



Understanding the Weathering Process of Antimony Minerals: Case Study Sb-Mine Sulzburg, Black Forest, Germany

Sakonvan Chawchai^{1,*}, Raphael Bissen²

¹ Morphology of Earth Surface and Advanced Geohazards in Southeast Asia Research Unit (MESA RU),
Department of Geology, Faculty of Science, Chulalongkorn University, Bangkok, Thailand

² Department of Mining and Petroleum Engineering, Faculty of Engineering, Chulalongkorn University,
Bangkok, Thailand

* Corresponding author: Email: sakonvan.c@chula.ac.th

Article History

Submitted: 20 July 2017/ Accepted: 11 November 2017/ Published online: 23 April 2018

Abstract

Concerns about heavy metal and metalloid contamination from mine dumps is one of the most intensively discussed issues in society, politics, and academia, because of the levels of pollution, and its toxic properties. During the Middle Ages the Black Forest was one of the most successful mining areas in Southwestern Germany. Historical records show that Sulzburg was a mining town in the Black Forest since the 10th century, but was abandoned in the 19th century. Nowadays this town is considered as an important recreation area in the country. Therefore, soil and water quality and any contamination are of great concern. The purpose of this research was to understand the weathering process and environmental impact of heavy metals and metalloids from the old antimony (Sb) mine sites in Sulzburg. In this study, we examined the mineralogy and whole-rock chemistry and performed soil sequential extraction and water chemical analysis around mine sites. The results show that the Sb deposits in Sulzburg contain mixtures of antimony-lead-bearing sulfides and sulfosalts in hydrothermal quartz veins. The primary ore stibnite (Sb_2S_3) and boulangerite ($Pb_5Sb_4S_{11}$) occur associated with pyrite, arsenopyrite, and sphalerite. The whole-rock chemistry of Sb-Mine Sulzburg is characterized by considerable Sb_2O_3 (4-25 %) and PbO contents (2-7 %). This agrees with the chemical composition of Sb minerals. Based on soil sequential extraction, toxic elements (Sb, Pb, As) mostly remain in the residual fraction. Comparing the water analysis at and around Sb-mine Sulzburg, Sb concentrations are lower than those of As and Pb for all water samples. This is possible due to the strong affinity of Sb to Fe-oxides-hydroxides and amorphous material and a lower mobility, from the source into water. Based on these findings, we argue that sources of toxic elements and weathering process in Sulzburg are important from the ecotoxicity perspective. Changes in oxidizing or reducing conditions can lead to release and mobilization of Sb, As, and Pb into the environment.

Keywords: Sb deposits; Black forest; Sulfides and sulfosalt minerals; Soil and water analysis

Introduction

Heavy metal and metalloid contamination from mine wastes (e.g. dumps, waste rocks, tailings) is a serious environmental concern [1-5]. Globally, acid mine drainage (AMD) from oxidation of sulfide minerals is a crucial problem for the global mining industry [6-10], because most sulfide minerals contain heavy metals and metalloids (i.e., As, Cu, Cd, Fe, Hg, Mn, Pb, Sb, and Zn). Contamination of antimony (Sb) in AMD-influenced water and soils has also been noted in several studies [11-24]. A recent study addresses the secondary and weathering process of Sb and their spreading contamination in sediments and water from abandoned mining areas [25-29]. However, few studies have been undertaken into Sb and weathering process compared to other potentially toxic metals such as Hg, Pb, Cd, and As. A greater understanding of mineralogy, rates and mechanisms of transformation and mobility of Sb in soil and natural waters is still needed [12-14, 18].

The Black Forest in southern Germany has a long and interesting mining history. Walenta [30] reported mining history in the middle and southern part of the Black Forest, described the minerals and ore formation in the area and investigated Sb occurrences. However, in mineralogical and geochemical analyses at Schweizergrund (Sb-Mine Sulzburg) and Sonnhalden valley, Sulzburg was not studied in detail (Figure 1c). Previous research mentioned only that these two locations contained different Sb minerals [31].

Sb mining has taken place in Sulzburg since the Middle Ages but was abandoned in the 19th century [32-33]. The purpose of this research was to investigate primary Sb minerals and their weathering products from the old mine sites, to find out how Sb deposits weather and transfer the mineral to soil and water. Therefore, we studied the mineralogy and whole-rock chemistry, performed soil sequential extraction as well as water chemical analysis.

Locations and geology of the study site

Sulzburg is a small town in the Breisgau-Hochschwarzwald District of Baden-Württemberg, Southwestern, Germany, which has a long tradition of mining since the 10th century. Records describe a successful mining town, with ample deposits of silver and lead. Nowadays, spoil heaps and dumps serve as reminders of this heritage. Sulzburg is situated on the western slope of the Black Forest, 25 km southwest of Freiburg (Figure 1a). The prospected area is located south of Sulzburg (Figure 1b).

The geology of Sulzburg is dominated by metamorphic and magmatic rocks, the basement consists of biotite-bearing paragneiss. On the south and southeast, the paragneiss is replaced by fine-grained foliated granite (Klemmbachgranit). Between Badenweiler and Neuenweg, there is a carboniferous conglomerate-filled graben c. 1.5 km wide oriented ESE and affected by fracturing associated with the Rheinische Disruption (NNE). A strong disruption lies to the south of Sulzburg, and is known as “Schweighof Fault” (Figure 1c), around 1 km from the graben [30, 32]. Ore mineralization is related to hydrothermal fluid flow along faults.

In 1981, the Landesamt für Geologie, Rohstoffe und Bergbau investigated the ore deposits in Sulzburg. Alluvial sediments with anomalously high ore concentrations were studied and a geochemical map of the Carboniferous sediments to the East of “Schweighof Fault” was produced. Hoffherr [31] reported the prospection of antimony ore in the southern part of Sulzburg (1 and 2; Figure 1c). This study refers to previous work of Walenta [30] and provides further details about Sb-mineralization in the Carboniferous sediments. A mineralized zone of approximately 5 km length with Pb, Zn, and Sb ores, and early pyrite-arsenopyrite occurs in the Carboniferous sediments. Several faults of

Rheinish direction (NW-SE) displace the zone by a few tens of meters, whereas the fault known as “Schweighof” caused a 1 km lateral displacement of the Carboniferous-gneiss border. Traces of old mining activities were found in this area.

Area1: Schweizergrund (Sb-mine Sulzburg)

The Sb mine lies on the southern hillside of Wegscheiderkopf (Schweizergrund; Figure 1c), In 2009 there was a passable gallery into the mine, leading to the mineral veins. The direction of the gallery is 20° N. From the gallery entrance, a ricochet running to the ore body is reached after 45 m. There is adit around 25 m long in NW direction, at the end of which there is a mine shaft filled with water. Outside the gallery heaps and dumps are recognizable on the right upper 250 m in a NW direction, along the entire footpath to Wegscheiderkopf (Figure 2).

Quartz is a major mineral. The oldest ore mineralization comprises pyrite (idiomorphic), marcasite, and arsenopyrite. The middle generation is characterized by sphalerite (xenomorphic, honey-yellow). The main ore mineralization includes stibnite and antimony sulfosalt (zinkenite, plagonite, semseyite, jemesonite, and boulangerite), because at the end phase there is more lead in the composition [30-31].

Area2: Sonnhalden Valley, Sulzburg

No detailed study of the antimony minerals exists for this locality. Some Sb-bearing material was found at the bottom of the valley, NW of the Sonnhalden Ridge. Major minerals are quartz and barite, with some traces of galena [32]. A shaft entrance and dump provide evidence of some mining in this area. Although there are 3 galleries in this ore mineral vein, a detailed study about this occurrence is lacking.

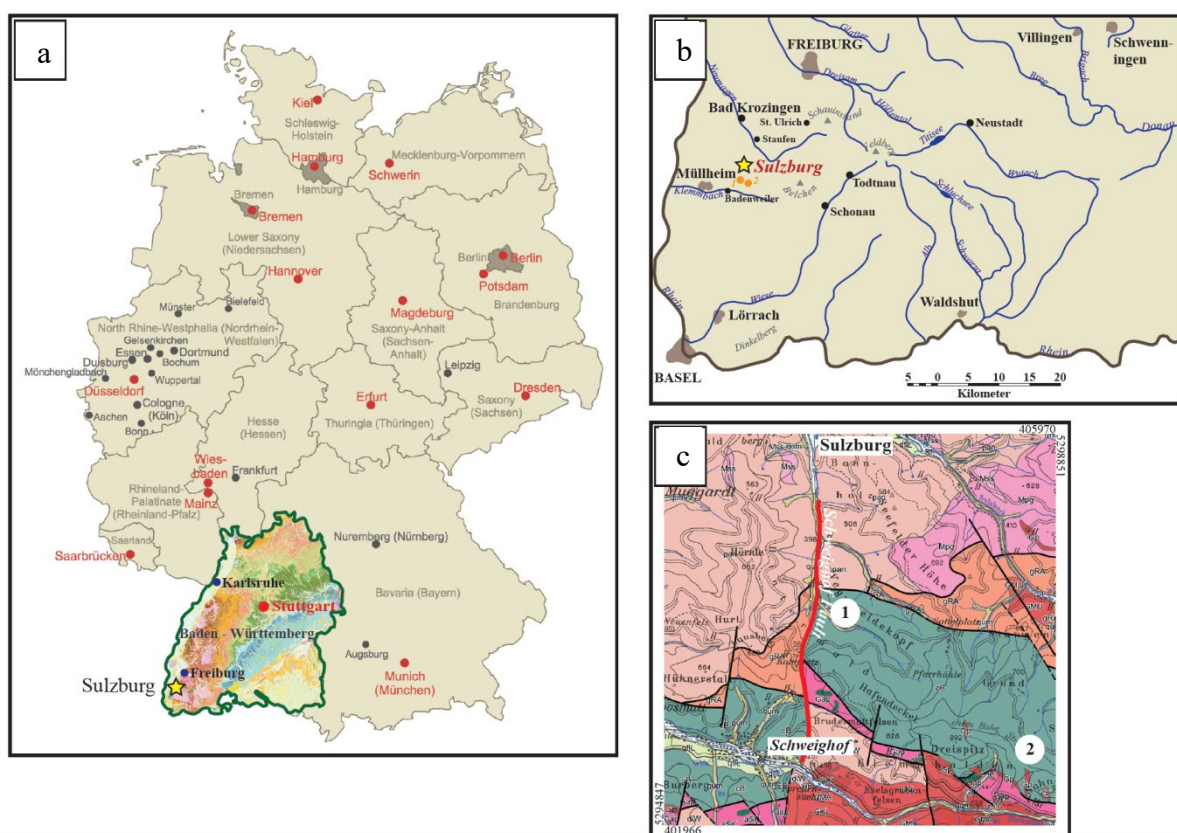


Figure 1 (a) Locations of Sulzburg in southwestern Germany, (b) sites of (1) Sb-Mine Sulzburg (2) and Sonnhalden and (c) geological map of Sulzburg “Schweighof Fault” is shown as a thick red line.

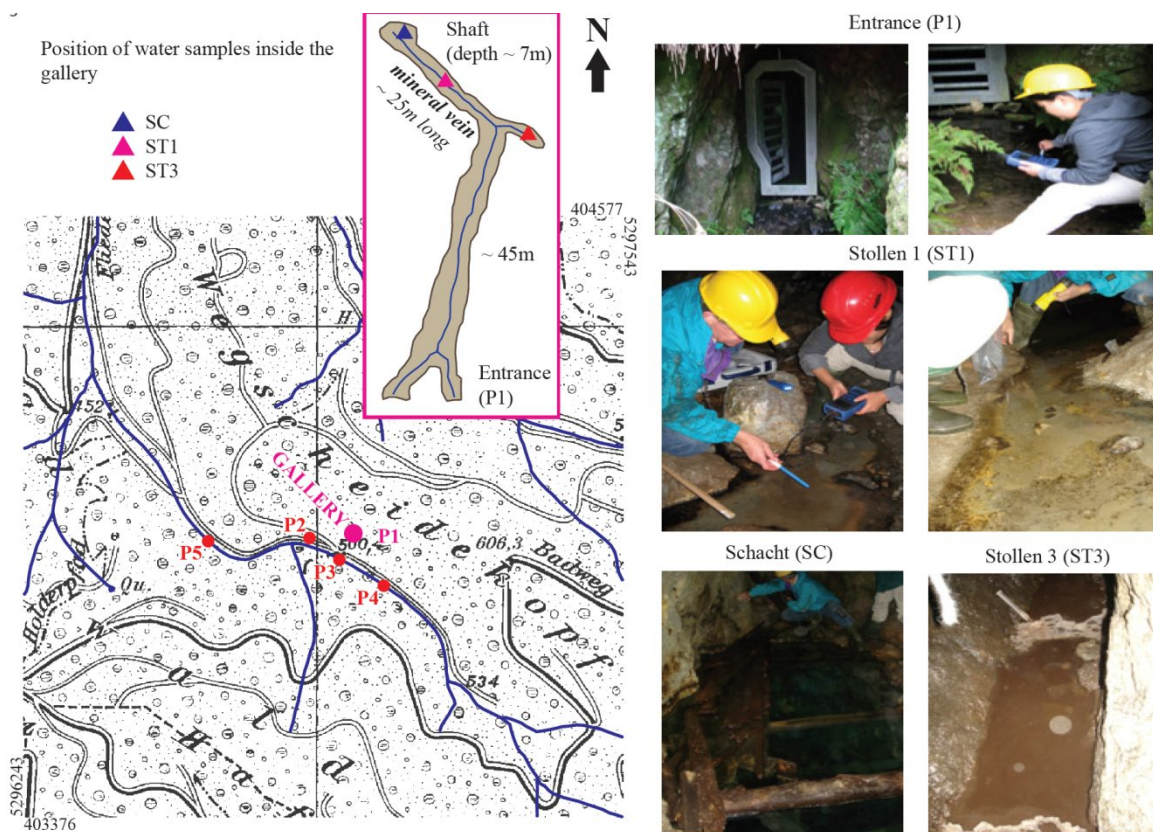


Figure 2 Map of the Sulzburg area, showing the location of the ore deposit at Sb-Mine with position of the water sampling sites inside and outside the gallery.

Materials and methods

1) Mineralogy

Sixty rock samples were collected from local heaps and dumps at Sb-Mine Sulzburg and at the bottom of valley to the NW of Sonnhalden ridge (location (1), (2); Figure 1b and c). The lithology was described and minerals were identified (Supplementary material Table 1 and 2). Seven polished sections were prepared for ore microscopy. Back-scattered electron (BSE) images along with the spectra of characteristic X-rays were generated using Scanning Electron Microscope (SEM; DSM960 (Link/Oxford)) at the Crystallography Institute, University of Freiburg, Germany (BSE mode, Acceleration Voltage 20 kV, beam current 70 μ A, working distance standard 25 mm).

After ore petrography and SEM analysis, the mineral chemistry was determined on polished and carbon coated ore samples using Electron Microprobe Analysis (EPM; 20 KV and beam

current of 29 nA) at the Institute of Earth and Environmental Sciences, University of Freiburg, Germany. Most of the standards used for calibration are mineral standards. The goal of the EPM investigation is to obtain quantitative data for the Sb minerals presented in the samples.

Macroscopic rock samples show different weathering colors. Therefore, three samples of the weathering crust were scraped off and analyzed by X-ray diffraction analysis (XRD) to identify secondary minerals. The XRD patterns were collected with a Bruker AXS D8 Advance diffractometer, equipped with a Cu K α radiation source, diffracted-beam graphite monochromator, and a scintillation detector. The diffraction patterns were collected from 2 to 90.0 $^{\circ}2\theta$, with a step of 0.02 $^{\circ}2\theta$ and a dwell time of 2 s at each step. Diffract plus EVA Program reference and Match Program were used for identifying minerals.

2) Total concentration

Whole-rock chemical data (Table 2) were obtained using Atomic Absorption Spectroscopy (AAS) for seven samples. For sample preparation, 0.1 g of rock powder were digested with 4.5 mL of HNO₃ 65 %, 1.5 mL of HClO₄ 60 %, and 0.5 mL of HF 48 %. The mixture was heated to 85°C for 2 hours by microwave (adapted from Yu et al. [34]). Then 2.5 mL of BH₃D₃ 5 % were added as well as 50 mL

deionized water before analysis with AAS. In this study, a Flame-AAS (Analytic Jena, AAS Vario6) and an ASS (Perkin-Elmer4100 ZL Zeeman) with microwave type μ PREP-A were used. Merck Certipur standard solution for AAS were applied (<http://www.merckmillipore.com>) together with rock standard. The complete set of data of AAS with detection limits is listed in Table 2 and Supplementary material (Table 3).

Table 1 Mineral occurrences at Sb mine Sulzburg and Sonnenhalde

Mineral compositions	Sulzburg	Sonnenhalde
Primary minerals		
Quartz (SiO ₂)	x	x
Pyrite (FeS)	x	x
Arsenopyrite (FeAsS)	x	x
Sphalerite (ZnS)	x	x
Stibnite (Sb ₂ S ₃)	x	x
Boulangerite (Pb ₅ Sb ₄ S ₁₁)	x	
Plagionite (Pb ₅ Sb ₈ S ₁₇)	x	x
Secondary minerals		
Stibiconite (Sb ₂ O ₃)	x	x
Bindheimite (Pb ₂ Sb ₂ O ₆ (O, OH))	x	

Table 2 Range of weight percentage (wt %) of whole-rock geochemical data

Elements	Detection limit	Sb-Mine Sulzburg (wt %)	Sonnhalden (wt %)
SiO ₂	0.050	46-73	62-69
Sb ₂ O ₃	0.010	4-25	3.5-13
PbO	0.001	2-7	0.01-0.03
Al ₂ O ₃	0.050	0.2-2.5	0.9-1
Fe ₂ O ₃	0.066	0.4-1	1-1.6
ZnO	0.037	0.1-1.7	0.0.9
Na ₂ O ₃	0.036	0.2-0.3	0.2-0.3
CaO	0.029	0.2-0.3	0.2-0.3
K ₂ O	0.038	0.1-0.4	3-3.7
MgO	0.041	0.04-0.09	0.1-0.2
BaO	0.003	0.02-0.07	0.01-0.02
CuO	0.022	0.01-0.04	0.01-0.04
CdO	0.014	0.01-0.02	-
As ₂ O ₃	0.005	0.01	0.2-0.4

Table 3 Total digestion and sequential extraction of Sb, Pb, As and Fe as determined from soil samples

Elements	Sample	Sulzburg (ppm)					Sonnhalden (ppm)					
		U1	U2	U3	Average	STDV	O1	O2	O3	Average	STDV	
	Fraction	pH	5.93	5.90	5.94	5.92	±0.02P	4.26	4.19	4.28	4.24	±0.05
Sb	1 Exchangeable	0.10	0.09	0.09	0.09	±0.01	0.04	0.04	0.04	0.04	±0.00	
Detection	2 Bound to Fe-Mn Oxide	2.43	2.55	2.64	2.54	±0.11	1.00	0.90	0.80	0.90	±0.10	
limit	3 Bound to organic matter	1.09	0.88	0.99	0.99	±0.11	0.49	0.36	0.42	0.42	±0.07	
0.01	4 Residual	308.00	288.00	293.00	296.33	±10.41	70.90	100.00	100.00	90.30	±16.80	
	Σ (Fraction 1-4)	311.62	291.52	296.72	299.95	±10.43	72.43	101.30	101.26	91.66	±16.66	
	5 Total digestion				368.00					92.10		
Pb	1 Exchangeable	0.01	0.01	0.01	0.01	±0.00	0.07	0.08	0.07	0.08	±0.00	
Detection	2 Bound to Fe-Mn Oxide	2.17	2.42	2.43	2.34	±0.15	1.40	1.40	1.47	1.42	±0.04	
limit	3 Bound to organic matter	1.23	1.46	1.51	1.40	±0.15	0.61	0.69	0.62	0.64	±0.04	
0.001	4 Residual	757.00	560.00	571.00	629.33	±110.70	45.60	68.60	62.30	58.83	±11.89	
	Σ (Fraction 1-4)	760.41	563.89	574.95	633.08	±110.41	47.68	70.77	64.46	60.97	±11.93	
	5 Total digestion				661.00					93.70		
As	1 Exchangeable	0.34	0.31	0.28	0.31	±0.03	0.01	0.04	0.03	0.03	±0.02	
Detection	2 Bound to Fe-Mn Oxide	86.80	90.90	84.10	87.27	±3.42	15.40	14.40	10.60	13.47	±2.53	
limit	3 Bound to organic matter	13.40	16.00	17.20	15.53	±1.94	2.67	1.74	2.17	2.19	±0.47	
0.005	4 Residual	2720.00	2739.00	2513.00	2657.33	±125.36	420.00	629.00	516.00	521.67	±104.62	
	Σ (Fraction 1-4)	2820.54	2846.21	2614.58	2760.44	±126.97	438.08	645.18	528.80	537.36	±103.81	
	5 Total digestion				3133.00					559.00		
Fe	1 Exchangeable	0.82	0.92	1.00	0.91	±0.09	0.27	0.35	0.46	1.08	±0.10	
Detection	2 Bound to Fe-Mn Oxide	524.00	505.00	514.00	514.33	±9.50	268.00	269.00	212.00	749.00	±32.62	
limit	3 Bound to organic matter	94.00	90.00	100.00	94.67	±5.03	54.00	43.70	48.40	146.10	±5.16	
0.066	4 Residual	18742.00	18094.00	18338.00	18391.33	±327.28	7132.00	10758.00	9785.00	9225.00	±1876.74	
	Σ (Fraction 1-4)	19360.82	18689.92	18953.00	19001.25	±338.04	7454.27	11071.05	10045.86	9523.73	±1864.07	
	5 Total digestion				24053.00					11001.00		

3) Fractionation/mobilization potential

Six soil samples were collected from the landfills at Sb-Mine Sulzburg and at Sonnhalden. Soil samples were taken with an aluminum shovel from the top soil and homogenized. For pH analysis, 10 g of a wet soil sample (< 2 mm) were brought in suspension with 50 ml of a CaCl₂ (0.01 mol L⁻¹) solution and shaken for five min. Afterwards, the suspension was left for 15 h before being shaken again followed International Organization for Standardization ISO 10390:2005 (<https://www.iso.org/standard/40879.html>). The pH was then measured in the sinking suspension using a Metrohm pH-electrode (719S Titrino).

The soil samples were dried overnight at 40 °C in a compartment drier (Binder). Subsequently, the dried samples were sieved to a grain size of 2 mm using a high-grade steel sieve. Clay clumps were broken up with a rubber hammer. Both, total digestion and sequential extraction were analyzed in this study.

For total digestion 0.5 g of soil were digested with 1.2 mL of HNO₃ 65 %, 3.6 mL HCl 32 %, and 0.5 mL of H₂O (mixture heated up to 85 °C for 2 h by microwave). This method follows that of the International Organization for Standardization ISO 11466:1995 (aqua regia: <https://www.iso.org/standard/19418.html>). Then 2.5 mL of BH₃O₃ 5 % were added as well as 25 mL deionized water before AAS analysis. Analytical chemistry standards are also applied per Merck Certipur standard no. 170204, 119776, 119733 and 119781 for Sb, Pb, As, and Fe, respectively.

The sequential extraction procedure used in this study was based on Tessier's method [35] with one modification: an oxalate solution was used in Fraction 2 to extract the Sb, Pb, As, and Fe from the amorphous Fe-hydroxides [36]. 10 mL of the samples were analyzed by AAS-flame analysis after each sequential extraction in the following four fractions;

- *Exchangeable (1)*: The sediment was extracted at room temperature for 1 h with 8 mL of sodium acetate solution (1 M NaOAc, pH 8.2) with continuous agitation.

- *Bound to Fe-Mn oxides (2)*: to the residual from (1) Oxalate acid (0.1 M C₂H₂O₄, pH 2.2) was added under continuous agitation for 1.5 h at room temperature.

- *Bound to organic matter (3)*: to the residual from (2) were added 3 mL of 0.02 M HNO₃ and 5 mL of 30 % H₂O₂ adjusted to pH 2 with HNO₃. The mixture was subsequently heated to 85 °C for 2 h with occasional agitation. Another 3 mL aliquot of 30 % H₂O₂ pH 2 with HNO₃ was then added and the sample was heated again to 85 °C until almost all the H₂O₂ had left with intermittent agitation. After cooling, 5 mL of 3.2 M NH₄OAc in 20 % (v/v) HNO₃ was added, the sample was diluted to 20 mL and agitated continuously for 30 min.

- *Residual (4)*: the residual from (3) was digested with a mixture of 5 mL of HNO₃, 1 mL of HF, and 1 mL of H₂O₂ by microwave digestion.

4) Contaminations output

Eight water samples were collected from inside and outside the gallery (Figure 2). Determination of pH, temperature, and conductivity were performed in the field with an Oxi 325-B Oximeter (WTH; water test handbag). For water sample collection, polyethylene plastic bottles were used to avoid any contaminants. All water samples were filtered. A Metrohm pH-electrode (719S Titrino) and a 712 conductivity-electrode were used to determine pH and conductivity, respectively. For anions (HCO₃⁻, SO₄²⁻, Cl⁻, F⁻, NO₃⁻), 6 mL of water samples were analyzed by DX-120 Ion Chromatograph. For cations (Ca, Mg, Na, K, Fe, Cu, Zn, Sb, As, Ba, Pb, Cd), the water samples were diluted with deionized water 1:10, 1:50, and 1:100 and 1 mL of CsCl (40 %) was added. Then

10 mL of water samples were analyzed by AAS-flame analysis after measuring Merck Certipur standard solution for each element. Si concentration was measured by Lambda40 UV/VIS spectrometer Perkin Elmer (DIN 38405-D21).

Results and discussion

1) Mineralogy and whole rock geochemistry

The main mineral of both locations is quartz, primary ore minerals are pyrite, arsenopyrite, sphalerite, stibnite, and antimony sulfosalts (Table 1). In this study, stibnite, antimony sulfosalts (boulangerite and plagionite) were identified based on quantitative data from EPM analysis (Figure 3 and Figure 4).

Stibnite (Sb_2S_3) and boulangerite ($Pb_5Sb_4S_{11}$) occur associated with pyrite, arsenopyrite, and sphalerite in the samples. Boulangerite is a major ore mineral in the analyzed samples at Sb-Mine Sulzburg. Texture observations show that boulangerite occurs together with stibnite at the rim; this indicates that it formed as late sequence of the mineralization, in which Pb formation was present. Stibnite is a major Sb

mineral in the analyzed samples at Sonnhalden, occurring associated with pyrite, arsenopyrite, and sphalerite. There is no boulangerite in the Sonnhalden samples, but they contain some plagionite ($Pb_5Sb_8S_{17}$). This infers that the analyzed samples of Sb minerals at Sonnhalden contain less Pb than those at Sb-Mine Sulzburg. According to Walenta [30] and Hoffher [31], the oldest ore mineralization consists of pyrite and arsenopyrite. The middle generation is sphalerite and the major Sb ore mineralizations are stibnite and antimony sulfosalts in the end stage (zinkenite, plagionite, semseyite, jemesonite, boulangerite, and berthierite) [30-31].

Stibiconite (Sb_2O_3) is a secondary mineral, which is present in the weathering crust of the samples from Sb-Mine and Sonnhalden. Bindheimite ($Pb_2Sb_2O_6$ (O, OH)) occurs only in the samples at Sb-Mine Sulzburg (Table 1 and Figure 5). The weathering crust probably contains more secondary minerals, but they are amorphous (e.g. metastibnite).

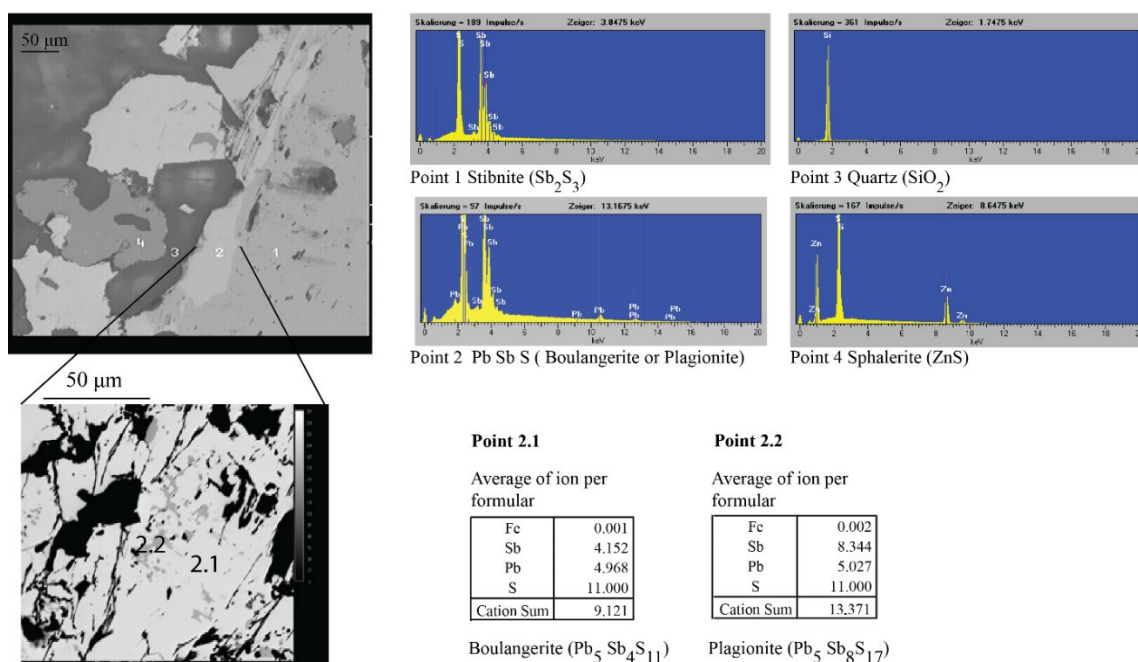


Figure 3 The BSE image shows sample points for EDX spectra 1, 2, 3, and 4. The EDX spectra show peaks of Sb, Pb, Zn, Si, and S and EPM data indicating that the composition depict stibnite (Sb_2S_3) at point 1, boulangerite ($Pb_5Sb_4S_{11}$) at point 2.1 and plagionite ($Pb_5Sb_8S_{17}$) at point 2.2, quartz (SiO_2) at point 3, and sphalerite (ZnS) at point 4.

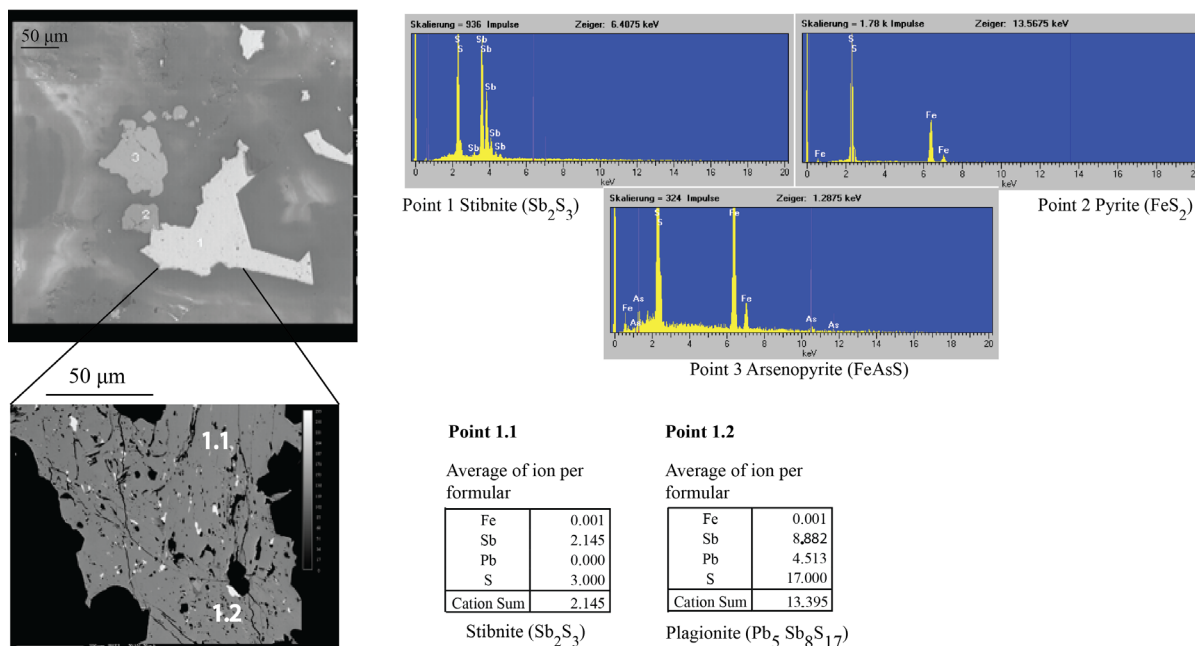


Figure 4 The BSE image shows sample points for EDX spectra 1, 2, and 3. The spectra show peaks of Zn, Fe, As, Sb, Pb, and S and EPM data indicating that the compositions represent Stibnite (Sb₂S₃) at point 1.1 and plagionite (Pb₅Sb₈S₁₇) at point 1.2, pyrite (FeS₂) at point 2 and arsenopyrite (Pb₅Sb₄S₁₁) at point 3.

The ore mineral veins, in the Carboniferous sediments, have a similar orientation at Sb-Mine Sulzburg and Sonnhalden (Figure 1c). Assuming the same age and composition of the fluid, a similar Sb mineralization could be expected for both localities. However, the analyzed samples showed variations in the chemical composition of Sb minerals. The whole rock chemistry in this area is heterogeneous and varies considerably in composition: SiO₂ (46-73 wt %), Sb₂O₃ (4-25 wt %); PbO (2-7 wt %); Al₂O₃ (0.2-2.5 wt %); Fe₂O₃ (0.4-1.6 wt %) (Table 2). The samples from Sb-Mine Sulzburg are characterized by considerable Sb₂O₃ and PbO contents, much higher than at Sonnhalden (Table 2). This agrees with the different mineral compositions. The high concentrations of Sb and Pb give rise to the presence of stibnite and antimony sulfosalts (boulangerite and

plagionite), which are less abundant in the samples of Sonnhalden.

2) Soil analysis

Generally, soil components include sand, silt, hydrous oxides of Fe, clay minerals, and organic matter. The soil samples from Sb-Mine Sulzburg have a pH value of around 5.9 and pH 4.2 at Sonnhalden. The soils at Sb-Mine Sulzburg have higher concentrations of Sb, Pb, As, and Fe. At both localities, the concentrations decrease in the following order: Fe > As > Pb > Sb (Table 3). Considerable amounts of these elements are bound to Fe-Mn oxides fraction. The exchangeable fraction of all analyzed elements is always lowest. Comparing the sum of the four fractions with the value for total digestion reveals relatively good agreement.

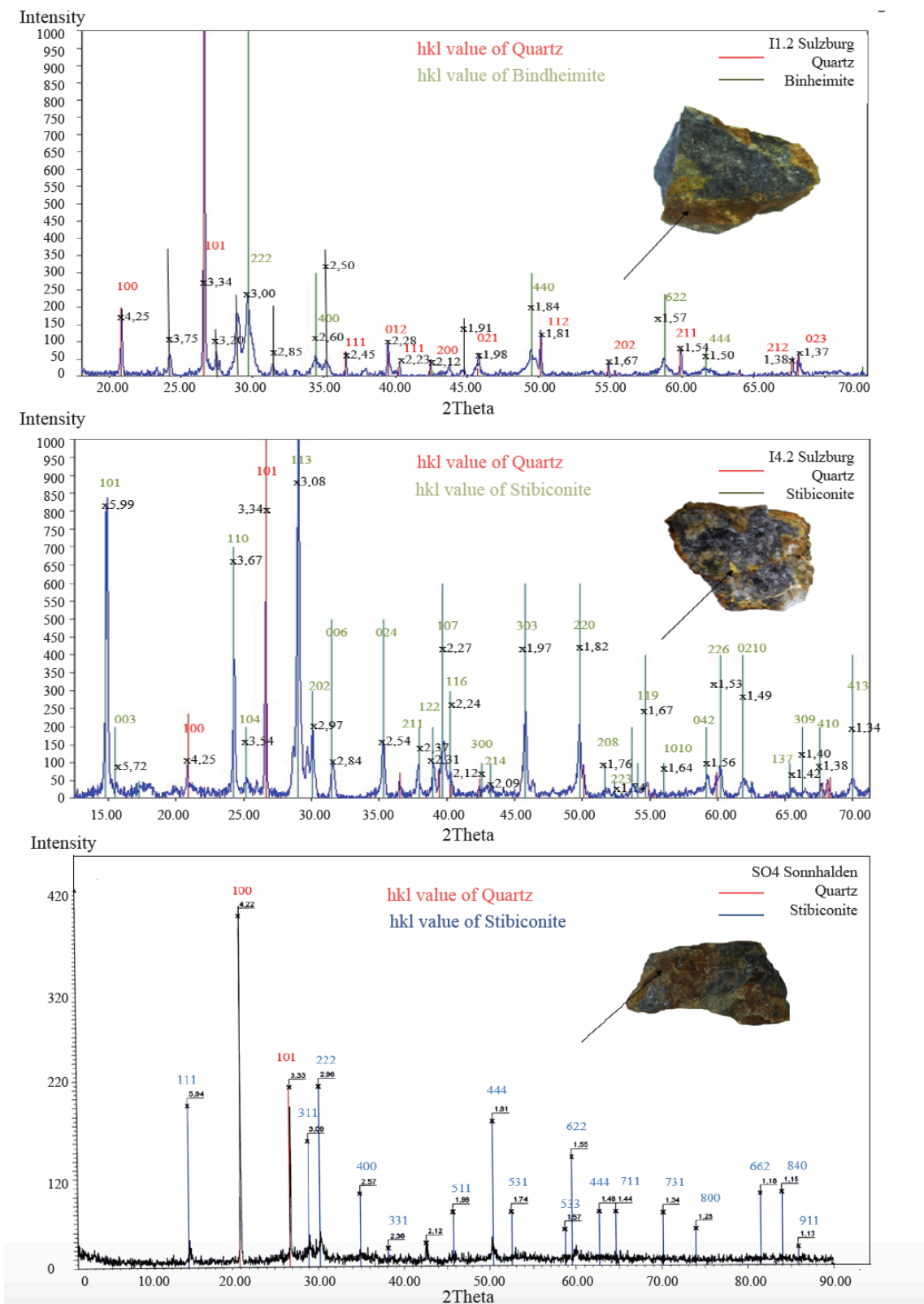


Figure 5 XRD diffraction patterns of samples I1.2, I4.2 from Sb-Mine Sulzburg and SO₄ from Sonnhalden. The main mineral is quartz and secondary minerals are stibiconite and binheimite.

The exchangeable fraction is potentially available to plants and is mobile in the environment [37]. Because the exchangeable fraction is so small, uptake by crops and a potential effect on animals and humans via the food chain is expected to be correspondingly small. The species bound to the Fe-Mn oxide fraction showed a higher element concentration than that bound to organic matter and the exchangeable fraction. This indicates that Sb, Pb, and As tend to bind with amorphous Fe-hydroxides [11, 15, 19, 38-39]. The species bound to the organic matter fraction is also small. The coordination ability of Fe to organic matter is stronger than that of the other elements. Under oxidizing conditions, organic matter can be degraded, potentially leading to release of the elements. The species in the residual represents the highest concentration of the elements. This means that almost the entire budget of the studied elements is not very mobile.

The Fe and As concentrations in soil are higher than Sb and Pb, but the opposite is observed in bulk-rock composition. Because the bulk rock samples are from dumps, they also contain a high Sb mineral concentration. The country rocks are conglomerates, which contain pyrite and arsenopyrite. Under reducing or oxidizing conditions in the environment, these are a source of Fe and As weathering to soil and water.

Both sites had been polluted by weathering of minerals containing heavy metals and metalloids (Pb, Fe, Sb, and As) from the old Sb mines since the Middle Ages. The soil sample from Sb-Mine Sulzburg has substantially higher concentrations of Sb, Pb, As, and Fe. The question arises: why there is such a difference between the two areas, given the similarity in physical behavior, age, and soil chemical properties, as well as the climatic conditions in the two locations? Our study indicated differences in the mineralogical compositions of the two sites. Several para-

meters control oxidation of minerals, particularly temperature, redox conditions, pH of the systems, organic matter decomposition, leaching and ion exchange processes, as well as microbial activity [40]. The differences in soil pH values between Sb-Mine Sulzburg and the Sonnhalden area is likely to play an important role in explaining differences in leaching processes.

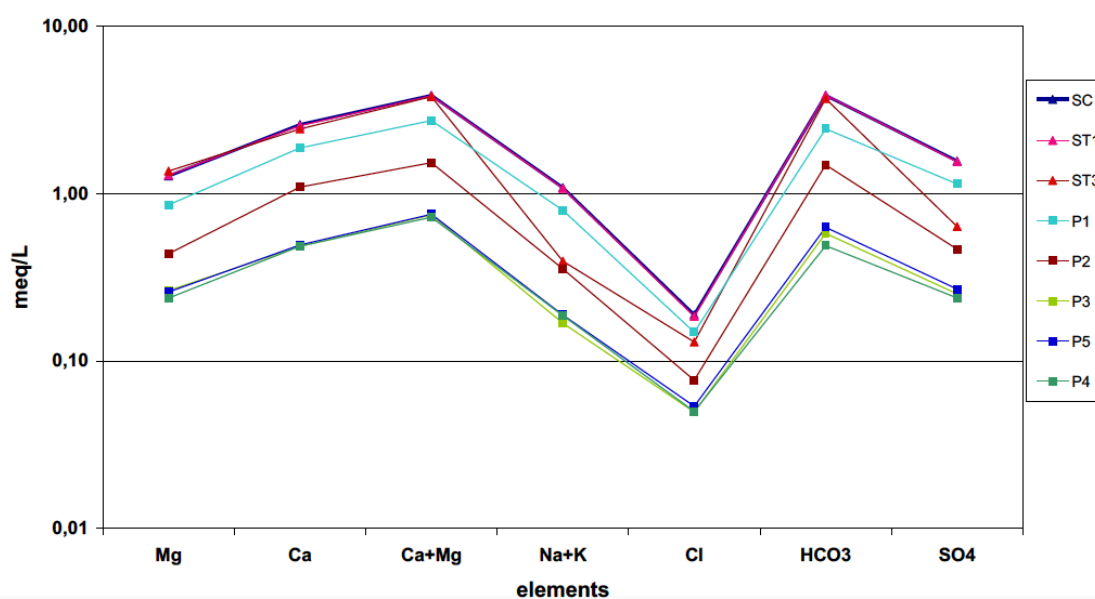
3) Water chemical analysis

The water samples from inside the gallery have a higher conductivity (EC), but a lower redox potential (Eh) and a lower concentration of oxygen than those from outside the gallery (Table 4, Figure 2). The water samples in the gallery and at the entrance have higher concentrations of major anions and cations than outside the gallery. The cations that are present in the greatest concentration are Ca^{2+} , Mg^{2+} , Na^+ , and K^+ (Figure 6). The water shows concentrations of $\text{Ca}+\text{Mg} > \text{Na}+\text{K}$. Calcium and magnesium in this area are predominantly sourced from dissolution of calcite and dolomite, which are dominant at ST3 and at the entrance (P1) of the gallery. The weathering of silicate minerals (e.g. feldspar and mica) is also a common source for dissolved Na and K.

The anions present in the highest concentrations are bicarbonate (HCO_3^-), and sulphate (SO_4^{2-}). The water samples have concentrations of $\text{HCO}_3^- > \text{SO}_4^{2-} > \text{Cl}^-$. Bicarbonate dissolved in water is derived from dissolution of calcite and dolomite. Sulphate dissolved in the water; originates from weathering of sulphide minerals, most commonly pyrite, arsenopyrite, and antimony sulfosalt. Comparing the water analysis, regarding toxic elements, at and around Sb-mine Sulzburg, Sb concentrations are lower than those of As and Pb for all water samples. This is possible due to the strong affinity of Sb to Al, Mn, and Fe oxides and a lower mobility, from the source into the soil and water, of Sb compared to As and Pb.

Table 4 Chemical analysis of water samples

Location	Schacht SC	Stollen1 ST1	Stollen3 ST3	Positon1 P1	Positon2 P2	Positon3 P3	Positon5 P5	Positon4 P4
Temperature/°C	10.00	10.30	10.13	10.40	11.57	9.67	10.23	9.90
pH in field	6.92	7.12	8.03	8.21	7.92	7.74	7.59	7.52
pH in Lab	7.32	7.20	7.99	8.10	7.60	7.09	6.82	7.33
EC ($\mu\text{S cm}^{-1}$) in field	517.00	515.00	440.00	372.00	420.00	106.00	108.00	95.00
EC ($\mu\text{S cm}^{-1}$) in Lab	512.40	510.40	410.50	362.90	202.50	109.00	127.10	95.64
Alk (HCO_3) (mmol L^{-1})	3.85	3.86	3.68	2.43	1.48	0.58	0.63	0.49
O ₂ (mg L^{-1})	0.25	1.25	6.30	9.25	9.15	10.40	12.10	11.95
Eh (mv)	47.7	45.9	187	198	214	273	392	413
Ca ²⁺ (mg L^{-1})	51.62	50.81	48.55	37.44	21.89	9.66	9.88	9.69
Mg ²⁺ (mg L^{-1})	15.43	15.61	16.50	10.37	5.30	3.20	3.14	2.89
Na ¹⁺ (mg L^{-1})	23.22	23.22	7.91	16.92	6.98	2.93	3.47	3.30
K ¹⁺ (mg L^{-1})	2.85	2.48	1.96	2.30	1.99	1.60	1.45	1.70
Sb ⁵⁺ (mg L^{-1})	0.00	0.00	0.00	0.03	0.01	0.00	0.00	0.00
As ⁵⁺ (mg L^{-1})	0.52	0.56	0.16	0.31	0.05	0.04	0.03	0.04
Ba ²⁺ (mg L^{-1})	0.87	0.80	0.94	1.00	1.10	1.17	1.30	1.23
Fe ²⁺ (mg L^{-1})	0.15	0.28	0.20	0.02	0.37	0.05	0.02	0.02
Cu ²⁺ (mg L^{-1})	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02
Pb ²⁺ (mg L^{-1})	0.04	0.01	0.06	0.06	0.09	0.08	0.11	0.10
Zn ²⁺ (mg L^{-1})	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02
Cd ²⁺ (mg L^{-1})	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
HCO ₃ ⁻ (mg L^{-1})	235.17	235.35	224.43	148.16	90.31	35.21	38.32	29.78
SO ₄ ²⁻ (mg L^{-1})	75.03	74.35	30.45	54.80	22.36	12.08	12.92	11.44
Cl ⁻ (mg L^{-1})	6.68	6.54	4.60	5.26	2.72	1.76	1.90	1.77
F ⁻ (mg L^{-1})	1.18	1.16	0.22	0.68	0.26	0.06	0.09	0.04
NO ₃ ⁻ (mg L^{-1})	0.00	0.00	0.39	2.42	1.02	10.46	9.87	11.33
SiO ₂ (mg L^{-1})	8.07	7.87	7.95	5.00	0.74	2.70	1.22	4.13
TDS (mg L^{-1})	420.88	419.09	344.38	284.80	155.21	81.05	83.74	77.50

**Figure 6** Schöller diagram.

All the water samples are in an oxidizing state. The water samples inside the gallery contain higher amounts of As than outside, but the Pb concentrations outside the gallery are higher. This can be interpreted as Pb being more mobile than As and Sb, from the gallery to the stream, or that Pb is derived from another source. The water sample at position P4 shows a high concentration of Pb. The Sb-Mine Sulzburg has a minor influence on the results at this position. The Sb concentration is highest at P1.

Considering Sb and As from water samples, we use computer programs MINTEQA2 (<https://vminteq.lwr.kth.se/>) to calculate the speciation under conditions (T, pH, Eh, and ion contents). The speciation results (Table 5) show that Sb in the water inside and outside mine are in V oxidation states (Sb^{5+}). Water inside the mine contains more As in III oxidation states (As^{3+}) than outside. The water outside the mine shaft are more in the As^{5+} field.

Table 5 Percentage distribution among dissolved and absorbed species of Sb and As

	Component	% of total concentration	Species name
Inside gallery (SC, ST1, ST3)	$\text{Sb}(\text{OH})_6^{-1}$	99.997	Sb^{5+}
	$(\text{HAsO}_4)^{-2}$	74.554	As^{5+}
	$(\text{H}_2\text{AsO}_4)^{-3}$	25.443	As^{3+}
Outside gallery (P2, P3, P4, P5)	$\text{Sb}(\text{OH})_6^{-1}$	99.999	Sb^{5+}
	$(\text{HAsO}_4)^{-2}$	84.632	As^{5+}
	$(\text{H}_2\text{AsO}_4)^{-3}$	15.362	As^{3+}

Conclusions

The Sb deposits in Sulzburg are mineralogically complex as they hold mixtures of antimony-lead-bearing sulfides and sulfosalts. Sources of toxic elements in this area are important for ecotoxicity, therefore, the release of Sb, As, and Pb are of concern, even at ppm level. In the soil samples at Sb-Mine Sulzburg and Sonnhalden, the entire budgets of these toxic elements are not very mobile. Based on soil sequential extraction, toxic elements mostly remain in the residual fraction. At Sb-Mine Sulzburg area, antimony from the weathered Sb minerals is possible bind to Fe-oxides-hydroxides and amorphous material in the sediments and soils, because Fe-oxides-hydroxides is a product from secondary minerals of pyrite and arsenopyrite. Therefore, only a small amount enters the aquatic phase. In this area, antimony was introduced into the aquatic cycle through natural processes such as weathering of minerals and soils. However, metals and metalloids bound to the Fe-Mn

oxides fraction and soil organic matter can be mobilized with increasing oxidizing or reducing conditions in the environment. The fraction associated with the residual fraction can only be mobilized by weathering, a long-term process. Soluble forms of antimony (Sb^{5+}) predominated in water both inside and outside the mine. Sb concentrations of water samples from the stream in Sulzburg remain below German drinking water limits, but the water from the creek is influenced directly from Sb-Mine. All water samples exhibit higher concentrations of As and Pb than of Sb. Arsenic (As^{5+}) from weathered arsenopyrites and Sb minerals is more mobile and hence enters the aquatic phase.

Acknowledgements

The authors would like to express their sincere thanks to Prof. Dr. Reto Gieré and Dr. Andreas Danislewsky for their valuable advice. We also thank the officers at Sulzburg, Dr. Justus Tonn and Friedlich Merkle for their

help in the field. S. Chawchai and R. Bissen acknowledge the Ratchadaphiseksomphot Endowment Fund, part of the 'Research Grant for New Scholar CU Researcher's project'.

References

- [1] Lottermoser, B.G. Introduction to mine wastes. In: Mine wastes. Springer, Berlin, Heidelberg; 2010. [Online] Available from: https://link.springer.com/chapter/10.1007/978-3-642-12419-8_1 [Accessed 19 July 2017].
- [2] Lottermoser, B.G. Tailings. In: Mine wastes. Springer, Berlin, Heidelberg; 2010. [Online] Available from: https://link.springer.com/chapter/10.1007/978-3-642-12419-8_4 [Accessed 19 July 2017].
- [3] Hudson-Edwards, K.A., Jamieson, H.E., Lottermoser, B.G. Mine wastes: Past, present, future. *Elements*, 2011, 1, 7(6), 375-80.
- [4] Macías, F., Pérez-López, R., Caraballo, M.A., Cánovas, C.R., Nieto, J.M. Management strategies and valorization for waste sludge from active treatment of extremely metal-polluted acid mine drainage: A contribution for sustainable mining. *Journal of Cleaner Production*, 2017, 10, 141, 1057-1066.
- [5] Oke, S., Vermeulen, D. Geochemical modeling and remediation of heavy metals and trace elements from artisanal mines discharge. *Soil and Sediment Contamination: An International Journal*, 2017, 2, 26(1), 84-95.
- [6] Lottermoser, B.G. Sulfidic mine wastes. In: Mine wastes. Springer, Berlin, Heidelberg; 2010. [Online] Available from: https://link.springer.com/chapter/10.1007/978-3-642-12419-8_2 [Accessed 19 July 2017].
- [7] Nordstrom, D.K. Mine waters: Acidic to circumneutral. *Elements*, 2011, 1, 7(6), 393-398.
- [8] Lindsay, M.B.J., Moncur, M.C., Bain, J.G., Jambor, J.L., Ptacek, C.J., Blowes, D.W. Geochemical and mineralogical aspects of sulfide mine tailings. *Applied Geochemistry*, 2015, 1, 57, 157-177.
- [9] Sephton, M.G., Webb JA. Application of Portland cement to control acid mine drainage generation from waste rocks. *Applied Geochemistry*, 2017, 81, 143-154.
- [10] Zhou, J., Nyirenda, M.T., Xie, L., Li, Y., Zhou, B., Zhu, Y., et al. Mine waste acidic potential and distribution of antimony and arsenic in waters of the Xikuangshan mine, China. *Applied Geochemistry*, 2017, 1, 77, 52-61.
- [11] Hammel, W., Debus, R., Steubing, L. Mobility of antimony in soil and its availability to plants. *Chemosphere*, 2000, 41(11), 1791-1798.
- [12] Filella, M., Belzile, N., Chen, Y.W. Antimony in the environment: a review focused on natural waters. *Earth-Science Reviews*, 2002, 1, 57(1), 125-176.
- [13] Flynn, H.C., Meharg, A.A., Bowyer, P.K., Paton, G.I. Antimony bioavailability in mine soils. *Environmental Pollution*, 2003, 124(1), 93-100.
- [14] Shotyck, W., Krachler, M., Chen, B. Antimony: Global environmental contaminant. *Journal of Environmental Monitoring*, 2005, 22, 7(12), 1135-1136.
- [15] Ettler, V., Mihaljevič, M., Šebek, O., Nechutný, Z. Antimony availability in highly polluted soils and sediments - A comparison of single extractions. *Chemosphere*, 2007, 68(3), 455-463.
- [16] Filella, M., Belzile, N., Lett, M.C. Antimony in the environment: A review focused on natural waters. III. Microbiota relevant interactions. *Earth-Science Reviews*, 2007, 1, 80(3), 195-217.
- [17] Murciego, A.M., Sánchez, A.G., González, M.A.R., Gil, E.P., Gordillo, C.T., Fernández, J.C., Triguero, T.B.

- Antimony distribution and mobility in topsoils and plants (*Cytisus striatus*, *Cistus ladanifer* and *Diuriscia viscosa*) from polluted Sb-mining areas in Extremadura (Spain). *Environmental Pollution*, 2007, 145(1), 15-21.
- [18] Smichowski, P. Antimony in the environment as a global pollutant: A review on analytical methodologies for its determination in atmospheric aerosols. *Talanta*, 2008, 15, 75(1), 2-14.
- [19] Wilson, S.C., Lockwood, P.V., Ashley, P.M., Tighe, M. The chemistry and behaviour of antimony in the soil environment with comparisons to arsenic: A critical review. *Environmental Pollution*, 2010, 1, 158(5), 1169-1181.
- [20] Okkenhaug, G., Zhu, Y.G., Luo, L., Lei, M., Li, X., Mulder, J. Distribution, speciation and availability of antimony (Sb) in soils and terrestrial plants from an active Sb mining area. *Environmental Pollution*, 2011, 159(10), 2427-2434.
- [21] Pérez-Sirvent, C., Martínez-Sánchez, M.J., Martínez-López, S., Hernández-Córdoba, M. Antimony distribution in soils and plants near an abandoned mining site. *Microchemical Journal*, 2011, 97(1), 52-56.
- [22] Wang, X., He, M., Xi, J., Lu, X. Antimony distribution and mobility in rivers around the world's largest antimony mine of Xikuangshan, Hunan Province, China. *Microchemical Journal*, 2011, 97(1), 4-11.
- [23] Hiller, E., Lalinská, B., Chovan, M., Jurkovič, E., Klimko, T., Jankulár, M., et al. Arsenic and antimony contamination of waters, stream sediments and soils in the vicinity of abandoned antimony mines in the Western Carpathians, Slovakia. *Applied Geochemistry*, 2012, 27(3), 598-614.
- [24] Hockmann, K., Lenz, M., Tandy, S., Nachtegaal, M., Janousch, M., Schulin, R. Release of antimony from contaminated soil induced by redox changes. *Journal of Hazardous Materials*, 2014, 30, 275, 215-221.
- [25] Tasev, G., Serafimovski, T., Djordjevic, T., Boev, B. Soil and groundwater contamination around the Lojane As-Sb mine, Republic of Macedonia. 17th International Multidisciplinary Scientific GeoConference SGEM 2017, 2017, 17(52), 809-817.
- [26] Radková, A.B., Jamieson, H., Lalinská-Voleková, B., Majzlan, J., Števkó, M., Chovan, M. Mineralogical controls on antimony and arsenic mobility during tetrahedrite-tennantite weathering at historic mine sites Špania Dolina-Piesky and Ľubietová-Svätodušná, Slovakia. *American Mineralogist*, 2017, 102(5), 1091-1100.
- [27] Li, X., Yang, H., Zhang, C., Zeng, G., Liu, Y., Xu, W., et al. Spatial distribution and transport characteristics of heavy metals around an antimony mine area in central China. *Chemosphere*, 2017, 1, 170 (Supplement C), 17-24.
- [28] Hu, X., He, M., Li, S., Guo, X. The leaching characteristics and changes in the leached layer of antimony-bearing ores from China. *Journal of Geochemical Exploration*, 2017, 1, 176 (Supplement C), 76-84.
- [29] Armiento, G., Nardi, E., Lucci, F., Cassan, M.D., Ventura, G.D., Santini, C., et al. Antimony and arsenic distribution in a catchment affected by past mining activities: influence of extreme weather events. *Rendiconti Lincei*, 2017, 1, 28(2), 303-315.
- [30] Walenta, K. Die Antimonerführenden Gänge des Schwarzwald. *GeolLandesamt Baden-Württ*, 1957, 2, 13-67.
- [31] Hofherr, I.M. Eine Antimon-Mineralisation südlich von Sulzburg im Südschwarzwald. *Ber Naturf Ges Freibg Br*, 1984, 74, 49-71.

- [32] Maus, H. Geologie und früher Bergbau bei Sulzburg, In: Geschichte der Stadt Sulzburg, Bd. 1. Freiburg, 1993.
- [33] Müller, A., Grosspietsch, J. Geschichte der Stadt Sulzburg: Von den Anfängen bis zum ausgehenden Mittelalter. Kehrer, 1993.
- [34] Yu, Z., Robinson, P., McGoldrick, P. An Evaluation of methods for the chemical decomposition of geological materials for trace element determination using ICP-MS. *Geostandards Newsletter*, 2001, 1, 25(2-3), 199-217.
- [35] Tessier, A., Campbell, P., Bisson, M. Sequential extraction procedure for the speciation of particulate trace metals. *Analytical Chemistry*, 1979, 51(7), 844-51.
- [36] Cornell, R.M., Schwertmann, U. The iron oxides: Structure, properties, reactions, occurrences and uses. John Wiley & Sons; 2003. 712.
- [37] Yutong, Z., Qing, X., Shenggao, L. Chemical fraction, leachability, and bioaccessibility of heavy metals in contaminated soils, Northeast China. *Environmental Science and Pollution Research*, 2016, 1, 23(23), 24107-24114.
- [38] Poulton, S.W., Canfield, D.E. Development of a sequential extraction procedure for iron: Implications for iron partitioning in continentally derived particulates. *Chemical Geology*, 2005, 25, 214(3), 209-221.
- [39] Assawincharoenkij, T., Hauzenberger, C., Sutthirat, C. Mineralogical and Chemical Characteristics of gossan waste rocks from a gold mine in Northeastern Thailand. *Applied Environmental Research*, 2017, 30, 39(2), 1-13.
- [40] Peng, J., Song, Y., Yuan, P., Cui, X., Qiu, G. The remediation of heavy metals contaminated sediment. *Journal of Hazardous Materials*, 2009, 30, 161(2), 633-640.