INTERPRETATION OF ISOTOPIC COMPOSITIONS OF DISSOLVED SULFATES IN ACID MINE DRAINAGE

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Abstract.--Sulfates produced by oxidation of sulfide minerals in mines, mine-and-mill tailings, and waste-rock dumps are characterized by (1) $\delta^{34}S$ values similar to those of the original sulfide minerals, and (2) low or negative $\delta^{18}O$ values similar to those for sulfates in acidic spring waters. Experimental oxidation of pyrite in waters with a wide range of $\delta^{18}O$ values has shown that the $\delta^{18}O$ value of the product sulfate depends not only on the experimental conditions (aerobic or anaerobic; submerged or intermittently wet and dry; sterile or containing *Thiobacillus ferrooxidans*), which may determine the actual reaction pathways, but also on the $\delta^{18}O$ value of the water in which the oxidation takes place. The experimental results can be interpreted as evidence that 29 to 100% of the oxygen in the sulfate was derived from water molecules, whereas dissolved sulfates in field samples incorporated 35 to 90% water oxygen. So far it has not been possible to determine whether the water oxygen is incorporated into the sulfate during the actual oxidation process (as implied by proposed stoichiometric equations), or through oxygen-isotope exchange between the water and one or more intermediates (e.g. sulfite or thiosulfate). At room temperature, the exchange of oxygen isotopes between water and sulfate ions is too slow to effect the observed $\delta^{18}O$ values. The range in $\delta^{18}O$ values for sulfate produced by oxidation of sulfides tends to widen as $\delta^{18}O$ values for rain and snow become more negative at higher latitudes and at greater distances from the oceans. Some uncertainty still exists regarding the actual $\delta^{18}O$ value for dissolved oxygen in subsurface waters. A further complication is background sulfate from sources such as marine evaporites, which might be detected using sulfur isotope data. The above components must be characterized before proper interpretation of the oxygen-isotope composition of sulfate produced during sulfide weathering is possible. Only then could oxygen-isotope data be used to monitor the effects of measures designed to reduce (or accelerate) the oxidation process in mines, tailings deposits, and waste-rock dumps.

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INTRODUCTION

It has been realized for some time that oxygen incorporated into sulfate during the oxidation of sulfide minerals is derived in part from molecular oxygen and in part from water molecules. The overall oxidation process is usually described by several stoichiometric equations. For example, Taylor et al. (1984b) cite the following:

$$2FeS_2+28Fe^{3+}+16H_2O \rightarrow 30Fe^{2+}+4SO_4^{2-}+32H^+ \quad [1]$$

$$28Fe^{2+} + 7O_2 + 28H^+ \rightarrow 28Fe^{3+} + 14H_2O \quad [2]$$

$$2FeS_2+7O_2+2H_2O \rightarrow 2Fe^{2+}+4SO_4^{2-}+4H^+ \quad [3]$$

If reaction [1] applies, all sulfate oxygen, Os, is derived from water molecules, Ow, whereas in reaction [3], 87.5% of the sulfate oxygen is derived from molecular oxygen, Om, and 12.5% from Ow. Reaction [2], which regenerates Fe^{3+} for reaction [1], produces H_2O from molecular oxygen. However, the amount of this H_2O is relatively minor and unlikely to affect the δ^{18}Ow and δ^{18}Os values.

It must be emphasized that the above equations, while convenient, may not describe the actual reaction mechanisms. For example, there is still considerable debate as to whether water dissociates and plays an oxidizing role, or whether exchange of oxygen isotopes between the water and intermediate sulfur species fully accounts for the presence of water oxygen in the product sulfate. According to Rimstidt et al. (1986), the process converting sulfide sulfur to sulfate may consist of as many as eight reaction steps, some of which occur at the mineral/solution interface, whereas others occur in the dissolved phase. Intermediate sulfur species may comprise polysulfides, elemental sulfur, polysulfonic acids, sulfite, and thiosulfate. Postulated pathways of sulfur oxidation by Thiobacilli invoke these intermediates (cf. review by Ralph 1979). There is, however, the question whether their concentrations and/or lifetimes, during natural oxidation of metal sulfides, are sufficiently large for exchange reactions to alter the oxygen isotope composition of the final sulfate product.

This paper examines published and new data for oxidation experiments and field samples, to determine how effectively oxygen-isotope data for dissolved sulfate in "acid mine drainage" can elucidate the conditions prevailing during the oxidation of metal sulfides. Isotopic data from laboratory experiments are available for oxidation of Na_2S and H_2S (Lloyd 1967, 1968); for oxidation of elemental sulfur (Mizutani and Rafter 1969); and for oxidation of pyrite (Schwarcz and Cortecci 1974; Taylor et al. 1984a; and current studies). Isotopic data for field samples have been published by Shakur (1979), Smejkal (1979), Taylor et al. (1984b), and van Everdingen et al. (1985); additional field samples have recently been analyzed by the authors.

METHODS

At the tailings deposit of an abandoned zinc mine in northern Ontario, water samples were collected from 2-inch (5-cm) ID piezometers, using a small-diameter bailer. The samples were stored in 1-L polyethylene and 125-ml glass bottles. The samples were used for the determination of δ^{34}S and δ^{18}Os values for dissolved sulfate, and δ^{18}Ow values for the water, respectively. At the same site, samples of tailings were collected from drillholes and testpits, and stored in plastic bags. Additional water samples were collected from mine drainage at two abandoned coal mines near Coleman (Alberta); from a tailings pond at a gold mine near Contwoyto Lake (N.W.T.); and from acidic creeks draining pyritic exposures near McBride (British Columbia), and near the Nanisivik lead/zinc mine on Baffin Island (N.W.T.).

In our oxidation experiments we used waters with four different δ^{18}Ow values, ranging from -33.5 to +34.0°/oo. For each type of water, two 125-mL vacuum flasks were prepared, each with 100 mL of water and 100 mg of pyrite that had been finely ground in dry air. The tops of the flasks were sealed with parafilm, while the side arms were left open to the atmosphere. After 31 days, the water was removed from one set of four flasks and analyzed to determine δ^{18}Os; after 547 days, 60 mL of water was removed from the second set of flasks and analyzed to determine both δ^{18}Os and δ^{18}Ow.

Sulfur and oxygen isotope analyses followed procedures described by Thode et al. (1961), van Everdingen et al. (1982), and Ueda and Krouse (1986).

In the following sections, oxygen and sulfur isotope data are reported as per mil (°/oo) δ^{18}O and δ^{34}S values, defined as:

$$\delta^{18}O = \left[\frac{[^{18}O/^{16}O]_{sample}}{[^{18}O/^{16}O]_{standard}} - 1\right] \times 10^3$$

$$\delta^{34}S = \left[\frac{[^{34}S/^{32}S]_{sample}}{[^{34}S/^{32}S]_{standard}} - 1\right] \times 10^3$$

The usual standards for δ^{34}S and δ^{18}O are troilite from the Cañon Diablo meteorite (CDT), and water approximating the mean isotopic composition of the ocean (SMOW).

Table 1.--Isotope data from oxidation experiments

SOURCE	DURATION (days)	δ^{18}Os °/oo SMOW	δ^{18}Ow °/oo SMOW	Δ °/oo
Current study - PYRITE	31	-5.9	-33.5	+27.6
(submerged/aerobic)	31	+0.7	-19.5	+20.2
	31	+16.0	+17.0	-1.0
	31	+22.6	+34.0	-11.4
	547	-14.2	-26.2 *	+12.0
	547	-5.7	-13.1 *	+7.4
	547	+15.6	+22.3 *	-6.8
	547	+29.5	+40.5 *	-11.0
Taylor et al., 1984a - PYRITE				
(submerged/anaer./sterile/+Fe^{3+})	30	-6.9	-10.9	+4.0
(submerged/aerobic/sterile/+Fe^{3+})	26	-6.0	-10.9	+4.9
(submerged/aerobic/sterile)	27	-4.8	-10.9	+6.1
(submerged/aerobic/+T.ferro.)	27	+1.8	-10.9	+12.7
(submerged/aerobic/+T.ferro.)	27	+0.5	-10.4	+10.9
(wet/dry, sterile)	29	+1.3	-10.9	+12.2
(wet/dry, sterile)	29	-0.9	-10.4	+9.5
(wet/dry, + T.ferro.)	29	+6.6	-10.9	+17.5
(wet/dry, + T.ferro.)	29	+7.7	-10.4	+18.1
Mizutani & Rafter, 1969 - SULFUR				
(in aerated water with soil)	14	-7.6	-7.0	-0.6
	17	-7.0	-7.0	0.0
	15	-1.3	-0.8	-0.5
	18	-0.4	-0.8	+0.4
	21	+2.0	-0.8	+2.8
Schwarcz & Cortecci, 1974 - PYRITE				
(in aerated water)	14	+3.5	-8.0	+11.5
	14	+71.0	+127.0	-56.0
Lloyd, 1967 - H_2S	-	+2.0	-4.7	+6.7
(through aerated water)	-	+18.0	+20.0	-2.0
	-	+29.3	+34.0	-4.7

* - Values at end of experiment reflect evaporation effects

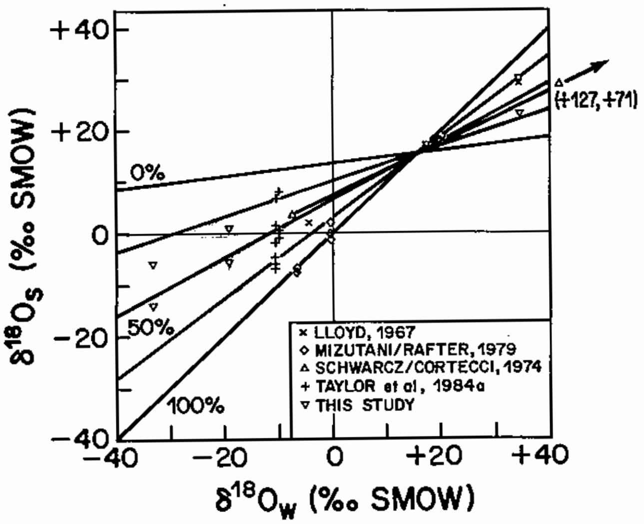

Figure 1.-- δ^{18}Os values of SO_4^{2-} versus δ^{18}Ow values of H_2O for oxidation experiments.

DATA FROM LABORATORY EXPERIMENTS

Isotopic data from oxidation experiments are listed in table 1 and illustrated by figure 1.

Previous Work

Lloyd (1967, 1968) concluded that the ratio of water oxygen to molecular oxygen used in the oxidation of Na_2S, at 25°C in water under an oxygen atmosphere, was 1:2. He suggested that the initial reaction (not balanced) was

$$S^{2-} + H_2O + O_2 \rightarrow SO_3^{2-} \qquad [4]$$

The isotope fractionation [εm] for the incorporation of molecular oxygen was deduced to be -8.7°/oo. Lloyd also found that the subsequent reaction

$$SO_3^{2-} + \tfrac{1}{2}O_2 \rightarrow SO_4^{2-} \qquad [5]$$

was comparatively slow, and that sulfite underwent oxygen-isotope exchange with the water (80% in one week at room temperature), as much as 10^5 times faster than the exchange between sulfate and water. The final $\delta^{18}Os$ for the sulfate would thus depend on the competing rates of (1) exchange of oxygen isotopes between sulfite and water, and (2) oxidation of sulfite to sulfate. It should be noted here that buildup and retention of SO_4^{2-} are pH dependent.

Oxidation of H_2S in aerated waters with three different $\delta^{18}Ow$ values resulted in 64 to 76 percent of the sulfate oxygen being derived from Ow (Lloyd 1967). The isotope fractionation [εw] for incorporation of water oxygen into SO_4^{2-} was found to be zero. The Δ values ($\delta^{18}Os$ minus $\delta^{18}Ow$) for individual samples ranged from -4.7 to +6.7^{o}/oo (table 1).

Bacterially mediated oxidation of elemental sulfur in an aerated soil/water slurry at 30°C produced sulfate with $\delta^{18}Os$ values almost identical to $\delta^{18}Ow$ (Mizutani and Rafter 1969). Sulfur isotope fractionations between sulfur and sulfate were less than 2.3^{o}/oo; Δ values ranged from -0.6 to +2.8^{o}/oo (table 1).

Oxidation of finely ground pyrite at 25°C in aerated slurries made with waters with two different $\delta^{18}Ow$ values revealed that $\delta^{18}Os$ increased about 0.6^{o}/oo for each ^{o}/oo increase in $\delta^{18}Ow$ (Schwarcz and Cortecci 1974). The Δ values ranged from -56.0 to +11.5^{o}/oo, and approximately half the sulfate oxygen was deduced to have been derived from the water (table 1).

A series of experiments was designed by Taylor et al. (1984b) to elucidate the pathways of pyrite oxidation. They used both aerobic and anaerobic sterile conditions, as well as aerobic conditions with *Thiobacillus ferrooxidans*. The pyrite was either submerged or subjected to the alternating wet and dry conditions often found in mine environments. For individual experiments, the Δ values ranged from +4^{o}/oo (anaerobic, sterile), to +18^{o}/oo (aerobic, with *T.ferro*.). The isotope fractionation (εm) for incorporation of molecular oxygen into sulfate was found to be -4.3^{o}/oo for chemical (abiological) oxidation, and -11.4^{o}/oo for bacterially-mediated oxidation (for an "average" value of -7.9^{o}/oo).

This Study

In our experiments, the samples extracted after 31 days showed Δ values ranging from -11.4 to +27.6^{o}/oo; for the samples extracted after 547 days, the Δ values ranged from -11.0 to +12.0^{o}/oo; the Δ value was smallest (1^{o}/oo) for the experiment using water with a $\delta^{18}Ow$ value of +17^{o}/oo.

DATA FOR FIELD SAMPLES

Isotopic data for most of the field samples are listed in tables 2 and 3, and illustrated in figure 2.

The Δ values ranged from +3.4 to +11.1^{o}/oo for samples from Bohemia (Smejkal 1979); from +2.6 to +15.2^{o}/oo for samples from Colorado and California (Taylor et al. 1984b); from +10.2 to +23.0^{o}/oo for samples from W. and N. Canada (van Everdingen et al. 1985); and from +4.0 to +22.0^{o}/oo for the samples analyzed during our current study. The Δ values for samples from the Pine Point area (N.W.T.), analyzed by Shakur (1979), were all higher, ranging from +26.4 to +34.0^{o}/oo.

DISCUSSION

Isotope Balance Calculations

To help determine the relative fractions of sulfate oxygen produced by the model reactions [1] and [3] during the various experiments, the isotopic composition of the oxygen incorporated in sulfate during sulfide oxidation can be expressed by the isotopic balance equation:

$$\delta^{18}Os = Y * (\delta^{18}Ow + \varepsilon w) + (1-Y) * \\ * (0.875 * (\delta^{18}Om + \varepsilon m) + \\ + 0.125 * (\delta^{18}Ow + \varepsilon w)) \qquad [6]$$

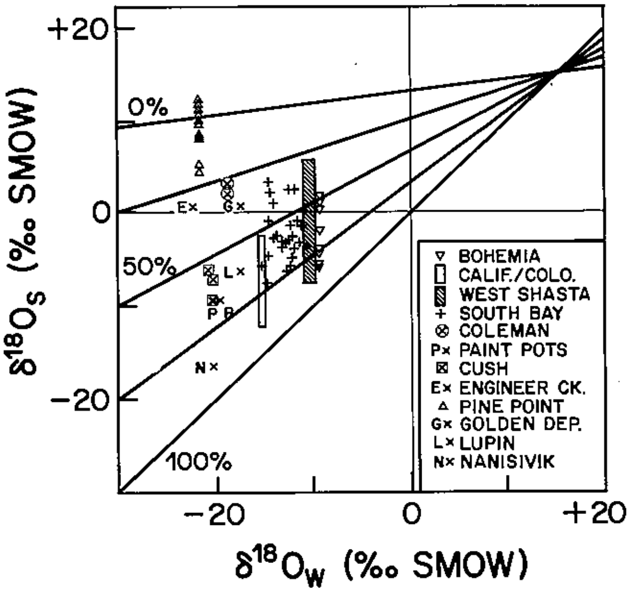

Figure 2.-- $\delta^{18}Os$ values of SO_4^{2-} versus $\delta^{18}Ow$ values of H_2O for field samples.

Table 2.-- Isotope data for field samples

	Sulfate		Water	
SOURCE	$\delta^{34}S$ °/oo CDT	$\delta^{18}O$ °/oo SMOW	$\delta^{18}O$ °/oo SMOW	Δ °/oo
A - ACIDIC SPRINGS				
PAINT POTS, B.C.				
Spring #12, 3-7-81	+10.8	-9.4	-20.5	+11.1
Spring #12, 28-4-84	+9.4	-9.5	-19.7	+10.2
GOLDEN DEPOSIT, N.W.T.				
Spring Water	-22.8	+0.5	-17.7	+18.2
ENGINEER CREEK, YUKON				
Acid Discharge	-23.2	+0.5	-22.5	+23.0
CUSH PROPERTY, B.C.				
Water 80158	+1.3	-6.2	-21.0	+14.8
Water 80159	+0.9	-9.4	-20.4	+11.0
Water 80160	+1.1	-7.2	-20.5	+13.3
NANISIVIK, N.W.T.				
Acid Creek #2	+15.3	-16.4	-20.4	+4.0
B - MINE WATERS				
W. and N. BOHEMIA (Smejkal (1979)				
Michael coal mine		+1.6	-9.5	+11.1
Antonin coal seam		+0.8	-9.5	+10.3
Josef coal seam		+0.1	-9.5	+9.6
Hromnice quarry, pyritic slates		-6.1	-9.5	+3.4
Berk quarry, pyritic slates		-2.1	-9.5	+7.4
Tisova sulfide mine		-4.1	-9.5	+5.4
Svornost sulfide mine		-4.7	-9.5	+4.8
Jachymov, Geier sulfide vein		-5.9	-9.5	+3.6
COLORADO/CALIFORNIA (Taylor et al. 1984a, Fig. 2)				
Mine waters Minima		-12.3	-15.7	+3.4
Maxima		-2.7	-15.1	+12.9
W. SHASTA, California (Taylor et al. 1984a, Fig. 2)				
Mine waters Minima		-7.6	-11.1	+2.6
Maxima		+5.7	-9.8	+15.2
COLEMAN, Alberta				
CC Mine Drainage	+19.6	+1.9	-19.1	+21.0
WCC Mine Drainage	+18.6	+3.0	-19.0	+22.0
LUPIN MINE, N.W.T.				
Tailings Pond	+3.2	-6.3	-17.6	+11.3
PINE POINT, N.W.T. (Shakur, 1979)				
Water from open pit	+14.4	+9.8	-22.0	+31.8
	+15.0	+8.6	(ave.)	+30.6
	+16.5	+9.8		+31.8
	+11.9	+5.2		+27.2
	+16.5	+12.0		+34.0
	+17.0	+11.0		+33.4
	+18.7	+11.0		+33.0
	+12.8	+8.2		+30.2
	+11.7	+4.4		+26.4
	+16.3	+11.4		+33.4
	+15.5	+8.8		+30.8
	+17.7	+10.4		+32.4
	+18.2	+12.0		+34.0
	+17.7	+11.0		+33.0

Table 3.-- Isotope data for South Bay mine tailings.

WATER SAMPLES

Piezometer #	Depth, m	Sulfate $\delta^{34}S$ $^o/oo$ CDT	Sulfate $\delta^{18}O$ $^o/oo$ SMOW	Water $\delta^{18}O$ $^o/oo$ SMOW	Δ $^o/oo$
H - 5	1.3 - 2.2	+4.5	-0.9	-11.7	+10.8
H - 5	1.3 - 2.2	+4.6	-3.3	-11.5	+8.2
H - 6	1.4 - 2.3	-0.8	-3.4	-12.9	+9.6
H - 7	1.8 - 2.7	+0.2	-6.3	-12.8	+6.5
H - 8	1.2 - 2.1	-0.6	-5.7	-15.5	+9.8
H - 8	1.2 - 2.1	-0.1	-7.6	-14.9 *	+7.3
M - 4	4.4 - 5.1	+0.6	-1.5	-12.4	+10.9
M - 5	10.3 - 10.6	+0.1	+2.4	-12.1	+14.5
M - 5b	4.8 - 5.1	-0.9	-5.7	-12.5	+6.8
M - 7a	3.8 - 4.6	0.0	-3.9	-12.0	+8.1
M - 7b	9.8 - 10.1	+0.6	-3.8 *	-10.8 *	+7.0
M - 8	7.9 - 8.2	-0.1	-4.8	-12.3	+7.4
M - 9	5.5 - 5.8	-0.2	-4.7	-14.9	+10.1
M - 11	5.9 - 6.8	+0.9	-3.1	-12.7 *	+9.7
M - 18	7.0 - 7.9	+8.3	+0.8	-14.2	+15.1
M - 24a	7.3 - 8.1	-0.2	-1.0	-14.8	+13.8
M - 24b	4.4 - 5.2	0.0	-2.8 *	-14.2	+11.4
M - 2	16.9 - 17.2	+0.3	+3.2	-14.8	+18.0
M - 32	9.9 - 10.2	+0.1	-3.7	-13.3	+9.5
M - 40	5.4 - 6.2	+2.5	-1.4	-11.4	+9.9
M - 41	4.1 - 4.9	+0.6	+2.4 *	-12.7	+15.0
M - 43	8.9 - 9.2	-0.2	-2.6 *	-14.0	+11.4
M - 45	5.9 - 6.2	-0.1	-3.3	-13.4 *	+10.2
M - 4	10.4 - 11.0	-0.3	-2.6	-12.3	+9.6
M - 49	2.6 - 2.9	-0.6	+2.0	-14.7	+16.7

TAILINGS SAMPLES

Source	Depth, m	State of oxidation	Sulfide $\delta^{34}S$ $^o/oo$ CDT	Sulfate $\delta^{34}S$ $^o/oo$ CDT	Sulfate $\delta^{18}O$ $^o/oo$ SMOW
H - 2 T1	0.41 - 0.45	OX	+0.8	+1.4	-4.8
H - 2 T2	1.83 - 2.43	UNOX	+0.8	+0.4	+0.8
M - 4 T	1.52 - 2.13	UNOX	+1.1	+0.3	-0.9
M - 26 T	1.52 - 2.13	UNOX	+0.5	-4.8 *	+4.0
M - 27 T	1.52 - 2.13	UNOX	+1.2	+0.6	-2.6
M - 40 T	1.52 - 2.13	UNOX	+0.9	+0.6	-5.9
M - 43 T1	0.43 - 0.50	OX	+1.2	+1.8	+4.2
M - 43 T2	1.22 - 2.43	UNOX	+0.8	+0.7	+5.6
M - 46 T1	0.41 - 0.50	OX	+1.2	+1.3	-4.2
M - 46 T2	0.51 - 0.60	OX	+1.0	+1.0	-6.4
M - 46 T3	1.52 - 2.13	UNOX	+1.3	+0.7	-6.2
CONCENTRATE SAMPLE		OX	+0.4	-1.3	+0.1

* - Average of two determinations

in which Y is the fraction of sulfate ions produced by reaction [1]; εm and εw represent the shifts in $\delta^{18}Om$ and $\delta^{18}Ow$ during incorporation of Om and Ow into sulfate.

Using $\varepsilon m = -8.7^o/oo$ and $\varepsilon w = 0.0^o/oo$ (Lloyd 1967), and the $\delta^{18}Om = \delta^{18}O$ of atmospheric $O_2 = +23.8^o/oo$ (Horibe et al. 1973), equation [6] can be rewritten as

$$\delta^{18}Os = \delta^{18}Ow * (0.875 * Y + 0.125) + $$
$$+ (1-Y) * 13.21 \qquad [7]$$

Lines for 100, 75, 50, 25, and 0 percent contribution by reaction [1], calculated using equation [7], have been plotted in figures 1 and 2. These lines converge and intersect at the point representing $\delta^{18}Os = \delta^{18}Ow \approx +15^o/oo$. The convergence suggests that at low latitudes, where $\delta^{18}Ow$ values are closer to $0^o/oo$, it will be more difficult to distinguish contributions from individual reactions than at high latitudes, where $\delta^{18}Ow$ values may approach $-30^o/oo$. It is noted that in the earlier analysis of van Everdingen and Krouse (1985), εw was chosen as $+2.6^o/oo$, as suggested by data of Taylor et al. (1984a). However, with that εw value, some of our recent data would fall below the 100 percent reaction [1] line on a $\delta^{18}Os$ vs. $\delta^{18}Ow$ plot. Therefore, an εw value of zero seems more appropriate.

Equation [7] can be rewritten to allow calculation of Y from the $\delta^{18}Os$ and $\delta^{18}Ow$ values for individual samples:

$$Y = (\delta^{18}Os - 0.125 * \delta^{18}Ow - 13.21) / $$

$$/ \ (0.875 * \delta^{18}Ow - 13.21) \qquad [8]$$

Finally, the fraction (X) of sulfate oxygen derived from Ow can be calculated either from

$$X = 0.875 * Y + 0.125 \qquad [9]$$

or directly from the isotopic data for Os, Ow, and Om:

$$X = (\delta^{18}Os - (\delta^{18}Om + \varepsilon m)) \ / $$

$$/ \ (\delta^{18}Ow - (\delta^{18}Om + \varepsilon m)) \qquad [10]$$

The position of individual data points in relation to the percent-reaction-[1] lines in figures 1 and 2 indicates the proportions of the sulfate produced by reactions [1] and [3]. The spread of the experimental data (fig. 1) shows that between 19 and 100% of the sulfate can be produced by reaction [1]. This corresponds with 29 to 100% of the sulfate oxygen being derived from Ow (calculated by equation [9]). The distribution of the field data (fig. 2), with the exception of the Point Point set, indicates that 26 to 88% of the sulfate was produced by reaction [1], with 35 to 90% of the sulfate oxygen provided by Ow.

Complications in Field Situations

Sulfate in waters associated with sulfide mineralization may have been derived from several sources (fig. 3). In the case of carbonate-hosted metal-sulfide deposits, anhydrite (or gypsum) may have been dissolved earlier from associated marine evaporite strata. Under anaerobic conditions in the presence of a suitable carbon source, sulfate reduction may occur, enriching the remaining SO_4^{2-} in both ^{34}S and ^{18}O (cf. Krouse 1987). Under more aerobic conditions, sulfur in lower valence states can oxidize, incorporating oxygen atoms from dissolved O_2 and from H_2O.

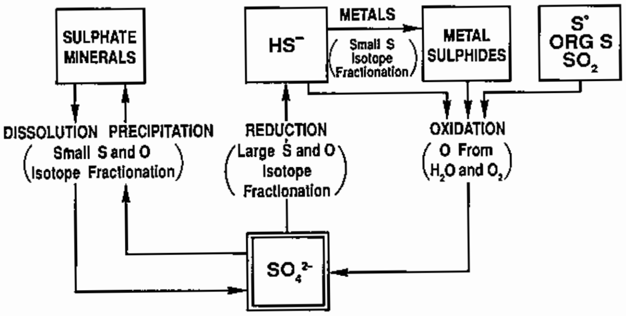

Figure 3.--Interactions between natural subsurface sulfate sources.

Interpreting isotopic data solely on the basis of metal-sulfide oxidation ignores the possibility that the water in which the oxidation process takes place may contain dissolved sulfate from non-sulfide sources. Where this is suspected, it is necessary to obtain information on both the concentration and the $\delta^{18}Os$ for the "original" sulfate.

The complexity of natural systems is illustrated by the data for water samples from a pumped open pit in the carbonate-hosted Pb/Zn deposit at Pine Point (Shakur 1979). The $\delta^{34}S$ and $\delta^{18}Os$ values varied by 6°/oo and 8°/oo, respectively (fig. 4), over a small area. The δ-values tended to increase with $[SO_4^{2-}]$ and $[Cl^-]$. The two known local sources of SO_4^{2-} are dissolution of anhydrite, and oxidation of metal sulfides, both with $\delta^{34}S$ values near +20°/oo (Sasaki and Krouse 1969).

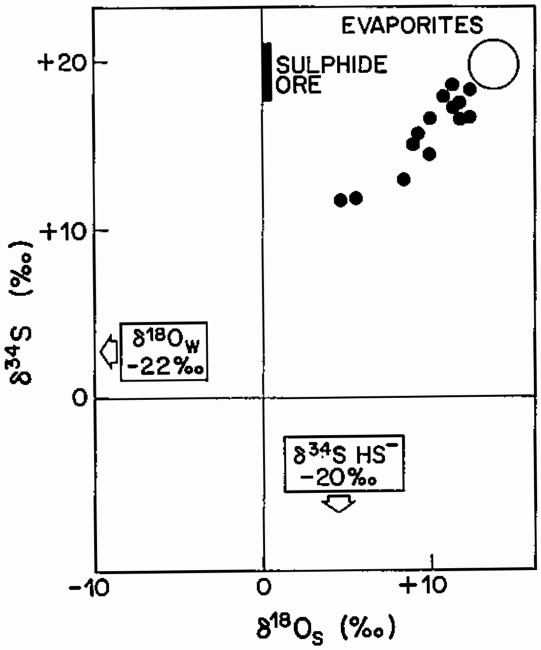

Figure 4.--$\delta^{34}S$ versus $\delta^{18}Os$ for SO_4^{2-} samples from an open pit near Pine Point, N.W.T. (after Shakur 1979). Ranges of $\delta^{34}S$ values for Pb-Zn ores, and of $\delta^{34}S$ and $\delta^{18}O$ values for evaporite sulfate are indicated.

A graphic tool for identifying sulfate sources is the plotting of δ-values versus the inverse of $[SO_4^{2-}]$ or $[Cl^-]$ concentrations. If a linear behaviour is invoked, the Y-intercept corresponds to the δ-value for one of the sources (cf. Krouse 1980). For the Pine Point $\delta^{18}Os$ data, figure 5 shows that the $\delta^{18}Os$ value at the intercept is 2 to 3 per mil higher than expected for the evaporite sulfate (Sasaki and Krouse 1969). Note that the line computed with the points for the two lowest sulfate concentrations excluded, gives an intercept close to the evaporite value.

It can also be argued that the $\delta^{18}Os$ values for many of these samples were somewhat elevated by bacterial sulfate reduction, because the Eh values of these waters average -250 mV (Shakur 1979). This would tend to give a lower Y-intercept, since higher $\delta^{18}O$ shifts

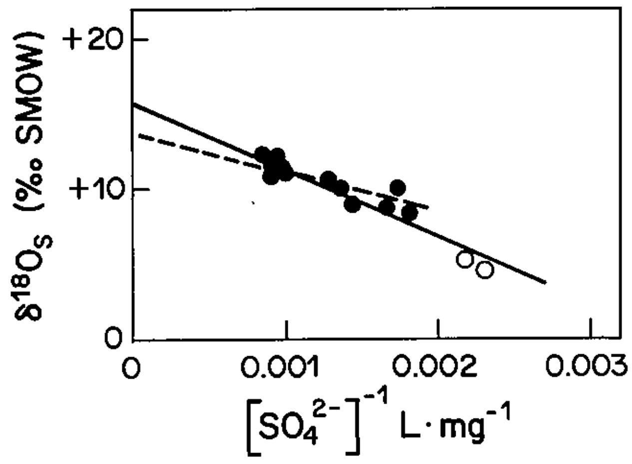

Figure 5--.δ^{18}Os versus the inverse of sulfate concentration, for water samples from an open pit near Pine Point, N.W.T. (after Shakur 1979). The dashed regression line represents the closed circles only (see text for discussion).

would be associated with lower sulfate concentration. The lower δ^{18}Os values in figure 5 imply that some sulfate was generated by oxidation of lower valence sulfur. The sulfide minerals cannot be the source for this, because their minimum δ^{34}S value is about +17°/oo, whereas figure 4 shows that lower δ^{34}S values were found for SO_4^{2-}. Note that the two samples with the lowest δ^{18}Os values and sulfate concentrations in figure 5 also have the lowest δ^{34}S values, and that they seem to fit a trend that differs from that suggested by the rest of the data in figure 4. Therefore, one may conclude that oxidation of another source of lower valence sulfur, with a lower δ^{34}S value, has produced some of the sulfate. Analysis of waters from boreholes some distance from the mining area revealed significant concentrations of δ^{34}S-depleted HS^-, generated by bacterial sulfate reduction (Weyer et al. 1979). Its re-oxidation would seem to be a good candidate for the third sulfate source. It can be readily appreciated that quantification of the sulfate contribution from the oxidation of sulfide ores in such a system would be impossible without detailed chemical and isotopic data.

Of our field data listed in tables 2 and 3, those for the Pine Point area are undoubtedly affected by the presence of marine sulfate, as discussed above. Those for the Golden Deposit and the Coleman mines are possibly affected; their δ^{18}Os values are relatively high, and evaporites are known to occur in their vicinity. No marine sulfates occur near the remaining sites; these include the South Bay and Lupin mines, located on the Canadian Shield, and the Nanisivik and Paint Pots discharges with the lowest δ^{18}Os values in table 2.

Other Uncertainties

Some uncertainty still exists regarding the δ^{18}Om value to be used in equations [6] and [10] for dissolved molecular oxygen participating in sulfide oxidation. In laboratory experiments, the δ^{18}Om value for atmospheric O_2 (+23.8°/oo, Horibe et al. 1973) has been assumed. However, the δ^{18}Om value of dissolved oxygen is usually not determined, although it may be drastically affected either by kinetic isotope effects during oxidation reactions, or by exchange processes. Determining δ^{18}Om values in natural waters presents a challenge because of difficulties during sampling. Even if a sample can be obtained without introducing atmospheric contamination, there is still the question as to whether the measured δ^{18}Om value represents that existing during sulfate formation. Nevertheless, attempts should be made to measure this parameter as it bears directly on the interpretation of δ^{18}Os versus δ^{18}Ow plots for field samples.

In addition it could be argued that the water associated with the sulfate at the time of sample collection may not properly reflect the δ^{18}Ow value of the water that provided the oxygen for incorporation into the sulfate. It should also be noted that water samples from a shallow tailings deposit can be expected to show a relatively wide range of, and some seasonal variation in, δ^{18}Ow values (reflecting δ^{18}Ow variations in infiltrating rain and snowmelt), as compared to water from natural acidic discharge or mine drainage, in which subsurface mixing would be more complete.

Holser et al. (1979, p. 14) asked: "Will field studies of pyrite oxidation, including isotope measurements on the oxygen of the air and water, ratify the ratio of 1:2 of those participants in Lloyd's experiments?". The authors believe that the data presented here have provided an answer to that question, even while raising several other questions. Careful selection and detailed analysis of samples from a variety of field situations should resolve some of the uncertainties outlined above. The paucity of experimental data on the proportions of Os derived from Om and Ow during oxidation of different sulfide minerals, elemental sulfur, and different organic sulfur species is being addressed by the authors in collaboration with a number of colleagues. Future oxidation experiments should be aimed at trapping (in sufficient quantity for isotopic analysis), one or more of the intermediate sulfur species that may be formed during the oxidation process, before they have a chance either to oxidize further or to exchange oxygen with the surrounding water.

CONCLUSIONS

Simplified stoichiometric equations describing pyrite oxidation, in combination with experimentally determined isotope parameters, define a field on a $\delta^{18}Os$ versus $\delta^{18}Ow$ diagram. Data from laboratory experiments, as well as data for samples from aerobic environments not affected by marine sulfate, were found to plot within this field. This suggests that the equations may present a reasonable, simplified description of the overall oxidation process. Calculations based on these equations indicate that the fraction of sulfate oxygen Os derived from water molecules ranges from about 29 to 100% for the experiments, and from 35 to 90% for the field samples.

The available experimental results also suggest that some of the water oxygen may be incorporated in the sulfate as a result of exchange of oxygen isotopes between the water and one or more intermediate sulfur species. The possibility that oxygen derived from H_2O molecules can act as an oxidant in purely chemical conversions, tends to be discounted.

The $\delta^{18}Os$ values for samples from some of the field sites reflect the presence of sulfate of marine-evaporite origin. In addition, the data for the Pine Point samples indicate the presence of sulfate derived from oxidation of HS^- which was generated earlier by bacterial sulfate reduction. Clearly, such background SO_4^{2-} must be characterized before $\delta^{18}Os$ and $\delta^{18}Ow$ data can be used to monitor sulfide oxidation in mining environments.

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LITERATURE CITED

Chiba, H. and Sakai, H. 1985. Oxygen isotope exchange rate between dissolved sulfate and water at hydrothermal temperatures. Geochimica et Cosmochimica Acta 49:993-1000.
http://dx.doi.org/10.1016/0016-7037(85)90314-X

Holser, W.T., Kaplan, I.R., Sakai, H., and Zak, I. 1979. Isotope geochemistry of oxygen in the sedimentary sulfate cycle. Chemical Geology 25:1-17.
http://dx.doi.org/10.1016/0009-2541(79)90079-2

Horibe, Y., Shigehara, K., and Takakuwa, Y. 1973. Isotope separation factor of carbon dioxide-water system and isotopic composition of atmospheric oxygen. Journal of Geophysical Research 78:2625-2629.
http://dx.doi.org/10.1029/JC078i015p02625

Krouse, H.R. 1980. Sulphur isotopes in our environment. In: Handbook of Environmental Isotope Geochemistry, Vol. 1, The Terrestrial Environment (Eds. P. Fritz and J. Ch. Fontes), Elsevier Scientific Publishing Co., Amsterdam, pp. 435-471.

Krouse, H.R. 1987. Relationships between the sulphur and oxygen isotope composition of dissolved sulphate. In: Studies on Sulphur Isotope Variations in Nature. International Atomic Energy Agency, pp. 19-29.
http://dx.doi.org/10.5962/bhl.title.103124

Lloyd, R.M. 1967. Oxygen-18 composition of oceanic sulfate. Science 156 1:1228-1231.
http://dx.doi.org/10.1126/science.156.3779.1228

Lloyd, R.M. 1968. Oxygen isotope behaviour in the sulfate-water system. Journal of Geophysical Research 73:6099-6110.
http://dx.doi.org/10.1029/JB073i018p06099

Mizutani, Y., and Rafter, T.A. 1969. Oxygen isotopic composition of sulphates-Part 4: Bacterial fractionation of oxygen isotopes in the reduction of sulphates and in the oxidation of sulphur. New Zealand Journal of Science 12:60-68.

Ralph, B.J. 1979. Oxidative reactions in the sulfur cycle. In: Biogeochemical Cycling of Mineral-Forming Elements (Eds. P.A. Trudinger and P.J. Swaine), Elsevier Scientific Publishing Co., Amsterdam, pp. 369-400.

Rimstidt, J.D., Chermak, J.A., and Newcomb, W.D. 1986. The oxidation of sulfide minerals. Extended Abstracts, 5th International Symposium on Water-Rock Interaction, Int. Assoc. Geochem. and Cosmochem., pp. 471-474.

Sasaki, A., and Krouse, H.R. 1969. Sulfur isotopes and the Pine Point mineralization. Economic Geology 64:718-730.
http://dx.doi.org/10.2113/gsecongeo.64.7.718

Schwarcz, H.P. and Cortecci, G. 1974. Isotopic analyses of spring and stream water sulfate from the Italian Alps and Apennines. Chemical Geology 13:285-294.
http://dx.doi.org/10.1016/0009-2541(74)90135-1

Shakur, M.A. 1979. Oxygen and sulfur isotope studies of natural sulfates. M.Sc. Thesis, Department of Physics, The University of Calgary, 115 pp.

Smejkal, V. 1979. Oxygen isotopic composition of sulphates from some mineral waters and mine waters in Western Bohemia. International Atomic Energy Agency, Vienna, Isotope Hydrology 1978, Vol. 1:83-98.

Taylor, B.E., Wheeler, M.C., and Nordstrom, D.K. 1984a. Stable isotope geochemistry of acid mine drainage: Experimental oxidation of pyrite. Geochimica et Cosmochimica Acta 48:2669-2678. http://dx.doi.org/10.1016/0016-7037(84)90315-6

Taylor, B.E., Wheeler, M.C., and Nordstrom, D.K. 1984b. Isotope composition of sulfate in acid mine drainage as measure of bacterial oxidation. Nature 308:538-541. http://dx.doi.org/10.1038/308538a0

Thode, H.G., Monster, J., and Dunford, H.B. 1961. Sulphur isotope geochemistry. Geochimica et Cosmochimica Acta 25:159-174. http://dx.doi.org/10.1016/0016-7037(61)90074-6

Ueda, A., and Krouse, H.R. 1986. Direct conversion of sulphide and sulphate minerals to SO_2 for isotope analyses. Geochemical Journal 20:209-212. http://dx.doi.org/10.2343/geochemj.20.209

van Everdingen, R.O. and Krouse, H.R. 1985. Isotope composition of sulfates generated by bacterial and abiological oxidation. Nature 315:395-396. http://dx.doi.org/10.1038/315395a0

van Everdingen, R.O., Shakur, M.A., and Krouse, H.R. 1982. ^{34}S and ^{18}O abundances differentiate Upper Cambrian and Lower Devonian gypsum-bearing units, District of Mackenzie, N.W.T. - An update. Canadian Journal of Earth Sciences 19:1246-1254. http://dx.doi.org/10.1139/e82-106

van Everdingen, R.O., Shakur, M.A., and Michel, F.A. 1985. Oxygen- and sulfur-isotope geochemistry of acidic groundwater discharge in British Columbia, Yukon, and District of Mackenzie, Canada. Canadian Journal of Earth Sciences 22:1689-1695. http://dx.doi.org/10.1139/e85-177

Weyer, K.U., Krouse, H.R., and Horwood, W.C. 1979. Investigation of regional geohydrology south of Great Slave Lake, Canada, utilizing natural sulphur and hydrogen isotope variations. International Atomic Energy Agency, Vienna, Isotope Hydrology 1978, Vol. 1:251-264.