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SULFUR AND OXYGEN ISOTOPE GEOCHEMISTRY OF ACID MINE DRAINAGE – THE POLYMETALLIC SULFIDE DEPOSIT "HIMMELFAHRT FUNDGRUBE" IN FREIBERG (GERMANY)

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We investigated physical, chemical and isotope (S, O) parameters of sulfate from acid mine drainage from the polymetallic sulfide ore deposit Freiberg (Germany), which was mined for more than eight hundred years. Two main groups of water were distinguished:

1. Flowing mine water with sulfate concentrations of less than 9000 mg/l and pH values higher than 3.2,
2. Pore water in weathered low grade ores and pools with sulfate concentrations higher than 9000 mg/l and pH values below 3.2.

The sulfur and oxygen isotope composition of sulfate from flowing mine waters reflects mixing of sulfate from two sulfur sources: a) atmospheric sulfur from precipitation and b) sulfate formed as a result of sulfide oxidation processes. Sulfur isotope values of mine water sulfate were used to estimate the contribution of sulfate derived through oxidation of sulfides. The sulfur isotope composition of pore water sulfate and precipitated sulfate (jarosite) from weathered low grade ore samples is identical to the sulfur isotope composition of primary sulfides. The oxygen isotope composition of pore water sulfate from low grade ore samples indicates that the oxidation process proceeds relatively slowly in O_2-depleted waters, probably without significant microbial catalysis.

Keywords: Acid-mine drainage; oxygen isotopes; sulfide deposit; sulfide oxidation; sulfur isotopes

INTRODUCTION

Acid mine drainage is often caused by supply of oxygen and water to sulfide-bearing rocks as a result of mining activity. Sulfate formed by oxidation of sulfides of ore bodies can produce acid drainage. Seepage water and groundwater penetrate the mine workings, seep into different mine levels, and finally discharge from culverts. Inflowing seepage water can be mineralised on its way from the surface via different mining levels to the discharge area

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("flowing mine waters") by mixing with acid solutions bearing high heavy metal contents. Discharge of acid waters into rivers pollute them and can cause tremendous environmental problems. We studied acid mine drainage in the sulfide ore deposit Freiberg (Germany), where mine water discharges from culverts into the rivers of the region.

The process of sulfide oxidation under natural conditions is rather complex. Different mechanisms and pathways have been proposed by different authors dependent on the specific conditions. The oxidation process involves dissolution, several intermediate sulfur species, and occasionally precipitation as secondary sulfates. Sulfur and oxygen isotope investigations are powerful tools to investigate the process of sulfide oxidation of acid main drainage [*e.g.* 1–9]. They are used to identify the mechanisms of sulfide oxidation as well as mixing processes of water.

We studied the sulfur and oxygen isotope composition of various oxidation products (very acid pore waters from weathered low grade ores, free flowing mine waters, secondary sulfate minerals) to determine their sulfur and oxygen sources and to obtain information on oxidation mechanisms. For comparison we also studied the sulfur and oxygen isotope composition of primary sulfides and sulfate in atmospheric precipitation, groundwater and seepage water to estimate the contribution of sulfate generated from sulfide oxidation.

GEOLOGIC AND HYDROLOGIC SETTING OF SAMPLING SITES

The polymetallic sulfide ore deposit Freiberg (Germany) was mined for more than eight hundred years (from 1168 to 1969) for silver, lead, copper and zinc [10, 11]. Numerous steep dipping veins and lodes comprise the sulfide ore bodies (Fig. 1). More than a thousand ore lodes were mined in the last eight hundred years. In the Freiberg mining district (Himmelfahrt Fundgrube), underground mine workings extend down to a depth of more than 700 m below the surface. In 1969 mine workings below 200 m under surface were flooded. The sulfide ores, composed dominantly of pyrite, sphalerite, galena with subordinate

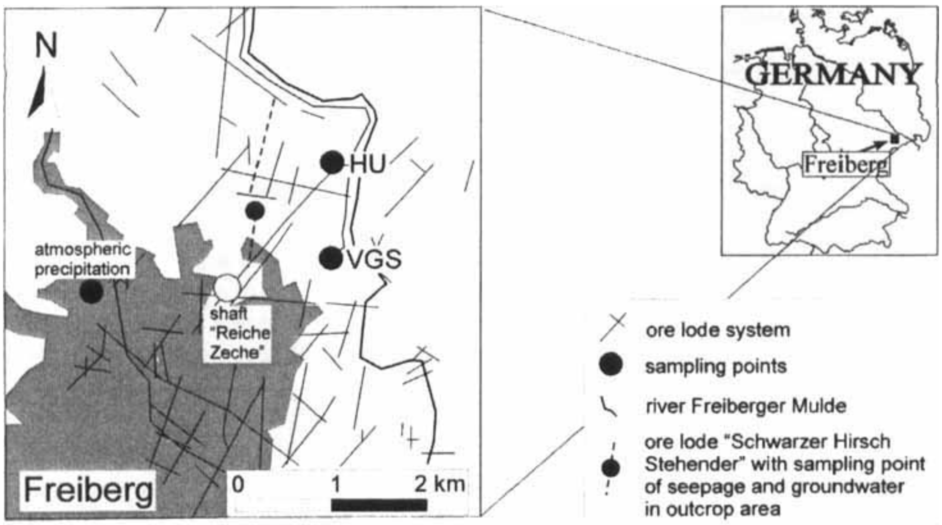

FIGURE 1 Map of the Freiberg mining district with sampling points of drainage galleries "Hauptstolln Umbruch" (HU), "Verträgliche Gesellschaft Stolln" (VGS), seepage water and groundwater in outcrop area of "Schwarzer Hirsch Stehender" (SH) and atmospheric precipitation (Institute of Mineralogy).

amounts of arsenopyrite and chalcopyrite, and traces of silver can be subdivided in high and low grade ores [11]. During mine operations high grade ores were brought to the surface and smelted. Low grade ores were back filled in open spaces in the mine. Most of the steep dipping ore veins and lodes were originally mined from the surface and later filled with host rock and low grade ores. The loosening of rocks and access of water and oxygen led to oxidation of back filled low grade ore and to the formation of acid pore waters, acid pools and secondary sulfate minerals.

The low grade ores (LGO) are the most important sites of sulfide oxidation [12]. They consist of broken host rocks (biotite gneisses) with dispersed sulfides. Weathering leads to the formation of clay minerals (mainly illite, kaolinite) from the silicates and secondary sulfates (mainly jarosite and gypsum, minor anglesite, scorodite, native sulfur). Oxidation of dispersed sulfide results in the generation of very acid solutions with high concentrations of sulfate and heavy metals. These solutions can drip out from weathered LGO and form red coloured pools in which $Fe(H_2O)_6^{3+}$ complexes are stable [13] (Fig. 2).

The ore vein system SH ("Schwarzer Hirsch Stehender") was selected for detailed isotope studies. This lode was mined and later filled with low grade ores between 1850 to 1896. We sampled low grade ore and water in very acid pools in 1997–1998 from several sites of this ore vein system on the first and second level of the mine.

Three mine levels are now accessible for sampling flowing mine water within the unsaturated zone of the ore vein system SH in the Freiberg mining district, the Himmelfahrt Fundgrube (Fig. 3). Mine waters are thought to originate from seepage water and groundwater, which penetrates into mine workings along faults and fractures.

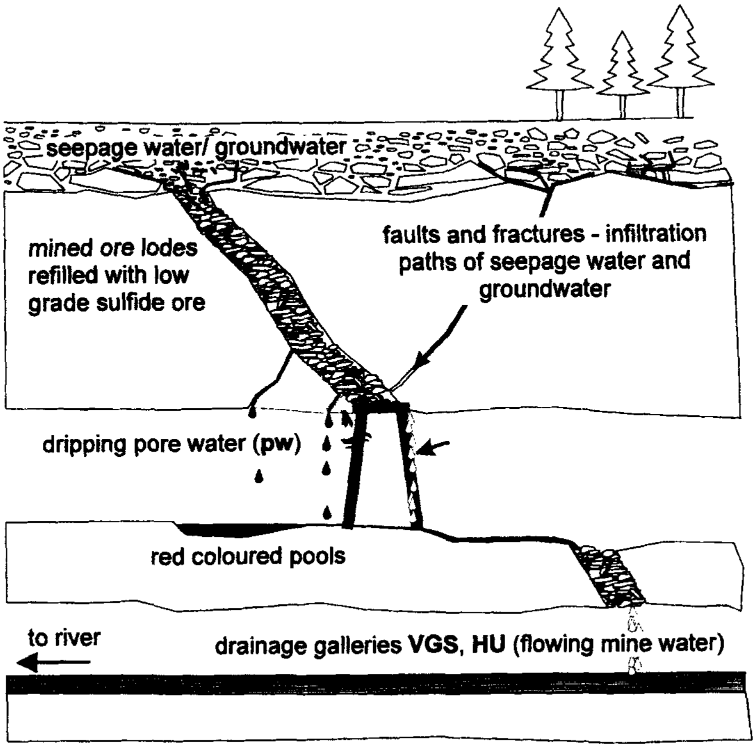

FIGURE 2 Oxidation environment of the mining district of Freiberg. Low grade ore becomes oxidised and can release highly concentrated acid, sulfate- and heavy metal-rich solutions, which are mixed with infiltrating seepage water and groundwater and drain via galleries into rivers.

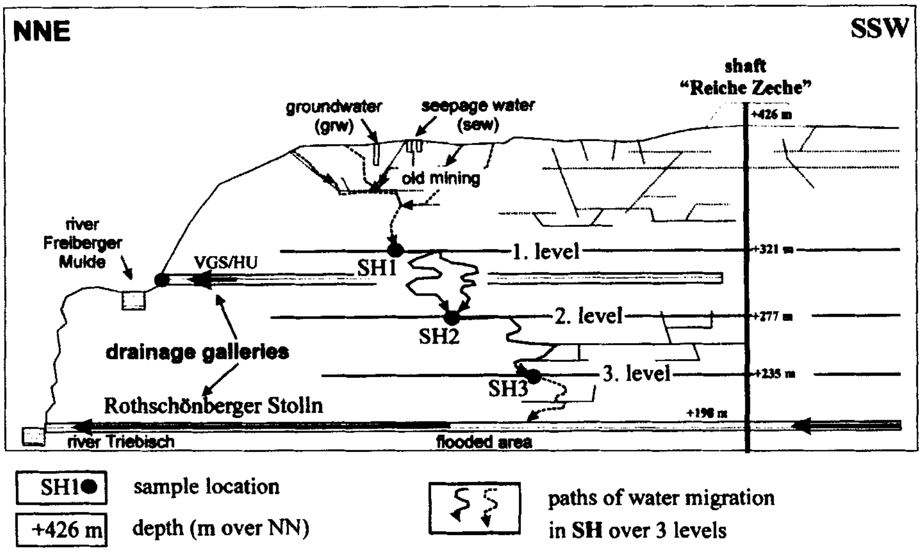

FIGURE 3 Schematic diagram of the unsaturated zone of the Freiberg mining district "Himmelfahrt Fundgrube" with three levels of the ore lode "Schwarzer Hirsch Stehender" (SH) and drainage galleries "Verträgliche Gesellschafts Stolln" (VGS) and "Hauptstolln Umbruch" (HU).

In order to gain information on water migration paths tracer experiments with NaCl were carried out in the mine workings of the vein system. Four liter of 1 N NaCl solution were added to the flowing mine water stream of SH at the first level. Arrival of these waters was detected at level 2 and 3 by increasing conductivity of mine waters due to their high NaCl content. Accordingly, flowing mine water takes about 50 minutes from the first level (sample point SH 1) to the second level (sample point SH 2) and another 40 minutes to the third level (sample point SH 3) Details are given in [14]. The flow rate of mine water was measured at sample point SH 2 to estimate sulfate fluxes during different sampling campaigns. We collected flowing mine waters on four occasions for isotope analyses.

Furthermore, two drainage galleries "Verträgliche Gesellschaft Stolln-VGS" and "Hauptstolln Umbruch – HU" were sampled. These drainage galleries collect flowing mine waters from different vein systems and finally drain into the river Freiberger Mulde (Figs. 1–3). For comparison, seepage water and groundwater as well as atmospheric precipitation was sampled. The first two were collected in the outcrop area of the vein system SH (Fig. 1). At sampling time the outcrop area was fallow land. The location of the sampling point for atmospheric precipitation was behind the Institute of Mineralogy (Freiberg, Brennhausgasse 14) in the City of Freiberg (Fig. 1).

METHODS

Sampling and Separation Procedures

Atmospheric precipitation was collected in containers over a period of 4 to 6 weeks. The collected water was adjusted to pH 9 with NaOH and evaporated until a volume of about 100 ml was reached. After filtration (0.45 µm cellulose nitrate – SARTORIUS) samples were acidified at pH 3.8–4 with HCl and sulfate was precipitated as $BaSO_4$ by adding $BaCl_2$ solution. The sulfate content was determined by the weight of $BaSO_4$.

Groundwater and **seepage water** were sampled in special suck devices in the outcrop area of the investigated ore system (SH) at 1–1.5 m and 5.5 m depth, respectively. All water samples (**flowing mine water**, seepage water and groundwater) were collected in one liter polyethylene bottles, filtered and sulfate was precipitated as $BaSO_4$ as described above.

Low grade ore samples were collected as one kilogram samples and stored in polyethylene bags. Pore water was extracted from low grade ores by centrifugation or leaching with deionized (milli pore) water. In order to precipitate Fe(III), the pore water was adjusted to pH 3.8–4 with 0.1 N NaOH. After coagulation and filtration of $Fe(OH)_3$, sulfate was precipitated as $BaSO_4$ as described above.

Jarosite ($KFe_3[(OH)_6/(SO_4)_2]$) was separated from low grade ores by wet screening (<20 µm) after separation of pore water. The preparation of $BaSO_4$ from jarosite was modified after Wassermann *et al.* [15]. One gram of the dry <20 µm fraction was heated to 50 °C for 5 minutes in 50 ml 2 N NaOH (pH 12). After dissolution of jarosite (causing a change in colour from yellow to brown) the solution was adjusted to pH 9 to precipitate Fe(III). The filtered solution was then adjusted to pH 3.8–4 and sulfate was converted to $BaSO_4$ as described above.

Sulfides (pyrite – FeS_2, sphalerite – ZnS and galena – PbS) from low grade ores were hand-picked under the binocular.

Microscopic Investigations

Separated sulfide minerals from low grade ore samples were characterised using an electron microscope. In some cases energy dispersive X-ray (EDX) analyses helped to identify very tiny new formed mineral phases (*e.g.* native sulfur).

Isotope Analysis

All isotope results are reported as $\delta^{34}S$ and $\delta^{18}O$ values in per mil ‰, where:

$$\delta(‰) = [(R_{sample}/R_{standard}) - 1] \times 1000$$

for $\delta^{34}S$ or $\delta^{18}O$, $R = {}^{34}S/{}^{32}S$ or ${}^{18}O/{}^{16}O$, respectively [9].

$\delta^{34}S$ analyses of $BaSO_4$ and sulfides were performed after conversion to SO_2 in the presence of V_2O_5 and SiO_2 [16] and subsequent determination of the sulfur isotope composition using a Finnigan MAT Delta E mass spectrometer. The reproducibility of the $\delta^{34}S$ analysis is better than ±0.2‰ (preparation of SO_2 + mass spectrometer analysis). All samples were analysed in duplicate. For routine measurements we used an internal standard (SO_2), which is calibrated against the international IAEA-standard NBS 127. Isotope values are reported relative to the international standard CDT.

$\delta^{18}O$ values of $BaSO_4$ were determined on CO_2 derived through reaction of $BaSO_4$ with graphite at high temperature [17, 18, 19]. Simultaneously generated CO was converted to CO_2 on a Ni-catalyst at 350 °C. After the complete conversion of CO to CO_2, all CO_2 gas was collected and analysed on a Finnigan MAT Delta plus mass spectrometer. As internal standard we used a synthetic $BaSO_4$ with a $\delta^{18}O$ value of 12.95‰ calibrated against the international IAEA standard NBS 19. The reproducibility of the $\delta^{18}O$ analysis of $BaSO_4$ is better than ±0.2‰.

$\delta^{18}O$ analyses of water samples were performed through equilibration with CO_2 according to Epstein and Mayeda [20] and subsequent oxygen isotope ratio measurement on a Finnigan MAT Delta plus mass spectrometer. The reproducibility of the $\delta^{18}O$ analysis of water samples is better than ±0.1‰. All oxygen isotope values are reported on the international V-SMOW scale.

RESULTS AND DISCUSSION

Microscopic Investigations

Weathered low grade ore samples contain primary sulfides (mainly pyrite, minor galena and sphalerite) as well as secondary sulfates (mainly jarosite, traces of anglesite). Microscopic investigations were used to reveal relationships between primary and secondary minerals.

Pyrite (FeS_2)*from low grade ore samples* shows solution cavities with regular rhombic or hexagonal forms (Figs. 4a and 4b). Hexagonal forms occur on [111] crystal faces, rhombic cavities on [100] crystal faces. Probably, these cavities resemble weak structural zones of the crystal. We were unable to resolve either a chemical or microbial solution mechanism for observed cavities.

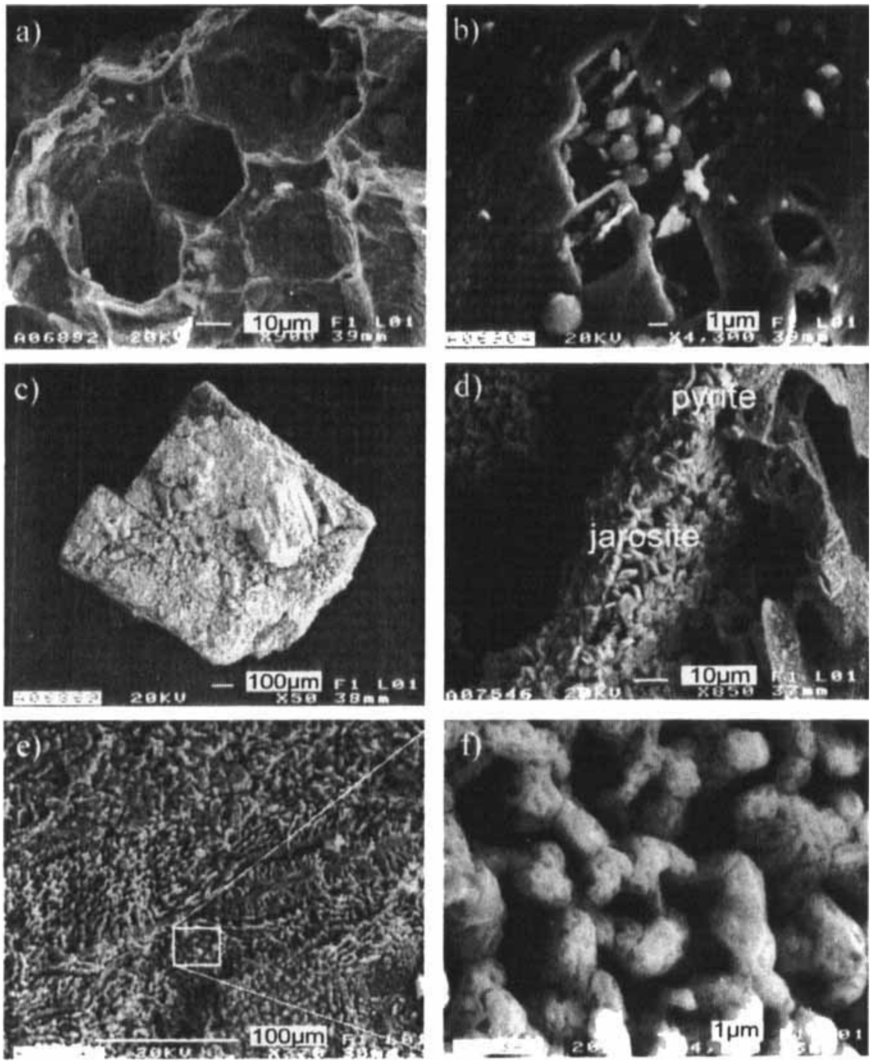

FIGURE 4 Secondary electron images from scanning electron microscope: pyrite with a) hexagonal and b) rhombic cavities; c) galena with anglesite cover; d) jarosite on surface of pyrite; e) f) native sulfur pseudomorphic after sphalerite.

On the surface of *galena* (PbS) crystals pseudomorphic *anglesite* ($PbSO_4$) was found (Fig. 4c). Anglesite crystals usually have a size of 0.5 mm in length and a diameter of up to 0.2 mm.

Jarosite (KFe_3 $[(OH)_6/(SO_4)_2]$ (Fig. 4d) is mostly found on the surface of pyrite. It forms tiny (1 to 10 μm) light-yellow-brownish crystals and is the most common sulfate mineral in weathered low grade ore.

Sphalerite (ZnS) forms black, claret and light yellow coloured crystals. The original colour of sphalerite is black due to its high iron content (the average Fe-content is 12.55% according to [21]). The claret and light yellow colour of sphalerite crystals in low grade ores is probably the result of selective removal of iron [12]. Beside colour changes, we sometimes observed native sulfur (pseudomorphic after sphalerite) with writhed structures (Figs. 4e, 4f). We believe that these structures could be an indication of microbial oxidation of sphalerite.

Gypsum ($CaSO_4 \times 2H_2O$) is omnipresent in all low grade ore samples and forms crystals or aggregates up to 2 mm in diameter. It is most abundant in mine workings with high aeration.

Isotope Investigations

Atmospheric Precipitation

Results are given in Table I and Figure 5. $\delta^{34}S$ values of sulfate in atmospheric precipitation vary from 3.1 to 8.5‰ with an average value of 5.0‰. Haubrich [12] determined $\delta^{34}S$ values on further 88 sulfate samples of atmospheric precipitation events in the region of Freiberg and obtained variations from 3 to 13.2‰ with a similar weighted mean value (5.5‰).

$\delta^{18}O$ values of sulfate in atmospheric deposition vary between 11.5 and 18‰ with an average of 14‰. Sulfate concentrations range from 2.40 to 3.85 mg/l. Haubrich [12] reported sulfate concentrations from 0.29 to 201.9 mg/l in atmospheric precipitation in Freiberg depending on the amount of rainfall.

Seepage Water and Groundwater

Data for seepage water and groundwater are given in Table II and shown in Figure 5.

Sulfate from seepage water shows $\delta^{34}S$ values from 3.9 to 4.6‰ and $\delta^{18}O$ values from 5.2 to 8.3‰. Sulfate from groundwater samples has similar $\delta^{34}S$ values (from 3.9 to 6.2‰) and

TABLE I Sulfate Concentrations and Isotope Data for Atomospheric Precipitation in Freiberg/Saxony (Sept. 1997 to Sept. 1998).

Atmospheric precipitation	*Sampling data*	*SO_4 [mg/l]*	*Rainfall [l/m^2]*	*Dissolved sulfate*	
				$\delta^{34}S_{CDT}$ [‰]	*$\delta^{18}O_{VSMOW}$ [‰]*
atm1	13.09.97–12.10.97	3.02	48.6	3.5	16.7
atm2	12.10.97–16.11.97	3.30	52.3	8.5	14.0
atm3	16.11.97–21.12.97	3.85	44.5	5.3	12.0
atm4	21.12.97–10.02.98	3.69	70.1	4.3	12.0
atm5	10.02.98–20.03.98	2.45	95.4	3.9	16.0
atm6	20.03.98–19.05.98	2.74	45.0	5.7	18.0
atm7	19.05.98–22.07.98	2.43	17.7	4.6	13.0
atm8	22.07.98–25.09.98	2.40	218.1	3.1	11.5
Mean		**2.74**		**5.0**	**14.1**

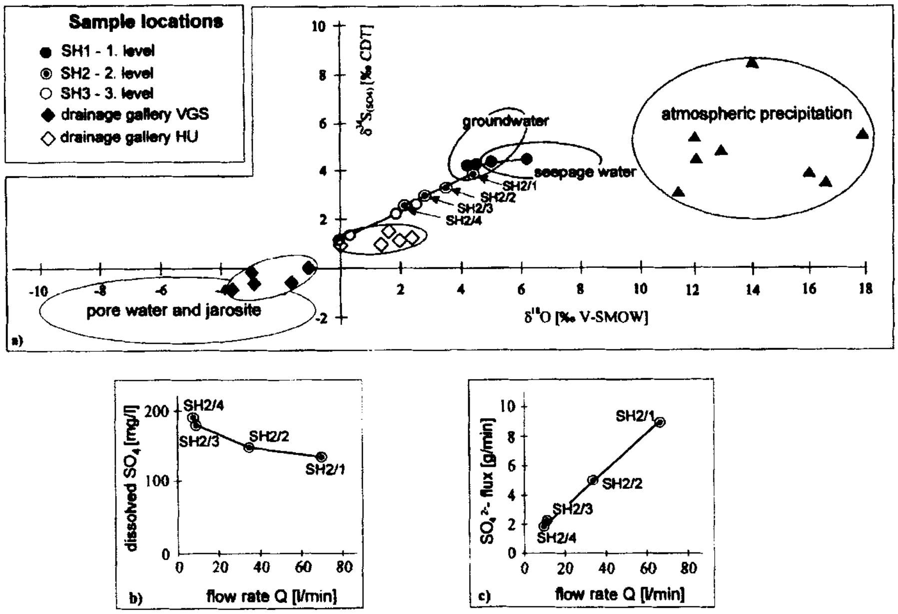

FIGURE 5 a) Sulfur and oxygen isotope composition of sulfate in atmospheric precipitation, seepage water, groundwater and flowing mine water (ore vein system SH, culverts VGS and HU) and low grade ore. Flowing mine water samples were taken at three different levels of the vein system SH during four sampling campaigns; b) water flow rates *vs.* sulfate concentrations and c) water flow rates *vs.* sulfate fluxes for sample location SH 2 at different sampling campaigns.

slightly tower $\delta^{18}O$ values (from 4.2 to 5.8‰). The $\delta^{34}S$ values of sulfate from seepage and groundwater samples are in good agreement with mean $\delta^{34}S$ values of sulfate from atmospheric precipitation in the Freiberg region, but $\delta^{18}O$ values are shifted. The depletion of $\delta^{18}O$ values in seepage water and groundwater was explained by Mayer *et al.* [22, 23] with sulfate immobilisation and mobilisation processes during the interaction of inorganic and organic sulfate in soil.

TABLE II Chemical and Isotope Data for Seepage Water and Groundwater Samples in the Outcrop Area of the Vein System SH ("Schwarzer Hirsch Stehender").

				Dissolved sulfate		*Water*
	Sampling data	*pH*	*SO_4 [mg/l]*	*$\delta^{34}S_{CDT}$ [‰]*	*$\delta^{18}O_{VSMOW}$ [‰]*	*$\delta^{18}O_{VSMOW}$ [‰]*
Seepage water						
sew1	16.10.1997-20.10.1997	5.8	120	4.6	8.3	−10.3
sew2	20.10.1997-24.10.1997	5.7	112	4.6	5.2	−9.3
sew3	24.10.1997-28.10.1997	5.4	112	3.9	6.6	−8.8
sew4	28.10.1997-03.11.1997	5.4	113	4.5	6.6	−9.4
sew5	03.11.1997-07.11.1997	5.3	113	4.5	6.6	−9.3
Groundwater						
grw1	30.09.97	6.2	140	6.2	5.8	
grw2	16.10.97	5.2	150	5.8	4.8	−9.9
grw3	24.10.97	4.9	141	5.0	4.2	−9.1
grw4	03.11.97	5.2	139	5.2	4.2	−9.0
grw5	07.11.97	5.3	143	3.9	4.5	−8.9

TABLE III Isotope Data for Sulfide from Weathered Low Grade Ore (LGO) and High Grade Ore (Mineral Collection of the Institute of Mineralogy, TU Bergakademie Freiberg), after [12,24*].

	pyrite	*sphalerite*	*galena*
	$\delta^{34}S_{CDT}$ [‰]	$\delta^{34}S_{CDT}$ [‰]	$\delta^{34}S_{CDT}$ [‰]
LGO1	−1.0		
LGO3	−1.1	−0.5	
Sulfide 1	−1.3		
Sulfide 2	−0.8		
Sulfide 3	−0.2		−3.0
Sulfide 4*			−2.6
Sulfide 5*	−0.7		−3.5
Sulfide 6*	−1.0	−0.8	−3.3
Sulfide 7*		−0.5	
Sulfide 8*		−0.5	
Sulfide 9*	−1.1	−0.4	−3.4
Sulfide 10*		−0.2	
Sulfide 11*		−1.9	
Sulfide 12*		−1.3	
Sulfide 13*		−0.8	−3.3
Sulfide 14*		−0.4	
Sulfide 15*		−0.8	
Mean	−0.9 ± 0.3‰ (n = 8, ±SD)	−0.7 ± 0.5‰ (n = 11, ±SD)	−3.2 ± 0.3‰ (n = 6, ±SD)

Low Grade Ore

Pore water in weathered low grade ore has very high concentrations of sulfates and pH values lower than 3.2 (Tab. IV). This suggests that weathered low grade ores to be the most important sites of sulfide oxidation.

Sulfides were sampled from low grade ore and high grade ore. The mean δ^{34}S values of sulfides are slightly different for various sulfide minerals (Tab. III): pyrite = −1.3 ± 0.3‰ ($n = 8$, ±SD); sphalerite = −0.6 ± 0.5‰ ($n = 11$, ±SD); galena = −3.3 ± 0.3‰ ($n = 6$, ±SD) [12, 24].

Pore water was studied from low grade ore (LGO) and from red coloured pools (RCP). Data are given in Table IV and Figures 5 to 7. The pore water from LGO and RCP is very acid with pH values ranging from 0.8 to 2.5 and has very high sulfate concentrations from 9200 to 157660 mg/l.

The sulfur isotope composition of the sulfate dissolved in these waters varies from −2.8 to −0.6‰ and is in range identical with that of source sulfides (Fig. 6a). This observation is in agreement with previous studies [3, 9], where no discernible sulfur isotope fractionation was found between sulfides and sulfates as a result of oxidation. Consequently, all sulfur of dissolved sulfate may be derived from oxidation of sulfides and no significant contribution of atmospheric precipitation is recorded in low grade ores. At present, it is impossible to establish which sulfide mineral was the main source for dissolved sulfate in pore water. Judging from δ^{34}S values, pore water sulfate could be considered as an oxidation product from a sulfide mix (pyrite – sphalerite – minor galena) with variable proportions of primary sulfides. Alternatively, minor isotope fractionation between primary sulfide and secondary sulfates could cause the observed variations of δ^{34}S of pore water sulfate. Finally, it cannot

TABLE IV Chemical and Isotope Data for Samples from Weathered Low Grade Ore (LGO) and from Red Coloured Pools (RCP).

		Dissolved sulfate (pore water)			*Jarosite*		*Water*
	pH	*SO_4 [mg/l]*	*$\delta^{34}S_{CDT}$ [‰]*	*$\delta^{18}O_{VSMOW}$ [‰]*	*$\delta^{34}S_{CDT}$ [‰]*	*$\delta^{18}O_{VSMOW}$ [‰]*	*$\delta^{18}O_{VSMOW}$ [‰]*
Low grade ore samples							
LGO1	0.8	57000	−1.9	−7.3	without jarosite		−8.8
LGO2			−1.1	−3.5	−2.3	−0.8	
LGO3			−1.6	−10.0	−2.7	−8.0	−9.4
LGO4	2.4	13016	−2.0	−5.2	−2.0	−1.0	−9.9
LGO5	1.9	157660	−0.6	−7.0	−1.0	−2.5	−9.3
LGO6	2.2	138700	−2.0	−4.4	−2.6	−3.0	−9.6
LGO7	1.6	9200	−2.1	−7.3	−3.4	−1.7	
LGO8			−2.2	−4.0	−2.2	−2.5	
Red coloured pool samples							
RCP9			−1.7	−3.7			
RCP10			−0.8	−2.1			−9.9
RCP11	2.4	15000	−2.5	−4.9			−9.8
RCP12			−2.3	−2.0			−7.5
RCP13	2.3	32800	−2.3	−6.3			−8.4
RCP14	2.5	19700	−2.8	−5.7			

be ruled out that small amounts of atmospheric precipitation led to slightly variable sulfur isotope compositions of pore water sulfate.

The oxygen isotope composition of pore water sulfate varies from −2.0 to −10.0‰. It is depleted in ^{18}O compared to sulfate from flowing mine water, but enriched in ^{18}O compared to the water ($\delta^{18}O_{H_2O}$, Tab. IV and Fig. 6b). Large variation of oxygen isotope composition was also found in previous studies. Taylor and Wheeler [3] concluded that the variation of $\delta^{18}O$ of sulfate can be mainly ascribed to fractionation between dissolved sulfate and water ($\Delta^{18}O_{SO_4-H_2O}$). Possible controls on $\delta^{18}O_{SO_4}$ of acid mine drainage are according to Van Stempvoort [4]:

a) Source of oxygen (O_2 (aqua, gas), H_2O);
b) Physico-chemical conditions, especially pH, $P_{(O_2)}$, temperature and time;
c) Oxidation agents, catalysts, abiotic or biotic oxidation paths.

The source of oxygen depends mainly on the oxidation pathway. In essence, oxygen required for the oxydation of sulfide may be derived from water with $\delta^{18}O < 0‰$ and from atmosphere with $\delta^{18}O = 23.8‰$ [25].

For the direct oxidation of pyrite the following reactions may apply:

- In the first pathway, pyrite is oxidised by ferric iron, as described by the reaction

$$FeS_{2(S)} + 14\ Fe^{3+} + 8\ H_20 \rightarrow 15\ Fe^{2+} + 2\ SO_4^{2-} + 16\ H^+ \qquad (1)$$

in which 100% of the sulfate oxygen is derived from water. Reaction (1) is rate limited by the rate of oxidation of ferrous to ferric iron, represented by reaction [26]:

$$Fe^{2+} + \tfrac{1}{4}\ O_{2(aq)} + H^+ \rightarrow Fe^{3+} + \tfrac{1}{2}\ H_2O \qquad (2)$$

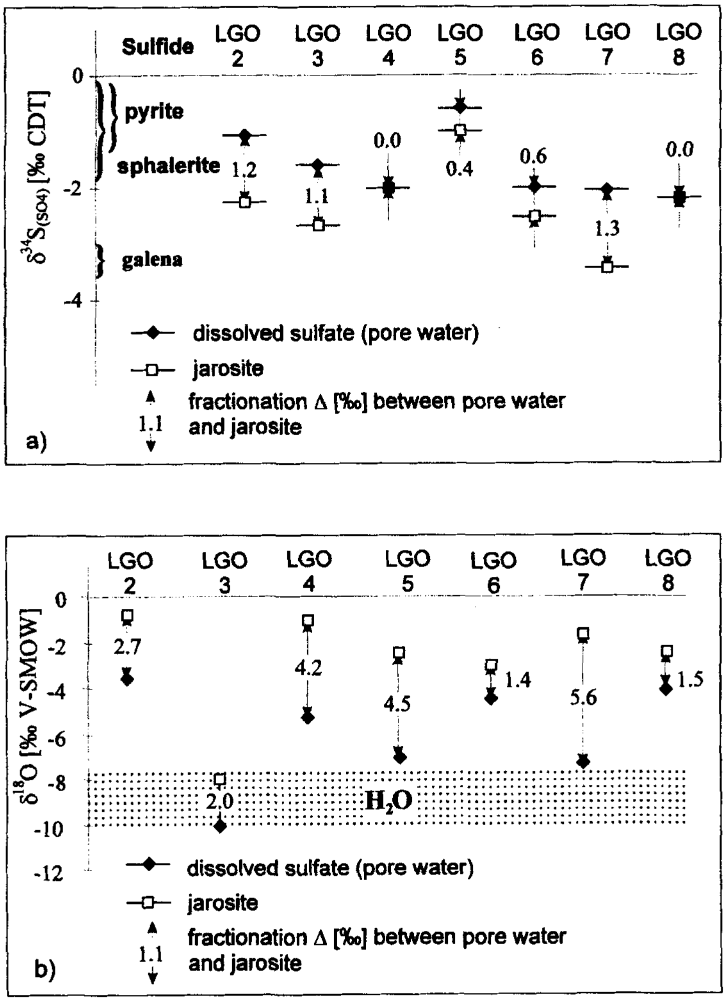

FIGURE 6 Sulfur (a) and oxygen (b) isotope composition of dissolved sulfate (pore water) and jarosite from low grade ore samples (LGO). $\delta^{34}S$ values for sulfides are from Hantsch [24] and Haubrich [12].

In environments with pH < 3.0 reaction (2) can be accelerated by the action of Thiobacillus ferrooxidans [27].

- In the second pathway the oxidation of pyrite is mainly caused by atmospheric oxygen, described by the reaction

$$FeS_{2(S)} + 3\tfrac{1}{2}\,O_2 + H_2O \rightarrow Fe^{2+} + 2\,SO_4^{2-} + 2H^+ \qquad (3)$$

Sulfate generated by this reaction incorporates 87.5% atmospheric oxygen and 12.5% oxygen from water [3]. Reaction (3) can be enhanced in the presence of bacteria (*e.g.* Thiobacillus ferrooxidans, [27]). Both reactions (2) and (3) are obviously rate limited by the availability of molecular oxygen [27]. However, sulfide oxidation reactions likely involve intermediate steps that produce intermediate species such as sulfite or thiosulfate depending on the environmental conditions. Consequently, the final $\delta^{18}O_{SO_4}$ value is a product of a complex interplay of several physico-chemical and biogeochemical conditions (*e.g.* pH, $P_{(O_2)}$, presence of bacteria) determining the main reaction pathway.

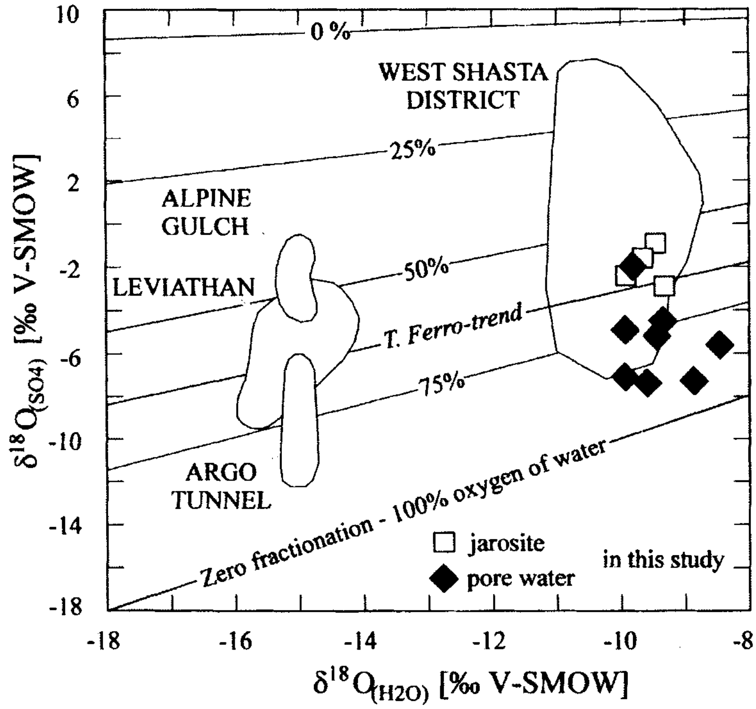

FIGURE 7 Plot of $\delta^{18}O_{SO_4}$ vs. $\delta^{18}O_{H_2O}$ for dissolved sulfate ("pore water") and jarosite from low grade ore samples. Isopleths for percent water derived oxygen, T. ferro trend and fields of data from West Shasta district, Alpine Gulch, Leviathan and Argo Tunnel are from [3].

Taylor and Wheeler [3] interpreted $\delta^{18}O_{SO_4}$ of acid mine drainage mainly on the basis of their experimental results [1], which suggest that $\Delta^{18}O_{SO_4-H_2O}$ values on the order of a few permil indicate O_2-depleted submersed conditions. Higher $\Delta^{18}O_{SO_4-H_2O}$ values reflect biologically mediated oxidation and/or higher contribution of dissolved atmospheric oxygen (O_2). Kinetic isotope fractionation factors between SO_4 and H_2O derived for different experimental conditions include the effect of several factors (*e.g.* pH, $P_{(O_2)}$, abiotic or biotic oxidation). For the enrichment of oxygen isotopes in comparison to water an empirical enrichment factor of 4‰ has been established [1]. However, because lower $\Delta^{18}O_{SO_4-H_2O}$ values have also been found both in nature and experiments, the enrichment factor ε_W was set by Taylor and Wheeler [3] to be 0‰. The enrichment factor for dissolved oxygen was established as $\varepsilon_{O2} = -4.3‰$ during oxidation in sterile environments and $\varepsilon_{O_2} = -11.4‰$ in the presence of Thiobacillus ferrooxidans. Using these enrichment factors, the contribution of water and dissolved oxygen for oxidation can be derived by the general isotope balance model

$$\delta^{18}O_{SO_4} = X(\delta^{18}O_W + \varepsilon_W) + (1 - X)(\delta^{18}O_{O_2} + \varepsilon_{O_2}) \qquad (4)$$

[3, 28]. Calculated estimates based on Eq. (4) (using $\varepsilon_W = 0‰$) suggest for most samples of pore water sulfate a contribution of water-derived oxygen of nearly 100% with lowest estimates of about 70% (compare Fig. 7).

This indicates predominantly sterile oxidation at O_2-depleted submersed conditions in low grade sulfide ore. This is in agreement with measured low contents of dissolved O_2 (< 2 mg/l) in mine waters and red colours of pore water indicating the presence of Fe^{3+}- ions and Fe^{3+}-aqua-complexes. The low $\Delta^{18}O_{(SO_4-H_2O)}$ values make an isotope exchange between water and sulfate unlikely since isotope equilibration corresponds to a fractionation factor of about 35‰ at a temperature of 10 °C with enrichment of ^{18}O in sulfate [28].

Jarosite High contents of the precipitated sulfate jarosite (up to 50%) are common in low grade ore of the Freiberg mining district. The mineral jarosite is formed mainly from Fe(III)-, potassium and sulfate ions: (K, H_3O^+) $Fe^{3+}[(OH)_6/(SO_4)_2]$.

Jarosite samples have $\delta^{34}S$ values from −3.4 to −1.0‰ and $\delta^{18}O$ values from −8.0 to −0.8‰ (Tab. IV). The sulfur is slightly depleted in ^{34}S compared to pore water sulfate (Fig. 6a), whereas ^{18}O is clearly enriched relative to dissolved sulfate (Fig. 6b).

Only few studies of acid main drainage consider the isotope composition of precipitated sulfate minerals in comparison to dissolved sulfate. Taylor and Wheeler [3] determined the sulfur isotope composition of native sulfur which was enriched by up to 5‰ compared to dissolved sulfate. Friese *et al.* [29] obtained similar results in lake sediments of a flooded open pit (Germany, Lusatia). Lloyd [30], Thode and Monster [31], Holser *et al.* [32] and Everdingen *et al.* [27] found enrichment of ^{18}O in precipitated versus dissolved sulfates. Everdingen *et al.* [27] suggested that oxygen isotope exchange at low pH and/or fractionation during formation of solid phases could be responsible for differences in the isotope composition. For a better understanding of the reason(s) of isotope differences of precipitated and dissolved sulfate the formation path and source material (primary sulfides or dissolved sulfate or intermediate species like sulfite) of precipitated sulfates need to be clarified.

Flowing Mine Water

Ore lode SH (Schwarzer Hirsch Stehender) Results of **SH** samples are given in Table V and plotted in Figure 5. Sulfate concentrations of mine water vary between 115 and 256 mg/l depending on depth and flow rate of mine water (Figs. 5a, b, c).

On the first level (location SH1), dissolved sulfate from mine waters shows isotope signatures and sulfate concentrations similar to seepage water and groundwater (Fig. 5a). With increasing depth both sulfur and oxygen isotope ratios decrease. Simultaneously, there is an increase in sulfate concentrations from the first to the third level in each sampling campaign (Tab. V), indicating an input of sulfate-rich solutions with depth. The host rocks of ore lodes are biotite gneisses and cannot contribute much to the increase of sulfate concentrations. The only available sulfur source is pore water of low grade ore, where high concentrations of sulfates were found caused by sulfide oxidation processes. We already mentioned, that mined ore lodes are now filled between levels with host rocks and low grade ore. We suggest that water becomes increasingly mineralised with depth by addition of sulfate formed as a result of sulfide oxidation. This assumption is supported by sulfur isotope ratios. Therefore, sulfate concentrations and sulfur isotope ratios indicate two sources of sulfate in flowing mine water: a) atmospheric sulfur from precipitation and b) sulfate formed as a result of sulfide oxidation processes. The two endmembers have quite different sulfate concentrations and isotope compositions (Tabs. I, IV). Large variations of sulfate concentrations and oxygen isotope ratios in pore water of weathered low grade ore make sulfur isotope ratios the most convenient tool for estimating the contribution of sulfate amounts derived through oxidation of sulfides.

The different flow rates at various sampling times (Tab. V) are attributed to different precipitation rates. Kolitsch [33] determined a retardation time of five to seven days between precipitation events and increased flow rates of mine water in the Freiberg mining district. Increasing flow rates (in wet periods) correspond to increasing sulfate fluxes but lower sulfate concentrations, as can be shown for sample location SH 2 (Figs. 5b, c). Therefore, in times

TABLE V Flow Rates, Chemical and Isotope Data for Flowing Mine Water Samples at Three Levels of the Ore Lode System SH ("Schwarzer Hirsch Stehender").

						Dissolved sulfate		*Water*
Sample	*Sampling data*	*Flow rate Q [l/min]*	*pH*	*SO_4 [mg/l]*	*Flux of SO_4 [g/min]*	$\delta^{34}S_{CDT}$ [‰]	$\delta^{18}O_{VSMOW}$ [‰]	$\delta^{18}O_{VSMOW}$ [‰]
SH1/1	23.04.97			115.0	7.7	4.5	6.2	−9.9
SH2/1	23.04.97	66.7	4.2	134.9	9.0	3.9	4.4	−9.9
SH3/1	23.04.97			162.0	10.8	2.6	2.5	−9.5
SH1/2	31.07.97			130.0	4.3	4.4	5.0	−9.8
SH2/2	31.07.97	33.3	4.0	150.0	5.5	3.3	3.5	−9.8
SH3/2	31.07.97			183.0	6.1	2.2	1.8	−9.8
SH1/3	19.09.97		5.6	150.0	1.8	4.3	4.5	−10.0
SH2/3	19.09.97	12	3.8	180.0	2.2	3.0	2.8	−8.8
SH3/3	19.09.97		3.3	247.8	3.0	1.4	0.3	−9.9
SH1/4	13.10.97			152.3	1.5	4.2	4.2	−8.3
SH2/4	13.10.97	10	3.8	190.0	1.9	2.6	2.2	−9.6
SH3/4	13.10.97			255.9	2.6	1.1	−0.1	−9.5

SH1 – 1. level; SH2 – 2. level; SH3 – 3. level

TABLE VI Chemical and Isotope Data for Water Samples from Culverts VGS ("Verträgliche Gesellschaftstolln") and HU ("Hauptstolln Umbruch").

				dissolved sulfate		water
Sample	*Sampling data*	*pH*	*SO_4 [mg/l]*	*$\delta^{34}S_{CDT}$ [‰]*	*$\delta^{18}O_{VSMOW}$ [‰]*	*$\delta^{18}O_{VSMOW}$ [‰]*
VGSI	23.06.91	5.5	657	−0.5	−1.7	
VGSII	20.10.91	4.1	552	−0.7	−2.8	
VGS1	05.06.97		665	−0.1	−1.0	
VGS3	30.09.97		647	−0.9	−3.5	−9.9
VGS4	06.02.98		557	−0.3	−2.7	−8.9
HUI	23.06.91	7.6	281	1.3	2.3	
HUII	20.10.91	6.8	233	1.1	2.0	
HU1	05.06.97		264	0.9	1.3	−9.9
HU3	30.09.97		243	1.5	1.5	−9.8
HU4	06.02.97		243	0.9	0.0	

with high flow rates a higher sulfate load is withdrawn from active sites of sulfide oxidation but diluted by a higher amount of precipitation water.

Drainage galleries VGS and HU Results for drainage galleries "Verträgliche Gesellschaft Stolln - VGS" and "Hauptstolln Umbruch - HU" are given in Table VI and Figure 5a.

Sulfate concentrations of water from HU vary between 233 and 281 mg/l similar to sample point SH 3 of the investigated ore lode system. $\delta^{34}S$ and $\delta^{18}O$ values vary between 0.9 and 1.5‰ and 0 and 2.3‰, respectively. Sulfate concentrations of water from VGS are higher (552 to 665 mg/l), whereas $\delta^{34}S$ and $\delta^{18}O$ values are lower (from −0.9 to −0.1‰ and from −3.5 to −1.0‰, respectively). Therefore, water from the VGS is highly mineralised. Low $\delta^{34}S_{SO_4}$ values indicate a high contribution of sulfate from sulfide oxidation processes.

CONCLUSIONS

Two main groups of water can be distinguished in the mine workings of the Freiberg district (Fig. 8a):

1. Pore water in weathered low grade ore and in very acid pools ("pool water") with SO_4 concentrations of more than 9000 mg/l and low pH values (<3.2).
2. Flowing mine water with SO_4 concentrations of less than 9000 mg/l and pH values higher than 3.2.

The sulfur isotope composition of sulfates of these two groups shows clear differences with lower values for very acid waters having high sulfate concentrations (Fig. 8b).

Sulfur and oxygen isotope compositions of flowing mine water of the mining district Freiberg have shown that the increase of sulfate concentrations on their way to lower levels and culverts is mainly caused by sulfide oxidation processes. Mine waters with a negligible sulfate input from sulfide oxidation (*e.g.* sample point SH1) have sulfur isotope compositions that are similar to that of seepage water and groundwater. The contribution of sulfate produced as a result of sulfide oxidation in mine waters can be estimated by means of sulfur isotope investigations. For example, a high discharge of sulfate from oxidation is detected for the culvert VGS ("Verträgliche Gesellschafts Stolln").

The most important sites of active sulfide oxidation are low grade ores. Isotope investigations on dissolved sulfate of low grade ores have shown that oxidation proceeds relatively

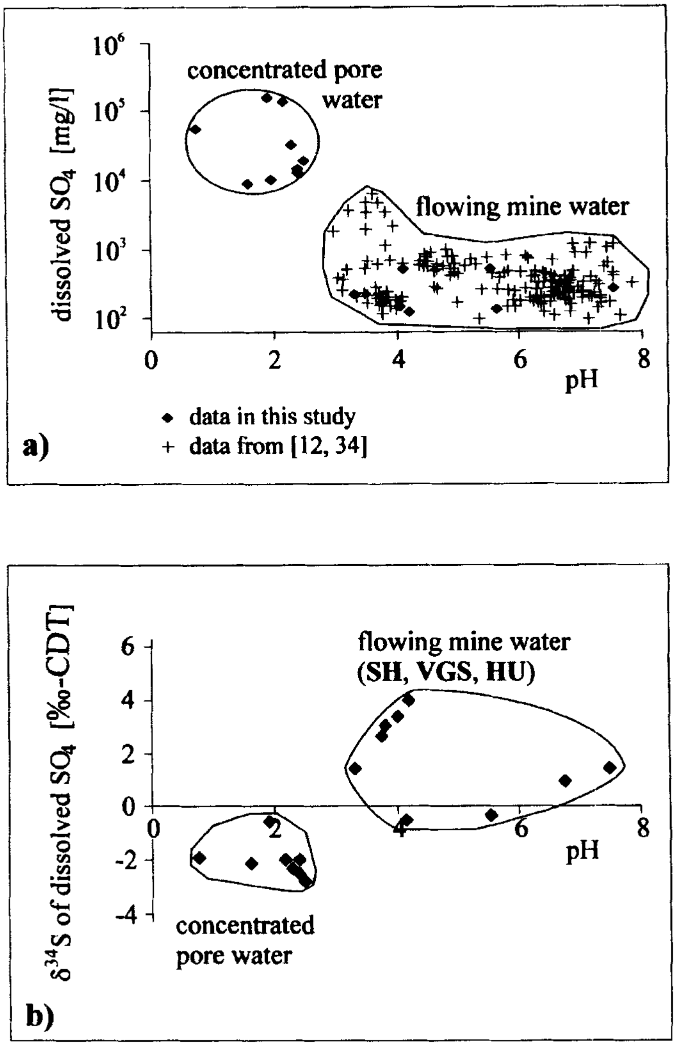

FIGURE 8 pH versus sulfate concentration (a) and pH versus $\delta^{34}S$ values (b) of pore water (dissolved sulfate from low grade ores and water from red coloured pools) and flowing mine water. Data are from [12, 34].

slowly in O_2-depleted waters, probably without significant microbial catalysis. Probably in times with a high flow rate (following periods with high precipitation rates), dissolved and/or precipitated sulfate can be released from low grade ore sites into flowing mine waters, culverts and finally pollute river water. Consequently, we focus present studies on detailed investigations of low grade ore sites and discharge regions.

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