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TOXIC ELEMENT COMPOSITION OF ACID MINE WATERS FROM SULFIDE ORE DEPOSITS

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ABSTRACT

Acid mine waters from metal sulfide deposits located in non-carbonate (silicate) bedrock have been analyzed from four different localities in the United States: Iron Mountain mine, California; Leviathan mine, California; Argo tunnel, Colorado and Sulfur mine, Virginia. The range of pH is 0.5-3.0 and concentrations of Fe, Al, Zn, Cu, As, Cd, Pb, Tl, Ni, Co, Cr, V and SO_4 are often extraordinarily high and certainly at toxic levels. Various plotting techniques, especially when combined with chemical equilibrium computations, are shown to be powerful tools for interpreting the source composition and downstream attenuation of metals during flow through a drainage basin. The results demonstrate that As and Tl are highly non-conservative and are rapidly removed from solution during downstream transport. However, Zn, Cd, Li and SO_4 are highly conservative and are only marginally removed from solution. Aluminum shows both conservative and nonconservative behavior with a clear break in this behavior at a pH of about 4.5; i.e., at higher pH values a strong solubility control by microcrystalline gibbsite is demonstrated, whereas at pH values less than 4.5, a simple dilution line indicates mixing with no solubility control.

INTRODUCTION

The oxidation of sulfide ore deposits during weathering is accelerated by mining activities, and any resulting effluent may be strongly acidic, containing several dissolved constituents at toxic concentrations. When the country rock is composed of crystalline silicates with little or no carbonates (granite or gneiss), extreme acidities can develop in effluent waters from the mining of sulfide ore deposits due to the lack of neutralizing minerals. These acidities and high metal concentrations can cause serious environmental degradation to receiving waters. This paper describes the types and concentrations of metals that are found in such mine waters, and demonstrates how analytical results can be effectively interpreted when the samples have been carefully collected and analyzed.

The fundamental process causing the production of acid mine water is the oxidation of pyrite by ferric iron:

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+$$

(Garrels and Thompson, 1960; Taylor, *et al.*, 1984) which is catalyzed by iron- and sulfur-oxidizing bacteria (Singer and Stumm, 1970; Nordstrom, 1982a). High concentrations of dissolved constituents are caused by two major processes: (1) the oxidation of metallic sulfides such as pyrite, sphalerite, chalcopyrite, galena, and arsenopyrite to produce high concentrations of iron, zinc, copper, lead and arsenic, respectively, in addition to high concentrations of sulfate and hydrogen ions, and (2) acid dissolution of the silicate bedrock (feldspars, micas, clays, etc.) that produce high concentrations of aluminum, silica, calcium, magnesium, sodium and potassium.

ACID MINE WATER ANALYSES

Acid mine waters have been collected, preserved and analyzed according to specialized techniques that include filtration through 0.1 micrometer pore size, HNO_3 acidification for most trace metals, and HCl acidification for preservation of oxidation states of iron and arsenic and analysis by flame atomic absorption spectrophotometry, flameless atomic absorption spectrophotometry, UV-visible spectrophotometry or plasma emission spectroscopy (direct current or inductively coupled), depending on concentration range and potential interferent problems (see Nordstrom, *et al.*, 1979, and Ball and Nordstrom, 1985, for details).

Field sites include four locations of widely varying geological and hydrological conditions. These waters have pH values ranging from 0.5 to 3.0 and high concentrations of a variety of metals, semi-metals and nonmetals, as shown in Table 1. The site in Shasta County is the Iron Mountain massive sulfide deposit containing pyrite, chalcopyrite, galena, sphalerite and other ore minerals emplaced in an altered rhyolite. The

Table 1. ACID MINE WATERS ANALYSES (mg/L)

	Shasta County** California	Alpine County* California	Clear Creek County** Colorado	Louisa County* Virginia
pH	1.1	1.8	2.7	2.0
Eh, V	0.612	0.465	0.731	----
Aluminum	1400	430	5.9	----
Antimony	(<0.2)	0.002	(0.001)	----
Arsenic	(25)	30	(0.14)	----
Barium	(<.005)	0.007	----	----
Beryllium	(0.014)	0.01	----	----
Bismuth	----	0.067	----	----
Boron	(0.7)	0.12	----	----
Cadmium	13	0.21	0.11	1.5
Calcium	173	140	290	560
Chloride	----	8.4	(2.7)	----
Chromium	(0.3)	2.6	(0.02)	----
Cobalt	(1.0)	4.9	----	----
Copper	340	5.3	6.4	516
Fluoride	----	3.4	(2.6)	----
Iron(Fe^{2+})	9,050	1,440	15.6	----
Iron(total)	11,700	1,570	175	16,200
Lead	(3)	0.22	(0.032)	<0.5
Lithium	(<0.1)	0.094	(0.04)	----
Magnesium	685	41	60	1600
Manganese	12	11	105	54
Molybdenum	(0.3)	0.02	(<.002)	----
Nickel	(0.5)	12	<0.06	----
Potassium	128	17	2.8	0.1
Selenium	(<0.01)	<.002	----	----
Silica	120	110	39	----
Sodium	93	29	17	3.7
Strontium	----	2.7	----	----
Sulfate	10,200	7,500	2,200	----
Thallium	(0.3)	2.0	----	----
Vanadium	(2.0)	1.1	----	----
Zinc	(1400)	1.4	40	400
Charge Balance	15%	-2.6%	----	----

*Exact locations are described in the text.

**Value in parentheses are analyses on a separate sample of the same water. These values are very representive of the mine water because other constituents that were analyzed in both samples gave good agreement.

water sample in Table 1 is effluent issuing from the Lawson tunnel of the Hornet ore body. The nearby Richmond ore body produces a similar acid water with pH values as low as 0.5 and sulfate concentrations up to 70 g/L (USEPA, unpublished data). These mine waters are some of the most acidic on record.

The site in Alpine County is the Leviathan mine tunnel no. 5 effluent that drains an ore body containing massive elemental sulfur and disseminated cryptocrystalline pyrite. Only the pyrite is oxidizing to any significant extent (Ball and Nordstrom, 1985). The country rock is mostly andesite tuff that is highly altered by shallow subsurface hydrothermal fluids.

The Argo tunnel, located in Clear Creek County, Colorado, was constructed in the 1890's to intersect the largest sulfide veins at greater depths than existing shafts in the Central City-Idaho Springs mining district and to provide a cheap and efficient means of draining the groundwater. The tunnel is built in Precambrian schists, gneisses and granites, and the ore is dominated by vein pyrite deposits containing variable amounts of other metals as sulfides, tellurides, arsenides, etc. The ore is often referred to as "complex ore", and it is distinctly different in chemistry and mineralogy from the ore at the other sites.

The last site is the Sulfur mine tailings leachates and some shaft outflow near Mineral, Louisa County, Virginia. The original ore body consisted of lenses of stratiform massive sulfides found within a sequence of silicic to mafic metavolcanic and metasedimentary rocks. The ore was again predominantly pyrite, but contained variable quantities of chalcopyrite, sphalerite, galena and pyrrhotite.

INTERPRETIVE TECHNIQUES

Element ratios for the ore metals in these acid waters should reflect those ratios found in the sulfide ore body, and may give a much more meaningful estimate of elemental abundances than direct sampling of the ore minerals. At the very least, they should reflect the proportion of sulfide ore minerals being weathered in the ore deposit. Variations in element ratios can be found when comparing drainage from one ore deposit with that from another. Figure 1 shows the Zn/Cd ratio, and Figure 2 shows the Zn/Cu ratio for several samples taken from each field site at different downstream dilutions. The Alpine County site gives a consistent ratio, but one which is different from other sites. At these low pH values it is not possible for precipitation or adsorption reactions to significantly change the ratios, and it seems unlikely that the oxidation rates for different metallic sulfides could vary enough to affect the ratios. Qualitative estimates of the metal ratios of the ore bodies seem consistent with the same ratios in the acid mine drainage (Nordstrom, *et al.*, 1977; Dagenhart, 1980). Weight ratios of Zn/Cd and Zn/Cu are shown in Table 2 for the mine water analyses shown in Table 1. These two ratios appear to give very distinct chemical fingerprints of the oxidizing sulfides.

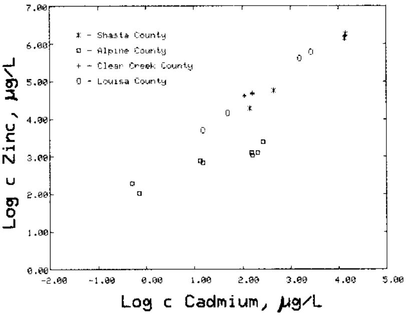

Figure 1. Concentrations of Zn vs. Cd in acid mine waters from four field sites.

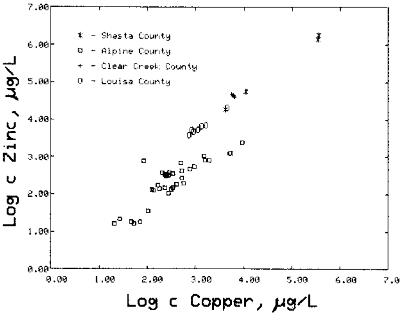

Figure 2. Concentrations of Zn vs. Cu in acid mine waters from four field sites.

Table 2. Zn/Cd and Zn/Cu weight ratios for acid mine waters

	Shasta County	Alpine County	Clear Creek	Louisa
Zn/Cd	108	6.7	364	267
Zn/Cu	4.1	0.26	6.3	0.78

Downstream attenuation of dissolved metals in a drainage basin will occur due to oxidation, precipitation, adsorption and dilution. Large decreases in concentrations will occur from these processes, and the non-conservative nature and relative attenuations can be viewed graphically by plotting the metal concentration against sulfate and against pH. Sulfate is probably the best conservative tracer during downstream dilution of acid mine waters because it is present at quite high concentration at the effluent source, and should be relatively unaffected by precipitation or adsorption processes. The alkali metals (except potassium) occasionally show conservative behavior during hydrogeochemical processes. Unfortunately, sodium concentrations are not elevated enough above background to permit them to be useful as conservative tracers; lithium, however, does appear to work rather well. Figure 3 is a plot of lithium against sulfate for 63 water samples collected from the Leviathan mine drainage basin. A linear correlation is apparent above 100 mg/L sulfate that suggests conservative mixing where mine portal effluent is the high-concentration end member (about 0.1 mg/L), and fresh surface water is the low-concentration end member (about 0.004 mg/L). Scatter in the data probably reflects analytical uncertainties. Zinc also behaves in a conservative manner, and a plot of zinc against lithium at sulfate concentrations above 100 mg/L correlates excellently as shown in Figure 4.

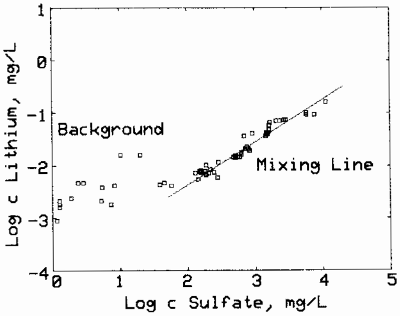

Figure 3. A plot of Li vs. SO_4 for Leviathan waters.

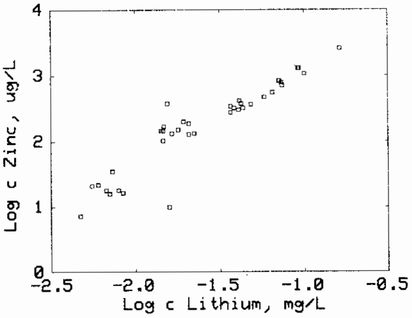

Figure 4. A plot of Zn vs. Li for Leviathan waters.

Data on aluminum concentrations from the Leviathan basin indicate both conservative and nonconservative behavior, depending on sulfate concentrations (Figure 5). A clear mixing line is obtained for sulfate concentrations greater than about 200 mg/L (pH <4.5). At lower sulfate concentrations (and pH >4.5), a distinct break in the correlation line occurs. Aluminum concentrations drop to much lower and nearly constant values around 0.03 mg/L at sulfate concentrations less than 100 mg/L. These trends for aluminum will be treated more quantitatively later with chemical equilibrium computations.

A very nonconservative constituent is arsenic which shows a very nonlinear concentration correlation when compared to sulfate (Figure 6). Arsenic must be reacting rapidly soon after the acid mine effluent leaves the mine portal.

To interpret the partially conservative behavior of elements like aluminum and the nonconservative behavior of elements like arsenic, other types of plots and techniques can be very useful. For example, when total dissolved arsenic concentrations are plotted against pH, it becomes clear that arsenic is removed very rapidly from acid mine waters with

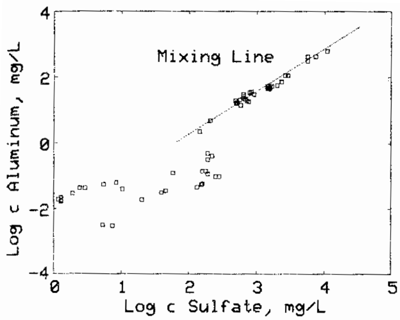

Figure 5. Aluminum concentrations in Leviathan waters as a function of sulfate concentrations.

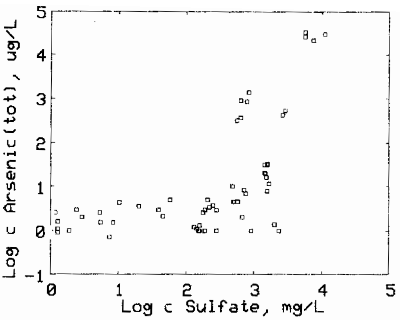

Figure 6. Arsenic concentrations in Leviathan waters as a function of sulfate concentrations.

only small increases in pH, as shown in Figure 7. At a pH of about 2-2.5 there is more than an order of magnitude decrease in arsenic, and by a dilution to pH = 4, the arsenic has nearly decreased to background levels for the drainage basin (about 1 µg/L). This dramatic decrease in arsenic concentrations is likely caused by the precipitation of scorodite, $FeAsO_4 \cdot 2H_2O$, and by adsorption on ferric oxyhydroxides, but the solubility data is inadequate at this time to quantitatively test this hypothesis even though new data has been obtained (Dove and Rimstidt, 1984).

Another element present at toxic concentrations in the Leviathan drainage basin is thallium. Its behavior is similar to arsenic in that it is rapidly removed from these waters with slight increases in pH, and background concentrations are reached at about a pH of 4.0, as seen in Figure 8.

Aluminum concentrations, on the other hand, show only a gradual decrease when plotted as a function of pH (see Figure 9). It might be tempting to assume that aluminum is conserved in the water over the whole range of pH, but this seems unlikely. Chemical equilibrium computations can be an effective tool to test this assumption regarding the aluminum data. The water samples collected from the Leviathan drainage basin were fully analyzed for all major constituents, and the results were subjected to equilibrium speciation computations, using the computer program WATEQ3 (Ball, et al., 1981). The various species forms for aluminum were computed, and activity coefficients applied so that the activities of all major species could be calculated. Figure 10 demonstrates the remarkable

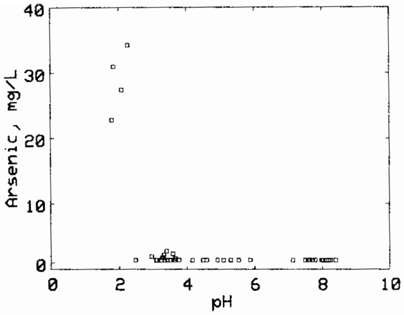

Figure 7. Arsenic concentrations as a function of pH for Leviathan waters.

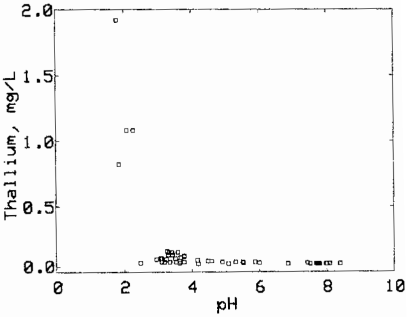

Figure 8. Thallium concentrations as a function of pH for Leviathan waters.

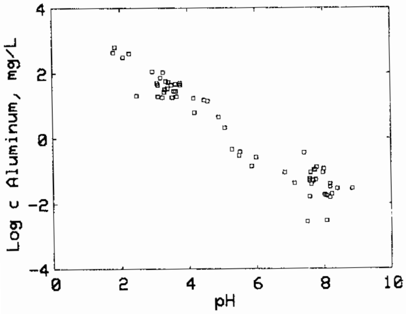

Figure 9. Aluminum concentrations as a function of pH for Leviathan waters.

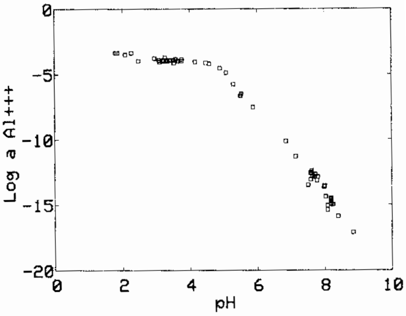

Figure 10. Free aluminum ion activities as a function of pH for Leviathan waters.

change from Figure 9 when the activity of the free aluminum ion is plotted against pH. Two near-linear trends appear with quite different slopes that meet at a pH of about 4.5. The shallow slope occurring at pH values of 1.8-4.5 is a dilution line. These points correspond exactly to the mixing line as shown by Figure 5. At higher pH values a steep slope is encountered that matches the stoichiometry of microcrystalline gibbsite, $Al(OH)_3$. The line itself correlates very well with a somewhat soluble microcrystalline form of gibbsite, hence a strong indication of solubility control by this mineral. This correlation is entirely consistent with the results of Driscoll (1984), who has done careful speciation analysis and computations with waters analyzed from the Adirondack Mountains in New York. The control on aluminum concentrations at pH <4.5 is kinetic in that it is governed by the leaching rate of aluminum from the bedrock and soils. It does not reflect a solubility control by a basic aluminun sulfate mineral, as suggested by van Breemen (1973) and Nordstrom (1982b) unless the most acid water at the source reflects a solubility control. This latter possibility has yet to be investigated. The Al:OH mole ratio for the dilution line is 1.7, which does not correlate with any known mineral. It does, however, correlate with ratios found in other drainage basins affected by acid mine waters, and thus, the leaching rate seems to be very similar regardless of location.

CONCLUSIONS

Several elements at toxic concentrations are found in acid mine waters issuing from sulfide ore deposits. The composition of these waters reflects the proportion of ore minerals being oxidized, and may be an easily accessible estimate of the ore grade for economic evaluation. The downstream attenuation of elements in acid mine drainage can be interpreted in terms of oxidation, precipitation and dilution trends by employing plotting techniques and chemical equilibrium computations. Sulfate, lithium and zinc appear to serve well as natural conservative tracers to distinguish dilution trends during downstream mixing, and pH works well as a master variable to demonstrate sorption and precipitation trends. Equilibrium computations can produce major transformations of the data to indicate mineral precipitation behavior, as shown by the interpretation of the aluminum data.

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