metal concentrations are unique events in at least this part of the Permian-Triassic section – there is no hint of another metallic anomaly in any of the other shaly interbeds, all fifty of which were analyzed in this program.

The oxidation of a large store of organic carbon at the end of the Permian would tend to raise the carbon dioxide and reduce the oxygen content of the atmosphere/ocean system. Calculation of the extent of this shift in atmospheric composition is beyond the scope of this paper, but other modelling suggest that it would be substantial (R.A. BERNER, 1987, 1989; R.A. BERNER & D.E. CANFIELD, 1989; J.F. KASTING et al., 1986; L.R. KUMP & R.M. GARRELS, 1987). The association that we infer, of raised atmospheric CO$_2$ during the strong P/Tr regression, is opposite to the theoretical model of F.T. MACKENZIE (e.g. 1990; F.T. MACKENZIE & J. PIGGOT, 1981) which postulates a high input of CO$_2$ to the atmosphere during his "submergent phase". But we believe that the MACKENZIE model is not consistent with the observations of sea level and stable isotopes in the geological record of the Lower Triassic.

The rise in pCO$_2$ would raise surface temperatures. Such a rise is supported by our tentative interpretation that the drop in $\delta^{18}O$ is real, and not a diagenetic effect; if so, the rise in temperature may have been about 6 degrees (W.T. HOLSER et al., 1989).

A sharp rise in temperature would decrease the solubility of gases in the world ocean. This would exacerbate the increase of atmospheric pCO$_2$. But – even more important – it would further decrease the content of dissolved O$_2$ in deep ocean waters, already wasted by the long-term oxidation of organic carbon. This would increase the width and shallow the depth of the deep-sea oxygen-minimum zone that was prevalent for much of the Paleozoic (W.D. GOODFELLOW, 1987; P. WILDE & W.B.N. BERRY, 1982). The changed ocean-atmosphere system may have also been more susceptible to the replacement of an Early Permian post-glacial circulation in the deep sea by a reverse circulation of warm salty bottom water (G. BRASS et al., 1982), although we do not yet see direct evidence of such a reversal. In contrast, K. MALIKOSKI et al. (1988) suggest that the Late Paleozoic oceanic anoxia was completely erased at the end of the Permian, converting an "overfed ocean" to a "hungry ocean", well ventilated by good deep-sea circulation.

A minimum zone of $\delta^{13}C$ at the base of the Early Triassic has been verified on a global scale. The other chemical changes that we see in GK-1 – high iridium,
other metals and sulfide — are certainly an important local signal, although they have not yet been found elsewhere. Whether they are local or worldwide, why have these chemical changes followed so closely upon the primary and worldwide shifts of the carbon cycle? The explanation may be that both the carbon isotope shift and the chemical changes were caused by the same regression of sea level, which first exposed organic carbon to oxidation and finally brought about anoxic conditions to precipitate metals in at least this part of the Tethys Sea. This all makes some sense if increased erosion of upraised red beds and volcanics (G. G. Oni et al., 1988) now exposed west of Bolzano (Text-Fig. 2) had brought metals into solution, to be finally reprecipitated when contacting the anoxic waters that had been generated in Tethys. Alternatively, the metals may have been dissolved from the red beds of the underlying Gröden Formation, and precipitated at an oxidation/reduction interface. Accumulation of metals may have been aided by algae (B.B. Dyer et al., 1989; N.F. Hurley & R. Van der Voo, 1990) whose presence is indicated by the lamellar textures seen in this interval (W.T. Holser, this volume). In a larger context, metal anomalies might have occurred only in those local basins where there was a simultaneous delivery into shallow sediments of metals from the hinterland and sulfide from the anoxic depths of the ocean.

9. Origin of the Permian/Triassic Regression

A common thread in the previous discussion leads back to the P/Tr regression-transgression as a proximate driving force. The obvious next question is, "what is the cause of the P/Tr regression?" This question has troubled geologists for some time (D.T. Donovan & E.J.W. Jones, 1979). A recent review (W. T. Holser & M. Magaritz, 1987) concluded that the P/Tr regression-transgression did not fit the criteria for a glacial origin, nor for an origin in the thermal expansion and contraction of mid-ocean ridges, and that other postulated origins were even more inadequate. The Late Paleozoic continental glaciation was already waning at the beginning of Early Permian time, and by mid-Permian all traces had disappeared, with the exception of Kazanian diamictites in the exotic Kolyma terrane (O.G. Epshteyn, 1981; S.M. Stanley, 1988). Glacial cycles have periods of x\(10^4\) a, whereas the time constant for the thermal cooling of mid-ocean ridges is x\(10^7\) a. The P/Tr regression was mostly accomplished in one or two stratigraphic stages, and may have come back even faster (W.T. Holser & M. Magaritz, 1987), perhaps in x\(10^8\) a. Thus we were left with a number of fast and large regressions (including P/Tr) within the long non-glacial intervals, and no feasible explanation.

This dilemma has possibly been resolved by a new tectonic model proposed by L.M. Cathles & A. Hallam (1991). The mechanism involves an initial worldwide regression consequent to the rifting of an elastically stretched plate (anywhere in the world). The elastic retraction of the rifted plate with delayed flow of mantle material from under the rifted plate to fill the rift, produces a worldwide regression followed by a transgression. Both of these processes are calculated to have time constants of the order of 30 ka, and a typical model calculation shows a regression peaking at -45 m in less than 20 ka followed by a transgression nearly as fast. The rifting that was the ultimate cause of the regression-transgression could have been anywhere: e.g., on the western edge of the Siberian Platform (R.M. Demenitskaya & S.V. Aplonov, 1988) associated with the Siberian Traps, or on the Tethyan margin of the India plate, associated with the Panjal Traps (A. Baud, J. Marcoux & G. Stampfli, 1989). This model for a non-glacial global regression-transgression couplet is somewhat faster and shallower than our evaluation of the P/Tr eustatic event, but it comes closer to explaining the P/Tr event than any other proposal. Further implications will be discussed elsewhere.

10. The Gartnerkofel Results in the Context of a Bolide Impact

The introductory chapter (W.T. Holser & H.P. Schönlau, 1989; see also H.P. Schönlau, 1989) briefly reviewed the hypothesis of L.W. Alvarez et al. (1980) that the extinctions and other events at the K/T boundary were the direct or indirect results of an impact by a large meteor or comet. By extension, and particularly because of a postulated periodicity among mass extinction events (D.M. Raup & J.J. Sepkoski, 1986, 1988), an analogous impact origin has been implied for the P/Tr events. Without attempting to review all of the lines of evidence on which these two hypotheses are based, our results at Gartnerkofel have the following consequences for attribution of the P/Tr events to a bolide impact:

1. The record of the late Permian provides geological evidence that the regression, the extinction and the carbon isotope decline were spread smoothly over at least two stratigraphic stages. The complicated variations in carbon isotope ratio extended through much of the succeeding Griesbachian Stage of the Lower Triassic, as now demonstrated in the Gartnerkofel area (Text-FIG. 4). The total interval was about 3 Ma (Text-FIG. 7). An impact origin for this whole record is difficult to conceive both because of its length and because of its measured progression. Even comet showers (P. Hut et al., 1987) seem unlikely to have been so extended in time or so smooth in effect.

2. A similar deterioration of conditions in the Late Cretaceous (although not as clearly evident as that in the Late Permian) has been postulated in combination with a bolide impact that delivered the coup de grace at the K/T boundary. A. Hoffman (1989) has pointed out that a coincidental impact does have a finite probability in view of the uncertainties of timing involved, but in the P/Tr even more than in the K/T it would be difficult to sort out the relative importance of medium-term endogenous changes and the short-term impact. Probabilities indicate that we should call on such a coincidence only if our evidence for medium-term changes is matched by equally good independent evidence for an impact.

3. The two Ir peaks observed in GK-1, although clearly above background and unique in that section (Text-
The strongest argument for an impact at the K/T boundary is the wide dissemination of shocked quartz grains (B.F. Bohor et al., 1984). At Gartnerkofel the thin shaly beds associated with each of the two Ir peaks in the core and outcrop were searched for shocked mineral grains without result (W.T. Holser, this volume). Thin sections, and oil-immersion and SEM mounts of disaggregated shale were examined. However, the methods of concentration and etching that have been successfully used on K/T samples (B.F. Bohor et al., 1984) were not applied. Consequently there still remains a possibility that shocked grains have been overlooked at the P/Tr boundary.

A wide variety of microspherules have been recovered from K/T boundary sediments, and they have been a prominent but controversial part of the argument for an impact. At Gartnerkofel H.P. Schönlau recovered five microspherules in the processing of outcrop samples for conodonts (W.T. Holser, this volume). However, the chemistry of these spherules strongly indicates that they are an industrial contaminant inadvertently introduced on the outcrop or in the laboratory.

At the K/T boundary an intense episode of volcanism has been strongly urged as an alternative to an extraterrestrial impact (e.g., C.B. Officer & C.L. Drake, 1985). In the arguments outlined above – the extended and complex nature of the anomalies, the weak Ir signal, the low ratios of Ir to other metals, and the lack of shocked quartz and of microspherules – all are more consistent with a volcanic than with an extra-terrestrial event. Furthermore, the associated hights of As and Sb (M. Attrep et al., this volume) are more agreeable with volcanic than with meteoritic contributions. The direct evidence for a volcanic influence at the P/Tr boundary in the Carnic Alps is not very strong – some grains of olivine in heavy mineral separates, and some trace element ratios, as described in a previous section. Local volcanism is not very evident, even as compared with earlier Permian (G.G. Ori et al., 1988) or later Triassic (Anisian) times (T. Bechstadt et al., 1987; A. Castellarin et al., 1980). D.M. McLean (1985) and others have suggested that the enormous outpourings of the Siberian traps were responsible for a major input of volcanic gases and dust into the atmosphere, as a cause of the P/Tr extinctions. But detailed palynological studies indicate that only a minor initial phase of the Siberian traps was erupted in the Late Permian – most of the output was spread throughout the Early Triassic (L.G. Sukhov et al., 1966).

Our conclusion is that while an impact(s) at the P/Tr boundary cannot be completely excluded, at least until a more thorough search is made for shocked quartz grains, the other evidence weighs heavily against the participation of an impact in the complex events of the P/Tr.

11. The Permian Triassic Mass Extinction Event

The pervasive dolomitization of the section at Gartnerkofel, and possibly its primary sedimentary facies as well, make it unlikely that this area can be expected to contribute directly to the paleontological description of the mass extinction events. However, one point may be worth making. In describing conodont fauna at the P/Tr boundary in the classic Meishan section on the South China block (Text-Fig. 1), D.L. Clark et al. (1986) found a sharp decrease of conodont population in the Lower Triassic (a single fragment) relative to that in the immediately underlying Dorashamian (Changsingian) beds (300/kg). Clark interpreted this decrease as evidence of a general decline of conodont population at the close of Permian time. But although we do not yet have any good recovery from the Permian Bellerophon Formation just below the P/Tr boundary at Gartnerkofel, the overlying Griesbachian beds contain an abundant conodont fauna (H.P. Schönlau, this volume). Through the Griesbachian section the abundance of conodonts varies extremely widely and unpredictably, a characteristic for which conodont faunas are notorious. In the absence of other evidence of a truly impoverished fauna, we suggest that the low recovery from the Triassic of the Meishan section was simply a further example of this common variability.

The emphasis of our research and its results is on the geochemical and geological aspects of the boundary. These results may, however, contribute indirectly to the search for a cause of the P/Tr mass extinction. The diagram of Text-Fig. 13 indicates some causal routes by which various aspects of a regressive pulse may have contributed to the Permian/Triassic extinctions. The classical connection between regression and extinction, and the one most often called on, is that when regression drops below the continental shelf edge, the shallow shelf zone that is most prolific in ecological niches is substantially narrowed. This venerable theory has its critics among ecologists, who point
out that such drops in sea level do not change the width of the photic zone on volcanic islands of constant hypsometric slope, thus providing a refuge untouched by regression (D. JABLONSKI, 1986).

However, we can see in Text-Fig. 13 several ways in which regression may contribute less directly or through oceanic overturns, through the mobilization of toxic metals that had been concentrated in these sediments, or through the sequestering of phosphorous in suboxic or reducing sediments, or through the mobilization of toxic metals that had been concentrated in these sediments. The relative effectiveness of these causal routes defiling from rifting and regression is not yet clear. The task that now confronts us, is to unravel the P/Tr system that has been mapped by geochemistry and to illuminate the critical paths leading to extinction.

References


