The Permian-Triassic of the Gartnerkofel-1 Core (Carnic Alps, Austria):
Sulfur, Organic Carbon and Microspherules

By WILLIAM T. HOLSER*)

With 1 Text-Figure and 3 Plates

Contents

Zusammenfassung

Der Gehalt an Corg liegt generell unter 0,1 %, obwohl einige der Mergelproben bis zu 0,5 % kommen. Pyritischer Schwefel, allgemein um 0,05 %, ist weit verbreitet, aber zwei Zonen höherer Konzentration sind an negative Abweichungen von δ34S direkt oberhalb schwacher Iridium-Anomalien gebunden. Framboid-Texturen und δ34S-Gehalte im Pyrit weisen auf einen frühdiagenetischen Ursprung hin.

Bei der Probenaufbereitung auf Conodonten wurden einige Mikrosphären geborgen, die aber als anthropogene Verunreinigungen interpretiert werden.

Abstract
All marly interbeds as well as numerous samples of the dominantly dolomitic limestone core Gartnerkofel-1 were analyzed for organic carbon and pyritic (as well as minor soluble) sulfur. Corg is generally less than 0.1 %, although some of the marls are as high as 0.5 %. Pyritic sulfur, generally in the range 0.05 % is widely distributed, but two zones of higher concentration are associated with negative excursions of δ34S just above weak iridium anomalies. The framboidal texture and δ34S levels in the pyrite point to an early diagenetic origin.

A few microspherules were recovered from conodont preparations, but were judged to be man-made contaminants.

1. Introduction
Previous studies have noted that the clay beds associated with the Cretaceous/Tertiary [K/T] boundary contain enhanced levels of pyrite (Schmitz, 1988, 1990; Schmitz et al., 1988; Hansen et al., 1986, 1988; Jehanno, 1987) and organic carbon in the form of kerogen, charcoal and soot (Wolbach et al., 1985, 1989, 1990; Hansen et al., 1986, 1987, 1988; Schmitz, 1988). Some of the pyrite occurs as microspherules; other microspherules are composed of potassium feldspar (Smit & Klaiver, 1981; Montanari et al., 1983; Naslund et al., 1986; Izett, 1987; Jehanno et al., 1987; Kyte, 1990), spinel-group minerals (magnetite, spinel, ma-

*) Author's address: Prof. Dr. WILLIAM T. HOLSER, Department of Geological Sciences, University of Oregon, Eugen, OR 97403, USA.
gnesioferrite, chromite or ferrite) (Montanari et al., 1983; Smit & Kyte, 1984; Kyte & Smit, 1986; Hansen et al., 1986, 1988; Izett, 1987; Jehanno et al., 1987; Cisowski, 1988), goethite (Kyte & Smit, 1986; Hansen et al., 1986; Jehanno et al., 1987; Schmitz, 1988) and other alteration products (kaolinite, glauconite, goyazite, jarosite, apatite) (Montanari et al., 1983; Kyte & Smit, 1986; Naslund et al., 1986; Bohor et al., 1987; Izett, 1987; Jehanno et al., 1987; Schmitz, 1988; Cisowski, 1988). The occurrences of these minerals at the K/T boundary have been emphasized by most of the above authors as important evidence for their respective explanations of the accumulations of iridium and other trace elements and the sequence of events that accompanied then. Consequently it is of interest to compare some related data from the P/Tr boundary at Gartnerkofel with those from the more intensively studied K/T boundary.

2. Chemical Analyses for Sulfur and Carbon

Cuts of all samples were analyzed for total sulfur, total carbon, and for S and C soluble in 2N HCl, in a LECO infrared analyzer, as described by Klein (this volume). The results are given in Tables 5, 6 and 7 of Klein’s paper (this volume).

3. Organic Carbon

The acid treatment obviously dissolved all dolomite and calcite. The acid-insoluble residue of C is designated as “organic carbon”, \( C_{\text{org}} \), in accordance with traditional laboratory practice. From the point of view of organic geochemistry it includes both kerogen and “elemental carbon”, and the latter may include carbon soot as well as coal-like components and charcoal (Bach & Anders, 1989). The content of \( C_{\text{org}} \) was very low, less than 0.1 %, even in some of the marly inter-beds (prefix “S” in the tables of Klein, this volume), which in other cases ranged as high as 0.5 %. Such low levels of \( C_{\text{org}} \) are probably not suitable for the separation of the components of elemental carbon (Bach & Anders, 1989), and these separations have not yet been attempted on P/Tr materials. A suite of samples of the marl/shale interbeds from GK-1 was subjected to standard palynological extraction procedures (with HF), by Dr. R. Zetter, but failed to recover identifiable spore/pollen materials. A single sample (88450) of marl from the Reppwand outcrop section, in the Bellerophon Formation 4.2 m below the lower Ir-peak, was submitted to J.M. Hayes for a trial analysis of geoporphyrins (Hayes et al., 1989). Soxhlet extraction with organic solvents failed to recover any significant amount of soluble organic material. After most of the contributions to this volume were already in press, new analyses were completed on the carbon isotope ratio of the \( C_{\text{org}} \) in a selected group of 36 of the marly samples from GK-1 (Magaritz et al., submitted). Although rocks with such a low content of \( C_{\text{org}} \) are not usually studied by isotope analysis, the results were very consistent and make an interesting and critical complement to the isotope studies of the carbonate fraction described here by Magaritz & Holser (this volume). One important conclusion is that the \( C_{\text{org}} \) in the inter-beds of the core material is substantially unaltered by weathering.

4. Pyrite

The significant sulfur determination is total sulfur, \( S_{\text{tot}} \). Sulfur soluble in the 2N HCl etch, \( S_{\text{sol}} \), is calculated by difference, \( S_{\text{tot}} - S_{\text{ins}} \), and with the precision of individual sulfur analyses as low as 10 %, the soluble differences are probably not significant unless they amount to over 15 % of \( S_{\text{sol}} \). It also seems likely that
the precision may be even worse where \( S_{\text{tot}} < 0.1 \% \).

Only five samples (S101, S117, S118B, S190 and S193) had \( S_{\text{tot}} > 0.1 \% \) (KLEIN, this volume). In one of these (S118B) FENNINGER (this volume) found 4 \% gypsum by X-ray diffraction, and it seems likely that the \( S_{\text{tot}} \) in the other four samples, as well as in many of those showing lower levels of \( S_{\text{sol}} \), is also accounted for by HCl-soluble sulfate in gypsum. Two of the samples with high \( S_{\text{sol}} \) showed equal and low sulfur isotope ratios in soluble and insoluble fractions (PAK & HOLSER, this volume). This indicates that the sulfate is not primary as sulfate, but was a product of recent oxidation of (insoluble) sulfide, either by oxidizing ground waters or by air exposure after coring. A minor amount of the sulfate formed in this way may have been lost from the rock through solution in ground water. We cannot firmly preclude the presence, in some of the five samples, of minor amounts of the mineral pyrrhotite, FeS, which is soluble in HCl, but examined by polarization reflection microscopy of a polished slab of core from next to sample S117 showed only pyrite and no pyrrhotite. Consequently for our interest in primary and diagenetic geochemistry, \( S_{\text{sol}} \) represents \( S \) as pyrite; in diagenetic geochemistry, \( S_{\text{tot}} \) is the original amount of pyrite. Consequently for our interest in primary and diagenetic geochemistry, \( S_{\text{sol}} \) represents \( S \) as pyrite; in the few samples with high \( S_{\text{sol}} \) it may slightly underestimate the original amount of pyrite.

The data for \( S_{\text{sol}} \) in the GK-1 core (KLEIN, this volume) reveal a wide distribution of minor amounts of pyrite, at levels generally in the range of 0.05 \% pyrite. Two zones of higher concentration of 1–10 \% pyrite are evident at 185.5–185.6 and 215.1–222.2 m, in each case just above the narrow intervals of shaly material. It may slightly underestimate the original amount of pyrite.

### 5. Microspherules

In view of the prominent occurrence of microspherules of various compositions in the K/T boundary clay, and their importance in the interpretation of that bed as fallout from an impact or volcanic event (see references in introduction to this paper), a concerted search as made for any microspherules in the Gartnerkofel P/Tr section. Thin sections, polished sections and oil-immersion samples of the marly interbeds of both the GK-1 core and the outcrop section, especially those with enhanced levels of Ir and other trace elements, were scanned by microscopy, and fracture surfaces were studied by scanning electron microscopy. No microspherules were found in these whole-rock preparations, except for the pyrite (and oxidized pyrite) microspherules described above.

However, in the course of examining acid-insoluble residues of samples from the outcrop section for conodonts, SCHÖNLAUB (this volume) separated five microspherules. Each single example turned up in a residue from solution in acetic acid of a large (0.7 to 2 kg) sample of dolostone. The result was unexpected, and no particular precautions had been taken to minimize contamination from atmospheric fallout on the outcrop or in the laboratory.

Examined under a binocular microscope, the microspherules appeared nearly perfectly spherical. Four were shiny black and from 50 to 150 \( \mu \text{m} \) in diameter; the other was matte white and about 250 \( \mu \text{m} \) in diameter. They were studied further by SEM; then they were ground to about mid-section and polished for study by vertical optical illumination and electron microprobe. In the sectioning process one of the four black microspherules was lost.

The black microspherules display a beautiful dendritic texture, with branching conforming closely to the spherical surface (Pl. 2, Figs. 1–3). Evidently an origi-
nally spherical mass crystallized (or re-crystallized) into a single dendritic crystal – or perhaps several sub-parallel crystals. Plate 2, Fig. 2 displays 4-fold symmetry around an axis in the upper right. One of the black spherules showed up as a hollow shell on sectioning (Pl. 2, Figs. 4, 5), but the other two were solid at the level sectioned (Pl. 2, Fig. 6).

Six microprobe analyses of two spots on each of three black microspherules were very similar, with mean values FeO 69.6 ± 1.9, MnO 0.7 ± 0.3, Cr₂O₃ 0.13 ± 0.07 wt %, and with NiO and CoO undetected at <0.10 and <0.23 %, respectively. Two black spherules were also analyzed for other elements using a silicate standard. Although this standard was inappropriate for this mainly iron oxide composition, the detection of BaO at 0.17 ± 0.04 and Al₂O₃ at 0.12 ± 0.05 % may be qualitatively significant in view of fact that these two elements are the principal constituents of the white microspherule (see below).

The mean of the iron analyses, equivalent to 69.7 ± 1.5 wt % Fe, corresponds closely to the ideal composition of Fe₂O₃, 69.94 % Fe. The phase could be either hematite or maghemite, but the 4-fold symmetry of the dendritic texture, and a lack of optical anisotropy in polished section, indicates that cubic maghemite is more likely. Maghemite is usually a metastable oxidation alteration of magnetite, and the crystal form we are seeing in Plate 2 may indeed be simply pseudomorphic after an initial crystallization as magnetite.

In Plate 3, Figs. 1 and 2, the surface of the white microspherule displays a texture of crystallinity that is superficially similar to that of the black microspherules. On closer examination (Pl. 3, Fig. 2), and especially in polished section (Pl. 3, Fig. 3), the crystal form is seen to be a radial-acicular texture of elongate crystals.

Microprobe analysis (n = 5) of the white microspherule gives as main constituents only BaO and Al₂O₃, whose mole ratio Ba/(Ba + Al) = 0.0760 ± 0.0045 corresponds rather well to an ideal for BaO : 6Al₂O₃ of 0.0769. The analysis also shows traces of a few tenths percent of Ca, Si, and Sr. Ba : 6Al₂O₃ has not been found in nature, but is found in the synthetic system BaO – Al₂O₃, melting congruently at 1915°C (LEVIN, et al., 1964, Fig. 206). Its minimum eutectic melting point in this binary system is 1620°C, at 36 wt % BaO.

Neither neighboring phase in the binary system, Al₂O₃ nor BaO : Al₂O₃, was evident in the material analyzed. BaO : 6Al₂O₃ is probably isostructural with the well-known synthetic compound barium ferrite, a layer stacking of hematite and BaO units. The uniqueness, purity and extremely high melting point of this material strongly indicates that it is a contaminant from atmospheric fallout during collection or processing of the natural sample. Microspherules routinely encountered in atmospheric fallout are magnetite from welding sputter, Bessemer converter operation, or fly ash from coal-fired electrical generating plants or trash incinerators (McCRONE & DELLY, 1973). In the last decade, however, there has been a great increase in microparticulate debris from spacecraft, most of it rich in alumina (ZOLENSKY et al., 1989). The main sources of this material are solid rocket fuel exhaust, solid rocket motor ablation, and thermal reflective spacecraft paint. According to ZOLENSKY et al. (1989) the most commonly used paint is composed of micron-sized particles of alumina, titania, and ZnO, but the equally high melting points of compounds in the system Al₂O₃ suggests that such material might also be applied to spacecraft surfaces, and subsequently contribute to particulate atmospheric fallout.

Black iron oxide spherules similar to those described above from Gartnerkofel samples have a wide range of both natural and anthropogenic origins. Black iron oxide microspherules, including hollow structures, associated with the Permian-Triassic boundary in South China, have been variously ascribed to an origin from ablation of an impacting meteorite (GAO et al., 1989), volcanism (ZHANG et al., 1989) or mineralization of algal remains (HANSEN et al, 1989). But the possible detection of traces of Ba in those from Gartnerkofel suggests an unusual common, and therefore man-made, source for all of our microspherules, black and white. It does not seem useful to speculate further on the origin of the black microspherules, pending further collections of material, carefully controlled to minimize contamination.

6. Conclusions

Sulfide is concentrated in narrow zones of pyrite (oxidized in part) above trace metal peaks in the Gartnerkofel section. Its form as lamina composed mainly of frambooidal microspherules, intersected by stylolites, and its light sulfur isotope ratio, indicate deposition of the pyrite during early diagenesis. The moderate concentrations of Ir, Co, and Ni in the underlying bed were probably formed in a related reduction process, as postulated by SCHMITZ (1985) for the marine K/T boundary. Organic carbon is relatively low in concentration (a few tenths percent), relative to C/S ratios commonly encountered in marine rocks, but its isotope profile verifies a primary origin. A few microspherules picked from conodont preparations are likely a contaminant from atmospheric fallout.

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Photomicrographs in reflected light of textures in the pyrite bed at 185.55 m.

Fig. 1: Fine-grained pyrite in wavy-lamellar and disseminated texture; a few grains are cubic.

Fig. 2: Framboidal microspherules of pyrite, some with atoll texture.

Fig. 3: Microspherules of pyrite, with later stylolites.

Fig. 4: Sieve-textured aggregates and microspherules of pyrite.

Fig. 5: Well-developed atoll texture in pyrite.

Fig. 6: Atoll microspherules of pyrite intersected by later stylolite.

White: pyrite; light gray: hematite and goethite; dark gray: quartz; black: open space, or clay-rich stylolite.

Scale bars: 100 μm.
Plate 2

Images of black iron oxide microspherules.

Fig. 1: SEM image, illustrating dendritic single(-)crystal of maghemite, with branching conforming to the spheroidal shape of the grain.
Scale bar 100 µm.

Fig. 2: Magnified view of the same spherule as in Fig. 1.
Scale bar 100 µm.

Fig. 3: Further magnification of spherule surface, showing detail of crystallographic parallel dendrite branches.
Scale bar 10 µm.

Fig. 4: Photomicrograph by vertical illumination of a polished mid-section of the same spherule, showing hollow structure and crystallinity.
Scale bar 100 µm.

Fig. 5: Same as (D), at higher magnification.
Scale bar = 100 µm.

Fig. 6: Another black iron oxide spherule with no hollow center, but crystallinity similar to Fig. 1.
Scale bar 100 µm.
Plate 3

Images of white barium aluminate microspherule.

Fig. 1: SEM view of spherule, with surface crystallinity superficially similar to the iron oxide spherules in Plate 2. However, the texture of the surface reflects a randomly oriented acicular crystallinity, compared with the regular orientation of the dendritic branching of the black spherules.
Scale bar 100 μm.

Fig. 2: Acicular intergrowths evident on a closer examination of the surface.
Scale bar 10 μm.

Fig. 3: Polished mid-section of the white spherule, showing the radiating to randomly oriented crystal needles of barium aluminate.
Scale bar 100 μm.
References


