CHAPTER 15. STABLE-ISOTOPE GEOCHEMISTRY OF MINE WATERS AND RELATED SOLIDS

ROBERT R. SEAL, II

U.S. Geological Survey, 954 National Center, Reston, Virginia 20192, U.S.A.

INTRODUCTION

The stable isotopes of hydrogen, carbon, nitrogen, oxygen, and sulfur provide a means of interrogating mine waters and related solids about their history. This history includes both information about the origins of the waters and solids, and about physical, chemical, and biological processes that may have acted upon these waters and solids. The usefulness of the application of stable isotopes to understanding the environmental geochemistry of minesites arises from the fact that the essential components of water are hydrogen and oxygen, and that much of the weathering of mine wastes involves the interaction of sulfide minerals with water and atmospheric oxygen. Thus, the stable isotopes of oxygen, hydrogen, and sulfur provide the most direct record of this interaction.

The usefulness of stable isotopes for understanding a variety of chemical, physical, and biological processes results from the mass differences among the various isotopes of a given element. The mass differences produce the preferential partitioning, or fractionation, of stable isotopes between two or more substances or species. Fractionation is attributable to differences in bonding strength between two or more isotopes in various molecules; in general, heavier isotopes form stronger bonds. For example, the heavier isotopes of oxygen will be preferentially concentrated in a solid, such as quartz, compared to its associated water, because chemical bonds in a solid are stronger. Similarly, water will concentrate the heavier isotopes of oxygen and hydrogen relative to water vapor because the chemical bonds in the liquid are stronger. Likewise, in biologically mediated processes, such as the bacterial reduction of sulfate in aqueous systems, organisms generally can more readily metabolize nutrients enriched in the lighter isotope because the bonds are weaker. For example, the sulfur-isotope composition of the residual sulfate used by sulfate-reducing bacteria will become enriched in the heavier isotopes relative to the sulfur-isotope composition of the hydrogen sulfide produced by the bacteria. Oxygen and hydrogen isotopes in waters can provide insights into water budgets at minesites, and the processes that affect the waters. Evaporation or mixing can be readily discernible by using stable isotopes, and isotopes can also provide information about the residence time of water in waste piles and mine workings. These processes are also important in the geochemical evolution of mine pit lakes.

The importance of stable-isotope techniques to understanding the processes of sulfide oxidation and acid generation in mine waters is readily apparent by considering mass-action relationships that describe the oxidation of pyrite [FeS_2]. In general terms, the various paths of pyrite oxidation require water and oxygen to yield sulfate, dissolved ferrous iron, and acid through a variety of pathways. Stable isotopes offer an independent means of evaluating the roles and relative importance of water and oxygen, and a variety of reaction mechanisms in mine-drainage settings. The stable-isotope geochemistry of acid mine drainage has been summarized Taylor & Wheeler (1994), which was largely based on the pioneering work of Taylor *et al.* (1984a,b). Van Stempvoort & Krouse (1994) reviewed the controls on the oxygen-isotope composition of sulfate, which included the processes relevant to the formation of mine drainage. The hydrogen, oxygen, and sulfur isotopic geochemistry of sulfate minerals from mine-drainage settings, mineral deposits, and other settings as it relates to the environments of their formation has been summarized by Seal *et al.* (2000). Likewise, the low-temperature reduction of dissolved sulfate, typically through processes mediated by bacteria, produces distinctive sulfur- and oxygen-isotope effects (Canfield 2001).

Stable isotopes are also useful for understanding the fate of cyanide that is used in the leaching of gold and silver ores. The fate can include volatilization, precipitation, adsorption, oxidation, biodegradation, and hydrolysis, many of which leave distinct carbon or nitrogen isotopic signatures. Analytical techniques that enable the application of stable isotopes to the study of these processes have been pioneered by Johnson (1996). The stable-isotope effects associated with these processes have been discussed by Rye & Johnson (1997), Johnson *et al.* (1998),and Johnson *et al.* (2000).

The first part of this chapter is designed to provide the reader with a basic understanding of the principles that form the foundations of stable-isotope geochemistry. That part is followed by a brief overview of analytical methods that are used to determine the stable-isotope compositions of a variety of media, and the overview is followed by a discussion of the geochemical processes that determine the stable-isotope characteristics of various solids, waters, and dissolved species. The chapter concludes with various examples of the application of stable isotopes to understanding the geochemical evolution of waters and related solids in mining environments.

FUNDAMENTAL ASPECTS OF STABLE ISOTOPES

Definitions

An isotope of an element is determined by the atomic mass (A) of an atom. The atomic mass is the sum of the number of protons (Z) and neutrons (N). For example, the element oxygen is defined by the presence of 8 protons, but can have 8, 9, or 10 neutrons. These various combinations of 8 protons and either 8, 9, or 10 neutrons are the isotopes of oxygen and are denoted as oxygen-16 ($8Z + 8N = 16$), oxygen-17 ($8Z + 9N = 17$), and oxygen-18 ($8Z + 10N = 18$). The isotopes of oxygen can be abbreviated as ^{16}O, ^{17}O, and ^{18}O, respectively. The terrestrial abundances of the three isotopes of oxygen ($Z = 8$), ^{16}O, ^{17}O, and ^{18}O, are 99.763, 0.0375, and 0.1995 percent, respectively (Garlick 1969). For oxygen, all of these isotopes are stable, meaning that they do not undergo radioactive decay at significant rates. In contrast, carbon ($Z = 6$) has two stable isotopes, ^{12}C and ^{13}C, and one unstable isotope, ^{14}C. The approximate terrestrial abundances of ^{12}C and ^{13}C are 98.89 and 1.11 percent, respectively. Unstable, or radiogenic isotopes undergo radioactive decay. For example, ^{14}C decays to ^{14}N, a stable isotope. The decay of radiogenic isotopes makes many of them useful for dating purposes.

Sulfur ($Z = 16$) has four stable isotopes: ^{32}S, ^{33}S, ^{34}S, and ^{36}S, with approximate terrestrial abundances of 95.02, 0.75, 4.21, and 0.02 percent, respectively (Macnamara & Thode 1950). Nitrogen ($Z = 7$) has two stable isotopes, ^{14}N and ^{15}N, with approximate terrestrial abundances of 99.64 and 0.36 percent (Sweeney *et al.* 1978). Hydrogen ($Z = 1$) has two stable isotopes: ^{1}H, and ^{2}H, with approximate terrestrial abundances of 99.9844, and 0.0156 percent, respectively (Way *et al.* 1950). Deuterium, ^{2}H, is commonly abbreviated as "D". In this context, ^{1}H is further abbreviated merely as "H".

Stable-isotope geochemistry is concerned with the relative partitioning of stable isotopes among substances, rather than their absolute abundances. Differences in the partitioning of stable isotopes, otherwise known as fractionation, result from equilibrium and kinetic effects. Stable-isotope geochemists investigate the variations of a minor isotope of an element relative to a major isotope of the element. For mine-drainage and sulfate minerals, the principal ratios of concern are D/H, $^{18}O/^{16}O$, and $^{34}S/^{32}S$. Studies of cyanide investigate $^{13}C/^{12}C$ and $^{15}N/^{14}N$. Fractionation processes typically cause variations in this ratio in the fifth or sixth decimal places. Because we are concerned with variations in isotopic ratios that are relatively small, the isotopic composition of substances is expressed in the "delta" (δ) notation as permil (or parts per thousand) variation relative to a reference material. The δ-notation for the $^{18}O/^{16}O$ composition of a substance is defined as:

$$\delta^{18}O = \left(\frac{\left(^{18}O/^{16}O\right)_{\text{sample}} - \left(^{18}O/^{16}O\right)_{\text{reference}}}{\left(^{18}O/^{16}O\right)_{\text{reference}}} \right) \times 1000 \tag{1}$$

expressed in units of parts per thousand or permil (‰). For most applications, the agreed-upon reference for oxygen isotopes is Vienna Standard Mean Ocean Water (VSMOW), for which $\delta^{18}O = 0.0$ ‰ by definition. VSMOW is a hypothetical water with oxygen and hydrogen isotopic compositions similar to those of average ocean water. A sample with a positive $\delta^{18}O$VSMOW value, such as +5.0 ‰, is enriched in ^{18}O relative to VSMOW. Conversely, a sample with a negative $\delta^{18}O$VSMOW value, such as –5.0 ‰, is depleted in ^{18}O relative to VSMOW.

Hydrogen isotopes are also defined relative to VSMOW, using the D/H ratio, such that the δD value for VSMOW is 0.0 ‰ by definition. The selection of seawater (VSMOW) as the reference for hydrogen-isotope and most oxygen-isotope applications in geochemistry is useful because the oceans are the foundation of the hydrological cycle.

For nitrogen isotopes, the $\delta^{15}N$ value for the $^{15}N/^{14}N$ ratio is defined relative to atmospheric nitrogen (N_2) with $\delta^{15}N = 0.0$ ‰ by definition. The selection of the atmosphere as the reference for nitrogen-isotope applications in geochemistry is useful because the atmosphere is the main nitrogen reservoir near the surface of Earth. For carbon isotopes, the $\delta^{13}C$ value for the $^{13}C/^{12}C$ ratio is defined relative to Vienna Pee Dee Belemnite (VPDB) with $\delta^{13}C = 0.0$ ‰ by definition.

For sulfur isotopes, the $\delta^{34}S$ value for the $^{34}S/^{32}S$ ratio is defined relative to Vienna Cañon Diablo Troilite (VCDT) with $\delta^{34}S = 0.0$ ‰ by definition. The reference was originally defined by the isotopic composition of troilite (FeS) from the Cañon Diablo iron meteorite. The selection of a meteoritic sulfide mineral as the reference for sulfur is useful because meteoritic sulfide is thought to represent the primordial (bulk) sulfur isotopic composition of Earth (Nielsen *et* *al.* 1991). For sulfur and oxygen, which have more than two stable isotopes, $^{34}S/^{32}S$ and $^{18}O/^{16}O$ are the ratios that are almost exclusively measured in studies of terrestrial systems. These ratios are mainly chosen because they represent the most abundant isotopes of these elements, which facilitate their ease of analysis.

The partitioning of stable isotopes between two substances, A and B, is quantitatively described by a fractionation factor, which is defined as:

$$\alpha_{A-B} = \frac{R_A}{R_B} \quad (2)$$

where R is either D/H, $^{15}N/^{14}N$, $^{18}O/^{16}O$, or $^{34}S/^{32}S$. This equation can be recast in terms of δ values as:

$$\alpha_{A-B} = \frac{1+\dfrac{\delta_A}{1000}}{1+\dfrac{\delta_B}{1000}} = \frac{1000+\delta_A}{1000+\delta_B} \quad (3)$$

Values of α are typically near unity, with variations normally in the second or third decimal place (1.0XX). For example, the $^{18}O/^{16}O$ fractionation between barite and water at 25 °C yields an $\alpha_{\text{barite-water}}$ value of 1.0252. In the literature, fractionation factors may be expressed in a variety of ways including α, 1000lnα, and Δ, among others. The value Δ_{A-B} is defined as:

$$\Delta_{A-B} = \delta_A - \delta_B \quad (4)$$

A convenient mathematical relationship is that 1000ln(1.00X) is approximately equal to X, so that

$$\Delta_{A-B} \approx 1000\ln\alpha \quad (5)$$

Isotopic fractionations may also be defined in terms of an enrichment factor (ε), where

$$\varepsilon_{A-B} = (\alpha_{A-B} - 1) \times 1000 \quad (6)$$

Analytical methods

Several procedures are available to determine the oxygen, nitrogen, carbon, sulfur, and hydrogen isotopic compositions of various sample types. All of the procedures involve conversion of the element of interest (O, N, S, or H) to a gaseous form that is amenable to mass-spectrometric analysis. The amount of sample required varies among laboratories and among mass-spectrometer technologies. Conventional techniques, using dual-inlet mass spectrometers, typically require from several up to tens of milligrams of pure mineral separate for $\delta^{18}O$, $\delta^{34}S$, $\delta^{13}C$, and $\delta^{15}N$, and up to several hundred milligrams of solid for δD. The $\delta^{18}O$ and δD of waters can be determined on samples ranging from several microliters up to several milliliters, depending on the techniques used for gas preparation. Newer techniques, using continuous-flow mass spectrometers interfaced with peripheral devices used to prepare gases, require significantly less sample (Giesemann *et al.* 1994, Kornexl *et al.* 1999). Hydrogen, nitrogen, oxygen, and sulfur isotopic compositions generally can be determined on samples of <1 mg. Typical analytical uncertainties (1σ) for both conventional and newer techniques are ±0.2 ‰ for $\delta^{18}O$, $\delta^{15}N$, $\delta^{13}C$, and $\delta^{34}S$, and ±1 ‰ for δD.

Sulfate for oxygen- and sulfur-isotope analysis from simple sulfate minerals, such as barite [$BaSO_4$], anhydrite [$CaSO_4$], gypsum [$CaSO_4{\cdot}2H_2O$], and many of the transition-metal salts, *e.g.*, melanterite [$FeSO_4{\cdot}7H_2O$], and chalcanthite [$CuSO_4{\cdot}5H_2O$], can be purified by reacting with a 5 mass % Na_2CO_3 solution to leach sulfate, followed by filtration of the solution, acidification (pH ≈ 4), and reprecipitation of the sulfate as $BaSO_4$ by addition of a 10 mass % $BaCl_2{\cdot}2H_2O$ solution. Similarly, aqueous sulfate can be extracted by filtration, acidification, and precipitation by the addition of $BaCl_2{\cdot}2H_2O$ solution. Details of the total isotopic analysis (δD, $\delta^{18}O_{SO_4}$, $\delta^{18}O_{OH}$, $\delta^{34}S$) of alunite- and jarosite-group minerals, including mineral separation techniques, have been described by Wasserman *et al.* (1992). Field and laboratory techniques for the extraction of dissolved sulfate and sulfide from waters for isotopic analysis have been summarized by Carmody *et al.* (1998).

The carbon and nitrogen isotopic compositions of solid and aqueous cyanides can be determined using conventional techniques by combusting solid cyanide salts with cupric oxide and native copper under vacuum to form CO_2 and N_2 gases; the procedures are presented by Johnson (1996). Aqueous cyanide must first be precipitated as a solid by reaction with cupric ferrocyanide.

Reference reservoirs

The isotopic compositions of substances (minerals, waters, gases, biological material) are typically discussed in terms of geochemical reservoirs, which may have served as sources for these constituents. For waters, the main reservoirs in modern surficial environments are seawater and meteoric water. Whereas seawater is only locally important at a few minesites, the oceans do form the basis of the hydrologic cycle, and thus warrant discussion here. Modern seawater has a fairly uniform isotopic composition, with δD and $\delta^{18}O$ ranging from −7 to +5 ‰, and −1.0 to +0.5 ‰, respectively, and with mean values close to the composition of VSMOW (δD = 0.0 ‰; $\delta^{18}O$ = 0.0 ‰) (Epstein & Mayeda 1953, Friedman 1953, Craig & Gordon 1965).

The δD and $\delta^{18}O$ of meteoric waters, those that originate as precipitation, vary systematically and predictably in a linear fashion (Epstein & Mayeda 1953, Friedman 1953, Craig 1961, Dansgaard 1964). The linear variation shown by meteoric waters is known as the "global meteoric water line" (Fig. 1; Craig 1961)

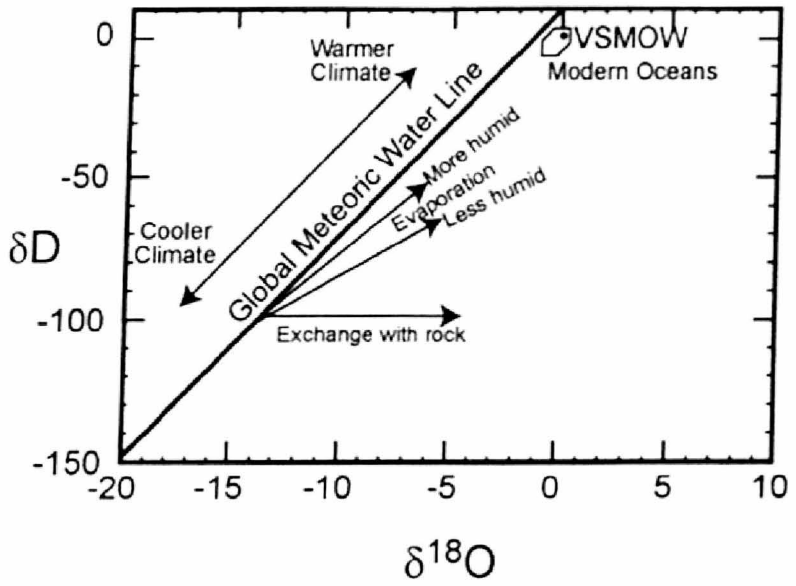

FIG. 1. Plot of δD and $\delta^{18}O$ for various water reservoirs and trends for physical and chemical processes that can alter the isotopic composition of water from values on the Global Meteoric Water Line (Craig 1961, Rozanski *et al.* 1993). VSMOW indicates Vienna Standard Mean Ocean Water. All isotopic values in permil (VSMOW).

and is described by the equation:

$$\delta D = 8\ \delta^{18}O + 10 \qquad (7)$$

Subsequent work, published more than 30 years later (Rozanski *et al.* 1993), has slightly refined this empirical relation:

$$\delta D = 8.13\ \delta^{18}O + 10.8 \qquad (8)$$

The linear relationship is the result of the kinetically controlled evaporation of moisture, dominantly from the oceans, and its subsequent isotopic distillation during condensation and precipitation. This linear relationship is well described as a Rayleigh distillation process, discussed below. Numerous factors determine the position of the isotopic composition of precipitation along the meteoric water line; chief among these are temperature, which is a function of latitude, altitude, and season, followed by the "continent effect" and the "rainout effect". The "continent effect" refers to systematic decrease of the isotopic composition of precipitation as one moves toward the interior of continents. The "rainout effect" refers to the systematic decrease of the isotopic composition of precipitation with increased amounts of precipitation. Both effects are the result of kinetic fractionation associated with distillation. The temperature effect results in a continuous increase in δD and $\delta^{18}O$ of precipitation from cold to warm climates (Fig. 1).

Several common chemical and physical processes can act upon waters to alter their isotopic composition; chief among these processes are evaporation, water–rock interaction, and mixing. Evaporation causes an enrichment in D and ^{18}O in the residual water, thereby producing a positive trend from the starting composition, typically with a slope between 4 and 6 (Fig. 1). Under very saline conditions, however, a different slope and a hook in the $\delta D - \delta^{18}O$ trajectory may be produced (Sofer & Gat 1975). Water–rock interactions in near-surface environments, such as in geothermal areas, generally only alter the oxygen isotopic composition of waters because of high water/rock ratios and the limited amount of hydrogen in rocks. An additional reservoir of oxygen contributes to sulfate derived from the weathering of sulfide minerals. The oxygen in sulfate oxygen can comprise mixtures of oxygen derived from water and oxygen derived from the atmospheric molecular oxygen. Atmospheric oxygen is globally homogeneous, averaging $\delta^{18}O = 23.5 \pm 0.3$ ‰ (Dole *et al.* 1954, Kroopnick & Craig 1972).

For sulfur, the most common reference reservoirs are meteoritic sulfur and seawater (Fig. 2). Meteoritic sulfur, such as Cañon Diablo troilite, provides a convenient reference because it approximates Earth's bulk composition. The iron meteorites have an average sulfur-isotope composition of $\delta^{34}S = 0.2 \pm 0.2$ ‰ (Kaplan & Hulston 1966), which is indistinguishable from that of pristine mid-ocean ridge basalts ($\delta^{34}S = 0.3 \pm 0.5$ ‰; Sakai *et al.* 1984). Geochemical processes, the most notable of which are oxidation and reduction, profoundly fractionate sulfur isotopes away from bulk-Earth values in geological systems (Fig. 2). Oxidation processes may produce species that are enriched in ^{34}S relative to the starting material, whereas reduction is likely to produce species that are depleted in ^{34}S.

Oxidation–reduction reactions involving reduced sulfur from the interior of Earth throughout its history have resulted in a $\delta^{34}S$ of +21.0 ±0.2 ‰ for dissolved sulfate in modern oceans (Rees *et al.* 1978). Because of the volume and importance of the ocean in the global sulfur cycle, this composition is another important reference reservoir from which to evaluate sulfur-isotope variations in geological systems. The $\delta^{34}S$ of sulfate in ancient oceans as recorded by marine evaporite sequences (Claypool *et al.* 1980) has varied from a low of approximately 10 ‰ during Permian and Triassic time to a high of 35 ‰ during Cambrian time.

For nitrogen, the atmosphere probably represents the most important reservoir for processes acting on or near Earth's surface (Fig. 3). For carbon, the same applies for atmospheric CO_2, which is in isotopic equilibrium with the oceans (Fig. 3). Atmospheric CO_2 also is the basis for the biological carbon cycle.

CAUSES OF ISOTOPIC FRACTIONATION

Isotopic fractionation is a result of variations in thermodynamic properties of molecules that are

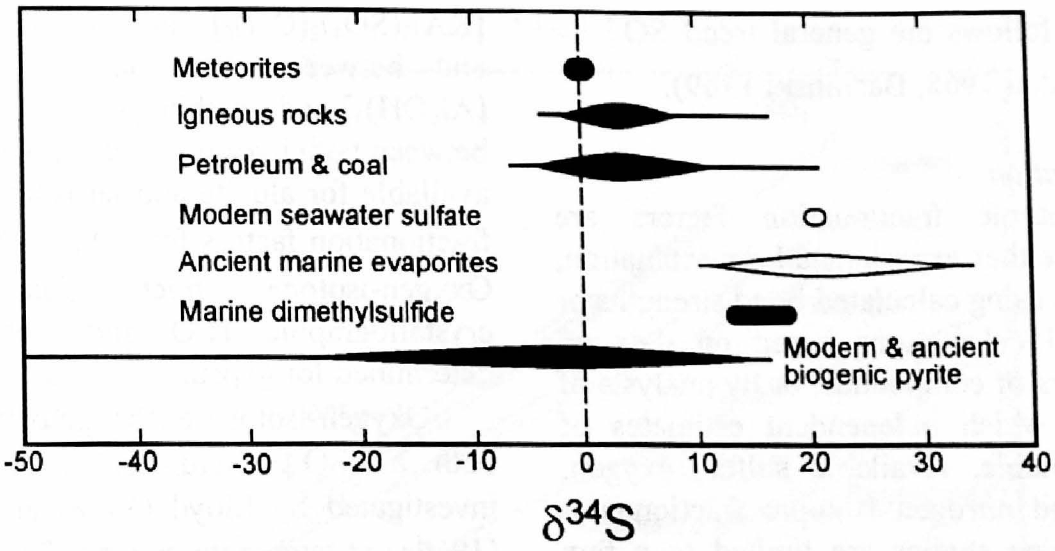

FIG. 2. The δ^{34}S of various geological reservoirs. Modified from Seal *et al.* (2000). All isotopic values are in permil (VCDT).

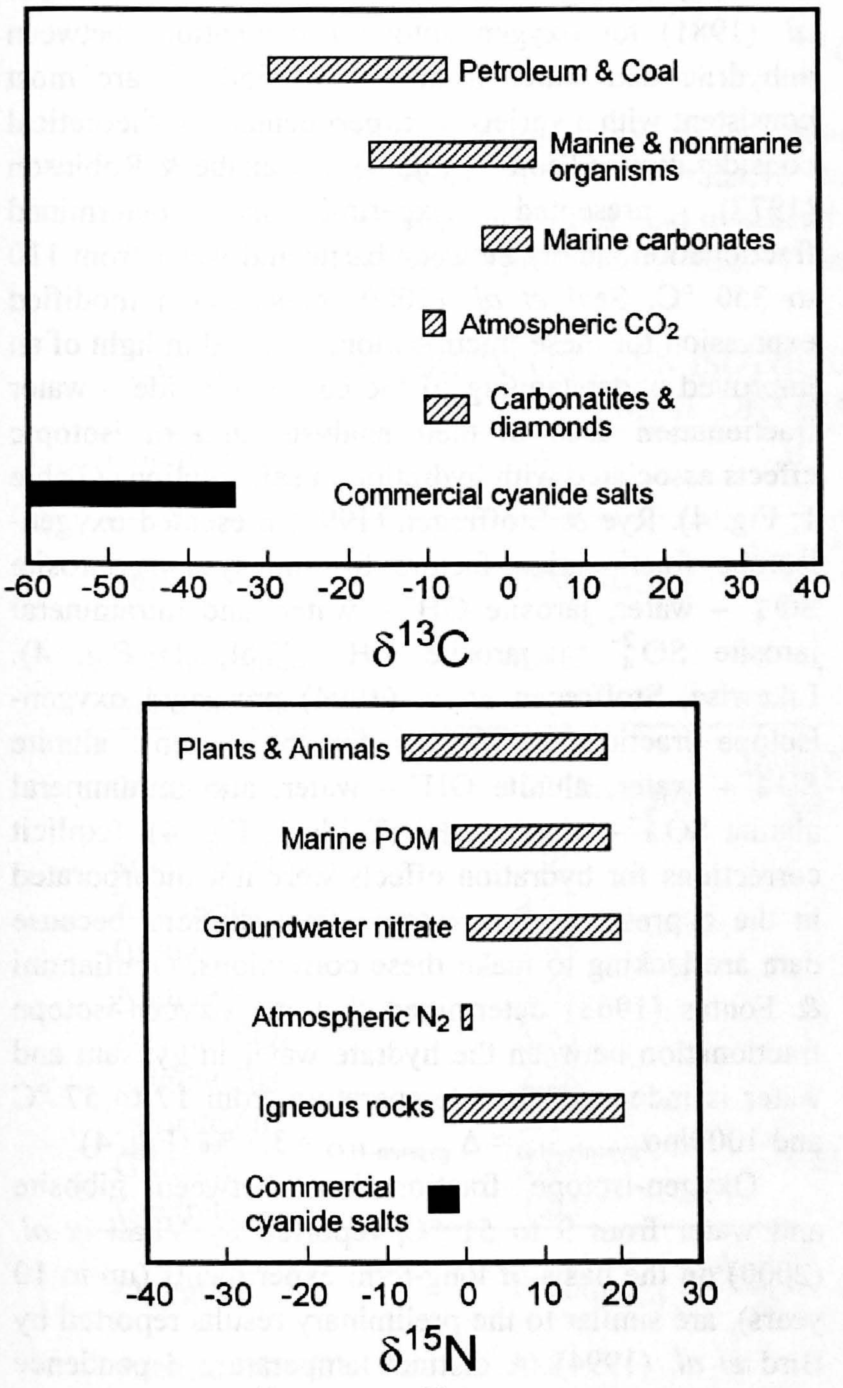

FIG. 3. The δ^{13}C and δ^{15}N of various reservoirs potentially relevant to mine-drainage settings. Modified from Rye & Johnson (1997) using data from Johnson *et al.* (2000). All isotopic values are in permil (VPDB or Air, respectively).

dependent on mass. Isotope fractionation results from equilibrium and kinetically controlled chemical and physical processes. Equilibrium processes include isotopic exchange reactions, which redistribute isotopes among molecules of different substances. Kinetic processes include irreversible chemical reactions and physical processes such as evaporation and diffusion (O'Neil 1986). Equilibrium isotope effects result from the effect of atomic mass on bonding; molecules containing a heavier isotope are more stable than those containing a lighter isotope. Kinetic isotope effects are related to greater translational and vibrational velocities associated with lighter isotopes. It is easier to break bonds between elements with lighter isotopes, for example the ^{32}S–O bond, compared with those with heavier isotopes, such as the ^{34}S–O bond, during the bacterially mediated reduction of dissolved sulfate to sulfide.

The most important factors that influence the magnitude of equilibrium stable-isotope fractionations at surficial conditions are temperature and chemical composition (O'Neil 1986). The temperature dependence of fractionation factors results from the relative effect of temperature on the vibrational energies of two substances. These fractionations are generally described well by equations of the form:

$$1000\ln\alpha = \frac{A}{T^2} + \frac{B}{T} + C \qquad (9)$$

where *A*, *B*, and *C* are empirically determined constants.

The dependence of isotopic fractionation on chemical composition includes such compositional variables as oxidation state, ionic charge, atomic mass, and the electronic configuration of the isotopic elements and the elements to which they are bound (O'Neil 1986). For sulfur-bearing systems, the effect of the oxidation state of sulfur is especially important. The higher oxidation states of sulfur are enriched in the heavier isotopes relative to lower oxidation states such that ^{34}S enrichment follows the general trend SO_4^{2-} > SO_3^{2-} > S_x^0 > S^{2-} (Sakai 1968, Bachinski 1969).

Equilibrium fractionation

Equilibrium isotopic fractionation factors are typically derived by either experimental determination, theoretical estimation using calculated bond strengths or statistical mechanical calculations based on data on vibrational frequencies of compounds, or by analysis of natural samples for which independent estimates of temperature are available. Available sulfur, oxygen, hydrogen, carbon, and nitrogen isotopic fractionation factors relevant to mine studies are limited to a few mineral and aqueous species. In many cases, fractionation factors at ambient temperatures have been derived from the extrapolation of high-temperature studies. This chapter provides a summary of the available fractionation data relevant to environmental studies at mines. A broader critical evaluation of fractionation factors associated with sulfate minerals has been presented by Seal *et al.* (2000).

Data for the sulfur isotopic fractionation of sulfate minerals that typically occur at minesites are limited. The gypsum-dissolved sulfate system has been investigated by Thode & Monster (1965), and the barite-dissolved sulfate system has been investigated by Kusakabe & Robinson (1977). Both studies observed limited sulfur-isotope fractionation between the mineral and the solution. At ambient temperature, Thode & Monster (1965) determined a sulfur-isotope fractionation between gypsum and dissolved sulfate of $\Delta_{\text{gypsum-sulfate}} = \delta^{34}S_{\text{gypsum}} - \delta^{34}S_{\text{sulfate}} = +1.65$ ‰. At temperatures between 110 and 350 °C, Kusakabe & Robinson (1977) observed no sulfur-isotope fractionation between barite and dissolved sulfate (*i.e.*, $\Delta_{\text{barite-sulfate}} = 0$ ‰). These results are consistent with the predictions by Sakai (1968) from statistical mechanics. Sakai (1968) concluded that the sulfur-isotope fractionation between a sulfate mineral and aqueous sulfate should be small. A major advantage of the small fractionation between sulfate minerals and aqueous sulfate is that the measured isotopic composition of the mineral approximates the isotopic composition of the parent fluid. In mine-drainage settings, sulfur-isotope fractionation between sulfate and sulfide is dominated by kinetic processes, as discussed below. Nevertheless, the estimated equilibrium sulfur-isotope fractionation between sulfate and H_2S ($1000\ln\alpha SO_4\text{–}H_2S$) is a useful reference. Extrapolation of the experimentally derived high-temperature expression of Ohmoto & Lasaga (1982) yields a value of ~73 ‰ at 25 °C.

Data are available for oxygen-isotope fractionation between water and aqueous sulfate (SO_4^{2-} and HSO_4^-), between water and the sulfates anhydrite, barite, alunite [$KAl_3(SO_4)_2(OH)_6$], and jarosite [$KFe_3(SO_4)_2(OH)_6$], and between water and the hydroxides gibbsite [$Al(OH)_3$] and goethite [$FeOOH$]. Fractionation factors between both hydroxyl and sulfate oxygen and water are available for alunite and jarosite; thus, the intramineral fractionation factors for $SO_4^{2-} - OH^-$ are also available. Oxygen-isotope fractionation factors between crystallographic H_2O and water have also been determined for gypsum.

Oxygen-isotope exchange between aqueous sulfate, both as SO_4^{2-} and HSO_4^-, and water has been investigated by Lloyd (1968) and Mizutani & Rafter (1969a) at temperatures from 70 to 350 °C; Seal *et al.* (2000) combined both data sets to produce the expression presented in Table 1 and shown in Figure 4. Seal *et al.* (2000) concluded that the results of Chiba *et al.* (1981) for oxygen-isotope fractionations between anhydrite and water from 100 to 550 °C are most consistent with a variety of experimental and theoretical considerations (Table 1; Fig. 4). Kusakabe & Robinson (1977) presented experimentally determined fractionation factors between barite and water from 110 to 350 °C. Seal *et al.* (2000) presented a modified expression for these fractionations, revised in light of an improved understanding of the carbon-dioxide – water fractionation used in their analysis, and of isotopic effects associated with hydration in salt solutions (Table 1; Fig. 4). Rye & Stoffregen (1995) presented oxygen-isotope fractionation factors for the systems jarosite SO_4^{2-} – water, jarosite OH^- – water, and intramineral jarosite SO_4^{2-} – jarosite OH^- (Table 1; Fig. 4). Likewise, Stoffregen *et al.* (1994) presented oxygen-isotope fractionation factors for the systems alunite SO_4^{2-} – water, alunite OH^- – water, and intramineral alunite SO_4^{2-} – alunite OH^- (Table 1; Fig. 4). Explicit corrections for hydration effects were not incorporated in the expressions for isotopic fractionations because data are lacking to make these corrections. Gonfiantini & Fontes (1963) determined that the oxygen-isotope fractionation between the hydrate water in gypsum and water is independent of temperature from 17 to 57 °C and $1000\ln\alpha_{\text{gypsum-H}_2\text{O}} \approx \Delta_{\text{gypsum-H}_2\text{O}} = 3.7$ ‰ (Fig. 4).

Oxygen-isotope fractionations between gibbsite and water from 9 to 51 °C, reported by Vitali *et al.* (2000) on the basis of long-term experiments (up to 10 years), are similar to the preliminary results reported by Bird *et al.* (1994). A distinct temperature dependence was observed, with fractionation increasing at lower temperatures (Table 1; Fig. 4). Oxygen-isotope fractionations between goethite and related ferric hydroxides and oxides, such as hematite and akaganéite, have been investigated by several workers. The results

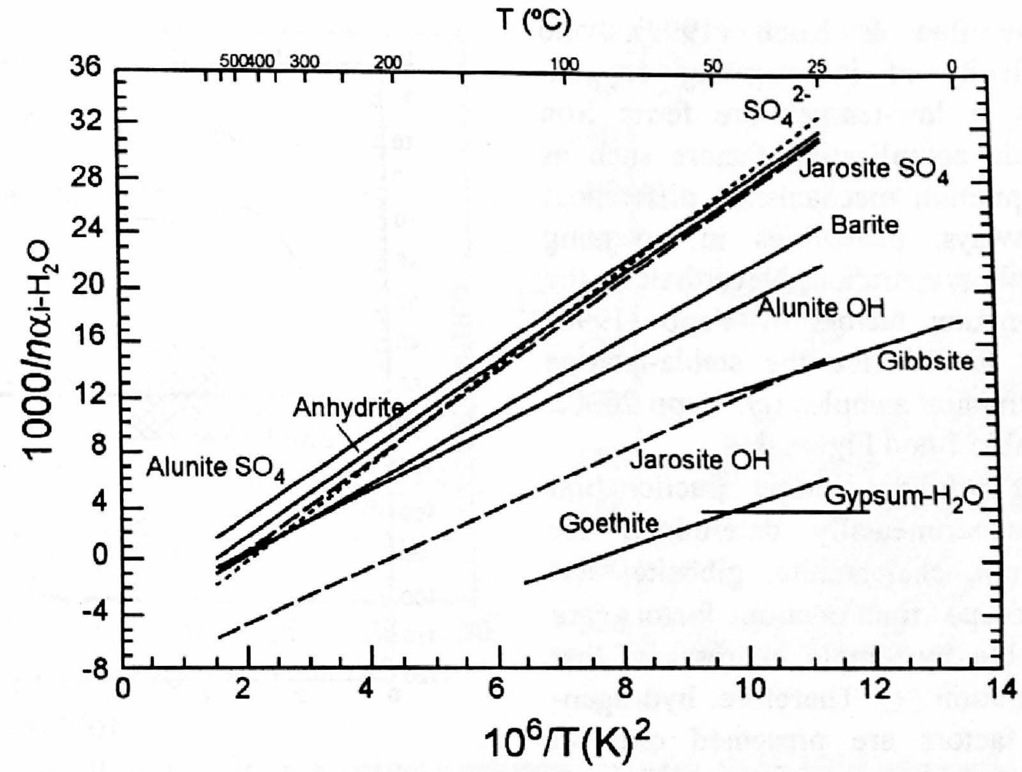

FIG. 4. Compilation of recommended equilibrium oxygen-isotope fractionation factors relative to H_2O for various compounds, mineralogical sites, and dissolved sulfate. Equations describing these curves are presented in Table 1. See text for sources of data.

TABLE 1. EQUILIBRIUM OXYGEN ISOTOPIC FRACTIONATION FACTORS RELEVANT TO MINE-DRAINAGE SETTINGS

Compound or component, i(-j)	A	B	C	T (°C) range*	Data sources
Sulfur	$1000\ln\alpha_{i-H_2S} = \frac{A\times10^6}{T^2} + \frac{B\times10^3}{T} + C$ (T in K)				
Sulfate minerals and aqueous sulfate	6.463		0.56	200–400	1
Oxygen	$1000\ln\alpha_{i-H_2O} = \frac{A\times10^6}{T^2} + \frac{B\times10^3}{T} + C$ (T in K)				
SO_4^{2-} (HSO_4^-)	3.26		–5.81	70–350	4, 5, 6
Anhydrite	3.21		–4.72	100–550	7
Barite	2.65		–4.97	110–350	4, 8
Alunite SO_4	3.09		–2.94	250–450	2
Jarosite SO_4	3.53		–6.91	100–250	3
Alunite OH	2.28		–3.9	250–450	2
Jarosite OH	2.1		–8.77	100–250	3
Gibbsite	2.04	–3.61	3.65	0–60	9
Goethite	1.63		–12.3	25–120	10
Oxygen	$1000\ln\alpha_{i-j} = \frac{A\times10^6}{T^2} + \frac{B\times10^3}{T} + C$ (T in K)				
Alunite SO_4–OH	0.8		0.96	250–450	2
Jarosite SO_4–OH	1.43		1.86	100–250	3

*Temperature range refers to the experimental temperature range; note that fractionation factors may extrapolate significantly beyond these ranges (see text). *Data sources:* 1 Ohmoto & Lasaga (1982); 2 Stoffregen *et al.* (1994); 3 Rye & Stoffregen (1995); 4 Seal *et al.* (2000); 5 Lloyd (1968); 6 Mizutani & Rafter (1969a); 7 Chiba *et al.* (1981); 8 Kusakabe & Robinson (1977); 9 Vitali *et al.* (2000); 10 Yapp (1990) were summarized by Bao & Koch (1999), who highlighted the difficulty of investigating oxygen-isotope fractionations in low-temperature ferric iron systems, which include complicating factors such as uncertainties in precipitation mechanisms, differences among reaction pathways, difficulties in reversing experiments, and sample preparation. Nevertheless, the goethite–water fractionation factors of Yapp (1990) seem to be the best to describe the stable-isotope variations observed in natural samples (*cf.* Yapp 2000), and are presented in Table 1 and Figure 4.

Mineral – water hydrogen-isotope fractionation factors have been experimentally determined for jarosite, alunite, gypsum, chalcanthite, gibbsite, and goethite. Hydrogen-isotope fractionation factors are generally not describable by simple expressions that follow the form of Equation (9). Therefore, hydrogen-isotope fractionation factors are presented only in Figure 5, without accompanying equations. Rye & Stoffregen (1995) experimentally measured hydrogen-isotope fractionation factors between jarosite and aqueous solutions and obtained $1000\ln\alpha_{jarosite-H_2O}$ ($\approx \Delta_{jarosite-H_2O}$) values that were generally independent of temperature from 150 to 250 °C and averaged –50 ‰. Alpers *et al.* (1988) proposed a jarosite–water fractionation of –59 ‰ at ambient temperature on the basis of data from a jarosite that was precipitated from mine water in the laboratory. In experiments by Stoffregen *et al.* (1994), hydrogen-isotope fractionation factors between alunite and aqueous solutions gave $1000\ln\alpha_{alunite-H_2O}$ values that ranged from –19 at 450 °C to –6 at 250 °C. Bird *et al.* (1989) proposed an alunite–water fractionation of 4 ‰ at ambient temperatures on the basis of data from natural samples.

Fontes & Gonfiantini (1967) investigated hydrogen-isotope fractionation between gypsum and water in solutions saturated with gypsum; values for $1000\ln\alpha_{gypsum-H_2O}$ were independent of temperature from 17 to 57 °C and averaged –15 ‰ (Fig. 5). Heinzinger (1969) measured the hydrogen-isotope fractionations of $1000\ln\alpha_{chalcanthite-H_2O}$ ($\approx \Delta_{chalcanthite-H_2O}$) = –22.7 ‰ between chalcanthite and a saturated aqueous solution at ambient temperature. Data are lacking to evaluate the effect of Cu-salt hydration on hydrogen-isotope fractionation (Seal *et al.* 2000). In addition, Heinzinger (1969) determined that there is a 57 ‰ intramineral fractionation in chalcanthite between one hydrogen-bonded water molecule and the four water molecules bonded to Cu^{2+}.

Vitali *et al.* (2001) investigated hydrogen-isotope fractionations between gibbsite and water, using the same samples as Vitali *et al.* (2000) had employed to determine oxygen-isotope fractionation. Vitali *et al.* (2001) concluded that the gibbsite–water hydrogen-isotope fractionation was independent of temperature from 9 to 51 °C, and that $1000\ln\alpha_{gibbsite-H_2O}$ averages –5 ‰ (Fig. 5). Yapp & Pedley (1985) and Yapp (1987) investigated hydrogen-isotope fractionation between goethite and water and also found that the fractionation factors were independent of temperature over the range 25 to 145 °C; they determined that $1000\ln\alpha_{goethite-H_2O}$ averages –100 ‰ (Fig. 5).

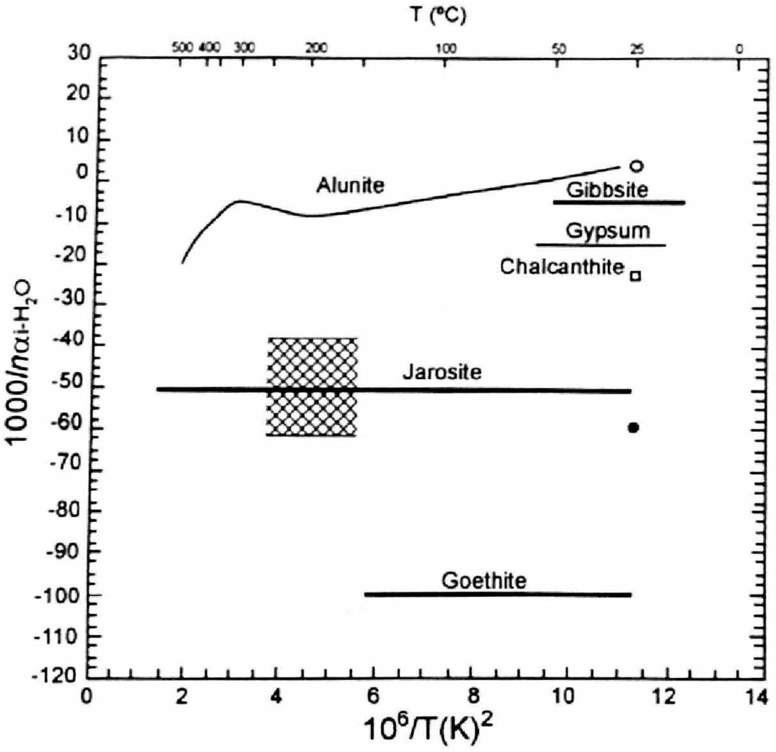

FIG. 5. Compilation of recommended equilibrium hydrogen-isotope fractionation factors relative to H_2O for various compounds. See text for sources of data.

Despite the importance of secondary precipitates in mine-drainage settings, studies of their stable-isotope geochemistry are limited. Rye *et al.* (1992) investigated samples of supergene alunite from a variety of mineral deposits, and determined that the combination of their $\delta^{34}S$, δD, $\delta^{18}OSO_4$, and $\delta^{18}OOH$ values were diagnostic of the environments of formation (Fig. 6). Rye & Alpers (1997) reached a similar conclusion for supergene jarosite. Haubrich & Tichomirowa (2002) reported $\delta^{34}S$ and $\delta^{18}O_{SO4}$ values for jarosite from the Freiberg mining district, Germany, which are consistent with the model outlined by Rye & Alpers (1997). The hydrogen-isotope composition of jarosite, alunite, gibbsite, and goethite should be especially useful at abandoned mines for understanding long-term variations in isotopically distinct water sources because the mineral–water hydrogen-isotope fractionations of these phases are independent of temperature.

General processes

Rayleigh distillation describes isotopic variations associated with continual depletion of a finite source or

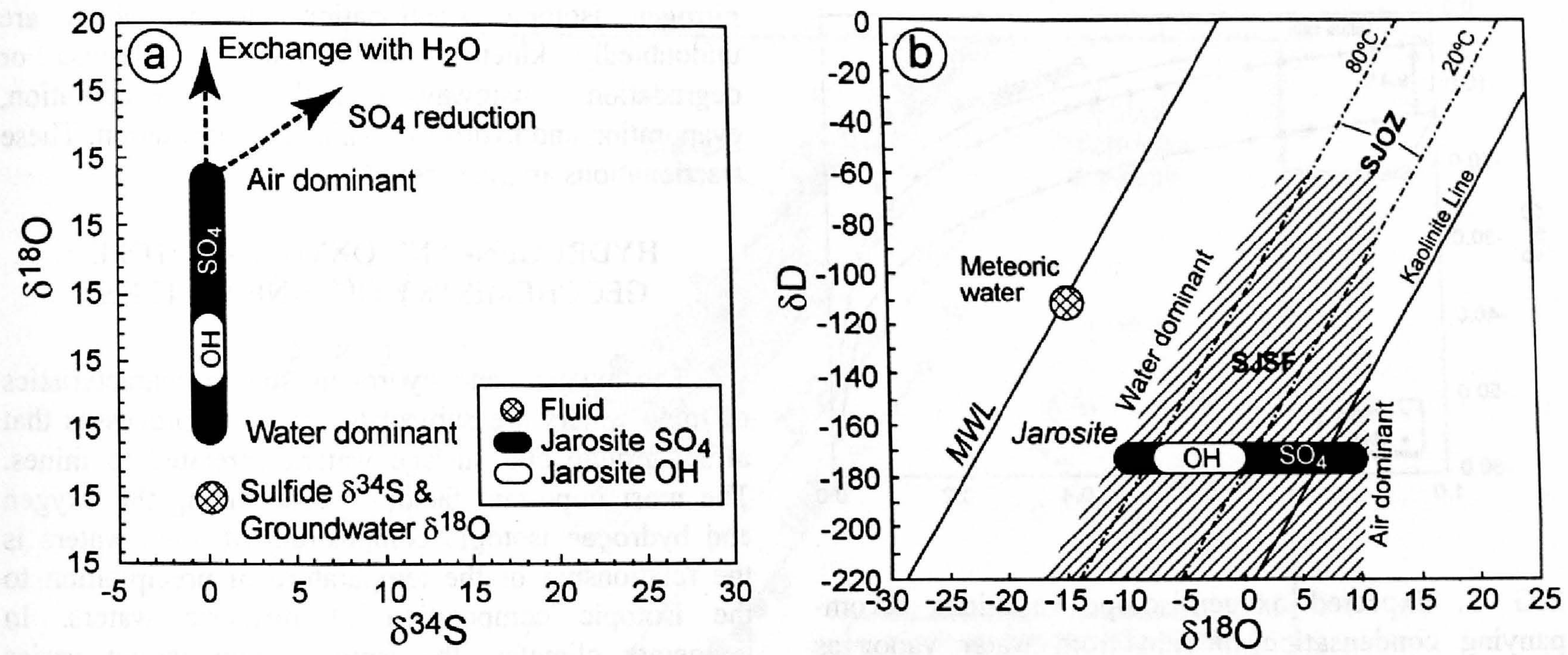

FIG. 6. Isotopic variations of jarosite from supergene environments for given fluid compositions. Modified from Rye & Alpers (1997). SJSF indicates the Supergene Jarosite Sulfate Field and SJOZ indicates the Supergene Jarosite OH Zone. These fields represent the likely ranges of values expected for natural samples for the two oxygen-bearing crystallographic sites in jarosite. Alunite displays similar isotopic variations (Rye *et al.* 1992). The meteoric water line (MWL) and the kaolinite line are shown for reference. (**a**) Oxygen and sulfur isotopic variations expected for supergene jarosites; (**b**) hydrogen and oxygen isotopic variations expected for supergene jarosite. All isotopic values in permil (VSMOW or VCDT).

the accumulation of a sink. For example, the sources and sinks may be dissolved sulfate remaining in solution (the source), which produces reduced sulfur, such as in pyrite (the sink); similarly, water vapor (the source) may be depleted during precipitation events (the sink). Rayleigh distillation describes both equilibrium and kinetically controlled processes equally well through the equation:

$$R = R_o f^{(\alpha-1)} \qquad (10)$$

where R_o is the initial isotopic ratio, R is the isotopic ratio when a fraction (f) of the starting amount remains, and α is the fractionation factor, either equilibrium or kinetic. This equation can be recast in the δ notation for oxygen isotopes as

$$\delta^{18}O = (\delta^{18}O_o + 1000)f^{(\alpha-1)} - 1000 \qquad (11)$$

The oxygen-isotope variations associated with the condensation of precipitation from the atmosphere can be modelled using Equation (11). If $\alpha_{L-V} = 1.0094$ at 25 °C (Majzoub 1971) and $\delta^{18}O_o = -13.0$ ‰ for the vapor, which is the average value obtained over oceans (Craig & Gordon 1965), then rain condensed from water vapor will preferentially remove ^{16}O and the first precipitation will have $\delta^{18}O \approx -3.7$ ‰. The preferential removal of ^{16}O will cause the $\delta^{18}O$ of the residual vapor to decrease, which in turn will lead to a decrease in the $\delta^{18}O$ of subsequent rain (Fig. 7). Similar relationships apply to hydrogen isotopes, for which $\alpha_{L-V} = 1.079$ at 25 °C (Majzoub 1971) and $\delta D_o = -94.0$ ‰ for the vapor, the average value found over oceans (Craig & Gordon 1965).

Mixing is another important process that can cause isotopic variations, and it can be modelled on the basis of simple mass-balance equations such as:

$$\delta_{\text{mixture}} = X_A\delta_A + X_B\delta_B \qquad (12)$$

where δ_{mixture} is the resulting isotopic composition of the mixture, δ_A and δ_B are the isotopic compositions of components A and B, and X_A and X_B are the mole fractions of components A and B.

Kinetic fractionations and processes

Variations in the stable isotopic composition of mine waters and wastes can result from a variety of kinetically controlled, reversible processes, such as isotopic exchange, and from irreversible processes, such as evaporation, sulfide and cyanide oxidation, and sulfate reduction. Irreversible processes are discussed separately below. Ohmoto & Lasaga (1982) determined that sulfur-isotope exchange rates between dissolved SO_4^{2-} and H_2S at elevated temperatures decrease proportionally with increasing pH at pH <3; from pH ≈ 4 to 7, the rates remain fairly constant; and at pH >7, the rate also decreases proportionally with increasing pH. In all cases, the rates at ambient temperatures are prohibitively slow; thus, equilibrium in mine-drainage

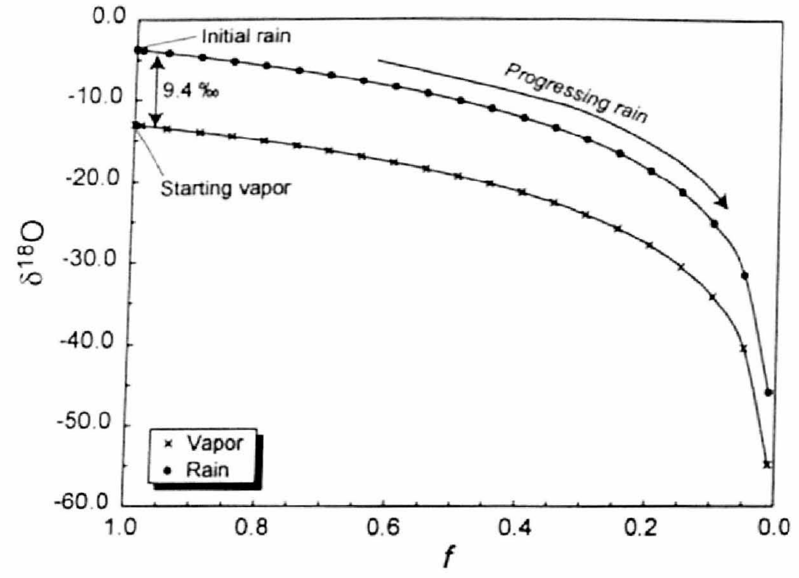

FIG. 7. Expected oxygen-isotope variations accompanying condensation of rain from water vapor as described by Rayleigh processes; "*f*" is the reaction progress variable, which is 1.0 before precipitation starts. The equilibrium fractionation between water and water vapor at 25 °C is 9.4 ‰, and it remains constant throughout the process if temperature remains constant. All isotopic values in permil (VSMOW).

settings where H_2S is present is not likely to have an effect on the sulfur isotopic composition of aqueous sulfate. Indeed, even in higher temperature low-pH hydrothermal systems, sulfur-isotope exchange between aqueous sulfate and H_2S may occur, but equilibrium is seldom observed (Ebert & Rye 1997).

The rate of oxygen-isotope exchange between dissolved sulfate and water was investigated by Hoering & Kennedy (1957) from 10 to 100 °C, by Lloyd (1968) from 25 to 448 °C, and by Chiba & Sakai (1985) from 100 to 300 °C. Seal *et al.* (2000) concluded that the studies of Hoering & Kennedy (1957) and Chiba & Sakai (1985) agreed with one another, and that the results of Lloyd (1968) were distinctly different. On the basis of the similarity of the results of Hoering & Kennedy (1957) and Chiba & Sakai (1985), their results can be used to fit expressions for the variation of the rate constants with pH at 25 and 100 °C. These expressions can then be used to interpolate rate constants between these temperatures, assuming that the variations in rate constants are proportional to inverse temperature ($1/T$). The results of these calculations are shown in Figure 8 as the logarithm of the half-life of the exchange reaction as a function of pH. These results indicate that the rates increase as both a function of temperature and pH. The significance of these results to the stable-isotope geochemistry of mine drainage is discussed below.

Rye & Johnson (1997) reported carbon and nitrogen isotopic fractionation factors, which are undoubtedly kinetic, for various cyanide-loss or degradation pathways, including evaporation, evaporation and hydrolysis(?), and complexation. These fractionations are discussed below.

HYDROGEN- AND OXYGEN-ISOTOPE GEOCHEMISTRY OF MINE WATERS

The oxygen- and hydrogen-isotope characteristics of mine waters are subject to the same processes that affect ground and surface waters unrelated to mines. The most important factor in determining the oxygen and hydrogen isotopic composition of mine waters is the relationship of the temperature of precipitation to the isotopic composition of meteoric waters. In temperate climates, the isotopic composition varies systematically with the seasons. On an annual basis, the lowest values of δD and $\delta^{18}O$ are generally associated with precipitation during the winter (cold season), and highest values are associated with precipitation during the summer (warm season), which is well illustrated by monthly composite samples from Ottawa (Fig. 9). In contrast, in tropical regions, such as the island of Barbados, the isotopic composition of precipitation is fairly constant, reflecting limited seasonal variations of temperature (Fig. 9).

Evaporation is another important process that can affect surface-water isotopic compositions. This effect has been modelled as a combination of equilibrium and disequilibrium effects (Craig & Gordon 1965). Evaporation produces a positive trend in terms of δD and $\delta^{18}O$ of the residual water away from the meteoric water line, with the slope ($\Delta\delta D/\Delta\,\delta^{18}O$) of the trend generally between 4 and 6 (Fig. 1). The slope is a function of the relative humidity accompanying evaporation. Higher slopes are associated with more humid conditions, whereas lower slopes are associated with less humid conditions. Thus, δD and $\delta^{18}O$ values of mine waters away from the meteoric water line at higher values than those of the local meteoric water serve to document environments in which evaporative concentration may have played an important role in the geochemical evolution of the drainage. Examples are presented below.

Lakes, including pit lakes, are subject to a variety of limnological processes that may affect their isotopic compositions. Lakes have complex water budgets that include inputs from precipitation, surface runoff, and groundwaters. The McLaughlin pit lake in California also includes input from geothermal waters, because the mine is located in an active geothermal area (Rytuba *et al.* 2000). Water outputs may include surface discharge, groundwater outflow, and evaporation. The isotopic and

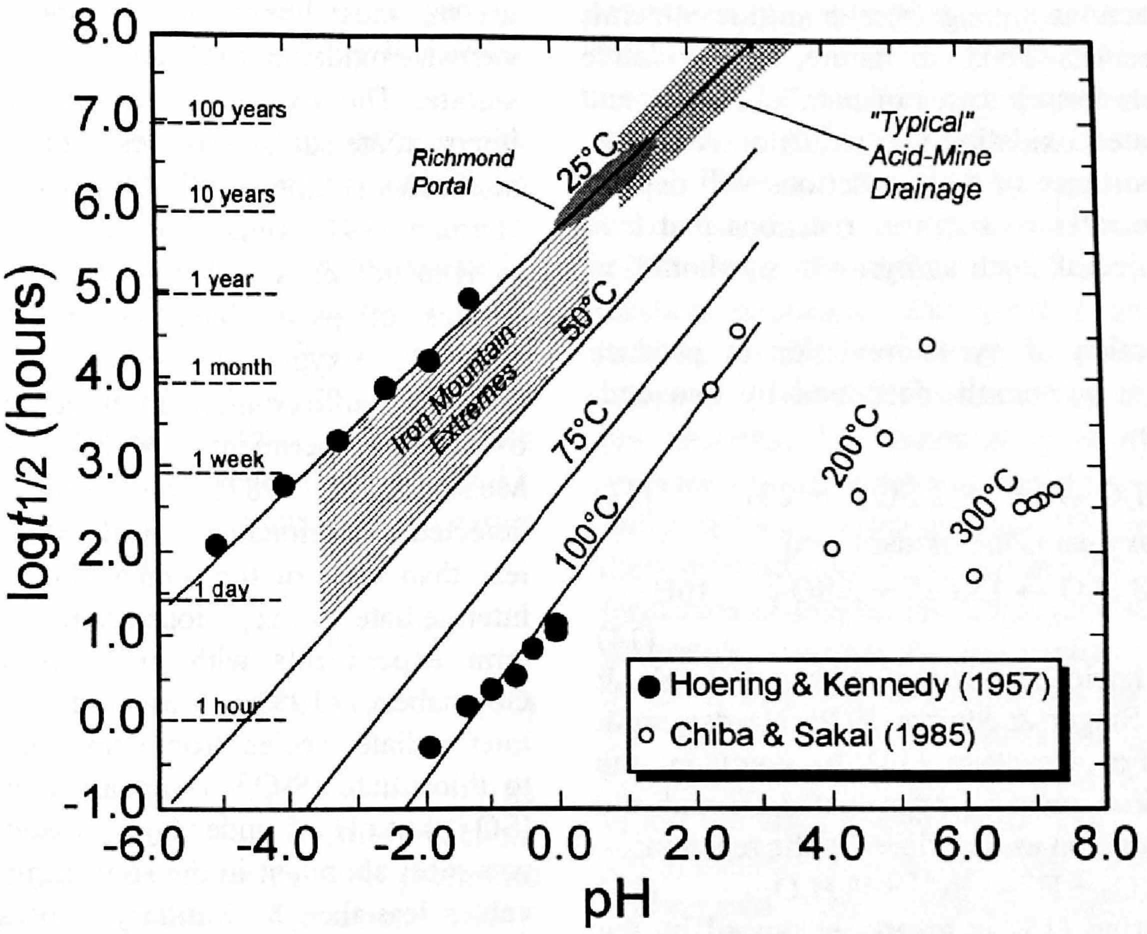

FIG. 8. Comparison of the kinetics of oxygen-isotope exchange data between dissolved sulfate and water in terms of pH and log$t_{1/2}$ (hours). Data from Hoering & Kennedy (1957) and Chiba & Sakai (1985). Fields for Iron Mountain, including the Richmond portal effluent, are from Alpers *et al.* (1994b), Nordstrom & Alpers (1999b), and Nordstrom *et al.* (2000). The field for "typical" acid mine drainage is from Seal & Hammarstrom (2003).

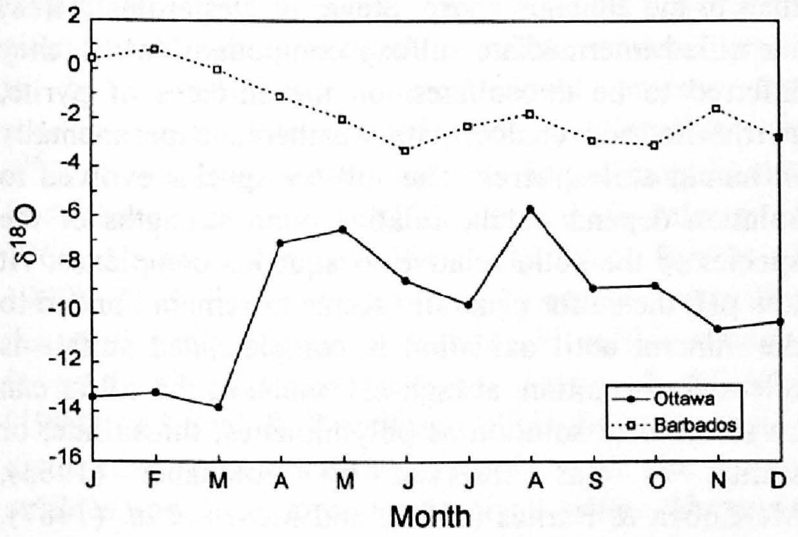

FIG. 9. Variations of the $\delta^{18}O$ of average precipitation from Ottawa and Barbados by month. Note the greater variations in temperate climates (Ottawa) compared to tropical climates (Barbados). Data are from I.A.E.A./W.M.O. (2001). Isotopic values in permil (VSMOW).

other geochemical signatures of lakes are also a function of the physical and chemical stratification in the lakes, and the residence time of the water in the lakes, which depends on factors such as whether the lake is a terminal lake (one with no surface discharge), or whether the lake represents constant-volume conditions in which the inputs equal the outputs. General aspects of the stable-isotope evolution of lakes, incorporating mass-balance and other physical constraints, which are also applicable to pit lakes, have been summarized by Gat (1981), Gilath & Gonfiantini (1983), and Gonfiantini (1986).

GEOCHEMISTRY OF SULFIDE WEATHERING

Stable-isotope fractionations associated with the oxidative weathering of pyrite and other sulfide minerals arise from the various reactions involved in the destruction of these minerals. Lowson (1982) provided an extensive review of the abiotic oxidation of pyrite, and Nordstrom (1982) reviewed both abiotic and biotic oxidation processes. Additional contributions have been made by Goldhaber (1983), Wiersma & Rimstidt (1984), McKibben & Barnes (1996), Luther (1987), Moses *et al.* (1987), Moses & Herman (1991), Williamson & Rimstidt (1994), and Rimstidt & Vaughan (2003). In laboratory settings, weathering of sulfide minerals can be conducted under abiotic or biotic conditions; in natural settings, weathering undoubtedly occurs in the presence of bacteria capable of mediating reactions among various sulfide minerals and aqueous species. Thus, in nature, the oxidative weathering results from a series of parallel abiotic and bacterially mediated oxidation and reduction reactions. The relative importance of these reactions will depend upon the relative rates of stepwise reactions that lead from a sulfide mineral, such as pyrite or pyrrhotite, to aqueous sulfate.

The mass action of pyrite oxidation to produce aqueous sulfate is commonly described by two end-member reactions:

$$FeS_2 + 7/2\ O_2 + H_2O \rightarrow Fe^{2+} + 2\ SO_4^{2-} + 2\ H^+ \qquad (13)$$

where dissolved oxygen is the oxidant, and

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

where dissolved ferric iron is the oxidant (Garrels & Thompson 1960, Singer & Stumm 1970, Nordstrom & Alpers 1999a). For Reaction (14) to continue, the supply of ferric iron must be rejuvenated through the oxidation of ferrous iron as described by the reaction:

$$Fe^{2+} + \tfrac{1}{4}\ O_2 + H^+ \rightarrow Fe^{3+} + \tfrac{1}{2}\ H_2O \qquad (15)$$

The rate of Reaction (15) is greatly enhanced by the bacterium *Acidothiobacillus ferrooxidans*, which can accelerate the rate of aqueous ferrous iron oxidation by a factor of at least 10^5 relative to the abiotic rate (Singer & Stumm 1968, 1970). Other bacteria, such as *Acidothiobacillus thiooxidans*, which oxidize sulfur, can also accelerate the rate of pyrite oxidation. Although Reactions (13) and (14) are commonly used to describe the mass balance of pyrite oxidation, the actual process is much more complex. Pyrite oxidation is largely an electrochemical process. The oxidation of pyrite to produce dissolved sulfate requires the transfer of seven electrons per sulfur atom to an aqueous oxidant; the oxidation of monosulfide minerals, such as pyrrhotite or sphalerite, requires the transfer of eight electrons. Incremental steps of oxidation–reduction reactions involve the transfer of one, or at most two electrons at a time (Basolo & Pearson 1967). Thus, pyrite oxidation may require up to seven discrete steps, and pyrrhotite oxidation may require eight. Each step offers the opportunity to affect the stable-isotope composition of the aqueous sulfate in the resultant mine drainage. The actual effect depends on the nature of the intermediate products and the kinetics of isotopic exchange among these products relative to the reaction rate at which these intermediate products are in turn destroyed.

The mechanism of pyrite oxidation involves concurrent cathodic-reaction, anodic-reaction, and electron-transport steps (Lowson 1982, Rimstidt & Vaughan 2003). The cathodic reaction involves an aqueous species accepting electrons from Fe(II) on the mineral surface. In mine-drainage settings, Fe^{3+} and O_2 are the most important. The anodic reaction involves stepwise oxidation of disulfide sulfur or sulfide sulfur to sulfate. The oxygen for the formation of sulfate or intermediate sulfoxy species is only derived from water molecules (Luther 1987, Moses *et al.* 1987, Moses & Herman 1991, Rimstidt & Vaughan 2003). According to Rimstidt & Vaughan (2003), sulfur atoms on the surface of pyrite have no direct interactions with molecular oxygen (O_2). At low pH, sulfate is the dominant sulfoxyanion observed in laboratory pyrite-oxidation experiments (McKibben & Barnes 1986, Moses *et al.* 1987). McKibben & Barnes (1986) detected polythionates at a pH of 3.6 in concentrations less than 10% of the total sulfur. At higher pH (>6), intermediate sulfoxyanions are more common. In short-term experiments with pH increasing from 6 to 9, Goldhaber (1983) observed a progression in intermediate species: from tetrathionate ($S_4O_6^{2-}$), thence to thiosulfate ($S_2O_3^{2-}$) appearing at pH >7, to sulfite (SO_3^{2-}) at pH >8 under O_2-saturated conditions; sulfate was most abundant in the short-term experiments at pH values less than 8. Similarly, Moses *et al.* (1987) did not identify any intermediate sulfoxy species below pH 7 in pyrite oxidation experiments; polythionates and thiosulfate were identified at pH = 7, and thiosulfate and traces of sulfite at pH = 9.

Rimstidt & Vaughan (2003) suggested that most of the oxidation steps occur on the mineral surface through interactions with disulfide (or polysulfide) groups rather than in the aqueous phase. Steger & Desjardins (1978) identified intermediate sulfoxy compounds, which they inferred to be thiosulfates, on the surfaces of pyrite, pyrrhotite, and chalcopyrite weathered experimentally in humid atmospheres. The sulfoxy species evolved to solution depend on the relative bond strengths of the species to the solid relative to aqueous complexes. At low pH, the sulfur generally seems to remain bonded to the mineral until oxidation is complete and sulfate is released to solution; at high pH, much of the sulfur can be released to solution as polythionates, thiosulfate, or sulfite, as was observed by Goldhaber (1983), McKibben & Barnes (1986), and Moses *et al.* (1987), which are then available for further reaction through oxidation or disproportionation. In the case of polythionates and thiosulfate, the formation of sulfite (SO_3^{2-} or HSO_3^-) seems to be a common step prior to the ultimate oxidation to sulfate (Williamson & Rimstidt 1992). Similarly, in the microbially mediated oxidation of sulfides, native sulfur, and intermediate sulfoxy species, the formation of sulfite is a common step prior to oxidation to sulfate (Suzuki *et al.* 1994). Theoretical and experimental studies have concluded that ferric iron (Fe^{3+}), rather than molecular oxygen (O_2), is the dominant oxidant of pyrite, regardless of pH

(Reaction 14). Nevertheless, molecular oxygen is important in the cycling of ferrous iron to ferric iron, as described by Reaction (15).

The oxidation of pyrrhotite may require the additional step of conversion to pyrite or marcasite as described by the reaction:

$$2\ \mathrm{Fe}_{1-x}\mathrm{S} + (½-x)\ \mathrm{O}_2 + (2-4x)\ \mathrm{H}^+ \rightarrow \mathrm{FeS}_2 + (1-2x)\ \mathrm{Fe}^{2+} + (1-2x)\ \mathrm{H}_2\mathrm{O} \quad (16)$$

Rims of marcasite around weathering grains of pyrrhotite are commonly reported in mine-waste environments, supporting this pathway of pyrrhotite oxidation (Jambor 1994, Hammarstrom *et al.*, 2001). Pyrrhotite can also react to form ferrous iron and native sulfur as described by the reactions:

$$\mathrm{Fe}_{1-x}\mathrm{S} + \left(\frac{1-x}{2}\right) \mathrm{O}_2 + (2-2x)\ \mathrm{H}^+ \rightarrow (1-x)\ \mathrm{Fe}^{2+} + \mathrm{S}^\circ + (1-x)\ \mathrm{H}_2\mathrm{O} \quad (17)$$

and

$$\mathrm{Fe}_{1-x}\mathrm{S} + (2-2x)\ \mathrm{Fe}^{3+} \rightarrow (3-3x)\ \mathrm{Fe}^{2+} + \mathrm{S}^0 \quad (18)$$

Native sulfur is then available for further reaction. Native sulfur has been reported as rims on pyrrhotite grains in mine-waste settings (Jambor 1994). Nevertheless, reaction of pyrrhotite to marcasite or pyrite appears to be more common than reaction to native sulfur.

Stable-isotope fractionations associated with pyrite oxidation have been studied experimentally under abiotic and biotic conditions. Additional insights have been gained from the study of field settings. With respect to sulfur isotopes, low-temperature oxidative alteration of sulfide minerals to sulfate minerals seems to be a quantitative, unidirectional process that produces negligible sulfur-isotope fractionation; the δ^{34}S of resulting sulfate minerals is indistinguishable from that of the parent sulfide mineral (Gavelin *et al.* 1960, Nakai & Jensen 1964, Field 1966, Rye *et al.* 1992). A similar conclusion can be reached regarding the relationship of aqueous sulfate with sulfide minerals in acid mine-drainage settings. Taylor & Wheeler (1994) and Seal & Wandless (1997) did not obtain a discernible difference between δ^{34}S in the parent sulfides and the associated dissolved sulfate. However, some experimental studies, particularly those involving oxidation of aqueous sulfide in neutral to alkaline conditions, some of which included a variety of bacteria, have documented negative sulfate–sulfide fractionations up to approximately 14 ‰ (Toran & Harris 1989), indicative of a kinetic isotope fractionation, which possibly resulted from the disproportionation of intermediate sulfoxy species rather than quantitative oxidation (Canfield 2001). Another notable exception without significant sulfur-isotope fractionation occurs when oxygenated mine waters subsequently become exposed to anoxic conditions, and bacterial sulfate reduction occurs. In these settings, the δ^{34}S of dissolved sulfate is higher than that of the parent sulfide minerals or the initial dissolved-sulfate composition, as discussed below.

In contrast, the δ^{18}O of aqueous sulfate formed during the biotic or abiotic oxidative weathering of sulfide minerals varies significantly, depending on reaction pathways. The greatest attention has been focused on the weathering of pyrite because of its common occurrence in numerous rock types, especially ore deposits. The weathering of pyrite is generally described by unidirectional Reactions (13) and (14) that differ in their oxidizing agent (O_2 versus Fe^{3+}) and in their inferred sources of oxygen (O_2 and H_2O) for the formation of sulfate. As discussed above, Reaction (14) accurately describes the mass action of pyrite oxidation by ferric iron, and also describes the source of oxygen for the formation of sulfate in a manner that is consistent with pathways of electron transfer proposed in the literature (Moses *et al.* 1987, Moses & Herman 1991, Rimstidt & Vaughan 2003). Taylor *et al.* (1984a) investigated the oxygen isotopic fractionation associated with Reaction (14) under abiotic and biotic conditions in which all of the oxygen in the resulting sulfate is derived from water. It was concluded that, at ambient conditions, the resulting sulfate should be enriched relative to the associated water by 4 ‰. Subsequent consideration of additional laboratory and field data led Taylor & Wheeler (1994) to conclude that 0 ‰ may be more appropriate to describe the oxygen-isotope fractionation associated with this reaction. Likewise, Mizutani & Rafter (1969b) observed no oxygen-isotope fractionation between sulfate and water associated with the oxidation of native sulfur (Van Stempvoort & Krouse 1994), and Lloyd (1967) found no oxygen-isotope fractionation between sulfate and water associated with the oxidation of Na_2S.

Reaction (13) does not accurately describe the role of molecular oxygen in the formation of dissolved sulfate during the oxidation of pyrite, even though the reaction can describe the mass action of the overall process. Instead, O_2 probably interacts with Fe^{2+} sites on the pyrite surface, but not directly with sulfur atoms (Lowson 1982, Rimstidt & Vaughan 2003). Thus, water molecules are probably the only source of oxygen interacting with sulfur atoms at the surface of sulfide minerals during oxidation. However, Krouse *et al.* (1991) demonstrated the incorporation of molecular oxygen into sulfate derived from the oxidation of sulfide minerals in experiments by using O_2 enriched in ^{18}O. Furthermore, compilations of oxygen-isotope data from mine-drainage settings clearly demonstrate that water alone cannot explain the source of oxygen in the resulting sulfate, and that molecular oxygen must be involved (Toran & Harris 1989, Taylor & Wheeler 1994). In nature, the pathways for the incorporation of molecular oxygen may be abiotic or biotic. Rye *et al.* (1992) and Rye & Alpers (1997) found that the isotopic compositions of samples of ancient supergene alunite and jarosite reflect the incorporation of both molecular oxygen and oxygen derived from water.

The oxidation of dissolved sulfite (SO_3^{2-}) is an attractive mechanism for incorporating molecular oxygen in dissolved sulfate during sulfide-mineral oxidation. The multistep oxidation process required to oxidize pyrite to sulfate involves the formation of sulfoxyanions with increasing oxidation states to accommodate a maximum transfer of one or two electrons per sulfur atom per step. These oxidation steps may occur as complexes on the mineral surface or in the aqueous phase. In either case, the oxidation will commonly proceed through sulfite before final oxidation to sulfate. The location of the site of oxidation will depend on the strength of the bonding of the sulfoxy species to the mineral surface relative to the bonding strength to the aqueous complexing agents. Oxidation in the solid phase can be expected to be isolated from isotopic exchange with the aqueous phase, but oxidation in the aqueous phase can be expected to have significant isotopic interactions with the aqueous phase if the rates of aqueous exchange reactions are fast relative to the residence time of the unstable intermediate species. At low pH, sulfate seems to be the first sulfoxyanion released to solution during sulfide oxidation (McKibben & Barnes 1986, Moses *et al.* 1987), but at higher pH (≥3.6) the intermediate sulfoxy species, such as polythionates, thiosulfate, and sulfite, have been identified in sulfide-mineral oxidation experiments, as noted above (Goldhaber 1983, McKibben & Barnes 1986, Moses *et al.* 1987). Thus, polythionates and thiosulfate are commonly oxidized to sulfite prior to oxidation to sulfate by both abiotic and biotic pathways (Williamson & Rimstidt 1992, Suzuki *et al.* 1994).

Considerable information is available about oxygen-isotope fractionations associated with sulfite because of the importance of SO_2 in acid rain. In contrast, little is known about oxygen-isotope fractionations associated with the oxidation of polythionates and thiosulfate (Van Stempvoort & Krouse 1994). Holt *et al.* (1981) investigated experimentally the abiotic aqueous-phase oxidation of SO_2, and Holt *et al.* (1983) investigated the nonaqueous phase (*i.e.*, humid atmosphere) oxidation of SO_2. The experiments of Holt *et al.* (1981) were conducted under a variety of conditions, many of which were relevant to mine-drainage environments, including temperatures between 1 and 24 °C and catalysis of reactions by ferric iron. For all of their experiments relevant to mine-drainage environments, the $\delta^{18}O$ of sulfate produced from the oxidation of sulfite varied systematically with the $\delta^{18}O$ of the water, with a slope of ~0.75. In other words, the isotopic composition of the water controlled the isotopic composition of three-quarters of the oxygen atoms in the resulting sulfate. Therefore, the isotopic composition of atmospheric oxygen controlled the other quarter. Their experiments indicate that the oxygen isotopic fractionation between dissolved sulfite and water is 12.6 ‰.

The rate of oxygen isotopic exchange between sulfite and water is known to be fast. Betts & Voss (1970) investigated the rate of isotopic exchange as a function of temperature, pH, and total sulfite concentration. It was determined that, for a 0.3 *M* total sulfite solution at 24.7 °C, the half-life for the exchange reaction was 25.3 h at pH 10.5, and 1.3 min at pH 8.9. Reliable results could not be obtained below pH 8.9 because of difficulty in quenching the experiments. Extrapolation of the rate constants to pH 7 suggests a half-life of approximately 0.5 sec; at pH 3, the half-life is on the order of fractions of a nanosecond. Likewise, attempts by Holt *et al.* (1983) to quench their 22 °C non-aqueous-phase SO_2 oxidation experiments by cryogenic methods at –79 °C failed, suggesting that exchange was rapid and continued to temperatures well below 0 °C. Thus, if aqueous sulfite is present in mine-drainage environments for even the briefest of times during sulfide-mineral oxidation to produce sulfate, its $\delta^{18}O$ will likely reflect equilibration of three of its four oxygen atoms with water, and the remaining oxygen atom will reflect the isotopic composition of atmospheric oxygen. Because of the rapid kinetics associated with oxygen-isotope exchange between sulfite and water, and the isotopic effects associated with its subsequent oxidation to sulfate, the isotopic signatures associated with precursor sulfoxyanions should probably be erased by the formation of sulfite.

The incorporation of molecular oxygen into sulfate derived from the oxidation of pyrite, with dissolved ferric iron as the primary oxidant, is better described by using sulfite as an intermediate species on the pathway to sulfate. Thus, the first step can be described by the reaction:

$$FeS_2 + 10\,Fe^{3+} + 6\,H_2O \rightarrow 11\,Fe^{2+} + 2\,SO_3^{2-} + 12\,H^+ \qquad (19)$$

where sulfite is then oxidized to sulfate according to the reaction:

$$SO_3^{2-} + \tfrac{1}{2}\,O_2 \rightarrow SO_4^{2-} \qquad (20)$$

Reactions (19) and (20) can be combined to describe

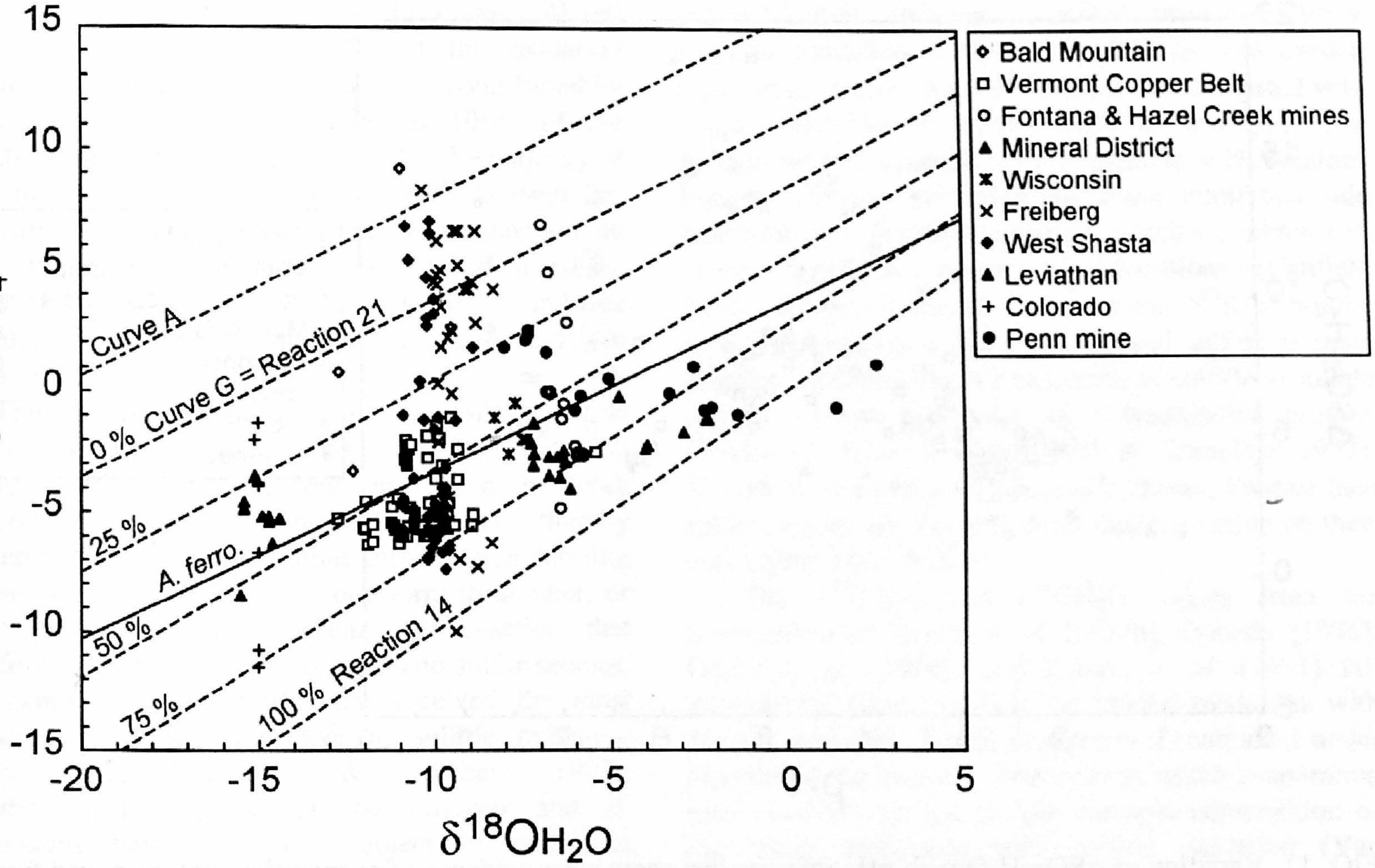

FIG. 10. Variation of $\delta^{18}OSO_4$ and $\delta^{18}OH_2O$ for various minesites and unmined mineral deposits. Data are from Toran (1987), Taylor & Wheeler (1994), Hamlin & Alpers (1995, 1996), Seal & Wandless (1997), Haubrich & Tichomirowa (2002), and Seal (unpub., 2003). Curve G represents isotopic effects associated with sulfite equilibration and oxidation under oxygen-excess conditions. Curve A represents isotopic effects associated with sulfite oxidation under oxygen-limited conditions. The lines marked 0, 25, 50, 75, and 100% represent the inferred contributions of Reaction (14), where Reactions (14) and (21) are the two end-members. The curve labeled "*A. ferro.*" is the best-fit to the data of Gould *et al.* (1990) for experiments on the oxidation of pyrite in the presence of the bacterium *Acidothiobacillus ferrooxidans*. All isotopic values are in permil (VSMOW).

the incorporation of molecular oxygen into sulfate derived from pyrite oxidation by the reaction:

$$FeS_2 + 10\,Fe^{3+} + 6\,H_2O + O_2 \rightarrow 11\,Fe^{2+} + 2\,SO_4^{2-} + 12\,H^+ \quad (21)$$

which should be a better representation of the mass action of the process because the multiple electron-transfer steps are implicit in its stoichiometry. The oxygen-isotope fractionations associated with this reaction should be the same as those associated with Reaction (20), which Holt *et al.* (1981) investigated experimentally (Fig. 10). Curve G from their experiments is probably the most relevant to mine-drainage settings because it was conducted with excess O_2 with Fe^{3+} as a catalyst, presumably at a temperature of 24 °C. Their results for Curve G are described by the equation:

$$\delta^{18}OSO_4 = 0.73\,\delta^{18}OH_2O + 11.1 \quad (22)$$

which should describe the general case for Reaction (21). Curve A from Holt *et al.* (1981), derived from experiments using stoichiometric proportions of sulfite and O_2 as described by Reaction (20), may also be useful for describing oxygen-isotope fractionation associated with pyrite oxidation in suboxic, oxygen-limited environments, such as in tailings piles. Curve A is described by the equation:

$$\delta^{18}OSO_4 = 0.74\,\delta^{18}OH_2O + 15.4 \quad (23)$$

Note that Curves A and G should represent upper limits on the $\delta^{18}OSO_4$ values expected from the oxidation of pyrite. Figure 10 shows that most data for mine drainage fall between Curve G and the curve corresponding to Reaction (14). It is worth noting that in the stoichiometry of Reaction (21) three-quarters of the oxygen atoms for sulfate formation are derived from water, and a quarter from molecular oxygen, consistent with the slopes of ~0.75 for Equations (22) and (23).

The viability of this model for the oxidation of pyrite and the role of molecular oxygen in the oxidation of sulfide minerals can be further assessed by considering the variation between $\Delta SO_4–H_2O$ from mine-drainage samples and pH (Fig. 11). Oxidation

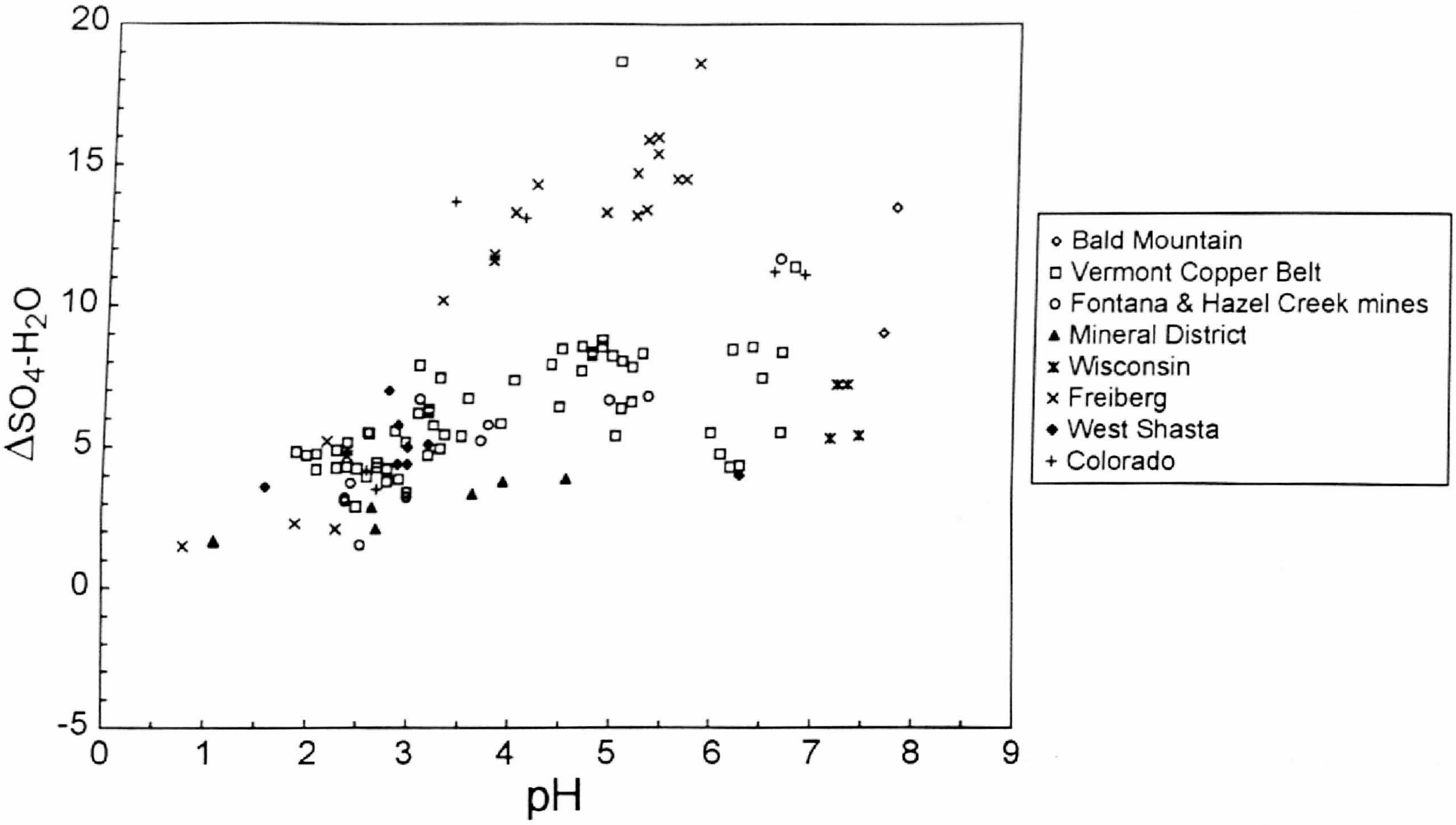

FIG. 11. Variation of ΔSO_4–H_2O with pH. Samples that show clear evidence of evaporation were removed from the set. The ΔSO_4–H_2O value is a measure of the relative contributions of Reactions (14) and (21). Note the positive correlation between ΔSO_4–H_2O and pH, and the greater range in ΔSO_4–H_2O values at higher pH, suggesting that Reaction (21) becomes more important as pH increases. Data are from Toran (1987), Taylor & Wheeler (1994), Hamlin & Alpers (1995, 1996), Seal & Wandless (1997), Haubrich & Tichomirowa (2002), and Seal (unpub., 2003). All isotopic values in permil (VSMOW).

dominated by Reaction (14) without direct interaction of O_2 with sulfur atoms would be expected to show minimal oxygen-isotope fractionation between dissolved sulfate and associated water (*i.e.*, ΔSO_4–$H_2O \approx 0$). In contrast, for oxidation dominated by Reaction (21) it would be expected that oxygen-isotope fractionation between dissolved sulfate and water would approach 11.1 ‰ for oxic environments and 15.4 ‰ for oxygen-limited environments. The laboratory oxidation studies of pyrite discussed above have concluded that intermediate sulfoxyanions that may act as precursors to sulfite, and sulfite itself, are more common at higher pH values. Therefore, a positive correlation between ΔSO_4–H_2O and pH would be expected, as would a larger range in ΔSO_4–H_2O values with increased pH, because of the greater abundance of sulfite and precursor sulfoxyanions (Fig. 11). The data plotted in Figure 11 have been screened to remove only those samples that show clear evidence of evaporation, which would disturb the primary isotopic signatures associated with sulfide oxidation, as discussed below. Thus, the covariation of ΔSO_4–H_2O with pH is in permissive support of the molecular-oxygen pathway for pyrite oxidation described by Reaction (21). Van Stempvoort & Krouse (1994) drew attention to the fact that the oxidation of sulfite and the oxidation of sulfide produce distinctive oxygen-isotope signatures in terms of the associated $\delta^{18}OSO_4$ and $\delta^{18}OH_2O$ values, consistent with the discussion above. Taylor & Wheeler (1994) also noted the importance of sulfite–water oxygen-isotope exchange at elevated pH.

Previous researchers have proposed that plots of $\delta^{18}OSO_4$ for dissolved sulfate and $\delta^{18}OH_2O$ for water can be used to assess the relative importance of Reactions (13) and (14) in the oxidation of pyrite (Taylor *et al.* 1984b, van Everdingen & Krouse 1985, Taylor & Wheeler 1994). A similar approach can be constructed for Reactions (14) and (21) to estimate the relative importance O_2 and H_2O in the formation of sulfate from the oxidation of pyrite (Fig. 10). As noted above, most samples fall between the curves corresponding to Reactions (14) and (21). Notable exceptions are some samples from the West Shasta district and the Penn mine (California), and from the Freiberg mining district (Germany), to be discussed below. In Figure 10, the lines marked 0, 25, 50, 75, and

100% refer to the relative effects of Reactions (14) and (21), where "0%" indicates 0% of the oxidation contributed by Reaction (14) (and 100% contributed by Reaction 21), and "100%" indicates 100% of the oxidation contributed by Reaction (14). The majority of the samples falls between the 25 and 75% isopleths, suggesting that, in general, subequal proportions of both reactions contribute to the oxidation of sulfide minerals. However, the covariations shown in Figure 11 indicate that the relative significance of these two reactions varies as a function of pH.

Thus far, the discussion of the role of bacteria in the stable-isotope fractionations associated with the oxidation of sulfide minerals has been minimal. Bacteria may either catalyze reactions, thereby accelerating their rates, without directly transforming oxygen or sulfur species from one form to another, or they may become involved in enzymatic reactions that transform and (or) sequester oxygen and sulfur species. The genus *Acidothiobacillus* has received the most attention from the perspective of sulfide oxidation (Kelly 1982, Nordstrom & Southam 1997). Specifically, the species *A. ferrooxidans* and *A. thiooxidans* have been the subject of numerous investigations. *A. ferrooxidans* is an acidophilic organism that catalyzes the oxidation of Fe^{2+} to Fe^{3+} (Singer & Stumm 1970). It also enzymatically oxidizes reduced sulfur to more oxidized species; *A. thiooxidans* exclusively oxidizes sulfur species through enzymatic pathways (Kelly 1982, Suzuki *et al.* 1994). Thus, microbes seem to be able to mediate several steps in the multiple-step process of sulfide-mineral oxidation, and compete with concurrent abiotic processes for many of these steps.

Experimental studies of oxygen isotopic fractionation associated with the oxidation of sulfide minerals mediated by bacteria have been conducted by Taylor *et al.* (1984a), Qureshi (1986), Gould *et al.* (1990), and Krouse *et al.* (1991). Invariably, these studies have demonstrated that greater than 50% of the oxygen for the formation of sulfate was derived from water. Gould *et al.* (1990) observed that pyrite oxidized under submersed conditions and pH 2.5 in the presence of *A. ferrooxidans* produced sulfate with $\delta^{18}OSO_4$ that varied systematically with $\delta^{18}OH_2O$, which could be described by the equation:

$$\delta^{18}OSO_4 = 0.69\,\delta^{18}OH_2O + 3.6 \qquad (24)$$

The location of this line between the curves for Reactions (14) and (21) suggests that a significant amount of molecular oxygen is incorporated into the sulfate as a result of bacterial activity. Schippers *et al.* (1996) obtained significant concentrations of polythionates in bacterially mediated oxidation experiments on pyrite at pH 1.9. Thus, the rapid oxygen-isotope exchange of sulfite, produced during stepwise oxidation of other sulfoxyanions, may exert a significant control on the $\delta^{18}O$ of sulfate associated with biotic oxidation of pyrite, even at low pH. The production and reaction of intermediate sulfoxyanions follows complex pathways involving numerous side reactions and disproportionation reactions, which can cause significant isotopic fractionations (Canfield 2001). However, the similarity of the $\delta^{34}S$ of source sulfide minerals and that of associated sulfate in mine drainage indicates that the oxidation of sulfide to sulfate can be viewed ultimately as a quantitative process (Taylor & Wheeler 1994, Seal & Wandless 1997). Therefore, regardless of reaction pathway, intermediate sulfoxyanions are likely to react through sulfite on their way ultimately to sulfate.

The $\delta^{18}OSO_4$ and $\delta^{18}OH_2O$ values from the experiments of Taylor *et al.* (1984a), Qureshi (1986), Gould *et al.* (1990), and Krouse *et al.* (1991) fall dominantly within the field for abiotic oxidation, with the exception of several experiments conducted under alternating wet and dry conditions in which evaporation may have altered the oxygen isotopic composition of the water associated with sulfide oxidation (Van Stempvoort & Krouse 1994). Thus, sulfate generated by bacterial or abiotic pathways seems to be indistinguishable in terms of $\delta^{18}OSO_4$ values, although bacterially mediated pathways may be biased toward slightly higher $\delta^{18}OSO_4$ values (Toran & Harris 1989, Taylor & Wheeler 1994, Van Stempvoort & Krouse 1994). Therefore, as noted by previous researchers, the oxygen-isotope composition of sulfate cannot be used as unequivocal evidence for the presence or absence of microbial activity during the oxidation of sulfide minerals.

GEOCHEMISTRY OF SULFATE REDUCTION

In low-temperature sulfur-bearing aqueous systems, biogenic sulfate reduction is a potentially important process if the proper conditions are met. The processes of sulfate reduction in natural systems commonly have associated characteristic, kinetically controlled, non-equilibrium oxygen- and sulfur-isotope fractionations. Isotopic variations associated with the biogenic reduction of sulfate have been studied by numerous researchers, most of whom have concentrated on the role of the dissimilatory sulfate-reducing bacteria such as *Desulfovibrio desulfuricans*. The activity of sulfate-reducing bacteria in marine sediments throughout most of geological time has had a profound effect on the sulfur-isotope composition of seawater sulfate.

Sulfate-reducing bacteria are active only in anoxic environments, such as below the sediment–water interface, in anoxic water bodies, in anaerobic wetlands, and in flooded mine workings. Various species of sulfate-reducing bacteria can survive over a range of temperature (0 to 110 °C) and pH (5 to 9.5) conditions, but prefer near-neutral conditions and can withstand a range of salinities, from dilute up to halite saturation (Postgate 1984). The metabolism of sulfate-reducing bacteria can be described by the general reaction:

$$2\ CH_2O + SO_4^{2-} = H_2S + 2\ HCO_3^- \qquad (25)$$

where CH_2O represents generic organic matter (Berner 1985). The H_2S can be lost to the water column, reoxidized, fixed as pyrite or other sulfide minerals if reactive metals are present, or fixed as organic-bound sulfur.

The fractionation of sulfur isotopes between sulfate and sulfide during bacterial sulfate reduction is a kinetically controlled process in which ^{34}S is enriched in the sulfate relative to the sulfide, in the same sense as equilibrium fractionation between sulfate and sulfide (Chambers & Trudinger 1979). The sulfate-reducing bacteria more readily metabolize ^{32}S and ^{16}O relative to ^{34}S and ^{18}O, respectively. Thus, the $\delta^{34}S$ and $\delta^{18}O$ of the residual aqueous sulfate increase during the progress of the reaction. In marine settings, the fractionation associated with bacterial sulfate reduction ($1000\ln\alpha SO_4$–H_2S) typically ranges from 15 to 60 ‰ (Goldhaber & Kaplan 1975) whereas an equilibrium, abiotic fractionation is approximately 73 ‰ at 25 °C. The magnitude of the fractionation has been shown to be a function of the rate of sulfate reduction, which can be related to sedimentation rates. The smaller fractionations (~15 ‰) correspond to faster rates of sulfate reduction and sedimentation, whereas the larger fractionations (~60 ‰) correspond to slower rates of sulfate reduction and sedimentation (Goldhaber & Kaplan 1975). In detail, the magnitude of the fractionation results from a complex series of reduction steps that produce intermediate sulfoxyanions, which undergo a variety of disproportionation, reduction, and oxidation steps, ultimately on their way to sulfide (Canfield 2001). Likewise, the fractionation of oxygen isotopes during bacterial reduction of sulfate is due to a complex combination of processes, among which are preferential reduction of isotopically light enzyme-bound sulfate to sulfite (SO_3^{2-}), reoxidation of sulfite to enzymes and sulfate, sulfite–water oxygen-isotope exchange, and reoxidation of sulfide (Van Stempvoort & Krouse 1994). Experimental studies to quantify coupled sulfur- and oxygen-isotope fractionation associated with bacterial sulfate reduction have determined that the sulfur-isotope systematics associated with bacterial sulfate reduction follow a Rayleigh pathway, but the oxygen-isotope systematics do not (Mizutani & Rafter 1969b, 1973, Fritz *et al.* 1989). The kinetics of direct oxygen isotopic exchange are sufficiently slow at ambient, near-neutral conditions to exclude direct sulfate–water exchange as a significant process during bacterial sulfate reduction. However, as previously mentioned, the exchange of oxygen isotopes between sulfite and water at ambient conditions (pH <9) is extremely rapid (Betts & Voss 1970, Holt *et al.* 1981). Oxygen-isotope exchange between sulfite and water, and the subsequent reoxidation of the sulfite to sulfate, seem to be important processes in determining the $\delta^{18}O$ of residual sulfate during bacterial reduction (Mizutani & Rafter 1969b, Fritz *et al.* 1989). The net result is that, even though sulfate-reducing bacteria preferentially metabolize ^{16}O relative to ^{18}O to produce a kinetic fractionation ranging between 25 and 29 ‰ (depending on the rate of reduction), the resulting $\delta^{18}O$ of the residual sulfate will reflect the $\delta^{18}O$ of the water if there is sufficient time for oxygen-isotope exchange to occur between the aqueous sulfite and water (Mizutani & Rafter 1969b, 1973, Fritz *et al.* 1989).

Mizutani & Rafter (1969b) found that the ratio of $\delta^{18}O$ variations to $\delta^{34}S$ variations with the progress of sulfate reduction was $(\delta^{18}O - \delta^{18}O_i)/(\delta^{34}S - \delta^{34}S_i) = 1/3.8$, where $\delta^{18}O_i$ and $\delta^{34}S_i$ are the initial oxygen and sulfur isotopic compositions, respectively, of the dissolved sulfate, and $\delta^{18}O$ and $\delta^{34}S$ are the compositions at the termination of the sulfate-reduction experiments. In contrast, data from the experimental studies of Mizutani & Rafter (1973) and Fritz *et al.* (1989) yielded $(\delta^{18}O - \delta^{18}O_i)/(\delta^{34}S - \delta^{34}S_i)$ ratios of 1/2.5 and 1/19.4, respectively; all three studies combined yield a ratio of 1/6.1. The significant differences among these three studies in terms of temperature, culture media, bacterial cultures, and experiment duration make it difficult to determine which data might be most applicable to natural systems. However, Zak *et al.* (1980) reported $\delta^{18}O$ and $\delta^{34}S$ data for porewaters from modern marine sediments in the Pacific Ocean, which yield a ratio of 1/2.1 associated with sulfate reduction in natural settings. This ratio suggests that an average fractionation of 19 ‰ may be more appropriate to describe oxygen-isotope variations associated with bacterial sulfate reduction in the oceans.

From the perspective of the environmental aspects of mining, sulfur and oxygen isotopes offer a powerful tool for understanding the role of bacterial sulfate reduction in various geochemical settings. When evaluated relative to the sulfur- and oxygen-isotope compositions of other dissolved sulfate at a site and in the context of the sulfur-isotope composition of ore and waste sulfide minerals, bacterial sulfate reduction imparts a distinctive and unequivocal isotopic fingerprint on residual dissolved sulfate, as discussed below. Stable-isotope investigations of dissolved sulfate in natural or constructed anaerobic (or aerobic) wetlands hold significant potential for elucidating the effectiveness of biogeochemical processes in determining overall water quality. The same applies to any remediation technology that uses or causes the reduction of sulfur. The environmental impact of Hg, either derived from ores or introduced through the beneficiation of gold by using amalgamation, is enhanced by its methylation. Mercury is dominantly methylated as a byproduct of the metabolism of sulfate-reducing bacteria (Compeau & Bartha 1985). Thus, stable isotopes offer a means of identifying and understanding environments conducive to Hg methylation at active and abandoned minesites.

STABLE-ISOTOPE GEOCHEMISTRY OF CYANIDE

Stable isotopes hold great potential for understanding the fate of cyanide in mineral processing operations at precious-metal mines as well as at abandoned heaps and spills because the carbon and nitrogen contained in cyanide can both undergo isotopic fractionation during degradation. The environmental geochemistry of cyanide use at gold mines has been summarized by Smith (1994) and Smith & Mudder (1999); the stable-isotope geochemistry of cyanide has been presented by Johnson (1996), Rye & Johnson (1997), Johnson *et al.* (1998), and Johnson *et al.* (2000). The following discussion is summarized from these papers. Gold (and silver) extraction using cyanide leaching is a two-step process. First, gold is dissolved from ores by applying a dilute solution of free cyanide, which forms soluble gold-cyanide complexes. To prevent the escape of free cyanide by volatilization, leach solutions are maintained at pH values above 10, at which the cyanide is dominantly in the non-volatile CN^- form. The gold is then recovered from the cyanide solution either by cementation with zinc or by adsorption onto activated charcoal. The presence of other metals and reactive sulfides, such as pyrrhotite, causes the formation of metallo-cyanide complexes and thiocyanate (SCN^-) that decrease the efficiency of gold recovery and lead to increased cyanide consumption.

Cyanide, because of its reduced nature, is unstable in most surficial environments. In natural settings, among the several processes that contribute to cyanide degradation or loss are complexation, precipitation, adsorption, oxidation to cyanate, volatilization, biodegradation, formation of thiocyanate, and hydrolysis (Smith & Mudder 1999). The relative importance and the reversibility of these processes varies among different hydrochemical settings, such as process-solution ponds, tailings and leach pads, adjacent soils, and groundwater.

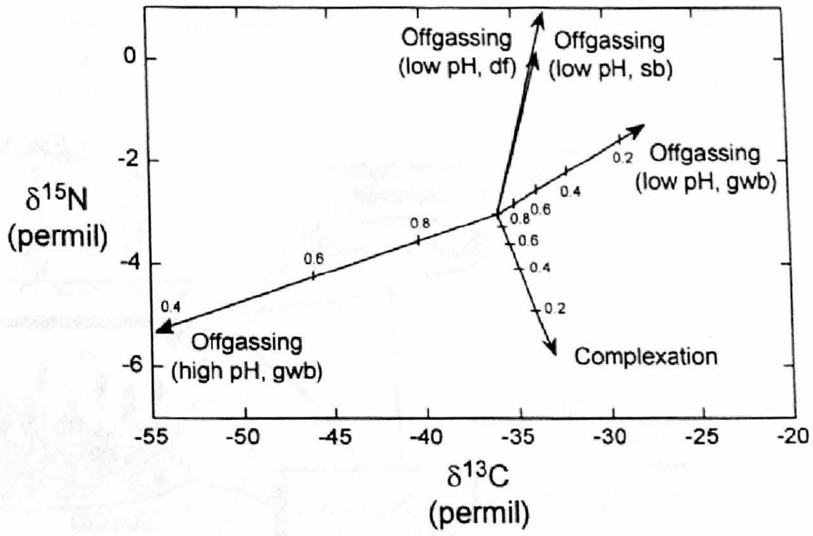

FIG. 12. Variation of $\delta^{15}N$ and $\delta^{13}C$ associated with various cyanide degradation or loss processes. Numbered tick marks refer to the fraction of cyanide remaining in solution. The abbreviations "df", "sb", and "gwb" refer to the different experimental set-ups of Johnson *et al.* (2000) – distillation flask, stirred beaker, and gas-washing bottle, respectively. Modified from Johnson *et al.* (2000). All isotopic values in permil (Air or VPDB).

Several cyanide-loss pathways produce distinctive isotopic signatures. Thus, carbon- and nitrogen-isotope analyses of cyanide and related compounds in mine waters may identify specific cyanide-loss pathways and give information on their relative importance (Johnson *et al.* 2000). For example, experiments conducted by Johnson *et al.* (2000) revealed that volatilization of cyanide produced pH-sensitive shifts in both $\delta^{13}C$ and $\delta^{15}N$ of the residual aqueous cyanide (Fig. 12). In contrast, oxidation of cyanide or complexation of cyanide with metals seems to cause minimal isotopic changes (Johnson *et al.* 2000). Isotopic studies of active mineral-processing operations at the Lone Tree, Pinson, and Getchell mines (Nevada) provide evidence that gaseous cyanide emissions from heap-leach circuits may be less important than has generally been thought (*cf.* Smith & Mudder 1999), and that significant amounts of cyanide may be retained within the ore heaps as precipitated or adsorbed cyanometallic species.

An additional point of note is that the $\delta^{13}C$ value of reagent cyanide can differ dramatically from one supplier to another. The isotopic differences reflect regional variations in the $\delta\ ^{13}C$ value of natural gas methane, which is the carbon feedstock for the common methods of cyanide manufacturing. Thus, measurements of the $\delta\ ^{13}C$ value of dissolved cyanide could prove to be useful at mineral-processing sites if there is a need to discriminate among multiple potential cyanide sources.

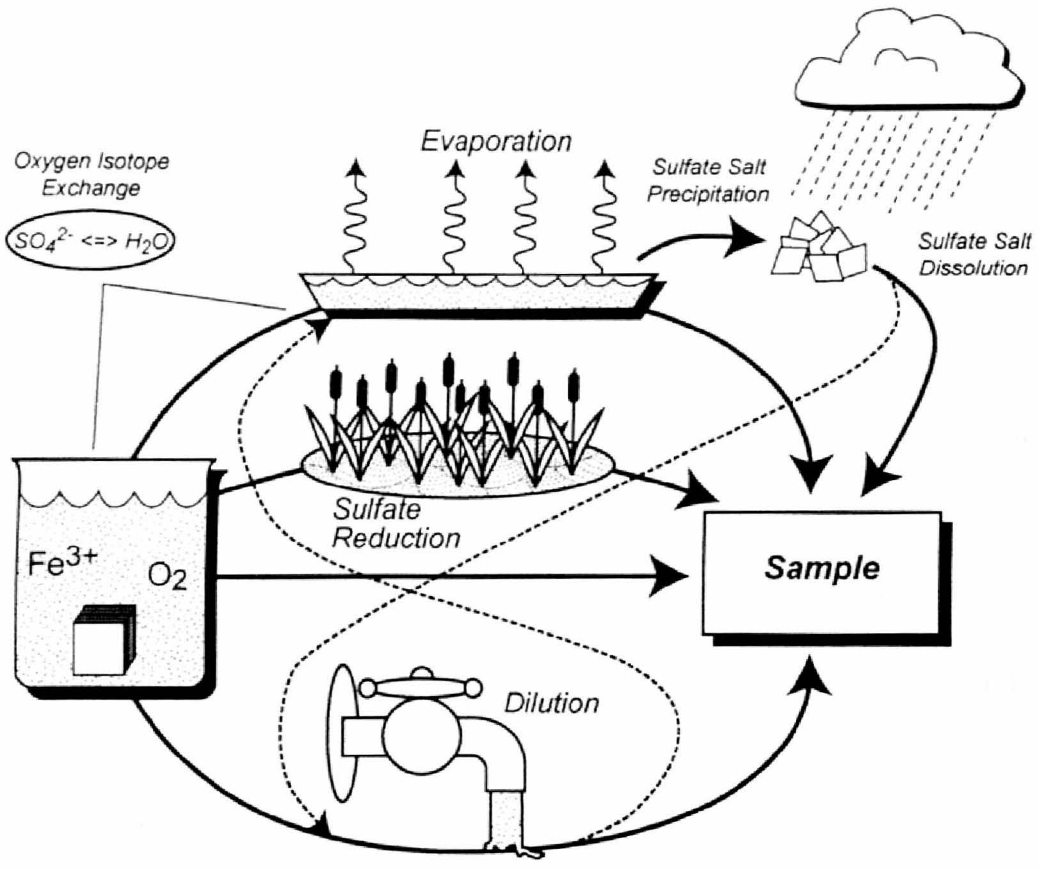

FIG. 13. Processes influencing the isotopic composition of samples derived from the oxidation of sulfide minerals. Accurate interpretation of the stable-isotope composition of a sample requires an understanding of all processes that may have affected the sample. Stable isotopes may provide insights to which of the processes may have been important in the evolution of a given sample. Note that in mine-drainage settings, there may be complex interactions among all of these pathways.

APPLICATIONS TO MINE DRAINAGE

The stable-isotope characteristics of acid mine drainage have been reviewed by van Everdingen & Krouse (1988) and Taylor & Wheeler (1994). In general, concentrations of dissolved sulfate typically range up to 5 g L^{-1}, but extreme concentrations up to 760 g L^{-1} have been reported where evaporation is important (Nordstrom *et al.* 2000). The present study seeks to extend the understanding of the behavior of stable isotopes in mine-drainage settings by drawing upon more recent studies.

The successful application of oxygen and sulfur isotopes from sulfates is possible because of the sluggish kinetics of isotopic exchange between sulfate and water or sulfide; except under extreme conditions of elevated temperature or very low pH, the isotopic signature of sulfate should preserve a record of the conditions of its origin. The oxygen-isotope composition of sulfate is best interpreted relative to the oxygen isotopic composition of the water associated with sulfide- mineral oxidation. However, mine-drainage settings represent complex environments where a multitude of physical and chemical processes may be operating, many of which can perturb the original isotopic signatures of the water or sulfate (Fig. 13). Among these processes are various combinations of evaporation, the formation of efflorescent metal-sulfate salts and their subsequent dissolution, sulfate reduction, and dilution. Thus, care must be taken when interpreting the oxygen-isotope composition of the dissolved sulfate and water in mine drainage. Nevertheless, even if the primary isotopic signatures associated with the oxidation of sulfide minerals have been masked by subsequent processes, stable-isotope data from mine drainage can provide useful insights into the variety of other physical and chemical processes that contribute to the geochemical evolution of mine waters; moreover, stable-isotope data may be extremely useful in deciphering which of these processes are most important.

For maximum utility, the minimum parameters required for rigorous investigation of the stable-isotope geochemistry of mine drainage include δDH_2O, $\delta^{18}OH_2O$, $\delta^{18}OSO_4$, and $\delta^{34}SSO_4$, and non-isotopic water-quality parameters such as pH and dissolved sulfate. In addition, an assessment of the mean $\delta^{34}S$ of ore-sulfide minerals, and the mean $\delta^{34}S$ and $\delta^{18}O$ of sulfate minerals, is beneficial. In areas where sulfate reduction is known or suspected, the $\delta^{34}S$ of dissolved sulfide will provide useful insights; in areas of cyanidation of precious-metal ores, $\delta^{13}C$ and $\delta^{15}N$ analyses may be essential.

The role of evaporation can be easily determined through the use of oxygen and hydrogen isotopes. Most surface waters and groundwaters originate as meteoric waters. Therefore, they can be expected to conform to the meteoric water line, and exhibit seasonal variations in composition due to variations in the mean temperature of precipitation (Fig. 9). Evaporation causes the hydrogen and oxygen isotopic composition of the residual water to depart from the meteoric water line along a positive trend, the slope of which depends on the temperature and relative humidity associated with evaporation. The partially evaporated waters may then be ponded or discharged from the site through surface runoff or groundwater infiltration. In any case, the $\delta^{18}OH_2O$ values are not representative of the conditions of initial sulfide oxidation; therefore, interpretations of the relative importance of Reactions (14) and (21) to sulfide oxidation on the basis of raw $\delta^{18}OH_2O$ and $\delta^{18}OSO_4$ values will be in error. Evaporation will cause the $\delta^{18}OH_2O$ value to shift to higher values, whereas the $\delta^{18}OSO_4$ value remains unchanged because of the sluggish kinetics of oxygen isotopic exchange between sulfate and water. The net result is that Reaction (14) will appear to have a greater importance than is actually the case. In extreme, but common cases, evaporation of mine waters can lead to the precipitation of a variety of secondary, efflorescent sulfate salts, such as gypsum, chalcanthite, melanterite [$FeSO_4 \cdot 7H_2O$], rozenite [$FeSO_4 \cdot 4H_2O$], szomolnokite [$FeSO_4 \cdot H_2O$], copiapite [$Fe^{2+}Fe^{3+}_4(SO_4)_6(OH)_2 \cdot 20H_2O$], and halotrichite [$Fe^{2+}Al_2(SO_4)_4 \cdot 22H_2O$], to name but a few (Alpers *et al.* 1994a, Nordstrom & Alpers 1999b, Jambor *et al.* 2000). These minerals store acidity and metals for later release through dissolution associated with storm events or during spring melt of snow packs.

Mine waters from the Penn mine in central California illustrate well the effects of evaporation on the stable-isotope characteristics of the mine waters (Hamlin & Alpers 1995, 1996). The Penn mine exploited a pyritic massive sulfide deposit. Surface, ground, and mine waters are affected by acid mine drainage before they reach the Camanche Reservoir. To mitigate the impacts of surface-water drainage on the Camanche Reservoir, dams were constructed in the watershed containing the mine workings and wastes to impound drainage and facilitate evaporation that would permit disposal of the resulting metal-rich salts. Instead, metal-rich, acid-sulfate plumes formed in the groundwater downgradient from the impoundment. The δDH_2O and $\delta^{18}OH_2O$ values of the deep mine waters and the groundwaters upgradient from the plume are indistinguishable from values on the meteoric water line; however, the groundwaters downgradient from the impoundments fall along a linear trend with a shallower slope than that of the meteoric water line (Fig. 14) – a clear indication that these waters have undergone significant evaporation. However, it should be noted that, on the basis of the stable-isotope data alone, it cannot be determined whether the trend represents strictly the effects of evaporation, or the mixing of unaltered meteoric waters with evaporated waters. Nevertheless, evaporation is clearly an important process contributing to the geochemical evolution of groundwaters at the Penn mine. The variation of $\delta^{18}OSO_4$ and $\delta^{18}OH_2O$ only provides indirect and ambiguous evidence that evaporation may have been important. The $\delta^{18}OSO_4$ values show limited variably, as would be expected, whereas the $\delta^{18}OH_2O$ values span a range of more than 12 ‰, consistent with evaporation (Fig. 10). In addition to the wide range in $\delta^{18}OH_2O$ values, probably the most telling feature of the $\delta^{18}OSO_4$ and $\delta^{18}OH_2O$ variations that signifies the influence of

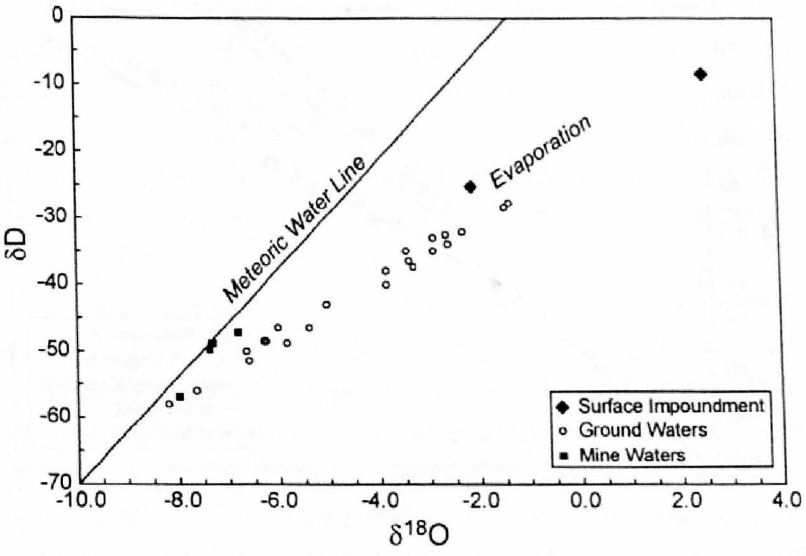

FIG. 14. Oxygen and hydrogen isotopic composition of surface and groundwaters from the Penn mine, California (Hamlin & Alpers 1995, 1996). The trend away from the Meteoric Water Line is a clear indication that evaporation was an important process at the abandoned Penn mine. Note that the regional groundwaters, as reflected by the mine waters, conform to the Meteoric Water Line. Waters in surface impoundments clearly show the effects of evaporation. Groundwaters either represent evaporated waters or mixtures of evaporated waters and regional groundwaters. The location of the Meteoric Water Line is from Craig (1961). All isotopic values in permil (VSMOW).

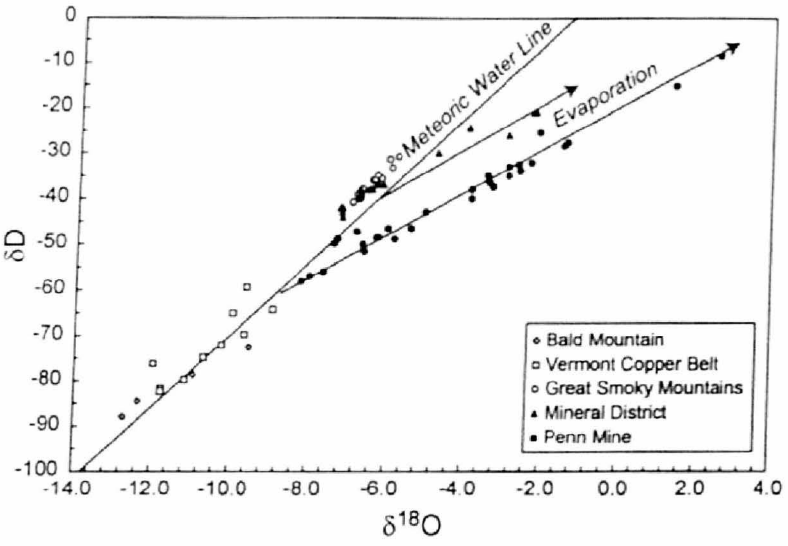

FIG. 15. Oxygen and hydrogen isotopic data for ground and surface waters from a variety of mines and unmined mineral deposits. Note that, with the exception of the Penn mine, most samples conform to the Meteoric Water Line. Data are from Hamlin & Alpers (1995, 1996), Seal & Wandless (1997), and Seal (unpub., 2003). The location of the Meteoric Water Line is from Craig (1961). All isotopic values in permil (VSMOW).

some other process beyond the environment of initial sulfide oxidation is the presence of several points which plot below the curve corresponding to Reaction (14), within an area that is theoretically impossible for sulfide oxidation alone (Fig. 10). Thus, only those samples that show no effects from evaporation can be used to constrain the environment of sulfide oxidation. However, it should be noted that on the basis of the stable-isotope data alone, it cannot be determined whether the trend of the hydrogen- and oxygen-isotope data from other abandoned mines clearly demonstrate the local importance of evaporation in the geochemical evolution of drainage (Fig. 15).

The precipitation of efflorescent metal-sulfate salts is a common outcome of evaporation of mine drainage; the salts can also form on sulfide-rich mine wastes under humid conditions, and at depth in tailings piles (Jambor 1994, Alpers *et al.* 1994a, Nordstrom & Alpers 1999b, Jambor *et al.* 2000). From the stable-isotope perspective, the $\delta^{18}OSO_4$ and $\delta^{34}SSO_4$ values of the salts should be similar to those of the drainage from which they formed. Their presence complicates the interpretation of stable-isotope data from mine drainage because waters that subsequently dissolve these salts have no genetic relationship to the waters that originally formed the salts. Thus, interpretations of the origins of the salts on the basis of the $\delta^{18}OSO_4$ and $\delta^{18}OH_2O$ variations of these waters will be in error. Unlike partially evaporated waters, as discussed above, additional stable-isotope systems offer no insights into the occurrence of this process in the history of a water sample. Therefore, insights into whether this process was operative must be obtained from other non-isotopic evidence, such as general knowledge of the hydrological setting of the samples.

Bacterial sulfate reduction is an important process in mine-drainage settings, but commonly occurs only locally. However, such reduction can play a dominant role in the evolution of mine drainage because it can lead to the removal of metals and sulfate from solution through the precipitation of metal-sulfide minerals. At abandoned minesites, environments conducive to bacterial sulfate reduction can be established in wetlands (natural and constructed) and in mine workings isolated from atmospheric oxygen. The stable-isotope data from the Penn mine (California) and the Fontana and Hazel Creek mines (North Carolina) indicate that bacterial sulfate reduction is locally important. At the Penn mine, surface waters and most groundwaters have evolved under oxygenated conditions; thus, the $\delta^{34}SSO_4$ and $\delta^{18}OSO_4$ values show limited variations. However, the $\delta^{34}SSO_4$ and $\delta^{18}OSO_4$ values from sulfate from wells that encountered isolated mine waters varied along a positive trend to higher values than oxygenated waters on the site (Fig. 16). In addition, the slope of this trend, ~½, is similar to the trend documented by Zak *et al.* (1980) for bacterial sulfate reduction in modern seafloor sediments, reflecting isotopic enrichment in residual sulfate accompanying the removal of isotopically light sulfide. Concentrations of dissolved gas rich in hydrogen, methane, and ethane attest to the reducing conditions in the mine waters (Hamlin & Alpers 1996). Similar conclusions can be reached for mine waters associated with the abandoned Fontana and Hazel Creek mines, which exploited pyrrhotite-rich massive sulfide deposits. Most of the $\delta^{34}SSO_4$ values for dissolved sulfate in mine waters from those mines are indistinguishable from the $\delta^{34}S$ of ore sulfide minerals; however, one sample from a caved adit filled with leaf litter and other abundant organic matter has significantly higher $\delta^{34}SSO_4$ and $\delta^{18}OSO_4$ values (Fig. 16), suggesting that the abundant organic matter is promoting local bacterial sulfate reduction (Seal *et al.* 1998). It should be noted that in geochemical settings that include sedimentary rocks, such as at the Penn, Fontana, and Hazel Creek mines, the $\delta^{34}S$ of sedimentary sulfide can be highly variable; thus, the combination of $\delta^{34}SSO_4$ and $\delta^{18}OSO_4$ values is essential for distinguishing bacterial sulfate reduction from an isotopically heterogeneous source of sedimentary sulfide minerals.

Dilution and fluid mixing may play important roles in determining the stable-isotope characteristics of mine

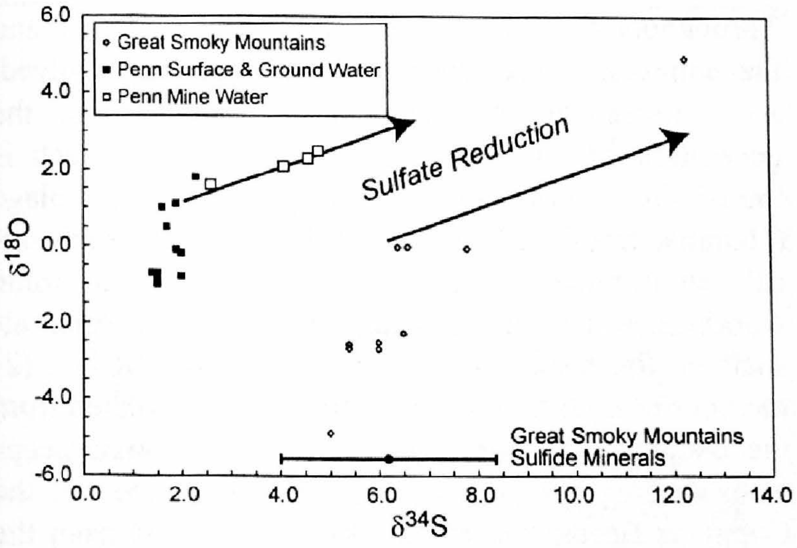

FIG. 16. Sulfur and oxygen isotopic composition of dissolved sulfate from the Penn mine, California (Hamlin & Alpers 1996), and the Fontana and Hazel Creek mines in Great Smoky Mountains National Park, North Carolina (Seal *et al.* 1998). The trend to higher $\delta^{34}S$ and $\delta^{18}O$ values of the sulfate reflects bacterial sulfate reduction. The slope plotted, 1/2.1, is the same as the slope documented by Zak *et al.* (1980) for modern marine sediments. "Mine water" from the Penn mine refers to anoxic waters from the flooded mine workings. The mean $\delta^{34}S$ and standard deviation (2σ) of ore sulfide minerals from the Fontana and Hazel Creek mines are indicated by the circle and bar at the bottom. All isotopic values are in permil (VSMOW or VPDB).

waters. The strength of stable isotopes in unraveling the effects of mixing are well illustrated by a recent study of mine drainage in the Freiberg mining district, Germany. Haubrich & Tichomirowa (2002) sampled atmospheric precipitation, shallow seeps and groundwater above mine workings, stagnant mine waters, and flowing mine waters associated with a polymetallic vein system in the district. The stagnant mine waters, which probably represent end-member acid mine drainage, have $\delta^{34}SSO_4$ values that are indistinguishable from the $\delta^{34}S$ values of source ore-sulfide minerals, as would be expected (Fig. 17a). The $\delta^{18}OSO_4$ values are consistent with those expected for sulfide oxidation dominated by a water source for the oxygen in the resulting sulfate. In contrast, the shallow ground and seep waters have $\delta^{34}SSO_4$ and $\delta^{18}OSO_4$ values that are significantly higher than the stagnant mine waters (Fig. 17a). Haubrich & Tichomirowa (2002) interpreted these values in terms of an atmospheric oxygen source, although local oxidation of host-rock sulfide minerals may also contribute to this end-member sulfate source. The sulfate concentrations of the precipitation that they sampled ranged from 2.4 to 3.9 mg L^{-1}, although they reported values as high as 202 mg L^{-1} from previous samplings, compared to the sulfate concentration of the shallow groundwaters and seep waters, which ranged from 112 to 150 mg L^{-1}. Regardless of the ultimate source of the shallow groundwaters, the flowing mine waters clearly fall along a mixing trend between the shallow groundwaters and the stagnant mine-waters in terms of their $\delta^{34}SSO_4$ and $\delta^{18}OSO_4$ values (Fig. 17a). The mixing trend is less evident in a plot of $\delta^{18}OSO_4$ and $\delta^{18}OH_2O$ variations because the $\delta^{18}OH_2O$ values are subject to seasonal variations related to the temperature of precipitation (Fig. 17b). Precipitation samples were collected on a monthly basis for a year, whereas groundwaters and flowing mine-waters were samples on several occasions spanning several months. The differences between Figures 17a and b highlight how interpretations of the environment of sulfide oxidation on the basis $\delta^{18}OSO_4$ and $\delta^{18}OH_2O$ variations can lead to erroneous conclusions if the effects of dilution or fluid mixing are not taken into account. Mixing of two sulfate sources can result in a variety of trajectories in Figure 17b, but dilution of a sulfate-rich water with a sulfate-poor water can cause significant increase or decrease in $\delta^{18}OH_2O$ depending upon seasonal variations in the isotopic composition of the sulfate-poor water, without producing variations in the $\delta^{18}OSO_4$ values. The significance of evaporation in the geochemical evolution of the Freiberg mine waters is difficult to assess because Haubrich & Tichomirowa (2002) did not report data for δDH_2O.

Oxygen-isotope exchange between sulfate and water, as discussed above, is only expected to occur to a significant degree in mine-drainage environments under conditions of elevated temperature and extremely low pH. The kinetic studies discussed above indicate that the exchange rate is strongly dependent upon temperature and pH (Fig. 8). The rate of isotopic exchange at the pH and temperature conditions "typical" of acid mine-drainage settings is sufficiently slow (half-life >10 years) that little or no oxygen-isotope equilibration would be expected between sulfate and water. However, at Iron Mountain (California), extreme conditions of temperature and pH have been identified in the mine workings, wherein the pH of mine waters reaches –3.6 and temperature is up to 47 °C at the source; the pH of discharge from the Richmond portal at Iron Mountain ranges between 0.0 and 1.5 (Alpers *et al.* 1994b, Nordstrom & Alpers 1999b, Nordstrom *et al.* 2000). Under the most extreme conditions, the half-life of the exchange reaction is of the order of a day (Fig. 8). Thus, oxygen isotopic exchange between aqueous sulfate and water may be an important process in the most extreme conditions at Iron Mountain. At 50 °C, SO_4^{2-} in equilibrium with a water with $\delta^{18}O = -10$ ‰ should have $\delta^{18}O = 15.4$ ‰.

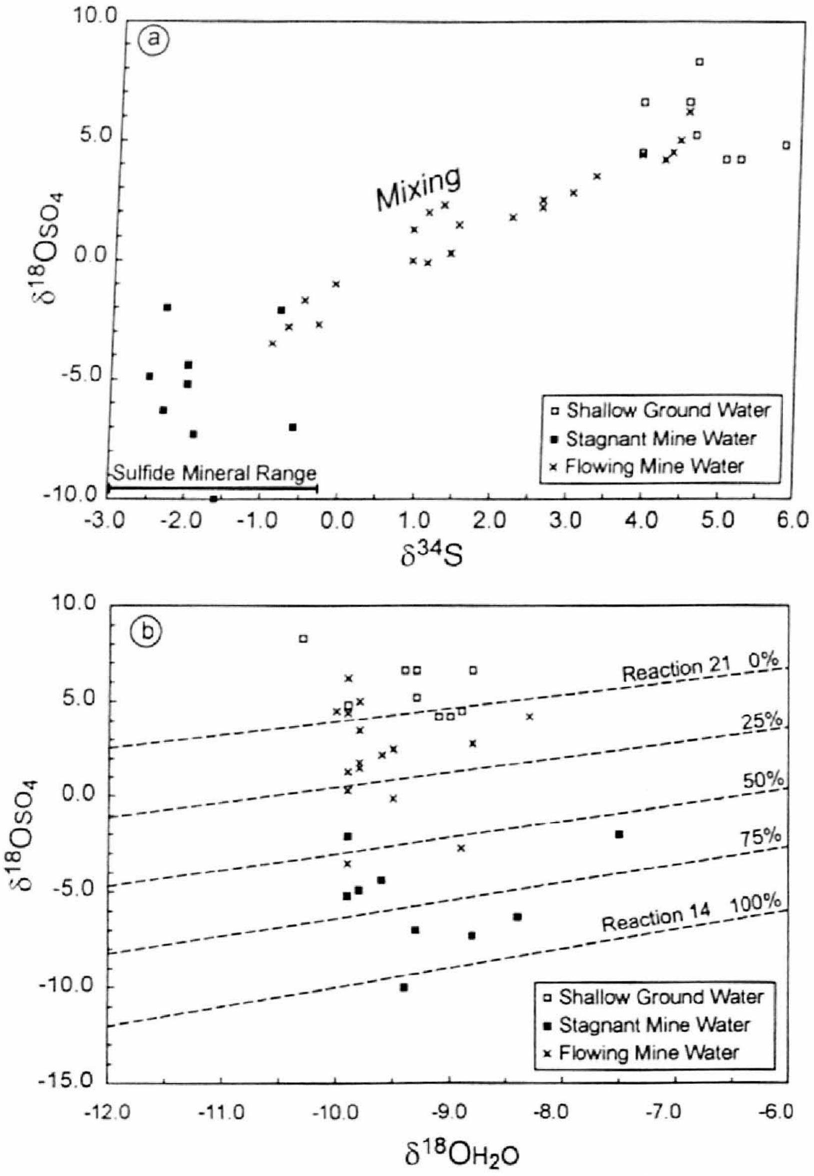

FIG. 17. Stable-isotope data for mine drainage from the Freiberg mining district, Germany (Haubrich & Tichomirowa 2002). All isotopic values in permil (VSMOW or VPDB). (**a**) Sulfur- and oxygen-isotope values of dissolved sulfate. The range of $\delta^{34}S$ values for ore sulfide minerals is shown at the bottom; (**b**) oxygen-isotope values of dissolved sulfate and water. Dashed lines represent the inferred relative proportions of Reactions (14) and (21).

Alpers *et al.* (1996) reported $\delta^{18}O$ values in aqueous sulfate and efflorescent salts from Iron Mountain to range from 10 to 15 ‰, indicating partial (80%) to total isotopic equilibration with the highly acidic mine waters.

DIVERSE ENVIRONMENTS AT THE ABANDONED ELIZABETH COPPER MINE

The abandoned Elizabeth mine in the Vermont copper belt is currently on the National Priorities (Superfund) list of the U.S. Environmental Protection Agency (Hathaway *et al.* 2001). The site has experienced a long mining history, from discovery in 1799 to final closure in 1958 (Kierstead 2001). Throughout this history, the commodities sought and the mining and ore-processing methods have evolved. As a result, the geochemical environments for the generation of mine drainage are diverse, but each is linked by a common ore and gangue assemblage (Hammarstrom *et al.* 1999, 2001). Distinct hydrochemical environments include (1) the flooded mine workings, which only discharge through an artesian air shaft on the banks of the Ompompanoosuc River; (2) the South Pit lake, which is hydrologically isolated from the underground workings; (3) oxic to suboxic seeps from shallow waste-rock piles at the headwaters of the Copperas Brook watershed; (4) anoxic seeps from the base of the thick tailings pile; (5) miscellaneous surface waters, which include a shallow pond on top of the tailings pile; and (6) Copperas Brook before it empties into the Ompompanoosuc River lake (Fig. 18; Seal *et al.* 2001, Seal & Hammarstrom's Chapter 2 in this Volume). Copperas Brook receives waters from all of the environments above, except from the artesian air vent and the South Pit. Flow in the lower reaches of Copperas Brook is dominated by snow melt and rain in the spring and early summer. Surface flow diminishes greatly as summer progresses, and most of the flow in the brook comes from seepage that exits at the base of the tailings pile at a fairly constant rate throughout the year.

Considerable uncertainty remains regarding the relative contributions of groundwaters and surface waters, and their residence times, particularly for groundwaters in the thick tailings pile and in the flooded mine workings. Another significant difference among these environments is the suboxic and anoxic evolution of waters in the underground workings and in the tailings pile, whereas all of the other waters evolve predominantly under oxidized conditions. The anoxic nature and corresponding dominance of dissolved ferrous iron in the seeps emerging from the tailings pile contributes to their near-neutral pH (6.0 to 7.0). Upon contact with the atmosphere, however, the ferrous iron oxidizes and pH rapidly drops below 3. Likewise, water emerging from the artesian air vent that drains the flooded mine workings is suboxic to anoxic, with pH typically varying between 4.5 and 5.5. The other waters at the site are acidic, with pH generally ranging from 2.0 to 4.0, and total dissolved solids ranging from 200 to 3700 mg L^{-1}. Stable-isotope data can provide important insights into the complexity of the mine waters at the minesite.

Seasonal variations in $\delta^{18}O$ of the water issuing from the artesian air vent and of the water from Copperas Brook prior to its confluence with the Ompompanoosuc River, for the period from October 1998 to September 1999, reflect the water sources and provide insights to the residence times (Fig. 19).

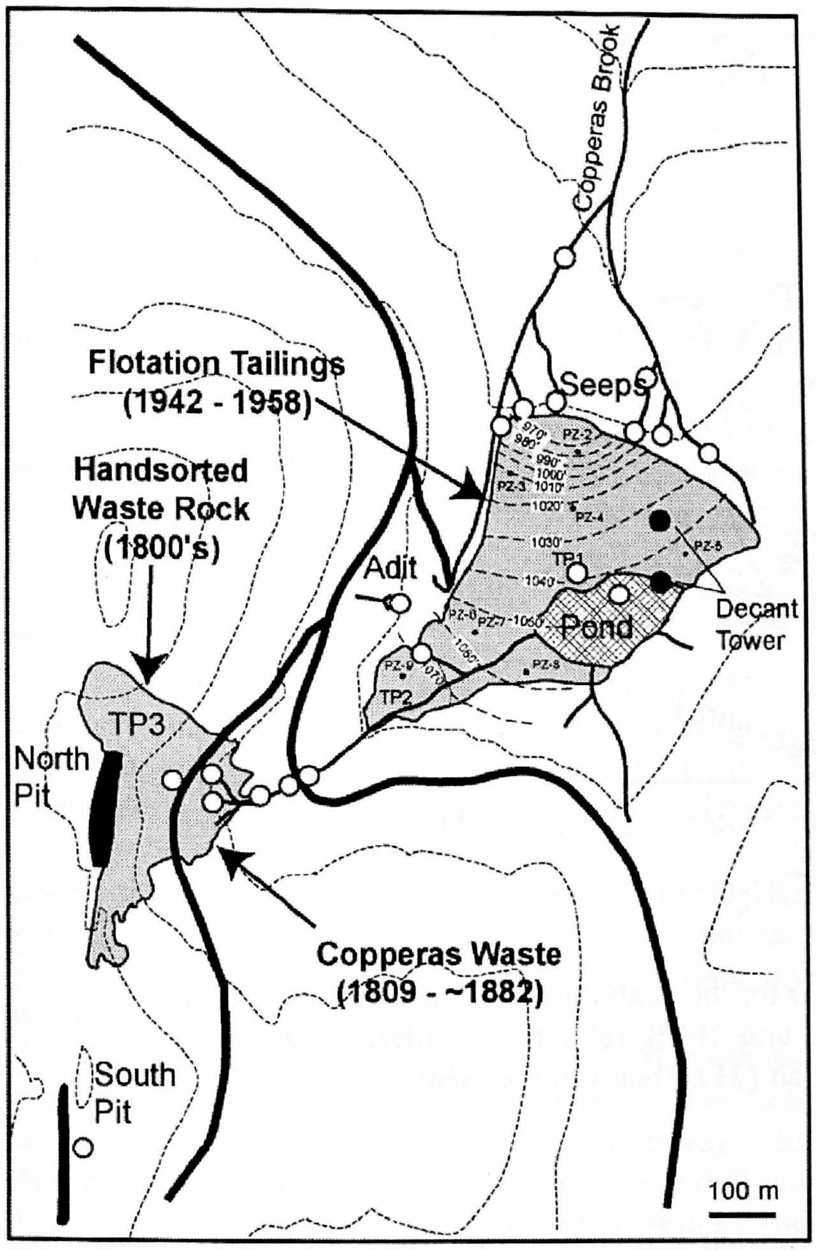

FIG. 18. Map of the abandoned Elizabeth copper mine, Vermont (modified from Seal *et al.* 2001). The South Pit is filled by a lake with no known connection to the underground mine workings. The North Pit is connected to underground mine workings and the associated mine pool, which discharges through the artesian air vent (not shown) located approximately 1.5 km north of the North Pit, on the banks of the Ompompanoosuc River. The waste-rock pile, TP3, is shallow and well-oxygenated, whereas the tailings piles, TP1 and TP2, are thicker, and develop an anoxic water column with depth. The shallow pond on TP1 flows through a decant system that discharges at the northeastern corner of TP1. The contours are in feet and represent the water table at depth in the tailings piles.

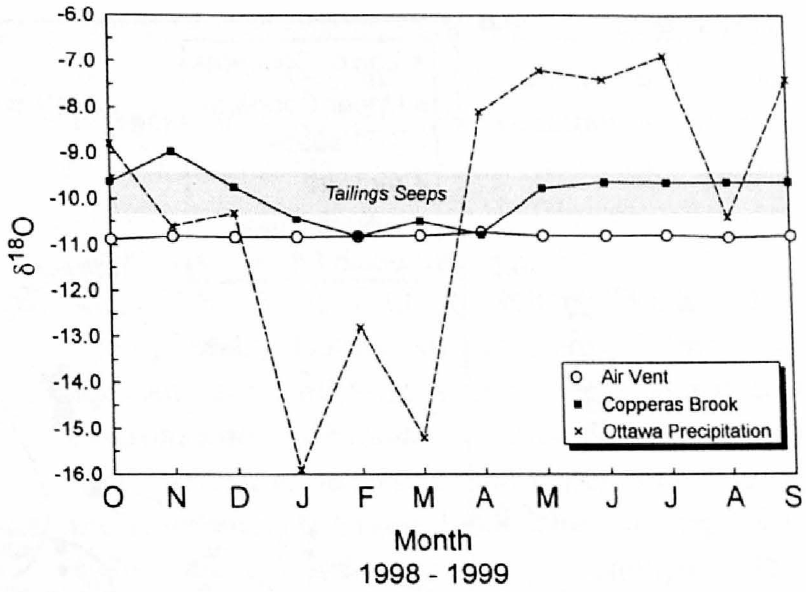

FIG. 19. Variations of $\delta^{18}O$ by month for drainage from Copperas Brook and the artesian air vent at the abandoned Elizabeth mine, and for mean monthly precipitation at Ottawa, Ontario (I.A.E.A./W.M.O. 2001). Note the lack of variations in waters from the Air Vent, reflecting a residence time of waters greater than one year. Note that the seasonal variations of waters in Copperas Brook are dampened relative to Ottawa precipitation, reflecting the residence time of water in the watershed. During the warm summer months, surface flow diminishes, and flow in the Copperas Brook watershed is dominated by waters seeping from the base of the tailings pile. All isotopic values are in permil (VSMOW).

For comparison, the variations in the monthly average $\delta^{18}O_{H_2O}$ of precipitation for the same period at the gauging station in Ottawa, 325 km to the northwest of Elizabeth, and of the Global Network of Isotopes in Precipitation are also presented in Figure 19 (IAEA/WMO 2001). The $\delta^{18}O_{H_2O}$ values of the precipitation show typical variations associated with seasonal changes in the temperature of precipitation; the winter months have the lowest values and the summer months have the highest values. The $\delta^{18}O_{H_2O}$ values of the air vent and Copperas Brook drainage fall between the extremes observed in precipitation at Ottawa, suggesting that the isotopic composition of precipitation at Ottawa provides a reasonable approximation for that in central Vermont. The more restricted variations in Vermont reflect the dampening effects of water storage in the catchment areas of the air vent and Copperas Brook. More important, the lack of variation in the $\delta^{18}O_{H_2O}$ of the air vent (beyond the analytical uncertainty of ±0.2 ‰) indicates that water in the mine pool has a residence time that is greater than one year; otherwise, seasonal variations would be expected. The variations observed for Copperas Brook are more complex. The variations from late fall through winter into spring reflect the dominance of surface-water flow in the watershed. The lack of variation from May through September, which are the dry summer months, represents the period when most of the flow in Copperas Brook is contributed by seepage from the tailings pile. As with the air vent, the lack of variation in

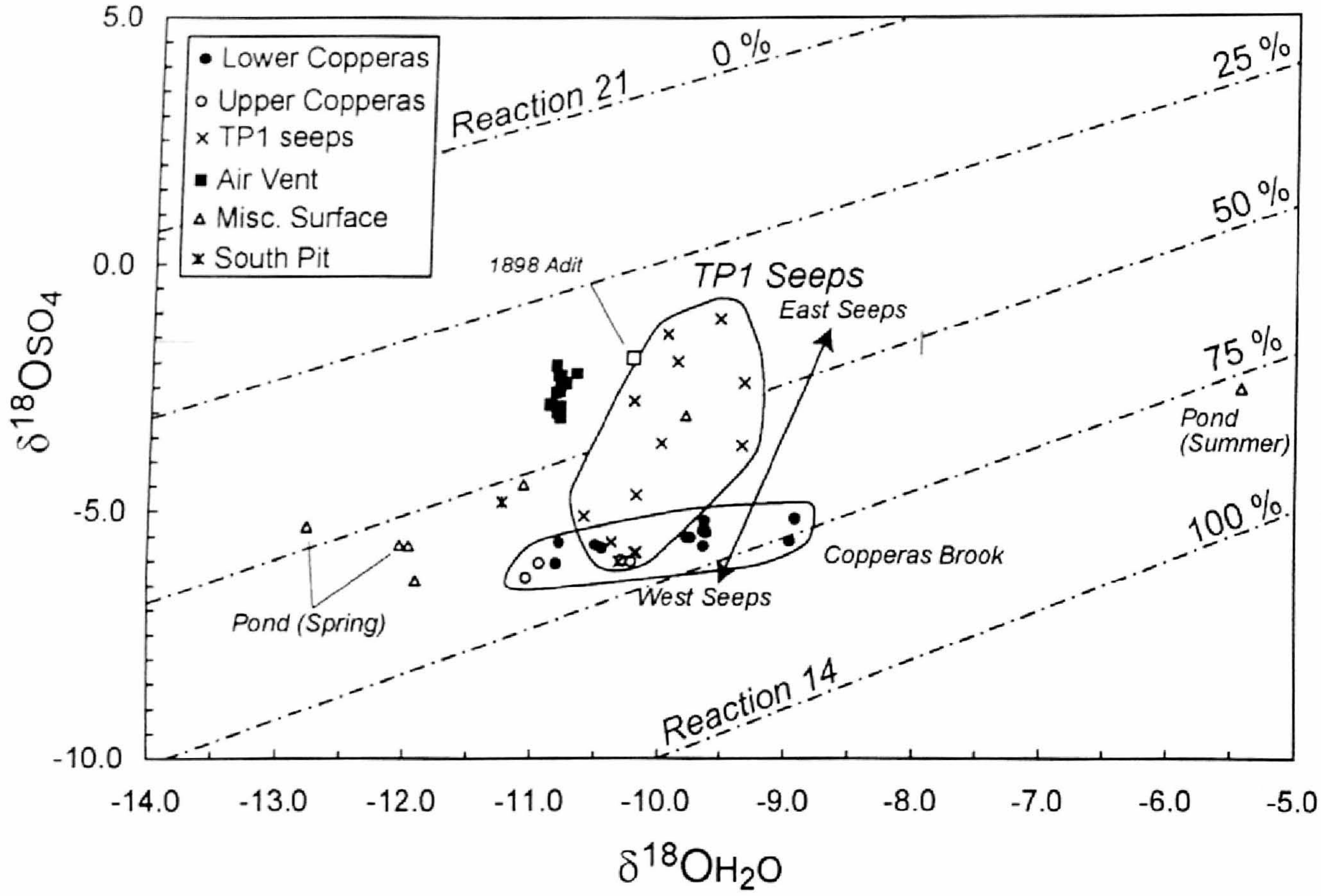

FIG. 20. Variations of $\delta^{18}OSO_4$ and $\delta^{18}OH_2O$ for the abandoned Elizabeth copper mine, Vermont. The lines marked 0, 25, 50, 75, and 100% refer to the inferred extent of participation of Reaction (14) versus Reaction (21). Data from R. Seal (unpub., 2003). All isotopic values are in permil (VSMOW).

$\delta^{18}OH_2O$ suggests that the residence time of water in the tailings pile is greater than a year.

The $\delta^{18}OSO_4$ and $\delta^{18}OH_2O$ values confirm the conclusions reached on the basis of the seasonal variations of $\delta^{18}OH_2O$ values for the air vent and Copperas Brook, and provide additional insights about the environments of sulfide oxidation at Elizabeth (Fig. 20). For the air vent, the $\delta^{18}OSO_4$ values show a limited range similar to that of the $\delta^{18}OH_2O$ values, which reflects the homogenizing effects of a long residence time for the waters in the mine workings. The high $\delta^{18}OSO_4$ values suggest that a significant amount of atmospheric oxygen is incorporated into the sulfate, which implies that most of the sulfide oxidation in the mine workings is occurring near the surface of the mine pool. The seeps emerging from the base of the tailings pile span the range of $\delta^{18}OSO_4$ values, with the highest values comparable to those from the air vent, and the lowest values comparable to those from lower and upper reaches of Copperas Brook. The highest $\delta^{18}OSO_4$ values from the seeps come from the eastern seeps, and the lowest values come from the western seeps. The range suggests variable contributions of atmospheric oxygen (Reaction 21) and water (Reactions 14 and 21) to the sulfate. The eastern seeps have shorter flowpaths and shallower thicknesses of overlying tailings than the western seeps (Fig. 18), which are consistent with the greater importance of atmospheric oxygen in reactions to produce sulfate in the east. The similarity of the isotopic composition of the western seeps and the range of values observed in Copperas Brook suggests that discharge from the tailings is dominated by the western seeps. The upper and lower reaches of Copperas Brook show a limited range of $\delta^{18}OSO_4$ values, with a wider range of $\delta^{18}OH_2O$ values, consistent with seasonal variations in $\delta^{18}OH_2O$. The range of $\delta^{18}OSO_4$ values implies that most of the oxygen in the sulfate is derived from water, as described by Reaction (14). The $\delta^{18}OH_2O$ values of the shallow pond on top of the tailings pile clearly show the effects of evaporation. During spring, the values are at their lowest (–12.8 to –12.0 ‰), but during the summer, they are up to –5.4 ‰ (Fig. 20).

SUMMARY

The underlying strength of applying stable isotopes to understanding geochemical processes associated with mine waters and mine wastes is that the elements which have traditionally been the mainstays of stable-isotope geochemistry, namely hydrogen, oxygen, sulfur, carbon, and nitrogen, are the key ingredients in the formation of acid mine drainage and in the processing of gold ores by use of cyanide. The greatest insights will be obtained from studies in which the results from multiple stable-isotope systems are integrated with other geochemical data. For studies concerned with acid drainage, analyses should include, at a minimum, δDH_2O, $\delta^{18}OH_2O$, $\delta^{18}OSO_4$, and $\delta^{34}SSO_4$ for waters, and $\delta^{34}S$ for source and products solids. Most processes associated with the stable-isotope geochemistry of mine waters and related solids result from kinetically controlled processes rather than equilibrium processes. Among these processes are the evaporation of water, the oxidation of sulfide minerals, and the bacterial reduction of sulfate.

The two key findings reported in this chapter are that:

(1) The rate of oxygen isotopic exchange between dissolved sulfate and water is sufficiently fast to play an important role in source-area processes where pH is anomalously low and temperatures are slightly elevated, such as in the mine workings of Iron Mountain, California; however, under conditions of "typical" acid mine drainage, oxygen-isotope exchange is unlikely because of the short residence times of sulfate and water.

(2) The sulfate formed from the oxidation of pyrite and other sulfide minerals can derive its oxygen from both water and molecular oxygen. The pathways for derivation from molecular oxygen may be different from that commonly reported in the literature; the pathway may involve dissolved sulfite, which exhibits extremely rapid oxygen-isotope exchange with water and which may form as an intermediate step during oxidation, prior to the oxidation to sulfate.

ACKNOWLEDGEMENTS

The preparation of this manuscript benefited from discussions with Charles N. Alpers, D. Kirk Nordstrom, J. Donald Rimstidt, Robert O. Rye, and James J. Rytuba. The manuscript also benefited from reviews by John L. Jambor, Craig A. Johnson, Robert O. Rye, and Gregory A. Wandless. Kathleen Johnson, Coordinator for the USGS Mineral Resources Program, provided support for the preparation of this paper, and Nadine M. Piatak assisted in literature searches.

REFERENCES

ALPERS, C.N., BLOWES, D.W., NORDSTROM, D.K. & JAMBOR, J.L. (1994a): Secondary minerals and acid mine drainage. *In* Environmental Geochemistry of Sulfide Mine-Wastes (J.L. Jambor & D.W. Blowes, eds.). *Mineral. Assoc. Can. Short Course Vol.* **22**, 247-270.

ALPERS, C.N., NORDSTROM, D.K. & THOMPSON, J.M. (1994b): Seasonal variations of Zn/Cu ratios in acid mine water from Iron Mountain, California. *In* Environmental Geochemistry of Sulfide Oxidation (C.N. Alpers & D.W. Blowes, eds.). *Am. Chem. Soc. Symp. Ser.* **550**, 324-344.

ALPERS, C.N., RYE, R.O. & NORDSTROM, D.K. (1996): Stable isotope systematics of S and O in aqueous and mineral sulfates from hyper-acid environments. Chapman Conference on crater lakes, terrestrial degassing, and hyper-acid fluids in the environment, Crater Lake, Oregon, Sept. 4-9, 1996. *Am. Geophys. Union*, Washington DC, (abs.).

ALPERS, C.N., NORDSTROM, D.K. & WHITE, L.D. (1988): Solid solution properties and deuterium fractionation factors for hydronium-bearing jarosites from acid mine waters. *EOS* **69**, 1480-1481.

BACHINSKI, D.J. (1969): Bond strength and sulfur isotopic fractionation in coexisting sulfides. *Econ. Geol.* **64**, 56-65.

BAO, H. & KOCH, P.L. (1999): Oxygen isotope fractionation in ferric oxide – water systems: low temperature synthesis. *Geochim. Cosmochim. Acta* **63**, 599-613.

BASOLO, F. & PEARSON, R.G. (1967): *Mechanisms of Inorganic Reaction – A Study of Metal Complexes in Solution*, 2nd ed. John Wiley & Sons, New York.

BERNER, R.A. (1985): Sulphate reduction, organic matter decomposition and pyrite formation. *Phil. Trans. Roy. Soc. London* **A315**, 25-38

BETTS, R.H. & VOSS, R.H. (1970): The kinetics of oxygen exchange between sulfite ion and water. *Can. J. Chem.* **48**, 2035-2041.

BIRD, M.I., ANDREW, A.S., CHIVAS, A.R. & LOCK, D. (1989): An isotopic study of surficial alunite in Australia: 1. Hydrogen and sulfur isotopes. *Geochim. Cosmochim. Acta* **53**, 3223-3238.

BIRD, M.I., LONGSTAFFE, F.J., FYFE, W.S., TAZAKI, K. & CHIVAS, A.R. (1994): Oxygen-isotope fractionation in gibbsite: synthesis experiments versus natural samples. *Geochim. Cosmochim. Acta* **58**, 5267-5277.

CANFIELD, D.E. (2001): Biogeochemistry of sulfur isotopes. *In* Stable Isotopes (J.W. Valley & D.R. Cole, eds.). *Rev. Mineral. Geochem.* **43**, 607-636.

CARMODY, R.W., PLUMMER, L.N., BUSENBERG, E. & COPLEN, T.B. (1998): Methods for collection of dissolved sulfate and sulfide and analysis of their sulfur isotopic composition. *U.S. Geol. Surv. Open-File Report* **97-234**.

CHAMBERS, L.A. & TRUDINGER, P.A. (1979): Microbiological fractionation of stable sulfur isotopes: A review and critique. *Geomicrobiol. J.* **1**, 249-293.

CHIBA, H. & SAKAI, H. (1985): Oxygen isotope exchange rate between dissolved sulfate and water at hydrothermal temperatures. *Geochim. Cosmochim. Acta* **49**, 993-1000.

CHIBA, H., KUSAKABE, M., HIRANO, S.-I., MATSUO, S. & SOMIYA, S. (1981): Oxygen isotope fractionation factors between anhydrite and water from 100 to 550 °C. *Earth Planet. Sci. Lett.* **53**, 55-62.

CLAYPOOL, G.E., HOLSER, W.T., KAPLAN, I.R., SAKAI, H. & ZAK, I. (1980): The age curves of sulfur and oxygen isotopes in marine sulfate and their mutual interpretations. *Chem. Geol.* **28**, 199-260.

COMPEAU, G.C. & BARTHA, R. (1985): Sulfate-reducing bacteria: principal methylators of mercury in anoxic estuarine sediment. *Appl. Environ. Microbiol.* **50**, 498-502.

CRAIG, H. (1961): Isotopic variations in meteoric waters. *Science* **133**, 1702-1703.

CRAIG. H. & GORDON, L.I. (1965): Deuterium and oxygen-18 variations in the ocean and marine atmosphere. Symposium on Marine Geochemistry, Narragansett Marine Laboratory. *University Rhode Island Pub.* **3**, 277-374.

DANSGAARD, W. (1964): Stable isotopes in precipitation. *Tellus* **16**, 436-468.

DOLE, M., LANE, G.A., RUDD, D.P. & ZAUKELIES, D.A. (1954): Isotopic composition of atmospheric oxygen and nitrogen. *Geochim. Cosmochim. Acta* **6**, 65-78.

EBERT, S.W. & RYE, R.O. (1997): Secondary precious metal enrichment by steam-heated fluids in the Crofoot-Lewis hot spring gold-silver deposit and relation to paleoclimate. *Econ. Geol.* **92**, 578-600.

EPSTEIN, S. & MAYEDA, T. (1953): Variations in the O^{18} content of waters from natural sources. *Geochim. Cosmochim. Acta* **4**, 213-224.

FIELD, C.W. (1966): Sulfur isotopic method for discriminating between sulfates of hypogene and supergene origin. *Econ. Geol.* **61**, 1428-1435.

FONTES, J.C. & GONFIANTINI, R. (1967): Fractionnement isotopique de l'hydrogéne dans l'eau de cristallisation du gypse. *Comptes Rendus Acad. Sci. Paris* **265**, 4-6.

FRIEDMAN, I. (1953): Deuterium content of natural water and other substances. *Geochim. Cosmochim. Acta* **4**, 89-103.

FRITZ, P., BASHARMAL, G.M., DRIMMIE, R.J., IBSEN, J. & QURESHI, R.M. (1989): Oxygen isotope exchange between sulphate and water during bacterial reduction of sulphate. *Chem. Geol.* **79**, 99-105.

GARLICK, G.D. (1969): The stable isotopes of oxygen. *In* Handbook of Geochemistry **8B** (K.H. Wedepohl, ed.). Springer, New York.

GARRELS, R.M. & THOMPSON, M.E. (1960): Oxidation of pyrite by iron sulfate solutions. *Am. J. Sci.* **258A**, 57-67.

GAT, J. (1981): Lakes. *In* Stable Isotope Hydrology: Deuterium and Oxygen-18 in the Water Cycle. *I.A.E.A. Tech. Report Ser.* **210**, 203-222.

GAVELIN, S., PARWEL, A. & RYHAGE, R. (1960): Sulfur isotope fractionation in sulfide mineralization. *Econ. Geol.* **55**, 510-530.

GIESEMANN, A., JÄGER, H.-J., NORMAN, A.L., KROUSE, H.R. & BRAND, W.A. (1994): On-line sulfur-isotope determination using an elemental analyzer coupled to a mass spectrometer. *Anal. Chem.* **66**, 2816-2819.

GILATH, C. & GONFIANTINI, R. (1983): Lake dynamics. *In* Guidebook on Nuclear Techniques in Hydrology. *I.A.E.A. Tech. Report Ser.* **91**, 129-161.

GOLDHABER, M.B. (1983): Experimental study of metastable sulfur oxyanion formation during pyrite oxidation at pH 6-9 and 30 °C. *Am. J. Sci.* **283**, 193-217.

GOLDHABER, M.B. & KAPLAN, I.R. (1975): Controls and consequences of sulfate reduction rates in recent marine sediments. *Soil Sci.* **119**, 42-55.

GONFIANTINI, R. (1986): Environmental isotopes in lake studies. *In* Handbook of Environmental Geochemistry (P. Fritz & J.Ch. Fontes, eds.) **2**, 113-168.

GONFIANTINI, R. & FONTES, J.C. (1963): Oxygen isotopic fractionation in the water of crystallization of gypsum. *Nature* **200**, 644-646.

GOULD, W.D., McCREADY, R.G.L., RAJAN, S. & KROUSE, H.R. (1990): Stable isotope composition of sulphate produced during bacterial oxidation of various metal sulphides. *In* Biohydrometallurgy 1989, Proceedings International Symposium on Biohydrometallurgy (J. Smalley, R.G.L. Ready & P. Wichlacz, eds.). *CANMET Spec. Publ.* **89-10**, 81-91. Natural Resources Canada, Ottawa, Ontario.

HAMLIN, S.N. & ALPERS, C.N. (1995): Hydrogeology and geochemistry of acid mine drainage in ground water in the vicinity of Penn Mine and Camanche Reservoir, Calaveras County, California:

First-year summary. *U.S. Geol. Surv. Water-Resources Investig. Report* **94-4040**.

HAMLIN, S.N. & ALPERS, C.N. (1996): Hydrogeology and geochemistry of acid mine drainage in ground water in the vicinity of Penn Mine and Camanche Reservoir, Calaveras County, California: Second-year summary, 1992-93. *U.S. Geol. Surv. Water-Resources Investig. Report* **96-4257**.

HAMMARSTROM, J.M., MEIER, A.L, JACKSON, J.C., BARDEN, R., WORMINGTON, P.J., WORMINGTON, J.D. & SEAL, R.R. II (1999): Characterization of mine waste at the Elizabeth copper mine, Orange County, Vermont. *U.S. Geol. Surv. Open-File Report* **99-564**.

HAMMARSTROM, J.M., SEAL, R.R. II, OUIMETTE, A.P. & FOSTER, S.A. (2001): Sources of metals and acidity at the Elizabeth and Ely mines, Vermont: Geochemistry and mineralogy of solid mine waste and the role of secondary minerals in metal recycling. *In* Environmental Geochemistry and Mining History of Massive Sulfide Deposits in the Vermont Copper Belt (J.M. Hammarstrom & R.R. Seal II, eds.). *Soc. Econ. Geol. Field Trip Guidebook Ser.* **35**, Pt. 2, 213-248.

HATHAWAY, E.M., LOVELY, W.P., ACONE, S.E. & FOSTER, S. (2001): The other side of mining: Environmental assessment and the process for developing a cleanup approach for the Elizabeth mine. *In* Environmental Geochemistry and Mining History of Massive Sulfide Deposits in the Vermont Copper Belt (J.M. Hammarstrom & R.R. Seal II, eds.). *Soc. Econ. Geol. Field Trip Guidebook Ser.* **35**, Pt. 2, 277-293.

HAUBRICH, F. & TICHOMIROWA, M. (2002): Sulfur and oxygen isotope geochemistry of acid mine drainage – the polymetallic sulfide deposit "Himmelfahrt Fundgrube" in Freiberg (Germany). *Isotopes Environ. Health Studies* **38**, 121-138.

HEINZINGER, K. (1969): Ein wasserstoffisotopieeffekt im $CuSO_4{\cdot}5H_2O$. *Zeits. Naturforsch.* **24a**, 1502-1511.

HOERING, T.C. & KENNEDY, J.W. (1957): The exchange of oxygen between sulfuric acid and water. *J. Am. Chem. Soc.* **79**, 56-60.

HOLT, B.D., KUMAR, R. & CUNNINGHAM, P.T. (1981): Oxygen-18 study of the aqueous-phase oxidation of sulfur dioxide. *Atmos. Environ.* **15**, 557-566.

HOLT, B.D., CUNNINGHAM, P., ENGELKEMEIR, A.G., GRACZYK, D.G. & KUMAR, R. (1983): Oxygen-18 study of the nonaqueous-phase oxidation of sulfur dioxide. *Atmos. Environ.* **17**, 625-632.

I.A.E.A./W.M.O. (2001): Global Network of Isotopes in Precipitation. The GNIP Database. URL: http://isohis.iaea.org

JAMBOR, J.L. (1994): Mineralogy of sulfide-rich tailings and their oxidation products. *In* Environmental Geochemistry of Sulfide Mine-Wastes (J.L. Jambor & D.W. Blowes, eds.). *Mineral. Assoc. Can. Short Course Vol.* **22**, 59-102.

JAMBOR, J.L, NORDSTROM, D.K. & ALPERS, C.N. (2000): Metal-sulfate salts from sulfide mineral oxidation. *In* Sulfate Minerals – Crystallography, Geochemistry, and Environmental Significance (C.N. Alpers, J.L. Jambor & D.K. Nordstrom, eds.). *Rev. Mineral. Geochem.* **40**, 305-350.

JOHNSON, C.A. (1996): Determination of $^{15}N/^{14}N$ and $^{13}C/^{12}C$ in solid and aqueous cyanides. *Anal. Chem.* **68**, 1429-1431.

JOHNSON, C.A., GRIMES, D.J. & RYE, R.O. (1998): Accounting for cyanide and its degradation products at three Nevada gold mines: constraints from stable C- and N-isotopes. *U.S Geol. Surv. Open-File Report* **98-753**.

JOHNSON, C.A., GRIMES, D.J. & RYE, R.O. (2000): Fate of process solution cyanide and nitrate at three Nevada gold mines inferred from stable carbon and nitrogen isotope measurements. *Trans. Inst. Mining Metall.* **C109**, 68-78.

KAPLAN, I.R. & HULSTON, J.R. (1966): The isotopic abundance and content of sulfur in meteorites. *Geochim. Cosmochim. Acta* **30**, 479-496.

KELLY, D.P. (1982): Biochemistry of the chemolithotrophic oxidation of inorganic sulphur. *Phil. Trans. Roy. Soc. London* **B298**, 499-528.

KIERSTEAD, M.A. (2001): History and historical resources of the Vermont copper belt. *In* Environmental Geochemistry and Mining History of Massive Sulfide Deposits in the Vermont Copper Belt (J.M. Hammarstrom & R.R. Seal II, eds.). *Soc. Econ. Geol. Field Trip Guidebook Ser.* **35**, Pt. 2, 165-192.

KORNEXL, B.E., GEHRE, M., HÖFLING, R. & WERNER, R.A. (1999): On-line $\delta^{18}O$ measurement of organic and inorganic substances. *Rapid Commun. Mass Spectrom.* **13**, 1685-1693.

KROOPNICK, P. & CRAIG, H. (1972): Atmospheric oxygen: isotopic composition and solubility fractionation. *Science* **175**, 54-55.

KROUSE, H.R., GOULD, W.D., McCREADY, R.G.L. & RAJAN, S. (1991): ^{18}O incorporation into sulphate during bacterial oxidation of sulphide minerals and the potential for oxygen isotope exchange between O_2, H_2O and oxidized sulphur intermediates. *Earth Planet. Sci. Lett.* **107**, 90-94.

KUSAKABE, M. & ROBINSON, B.W. (1977): Oxygen and sulfur isotope equilibria in the $BaSO_4$–HSO_4^-–H_2O system from 110 to 350 °C with applications. *Geochim. Cosmochim. Acta* **41**, 1033-1040.

LLOYD, R.M. (1967): Oxygen-18 composition of oceanic sulfate. *Science* **156**, 1228-1231.

LLOYD, R.M. (1968): Oxygen isotope behavior in the sulfate–water system. *J. Geophys. Research* **73**, 6099-6110.

LOWSON, R.T. (1982): Aqueous pyrite oxidation by molecular oxygen. *Chem. Rev.* **82**, 461-497.

LUTHER, G.W. II (1987): Pyrite oxidation and reduction –molecular orbital theory considerations. *Geochim. Cosmochim. Acta* **51**, 3193-3199.

MACNAMARA J. & THODE, H.G. (1950): Comparison of the isotopic constitution of terrestrial and meteoritic sulphur. *Phys. Rev.* **78**, 307.

MAJZOUB, M. (1971): Fractionnement en oxygene-18 et eu deuterium entre l'eau et sa vapeur. *J. Chim. Phys.* **197**, 1423-1436.

McKIBBEN, M.A. & BARNES, H.L. (1986): Oxidation of pyrite in low temperature acidic solutions: rate laws and surface textures. *Geochim. Cosmochim. Acta* **50**, 1509-1520.

MIZUTANI, Y. & RAFTER, T.A. (1969a): Oxygen isotopic composition of sulphates, Part 3: Oxygen isotopic fractionation in the bisulphate ion–water system. *New Zealand J. Sci.* **12**, 54-59.

MIZUTANI, Y. & RAFTER, T.A. (1969b): Oxygen isotopic composition of sulphates, Part 4: Bacterial fractionation of oxygen isotopes in the reduction of sulphate and in the oxidation of sulphur. *New Zealand J. Sci.* **12**, 60-68.

MIZUTANI, Y. & RAFTER, T.A. (1973): Isotopic behavior of sulphate oxygen in the bacterial reduction of sulphate. *Geochem. J.* **6**, 183-191.

MOSES, C.O. & HERMAN, J.S. (1991): Pyrite oxidation at circumneutral pH. *Geochim. Cosmochim. Acta* **55**, 471-482.

MOSES, C.O., NORDSTROM, D.K., HERMAN, J.S. & MILLS, A.L. (1987): Aqueous pyrite oxidation by dissolved oxygen and ferric iron. *Geochim. Cosmochim. Acta* **51**, 1561-1571.

NAKAI, N. & JENSEN, M.L. (1964): The kinetic isotope effect in the bacterial reduction and oxidation of sulfur. *Geochim. Cosmochim. Acta* **28**, 1893-1912.

NIELSEN, H., PILOT, J., GRINENKO, L.N., GRINENKO, V.A., LEIN, A.Y., SMITH, J.W. & PANKINA, R.G. (1991): Lithospheric sources of sulphur. *In* Stable Isotopes in the Assessment of Natural and Anthropogenic Sulphur in the Environment (H.R. Krouse & V.A. Grinenko, eds.). SCOPE 43. J Wiley & Sons, New York (65-132).

NORDSTROM, D.K. (1982): Aqueous pyrite oxidation and the consequent formation of secondary iron minerals. *Soil Sci. Soc. Am. Special Pub.* **10**, 37-56.

NORDSTROM, D.K. & ALPERS, C.N. (1999a): Geochemistry of acid mine waters. *In* The Environmental Geochemistry of Mineral Deposits. Part A: Processes, Techniques, and Health Issues (G. S. Plumlee & M.J. Logsdon, eds.). *Rev. Econ. Geol.* **6A**, 133-160.

NORDSTROM, D.K. & ALPERS, C.N. (1999b): Negative pH, efflorescent mineralogy, and consequences for environmental restoration at the Iron Mountain Superfund site, California. *Proc. National Acad. Sci. USA* **96**, 3455-3462.

NORDSTROM, D.K. & SOUTHAM, G. (1997): Geomicrobiology of sulfide mineral oxidation. *In* Geomicrobiology: Interactions between Microbes and Minerals (J.F. Banfield & K.H. Nealson, eds.). *Rev. Mineral.* **35**, 361-390.

NORDSTROM, D.K., ALPERS, C.N., PTACEK, C.J. & BLOWES, D.W. (2000): Negative pH and extremely acidic mine waters from Iron Mountain, California. *Environ. Sci. Technol.* **34**, 254-258.

OHMOTO, H. & LASAGA, A.C. (1982): Kinetics of reactions between aqueous sulfates and sulfides in hydrothermal systems. *Geochim. Cosmochim. Acta* **46**, 1727-1745.

O'NEIL, J.R. (1986): Theoretical and experimental aspects of isotopic fractionation. *In* Stable Isotopes in High Temperature Geological Processes (J.W. Valley, H.P. Taylor Jr & J.R. O'Neil, eds.). *Rev. Mineral.* **16**, 1-40.

POSTGATE, J.R. (1984): *The Sulfate-Reducing Bacteria*, 2nd ed. Cambridge University Press, Cambridge, UK

QURESHI, R.M. (1986): *The Isotopic Composition of Aqueous Sulfate (A Laboratory Investigation)*. Ph.D. thesis, Univ. of Waterloo, Waterloo, Ontario.

REES, C.E., JENKINS, W.J. & MONSTER, J. (1978): The sulphur isotope composition of ocean water sulphate. *Geochim. Cosmochim. Acta* **42**, 377-382.

RIMSTIDT, J.D. & VAUGHAN, D.J. (2003): Pyrite oxidation: a state-of-the-art assessment of the reaction mechanism. *Geochim. Cosmochim. Acta* **67**, 873-880.

ROZANSKI, K., ARAGUÁS-ARAGUÁS, L. & GONFIANTINI, R. (1993): Isotopic patterns in modern global precipitation. *Geophys. Monogr.* **78**, 1-36.

RYE, R.O. & ALPERS, C.N. (1997): The stable isotope geochemistry of jarosite. *U.S. Geol. Surv. Open-File Report* **97-88**.

RYE, R.O. & JOHNSON, C.A. (1997): The use of stable carbon- and nitrogen-isotope data in quantifying cyanide loss from mine wastewaters. *U.S. Geol. Surv. Open-File Report* **97-82**.

RYE, R.O. & STOFFREGEN, R.E. (1995): Jarosite-water oxygen and hydrogen isotope fractionations: preliminary experimental data. *Econ. Geol.* **90**, 2336-2342.

RYE, R.O., BETHKE, P.M. & WASSERMAN, M.D. (1992): The stable isotope geochemistry of acid sulfate alteration. *Econ. Geol.* **87**, 225-262.

RYTUBA, J.J., ENDERLIN, D., ASHLEY, R., SEAL, R. & HUNERLACH, M.P. (2000): Evolution of the McLaughlin gold mine pit lakes, California. *In* Proceedings from the Fifth International Conference on Acid Rock Drainage **1**. Society for Mining, Metallurgy, and Exploration, Littleton, Colorado (367-375).

SAKAI, H. (1968): Isotopic properties of sulfur compounds in hydrothermal processes. *Geochem. J.* **2**, 29-49.

SAKAI, H., DES MARAIS, D.J., UEDA, A. & MOORE, J.G. (1984): Concentrations and isotope ratios of carbon, nitrogen, and sulfur in ocean-floor basalts. *Geochim. Cosmochim. Acta* **48**, 2433-2442.

SCHIPPERS, A., JOZSA, P.-G. & SAND, W. (1996): Sulfur chemistry in bacterial leaching of pyrite. *Appl. Environ. Microbiol.* **62**, 3424-3431.

SEAL, R.R. II & HAMMARSTROM, J.M. (2003): Geoenvironmental models of mineral deposits: examples from massive sulfide and gold deposits (Chapter 2, this Volume).

SEAL, R.R. II & WANDLESS, G.A. (1997): Stable isotope characteristics of waters draining massive sulfide deposits in the eastern United States. *In* Fourth International Symposium on Environmental Geochemistry, Proceedings (R.B. Wanty, S.P. Marsh & L.P. Gough, eds.). *U.S. Geol. Surv. Open-File Report* **97-496**.

SEAL, R.R. II, HAMMARSTROM, J.M., SOUTHWORTH, C.S., MEIER, A.L., HAFFNER, D.P., SCHULTZ, A.P., PLUMLEE, G.S., FLOHR, M.J.K., JACKSON, J.C., SMITH, S.M. & HAGEMAN, P.L. (1998): Preliminary report on water quality associated with the abandoned Fontana and Hazel Creek mines, Great Smoky Mountains National Park, North Carolina and Tennessee. *U.S. Geol. Surv. Open-File Report* **98-476**.

SEAL, R.R. II, ALPERS, C.N. & RYE, R.O. (2000): Stable isotope systematics of sulfate minerals. *In* Sulfate Minerals – Crystallography, Geochemistry, and Environmental Significance (C.N. Alpers, J.L. Jambor & D.K. Nordstrom, eds.). *Rev. Mineral. Geochem.* **40**, 541-602.

SEAL, R.R. II, KORNFELD, J.M., MEIER, A.L. & HAMMARSTROM, J.M. (2001): Geochemical settings of mine drainage in the Vermont copper belt. *In* Environmental Geochemistry and Mining History of Massive Sulfide Deposits in the Vermont Copper Belt (J.M. Hammarstrom & R.R. Seal II, eds.). *Soc. Econ. Geol. Field Trip Guidebook Ser.* **35**, Pt. 2, 255-276.

SINGER, P.C. & STUMM, W. (1968): Kinetics of the oxidation of ferrous iron. *In* Proceedings Second Symposium on Coal Mine Drainage Research: Bituminous Coal Research Inc., Monroeville, Pennsylvania (12-34).

SINGER, P.C. & STUMM, W. (1970): Acid mine drainage: the rate-determining step. *Science* **167**, 1121-1123.

SMITH, A. (1994): The geochemistry of cyanide in mill tailings. *In* Environmental Geochemistry of Sulfide Mine-Wastes (J.L. Jambor & D.W. Blowes, eds.). *Mineral. Assoc. Can. Short Course Vol.* **22**, 293-332.

SMITH, A.C.S. & MUDDER, T.I. (1999): The environmental geochemistry of cyanide. *In* The Environmental Geochemistry of Mineral Deposits. Part A: Processes, Techniques, and Health Issues (G.S. Plumlee & M.J. Logsdon, eds.). *Rev. Econ. Geol.* **6A**, 229-248.

SOFER, Z. & GAT, J.R. (1975): The isotope composition of evaporating brines: effect of the isotopic activity ration in saline solutions. *Earth Planet. Sci. Lett.* **26**, 179-186.

STEGER, H.F. & DESJARDINS, L.E. (1978): Oxidation of sulfide minerals, 4. Pyrite, chalcopyrite and pyrrhotite. *Chem. Geol.* **23**, 225-237.

STOFFREGEN, R.E., RYE, R.O. & WASSERMAN, M.D. (1994): Experimental studies of alunite: I. ^{18}O-^{16}O and D-H fractionation factors between alunite and water at 250-450 °C. *Geochim. Cosmochim. Acta* **58**, 903-916.

SUZUKI, I., CHAN, C.W. & TAKEUCHI, T.L. (1994): Oxidation of inorganic sulfur compounds by Thiobacilli. *In* Environmental Geochemistry of Sulfide Oxidation (C.N. Alpers & D.W. Blowes, eds.). *Am. Chem. Soc. Symp. Ser.* **550**, 60-67.

SWEENEY, R.E., LIU, K.K. & KAPLAN, I.R. (1978): Oceanic nitrogen isotopes and their uses in determining the source of sedimentary nitrogen. *In* Stable Isotopes in Earth Science (B.W. Robinson, ed.). *Dept. Sci. Ind. Research New Zealand Bull.* **220**, 9.

TAYLOR, B.E. & WHEELER, M.C. (1994): Sulfur- and oxygen-isotope geochemistry of acid mine drainage in the western United States. *In* Environmental Geochemistry of Sulfide Oxidation (C.N. Alpers & D.W. Blowes, eds.). *Am. Chem. Soc. Symp. Ser.* **550**, 481-514.

TAYLOR, B.E., WHEELER, M.C. & NORDSTROM, D.K. (1984a): Stable isotope geochemistry of acid mine drainage: experimental oxidation of pyrite. *Geochim. Cosmochim. Acta* **48**, 2669-2678.

TAYLOR, B.E., WHEELER, M.C. & NORDSTROM, D.K. (1984b): Isotope composition of sulfate in acid mine drainage as measure of bacterial oxidation. *Nature* **308**, 538-541.

THODE, H.G. & MONSTER, J. (1965): Sulfur-isotope geochemistry of petroleum, evaporites, and ancient seas. *Am. Assoc. Petrol. Geol. Mem.* **4**, 367-377.

TORAN, L. (1987): Sulfate contamination in groundwater from a carbonate-hosted mine. *J. Contam. Hydrol.* **2**, 1-29.

TORAN, L. & HARRIS, R.F. (1989): Interpretation of sulfur and oxygen isotopes in biological and abiological sulfide oxidation. *Geochim. Cosmochim. Acta* **53**, 2341-2348

VAN EVERDINGEN, R.O. & KROUSE, H.R. (1985): Isotope composition of sulphates generated by bacterial and abiological oxidation. *Nature* **315**, 395-396.

VAN EVERDINGEN, R.O. & KROUSE, H.R. (1988) Interpretation of isotopic compositions of dissolved sulfates in acid mine drainage. *U.S. Bureau Mines Info. Circular* **9183**, 147-156.

VAN STEMPVOORT, D.R. & KROUSE, H.R. (1994): Controls on $\delta^{18}O$ in sulfate. *In* Environmental Geochemistry of Sulfide Oxidation (C.N. Alpers & D.W. Blowes, eds.). *Am. Chem. Soc Symp. Ser.* **550**, 446-480.

VITALI, F., LONGSTAFFE, F.J., BIRD, M.I. & CALDWELL, W.G.E. (2000): Oxygen-isotope fractionation between aluminum-hydroxide phases and water at <60°C: results of decade-long synthesis experiments. *Clays Clay Minerals* **48**, 230-237.

VITALI, F., LONGSTAFFE, F.J., BIRD, M.I., GAGE, K.L. & CALDWELL, W.G.E. (2001): Hydrogen-isotope fractionation between aluminum hydroxides: synthesis products versus natural samples from bauxites. *Geochim. Cosmochim. Acta* **65**, 1391-1398.

WASSERMAN, M.D., RYE, R.O., BETHKE, P.M. & ARRIBAS, A. Jr (1992): Methods for separation and total stable isotope analysis of alunite. *U.S. Geol. Surv. Open-File Report* **92-9**.

WAY, K., FANO, L., SCOTT, M.R. & THEW, K. (1950): Nuclear data. A collection of experimental values of halflifes, radiation energies, relative isotopic abundances, nuclear moments and cross-sections. *U.S. Nat. Bureau Standards Circular* **499**.

WIERSMA, C.L. & RIMSTIDT, J.D. (1984): Rates of reaction of pyrite and marcasite with ferric iron at pH 2. *Geochim. Cosmochim. Acta* **48**, 85-92.

WILLIAMSON, M.A. & RIMSTIDT, J.D. (1992): Correlation between structure and thermodynamic properties of aqueous sulfur species. *Geochim. Cosmochim. Acta* **56**, 3867-3880.

WILLIAMSON, M.A. & RIMSTIDT, J.D. (1994): The kinetics and electrochemical rate-determining step of aqueous pyrite oxidation. *Geochim. Cosmochim. Acta* **58**, 5443-5454.

YAPP, C.J. (1987): Oxygen and hydrogen isotope variations among goethites (α-FeOOH) and the determination of paleotemperatures. *Geochim. Cosmochim. Acta* **51**, 355-364.

YAPP, C.J. (1990): Oxygen isotopes in iron (III) oxides: 1. Mineral–water fractionation factors. *Chem. Geol.* **85**, 329-335.

YAPP, C.J. (2000): Climatic implications of surface domains in arrays of δD and $\delta^{18}O$ from hydroxyl minerals: goethite as an example. *Geochim. Cosmochim. Acta* **64**, 2009-2025.

YAPP, C.J. & PEDLEY, M.D. (1985): Stable hydrogen isotopes in iron oxides – II. D/H variations among natural goethites. *Geochim. Cosmochim. Acta* **49**, 487-495.

ZAK, I., SAKAI, H. & KAPLAN, I.R. (1980): Factors controlling $^{18}O/^{16}O$ and $^{34}S/^{32}S$ isotope ratios of ocean sulfates, evaporites and interstitial sulfates from modern deep sea sediments. *In* Isotope Marine Chemistry (E.D. Goldberger, Y. Horibe & K. Saruhashi, eds.). Uchida Rokakuho Publ. Co., Tokyo, Japan (339-373).