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Technical Article

The Hydrogeochemistry of Arsenic in the Clara Mine, Germany

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Abstract. The oxidative dissolution of primary arsenic-bearing sulfide minerals in barite-fluorite veins is a potential source of arsenic in the Clara Mine. Geological structures, especially the mineral veins, provide potential pathways for the water. The highest arsenic concentrations are found in ground water within the eastern part of the mine. Arsenic and major ions are positively correlated and provide evidence that arsenic is likely derived locally from the water-vein/water-rock interaction. Geochemical modeling with PHREEQC shows all the arsenate mineral phases to be significantly undersaturated, although secondary arsenate minerals are common in the oxidized part of the deposit. The mine waters plot near the boundary of $Fe(OH)_3$ and Fe^{2+} in the pH-Eh diagram for the As-Fe-S-H_2O-system. Arsenic occurs as the 5-valent species $H_2AsO_4^-$ and $HAsO_4^{2-}$. Statistical analysis illustrates a strong association between As, Fe, pH, and HCO_3. Oxidation of the primary As-bearing minerals, such as pyrite and arsenopyrite, and the subsequent behavior of the oxyanion, arsenate, generally controls the distribution and speciation of arsenic. The low concentrations of dissolved As is due to co-precipitation and adsorption of arsenate by Fe, Al, and Mn (oxy)hydroxides.

Key words: Adsorption; arsenic; Black Forest; Clara Mine; co-precipitation; Fe(oxy)hydroxides; hydrogeochemistry; modeling; statistical analysis; water-rock interactions

Introduction

Arsenic (As) has received increased attention in recent years, especially since it has been linked to increased cancer risk. Because As in ground and surface water poses a risk to the ecosystem and to human health, more detailed information is needed on the factors that govern the fate of arsenic and its mobility in the environment. Arsenic in natural systems is often linked to iron and sulfur cycling at redox boundaries, apparently due to co-precipitation reactions of arsenic with poorly crystalline iron (oxy)hydroxides, iron monosulfides, and pyrite (Moore et al. 1988; Wilkin 1996).

The Clara Mine is in the upper Rankachtal, about 8 km north of Wolfach in the Black Forest, Germany. It is part of the Kinzigtal mine area, where Co, Ag, Pb, and Cu have been exploited since the Middle Ages. In recent decades, barite and fluorite veins were intensively mined. Elevated arsenic concentrations in the mine water have raised concerns that groundwater quality could also be impacted. This study was conducted to examine the factors controlling the concentrations of dissolved As in the mine water.

Geological and Hydrological Settings

The barite and fluorite mineralisation occurs in three major vein systems in the central Black Forest gneiss complex: the Clara barite veins, the Stollen barite veins, and quartz veins (Figure 1). The mineralisation is associated with sellaite, quartz, carbonate, various sulfides, natural alloys and >250 species of secondary minerals. The barite-fluorite-quartz veins contain native elements, sulfides, halides, oxides, hydroxides, carbonates, sulfates, arsenates, phosphates, and silicates. Arsenic-bearing minerals are abundant, with arsenopyrite (FeAsS) being the most common. The other primary arsenic minerals include enargite (Cu_3AsS_4), geocronite ($5PbS{\cdot}AsSbS_3$), gersdorffite (NiAsS), luzonite (Cu_3AsS_4), rammelsbergite ($NiAs_2$), and safflorite ($CoAs_2$). In addition, As-bearing secondary minerals are common in the oxidized zone. There are more than 35 of these, including arsenates of Fe, Cu, Pb, Zn, Ca, Ba, Co, Bi, and Al (Cruse 1981; Kaiser 1984; Huck 1986).

The gneisses are partly interstratified by small granite veins. Locally, the gneisses are mostly biotite-plagioclase-gneisses with coarsely granular to dense texture, interbedded with a few layers of garnet-bearing amphibolites and garnet-biotite gneisses. They consist mainly of plagioclase (An20-An40), orthoclase, biotite, quartz, amphibole, and accessory minerals. Small fractures in the gneisses are sometimes filled with gypsum, pyrite, arsenopyrite, and pyrrhotine. The crystalline basement in the mine is partly covered by about 35 m of thick Triassic red sandstone, in which mineral veins outcrop.

The Clara barite veins are the most important barite and fluorite veins of the mine and strike 150°NW-SE with a dip of 70-80°NE. They are about 650 m long and several meters thick. The Stollen barite veins

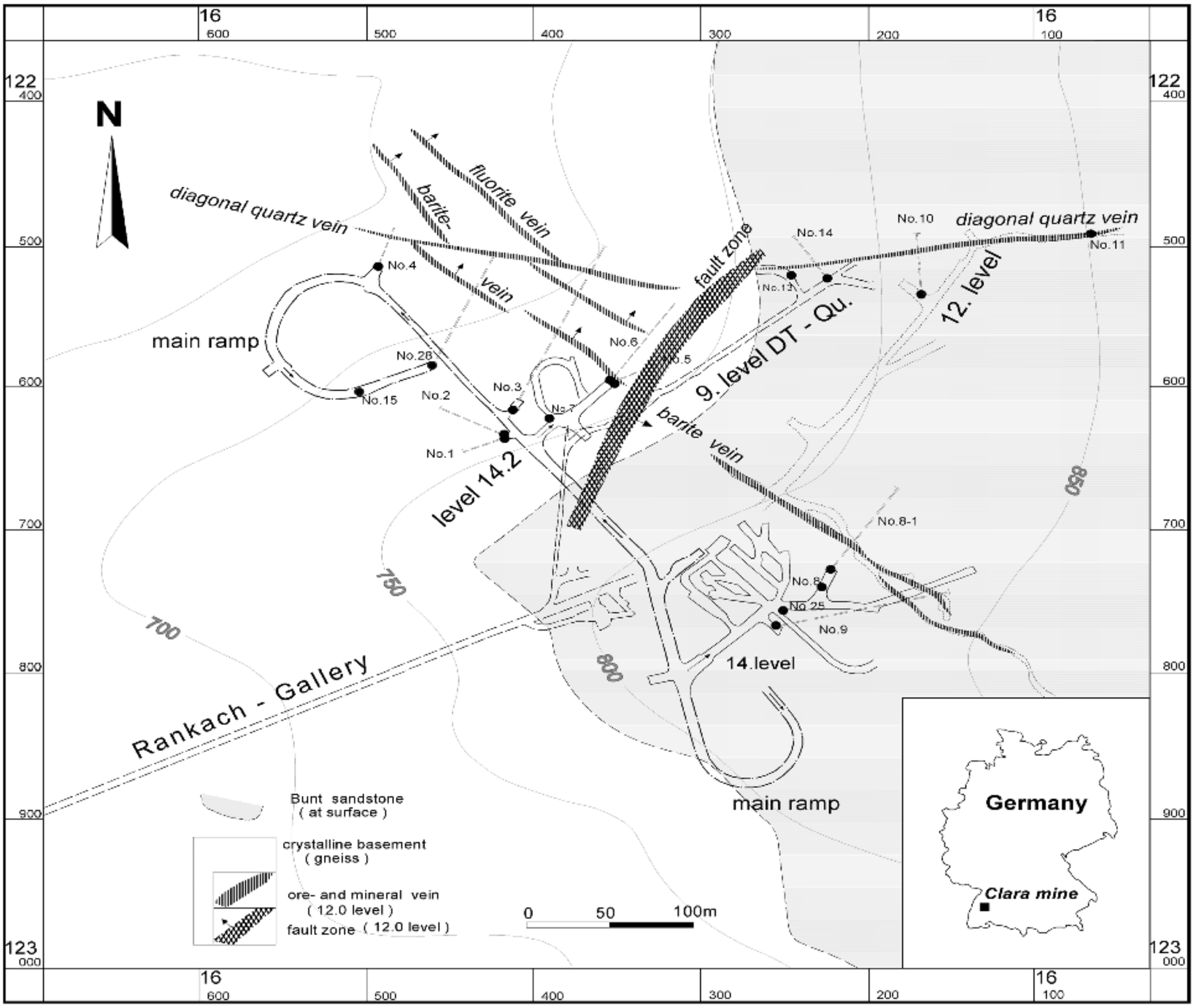

Figure 1. Map showing the underground water sampling locations (Geological map modified from Huck 1986; Kaiser 1984; Biehler 1991; and Sachtleben Bergbau GmbH)

strike in a N-S direction. The third vein system consists of the quartz veins that strike E-W and also bear barite and fluorite. Water is very strongly bound by absorption within the rock matrix (Stober 1995). Water transport in the mine is strongly related to the mineral veins due to their high fracture and cavity-related permeability. Generally, water descends along the mineral veins. The transmissibility coefficient of the barite and fluorite veins was measured between $T=2.26\cdot10^{-5}m^2/s$ and $5.21\cdot10^{-4}$ m^2/s, which is much higher than the mean value of the Black Forest gneisses ($T=6.92\cdot10^{-6}m^2/s$) (Biehler 1991). Some hollows at the 12 level reach a diameter of several meters. These hollows are often filled with red clay, which apparently is derived from the overlying red sandstone. In contrast to the mineral veins, the two major fault and shear zones in the mine are nearly impermeable, though their width and hydraulic property change considerably and their permeability increases where they are disturbed by younger faults.

Methodology

Water samples

Water samples were collected monthly between July 1997 and Oct 1998 in and around the mine. Some of the sample sites within the mine are shown in Figure 1. We took water samples at different levels of the 650 m deep mine: most came from drillholes (sites 1, 2, 3, 4, 5, 6, 8-1, 9, 10, 11, 14, 28) while some were collected from open fractures and veins (8, 12, 13, 15, 26, 29). Sample sites 7 and 25 were from fast flowing water in open trenches in the mine. Surface water samples were also taken from springs (20, 21, 22, 23), streams (16, 24) and a waste water pool filled with mine water (16-1). In Sept 1998, rain water, and in Dec 1997 and Jan 1998, snow water, were also collected and analyzed; no arsenic was detected.

Water temperature, pH, electrical conductivity (EC), Eh, and dissolved O_2 (D.O.) were measured using portable instruments. Samples were collected in two bottles, with care taken to fill the bottles completely to avoid any gas exchange. One sample was preserved at 4°C for determination of dissolved major cations and anions and alkalinity; the second sample was filtered through a 0.45 µm pore-size filter and acidified with HNO_3 for dissolved minor metals analysis. Major cations (Li^+, Na^+, K^+, Ca^{2+}, Mg^{2+}) and anions (Cl^-, SO_4^{2-}, NO_3^-, F^-, Br^-) were analyzed by ion chromatography (Dionex DX-120). Some elements (Sr, Fe, Zn, Ni) were measured using flame atomic absorption spectrometry (Perkin-Elmer 3030 AAS), and others (Al, Ba, Mn, Cu, Pb, Cd, As, Cr) were determined using graphite furnace AAS (Perkin-Elmer 4110ZL). Alkalinity was determined by titration, and dissolved SiO_2 was determined using a Merck SQ 200 spectrophotometer, using the molybdate blue method.

Results

Water geochemistry

The temperature of the groundwater increased with depth by about 2°C/100m. Surface waters had an EC under 100 µS/cm and groundwater ranged between 200 and 1400µS/cm. The in situ pH across all of the sampling locations ranged between 4.75 and 9.30. Water flowing out of drillholes had a D.O. of 3.0-9.0 mg/L. In the stagnant water in the drillholes, the D.O. ranged between 2.0 and 8.5 mg/L. The surface waters had a higher D.O. (7.0-11.5 mg/L) than the ground water. The D.O. decreased with increasing EC. The mine water had an Eh between 200 and 300 mV, plotting in the transition between an oxidizing and reducing environment. The D.O. and Eh values decreased with increasing depth. The relationship between HCO_3^- and pH indicates that the carbonate-CO_2-equilibrium is an important pH buffer system in the mine. Four types of water can be distinguished on the basis of the relative proportions of the major ions: (1) Ca-HCO_3 water, (2) Ca-HCO_3-SO_4 water, (3) Ca-SO_4 water and (4) Ca-SO_4-(Na-Cl) water. From the type 1 to type 4, EC increased from about 100 µS/cm to more than 1000 µS/cm.

Relationships between arsenic and major ions

Concentrations of As were measured in groundwater samples from the exploration drill holes, and in some surface and mine water samples between July 1997 and Oct 1998. Arsenic was not detected frequently in the surface and shallow ground waters, but exceeded 10 µg/L in mine water and some groundwater samples. The highest concentration of As (146 µg/L) was found in stagnant water in the mine's barite vein (sample site 26).

Arsenic, physical parameters, major ions and other trace elements in water were plotted in correlation diagrams (Figures 2, 3). The scatter plots show that As concentrations increase as the concentrations of major cations, such as Na, K, Ca, Mg, and Sr, increase. Because all water samples from the mine were undersaturated with respect to the arsenates of Na, K, Ca, Mg, and Sr, it is assumed that their concentrations in water are all positively correlated with the water-rock reaction time, although they had different sources. Most of the As is derived from the oxidation of As-bearing minerals, while Na, K, Ca, Mg, and Sr may stem from many geochemical processes, such as the weathering and dissolution of neighboring rock, dissolution of the barite-fluorite veins, and fluid inclusions in minerals.

In waters with relatively high EC, Cl and SO_4 are the major anions. The As-concentration was positively but not linearly correlated with Cl, Br, or SO_4 in the water. The correlation became weaker as the EC increased. Cl and Br stem mainly from the leaching of fluid inclusions in minerals, especially from fluid inclusions in sulfide minerals that had high Cl and Br concentrations. The most important source for SO_4 is the oxidation of pyrite, arsenopyrite, and other sulfides that might contain high As. In addition, the dissolution of barite ((Ba, Sr, Ca)SO_4 solid solution) and the small gypsum veins in neighboring rocks are also possible sources for SO_4.

The As concentration is nearly linearly correlated with the HCO_3 concentration, which is possibly related to the close relation between As and pH. The samples with As>20µg/L range in pH from 6.5-7.5. The pH of the water is mainly controlled by the H_2O-CO_2-H_2CO_3- HCO_3^- - CO_3^{2-} buffer system. The plot also indicates that the correlation between As and HCO_3 is different for water from different sources. There are two major different linear relations with different slopes. One group (the Ca-Na-SO_4-Cl type) includes mostly stagnant water samples from drillholes through the barite veins (sites 8-1 and 9). The water-rock interaction for this group is considered to be in equilibrium, with relatively high EC and As (>20µg/L). The As-HCO_3 correlation line has a small slope. Another group of samples is Ca-HCO_3 or Ca-HCO_3-SO_4 type water with relatively low EC and As concentration (<20µg/L). The As-HCO_3 regression line has a steep slope.

The As concentration was negatively correlated with D.O., presumably due to the oxidation and dissolution of As-bearing sulfides in water. During this process, O_2 is consumed and D.O. decreases; at the same time, SO_4 and As concentrations increase (Figure 2).

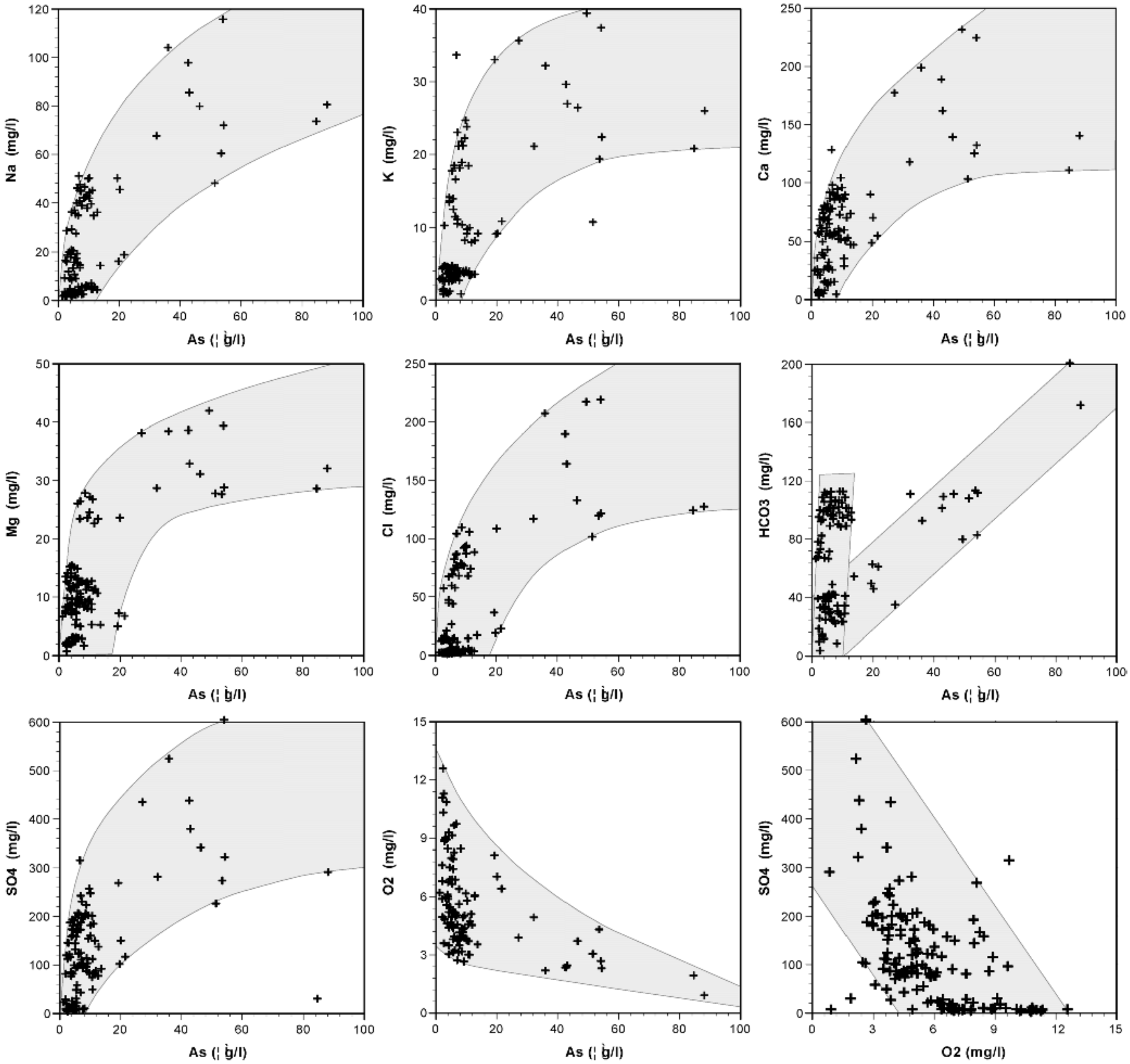

Figure 2. Compositional relationships among As and major ions for the water from the Clara Mine

Relationships between arsenic and other elements

Generally, water with high Fe, Mn, Al, Ba, Cu, Pb, Zn, and Ni concentrations contains little As (Figure 3). The geochemical speciation model PHREEQC (Parkhurst and Appelo 1999) was used to calculate the distribution of As species and the values of the saturation index (SI) for certain arsenate minerals containing Fe, Mn, Al, Ba, Cu, Pb, Zn, Ni, etc. Equilibrium-speciation modeling indicates that saturation was not approached for these minerals; thus, sorption reactions of As onto iron-(oxy)hydroxide minerals (especially in red clay) might control concentrations of As in the mine water. Arsenic mobility in natural systems is often linked to iron cycling at redox boundaries due to co-precipitation reactions of As with poorly crystalline iron (oxy)hydroxides, iron monosulfides, and pyrite (Moore et al. 1988). The strong adsorption of arsenate and to a lesser extent arsenite onto amorphous or poorly crystalline hydrous ferric oxide (HFO) can cause the As concentration to be controlled by the Fe concentration (Belzile and Tessier 1990; Waychunas et al. 1993; Bowell 1994). The ability of the HFO to adsorb As species is influenced by the speciation and crystallinity of the iron, pH, presence of competing oxyanions such as organic acids and phosphate, and by the presence of other adsorbent surfaces.

Similar to its adsorption onto HFO, As can also be adsorbed onto Al and Mn-phases, in particular gibbsite (Korte and Fernando 1991; Foster et al.

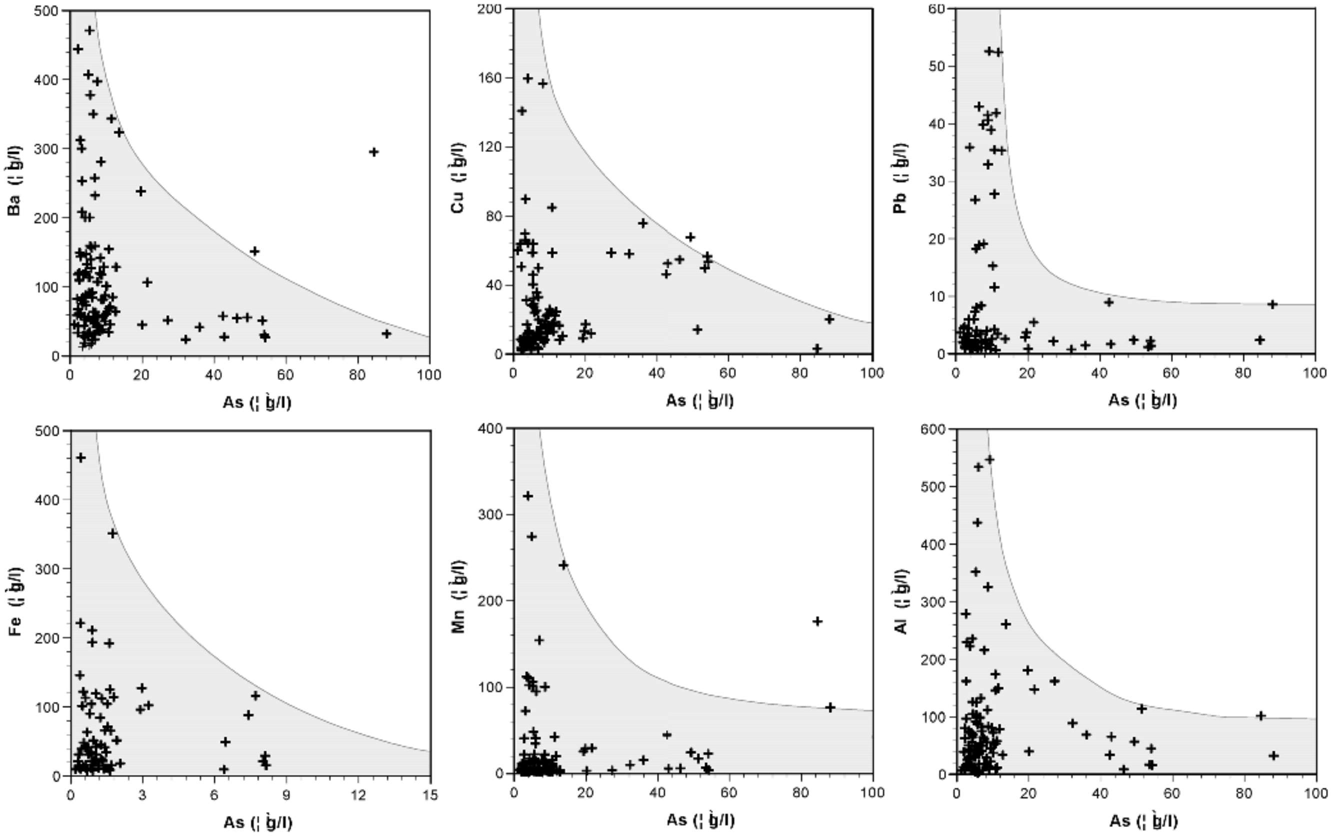

Figure 3. Compositional relationships among As and minor elements for the waters from the Clara Mine

1998). PHREEQC calculations indicate that most of the samples were oversaturated with respect to gibbsite, goethite, and amorphous $Fe(OH)_3$. The mobility of As in natural waters is, in most circumstances, controlled by sorption onto particulate phases (Mok and Wai 1994). Scavenging of elements into and onto metal hydroxides is a result of co-precipitation, adsorption, surface complex formation, ion exchange, and penetration of the crystal lattice (Chao and Theobald 1976). In natural systems, it is often impossible to distinguish between co-precipitation and adsorption (Drever 1997).

Statistical Analysis and Interpretation

An important approach to understanding the chemistry of natural waters is to investigate statistical associations among dissolved constituents and environmental parameters. A statistical association does not establish a cause-and-effect relationship, but it frequently presents data in such a way that cause-and-effect relationships can be deduced (Drever 1997). We carried out multivariate factor and cluster analysis using SPSS8.0 to investigate the geochemical correlation of As and other components. Hierarchical cluster analysis was carried out with a proximity matrix and between-groups average linkage clustering for standardized data. Scaling of variables is important, since differences in scaling may affect the cluster solution. The raw data was transformed by variables using the standardizing procedure "maximum magnitude of 1", which divides each value for the item being standardized by the maximum of the values. The measure for interval data was carried out by Pearson correlation. The clustering of variables (R-mode cluster analysis) has essentially the same arrangement as the factor analysis. The cluster diagram for variables (Figure 4) shows two clusters that can be interpreted in terms of natural geochemical association. There is a Ca- SO_4-Ca- Cl cluster with EC, Sr, K and Mg; this cluster is the same as factor 1 of the factor analysis, and results from the interaction of the water, rock, and mineral veins. There is another cluster around Fe, As, pH and HCO_3, which can be explained by oxidation and dissolution of As-bearing sulfides in contact with meteoric waters and secondary carbonates.

The principal component-analysis method was selected for factor analysis. The rotation was carried out on the basis of the Varimax-criterion with Kaiser-normalization. Five factors (or principal components) were extracted that together can explain 86.2% of the total variance of the 20 variables. The first factor accounts for 36.4%, the second, 18.2%, the third, 14.5%, the fourth, 9.3% and the fifth, 7.8% of the total variance of the data set. The factors are displayed in Figure 5. The rectangular boxes represent the factors, and the central line represents zero loading for the variables. Points near the top of the boxes represent high positive loadings and points near the bottom represent high negative loadings.

Factor 3 had high positive loadings for Fe(0.80), As(0.66), HCO_3(0.78) and small negative loading for NO_3(0.52). It is essentially a Fe-As factor, and was interpreted as representing the oxidation and dissolution of Fe-As sulfide in the barite and fluorite veins and further reaction with carbonates. The small negative loading for NO_3 is possibly related to the use of explosives during mining. Factor 4 was an acidity-pH factor with a high negative loading for acidity (0.93) and a positive loading for pH value (0.69), and was regarded as the pH buffer system of CO_2-H_2CO_3-HCO_3-carbonate in groundwater.

Eh (pe)-pH-diagram

The pe-pH diagram provides an insight into the hydrochemistry of As under differing pH (5-9) and Eh (0 to 400 mV) regimes. All samples either plot in the $H_2AsO_4^-$ or the $HAsO_4^{2-}$ fields, both As(V) species. The hydrogeochemistry of As is dominated in aerobic groundwater by arsenate species, and in anaerobic groundwater by the reduced form, arsenite. The presence of both arsenite and arsenate may reflect a lack of redox equilibrium or active oxidation-reduction reactions as a result of mineral-water interactions. Dissolved As is mobile across a wide pH-Eh range; however, its initial liberation from primary sulfides is strongly pH and Eh dependent. In mine waste management, an understanding of the thermodynamic controls of sulfide oxidation is thus fundamental to minimizing the flux of As (and also heavy metals) into the hydrosphere.

The stabilization of soluble oxyanionic As species at low pH is subject to a high redox potential. At a pH>10, Eh can range from 150 to 700 mV. Both variables exert an important control on As mobility and attenuation. The influence of pH is typically indirect, affecting As by regulating the saturation indices of other solutes such as Fe, with which As is prone to co-precipitate (Williams 2001). Redox variation in water produces an analogous effect, particularly across the critical ferric-ferrous threshold. Direct Eh control is, however, probably caused by the differential adsorption-desorption of As(III) and As(V) species (Bowell 1994). The dynamics of Fe constitute an important control on aqueous As mobility, particularly in acid (pH<4.0) mine water. The heterogeneous surface charge properties of hydrous oxides make them efficient scavengers of both cations and anions. The precise mechanisms may involve co-precipitation, adsorption, surface complex formation, ion exchange, and lattice penetration (Williams 2000). For common Fe oxides, including goethite and ferrihydrite, Schwertmann and Fechter (1982) give isoelectric points of pH 5.0, indicating a propensity for the adsorption of oxyanionic solutes such as $H_2AsO_4^-$ at pH levels below this threshold.

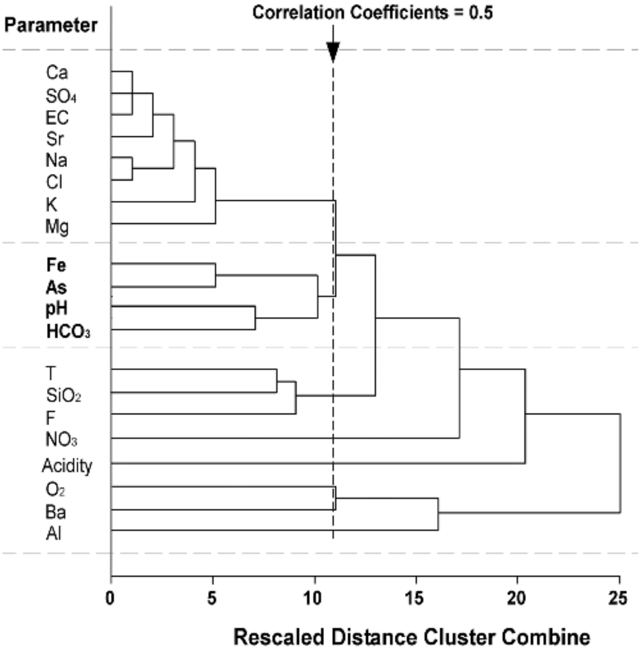

Figure 4. Dendrogram produced by clustering water samples with 20 parameters. Hierarchical cluster analysis was performed using average linkage (between groups) and rescaled distance by Pearson correlation measure.

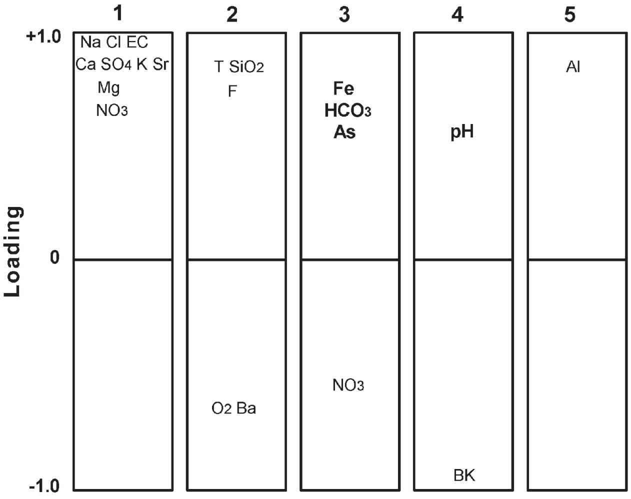

Figure 5. Diagrammatic representation of factors from principal component analysis of chemical data for waters from the Clara Mine

Negative correlation between As and Fe concentrations has also been found in other naturally contaminated aquifers (Armienta et al. 2001). The highest Fe concentration that we measured was in samples from the drillholes through the barite veins in the eastern part of the mine. The Fe concentration seems to be controlled by the pH and Eh of the water and the precipitation of $Fe(OH)_3$ since all of the samples plot in the $Fe(OH)_3$ field or in the Fe^{2+} field. Water samples containing As above the detection level were plotted in the pe–pH diagram developed for the As-Fe-S-H_2O system (Figure 6). All the samples plot near the boundary between $HAsO_4^{2-}$ and $H_2AsO_4^-$ stability fields, and near the boundary between amorphous $Fe(OH)_3$ and Fe^{2+} stability fields. Water samples with low pH and Eh values collected from low levels of the mine were in the Fe^{2+} stability field and had higher As concentrations. In contrast, water samples in the $Fe(OH)_3$ field had lower As concentrations, due to As adsorption on $Fe(OH)_3$.

Figure 6 shows that arsenopyrite is not stable at the Eh and pH values of the sampled waters. Oxidative dissolution of arsenopyrite should be expected in the veins. The paragenetic sequence that follows the oxidation of As-bearing sulfides exerts a major control on aqueous As mobilization. In most cases, arsenopyrite is the primary carrier, the oxidation of which generally results in the in situ formation of scorodite ($FeAsO_4{\cdot}2H_2O$), similar ferric arsenate coatings, and ferric hydroxides, which can simultaneously adsorb As. Scorodite has limited solubility under most pH-Eh conditions. Arsenopyrite oxidation, which could be the source of the As, the high sulfate concentrations, and the low pH, proceeds by the following reaction:

$$FeAsS+3.25O_2+1.5H_2O \rightarrow Fe^{2+}+SO_4^{2-}+HAsO_4^{2-}+2H^+$$

Arsenopyrite oxidation, leading to scorodite precipitation followed by incongruent dissolution of scorodite, has been suggested by Dove and Rimstidt (1985). Scorodite, which is stable at low pH and high Eh, may be dissolved by infiltrating rainwater or shallow groundwater (Armienta et al. 2001).

Discussion and Conclusion

An understanding of factors controlling the distribution of As in groundwater requires knowledge of the sources of the As and the processes controlling As mobility (Hinkle and Polette 1999). The apparent source of As in the mine water is the oxidation and dissolution of As-bearing sulfides. Primary and secondary As minerals are abundant. Arsenic can enter through various pathways into soils, aquifer sediments, and drinking water. For instance, the weathering of arsenopyrite (FeAsS) is usually associated with iron sulfide ore-deposits (Lin and Puls 2000). The concentration of As was negatively correlated with the D.O., indicating that it is related to the oxidation and dissolution of As-bearing sulfides.

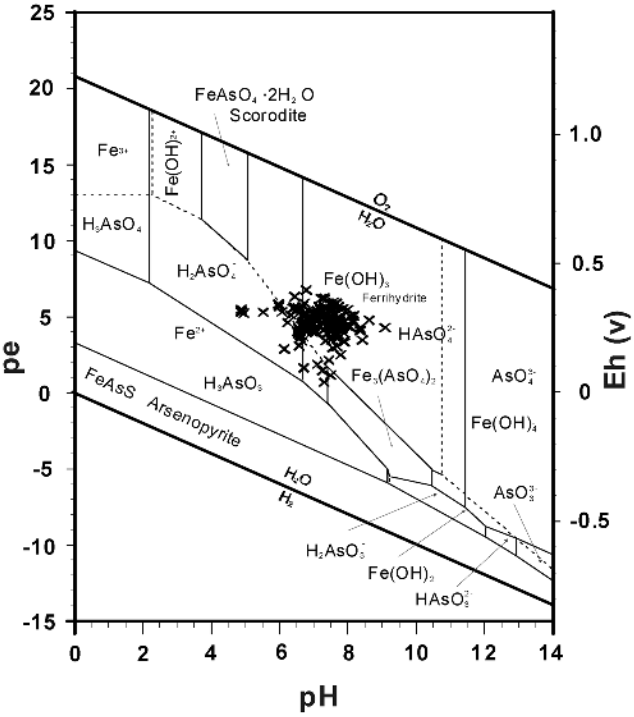

Figure 6. A pe-pH diagram for the As-Fe-S-H_2O system (calculated using Wateq4f data with PHREEQC)

Cluster analysis illustrates a strong association of As, Fe, and HCO_3, which is associated with the weathering of As-Fe bearing minerals such as pyrite and arsenopyrite. Factor analysis also yields an As-Fe-HCO_3 factor that accounts for 14.5% of the variance in the geochemical data set. Arsenic was likely attached to iron (oxy)hydroxide particles.

Adsorption/desorption and oxidation/reduction at red clay surfaces was found to be very important to the natural attenuation of As in the subsurface environment. Arsenic appears to be sorbed on to clay minerals, and transported in solution and co-precipitated with, or scavenged by Fe(III), Al(III), and Mn(IV) in the red clay.

The dissolved As concentrations are positively correlated (but in a non-linear manner) with the concentrations of Na, K, Ca, Mg, Sr, Cl, SO_4, and HCO_3, and controlled by the concentrations of elements such as Fe, Al, Mn, Cu, Pb, Zn, and Ni. Equilibrium-speciation modeling using PHREEQC indicates that the arsenates of Na, K, Ca, Mg, Sr, Fe, Al, Mn, Cu, Pb, Zn, or Ni were unsaturated, which means that the As concentration in water is not controlled by the precipitation and dissolution of arsenate minerals. Sorption and/or co-precipitation reactions of As onto iron-, aluminum- and manganese-hydroxide minerals likely control the concentrations of As in groundwater.

The water from the Clara Mine has a pH range from 5 to 9, and an Eh range from 0 to 400 mV. In the Eh-pH diagram of the As-Fe-S-H_2O-system (Figure 6), water samples plotted near the boundary between $Fe(OH)_3$ and Fe^{2+}. At the same time, As existed as $H_2AsO_4^-$ and $HAsO_4^{2-}$, both As(V) species. The Eh of the Clara Mine water is likely controlled by Fe^{2+} and Fe^{3+}. It is almost impossible that $FeAsO_4{\cdot}2H_2O$ or $Fe_3(AsO_4)_2$ precipitated from the water.

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