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The Permian-Triassic of the Gartnerkofel-1 Core (Carnic Alps, Austria): Sulfur Isotopes

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With 1 Text-Figure and 1 Table

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*Carinthia
Carnic Alps
Permian/Triassic Boundary
Sulfur Isotopes*

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Zusammenfassung

Die Schwefelisotopenuntersuchung von Pyriten ergab stark negative Werte, die aber für die jeweiligen Niveaus verschieden sind. Dies spricht für die syngenetische Herkunft der Sulfide. Zwei Gipsproben ergaben fast gleiche Werte wie die zugehörigen Pyritproben, woraus folgt, daß sie nicht etwa Evaporite, sondern Oxidationsprodukte des Pyrits sind.

Abstract

Sulfur isotope ratios in pyrite have high negative values characteristic of each level, confirming a syngenetic origin of the sulfide. Two samples of gypsum have high negative values corresponding to pyrite in the same samples, indicating that the gypsum is from oxidation of the pyrite and not an evaporite sediment.

1. Introduction

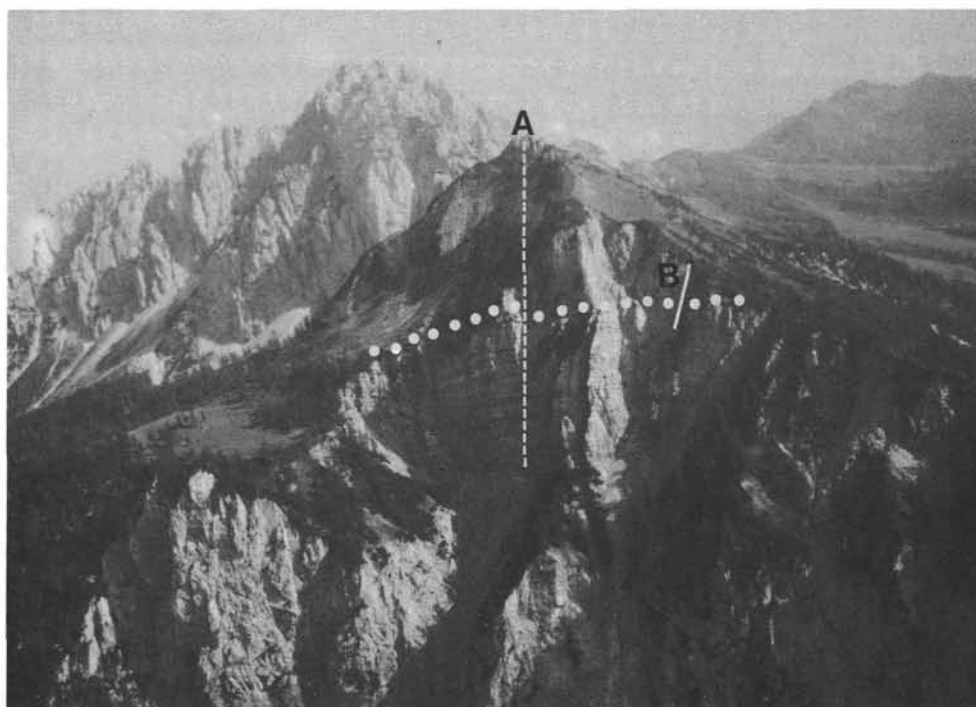
Sulfur isotope ratios in sedimentary regimes are mainly controlled by the biogenic reduction of sulfate from the sea water reservoir, fixed eventually as pyrite in the sediments (HOLSER et al., 1988). The strong negative isotopic fractionation during reduction gives $\delta^{34}\text{S}_{\text{std}}$ in the sediments that is highly negative but variable with time and place of deposit. The sulfate remaining in sea water is thus pushed to higher positive values, which are mixed worldwide to give a $\delta^{34}\text{S}_{\text{sft}}$ characteristic of that geological age. Through geological time, the shifting balance of reduction and oxidation generates an "isotope age curve" for marine sulfate, as sampled in sulfate evaporite rocks (e.g. CLAYPOOL et al., 1980). Low values in the range $\delta^{34}\text{S} = +10$ to $+12$ ‰ are characteristic of the late Permian and earliest Triassic. At the end of the Early Triassic, an anomalous very sharp rise in the sulfur isotope age curve, to about $+27$ ‰ (HOLSER, 1977) may reflect a

final phase of the geochemical changes that characterized the Permian-Triassic transition (HOLSER & MAGARITZ, 1987).

In contrast to this secular regularity of $\delta^{34}\text{S}$ in marine sulfate, $\delta^{34}\text{S}_{\text{std}}$ in sedimentary rocks depends not only on the $\delta^{34}\text{S}_{\text{sft}}$ of sea water at that time, but mainly on the local sedimentary conditions under which reduction took place. Sulfides in hydrothermal deposition have a variety of sources and corresponding values of $\delta^{34}\text{S}_{\text{std}}$ but are relatively constant throughout a particular hydrothermal deposit. Gypsum formed by weathering oxidation of either sedimentary or hydrothermal sulfide generally retains the same $\delta^{34}\text{S}$ of the sulfide from which it was formed.

The core from Gartnerkofel-1 contained pyrite at several levels, and occasionally gypsum (KLEIN, this volume; FENNINGER, this volume). Sulfur isotope studies of these materials may contribute to our understanding of their origin.

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Text-Fig. 1.
Aerial photograph from the north of the Reppwand with the Gartnerkofel (2195 m) in the background. A: Drill site on Kammleiten (1998 m); B: Top of the outcrop section. Dotted line indicates the Permian-Triassic boundary between the Bellerophon Formation (below) and the Werfen Formation above. Photo: G. FLAJS, Aachen.

2. Method

Eleven samples containing pyrite were selected from the core between 182 and 222 m; two of these also contained gypsum. All of these samples were from Unit 3A of the Lower Triassic Werfen Formation – the zone of minimal $\delta^{13}\text{C}$, just above the P/Tr boundary.

Several grams of pulverized samples were leached with HCl. From the solution any sulfate that may have been present was precipitated as BaSO_4 ; the remainder was treated with an oxidizing mixture of HNO_3 and HCl in order to extract sulfide sulfur as BaSO_4 . Then standard sample chemistry and mass spectrometric analysis was applied (PAK & FELBER, 1974).

3. Results and Discussion

The analytical results are listed in Table 1. The range for pyrite from $\delta^{34}\text{S} = -18$ to -27 ‰ is about as expected for syngenetic sedimentary sulfides, in agreement with their microscopic texture (HOLSER, this volume). The clustering of $\delta^{34}\text{S}$ values at differing levels of the core is also characteristic of syngenetic sulfide; if the sulfide had been introduced by later hydrothermal alteration it would more likely have been uniform over this relatively short distance. A syngenetic origin of the sulfide in this stratigraphic interval suggests that it may have an origin in common with the minima of $\delta^{13}\text{C}$ and maxima of trace metals that also characterize these levels (HOLSER et al., 1989; this volume).

The $\delta^{34}\text{S}$ values in the gypsum fraction of each of two samples match that for pyrite in the same samples, indicating that the gypsum was derived from the pyrite – probably by weathering – and not from a marine evaporite. Unfortunately the Gartnerkofel boring had to be stopped short of reaching the lowermost Bellerophon Formation, which displays some bedded gypsum in the nearby Reppwand outcrop (BUGGISCH et al., 1976). Sulfur isotope analyses from marine sulfate

Table 1.
Sulfur isotope data of some samples near the Permian/Triassic boundary.

Lab. No.	Sample No.	Depth [m]		$\delta^{34}\text{S}$ [‰ CDT] $\pm 0,2$ (st. dev.)
VRI-S-1947	S101	182.00	sulfide	-27.3
VRI-S-1941A	S117	185.57	HCl sol. sulfate	-18.5
VRI-S-1941B	S117	185.57	sulfide	-19.5
VRI-S-1944A	S118B	185.80	HCl sol. sulfate	-18.4
VRI-S-1944B	S118B	185.80	sulfide	-19.0
VRI-S-1948	183	215.35	sulfide	-23.3
VRI-S-1945	S190	220.35	sulfide	-26.8
VRI-S-1949	190C	220.90	sulfide	-24.4
VRI-S-1950	191C	221.37	sulfide	-25.5
VRI-S-1951	191D	221.54	sulfide	-25.3
VRI-S-1952	191F	222.05	sulfide	-25.0
VRI-S-1946	192	222.08	sulfide	-27.1
VRI-S-1943	S193	222.20	sulfide	-22.8

evaporites that are more extensive in both the Bellerophon and Werfen Formations, farther west in the Southern Alps, have been published previously (PAK, 1981; CORTECCI et al., 1981; HOLSER & MAGARITZ, 1985).

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