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The first occurrence of schwertmannite in a natural stream environment

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Abstract: After being frequently identified in precipitates from acid mine waters, a fully natural occurrence of schwertmannite, $Fe_{16}O_{16}(OH)_{12}(SO_4)_2$, has now been found in a small stream draining a pyritic schist at the Pfitscher Joch, Zillertaler Alps, Austria. The characteristics of specimens from this location are in full agreement with those of synthetic samples and samples from acid mine waters described elsewhere. This natural occurrence also demonstrates the genetic relationship between schwertmannite, jarosite and goethite/ferrihydrite as products of pyrite oxidation, which is governed mainly by the pH and the sulfate and iron concentrations of the stream.

Key-words: schwertmannite, jarosite, goethite, stream, pyrite oxidation.

Introduction

Schwertmannite was recently described and approved as a new mineral occurring widely as a yellow-orange precipitate in strongly acid, sulfate-rich waters draining through pyritic soils, ores and mine spoils (Bigham *et al.*, 1990, 1992, 1994). In these waters, schwertmannite precipitates after microbial oxidation of Fe^{2+} by acidophilic bacteria such as *Thiobacillus ferrooxidans*. It is often associated with jarosite, goethite and ferrihydrite. The mineral is poorly crystalline, and its proposed structure is akin to that of akaganéite [FeO(OH,Cl)], with sulfate instead of chloride as a stabilizing element in the tunnel cavities. Its ideal formula is $Fe_{16}O_{16}(OH)_{12}(SO_4)_2$, but it may range to $Fe_{16}O_{16}(OH)_9(SO_4)_{3.5}$, depending on the degree to which tunnel and surface sites are saturated with SO_4. The mineral can be synthesized abiotically as well as biotically. Further details are given in Bigham *et al.* (1990, 1994).

The occurrences of schwertmannite described so far from Europe, North America and Australia stem from localities created by mining or other anthropogenic activities. It should, however, also occur wherever pyritic rocks undergo surface weathering, provided a pH of 3 to 4 is maintained long enough to make precipitation possible. This depends mainly on the acid neutralizing capacity of the surrounding environment (soils, sediments and fresh-water diluents). This article briefly describes the first fully natural occurrence of schwertmannite.

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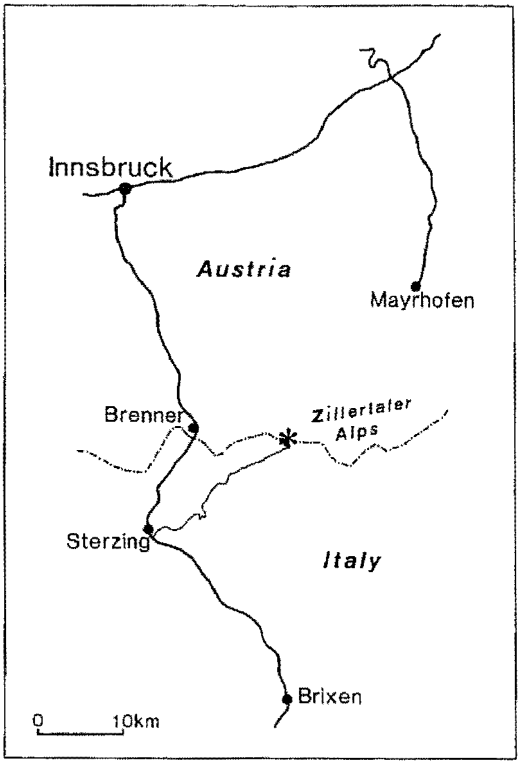

Fig. 1. Location of the Rötlbach.

Locality

The schwertmannite was detected in a stream (Rötlbach) near the Pfitscher Joch in the Zillertaler Alps, Austria (Fig. 1). The source of the Rötlbach is a spring located *ca.* 1 km west of the Rotbachlspitze (2895 m asl), at an altitude of *ca.* 2600 m. This spring drains a schist containing about 5% pyrite that belongs to the Penninikum zone of the Alps. As the acid spring water (pH as low as 2.3) is diluted by an increasing number of non-contaminated tributaries, the pH gradually approaches 7. The Rötlbach flows NW to join the Zamser Bach at *ca.* 2000 m, and throughout most of its course is characterized by an eye-catching, bright-orange to reddish precipitate deposited mainly on rock fragments. The average color is 7.5 YR 6/8 in the Munsell notation and L* = 55.2, a* = 13.4 and b* = 33.1 in CIELab notation (as measured with a Minolta Chromameter CR-300). Both notations indicate that the material is redder than goethite. Because of its unusual color, the stream was described by Lammerer (1989) in a recent geologic guide to the region.

Methods

Four samples were taken at various localities from the schwertmannite zone of the Rötlbach and air-dried after sieving off the coarse material (plant debris, rock fragments).

In brief, the methods of characterization were as follows (for details see Bigham *et al.*, 1990):

Chemical analysis: After dissolution in cold 5*M*HCl, Fe by AAS Unicam 939 + 939OX, SO_4 by ion chromatography, Dionex 2000i/SP, CO_2 by dry combustion Leybold-Heraeus CSA 302, H_2O by drying at 110°C and 800°C. Oxalate soluble Fe after Schwertmann (1964).

Electron microscopy: Zeiss EM 10 A for transmission, Leica (Cambridge Instr.) S 360 for scanning.

X-ray diffraction: Philips PW 1820 goniometer with a diffracted beam monochrometer, step scanning with 0.05° 2Θ step size and 20 s counting time per step.

FTIR spectroscopy: KBr tablets, Nicolet Magna 550.

Mössbauer spectroscopy: RT and 4 K spectra in transmission geometry with a ^{57}Co source in a Rh-matrix.

Thermoanalysis: Combined DTA and TGA, Linseis, heating rate 10°C min^{-1}, hematite as reference material.

Characterization

Where the water has attained a pH of 3 to 4, the precipitate is dominated by schwertmannite. Schwertmannite is metastable with regard to goethite, and the latter is, therefore, a common subdominant phase. Scanning electron micrographs show subrounded aggregates (Fig. 2a) which, at higher magnifications in transmission mode (Fig. 2b), exhibit a typical hedgehog-like appearance. The needles indicate a preferential crystal growth in the tunnel direction, *i. e.* along the c-axes, whereas the development perpendicular to the tunnel is minimal.

A representative X-ray diffractogram shows 8 broad peaks due to schwertmannite, which compares well with a specimen produced by biotic

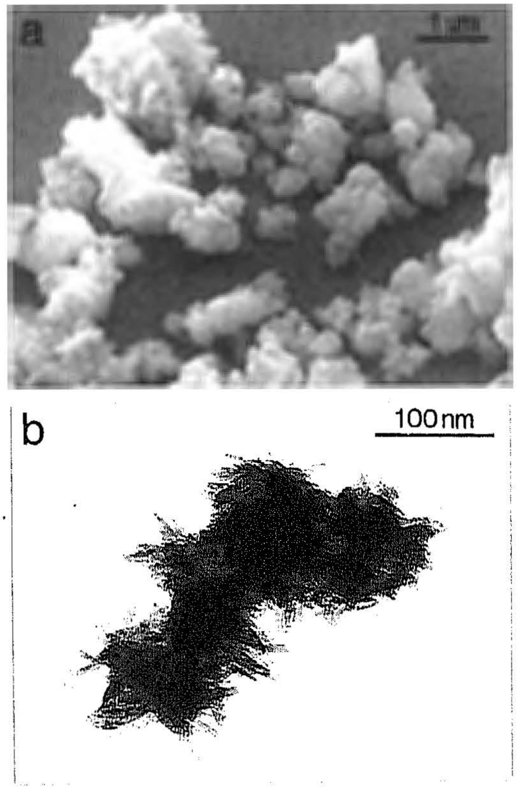

Fig. 2. Scanning electron (a) and transmission electron (b) micrographs of Rötlbach schwertmannite.

oxidation of Fe^{2+} in the laboratory (Fig. 3). The 110 diffraction line, prominent for akaganeite, is missing, probably because of the reduced crystal development perpendicular to the tunnel direction (Fig. 2b). A weak, 0.42 nm peak in the Rötlbach sample indicates a small amount of goethite.

The chemical composition of four samples from this location provided in Table 1 are in agreement with values given by Bigham *et al.* (1990, 1994). Schwertmannite is completely soluble in an oxalate solution of pH 3 (Fe_o), whereas goethite is not. Both minerals dissolve readily in a dithionite solution (Fe_d). The Fe_o/Fe_d ratio for these samples is around 0.85 and also reflects the small goethite admixture.

Thermal analyses (DTA/TGA) (Fig. 4) typically show an exothermic-endothermic pair of peaks at about 600 and 700°C, which are due to the formation of $Fe_2(SO_4)_3$ and its decomposition to hematite, respectively. The latter is associated with a weight loss as seen in the TGA curve. The small endotherm at about 300°C is again due to goethite.

The infra-red spectrum after heating the KBr disc at 100°C for 64 h to remove adsorbed water (Fig. 5) is characterized by a splitting of the $\nu_3(SO_4)$ fundamental into well-resolved bands at 1212, 1135, and 1036 cm^{-1}, indicating a distorted SO_4 tetrahedron, and by an associated $\nu_1(SO_4)$ band at 972 cm^{-1}. A broad band centering at 3185 cm^{-1} is attributed to OH stretching. The two bands at 885 and 796 cm^{-1} can be assigned to OH bending vibrations from the goethite impurity.

A Mössbauer spectrum taken at room temperature (not shown) consists of an asymmetric Fe^{III} doublet which can be best fitted with two distributions of quadrupole splittings (Bigham *et al.*, 1990). The spectrum taken at 4.2 K (Fig. 6) shows two magnetically ordered Fe^{III} components, and resembles that of an acid mine

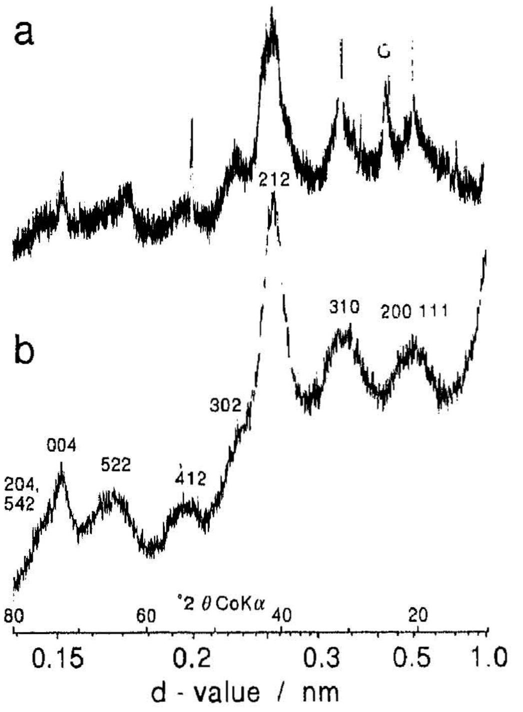

Fig. 3. Representative X-ray powder diffractogram from Rötlbach schwertmannite (a); G = goethite. An X-ray pattern from pure schwertmannite synthesized by biotic oxidation of Fe^{2+} with *Thiobacillus ferrooxidans* is also shown for comparison (b).

Table 1. Chemical composition of samples from Rötlbach[1].

Sample	Fe_2O_3	SO_3	CO_2	H_2O_{110}[2]	H_2O_{800}[3]	Σ	Fe/S	Fe/S[4]
				%			--mol/mol--	
Rö4	59.6	9.36	2.98	17.7	8.13	97.8	6.4	6.2
Rö5a+b	57.7	9.40	2.95	20.1	8.72	98.9	6.2	5.6
Fe325a	61.6	8.04	n.d.[5]	n.d.	n.d.	-----	7.9	6.9
Sh 1/2	60.8	8.65	4.12	n.d.	n.d.	-----	7.0	6.9

[1] Data corrected for acid insoluble residue

[2] H_2O_{110} = weight loss after drying to 110°C

[3] H_2O_{800} = weight loss after drying to 800°C minus H_2O_{110}

[4] Based on oxalate-soluble Fe

[5] n.d. = not determined

drainage precipitate of similar mineralogy described by Murad *et al.* (1994). A two-sextet fit indicates the dominant component (*i.e.*, that constituting the inner component in Fig. 6) to have a magnetic hyperfine field of 46.0 T and a quadrupole interaction of -0.18 mm s^{-1}. These parameters are characteristic for schwertmannite (Bigham *et al.*, 1994). The subdominant component with a hyperfine field of 49.7 T ensues from goethite.

Discussion

With regard to its OH/Fe (and Fe/S) ratio, schwertmannite fills a gap in the genetic series of secondary Fe^{III} minerals formed as oxidation products of pyrite. These minerals span the range between pure Fe sulfates (OH/Fe = 0) on one side and goethite/ferrihydrite (OH/Fe = 3) on the other. Within this series, jarosite [$KFe_3(OH)_6(SO_4)_2$] (OH/Fe = 2.0) occurs at the strongly acid source of the Rötlbach, followed by schwertmannite (OH/Fe = 2.625 - 2.75) at pH 3 - 4 over most of the stream course, and by goethite/ferrihydrite at pH 5 - 7 as dilution with fresh water progresses. Most of the stream is, thus, conducive to schwertmannite formation.

Two other observations support these general conlusions: (1) In a transect across the first confluence of the acid (pH 2.8) Rötlbach with a fresh water tributary (pH ~ 7), an ochreous precipitate

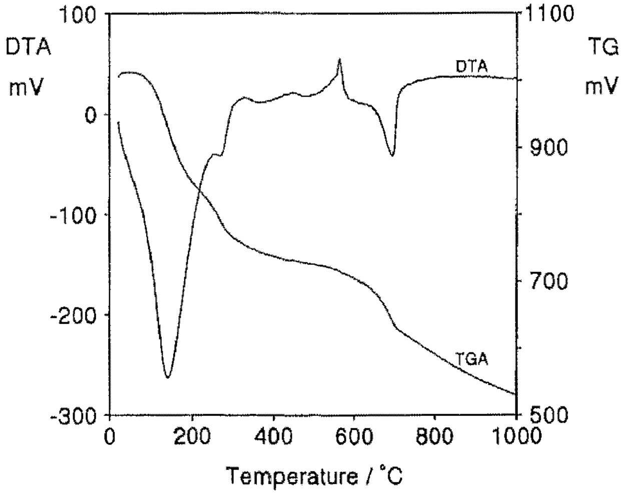

Fig. 4. DTA and TGA curves from Rötlbach schwertmannite.

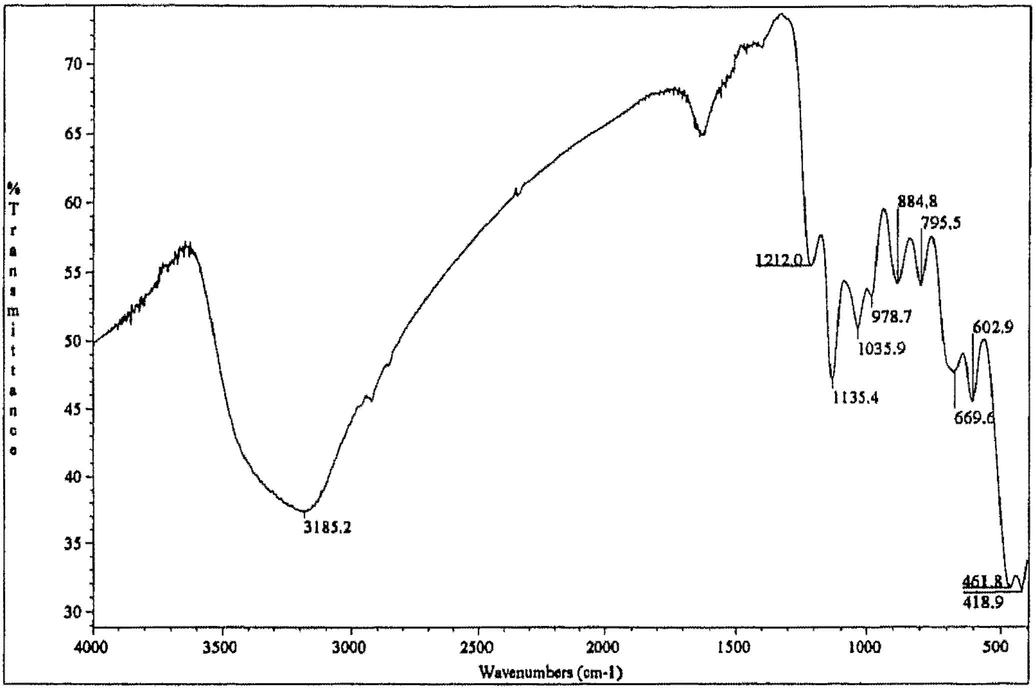

Fig. 5. FTIR spectrum from Rötlbach schwertmannite.

of schwertmannite immediately forms when the pH exceeds 3.0 (Bigham *et al.*, submitted). (2) A second, Fe-rich spring appears several km west of the Rötlbach in Italy. Here, the spring water has a pH of 6.5 and contains 200 mg SO_4/L and 6-9 mg Fe/L which is essentially all Fe^{2+}. The Fe^{2+} rapidly oxidizes and precipitates as ferrihydrite and some goethite upon aeration of the spring water, as would be expected from the higher pH. In this situation, the sulfide but not the iron is oxidized before the groundwater surfaces, and the initial acidity from pyrite oxidation

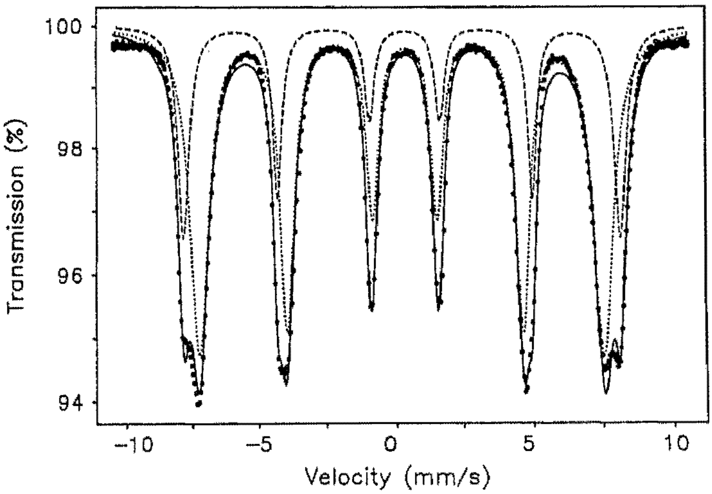

Fig. 6. Mössbauer spectrum from Rötlbach schwertmannite.

is completely neutralized as the water flows through the local aquifer. All these observations are in general agreement with mineral stability considerations which will be discussed elsewhere (Bigham *et al.*, submitted).

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