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

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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 localities in Austria 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). Kairo 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 have survived 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. DR1). In terms of general stratigraphy, the uppermost Permian deposits in the area are represented by the Belleroophon 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 Belleroophon 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...
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 chem stratigraphic 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 $\gamma$-$\gamma$ 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 meteoritic 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 $^{187}$Os/$^{188}$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 $^{187}$Os/$^{188}$Os ratio has increased rapidly with time (average upper-crustal $^{187}$Os/$^{188}$Os $\approx 1$). In contrast, meteorites have low $^{187}$Os/$^{188}$Os ratios of $\sim 0.11-0.18$; even the addition of a small (<1%) meteoritic component to terrestrial rocks would result in a drastic change of the $^{187}$Os/$^{188}$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 Schönlau (1991).

At Val Badia, the maximum Ir level is fol-
lowed by a dramatic shift to more negative δ13C 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 187Os/188Os ratios as well as Re, Os, Ir, Ru, Pd, and Pt concentrations for a subset of samples. The results show that initial 187Os/188Os 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 187Re/188Os ratios typically >250. Gartnerkofel samples show that initial 187Os/188Os 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 187Re/188Os ratios typically >250. Gartnerkofel samples show that initial 187Os/188Os ratios are variable and entirely nonchondritic.

Helium data are listed in Table DR3 (see footnote 1); He concentrations ranged from a few tens to ~1000 × 10^-9 cm³/g (standard temperature and pressure, STP), except for a single sample that had ~4000 × 10^-9 cm³/g (STP). In general there is a good correlation between 3He 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 × 10^-15 cm³/g (STP); most samples are an order of magnitude lower. The 3He/4He 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-
these samples is $\sim 10$ cm/k.y. (Rampino et al., 2002). Coupled with a density of 2.5 g/cm$^3$, this rate yields $\alpha = 25$ g/cm$^2$/(k.y. Ignoring possible diagnostic loss (i.e., $R = 1$), we obtain a maximum extraterrestrial $^3$He flux of $\sim 0.24$ pcc/cm$^2$/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 $\sim 0.5$ pcc/cm$^2$/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 $^3$He retention.

3. Although long-term preservation of extraterrestrial $^3$He has been suggested on the basis of high extraterrestrial $^3$He concentrations in Cenozoic, Cretaceous, and Ordovician rocks, it is possible that the Gartnerkofel samples were subjected to more extreme conditions, which promoted $^3$He loss from the in-situ atmosphere. We are grateful to G. Retallack, J. Smit, and P. Wignall for constructive reviews.

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