

Geochemistry of the end-Permian extinction event in Austria and Italy: No evidence for an extraterrestrial component

Christian Koeberl* Department of Geological Sciences, University of Vienna, Althanstrasse 14, A-1090 Vienna, Austria

Kenneth A. Farley* Division of Geological and Planetary Sciences, MS 170-25, California Institute of Technology, Pasadena, California 91125, USA

Bernhard Peucker-Ehrenbrink* Department of Marine Chemistry and Geochemistry, Woods Hole Oceanographic Institution, Woods Hole, Massachusetts 02543-1541, USA

Mark A. Sephton* Planetary and Space Sciences Research Institute, Open University, Milton Keynes MK7 6AA, UK

ABSTRACT

The end-Permian mass extinction (251 Ma) was the largest in Earth's history, and the great extent of biospheric perturbation is recorded as dramatic shifts in carbon isotope ratios of sedimentary materials. Both terrestrial and extraterrestrial events are commonly invoked as causative mechanisms for the crisis, and the primary reason for the event remains the subject of controversy. Geochemical indicators sensitive to the influence of extraterrestrial material involve platinum group elements and osmium and helium isotope ratios. Analyses of extinction levels in two sections from Austria and Italy reveal no evidence of an extraterrestrial impact. The end-Permian crisis, it appears, was a homegrown catastrophe.

Keywords: Permian-Triassic boundary, impacts, mass extinctions, Os isotopes, He isotopes.

INTRODUCTION

The end of the Permian is associated with the largest mass extinction known in Earth history. Profound changes occurred in the marine and terrestrial biospheres, with the loss of 90% of marine species and 70% of land vertebrate species (cf. Benton and Twitchett, 2003, and references therein). Upper Permian sedimentary rocks record remarkable shifts in carbon isotope ratios, testifying to significant changes in oceanic and atmospheric chemistry (e.g., Holser et al., 1989). Traditionally these biological and chemical changes were thought to have occurred over a period of several million years (Holser et al., 1989). However, recent radiometric dating methods have constrained their duration to <165 k.y. (Bowring et al., 1998), making the end-Permian disturbances appear all the more dramatic.

The close association of the biological and chemical phenomena suggests a common cause. A variety of triggers for the end-Permian event have been proposed, including a period of extreme volcanism (Renne et al., 1995), catastrophic overturn or transgression (e.g., Wignall and Hallam, 1992) of a stagnant ocean, or rapid decomposition of a gas hydrate reservoir (e.g., Erwin, 1993). Following the recognition of a large-scale impact event associated with the Cretaceous-Tertiary (K-T) boundary and a possible causal link between that impact and the K-T mass extinction, speculations bloomed that other major mass extinctions—in particular, the end-Permian

event—might also be related to an impact event. However, so far the evidence in favor of such a proposal is controversial and inconclusive.

The extraterrestrial nature of siderophile element anomalies at some end-Permian locations (e.g., Holser et al., 1989; Retallack et al., 1998) still needs confirmation. Retallack et al. (1998) reported on the possible discovery of shocked quartz grains from end-Permian locations in Australia and Antarctica, but photographs of the putative shocked quartz grains are not convincing, and the statistics of what the authors cautiously call “planar features” are insufficient. Even these authors admitted that, in comparison to the K-T boundary, the evidence “yields only the scent of an impact” and that “the much more severe extinction at the close of the Permian demands evidence of a much larger impact if that were its primary cause” (Retallack et al., 1998, p. 982). Kaiho et al. (2001) reported sulfur isotope and chemical data for samples from the Meishan (China) end-Permian section. Koeberl et al. (2002) noted that none of the points raised by Kaiho et al. (2001) provides conclusive evidence of an impact event. Most recently, Basu et al. (2003) claimed that the presence of fresh fragments of chondritic meteorites (up to a few hundred micrometers in size) in samples from Graphite Peak, Antarctica, provides confirming evidence of an end-Permian impact event. However, it is unclear how such meteorite fragments could survive unaltered for ~250 m.y., when even larger meteorites were destroyed in both hot and cold deserts by weathering in fractions of that time period (e.g., Bevan et al., 1998, and references therein). In

addition, the placement of the end-Permian event at some locations studied by Retallack et al. (1998) is uncertain (Isbell and Askin, 1999).

This study was aimed at confirming the existence of Ir anomalies noted earlier in end-Permian samples and, if found, to determine whether they represent an extraterrestrial signature associated with an impact event.

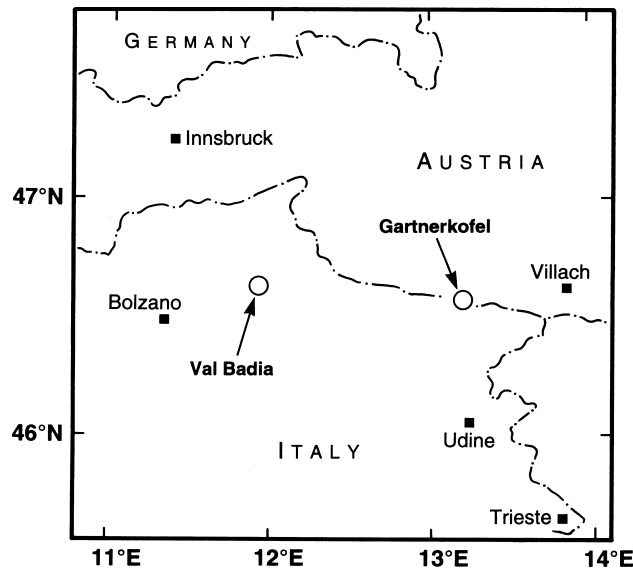
SAMPLES AND EXPERIMENTAL METHODS

Samples spanning the end-Permian event from two locations were analyzed for this study (Fig. 1), from drill core through the Gartnerkofel section in the Carnic Alps, southern Austria, and from the Val Badia section in the western Dolomites, northeast Italy. Both locations represent marine sites within the western Tethys (Fig. DR1¹). In terms of general stratigraphy, the uppermost Permian deposits in the area are represented by the Bellerophon Formation, which consists of limestones, dolomites, and evaporites deposited in a shallow-marine inner shelf or lagoon in the western Tethys Ocean (e.g., Hallam and Wignall, 1999). The Bellerophon Formation is overlain by the Tesero Oolite Horizon, the laterally widespread basal unit of the Werfen Formation, which is an oolitic grainstone thought to have been deposited almost synchronously throughout the Southern Alps during a rapid marine transgression. The Tesero Oolite Horizon is overlain by the fine-grained marly limestones of the Mazzin Member, which were deposited in a distal deep-water setting. Details on the Austrian and Italian locations (including carbon isotope data) were given by Holser and Schönlaub (1991) and Sephton et al. (2002), respectively. On the basis of cyclostratigraphic studies, sedimentation rates for the Gartnerkofel section have been estimated as ~10 cm/k.y. (Rampino et al., 2002), a rate within the range suggested for

¹GSA Data Repository item 2004166, Figures DR1–DR2 and Tables DR1–DR3, is available online at www.geosociety.org/pubs/ft2004.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301-9140, USA.

*E-mails: christian.koeberl@univie.ac.at; farley@gps.caltech.edu; behrenbrink@whoi.edu; m.a.sephton@open.ac.uk.

Figure 1. Locations of Gartnerkofel (Austria) and Val Badia (Italy) Permian-Triassic boundary sites.



the end-Permian sedimentary sequences in the Italian Dolomites (Magaritz et al., 1988).

Historically, the contact between the Bellerophon Formation and Werfen Formation has been taken to indicate the boundary between the Permian and the Triassic, which also agrees with the biostratigraphic and chemostratigraphic indicators of the crisis. Paleontologically, however, the first appearance of the conodont *Hindeodus parvus* is currently recommended to mark the onset of the Triassic. At our locations, this first appearance places the Permian-Triassic boundary in the base of the Mazzin Member, implying that the crisis—as shown by the formation boundary—occurred before, not at, the Permian-Triassic boundary as currently defined.

The samples were analyzed for Ir abundances by the highly sensitive multiparameter γ - γ coincidence spectrometry method (Koeberl and Huber, 2000) and for Os isotope composition and abundances of platinum group elements (Hassler et al., 2000). In addition, He concentration and isotope compositions (Table DR3; see footnote 1) were measured on 18 samples from the Gartnerkofel core.

SEARCH FOR EXTRATERRESTRIAL SIGNATURE

The detection of an extraterrestrial component in melt rocks or breccias as well as ejecta layers can be of diagnostic value and provide confirming evidence for an impact origin of a geologic structure. During impact, a small amount of the finely dispersed meteoritic melt (droplets) or vapor is mixed with a much larger quantity of target-rock vapor and melt. This mixture later forms impact melt rocks, melt breccias, or impact glass. In most cases, the contribution of meteoritic matter to these impactite lithologies is very small, leaving only subtle geochemical signatures.

The detection of small amounts of meteor-

itic matter within the crustal compositional signature of the target rocks is difficult (e.g., Koeberl, 1998). Only elements that have high abundances in meteorites, but low abundances in terrestrial crustal rocks (e.g., siderophile elements, noble gases), are useful. Most meteorites have high siderophile element contents; however, it is also necessary to reliably constrain the target-rock contribution of such elements. Commonly determined are the concentrations and interelement ratios of siderophile elements, especially the platinum group elements (PGEs), which are several orders of magnitude more abundant in most meteorites than in terrestrial upper-crustal rocks.

Iridium is most often determined as a proxy for all PGEs, because it can be measured with the best detection limit of all PGEs by neutron activation analysis.

However, Ir and other PGEs are, under certain conditions, mobile and can also be concentrated by purely terrestrial processes (e.g., Colodner et al., 1992). In such cases, the Re-Os isotope system can be used to establish the presence of a meteoritic component. The use of this method is based on the fact that the $^{187}\text{Os}/^{188}\text{Os}$ ratios of meteorites (and mantle rocks) and terrestrial crustal rocks are significantly different. As a result of the high Re and low Os concentrations in old crustal rocks, their $^{187}\text{Os}/^{188}\text{Os}$ ratio has increased rapidly with time (average upper-crustal $^{187}\text{Os}/^{188}\text{Os} \approx 1$). In contrast, meteorites have low $^{187}\text{Os}/^{188}\text{Os}$ ratios of ~ 0.11 – 0.18 ; even the addition of a small ($\ll 1\%$) meteoritic component to terrestrial rocks would result in a drastic change of the $^{187}\text{Os}/^{188}\text{Os}$ ratio (Koeberl and Shirey, 1997).

RESULTS

Patterns of Ir abundance are similar at Gartnerkofel and Val Badia (Figs. 2 and 3; Table DR1 [see footnote 1]). Background values of <100 ppt are interrupted by at least two maxima, the youngest of which is the greater and reaches 216 ppt at Gartnerkofel and 242 ppt at Val Badia. The Gartnerkofel data are in good agreement with previously reported data reported by Holser et al. (1989) and Holser and Schönlaub (1991).

At Val Badia, the maximum Ir level is fol-

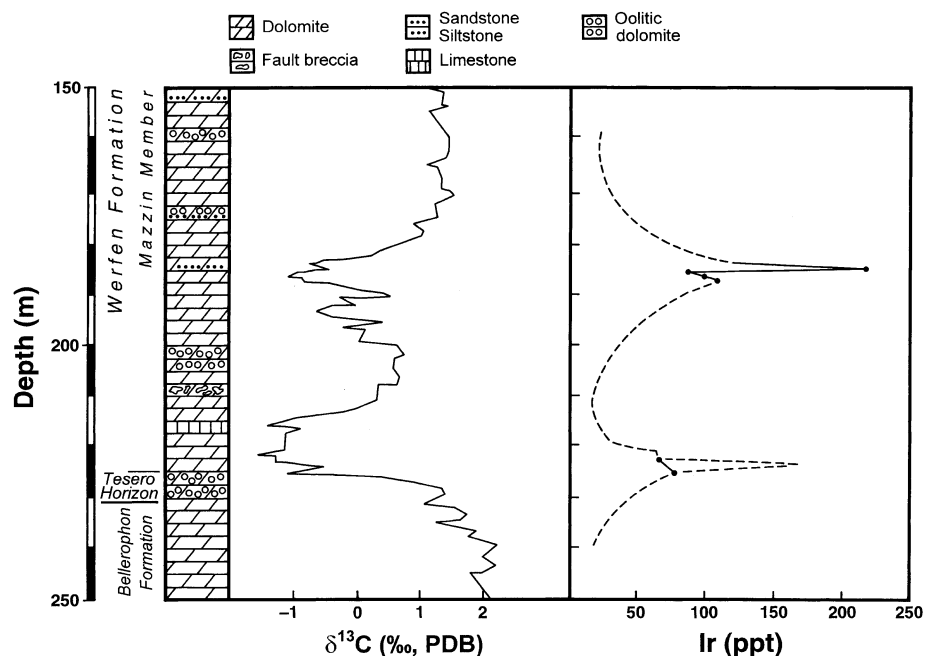


Figure 2. Plots of $\delta^{13}\text{C}$ (after Holser and Schönlaub, 1991; PDB—Peedee belemnite) and Ir abundance data (dashed parts of line after Holser et al., 1989) for Gartnerkofel (Austria) Permian-Triassic section. Lithostratigraphy is shown on left.

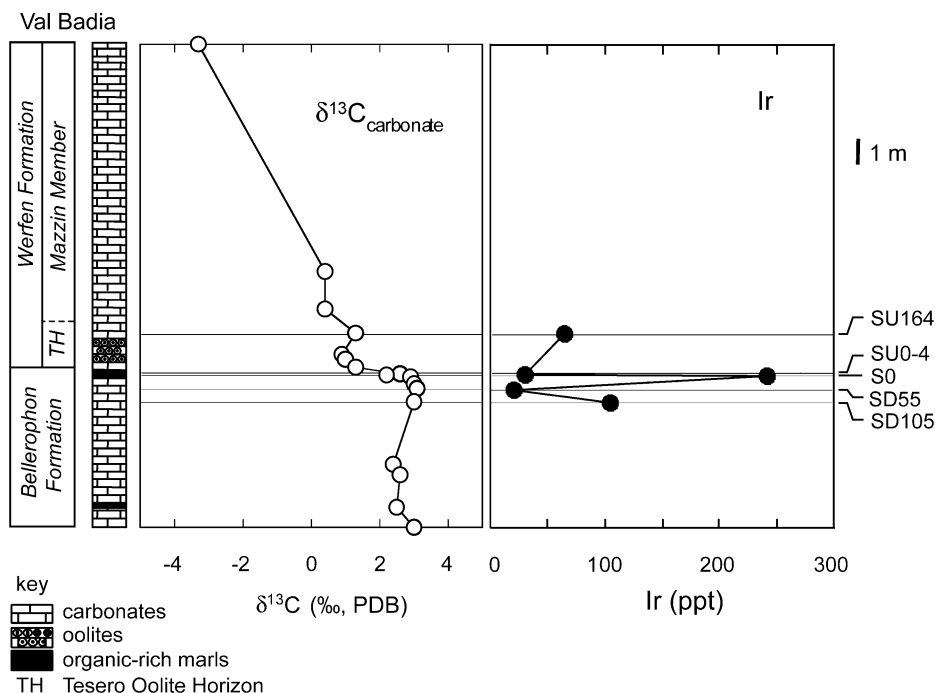


Figure 3. Plots of $\delta^{13}\text{C}$ (after Sephton et al., 2002; PDB—Peedee belemnite) and Ir abundance data for Val Badia (Italy) Permian-Triassic section. Lithostratigraphy is shown on left.

lowed by a dramatic shift to more negative $\delta^{13}\text{C}$ values for both marine carbonates and molecular fossils of land plant cuticles (alkanes) that is associated with the end-Permian crisis (Sephton et al., 2002). Thus, the presence of an Ir anomaly in close association with the end-Permian extinction, e.g., as noted by Holser et al. (1989) and Retallack et al. (1998), is confirmed. However, the extent of the Ir anomaly is very small compared to that observed at the K-T boundary (but only slightly less than values observed for the layers formed during the late Eocene impact).

To determine whether the Ir in the end-Permian samples represents an extraterrestrial signature, we determined the $^{187}\text{Os}/^{188}\text{Os}$ ratios as well as Re, Os, Ir, Ru, Pd, and Pt concentrations for a subset of samples. The results show that initial $^{187}\text{Os}/^{188}\text{Os}$ ratios for the Val Badia samples are significantly more radiogenic than average upper crust. This probably reflects open-system behavior and loss of Re and/or addition of Os after deposition of the organic-rich sediments. Such sediments are characterized by high Os/Ir and $^{187}\text{Re}/^{188}\text{Os}$ ratios typically >250 . Gartnerkofel samples have much less radiogenic initial $^{187}\text{Os}/^{188}\text{Os}$ ratios (0.4–0.6), comparable to Cenozoic seawater. Though the $^{187}\text{Os}/^{188}\text{Os}$ ratios of end-Permian seawater have not yet been reconstructed, it is possible that the initial ratios of 0.45–0.58 for the Gartnerkofel samples represent the $^{187}\text{Os}/^{188}\text{Os}$ ratios of contemporaneous seawater. The sample with the highest PGE concentration has negative initial $^{187}\text{Os}/^{188}\text{Os}$ ratios indicative of Re addition or Os

loss after deposition (Table DR2; see footnote 1). On the basis of the high $^{187}\text{Re}/^{188}\text{Os}$ ratios (1022), this sample also appears to have been deposited under reducing conditions. The abundance ratios of the measured PGEs are variable and entirely nonchondritic.

Helium data are listed in Table DR3 (see footnote 1); He concentrations ranged from a few tens to $\sim 1000 \times 10^{-9} \text{ cm}^3/\text{g}$ (standard temperature and pressure, STP), except for a single sample that had $\sim 4000 \times 10^{-9} \text{ cm}^3/\text{g}$ (STP). In general there is a good correlation between ^4He content and the fraction of acid-insoluble residue in the sample (Fig. DR2A; see footnote 1). This correlation is consistent with the presence of radiogenic helium within detrital minerals, such as clays and possibly zircons, in these rocks.

The ^3He contents are all very low, $< 2 \times 10^{-15} \text{ cm}^3/\text{g}$ (STP); most samples are an order of magnitude lower. The $^3\text{He}/^4\text{He}$ ratios span an order of magnitude, from 6×10^{-8} to 6×10^{-9} . As shown in Figure DR2B (see footnote 1), these values are typical for purely terrestrial helium in which ^3He is produced from neutron reactions on ^6Li . Thus, there is no evidence for extraterrestrial He in these samples, as proposed by, e.g., Poreda and Becker (2003).

DISCUSSION

The level that approximates the peak in Ir contains evidence of local anoxia at both Val Badia and Gartnerkofel. This observation is important because elevated Ir, Os, Pt, and Re concentrations can be produced in anoxic de-

positional environments (Colodner et al., 1992). At Val Badia, Cirilli et al. (1998) recognized an increase in the amount of amorphous organic matter at the base of the Tesero Horizon, whereas at Gartnerkofel, Holser et al. (1989) documented framboidal pyrite and high cerium to lanthanum ratios, indicating oxygen-poor conditions. Although Val Badia and Gartnerkofel sedimentary rocks record relatively local conditions within the Tethys Ocean, there is also evidence of more widespread anoxia in the hemispheric Panthalassan Ocean at that time. Isozaki (1997) recognized framboidal pyrite and other reduced minerals in end-Permian pelagic cherts from Panthalassa that had been preserved in Jurassic accretionary wedges in Japan and Canada. This evidence suggests that the widespread development of anoxia may explain the anomalous PGE concentrations in end-Permian marine sedimentary rocks. Such an interpretation is supported by nonchondritic PGE abundance ratios and the lack of low initial $^{187}\text{Os}/^{188}\text{Os}$ ratios, all of which point to a terrestrial origin of the PGE anomaly.

The peak in Ir and drop in $\delta^{13}\text{C}$ values also point to a proliferation of fungal remains thought to represent the response of the terrestrial ecosystem to acidifying emissions of the Siberian Traps (Visscher et al., 2004). This volcanic event would have released large amounts of carbon dioxide to the atmosphere, generating global warming, a reduction of the solubility of oxygen in seawater, and less vigorous oceanic circulation, conditions that would promote oceanic anoxia (e.g., Wignall and Twitchett, 1996). Hence it is possible that the biotic crisis, decline in $\delta^{13}\text{C}$, and elevated Ir concentrations may all be ultimately linked to massive end-Permian volcanism (cf. Maruoka et al., 2003).

The most important observation regarding the He data is the lack of evidence for extraterrestrial helium. The ^3He concentration is in all cases at or below reasonable estimates for nuclear production (Fig. DR2B; see footnote 1). By assuming that all measured ^3He is from the sample (rather than the blank) and is not derived from nuclear processes, we obtain a firm upper limit on the mean extraterrestrial ^3He concentration in these samples of $\sim 0.01 \text{ pcc/g}$.

The concentration of interplanetary dust particle-hosted ^3He in sediment samples is governed by the relationship $[^3\text{He}] = fR/\alpha$, where f is the flux from space, α is the sediment mass-accumulation rate, and R is an unknown retention parameter that accommodates diffusive and diagenetic loss of He. On the basis of this relationship the absence of extraterrestrial ^3He in these samples may be explained in one or more of the following ways:

1. The sedimentation rate estimated for

these samples is ~ 10 cm/k.y. (Rampino et al., 2002). Coupled with a density of 2.5 g/cm^3 , this rate yields $\alpha = 25 \text{ g/cm}^2/\text{k.y.}$ Ignoring possible diagenetic loss (i.e., $R = 1$), we obtain a maximum extraterrestrial ^3He flux of $\sim 0.24 \text{ pcc/cm}^2/\text{k.y.}$ This is just 24% of the modern value and is mostly lower than is observed in rocks deposited at any time in the Cenozoic, Cretaceous, or Ordovician.

2. Alternatively, this sedimentation-rate estimate may be incorrect. The mean flux measured throughout all time obtained by simply averaging all available data is $\sim 0.5 \text{ pcc/cm}^2/\text{k.y.}$ If this were the actual flux at the time of the Permian-Triassic boundary, then the sedimentation rate must have been at least two times higher than has been estimated, again assuming quantitative extraterrestrial ^3He retention.

3. Although long-term preservation of extraterrestrial ^3He has been suggested on the basis of high extraterrestrial ^3He concentrations in Cenozoic, Cretaceous, and Ordovician rocks, it is possible that the Gartnerkofel samples were subjected to more extreme conditions, which promoted ^3He loss from the interplanetary dust particles. Such conditions might include high temperatures or extensive chemical alteration. Optical and molecular maturity parameters from the Val Badia section suggest that temperatures of at least 100°C were achieved following burial (Sephton et al., 1999).

CONCLUSIONS

We attempted to confirm the presence of an Ir anomaly associated with the end-Permian crisis by using samples from two well-studied locations in Austria (Gartnerkofel, Carnic Alps) and Italy (Val Badia, Dolomites). Elevated Ir contents to ~ 0.24 ppb were found. Additional PGE determinations and, for the first time, $^{187}\text{Os}/^{188}\text{Os}$ measurements revealed that these anomalies lack the characteristics of a large extraterrestrial impact. The elevated element concentrations can be explained by the reducing nature of the sediments deposited at the boundary. The absence of an extraterrestrial component is confirmed by He data. The weak and inconsistent evidence for an extraterrestrial impact event marking the end-Permian extinction event needs to be reevaluated.

ACKNOWLEDGMENTS

This work was supported by the Austrian Science Foundation, project Y58-GEO, the United Kingdom Particle Physics and Astronomy Research Council (PPARC), and the U.S. National Science Foundation. Peucker-Ehrenbrink thanks T. Abbruzzese and D. Schneider (Woods Hole Oceanographic Institution In-

ductively Coupled Plasma Facility) for analytical assistance. We are grateful to G. Retallack, J. Smit, and P. Wignall for constructive reviews.

REFERENCES CITED

- Basu, A.S., Petaev, M.I., Poreda, R.J., Jacobsen, S.B., and Becker, L., 2003, Chondritic meteorite fragments associated with the Permian-Triassic boundary in Antarctica: *Science*, v. 302, p. 1388–1392.
- Benton, M.J., and Twitchett, R.J., 2003, How to kill (almost) all life: The end-Permian extinction event: *Trends in Ecology and Evolution*, v. 18, p. 358–365.
- Bevan, A.W.R., Bland, P.A., and Jull, A.J.T., 1998, Meteorite flux on the Nullarbor region, Australia, in Grady, M.M., et al., eds., *Meteorites: Flux with time and impact effects*: Geological Society [London] Special Publication 140, p. 59–73.
- Bowring, S.A., Erwin, D.H., Jin, Y.G., Martin, M.W., Davidek, K., and Wang, W., 1998, U/Pb zircon geochronology and tempo of the end-Permian mass extinction: *Science*, v. 280, p. 1039–1045.
- Cirilli, S., Pirini Radrizzani, C., Ponton, M., and Radrizzani, S., 1998, Stratigraphical and palaeoenvironmental analysis of the Permian-Triassic transition in the Badia Valley (Southern Alps, Italy): *Palaeogeography, Palaeoclimatology, Palaeoecology*, v. 138, p. 85–113.
- Colodner, D.C., Boyle, E.A., Edmond, J.M., and Thomson, J., 1992, Post-depositional mobility of platinum, iridium and rhenium in marine sediments: *Nature*, v. 358, p. 402–404.
- Erwin, D.H., 1993, *The great Palaeozoic crisis: Life and death in the Permian*: New York, Cambridge University Press, 327 p.
- Hallam, A., and Wignall, P.B., 1999, Mass extinctions and sea-level changes: *Earth-Science Reviews*, v. 48, p. 217–250.
- Hassler, D.R., Peucker-Ehrenbrink, B., and Ravizza, G.E., 2000, Rapid determination of Os isotopic composition by sparging OsO_4 into a magnetic-sector ICP-MS: *Chemical Geology*, v. 166, p. 1–14.
- Holser, W.T., and Schönlaub, H. P., eds., 1991, *The Permian-Triassic boundary in the Carnic Alps of Austria (Gartnerkofel region)*: Wien, Abhandlungen der Geologischen Bundesanstalt, v. 45, 232 p.
- Holser, W.T., Schönlaub, H.P., Attrep, M., Jr., Boeckelmann, K., Klein, P., Magaritz, M., Orth, C.J., Fenninger, A., Jenny, C., Kralik, M., Mauritsch, H., Pak, E., Schramm, J.M., Stattegger, K., and Schmöller, R., 1989, A unique geochemical record at the Permian-Triassic boundary: *Nature*, v. 337, p. 39–44.
- Isbell, J.L., and Askin, R.A., 1999, Search for the evidence of impact at the Permian-Triassic boundary in Antarctica and Australia: *Comment: Geology*, v. 27, p. 859.
- Isozaki, Y., 1997, Permo-Triassic boundary superanoxia and stratified superocean: Records from lost deep sea: *Science*, v. 276, p. 235–238.
- Kaiho, K., Kajiwar, Y., Nakano, T., Miura, Y., Kawahata, H., Taziki, K., Ueshima, M., Chen, Z., and Shi, G.R., 2001, End-Permian catastrophe by bolide impact: Evidence of a gigantic release of sulfur from the mantle: *Geology*, v. 29, p. 815–818.
- Koerberl, C., 1998, Identification of meteoritic components in impactites, in Grady, M.M., et al., eds., *Meteorites: Flux with time and impact effects*: Geological Society [London] Special Publication 140, p. 133–152.
- Koerberl, C., and Huber, H., 2000, Optimization of the multiparameter-coincidence spectrometry for the determination of iridium in geological materials: *Journal of Radioanalytical and Nuclear Chemistry*, v. 244, p. 655–660.
- Koerberl, C., and Shirey, S.B., 1997, Re-Os systematics as a diagnostic tool for the study of impact craters and distal ejecta: *Palaeogeography, Palaeoclimatology, Palaeoecology*, v. 132, p. 25–46.
- Koerberl, C., Gilmour, I., Reimold, W.U., Claeys, P., and Ivanov, B.A., 2002, End-Permian catastrophe by bolide impact: Evidence of a gigantic release of sulfur from the mantle: *Comment: Geology*, v. 30, p. 855–856.
- Magaritz, M., Bär, R., Baud, A., and Holser, W.T., 1988, The carbon-isotope shift at the Permian/Triassic boundary in the southern Alps is gradual: *Nature*, v. 331, p. 337–339.
- Maruoka, T., Koerberl, C., Hancox, P.J., and Reimold, W.U., 2003, Sulfur geochemistry across a terrestrial Permian-Triassic boundary section in the Karoo Basin, South Africa: *Earth and Planetary Science Letters*, v. 206, p. 101–117.
- Poreda, R.J., and Becker, L., 2003, Fullerenes and interplanetary dust at the Permian-Triassic boundary: *Astrobiology*, v. 3, p. 75–90.
- Rampino, M.R., Prokoph, A., Adler, A.C., and Schwindt, D.M., 2002, Abruptness of the end-Permian mass extinction as determined from biostratigraphic and cyclostratigraphic analyses of European western Tethyan sections, in Koerberl, C., and MacLeod, K.G., eds., *Catastrophic events and mass extinctions: Impacts and beyond*: Geological Society of America Special Paper 356, p. 415–427.
- Renne, P.R., Zichao, Z., Richards, M.A., Black, M.T., and Basu, A.R., 1995, Synchrony and causal relations between Permian-Triassic boundary crises and Siberian flood volcanism: *Science*, v. 269, p. 1413–1416.
- Retallack, G.J., Seyedolali, A., Krull, E.S., Holser, W.T., Ambers, C.P., and Kyte, F.T., 1998, Search for evidence of impact at the Permian-Triassic boundary in Antarctica and Australia: *Geology*, v. 26, p. 979–982.
- Sephton, M.A., Looy, C.V., Veeffkind, R.J., Visscher, H., Brinkhuis, H., and de Leeuw, J.W., 1999, Cyclic diaryl ethers in a Late Permian sediment: *Organic Geochemistry*, v. 30, p. 267–273.
- Sephton, M.A., Looy, C.V., Veeffkind, R.J., Brinkhuis, H., de Leeuw, J.W., and Visscher, H., 2002, Synchronous record of $\delta^{13}\text{C}$ shifts in the oceans and atmosphere at the end of the Permian, in Koerberl, C., and MacLeod, K.G., eds., *Catastrophic events and mass extinctions: Impacts and beyond*: Geological Society of America Special Paper 356, p. 455–462.
- Smoliar, M.I., Walker, R.J., and Morgan, J.W., 1996, Re-Os ages of group IIA, IIIA, IVA and IVB iron meteorites: *Science*, v. 271, p. 1099–1102.
- Visscher, H., Looy, C., Collinson, M.E., Brinkhuis, H., Konijnenburg-van Cittert, J.H.A., Kürschner, W.M., and Sephton, M.A., 2004, Environmental mutagenesis during the end-Permian ecologic crisis: *National Academy of Sciences Proceedings*, doi: 10.1073/pnas/0404472101.
- Wignall, P.B., and Hallam, A., 1992, Anoxia as a cause of the Permian/Triassic extinction: Facies evidence from northern Italy and the western United States: *Palaeogeography, Palaeoclimatology, Palaeoecology*, v. 93, p. 21–46.
- Wignall, P.B., and Twitchett, R.J., 1996, Oceanic anoxia and the end Permian mass extinction: *Science*, v. 272, p. 1155–1158.

Manuscript received 23 June 2004

Revised manuscript received 30 August 2004

Manuscript accepted 30 August 2004

Printed in USA