Antimony Anomalies around abandoned Silver Mines in Tyrol/Austria

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Abstract

Austria was one of the richest Silver producers in Medieval Times, with most of the important mines located in Tyrol. Nearly all those mines in the Inntal Valley mined Fahlores of which the Silver contents were the basis for Tyrol's political power by that time. In 1999 a large rock slide caused the last working mine to shut down, and intensive geotechnical, geological, and hydrogeological investigations started around the sliding area. These investigations found Sb anomalies in many springs around the dolomite underground mine and in the underground mine itself. While some scientists recognized a close relation to the former Silver mine, the mine owner suggested a relation to the geological situation.

About 50 sampling points in different geological strata near the Großkogel and Schwaz dolomite and visitor's mines were sampled in summer and winter and analysed for the main and trace elements. As a result of those investigations we were able to show, that the anomalies are closely linked to the geological situation and that mined as well as unmined areas are subject to Sb anomalies of up to 2.2 mg L^{-1}.

It is clear from our investigations, that the Antimony anomalies are linked to the geological situation and that the current operators are not responsible for the Antimony concentrations that can be found today.

1 Introduction

1.1 Locations and Mining History

One of the most important Austrian silver production regions in medieval and the early modern times was Tyrol. Between Schwaz and Brixlegg, both located in the Inntal valley north-east of Innsbruck, numerous silver mines existed that mined silver-bearing fahlore (fig.1). Both, Tyrol's political power and the economical power of the Augsburg Fugger family, are due to the silver mined there. The investigations described here concentrated on the Schwaz and the St. Gertraudi mining districts, covering an area of 10 km² and 5 km², respectively. Originally, the investigations were carried out to conduct mine water tracer tests in the Georgi-Unterbau mine south-east of Brixlegg, but after identifying the antimony anomalies, they were extended to cover the Schwaz area as well.

Two main adits were used to dewater the mined areas of St. Gertraudi and Schwaz: the Georgi-Unterbau adit and the Wilhelm-Erbstollen adit. Those to adits were the basis for the underground sampling described here.

Mining in the Schwaz area dates back to Bronze Age times (Rieser and Schrat-

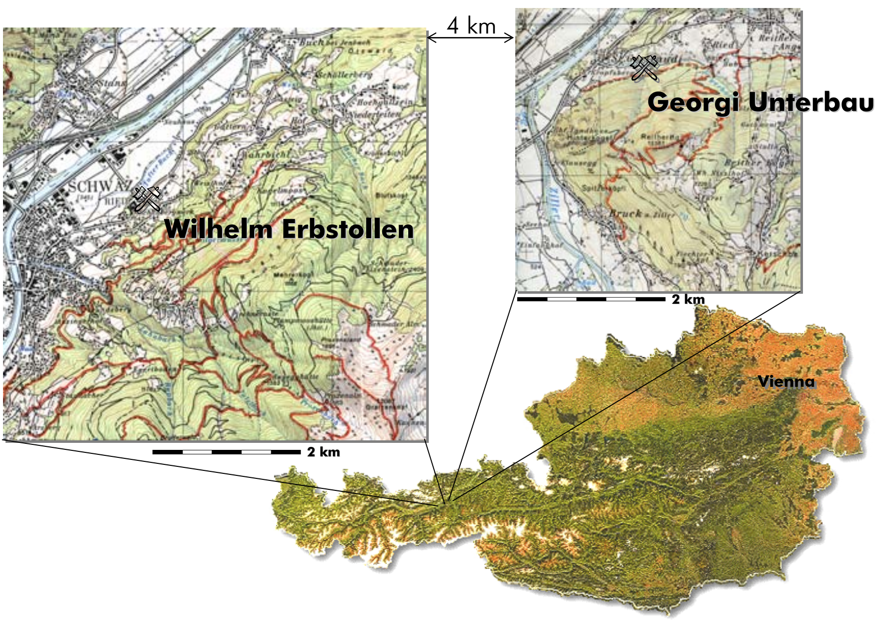

Fig. 1: Location of the mining and investigation areas of Schwaz (left) and Großkogel (right) in central Tyrol/Austria. Ming symbols mark the entrances to the two main dewatering adits.

tenthaler 2002) and started again in the 13th century (Hanneberg and Schuster 1994; Palme et al. 2002). By far the most important mining area was the Falkenstein mining area limited by the Bucher Bach in the east and the Lahnbach in the west. Details about the mining in the surroundings of Brixlegg can already be found in a goods list from the year 1416. Many miners from Bohemia, Saxony and other Central European mining regions came to the Inn valley, attracted by the message of rich silver findings. 1427 Duke Friedrich released a mining order for Schwaz to regulate the pit lending and the operational procedures. The freedom of mining promoted the prospering of the mining area decisively. Twenty-six pits were working at the Falkenstein before the year 1460, and within the years to 1499 another 231 mining leases were awarded. Because of this development more than 10,000 miners were employed in over 1,000 galleries soon and Schwaz became the most important silver mining area in Europe. Thus, the Falkenstein mines achieving the highest production with a peak of 15.7 t of fine silver in 1523. Due to mismanagement and the increasing import of silver from the Americas, silver mining in the Schwaz area ended in the late 17th century.

As a result of exploration in the Schwaz area, in 1873 the Wilhelm Erbstollen was driven to undermine the Falkenstein area. Rich fahlores were found in the Krummörter pit, but ore mining ceased in 1957. Since then the Montanwerke Brixlegg AG mined high quality dolomite until a mountain collapse caused the mines closure by the authorities in 1999.

In 1887 the miners started to drive the Georgi-Unterbau at St. Gertraudi, which opened up rich fahlore and barite resources. Starting in 1900, a 100 m deep two compartment blind shaft was sunk, connecting the 20, 40, 70 and 100 m main levels and the 10, 75 and 80 m sublevels (Pirkl 1961; Mutschlechner 1984; Krischker 1990; Hanneberg and Schuster 1994) as well as the 14-Nothelfer pit and the Barbara pit with each other. It was partially to fully flooded since the 1950's (Hießleitner 1951; Schmidegg 1953) and pumped out again in 1984 and 1988 for ore prospecting (Krischker 1990). Since 1990 the blind shaft has been flooded and therefore, stationary hydraulic conditions exist.

1.2 Geological situation

Most parts of the mines are within the Devonian Schwaz Dolostone (*Schwazer Dolomit*) of the Northern Tyrol Greywacke area (*Nordtiroler Grauwackenzone*). Typically, the Schwaz Dolostone is a very hard, light white to light grey dolostone, being highly brecciated and fissured in the area investigated. The dolostone hosts silver and mercury bearing fahlores (there under Schwazite) as well as barite, the mineralisation being bound, but not restricted, to the breccia zones (Pirkl 1961; Wöbking 1982). Grundmann and Martinek (1994) and Schnorrer (1994) and Schnorrer (1996) described 20 ore minerals being characteristic for the Schwaz Dolostone and a total of over 132 minerals for the Schwaz-Brixlegg area, there under REE minerals. According to Arlt and Diamond (1998), who investigated fahlores of the Schwaz-Brixlegg mining area, the fahlores of the Georgi-Unterbau comprise of 41% Cu; 0.5% Ag; 2% Fe; 5% Zn; 0.7% Hg; 0.02% Mn; 16% Sb; 9%

As; and 26% S. Unfortunately, no data on REE concentrations in the rocks of the Greywacke and their interpretation can be found in the literature.

A first physico-chemical investigation of the flooded blind shaft was conducted in December 2000. In addition to the temperature and salinity measurements water samples were taken to be analysed on site and in the laboratory. Further investigations, including two tracer tests with 15 µm microspheres and Na-fluorescein, were conducted in August 2001 and February 2002 (Wolkersdorfer et al. 2002; Wolkersdorfer 2002).

1.3 Eiblschrofen Rock Slide

On July 10th 1999 a large rock slide occurred at the Eiblschrofen above the city of Schwaz. Several hundred of inhabitants had to be evacuated and the Schwaz dolomite mine (run by Montanwerke Brixlegg AG) as well as the Schwaz visitor mine (run by Silberbergwerk Schwaz Besucherführungsgesellschaft m.b.H.) had to be closed immediately (Weber and Schneider 2000). Whilst the visitor mine since then started its operation, the dolomite mine is still closed as a result of missing permissions by the authorities.

As a result of the rock slide, intensive investigations, including the hydrogeological situation, were initiated. Those investigations resulted in unusually high antimony concentrations in the surface and mine waters of the Schwaz mining area (Millen 2003). It was assumed by the authorities, that those anomalies are a result of the current mining operations. Therefore, the dolomite mine operator initiated a hydrogeological sampling programme to investigate the natural antimony background of the Schwaz and the Großkogel mining areas.

The aim of those hydrogeological investigations was to find relations between the lithology and antimony anomalies, the aerial distribution of the antimony concentrations and potential remediation methods for the mine water. Furthermore, it should be shown, if there is a potential anthropogenic cause for the anomalies.

2 Investigations

A total of 138 water samples from the Großkogel and the Schwaz mining areas were used for the investigations described here. 98 samples were collected by the authors, 21 are cited by Weber and Schneider (2000) and 19 samples were added by the Montanwerke Brixlegg AG. Details of the sampling procedure can only be given for the 98 samples collected by the authors. They were collected from 29 sampling points in the Schwaz area and 19 from the Großkogel area, there under 27 surface and 21 underground sampling points. All sampling points were chosen to represent the main rock types outcropping at the Großkogel and around Schwaz at the surface and the main underground workings in the Großkogel barite and the Schwaz dolostone mines. Furthermore, depth dependent antimony profiles were measured in the 100 m deep Georgi Unterbau shaft.

All samples were filtered on-site with a 0.45 µm cellulose acetate filter and filled into 500 mL bottles for the main ions and 50 mL bottles for the trace elements, the latter acidified for stabilisation. Those bottles were labelled with the sample number, the date, and the sampling point and stored in a cold and cool place thereafter. On site the pH, conductivity, temperature, redox-potential, oxygen-content, acidity (base capacity k_B 8.2), alkalinity (acid capacity k_S 4.3), and the iron contents (ferric and ferrous) were evaluated. Oxygen was measured with a WTW (Wissenschaftlich Technische Werke, Weinheim/Germany) oxygen sensor, iron with a Hach DR890 field photometer (Hach Company, Loveland CO/USA), and all other parameters with an Ultrameter 6P (MYRON L Company, Karlsbad/USA).

Main ions (Li, Na, K, Ca, Mg, Cl, NO_3, SO_4) were measured by ion chromatography with a D6000 of Merck-HITACHI, trace elements (Ag, As, Au, Ba, Bi, Cd, Co, Cs, Cu, Hg, Mn, Mo, Ni, Pb, Pd, Rb, Sb, Sc, Se, Sn, Sr, U, W, Zn) with the ICP-MS of the Fakultät Forst, Geo- und Hydrowissenschaften (Tharandt; Dresden University). Fluoride was measured with ion selective probes F500 (WTW Weinheim) and reference electrode SE 20/EB (Sensortechnik Meinsberg) as well as probe 94-09 (Orion, Boston, USA; with reference electrode included).

To compare the reliability of the low antimony concentrations in the river Inn, those samples were also measured by neutron activation analyses (Freiberg Institute for Archeometry, Prof. E. Pernicka).

Using those results, statistical (SPSS) and chemico-thermodynamical (PHREEQC) investigations were carried out to interpret the data obtained. Over and above an extensive literature review was conducted, which showed that antimony anomalies in mine and surface water had not been of concern so far.

3 Results

European and Austrian regulations require an antimony content of 5 µg L^{-1} in the drinking water (EU 98/83; TWV BGBl 304/2001). No regulations exist for surface waters, but the German Länderarbeitsgemeinschaft Wasser (LAWA) published a list of antimony values which require inspection or action when exceeded in groundwaters (Länderarbeitsgemeinschaft Wasser [LAWA] 1994). Thereafter, inspections are necessary if the antimony concentrations exceed 2–10 µg L^{-1} and remediation actions are required if 20–60 µg L^{-1} are exceeded.

According to investigations conducted by the Austrian Environment Agency (Philippitsch and Grath 2003), antimony in Austrian karst waters has a mean of 0.2 µg L^{-1} and a maximum of 0.7 µg L^{-1} ($n = 50$). Drinking waters in Austria regularly are below the drinking water standards. This complies with other investigations, showing, that surface water concentrations range between < 0.05 and 0.08 µg L^{-1}, ground water between < 0.02 and 1.33 µg L^{-1} and mine waters between < 0.1 and 250 µg L^{-1} (Mattheß 1994; Merkel and Sperling 1998). Extreme antimony concentrations were observed in brines or thermal waters, reaching 8–1,000 µg L^{-1} (Wedepohl et al. 1969–1978).

Both, the Schwaz and the Großkogel areas revealed mean and maximum antimony concentrations which are far higher then those reported so far (Tab. 1), but in both areas, though geologically slightly different, the means and maxima are

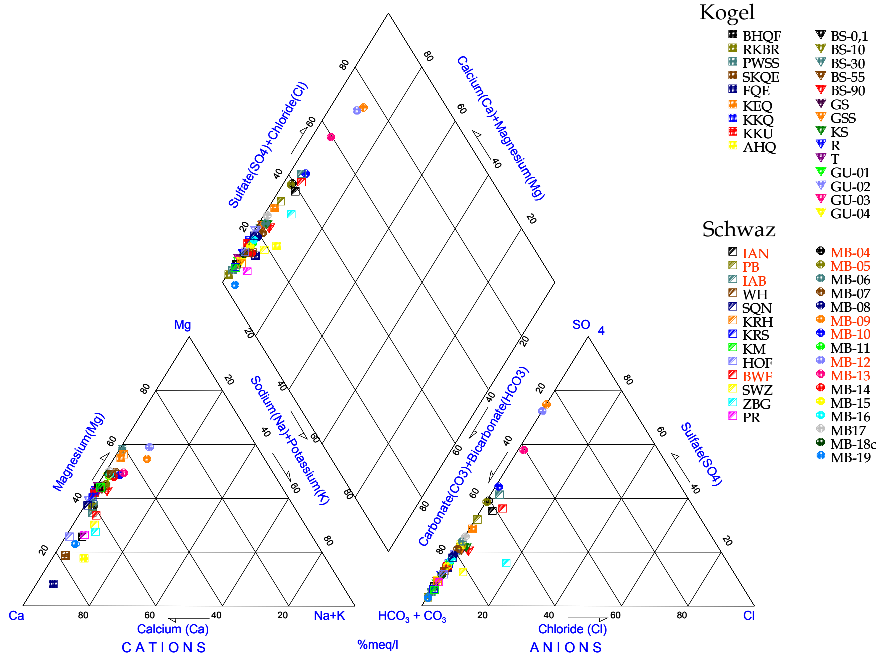

Fig. 2: Hydrogeochemical classification of the analysed surface and mine waters in the PIPER-diagram (explanation in the text).

very similar (539 and 512 µg L^{-1}; 1768 and 1758 µg L^{-1}, respectively). Other sources also report antimony concentrations of up to 2200 µg L^{-1}, but no particular information about the sampling procedure is given, therefore those values will not be included in the detailed interpretation (Montanwerke Brixlegg AG; Weber and Schneider 2000).

Hydrogeochemically, the surface and ground waters of Schwaz and Kogel are very similar, plotting into the Ca-Mg-HCO_3 and the Mg-Ca-HCO_3 fields (fig. 2). Only some of the Schwaz mine waters are enriched in sulphate and therefore plot into the Ca-Mg-HCO_3-SO_4 and Mg-Ca-HCO_3-SO_4 fields. This can also be seen from table 1, with the mean Schwaz sulphate concentrations being twice as high as the Kogel values. With principal component analyses the relationship of all parameters analysed were investigated. It could clearly be seen that Cu, Sb, As, and Zn, the main metals in the fahlores, plot into the same field. Ag, Bi, Mn, Pb, Cd, and Hg, some of the other metals in the fahlore, plot in different areas, because their hydrogeochemical behaviour differs from their behaviour during rock and mineral formation processes. Their relative concentrations in the waters equal those of the fahlores (fig. 3).

46 water samples of the Schwaz area could directly be assigned to one of the five rock types outcropping there: Schwaz Dolomite (8 samples); Triassic Buntsandstein (6 samples); Phyllites (18 samples); Triassic Limestones (4 samples) and

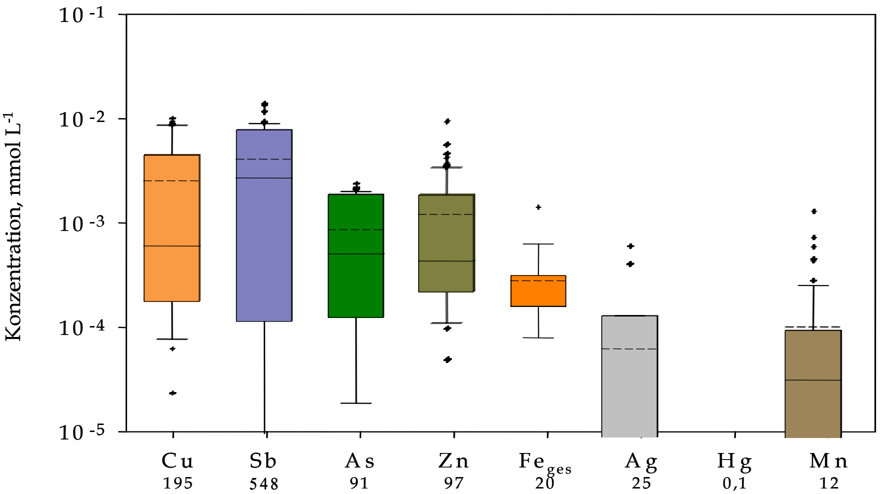

Fig. 3: Box plots of the main heavy and semi-metal concentrations selected in accordance with their abundance in the Schwaz and Kogel fahlores. All concentrations in mmol L^{-1}; the small numbers under the elements show the concentration in µg L^{-1}.

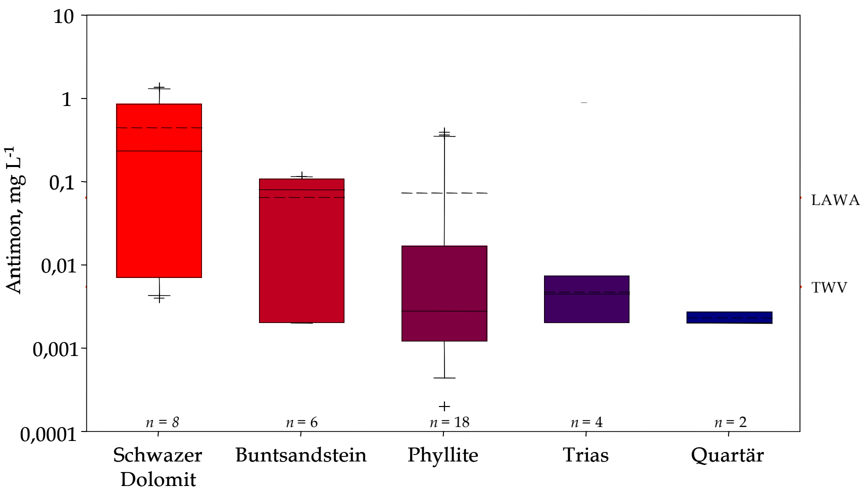

Fig. 4: Box plots of antimony in relation to the five main lithological units of Schwaz. TWV: standard of Austrian drinking water regulation; LAWA: standard for action.

Quaternary Sediments (2 samples). Only the samples from the Quaternary Sediments were under the Austrian drinking waters standards, while the samples from the phyllites and the Triassic Limestones were under the German LAWA limits. More than half of the samples taken from the Schwaz Dolomite and the Buntsandstein exceeded the LAWA standard (fig. 4).

In the mine waters of the Schwaz dolomite mine, antimony concentrations above 600 µg L^{-1} were related to the old workings in the "Abbau I – III" and in the Georgi Unterbau to the flooded shaft. All the other mine waters were below 600 µg L^{-1}, and in the Georgi Unterbau below 200 µg L^{-1}. At the dewatering adits of the Wilhelm Erbstollen and the visitor's mine the antimony concentrations were 326 µg L^{-1} and 185 µg L^{-1} respectively. More important than the concentrations are the mass loads. At "Abbau III", with the highest antimony concentration, a load of 0.4 kg day^{-1} and at the dewatering adit of the old workings of the "Messerschmitt Halle" about 13 kg day^{-1} were measured. Comparing the three dewatering adits results in loads of 0.2 kg day^{-1} for the visitor's mine, 16 kg^{-1} day for the Wilhelm Erbstollen, and 0.1 kg day^{-1} for the Georgi Unterbau.

4 Discussion

As could be shown, the high antimony anomalies are closely linked to the Schwaz Dolomite, which is the host rock for the silver bearing fahlores. To a lesser extend, the Buntsandstein outcrops at the surface are subjected to higher antimony concentrations. All the other lithologies investigated may contain local springs with antimony contents exceeding the LAWA standards, but in some cases it was not clear, if the springs couldn't be abandoned adits which are now covered by rock debris. Antimony contents in waters from the Triassic limestones and the Quaternary Sediments were regularly under the limits of the drinking water regulations.

Within the mine workings, both, in the Schwaz and the Kogel cases, high antimony contents are clearly linked to the abandoned mine workings and to the "Abbau III", which was subject to a surface collapse in 1995. In this area, surface water flows through old abandoned mine workings of medieval and Bronze Age times and is therefore enriched in antimony and in sulphate. The new workings in "Abbau IV" had antimony concentrations lower than 200 µg L^{-1} and the extreme mine water inflows in the Georgi Unterbau away from the flooded shaft also had low antimony concentrations.

It can therefore be concluded that the high antimony concentrations are clearly linked to the Schwaz Dolomite and to the abandoned mine workings which were not subject of the dolomite mining of the Montanwerke Brixlegg AG. Nonetheless, in case of a continuation of the dolomite mining, the operator shall ensure that the contact time between the fahlore bearing dolomite and the mine water is as short as possible. By using flexible tubes at the most dominant water inflows and foils to protect the excavated material from dropping water the antimony load can be reduced significantly. In the case of the three dewatering adits it is advisable to use the area owned by the operators for constructing wetlands which can reduce some of the metals in the mine water. Taking into account that arsenic and antimony have a similar chemical behaviour this passive treatment technique for antimony must not be excluded.

	Kogel			Schwaz			
parameter	min	max	mean	min	max	mean	*n*
Temperature; °C	7.5	17.2	9.2	3.4	15.2	10.5	94
pH; –	6.9	8.4	7.8	7.3	8.9	8.0	100
Conductivity; µS/cm	230	486	393	66	1107	407	101
Redox, mV	320	530	450	270	480	440	80
HCO_3; mg/L	131	262	213	46	272	188	60
SO_4^{2-}; mg/L	2	45	29	3	470	67	62
Sb; mg/L	0.001	1.768	0.593	0.0002	1.758	0.512	77

Tab. 1: Main results of the hydrogeological investigations at the Kogel and Schwaz mining areas. *n*: number of measurements (varies due to sampling conditions).

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