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Redox Equilibria of Iron in Acid Mine Waters

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As the fourth most abundant element in the earth's crust, no other metal is as important as iron in geochemistry (1), natural water systems (2), microbial metabolism (3), the evolution of the earth's past and the formation of ore deposits (4,5). The chemical behavior of iron is known to be a key to the interpetation of processes involving trace elements, nutrients and oxidation-reduction reactions in natural waters, soils, sediments and groundwaters (6-13). An appropriate starting point for the cycling of iron through the lithosphere is the weathering of iron minerals, especially pyrite because it commonly occurs in many rock types and it provides a major source of sulfate and acidity as well as iron to natural water systems. Pyrite weathering also leads to the formation of acid mine drainage, a major cause of water pollution in many freshwater rivers and lakes.

Unlike iron transformations in marine systems or freshwaters of neutral to alkaline pH, acid mine waters contain very high concentrations of iron, which are therefore more easily determined. There are also minimal problems in these waters with non-equilibrium polymerization and colloid formation. Attempts at chemical modeling, however, are complicated by the large quantities of aqueous complexes that must be considered and the inadequacy of individual ion activity coefficients at moderate ionic strengths (up to 0.6 molal) when the ion association method is used. Calculations which are based on ion association and assume mineral-water equilibrium have been applied to problems of aqueous geochemistry with encouraging results (14-19). Although we consider our initial efforts as estimates, our calculations can be checked against field obser-

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vations. Our results should indicate where the major weaknesses of this approach remain. We believe that any chemical model must be continually tested against many different field situations so that it can be improved and modified and thereby enhance our understanding of natural systems. In this paper we shall focus on three important aspects of acid mine water equilibria: 1) the measurement and interpretation of redox reactions, 2) the formation of aqueous complexes and 3) solution-mineral reactions.

Formation of Acid Mine Waters

Numerous investigations of pyrite oxidation and the production of acid mine drainage have partially unravelled the mechanisms of this complex process. The initial step in pyrite oxidation was demonstrated by Sato (20) to be the release of ferrous ions and elemental sulfur:

$$FeS_2 \rightarrow Fe^{2+} + S_2^{\circ} + 2e^- \quad (1)$$

Likewise, the initial oxidation step of other metals sulfides (chalcocite, covellite, galena and sphalerite) appeared to produce the aqueous divalent metal ion and elemental sulfur.

In the next step of the oxidation, sulfur is oxidized to sulfate and protons are produced

$$S_2^{\circ} + 8H_2O \rightarrow 2SO_4^{2-} + 16H^+ + 12e^- \quad (2)$$

Iron will remain in the reduced ferrous state for quite some time as long as the solution is acid (pH $\leq$ 4). Although the overall oxidant which drives this reaction is oxygen from the atmosphere, several investigators have demonstrated that dissolved ferric iron is the primary oxidant which directly attacks the pyrite surface (21,22). Since the reaction rate depends upon the availability of Fe^{3+}, the oxidation half-reaction

$$Fe^{2+} \rightarrow Fe^{3+} + e^- \quad (3)$$

has been called the rate-determining step in the formation of acid mine drainage (23). Reaction 3 proceeds so slowly under acid conditions that acid mine waters would not commonly occur were it not for the acidophilic iron-oxidizing bacterium *Thiobacillus ferrooxidans*. This bacterium is such an effective catalyst that the oxidation rate is increased by 5 or 6 orders of magnitude over the abiotic rate (24,2). The bacterium can grow in the absence of light and it is found deep inside mines as long as some minimal amount of oxygen is available. The production of acid mine drainage is thus a rapid, self-perpetuating process catalyzed by bacteria which continues as long as air, water and pyrite are available. The geochemical formulation of this process is summarized in Figure 1. Pyrite is attacked by ferric iron, an acid ferrous sulfate solution is produced, and the ferrous iron is catalytically reoxidized to ferric by T. ferroxidans. This cycle continues until the pyrite is gone or the mine water leaves the sulfide surfaces (issues from the mine) where it will fully oxidize and hydrolyse to form amorphous ferric hydroxide (yellow-boy), goethite or jarosite depending upon the acid, iron, sulfate content of the water and the degree of ageing. Oxygen enters this reaction scheme by accepting the electron donated from the iron oxidation of reaction 3 through the metabolic pathways of the bacterium. The reduction half-reaction is:

$$\tfrac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O \qquad (4)$$

Since these bacteria are aerobic, this scheme implies that an important function of oxygen is to provide oxic conditions for adequate respiration. These half-reactions (3 and 4) need not be in equilibrium with each other; only a small amount of oxygen, enough for respiration, is necessary to drive this process. In this study, we are chiefly concerned with the reactions occurring in the effluent water after it has left the mines and has entered natural streams.

Field Site, Sampling and Analytical Methods

In Shasta County, California, inactive copper mines containing several millions of tons of sulfides are being weathered to produce highly acidic mine waters. The watershed surrounding Iron Mountain (Figure 2) was chosen for detailed investigations because it was the largest source of acid drainage in the region (25,26). Approximately 14 km of stream waters are affected by acid effluent issuing from the mines at Iron Mountain. These streams show a large gradient in redox state, pH and total dissolved solids during downstream transport due to mixing and dilution as well as rapid oxida-

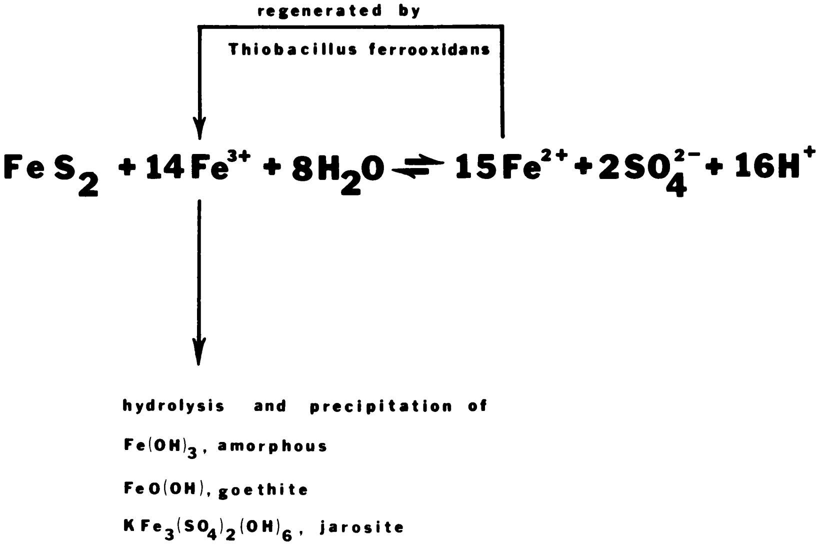

Figure 1. Mechanism of acid mine water formation

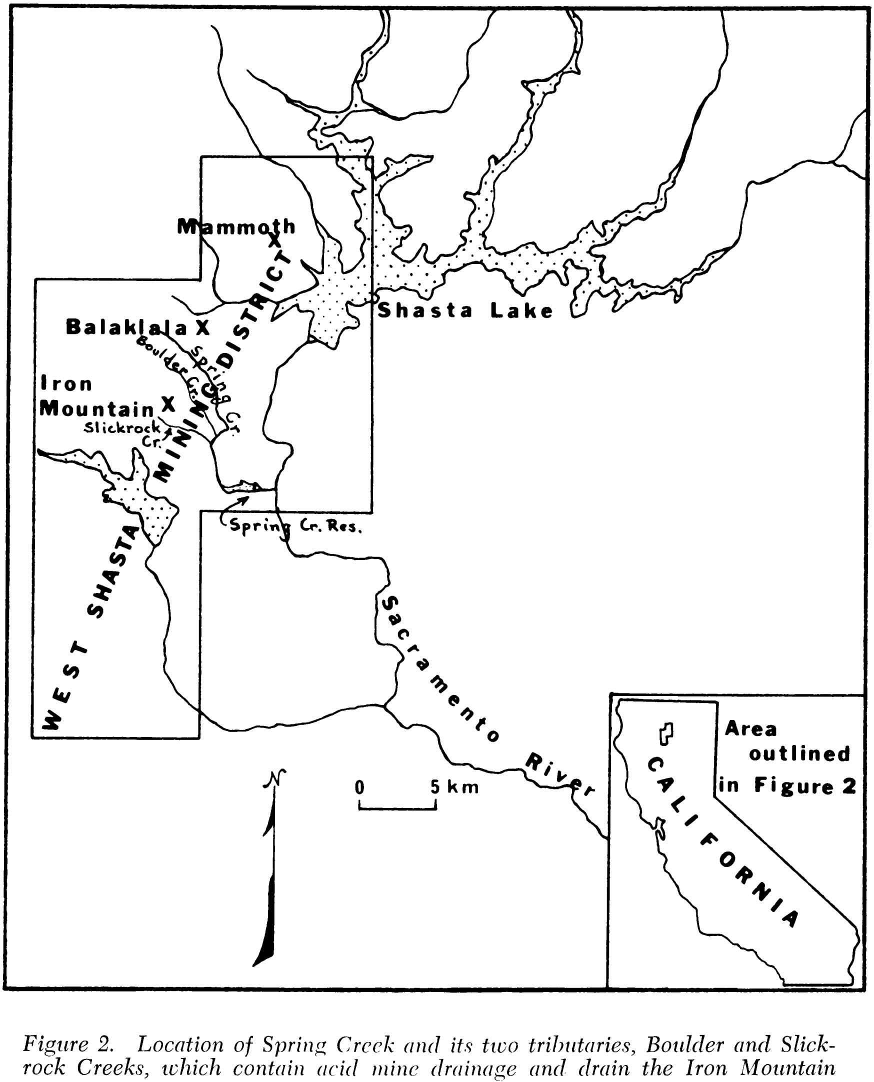

Figure 2. Location of Spring Creek and its two tributaries, Boulder and Slickrock Creeks, which contain acid mine drainage and drain the Iron Mountain watershed

tion rates. The weathering ore bodies are typical massive sulfide deposits, and they contain fine-grained pyrite with variable amounts of chalcopyrite and sphalerite occurring as pods or lenses within a rhyolite of Devonian age. Both air and groundwaters easily infiltrate the ore bodies and stoped out areas where the acid waters develop. The acid waters eventually find their way to a portal or adit and are finally discharged into either Boulder Creek or Slickrock Creek, the principal tributaries of Spring Creek (Figure 2). During an 18-month period over 100 water samples were collected at several different locations on these streams in order to interpret the hydrogeochemical processes controlling the heavy metal chemistry (26).

Temperature, conductivity, pH, Eh and dissolved oxygen (D.O.) were measured on site. Water samples collected for analysis were filtered on site through 0.10 µm membranes in an acid-cleaned plastic filtering apparatus (27) connected to a portable peristaltic pump via acid cleaned silicone tubing. Samples were preserved by acidification to a pH of about 1 with nitric acid for heavy metal analysis and with hydrochloric acid for ferrous iron, aluminum, alkali metals and alkaline earth metals. Filtration through 0.10 µm membranes remove iron-oxidizing bacteria and prevents biological oxidation while acidification minimizesinorganic oxidation. Anion analyses were carried out on samples which were filtered but otherwise were not preserved. Eh measurements were made with a combination polished platinum electrode which was checked at least once in a sampling day with ZoBell's solution (28). The precision on emf readings was ± 5 mv; the precision on pH readings was ± 0.02, although the accuracy cannot be considered better than ± 0.05. Measurement of pH in the most concentrated acid mine effluent (pH ≃ 1.0) were quite slow to come to a steady value but were always reproducible. Measurements of D.O. were made by a commercial oxygen electrode which was calibrated by a Winkler titration on a clean oxygen-saturated stream water.

Aluminum, silicon and zinc were determined by d.c.-argon plasma jet emission spectrophotometry. The remaining cations were analyzed by atomic absorption spectrophotometry (AAS) except ferrous iron which was done by a modification of the Ferrozine method (29,30,31). Total iron was determined by AAS and Fe^{3+} by difference. Sulfate was analyzed by the Thorin method after removal of interfering cations by ion exchange. Fluoride and chloride were extremely difficult to analyze because of the high concentration of interfering ions, and they were present at very low concentrations (about 0.1 mg/L or less). For chemical equilibrium computations they were assumed to be 0.1 mg/L for all samples.

Water samples collected from the Iron Mountain watershed provided a large variation in pH (1 to 7), Eh (350 to 900 mv), total dissolved iron (10 to 12,000 mg/L), temperature (4° to 31°C) and the ionic strength varied up to 0.6 molal.

Calculations of Activities and Saturation Indices

The water analyses were coded and then processed with the computer program WATEQ2. This program was modified in several ways to handle acid mine waters: (a) the Eh could be calculated from the Fe^{2+}/Fe^{3+} activity ratio or vice versa, (b) several sulfate minerals were added, (c) metal sulfate and hydroxide complex constants were carefully evaluated and included, and (d) Mn, Cu, Zn and Cd species were added since they are major constituents for several of the water samples. These modifications and the evaluated thermodynamic data are described by Ball, Jenne and Nordstrom in this symposium (32).

Redox Status of Acid Mine Waters: Equilibrium or Disequilibrium?

What we mean in this report by equilibrium and disequilibrium requires a brief discussion of definitions. Natural physicochemical systems contain gases, liquids and solids with interfaces forming the boundary between phases and with some solubility of the components from one phase in another depending on the chemical potential of each component. When equilibrium is reached by a heterogeneous system, the rate of transfer of any component between phases is equal in both directions across every interface. This definition demands that all solution reactions in the liquid phase be simultaneously in equilibrium with both gas and solid phases which make contact with that liquid. Homogeneous solution phase reactions, however, are commonly much faster than gas phase or solid phase reactions and faster than gas-liquid, gas-solid and liquid-solid transfer reactions. Therefore it seems appropriate to assume that natural waters would be in equilibrium with respect to dissolved species in the aqueous phase but might be in varying stages of disequilibrium with respect to gaseous and solid phases. Such a system is in partial or local equilibrium (33). In fact, there may be multiple and diverse local equilibrium states in such a heterogeneous environment. Equilibrium thermodynamics defines the extent to which a natural water has reached chemical equilibrium even though it may be undergoing dynamic changes in fluid flow, heat flow, biologic activity or mass transfer. This assumption of local equilibrium is a fundamental postulate of irreversible thermodynamics which justifies the calculations of equilibrium properties for a restricted spatial or temporal element in an irreversible process (33,34,35). With these concepts in mind, we can appreciate that a natural water may have one fixed, representative Eh but it may not be in equilibrium with dissolved gases or the solid surface of a platinum electrode. We now consider Eh measurements and chemical equilibrium in natural water systems.

The Eh of natural waters has been calculated theoretically (2,36), measured with inert metal electrodes, calculated from analyses of individual redox species (37) and measured by equilibration with known redox couples (38,39). Eh measurements have been used qualitatively as an operational parameter and quantitatively as an indication of a dominant redox couple. The qualitative use of Eh, advocated by ZoBell (40), has resulted in a great many measurements (41). As a quantitative tool, the use of Eh has not enjoyed widespread success. Several criteria must be met before the Eh can be related to a specific redox couple or mechanism: 1) the net exchange current at the electrode-solution interface, i.e., the difference in the rates of electron transfer to and from the platinum surface, must be negligible (an equilibrium criterion required for the application of the Nernst equation), 2) the individual exchange current, i_o, should be greater than about 10^{-7} ampere/cm^2 (43), 3) all aqueous electroactive redox species should be in homogeneous equilibrium, 4) the electrode surface must be free of electroactive surface coatings and adsorbed impurities and 5) activities of the redox species must be either measured or calculated by considering the effects of complexing and ionic strength on activity coefficients, since the activities, rather than the concentrations of the participating species are the quantities that determine the potential due to the redox couple. These criteria are difficult to meet and have led to the skeptical outlook that most Eh measurements are not amenable to quantitative interpretation (2,42,43). Contamination of platinum electrode surfaces by oxygen in aerated waters (43,44), by sulfur in anaerobic waters (44) and by iron in surface sediments (45) may cause errors in the measured values. Furthermore, many Eh measurements are thought to be mixed potentials (43). For these reasons, most Eh measurements have been used only in a qualitative sense.

In contrast to this general pessimism, several investigators have found good agreement between measured Eh and a dominant redox couple. Sato (20) found a relation between the measured Eh and pH of subsurface waters and the peroxide-oxygen redox couple. Berner (46) demonstrated a Nernstian relationship between measured Eh and the S^{2-}/S° couple in anoxic marine sediments. This equilibrium has also been substantiated by Kryukov, et al. (47), Skopintsev, et al. (48) and Whitfield (49). Thorstenson (37) found good agreement between the redox couples of sulfur and nitrogen species for five different reducing environments, implying that mixed potentials may not be a major problem. In laboratory experiments, Natarajan and Iwasaki (50) found Nernstian behavior of platium electrodes in the presence of varying dissolved oxygen and ferrous-ferric ratios. Bricker (51) achieved reversible equilibrium behavior with a platinum electrode in solubility studies of manganese oxides and hydroxides. Eh measurements of sulfur-rich waters can deviate from calculated sulfide redox values due to the presence of colloidal sulfur, but Boulegue (52) has shown that these interferences can be identified by acid-base titrations of the sample. Thus, amid the skepticism, there is already evidence from several different environments indicating that Eh measurements can be amenable to quantitative, thermodynamic interpretations.

Acid mine waters should be particularly well-suited to reliable Eh measurements because the high concentrations of electroactive iron species would clearly satisfy criteria 1) and 2) above (42,43). In addition, the acid conditions inhibits surface coatings of iron oxides on the electrode. The measured Eh values in this study were compared with calculated values based on ferrous-ferric analyses of 60 samples all of which had cation-anion balances better than 30 percent. Calculated values were derived from the Fe^{2+}/Fe^{3+} activity ratios after species distribution and temperature corrections to the standard ferrous-ferric couple had been computed with WATEQ2. The Nernst equation used for the calculation is

$$Eh = E^\circ\ (T,\ Fe^{2+}/Fe^{3+}) - \frac{RT}{F} \ln \frac{[Fe^{2+}]}{[Fe^{3+}]}$$

where the square brackets indicate activities, R is the ideal gas constant, T is the Kelvin temperature, F is the Faraday constant and E° is the temperature-dependent standard electrode potential for the ferrous-ferric couple. The results are shown in Figure 3, where the solid line represents perfect agreement. Seventy-seven percent of the values fall within ± 30 mv, which would be an anticipated uncertainty for most Eh measurements. No value is greater than 80 mv from the other and over half of the values agree to within ± 10 mv, which is twice the precision of the emf readings. This excellent agreement suggests a simultaneous validation of the equilibrium condition of acid mine waters, of the chemical model and its ability to represent that equilibrium, and of the accuracy of the Eh measurement.

Several features of this study should be pointed out. First, the reliability of the Eh measurement depends greatly on the technique. We used a closed line to pump water from the stream to a flow-through cell where a continuous supply of fresh sample water made contact with the electrode. No streaming potential effects were noticed because there was little or no change in potential when the pumping was stopped. The lack of streaming potential was probably due to the slow flow velocities and the high iron concentrations. The method of using a closed flow-through cell supplying a large volume of water to the surface of the Eh and pH electrodes has been found to be quite successful for a wide range of natural waters (53). We also would commonly remove the platinum electrode and gently buff the polished surface with a soft cloth and repeat the measurement if we noticed any drift. Second, we felt it was valuable to see the amount of change in the calculated Eh when activity coefficients and complexes were not considered, that is, when measured total concentrations of ferrous and ferric iron, rather than their respective calculated activities, were used to compute the Eh. We chose two measured Eh values, one which agreed to within 1 mv of the calculated value and another which differed from the calculated value by 79 mv. Without activity and complexing corrections, the discrepancies increased to 30 and 180 mv, respectively, a large error in each case.

It appears that the largest source of error in these comparisons is the analytical data. The next largest source of error seems to be the adequacy of activity coefficients and stability constants used in the model and last is the reliability of the field Eh measurement. Close inspection of Figure 3 shows a slight bias of calculated Eh values towards more oxidizing potentials. Fe(III) complexes are quite strong and it is likely that some important complexes, possibly $FeHSO_4^{2+}$ (54,55), should be included in the chemical model, but the thermodynamic data are not reliable enough to justify its use.

Finally, we return to a clarification of what parts of the system are in equilibrium. The comparison of calculated with measured Eh values gives strong evidence for homogeneous solution equilibrium and for equilibrium conditions at the surface of a platinum electrode in these waters. To determine whether the D.O. content of the water related to these equilibria and whether the oxidation of iron consumed oxygen from the stream water, we made measurements at the mouth of Boulder Creek and downstream in Spring Creek where most of the iron has been oxidized. We compared our D.O. measurements with the saturation oxygen solubility for the appropriate temperature and barometric pressure and found each part of the stream very close to saturation. The streams should contain saturated amounts of D.O. since they are commonly turbulent and well-mixed. The results in Table I, however, show that the Eh calculated using the O_2/H_2O couple is considerably higher than the measured value. The redox state of the water is thus determined by the ferrous-ferric ratio; oxygen dissolved in the water, while in equilibrium with the atmosphere, is not in equilibrium with the ferrous-ferric couple. This situation also reflects the fact that the exchange current for the O_2/H_2O couple is far less than for

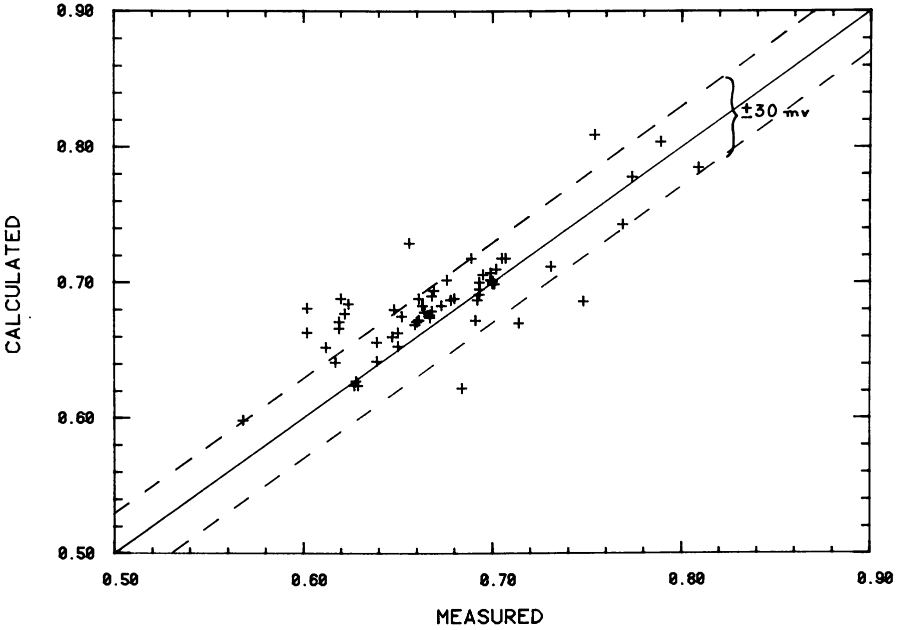

Figure 3. Comparison of measured and calculated Eh values. Errors of ±30 mV are given for the uncertainty in the Eh measurements.

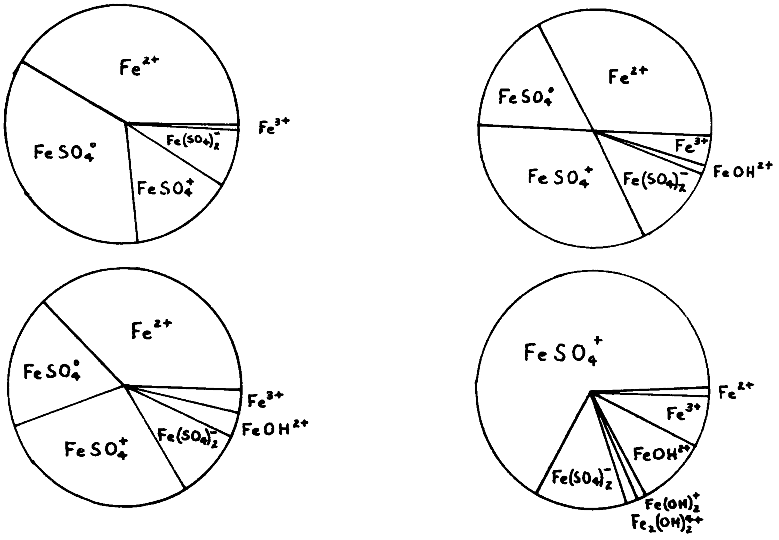

Figure 4. Distribution of dissolved iron redox species for varying concentrations of reduced and oxidized iron. (a) Hornet effluent; (b) Boulder Creek; (c) Spring Creek; (d) Spring Creek reservoir. Analyses for these four samples are shown in Table II.

Table I
Comparison of measured Eh values with those calculated from dissolved oxygen and the O_2/H_2O redox couple

	(H)Spring Cr.	(C)Boulder Cr.	(G)Boulder Cr.	(J) Spring Cr.
pH	6.40	3.02	1.85	2.32
D.O.(mg/L)	10.3	10.5	11.0	11.8
Eh, measured (V)	.385	.694	.625	.640
Eh, O_2/H_2O (V)	0.948	1.156	1.227	1.197

Table II
(Concentrations in mg/L except where noted)

Site	B*	G	J	N
T°C	25.5	6.0	5.5	5.5
pH	1.10	2.00	2.50	2.90
Eh (V)	.622	.378	.650	.770
Spec. Cond.**	65000	9900	2970	1810
Ca	173	45	17	18
Mg	685	107	27.5	30.8
Na	92.5	14.2	6.00	5.40
K	128	13.8	3.75	2.40
Fe (II)	9050	-	260	-
Fe (III)	2650	1280	354	208
Al	1400	188	47	47
SiO_2	130	55	26	32
SO_4	60000	5310	1280	1080

*B - Hornet Effluent, G - Boulder Creek, J - Spring Creek, N - Spring Creek.
**Units for specific conductance are microSiemens.

the Fe^{2+}/Fe^{3+} couple (43) and does not affect the measured potential.

Solution Complexes of Iron in Acid Mine Waters

The wide range of Eh, pH and dissolved solids for the acid mine waters in the Iron Mountain watershed provides an opportunity to survey the dominant complexes which are calculated from an ion association model. Rather than choosing some "average" composition for acid mine water, we have used naturally-occurring waters which represent the range of conditions found in the study site. The analyses shown in Table II are a series of water samples containing the most ferrous-rich to the most ferric-rich in iron content. These analyses show progressive downstream dilution and oxidation beginning with the source water coming from the Hornet tunnel which discharges into Boulder Creek (see Figure 2). The two Spring Creek samples were taken at 1) a point just below Boulder Creek confluence and 2) a point 4 km below the Boulder Creek confluence at the mouth to the Spring Creek Reservoir. The list of iron complexes which were used in the aqueous modeling computations are shown in Table III. Of these complexes, the major ones are expected to be hydroxide and sulfate. The distribution of species is shown in Figure 4 as percentages of the total dissolved iron. Only species which contributed 0.2 percent or more of the total dissolved iron were included. From Figure 4, it is clear that only the $FeSO_4^\circ$ contributes to the complexing of ferrous iron but that this complex alone can constitute up to nearly 50 percent of the total ferrous iron. Ferric iron is much more highly complexed than ferrous and under most conditions the free ferric iron is never more than about 8 percent of the total iron. $FeSO_4^+$ is always the dominant ferric complex, followed by $Fe(SO_4)_2^- > Fe(OH)^{2+} > Fe_2(OH)_2^{4+} > Fe(OH)_2^+$ in order of decreasing abundance. An objection might be raised that organic complexing plays an important role in the species distribution of these waters. This possibility is certainly very real, and there is some evidence that the dissolved organic carbon in these waters is very high, but the good agreement on the Eh calculations and the low pH values of these waters suggest that any organics present are probably fully protonated and have only a minor effect on complexing.

Any chemical modeling of acid mine waters

Table III

Aqueous complexes and solid phases of iron considered for computation

a) Complexes:

$FeOH^{+}$, $Fe(OH)_2^{\circ}$, $Fe(OH)_3^{-}$, $FeSO_4^{\circ}$

$FeOH^{2+}$, $Fe(OH)_2^{+}$, $Fe(OH)_3^{\circ}$, $Fe(OH)_4^{-}$, $Fe_2(OH)_2^{4+}$, $Fe_3(OH)_4^{5+}$ $FeSO_4^{+}$, $Fe(SO_4)_2^{-}$

$FeCl^{2+}$, $FeCl_2^{+}$, $FeCl_3^{\circ}$, FeF^{2+}, FeF_2^{+}, FeF_3°

b) Solids:

Melanterite	$FeSO_4 \cdot 7H_2O$
Copiapite	$Fe^{2+}Fe_4^{3+}(SO_4)_6(OH)_2 \cdot 20H_2O$
Coquimbite	$Fe_2(SO_4)_3 \cdot 9H_2O$
Jarosite	$KFe_3(SO_4)_2(OH)_6$
Ferric hydroxide, amorphous	$Fe(OH)_3$

relies heavily on accurate thermodynamic data for iron sulfate complexes. Unfortunately, data for ion triplets such as $Fe(SO_4)_2^-$ are not accurately known and possible complexes such as $FeHSO_4^{2+}$ and $Fe(HSO_4)_2^0$ have not been properly identified. Better data are needed for these species in order to enhance the capability of generalized chemical models.

Water-Mineral Equilibrium Relationships

A suite of both oxidized and reduced iron minerals has been found as efflorescences and precipitates in or near the acid mine water of Iron Mountain. The dominant minerals tend to be melanterite (or one of its dehydration products), copiapite, jarosite and iron hydroxide. These minerals and their chemical formulae are listed in Table III from the most ferrous-rich at the top to the most ferric-rich at the bottom. These minerals were collected in air-tight containers and identified by X-ray diffractometry. It was also possible to check the mineral saturation indices ($\log_{10}(AP/K)$, where AP = activity product and K = solubility product constant) of the mine waters with the field occurrences of the same minerals. By continual checking of the saturation index (S.I.) with actual mineralogic occurrences, inaccuracies in chemical models such as WATEQ2 can be discovered, evaluated and corrected (19), provided that these occurrences can be assumed to be an approach towards equilibrium.

We have chosen an equilibrium zone around the S.I. equal to the estimated uncertainty of the solubility product constant. Outside of these limits, the solution is either supersaturated (positive direction) or undersaturated (negative direction). The S.I. values were then plotted vs. the log conductivity to show approaches to mineral saturation as an approximate function of the total dissolved solids. Conductivity was chosen as a convenient parameter because 1) it points out dilution trends or undersaturation and corresponds to a spatial trend for downstream sites, 2) it changes more consistently than other parameters, and 3) it covers a larger range of values than Eh, pH or an individual ion. Activity diagrams (53) could have been used but then certain assumptions have to be made about the mineral stability boundaries such as constant activity of water or of pH or of sulfate.

Melanterite. The most concentrated acid mine waters, such as those flowing from the Hornet tunnel, commonly precipitate melanterite, a pure ferrous sulfate, along their edges. Water which had infiltrated a massive ore body would also precitipate melanterite along the surface of an open cut exposed to dry outside air. But melanterite was found only on sulfide surfaces which were regularly washed by rainfall or running water. In sheltered areas, such as the entrance to the Richmond mine, the dominant mineral occurring on open cuts is copiapite or a mixture of copiapite and coquimbite.

In Figure 5 we have plotted S.I. values for melanterite indicating a trend towards saturation for the Hornet effluent (labeled B). All of the other waters (collected at downstream sites) have been diluted and oxidized and therefore appear undersaturated. The results of these calculations compare quite favorably with field observations. Unfortunately, there is a large uncertainty associated with the thermodynamic solubility constant for melanterite. Although its solubility is well-known, the thermodynamic equilibrium constant is difficult to obtain because the compound is highly soluble and therefore becomes saturated only at high ionic strenths.

More importantly, it should be noted that melanterite commonly forms on rock surfaces, especially along fractures where water can be pulled up from a water-saturated zone to the surface by capillary forces. Thus, melanterite saturation is occurring in a microenvironment in many instances which makes sampling and interpretation difficult.

Copiapite. Theoretically, melanterite can oxidize to form copiapite by the reaction:

$$5FeSO_4 \cdot 7H_2O + O_2 + H_2SO_4 \rightarrow$$
$$Fe^{2+}Fe^{3+}_4(SO_4)_6(OH)_2 \cdot 20H_2O + 15H_2O.$$

As mentioned earlier, large amounts of copiapite have been found accumulating on ore surfaces in areas protected for direct rainfall. The mechanism of its formation is not at all clear but from field observations it appears that acid mine water is being drawn by capillary forces to an exposed surface where it quickly evaporates to melanterite and/or copiapite. Coquimbite is intimately associated with copiapite and these two minerals appear to be very stable as long as they are protected from rainfall or running water. No thermodynamic data

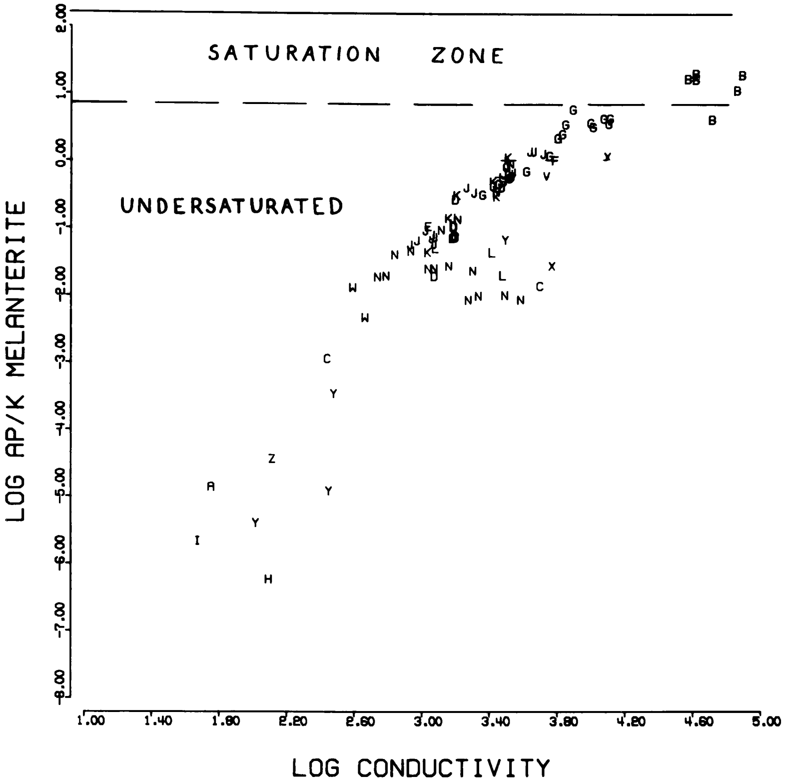

Figure 5. Saturation indices for melanterite plotted as a function of the log conductivity showing an approach to saturation for the most concentrated ferrous-rich waters of the Hornet effluent (B)

are available on either copiapite or coquimbite so that S.I. values cannot be calculated. Copiapite contains both ferrous and ferric iron but a form called ferricopiapite containing only iron in the oxidized ferric state may also occur. There is little information on the relative abundance of these minerals nor whether copiapite is a necessary precursor to the formation of ferricopiapite and coquimbite. A further complication to the interpretation of mineral reactions is the solid substitution properties of copiapite. It not only can have a change in the ferrous/ferric ratio but the divalent and trivalent sites can accept a large number of divalent and trivalent ions such as Mg^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+} and Al^{3+}.

Jarosite. The waters which are associated with such soluble salts as melanterite and copiapite commonly have pH values of 0.8 to 1.5. As the pH rises to the range of 1.5 to 2.5, jarosite will commonly precipitate if the dissolved iron content is high enough. A fine-grained yellow precipitate forms in Boulder Creek every summer and fall, which when washed and filtered, gives a good X-ray pattern for potassium jarosite. This mineral is precipitating directly from the water and it appears to have good crystallinity. Both copiapite and jarosite are a bright yellow color and may easily be confused with sulfur.

In Figure 6, the S.I. values for potassium jarosite are given for all the samples. The values show supersaturation for nearly every sample and prompts us to ask several questions: (a) are these waters truly supersaturated and is this a kinetic requirement for precipitation? (b) are organic complexes important for these waters? (c) are the thermodynamic data reliable? Some of these questions can be answered. First, the amount of supersaturation is more than the ± 1.1 log K unit uncertainty in the thermodynamic data. Second, the model does not appear to be inadequate for the Eh comparison and other calculations, and if organic complexing were introducing a significant error it would have shown up in the cation-anion balance or other calculations. Downstream in Spring Creek where no jarosite has been found the S.I. is often more supersaturated than in Boulder Creek. This supersaturation suggests that jarosite solubility does not control the water chemistry of any of the streams. The remaining possibility is that jarosite is precipitating only in microenvironments where the

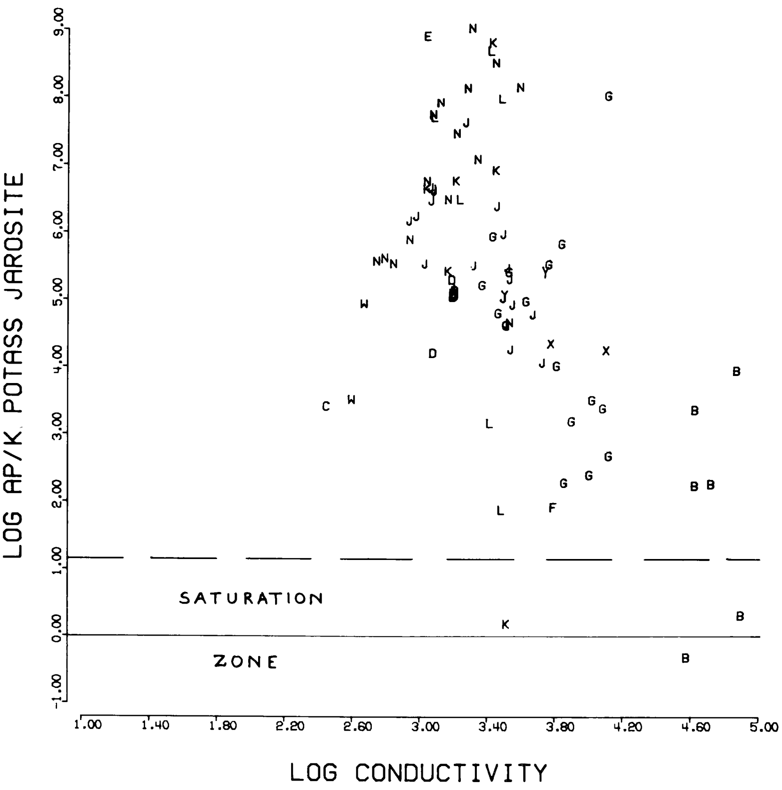

Figure 6. Saturation indices for jarosite plotted as a function of the log conductivity showing supersaturation for nearly all values

water chemistry is different than in the bulk solution. The evidence for this is that jarosite precipitation is always found on stream bed surfaces where bacteria have been growing, and is also found inside of acid slime streamers produced by these bacteria. Beyond this, there may be important particle size effects (12). There could still be local equilibrium conditions existing here, but they are probably below the resolution of the sampling techniques. Clearly, more work is needed before the jarosite geochemistry can be adequately interpreted.

Amorphous ferric hydroxide. Most of Spring Creek below the Boulder Creek confluence is iron stained and actively precipitates iron hydroxide. The pH values are commonly in the range of 2.5 to 3.5 depending on the season. The iron precipitates are amorphous to X-rays and appear to be amorphous ferric hydroxide from their color and texture. S.I. values calculated for amorphous ferric hydroxide show a trend towards saturation with downstream dilution and oxidation (Figure 7). We have used the upper solubility limit of pK = 37.1, where pK is the apparent stability constant for ferric oxyhydroxides (12) and most of the downstream sites (labeled N) fall neatly into the region of pK = 37 to 39 as would be expected for a freshly precipitated material. Very little supersaturation appears in our computations. Again, the S.I. calculations match very well with the field observations and with previous studies of ferric hydroxide equilibrium in natural waters (12,15,17). A noticeable hiatus occurs at about log K = 41. Below this value the samples plotted in Figure 7 are very high in ferrous iron, low in pH and show no sign of ferric hydroxide precipitation.

Conclusions

We have utilized a chemical model in this investigation to interpret the equilibrium behavior of iron in acid mine waters. A successful correlation between calculated and measured Eh values has been found, using WATEQ2, the computerized ion association model. This correlation supports the basic assumption of homogeneous solution equilibrium in these waters and simultaneously corroborates both the validity of the aqueous model and the quantitative interpretation of Eh measurements in these waters. This interpretation makes it possible to calculate the distribution of iron

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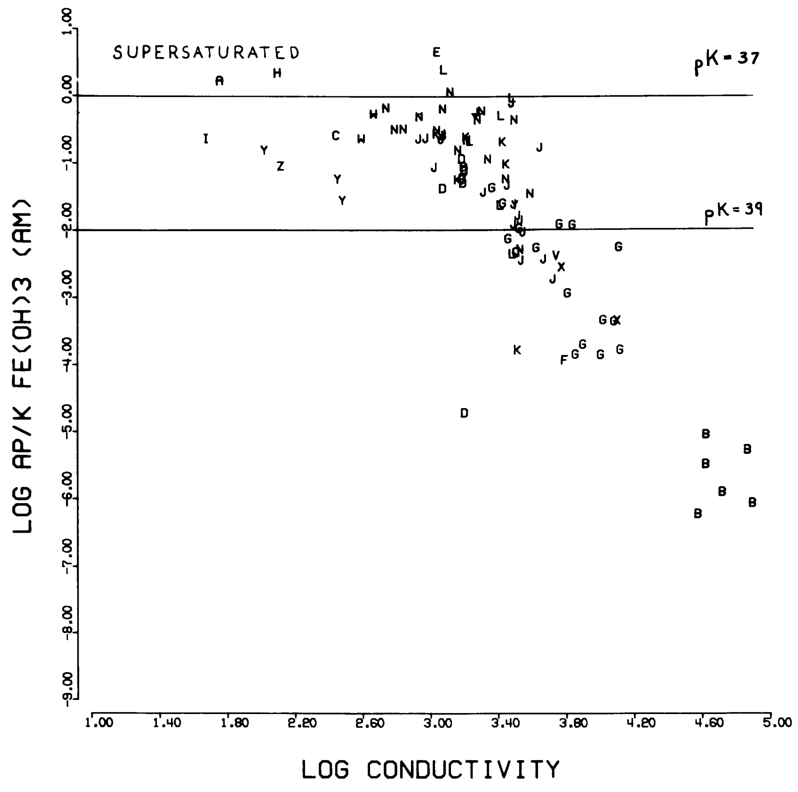

Figure 7. Saturation indices for amorphous ferric hydroxide plotted as a function of the log conductivity showing an approach to saturation for the more dilute and more oxidized downstream waters

species based on Eh measurements when ferrous-ferric analyses are not available. Although the stream waters show equilibrium saturation with dissolved oxygen, there is no equilibrium between the dissolved oxygen and ferrous-ferric redox couple.

Mineral saturation indices for melanterite and amorphous iron hydroxide agree quite well with field occurrences of the same minerals. Jarosite, however, appears to be supersaturated for nearly all of the samples regardless of the presence or absence of the mineral in these streams. Field observations indicate that jarosite precipitation occurs in the microenvironment of bacterial colonies where the chemical conditions may be quite different from the bulk solution. These considerations lead us to suggest that there is a kinetic barrier which hinders jarosite precipitation but does not hinder ferric hydroxide precipitation and that this barrier is overcome by the surfaces of bacterial colonies (both iron-oxidizers and unidentified non-oxidizers).

The chemical equilibria approach used in this study have enabled us to identify which parts of an acid mine drainage system are in equilibrium and which parts are not. Our results have provided greater insight into the chemical processes of acid mine waters in particular and the redox relations of iron in general.

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Abstract

A detailed hydrogeochemical investigation of 14 km of stream waters contaminated by acid mine drainage in Shasta County, California provides insight into the

equilibrium transformations of iron during the oxidative weathering of pyritic ore. Over 60 water analyses covering a range of pH, redox state, total iron concentration, temperature and ionic strength were processed with the computerized chemical model WATEQ2 so that activities of free ions and complexes and satutation indices could be determined. The results demonstrate (a) measured Eh values agree quite well with Eh values calculated from the ferrous/ferric activity ratio, (b) the dominant complexes in acid mine waters are $FeSO_4^\circ$, $FeSO_4^+$, $Fe(SO_4)_2^-$, $Fe(OH)^{2+}$, $Fe_2(OH)_2^{4+}$ and $Fe(OH)_2^+$ and (c) acid mine waters low in pH (1 to 2) and high in reduced iron approach saturation with respect to melanterite whereas progressive downstream oxidation and dilution (pH = 2 to 3.5) of these waters forces these waters to become saturated with respect to amorphous iron hydroxide. For these two minerals, the field observations match the saturation calculations very well. However, all of the waters show supersaturation with respect to jarosite regardless of the presence or absence of jarosite in the stream waters. These results suggest a strong kinetic hindrance to the precipitation of jarosite.

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