GEOCHEMICAL EVOLUTION OF EXTREMELY ACID MINE WATERS AT IRON MOUNTAIN, CALIFORNIA: ARE THERE ANY LOWER LIMITS TO pH?

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ABSTRACT

Oxidation of pyrite is well known to cause acidification of surface and ground waters. Minimum pH values tend to be in the range of 1.5 to 2.5 for natural waters infiltrating disseminated sulfide deposits, base metal tailings, and sulfidic waste rocks, where some degree of neutralization by gangue minerals accompanies pyrite oxidation. However, within massive sulfide deposits and in sulfide-rich tailings and waste rock, extremely high aqueous concentrations of sulfate, iron, and other metals can develop, accompanied by pH values less than 1.0. In at least one extreme case, at Iron Mountain, California, pH values less than 0.0 have now been documented. In this paper, we discuss geochemical mechanisms which can lead to the attainment of these extremely low pH values.

Computer simulations of sulfide oxidation using the programs PHREEQE and PHRQPITZ indicate that oxidation of 1.55 moles of pyrite in one kg of pure water will lead to a pH near 0.0, at which point saturation with melanterite ($FeSO_4 \cdot 7H_2O$) is achieved. Continued pyrite oxidation accompanied by precipitation of melanterite or other Fe-sulfates can drive pH below zero. The acidity will be reduced by dissolution and hydrolysis of gangue minerals and oxidation of Fe^{2+} to Fe^{3+}, which is accompanied by a pH increase at pH values below 2.

Given the relatively high ratio of Fe^{III}/Fe^{II} in efflorescent Fe-sulfate salts (e.g., rhomboclase, voltaite, and coquimbite) found in the mine workings at Iron Mountain, it seems likely that oxidation and evaporative processes have contributed significantly to the evolution of mine waters with negative pH values. Conditions at Iron Mountain which favor this phenomenon are: high pyrite content of ore (95-98%), low abundance of carbonate and other neutralizers, availability of oxygen and water in the mine workings, and elevated temperatures (38-47°C) from exothermal pyrite oxidation.

Keywords: acid mine drainage, pH, massive sulfide, pyrite, iron sulfates, Iron Mountain, West Shasta district, California

INTRODUCTION

Iron Mountain mine in Shasta County, California, is producing some of the most acidic and metal-rich mine drainage in the world. The Iron Mountain site (Fig. 1) is listed on the National Priority List of the U.S. Environmental Protection Agency for Superfund cleanup (Nordstrom et al., 1990). Renovations and reconnaissance of underground workings in the Richmond mine at Iron Mountain were completed during 1988-1990 at a cost of more than $1 million (US), allowing access to stopes which had been abandoned since the early 1950's.

In this paper, we document the occurrence of extremely acid mine waters at Iron Mountain, including the first negative values of pH recorded from such an environment, and discuss the geochemical mechanisms which contribute to the attainment of these extreme conditions.

HYDROGEOCHEMICAL CHARACTERISTICS OF IRON MOUNTAIN, CALIFORNIA

Subsurface conditions at Iron Mountain appear to be nearly optimal for the maximum production of acid mine waters. In particular, there are five characteristics of the hydrogeochemistry causing extremely acid mine waters: (1) high pyrite concentration, (2) easy access of oxygen, (3) elevated temperatures enhancing evaporation, (4) site-specific hydrologic factors, and (5) low neutralizing capacity of wall rocks.

First, the concentration of pyrite is nearly 100 percent in large single masses. The largest, the Richmond ore body, is a well-defined massive sulfide about 60 m wide, about 45 m high and about 800 m long. The original Richmond and Richmond Extension ore bodies were estimated to be about 11.5 M tons, or 80.5 M ft^3, averaging around 1 wt. % Cu and 3 wt. % Zn, although the assays show a large range of values. Given the low abundance of gangue minerals in the massive sulfide ore, the pyrite content averages 95 % or more. Hence, the concentration of sulfide is essentially at a maximum.

Second, the massive sulfides are largely within the unsaturated zone. The deposits have been drilled full of exploration holes and are honeycombed with tunnels, shafts, manways, and stopes, resulting in considerable availability of oxygen. Most of the oxygen reaches the Richmond sulfides by advective air currents that flow between open portals, adits, shafts, and caved-in or weakened ground on the surface. The airflow is probably aided by thermally driven convective cells due to the high heat output from pyrite oxidation. About 1,500 kilojoules of heat are released per mole (about 120 grams) of pyrite oxidized; this amount of heat could raise the temperature of the groundwater to the boiling point of pure water (Nordstrom and Munoz, 1987). "Hot chimneys" have been noted in many waste rock piles, and the occurrence of fires in underground sulfide mines is well-documented (Ninteman, 1978).

Third, the heat effect is strong enough to induce evaporation of the subsurface mine waters and we suspect this contributes further to the acidity. Evaporation also can induce the formation of acid iron sulfate minerals. These minerals, e.g., rhomboclase, are known to form only under conditions of extreme acidity and can be thought of as acidity stored in solid form.

Fourth, with the structure and position of the Brick Flat open pit above the underground Richmond mine workings, ground water is effectively drawn inwards towards the center of Iron Mountain. The Richmond mine workings are drained primarily by a single portal.

Fifth, the surrounding bedrock is a series of submarine extrusive and intrusive volcanic rocks collectively called the Balaklala Rhyolite (Kinkel et al., 1956). This rock has been affected previously by hydrothermal alteration and now has little capacity to neutralize acid mine waters. There is little carbonate mineral present, therefore there is little opportunity for any significant alkalinity to develop. Whatever alkalinity does develop is overwhelmed by the acidity produced from pyrite oxidation.

These five factors make Iron Mountain a unique hydrogeochemical reactor that is nearly optimal for maximum production of acid mine waters.

RESULTS OF UNDERGROUND SAMPLING AT IRON MOUNTAIN

Water and mineral samples were collected by the authors from the Richmond workings of Iron Mountain during September, 1990. The water sample locations are shown on the map in Figure 1. Both seepage drip waters and floor drainage waters were sampled. The twelve acid mine waters sampled were found to range in pH from 1.5 to <-1.0; four complete chemical analyses are shown in Table 1 (for additional data, see Nordstrom and Alpers, written communication, 1990; available from the authors). Sample 90WA103 (pH 0.48) was a floor drainage sample taken at the five-way intersection shown in Figure 1 and is fairly representative of the effluent leaving the Richmond portal during low-flow conditions. The other three samples in Table 1 are drip waters with negative pH values.

From the definition pH ≡ $-\log[a_{H^+}]$, it can be seen that values of pH less than zero correspond simply to aqueous activities of H^+ greater than 1. The activity of H^+ is equal to the molal concentration multiplied by an activity coefficient ($a_{H^+} = m_{H^+}\gamma_{H^+}$). As shown in Figure 2A, molalities of sulfuric acid greater than about 1 (or normalities > 2) correspond to negative pH values.

Unfortunately, pH measurements below values of about 1.0 are subject to significant errors due to: (1) the lack of an adequate definition of pH, (2) the lack of standard buffers, (3) the non-ideal behavior of acids at high concentrations, (4) the non-linear response of glass electrodes at high acid concentrations, and (5) the possible interfering reactions of acid anions at the hydrated glass electrode surface. Some of these problems can be resolved. The application of the Pitzer ion interaction theory to sulfuric acid (Pitzer et al., 1977) makes it possible to develop a set of standardized sulfuric acid solutions for calibration purposes. Among acids, sulfuric appears to be the best behaved in terms of electrode response time, non-ideal behavior and stability of the hydrated glass membrane.

Water samples were filtered on site at Iron Mountain using Millipore[1] hand-pumped, enclosed containers that hold 150 mL of solution. Samples were diluted in the field by 1:10 with 0.1 M HCl for cation and Fe(II/III) determinations and by 1:10 with distilled water for sulfate determinations.

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[1] The use of brand names in this report is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

The dilutions were found to be essential because some undiluted samples precipitated a large mass of iron sulfate crystals within minutes to hours after cooling to ambient temperatures and later chilling on ice. Temperature and pH were measured on site using four sulfuric acid solutions of 0.100 N, 0.3275 N, 1.81 N and 3.275 N standardized against primary sodium carbonate. The pH of these solutions were defined by the Pitzer method (Pitzer et al., 1977) and the MacInnes convention for scaling individual ion activity coefficients. The computations for this were done with a revised version of PHRQPITZ (Plummer et al., 1988), a thermodynamic mass transfer program that calculates chemical equilibria in brines. The results are shown in Figure 2. The pH, defined by the Pitzer method, is shown in Figure 2A as a function of sulfuric acid molality. A sample calibration curve for a Sargent-Welch electrode is shown in Figure 2B. Calibration curves for two different electrodes were obtained: an Orion Ross combination glass electrode with a 3.0 M KCl filling solution and a Sargent-Welch combination glass electrode with a saturated KCl (4.8 M) filling solution. The calibration curves were checked with additional buffer standards of HCl-KCl (pH 1.0 and 2.0), potassium tetraoxalate (pH 1.68), potassium hydrogen phthalate-HCl (pH 3.00) and potassium hydrogen phthalate (pH 4.00) and were found to be consistent to within ± 0.02 of a pH unit on both electrodes.

During sample collection at site 90WA110 (Fig. 1) three waters were found to have pH values much lower than the most concentrated sulfuric acid standard; our estimates of pH < -1.0 for these samples (Table 1) are conservative estimates, subject to better quantification pending calibration of our electrodes with more concentrated standards. In contrast, the pH determinations of -0.35 and -0.7 for samples 90WA108 and 90WA109, respectively, have a precision of ±0.1 units or less. Temperature dependence was determined by measuring the electrode potentials (in mV) of both standards and samples at ambient mine temperatures (20 to 47°C). These measurements resulted in pH calibration curves at 25.0, 38.0 and 47.1°C.

The two lowest pH values in Table 1 were drippings of ground water seeps from stalactites of either melanterite (90WA109) or rhomboclase (90WA110) under humid, warm conditions. Abundant efflorescences, stalactites and stalagmites made up of soluble sulfate minerals were found throughout most of the accessible passages. They were identified (in approximate order of abundance) as rhomboclase, voltaite, melanterite, coquimbite, copiapite, römerite, kornelite, gypsum, halotrichite, and chalcanthite by X-ray diffraction and optics (R. Erd, oral communication, 1990). The stoichiometric formulas for these minerals are given in Table 2. Some stalagmites made up mostly of rhomboclase and voltaite were found with dimensions greater than 3 m in height and 1 m in diameter. We estimate that the sulfate salts, having accumulated over nearly 40 years, now occupy about 5 % of the open space in the mine workings (Nordstrom and Alpers, written communication, 1990).

Based on energy dispersive spectra and wet chemical analysis, it is likely that considerable solid solution substitution is present in several of the sulfates, most notably Zn and Cu replacing Fe^{II} in melanterite and Al replacing Fe^{III} in coquimbite and copiapite. Iron oxides and hydroxides (e.g., goethite, ferrihydrite) were observed locally but not sampled. Water sample 90WA109 must have been at or above saturation with respect to melanterite because it was dripping from a large melanterite stalactite and an undiluted sample precipitated a large mass of melanterite crystals on cooling. Similarly, samples 90WA110 A and B must have been at or above saturation with respect to rhomboclase because they precipitated large crystalline masses (approximately 90 percent of sample volume) of rhomboclase on cooling and extensive deposits of rhomboclase were observed in the drip zone.

Ritcey (1989) tabulated mine and tailings water analyses from hard-rock metal mines in Canada and the Unites States and showed that the typical range for pH is 1.8-7.0, and that the concentration range for sulfate is 9.2-30 g/L, for copper is 1-791 mg/L, for zinc is 1.6-1360 mg/L, and for arsenic is 0.2-5.06 mg/L. Acid mine waters from Iron Mountain have the lowest pH, highest iron, highest cadmium, and highest sulfate of any that we have been able to find in the field or in the literature. The arsenic concentrations are second only to one value reported in the Soviet Union by Goleva (1977) and the zinc concentrations are second only to those reported from the Bawdwin zinc mine in Burma (Braeuning, 1977) (Table 3).

In most respects, the chemistry of the mine waters and the mineralogy of secondary salts inside the Richmond workings reflect the most extreme conditions of natural acidity developed from pyrite oxidation yet reported.

EVOLUTION OF EXTREMELY ACID MINE WATERS

The water samples of lowest pH at Iron Mountain have been affected by at least five processes: (1) sulfide oxidation, (2) oxidation of iron from Fe^{II} to Fe^{III}, (3) dissolution and hydrolysis of gangue minerals, (4) concentration by evaporation, and (5) efflorescent mineral formation. In the following subsections, the relative importance of these processes is addressed in an effort to understand the origin of these extremely acid mine waters.

Sulfide Oxidation

The complete oxidation of pyrite at near-neutral to weakly acid (pH 4-7) conditions can be summarized as:

$$FeS_2 + 15/4\ O_2 + 7/2\ H_2O \Longrightarrow Fe^{III}(OH)_{3(s)} + 2\ SO_4^{2-} + 4\ H^+ . \qquad (1)$$

At pH values less than 4, ferric iron can act as the direct oxidant of pyrite:

$$FeS_2 + 14\ Fe^{3+} + 8\ H_2O \Longrightarrow 15\ Fe^{2+} + 2\ SO_4^{2-} + 16\ H^+ . \qquad (2)$$

This reaction is fast (e.g., McKibben and Barnes, 1986), but its rate is limited in an abiotic system because the reoxidation of iron from ferrous to ferric by oxygen is extremely slow at pH values below 4. However, the catalytic effect of the iron-oxidizing bacterium *Thiobacillus ferrooxidans* speeds up the rate for the reaction:

$$Fe^{2+} + 1/4\ O_2 + H^+ \implies Fe^{3+} + 1/2\ H_2O \tag{3}$$

by five to six orders of magnitude over the abiotic rate (Nordstrom, 1985) so that the rate of regeneration of ferric iron (reaction 3) is about three orders of magnitude greater than the rate of pyrite oxidation by ferric iron (reaction 2). In the absence of abundant bacteria, reaction (3) is the rate-determining step in the production of acid mine drainage (Singer and Stumm, 1970). Combining reactions (2) and (3), an acidic ferrous-sulfate solution is produced by the oxidation of pyrite according to the reaction:

$$FeS_2 + 7/2\ O_2 + H_2O \implies Fe^{2+} + 2\ SO_4^{2-} + 2\ H^+ . \tag{4}$$

Geochemical modelling of sulfide oxidation reactions was carried out using the mass transfer programs PHREEQE (Parkhurst et al., 1980) and PHRQPITZ (Plummer et al., 1988). The specific ion interaction (Pitzer) approach to aqueous speciation in PHRQPITZ is preferable to the ion association model in PHREEQE for this problem because the Pitzer approach is generally more successful in highly concentrated solutions, such as the mine waters in the vicinity of pH 0. For example, in Table 1 it can be seen that these mine water samples from Iron Mountain have sulfate concentrations in excess of 100 g/L (about 1 molar) and that the samples with negative pH have sulfate concentrations between 360 and 760 g/L (3.7 to 7.9 molar). Because Pitzer coefficients are not available for Fe^{III}-bearing systems, the use of PHRQPITZ is somewhat limited in this application, so some calculations were made using the PHREEQE program. Agreement between the two programs is very close for simulations at pH $\geq$ 0.5 and the observed deviations at pH = 0 do not affect the conclusions in this paper.

Reaction of pyrite with pure water according to reaction (4) was modelled with PHRQPITZ. A plot of moles of pyrite consumed versus pH (Fig. 3A) shows a rapid decline in pH from an initial value of 7.0 for pure water to pH 3.7 for .0001 moles of reaction (4), and then further decline in pH to 1.96 for .01 moles (corresponding to about 1.2 g pyrite per liter of water). Continued dissolution of pyrite leads to pH < 1.0 after 0.17 total moles reacted and finally to a pH just below zero (-0.02) after 1.5485 moles of reaction (4), at which point the solution reaches saturation with respect to melanterite. Continued pyrite oxidation would allow melanterite to precipitate by reaction (5):

$$Fe^{2+} + SO_4^{2-} + 7\ H_2O \implies Fe^{II}SO_4 \cdot 7H_2O . \tag{5}$$

Continuation of reaction (4) at melanterite saturation generates one mole of melanterite and one mole of sulfuric acid for each mole of pyrite consumed, as shown by combining equations (4) and (5):

$$FeS_2 + 7/2\ O_2 + 8\ H_2O \implies Fe^{II}SO_4 \cdot 7H_2O + 2\ H^+ + SO_4^{2-} . \tag{6}$$

Therefore, melanterite saturation poses no barrier to further decrease of pH to values below zero. Continued pyrite oxidation at melanterite saturation leads to decreasing pH along the curves shown in Figure 3. In Figure 3B, results of the above simulation can be seen on a plot of pH versus moles of reaction (4) on a logarithmic scale. The deviations from linearity in Figure 3B are due to changes in activity coefficients with increasing ionic strength.

Oxidation of Fe^{II} to Fe^{III}

By reaction (3), the oxidation of aqueous Fe^{2+} to Fe^{3+} consumes one mole of H^+ for each mole of iron oxidized. Near and above pH values of 2, Fe^{3+} hydrolyzes according to the reactions

$$Fe^{3+} + H_2O <==> Fe^{III}(OH)^{2+} + H^+ , \tag{7A}$$

$$Fe^{3+} + 2\ H_2O <==> Fe^{III}(OH)_2^{+} + 2\ H^+ \text{ , and} \tag{7B}$$

$$Fe^{3+} + 3\ H_2O <==> Fe^{III}(OH)_3 + 3\ H^+ . \tag{7C}$$

This hydrolysis causes a net decrease in pH for Fe^{2+} oxidation, as can be seen by combining reactions (3) and (7C):

$$Fe^{2+} + 1/4\ O_2 + 5/2\ H_2O ==> Fe^{III}(OH)_3 + 2\ H^+ . \tag{8}$$

Below pH 1, no significant Fe^{3+} hydrolysis occurs, so the oxidation of Fe^{2+} leads to a net loss of acidity by reaction (3) and therefore an increase in pH.

A similar loss of acidity occurs if Fe^{II} is oxidized in the solid phase. When melanterite oxidizes to copiapite, one mole of sulfuric acid is consumed for each mole of copiapite produced according to the reaction (Nordstrom, 1982)

$$5\ Fe^{II}SO_4 \cdot 7H_2O + O_2 + H_2SO_4 ==> Fe^{II}Fe^{III}_4(SO_4)_6(OH)_2 \cdot 20H_2O + 15\ H_2O . \tag{9}$$

Oxidation of melanterite to other ferric sulfate minerals such as coquimbite, voltaite, or rhomboclase also consumes acidity; e.g., for rhomboclase:

$$Fe^{II}SO_4 \cdot 7H_2O + H_2SO_4 + 1/4\ O_2 ==> (H_3O)Fe^{III}(SO_4)_2 \cdot 3H_2O + 7/2\ H_2O . \tag{10}$$

The production of rhomboclase indicates that extensive oxidation of Fe^{II} to Fe^{III} has occurred. Under these circumstances the overall reaction for pyrite oxidation becomes

$$FeS_2 + 9/2\ H_2O + 15/4\ O_2 ==> (H_3O)Fe^{III}(SO_4)_2 \cdot 3H_2O \tag{11}$$

and the acidity is stored as H_3O^+ in the mineral rhomboclase.

The formation of Fe^{III}-sulfate minerals has two effects on the acidity of the mine waters. During oxidation of the iron there is an irreversible loss of acidity, which tends to keep the pH from going much lower. During solidification of the ferric sulfate minerals, especially rhomboclase, some of the remaining acidity is stored in solid form. Fe^{III}-sulfate salts appear to be more abundant than Fe^{II}-sulfates in the areas sampled underground at Iron Mountain, and the most acidic mine water (samples 90WA110A, Table 1) has a high proportion of Fe^{3+}. Because the oxidation of iron from Fe^{II} to Fe^{III} causes an increase in pH at values below 2, other geochemical mechanisms, especially evaporation and pyrite oxidation at saturation with melanterite or other Fe-sulfate salts, must be responsible for the attainment of pH values below zero.

Dissolution and Hydrolysis of Gangue Minerals

The presence of relatively high concentrations of Mg, Si, and Al in the Iron Mountain mine waters (Table 1) indicates that considerable reaction of wall-rock silicates has occurred. With a knowledge of the composition of the minerals likely to have dissolved or precipitated, it is possible using mass balance and thermodynamic mass transfer calculations to quantify the amount of each mineral which must dissolve or precipitate to produce the extremely acidic mine waters. Additional information from this type of calculation is the neutralization potential of the wall rock.

Previous work by Alpers and Nordstrom (1990) established the identity of the principal minerals contributing dissolved constituents to the mine waters in the Richmond mine at Iron Mountain. In that study, eight mine water samples were chosen to represent the range of hydrologic conditions at the site, from high-flow to low-flow. In the present analysis, we use water sample 90WA103 (Table 1), which represents the combined effluent at the five-way intersection shown in Figure 1. Because of an exceptional multi-year drought affecting northern California between January, 1986 and the time of sampling in September, 1990, the conditions represented by data in Table 1 are considered minimum low-flow conditions.

Program BALANCE (Parkhurst et al., 1982) was used to compute the mass transfer between minerals and aqueous solution necessary to account for the observed mine water compositions. Geologic, mineralogic, and electron microprobe data from previous reports (Kinkel et al., 1956; Nordstrom, 1977; Reed, 1984) were used to define the identity and solid solution composition of possible source minerals (for mineral formulas, see Alpers and Nordstrom, 1990). The principal gangue minerals in the altered rhyolite are albite, sericite (white mica), chlorite (green mica), quartz, and calcite. The sulfides pyrite and chalcopyrite were assumed to be stoichiometric FeS_2 and $CuFeS_2$, respectively, whereas electron microprobe data for sphalerite $(Zn_{.933}Fe_{.062}Cu_{.005}S)$ from Reed (1984) were used. The solids melanterite and amorphous silica as well as gases O_2 and CO_2 were also included in the BALANCE model as potential reactants and/or products.

Table 4 displays the results from a BALANCE calculation using as input the mine water composition (90WA103) and the phases listed above. As expected, large amounts of O_2 were consumed during sulfide oxidation; by weight, O_2 makes up about 45 percent of the reactant mass. Of the solid phase reactants consumed to produce the dissolved concentrations in the mine water, by weight about 48 percent are sulfides and 7 percent are gangue (silicate and minor carbonate). In addition to the dissolution of the gangue minerals and sulfides listed above, precipitation of Si- and Fe-bearing phases has clearly occurred. We consider amorphous silica and melanterite to be the most likely secondary phases to have formed containing these elements. The silica concentrations in the mine waters are consistently near to amorphous silica saturation levels; in fact, the temperature sensitivity of amorphous silica solubility led Nordstrom and Potter (1977) to speculate that temperatures within the Richmond Mine workings approach 50°C. Subsequent observations of mine temperatures indicate that this estimate was a good one, confirming that amorphous silica saturation most likely controls aqueous silica concentrations within the Richmond Mine workings.

The choice of melanterite as the secondary Fe-sulfate in the BALANCE model was based in part on the observation of this phase forming as stalactites and stalagmites at the site of sample 90WA109 (Fig. 1). The rate of drip during collection of sample 90WA109 was sufficiently fast and the location of this flow was such that these Fe^{2+}-rich waters were contributing to the portal effluent. In contrast, the drip sampled as 90WA110A was Fe^{3+}-rich (Table 1) and was taken from an area of abundant Fe^{III}-rich salts, which represents a hydrologic "dead end" where the waters tend to oxidize and evaporate.

The solubility of the precipitated minerals limits the aqueous concentrations of Si and Fe. In contrast, there appear to be no solubility constraints on the other major cations in the mine effluent (Mg, Al, Ca, Na, Zn, and Cu).

To test the results of the BALANCE model, mass transfers were calculated using the PHREEQE program (Parkhurst et al., 1980). BALANCE results for sample 90WA103 were used as input to PHREEQE by simulating the dissolution of one reactant mineral at a time, in the order listed in Table 4, followed by precipitation of the product minerals. After the indicated amount of each mineral is dissolved or precipitated, PHREEQE calculates the speciation of the aqueous solution including the pH and the saturation index of the solution with respect to various minerals. The final pH from the PHREEQE simulation together with the values of mineral saturation indices provide a thermodynamic check on the validity of the BALANCE model, which is based entirely on mineral stoichiometry and bulk solution composition.

The pH values calculated by PHREEQE for sample 90WA103 are shown in Figure 4 as a function of reaction progress, expressed as moles of minerals dissolved or precipitated per kg H_2O. Starting with 1 kg of pure water at pH 7.0, the first part of the PHREEQE calculation was to add pyrite and O_2 in the molar proportion 1 to 3.5, causing complete oxidation of S to SO_4 but leaving essentially all dissolved iron as Fe^{2+} as in reaction (4). For sample 90WA103, an O_2 coefficient of 3.5092 was necessary to match the oxygen consumption indicated by the BALANCE computation (Table 4). Pyrite (plus O_2) was added incrementally up to 0.9816 moles (Table 4), resulting in a pH value of 0.50. Calculated pH values are shown in Figure 4 as a function of moles of minerals dissolved and/or precipitated in the PHREEQE simulation. Chalcopyrite and then sphalerite were added, each together with sufficient O_2 to oxidize their S completely (4 and 2 moles O_2 per mole of solid, respectively). Dissolution of these two sulfide minerals did not cause an appreciable change in pH (Fig. 3) in part because the metal to sulfur molar ratio in these phases is 1:1, in contrast with the 1:2 ratio in pyrite (Alpers and Brimhall, 1989). The **PHREEQE** simulation continued with dissolution of calcite, albite, sericite, chlorite, and kaolinite; of these, chlorite caused the largest increase in pH, from a value of 0.57 to 0.66. Precipitation of SiO_2 (amorphous) had no effect on pH. The final step in the PHREEQE simulation is the precipitation of melanterite, which causes a decrease in pH from 0.67 to the final simulated value of 0.46. According to reaction (5), melanterite precipitation should have no direct effect on pH, so this change is caused by the removal of Fe^{2+} and SO_4^{2-} from solution, which liberates H^+ from bisulfate complexes such as HSO_4^- and $FeHSO_4^-$ and therefore causes pH to decrease.

The actual pH of sample 90WA103 was measured at 0.48 ±0.02 in the field using a Sargent-Welch electrode and 0.5 ±0.05 using a Orion Ross electrode (see calibration curve in Fig. 2). Measurements of pH at such low values are subject to considerable uncertainties, including problems with electrode conditioning and junction potentials (Stipp, 1990). Nevertheless, the observed agreement of pH values between the two electrodes was within 0.05 on all samples and usually within 0.02 pH units. Furthermore, the close agreement between measured pH and that calculated by the mass balance/mass transfer modelling gives confidence that the computer simulations afford a reasonable approximation for the mineral dissolution and precipitation reactions actually occurring in the subsurface. Saturation indices from the **PHREEQE** simulation shown in Figure 4 are in close agreement with those computed using the **WATEQ4F** program for the original mine water.

CONCLUSIONS

Five hydrogeochemical factors required for the production of acid mine waters are sulfide minerals, oxygen, water, iron-oxidizing bacteria, and the absence of any strongly neutralizing ground-water or rock mass. Iron Mountain, California, contains optimal conditions for all of these factors and, consequently, produces some of the most acidic mine waters in the world. In this report we have provided the first published documentation of mine waters with pH below zero.

Computer simulations of sulfide oxidation using programs **PHREEQE** (Parkhurst et al., 1980) and PHRQPITZ (Plummer et al., 1988) indicate that oxidation of 1.55 moles of pyrite in one kg of pure water can lead to a pH near 0.0 in water saturated with melanterite ($Fe^{II}SO_4 \cdot 7H_2O$). Continued pyrite oxidation accompanied by precipitation of melanterite or other Fe-sulfates can drive pH below zero. Acidity will be reduced by the dissolution and hydrolysis of gangue minerals and by the oxidation of Fe^{2+} to Fe^{3+} at pH values below 1, where Fe^{3+} hydrolysis is minimal.

Given the relatively high ratio of Fe^{III}/Fe^{II} in efflorescent Fe-sulfate salts (e.g., rhomboclase, voltaite, and coquimbite) found in the mine workings at Iron Mountain, it appears that considerable oxidation of Fe^{II} has occurred in "dead end" stopes, where the most acidic mine waters are found. In addition to the acidity consumed by Fe^{II} oxidation, some acid was also consumed by the hydrolysis of silicate and minor carbonate gangue minerals, accounting for about 11% of the total dissolved solids. Given that Fe^{II} oxidation and gangue mineral hydrolysis have occurred and that these processes tend to raise pH, it seems likely that evaporative processes have contributed significantly to the concentration of H^+ in the extremely acid mine waters at Iron Mountain. Work is in progress to confirm the role of evaporative processes in the evolution of these extremely acid waters using stable isotopes of oxygen and hydrogen.

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Sample number	90WA103	90WA108	90WA109	90WA110A
Water temperature (°C)	34.8	41.8	32.2	42 ±0.5
pH (field)	0.48 ±0.02	-0.35 ±0.05	-0.7 ±0.1	< -1.0
Element[1]		(mg/L)		
Ca	183	424	330	279
Mg	821	1,380	1,450	437
Sr	0.25	0.30	0.49	0.90
Ba	0.068	0.25	0.10	0.20
Na	251	355	939	416
K	261	704	1,170	194
Fe(II)	18,100	50,800	79,700	34,500
Fe(total)	20,300	55,600	86,200	111,000
Al	2,210	4,710	6,680	1,420
Mn	17.1	41.8	42.1	22.9
Zn	2,010	6,150	7,650	23,500
Cd	15.9	43.0	48.3	211
Cu	290	578	2,340	4,760
Cr	0.12	4.5	0.75	0.60
Co	1.3	2.2	15.5	5.3
Ni	0.66	2.8	2.9	3.7
Mo	0.59	1.0	3.7	4.2
Ag	0.16	0.49	0.65	2.4
Pb	3.6	4.3	3.8	11.9
Tl	0.44	0.15	0.15	0.39
Sb	4.0	11.2	15.9	29.0
Se	0.42	2.1	2.1	4.2
As(III)	8.14	27.2	38	32.3
As(total)	56.4	169	154	340
Sn	1.6	6.5	14.7	41
Ti	5.9	8.6	125	1.0
Be	0.026	0.10	0.10	0.20
V	2.9	17.4	10.8	14.9
SO_4	118,000	420,000	360,000	760,000
B	1.5	2.5	2.5	17.3
SiO_2	165	69	34	35

[1] Fe(II) and Fe(total) determinations by Ferrozine method; As(III) and As(total) by hydride generation atomic absorption spectroscopy; SO_4 by ion chromatography; all other elements by inductively coupled plasma spectroscopy.

Table 1. Selected Analytical Data on Groundwater Samples from the Richmond Mine, Iron Mountain, California (modified from Nordstrom and Alpers, written communication, 1990).

MINERAL	FORMULA
Melanterite	$Fe^{II}SO_4 \cdot 7H_2O$
Ferricopiapite and/or	$Fe_4^{III}(SO_4)_5(OH)_2 \cdot 16H_2O$
Copiapite	$Fe^{II}Fe_4^{III}(SO_4)_6(OH)_2 \cdot 20H_2O$
Römerite	$Fe^{II}Fe_2^{III}(SO_4)_4 \cdot 14H_2O$
Kornelite	$Fe_2^{III}(SO_4)_3 \cdot 7H_2O$
Coquimbite	$Fe_2^{III}(SO_4)_3 \cdot 9H_2O$
Rhomboclase	$(H_3O)Fe^{III}(SO_4)_2 \cdot 3H_2O$
Voltaite	$K_2Fe_5^{II}Fe_4^{III}(SO_4)_{12} \cdot 18H_2O$
Gypsum	$CaSO_4 \cdot 2H_2O$
Chalcanthite	$CuSO_4 \cdot 5H_2O$
Halotrichite	$Fe^{II}Al_2(SO_4)_4 \cdot 22H_2O$

Table 2. Efflorescent Sulfate Minerals Identified at Iron Mountain

	IRON MOUNTAIN (this study)	OTHER	REFERENCE
pH	<-1.0, -0.7	0.67	Goleva et al.(1970)
		0.97	Dubrovsky (1986)
Cu	4.8 g/L	46 g/L	Clarke (1916)
Zn	23 g/L	50 g/L	Braeuning (1977)
Cd	211 mg/L	41 mg/L	Lindgren (1928)
Fe	141 g/L	48 g/L	Blowes et al.(1991)
SO_4	790 g/L	209 g/L	Lindgren (1928)
As	340 mg/L	400 mg/L	Goleva (1977)

Table 3. Comparison of Other Extreme Mine Water Compositions With Those From Iron Mountain

	moles/ kg H_2O	g/mole	g/kg H_2O	wt% of total reactants
REACTANTS				
pyrite	.9816	120	117.8	
chalcopyrite	.0051	184	0.9	
sphalerite	.0385	96	3.7	
TOTAL SULFIDES			122.4	48
calcite	.0047	100	0.5	
albite	.0119	263	3.1	
sericite	.0111	389	4.3	
chlorite	.0132	567	7.5	
kaolinite	.0063	258	1.6	
TOTAL GANGUE			17.0	7
O_2 gas	3.5421	32	113.3	45
TOTAL REACTANTS			252.7	100
PRODUCTS				
melanterite	.5759	152[1]	87.5	
silica (amorphous)	.1162	60[1]	7.0	
CO_2 gas	.0047	40	0.2	
TOTAL PRODUCTS			94.7	37
NET TOTAL (REACTANTS-PRODUCTS)			158.0	63

[1] Melanterite and amorphous silica formula weights without waters of hydration; H and O are not included in mass balance.

Table 4. Results of Mass Balance Computation for Water Sample 90WA103 Using the Program BALANCE (Parkhurst et al., 1982).

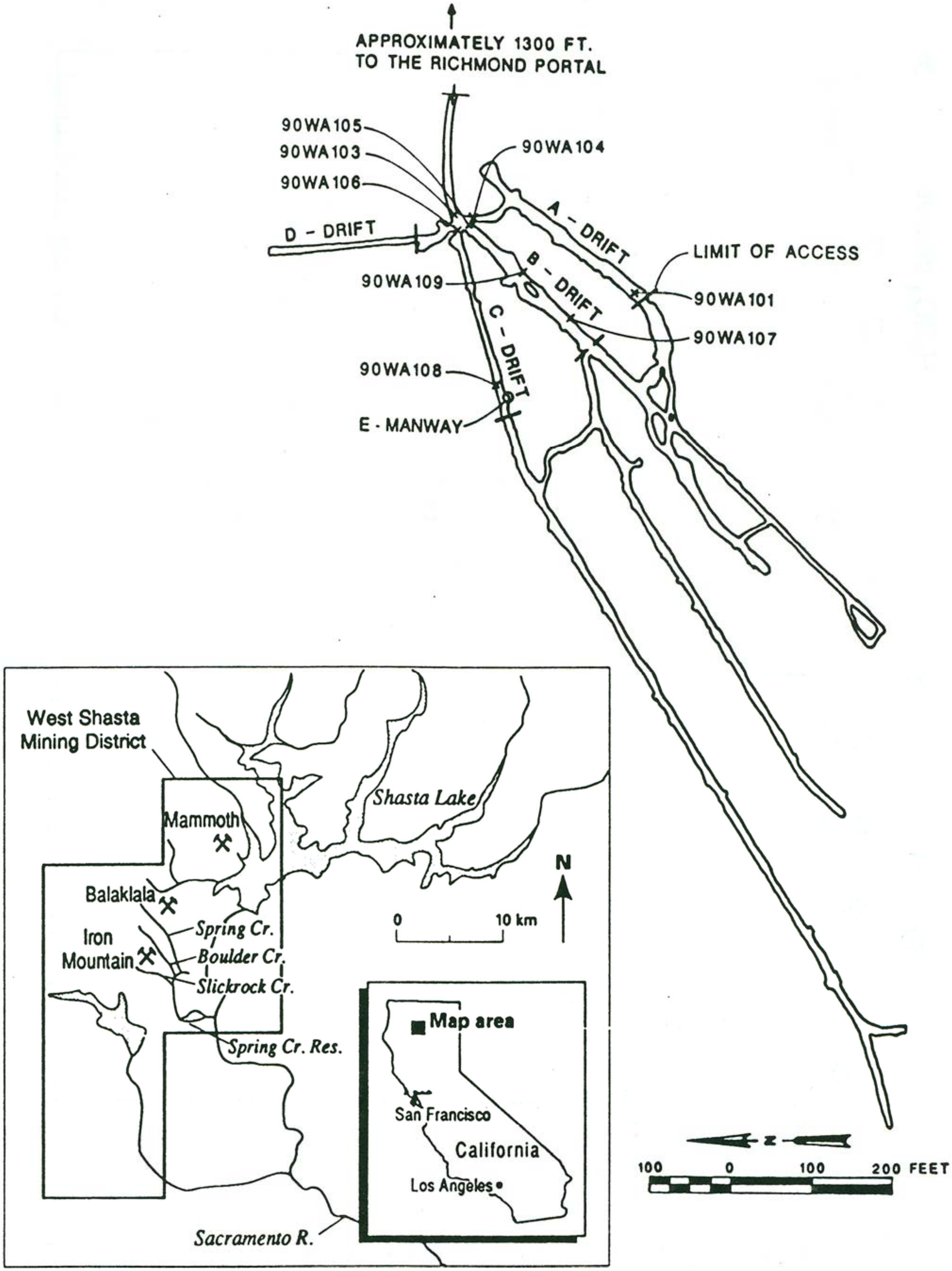

Figure 1. Location map for Iron Mountain deposit and map of 2,600 Level, Richmond mine, showing location of water samples taken in September, 1990.

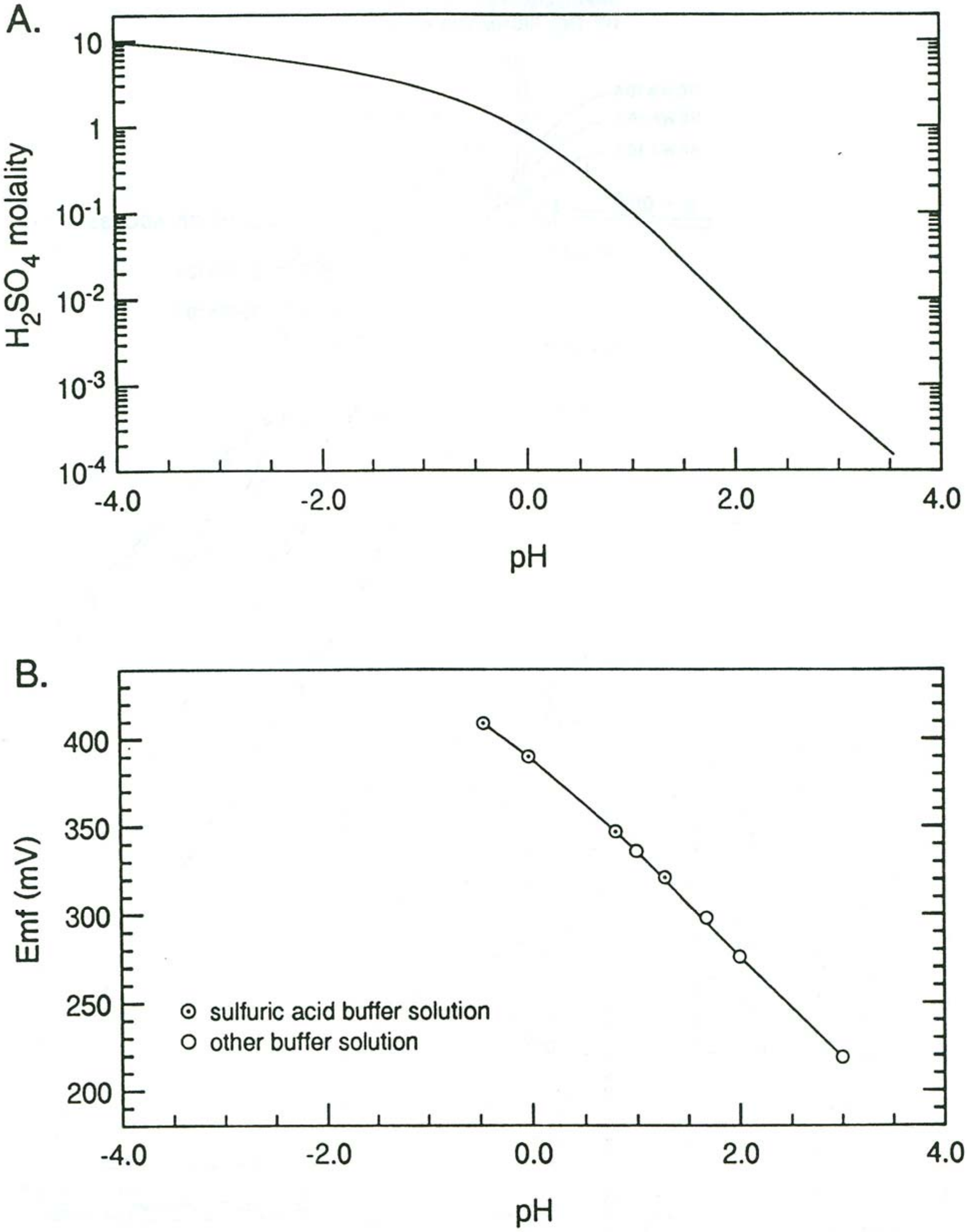

Figure 2. Calibration curves for measurement of extremely low pH. A. pH of pure sulfuric acid solutions at 25°C calculated with the program PHRQPITZ (Plummer et al., 1988). B. Electrode potential (EMF) at 25°C for a Sargent-Welch combination glass membrane electrode against pH taken from curve in A.

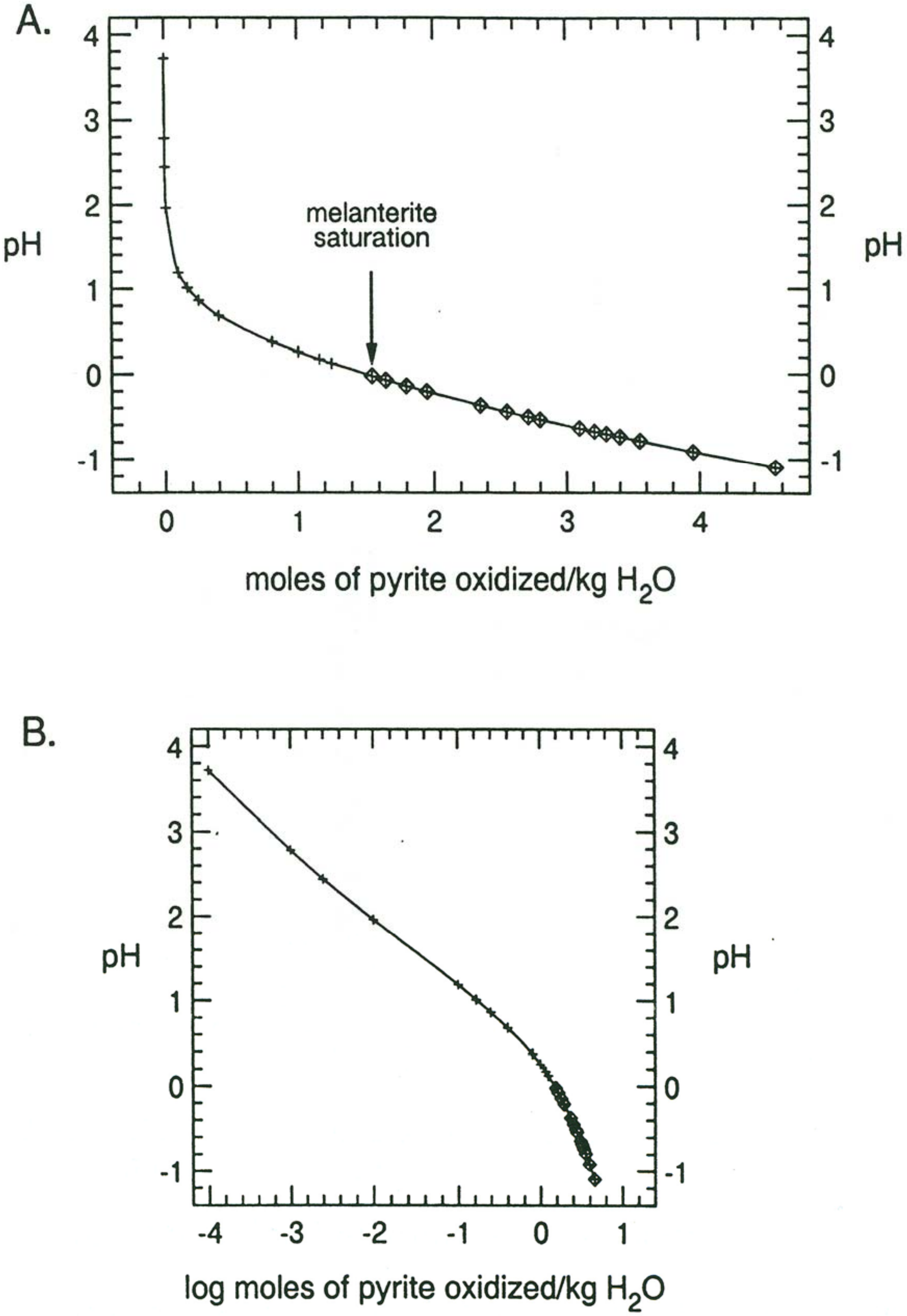

Figure 3. Simulation of pyrite oxidation in pure water according to reaction (4) using the program PHRQPITZ; diamonds indicate calculated points with melanterite precipitation.

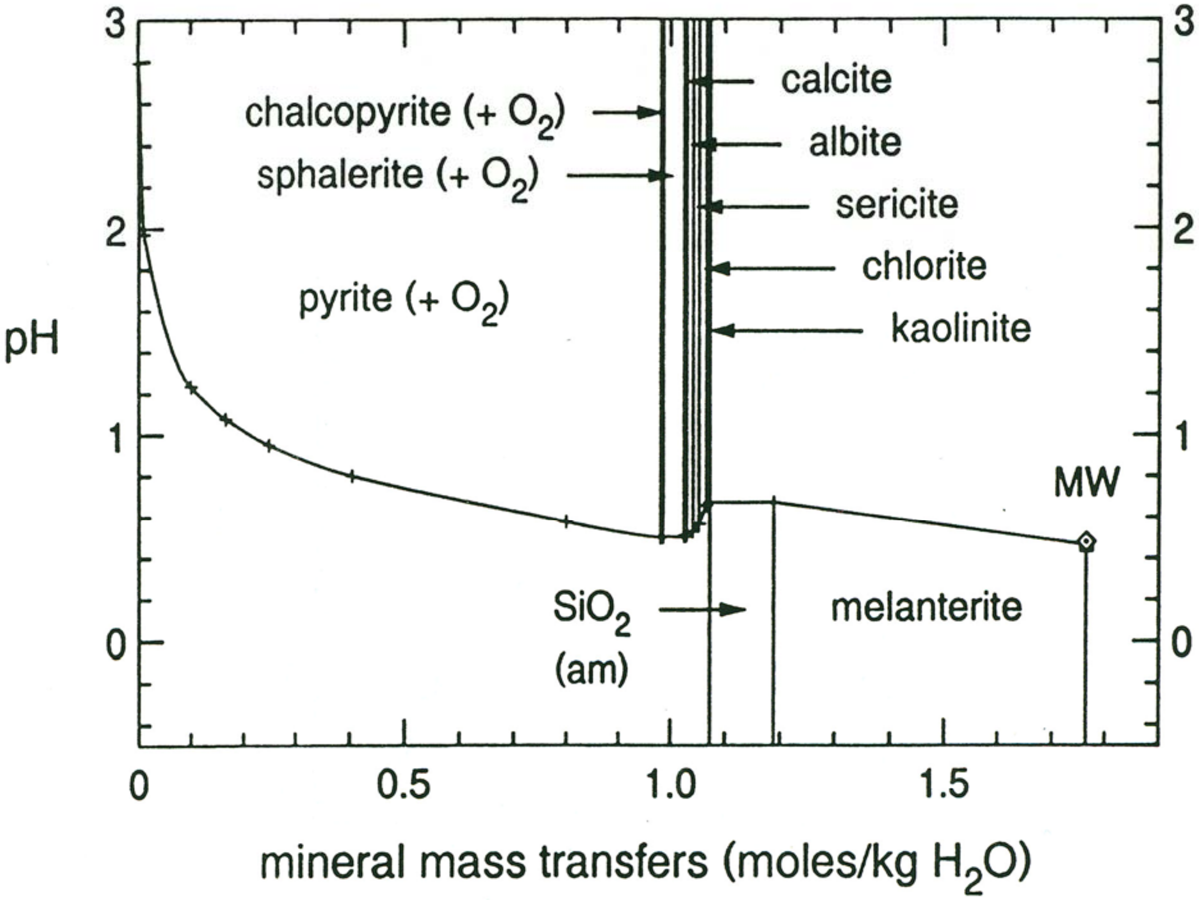

Figure 4. Results of simulation using the program PHREEQE for water sample 90WA103 based on mass transfer coefficients from the program BALANCE (Table 4); final simulated pH = 0.46 (open square); MW = measured pH of mine water = 0.48 (open diamond).