Oxygen- and sulfur-isotope geochemistry of acidic groundwater discharge in British Columbia, Yukon, and District of Mackenzie, Canada

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The Paint Pots in Kootenay National Park (British Columbia) appear to derive the Fe, Zn, Pb, and SO_4^{2-} contents of their water from sulfide mineralization in Lower and Middle Cambrian carbonates. The Fe, Zn, Ni, and SO_4^{2-} contents of groundwater discharging into a tributary of Engineer Creek (Yukon) are likely derived from sulfide mineralization in Devonian or Ordovician black shales exposed in the area. The high Fe and SO_4^{2-} contents of a natrojarosite deposit northeast of Fort Norman (Northwest Territories) are probably derived from pyritiferous Cretaceous shales in that area. Isotope analyses of water and of dissolved and precipitated sulfur species from these three sites where acidic, heavy-metal-bearing groundwater is being discharged revealed that between 38 and 74% of the oxygen used in the subsurface oxidation of metal sulfides is supplied by H_2O molecules rather than by molecular (dissolved) oxygen. The available data also suggest that lower percentages of water oxygen in the secondary sulfates reflect increasing activity of *Thiobacillus ferrooxidans* or similar bacteria in the oxidation process.

Les ions Fe, Zn, Pb et SO_4^{2-} des sources "Paint Pots" dans le parc national de Kootenay (Colombie-Britannique) semblent provenir des sulfures contenus dans les calcaires d'âge cambrien inférieur et moyen. Les teneurs en Fe, Zn, Ni et SO_4^{2-} des eaux souterraines qui se déchargent dans un affluent du ruisseau Engineer (Yukon) semblent dériver de sulfures présents dans les schistes argileux noirs dévoniens ou ordoviciens qui affleurent dans cette région. Les schistes argileux pyriteux de cette région semblent responsables des teneurs élevées en Fe et en SO_4^{2-} du dépôt de natrojarosite situé au nord-est de Fort Norman (Territories-Nord-Ouest). Les analyses des isotopes de l'eau et des solutions et des précipités des sulfures à ces trois emplacements où se déchargeaient des eaux souterraines acides contenant des métaux lourds révèlent qu'entre 38 et 74% de l'oxygène utilisé pour l'oxydation des sufures métalliques en subsurface est fourni par les molécules H_2O plutôt que par l'oxygène moléculaire (dissous). Les données connues actuellement indiquent en plus que les faibles pourcentages d'oxygène de l'eau dans les sulfates secondaires reflètent une activité croissante de *Thiobacillus ferrooxidans* ou de bactéries analogues dans le processus d'oxydation.

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Introduction

The Paint Pots, a group of springs located in Kootenay National Park, British Columbia, at latitude 51°10′08″ N, longitude 116°09′28″ W, produce acidic water high in Fe, Zn, and Pb. They were described in detail by van Everdingen (1970), who reported that the Fe minerals deposited by the spring water in the Ochre Beds were amorphous iron oxihydroxides (Fe_2O_3 with 1.5 or 2 molecules H_2O, about 75%) and crystalline hematite (Fe_2O_3, about 20%).

The water chemistry of an occurrence of similarly acidic, Fe-bearing groundwater discharge, 54 km northeast of Fort Norman, Northwest Territories (latitude 65°11′58″ N, longitude 124°38′15″ W), was described by Michel (1977), who also presented data on the oxygen-isotope composition and tritium (^3H) abundances in the spring water. The spring-water deposit at this site, named the "Golden Deposit" because of its vivid appearance, consists of amorphous iron hydroxides and natrojarosite, $NaFe_3(SO_4)_2 \cdot (OH)_6$ (Michel 1977).

A third natural occurrence of acidic, Fe-bearing groundwater discharge, in a tributary of Engineer Creek near kilometre 181 on the Dempster Highway, Yukon (latitude 65°15′10″ N, longitude 138°17′15″ W), was reported by Jonasson and Goodfellow (1976). A partial chemical analysis of that water was presented by Schreier (1978). Similar occurrences were described by Norris (1979*a*) in the Porcupine River, Yukon, map area.

Sulfur- and oxygen-isotope analyses of dissolved sulfate from the Paint Pots and of dissolved and precipitated sulfates from the Golden Deposit have been presented by Shakur (1982). We have recently made additional oxygen-isotope and tritium analyses of waters from the Paint Pots and from the Engineer Creek tributary, as well as sulfur- and oxygen-isotope analyses of dissolved and precipitated sulfates from all three sites. Samples from the three mineral deposits have also been analysed for their mineralogical composition.

We present a compilation of all available data, which allows the identification of the most probable sources for the sulfate contents in the three groundwaters and of the sulfur transformation processes that may be involved.

Sampling and analytical procedures

One-litre water samples were collected from each site for major-ion analysis; 0.25 − 1.0 L samples, acidified with nitric acid to a pH of <2.0, were analysed for metals. The chemical analyses were performed by the Calgary laboratory of the Water Quality Branch, Environment Canada.

Samples for isotope analyses of the water were collected in 125 mL glass bottles. Analyses for $^2H/^1H$, $^{18}O/^{16}O$, and ^3H

TABLE 1. Chemical and physical data for acidic Fe-bearing spring waters[a]

	Paint Pots[b]			Golden Deposit	Engineer Creek (Dempster Hwy.)
Source	Spring 12	Spring 16	Spring 19	Spring near edge[c]	Acidic trib., km 181
Constituents (mg/L)					
Ca	137	241	193	341	40.3
Sr	0.48	0.73	0.72	—	—
Mg	61.9	61.7	65.4	800	374
Fe	300	440	300	220	450
Mn	0.46	0.78	0.61	6.5	6.7
Al	5.0	7.2	7.1	—	—
Cu	0.017	0.011	0.008	0.03	0.19
Pb	0.15	1.2	0.72	0.12	0.10
Zn	52.0	177	114	0.17	29.0
Cd	—	—	—	—	0.09
Co	—	—	—	—	0.65
Ni	—	—	—	—	9.0
Na	1.8	1.5	1.7	500	14.0
K	1.0	0.9	0.9	7.0	3.6
HCO_3	*	*	*	*	*
SO_4	1167	2138	1883	5300	4160
Cl	0.2	0.4	0.3	24	0.2
F	0.27	0.09	—	0.15	0.33
SiO_2	16.7	15.9	16.7	37.0	11.0
Sum	1744	3086	2584	7236	5099
pH[d]	3.7 (3.1)	2.4 (2.5)	2.6 (2.6)	2.9 (2.6)	4.0 (2.8)
Conductivity (μS/cm)	2030	4500	3120	8700	4570
Temp. (°C)	10.7	6.7	7.9	3.7	5.5

*No value, because of low pH; as much as 350 ppm carbonic acid ($H_2CO_3{}^0$) may have been present.

[a] Analyses by Water Quality Branch, Inland Waters Directorate, Environment Canada, Calgary.

[b] From van Everdingen (1970, Fig. 2 and Table V).

[c] From Michel (1977).

[d] Values in parentheses measured in the laboratory.

TABLE 2. Isotopic data for acidic Fe-bearing spring waters and spring deposits[a]

				δ^{18}O (‰ SMOW ± 0.2)		δ^{34}S (‰ CDT ± 0.2)
Source and material	Date collected	^{3}H (TU ± 10)	δ^{2}H (‰ SMOW ± 3.0)	In H_2O	In sulfate	In sulfate
Paint Pots, B.C.						
Water, spring 12	3-7-81	—	−162	−20.5	−9.4[b]	+10.8[b]
	5-11-83	46	−157	−19.9	—	—
	28-4-84	148	−156	−19.7	−9.5	+9.4
Deposit, crust	28-4-84	×	×	×	−7.6	+9.9
Deposit, red ochre	28-4-84	×	×	×	−5.3	+8.2
Golden Deposit, NWT						
Water from spring	15-9-75	78[c]	—	−17.7[c]	+0.5[b]	−22.8[b]
Deposit, crust	15-9-75	×	×	×	+2.4[b]	−22.3[b]
Deposit, yellow ochre	15-9-75	×	×	×	+4.4	−24.9
Crystals on plants	3-7-75	×	×	×	−0.8[b]	−19.1[b]
Engineer Creek, Yukon						
Acidic discharge, km 181	31-7-82	92	—	−23.0	—	—
	28-7-83	55	−181	−22.5	+0.5	−23.2
Ochre deposit, km 181	31-7-82	×	×	×	−0.9	−22.0
	28-7-83	×	×	×	—	−22.5

NOTES: Dash indicates not determined; × indicates not applicable.

[a] Analyses for ^{2}H, ^{18}O, and ^{3}H in water by Environmental Isotope Laboratory, Department of Earth Sciences, University of Waterloo; others by Stable Isotope Laboratory, Physics Department of the University of Calgary.

[b] From Shakur (1982).

[c] From Michel (1977).

TABLE 3. Mineralogical composition (%) of deposits from acidic Fe-bearing springs[a]

	Paint Pots			Golden Deposit			Engineer Creek	
	Red ochre	Yellow ochre	Crust	Yellow ochre	Crust	Crystals on plants	Ochre deposit	Shale
Hematite	—	3	—	—	—	—	—	2
Goethite (limonite)	100	10	76	9	56	—	70	—
Jarosite	—	—	24	66	9	—	3	14
Gypsum (anhydrite)	—	5	—	—	8	4	5	3
Bloedite	—	—	—	—	—	56	—	—
Rozenite	—	—	—	—	—	18	—	—
Variscite	—	—	—	—	—	14[b]	—	—
Pyrite	—	—	—	—	—	—	—	2
Carbonates	—	—	—	tr	—	tr	—	—
Silicates[c]	—	82	—	25	27	8	22	76

[a] X-ray diffraction analyses by Institute of Sedimentary and Petroleum Geology, Geological Survey of Canada, Calgary (J. Wong and A. G. Heinrich).
[b] Probable; supported by results of X-ray fluorescence scan.
[c] Quartz, feldspar, and clay minerals, probably representing sediment contributed by surface runoff.

were carried out in the Environmental Isotope Laboratory of the Department of Earth Sciences, University of Waterloo.

Samples for determination of ^{34}S and ^{18}O abundances in dissolved sulfate were collected at each site in 1 L wide-mouth polyethylene bottles with removable plastic liners. Excess $BaCl_2 \cdot 2H_2O$ and some HCl were added to precipitate sulfate as $BaSO_4$, while preventing precipitation of carbonate and sulfide. After approximately 24 h, the supernatants were decanted and the precipitates sealed inside the plastic liners within the sample bottles. Samples of the mineral deposits at each site were collected in heavy-duty, roll-top plastic bags.

All sulfur- and oxygen-isotope analyses on sulfates were carried out in the Stable Isotope Laboratory of the Physics Department of the University of Calgary, following procedures described by Thode *et al.* (1961), Halas *et al.* (1982), and van Everdingen *et al.* (1982).

Results and interpretation

Results of the chemical, isotopic, and mineralogical analyses are listed in Tables 1, 2, and 3, respectively.

The results of the hydrogen and oxygen isotope analyses are presented in Table 2 as δ^2H and $\delta^{18}O$ values, expressed as per mil deviations from standard mean ocean water (SMOW). The results of the sulfur-isotope analyses are expressed as per mil deviations from the usual sulfur standard, troilite from the Cañon Diablo meteorite (CDT).

The data in Tables 1 and 2 reveal that the acidic waters from the three sites studied have a number of characteristics in common. These common characteristics will be discussed first, followed by discussion of the peculiar characteristics of the individual sites.

Common characteristics

All three sites produce water with low pH values (2.4–4.0). The decreases in pH observed between the field and the laboratory measurements reflect oxidation of Fe^{2+} to Fe^{3+}, followed by precipitation of $Fe(OH)_3$. The cation composition of the waters is dominated by SO_4^{2-}. Because of the low pH levels, no HCO_3 could be detected; however, carbonic acid ($H_2CO_3^0$) may have been present.

The excess of SO_4^{2-} over Ca^{2+} in these waters (epm ratios $[SO_4]/[Ca]$ ranging from 3.5 to 43.1) cannot be derived from dissolution of gypsum or anhydrite evaporites. Similarly, the high [Na]/[Cl] ratios cannot be derived from dissolution of halite evaporites. The high iron and sulfate concentrations and the results of isotopic analyses of dissolved sulfates strongly suggest that iron sulfide minerals are the main source for the excess sulfate and metal ions in these waters.

The δ^2H and $\delta^{18}O$ values given in Table 2 show that the acidic groundwater discharges represent local precipitation. The ^3H values in Table 2 indicate that the waters represent recent precipitation; the relatively short subsurface residence times implied are presumed to reflect relatively short subsurface flow paths.

The Paint Pots

The acidic discharge at the Paint Pots is an $Fe-Ca-Mg-SO_4$ water. The [Mg]/[Ca] ratios in the available samples range from 0.42 to 0.74, indicating that the acidic water has encountered both limestone and dolomite along its flow path through the Cambrian strata in the area. The elevated Zn and Pb concentrations suggest that both sphalerite and galena occur with the iron sulfide being oxidized. Such mineral assemblages are known to exist in Cambrian carbonates north, northeast, and southeast of the Paint Pots (Evans 1965; van Everdingen 1970).

The $\delta^{34}S$ values for dissolved and precipitated sulfates of the Paint Pots and Ochre Beds (Table 2) indicate a sulfur source with $\delta^{34}S$ values between +8 and +11‰. Although bacterial oxidation of pyrite might produce a small negative sulfur-isotope fractionation under special conditions, it is to be expected that quantitative conversion of sulfide will produce sulfate with a $\delta^{34}S$ value very similar to that of the source sulfide (Schwarcz and Cortecci 1974; Taylor *et al.* 1984*b*). According to Evans (1965), sulfide mineralization in the Lower and Middle Cambrian carbonates in the Eldon deposit, about 19 km north of the Paint Pots, has $\delta^{34}S$ values between +8 and +12.5‰; a galena sample from the Baker Creek claim, 25 km north-northeast of the Paint Pots, gave a $\delta^{34}S$ value of +9.2‰. If present in the Cambrian strata in the Paint Pots area, sulfide mineralization similar to the above occurrences would be the most probable source for the Paint Pots sulfates. Sulfides from the Hawk Creek prospect, in Cambrian carbonates only 11 km southeast of the Paint Pots, have $\delta^{34}S$ values ranging from

+24.8 to +27.9‰, too high to produce the sulfates of the Paint Pots.

The $\delta^{18}O$ values for dissolved and precipitated sulfates from the Paint Pots, ranging from −9.5 to −5.3‰, again rule out marine evaporites as the sulfur source, because marine sulfates invariably have positive $\delta^{18}O$ values (Claypool *et al.* 1980; Holser *et al.* 1979). Negative $\delta^{18}O$ values are found in dissolved sulfate in acidic mine waters that derive their high iron and sulfate contents from oxidation of pyrite and, possibly, other sulfide minerals (e.g., Šmejkal 1979; Taylor *et al.* 1984*a*). The negative $\delta^{18}O$ values of those minewater sulfates reflect the uptake of oxygen from water with negative $\delta^{18}O$ values during the oxidation process.

Experiments described by Lloyd (1967) suggested that as much as 75% of the oxygen in secondary sulfate (O_s), produced by oxidation of hydrogen sulfide in the presence of both air and water, could be derived from water molecules (O_w). Sulfate produced in pyrite-oxidation experiments by Schwarcz and Cortecci (1974), in which air was bubbled through pyrite−water slurries, incorporated about equal amounts of molecular (atmospheric or dissolved) oxygen (O_a) and water oxygen (O_w).

The oxidation of pyrite can be described by the reaction (Stumm and Morgan 1970)

$$[1]\quad 4FeS_{2(s)} + 15O_2 + 14H_2O \rightarrow 4Fe(OH)_3 + 8SO_4^{2-} + 16H^+$$

or the reaction (Garrels and Mackenzie 1971)

$$[2]\quad 4FeS_{2(s)} + 15O_2 + 8H_2O \rightarrow 2Fe_2O_3 + 8SO_4^{2-} + 16H^+$$

Nordstrom (1982) has suggested that, in order to follow the isotopic-reaction kinetics of sulfate formation by this process, the two possible pathways identified by Ehrlich (1981) should be considered.

In the first pathway, pyrite is oxidized by ferric iron, as described by the reaction

$$[3]\quad FeS_{2(s)} + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+$$

in which 100% of the sulfate oxygen is derived from water. Reaction [3] is rate limited by the rate of oxidation of ferrous to ferric iron, represented by the reaction

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

Reaction [4] can be speeded up, in environments with pH of <3.0, by the action of *Thiobacillus ferrooxidans* (Ehrlich 1981).

In the second pathway, the oxidation of pyrite by atmospheric oxygen, described by the reaction

$$[5]\quad 2FeS_{2(s)} + 7O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4SO_4^{2-} + 4H^+$$

produces sulfate in which O_s incorporates 87.5% O_a and 12.5% O_w. Reaction [5] can be promoted by direct bacterial action in which *Thiobacillus ferrooxidans*, attached to pyrite surfaces, enzymatically oxidizes both ferrous iron and sulfide (Ehrlich 1981). Both reactions [4] and [5] are obviously rate limited by the availability of molecular oxygen, particularly in submersed environments.

Because of the large difference between the $\delta^{18}O$ values for atmospheric oxygen (+23.8‰, Horibe *et al.* 1973) and for groundwater in our study area (Table 2), reactions [3] and [5] will produce sulfates with very different $\delta^{18}O$ values. These two reactions, however, which are assumed to represent the extreme overall pathways for pyrite oxidation, likely involve intermediate steps that produce intermediate species like sulfite or thiosulfate, depending on the environmental conditions. The effects of such intermediates on the oxygen-isotope composition of the SO_4^{2-} generated will depend on the competing rates of oxygen exchange (between the intermediates and the water) and oxidation of the intermediates to sulfate. Sorting out these effects is still extremely difficult, but there are indications that they may be relatively small.

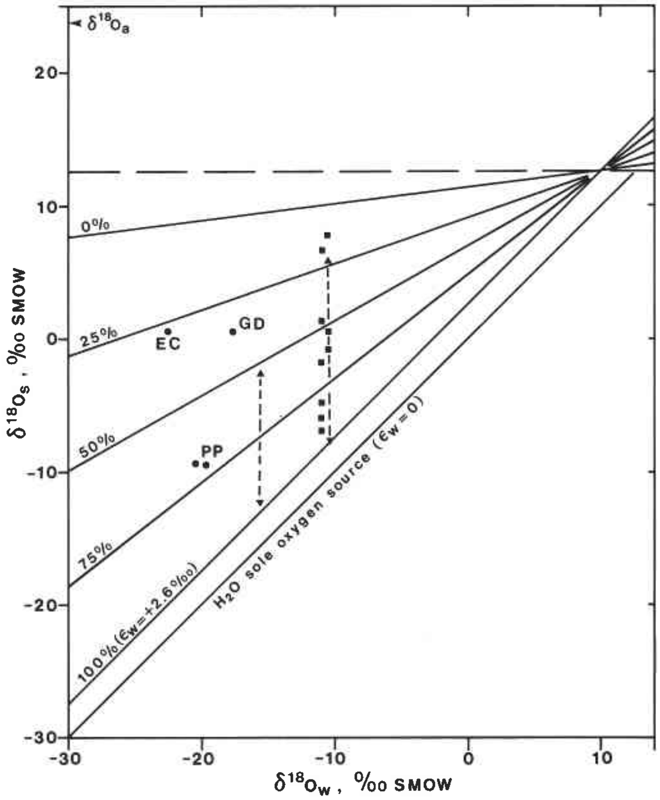

FIG. 1. Relationship between $\delta^{18}O_s$ and $\delta^{18}O_w$ for acidic groundwater discharges and mine waters. PP = Paint Pots; GD = Golden Deposit; EC = Engineer Creek. Interconnected triangles represent approximate ranges for samples of acidic mine waters (Taylor *et al.* 1984*a*); squares represent experimental results of Taylor *et al.* (1984*b*). Lines labelled 0−100% indicate expected $\delta^{18}O_s$ vs. $\delta^{18}O_w$ relations for increasing contributions by reaction [3] to the secondary sulfate.

Lloyd (1967) did not find sulfite in his hydrogen-sulfide oxidation experiments, which suggested that rapid oxidation allowed little isotopic exchange. Taylor *et al.* (1984*b*) found only HSO_4^- and SO_4^{2-} during their pyrite oxidation experiments (using minimal stirring rates at pH = 2.0), indicating rapid pyrite-to-sulfate oxidation at pyrite−water interfaces. Sulfur-isotope fractionations between pyrite and sulfate were less than 1.0‰, suggesting that sulfur-isotope exchange among species was also minimal. We have therefore assumed that the effects of intermediate reaction steps on the $\delta^{18}O$ values of the product sulfates will be small and that the $\delta^{18}O_s$ values for our acidic waters will enable us to identify the extent to which the conditions implied by reactions [3] and [5] are occurring in these acidic drainage systems.

The equation for the isotopic composition of sulfate oxygen O_s can be written as

$$[6]\quad \delta^{18}O_s = W(\delta^{18}O_w + \epsilon_w) + (1 - W)(\delta^{18}O_a + \epsilon_a)$$

in which W represents the fraction of O_s derived from water;

$\delta^{18}O_s$ and $\delta^{18}O_w$ have the values given in Table 2; and $\delta^{18}O_a = +23.8‰$. The variables ϵ_a and ϵ_w represent shifts in the δ values due to kinetic isotope effects during incorporation of O_a and O_w into sulfate. Values for ϵ_a and ϵ_w have been published by Lloyd (1967): $\epsilon_a = -8.7‰$ and $\epsilon_w = 0.0‰$. Taylor *et al.* (1984*a*) determined a value of $-11.2‰$ for ϵ_a during oxidation facilitated by *T. ferrooxidans* and a value of about $+3.5‰$ for ϵ_w. The $\delta^{18}O$ values for sulfates in their samples of acid mine drainage, however, indicated that ϵ_w could be as low as $+2.6‰$.

Using Lloyd's (1967) values for ϵ_a and ϵ_w, we find that 69–71% of the oxygen in the Paint Pots sulfate may have been supplied by the water (O_w). Using the ϵ_a and ϵ_w values from Taylor *et al.* (1984*a*), we find that as much as 72–74% of the sulfate oxygen may have been derived from O_w. Comparison of these results with the ratio of O_w/O_a close to unity found by Schwarcz and Cortecci (1974) leads us to the conclusion that reaction [5] must have made a larger contribution in their experiments than it does at the Paint Pots, presumably because of the free availability of atmospheric oxygen in their experiments.

Our results are illustrated by Fig. 1, in which $\delta^{18}O_s$ is plotted against $\delta^{18}O_w$ for the Paint Pots and the other acidic water sources. Squares and triangles represent experimental results from Taylor *et al.* (1984*b*) and the $\delta^{18}O$ ranges for samples of acidic mine drainage (Taylor *et al.* 1984*a*). The line labelled "H_2O sole oxygen source" represents zero difference between $\delta^{18}O_s$ and $\delta^{18}O_w$. The line labelled 100% represents sterile, submersed conditions in which all of the sulfate would be produced by reaction [3]; its offset relative to the "H_2O sole oxygen source" line is based on the lowest value for ϵ_w ($+2.6‰$) suggested by the acid mine drainage data of Taylor *et al.* (1984*a*).

The lines labelled 75, 50, 25, and 0% in Fig. 1 indicate expected isotopic compositions for product sulfates ($\delta^{18}O_s$) relative to $\delta^{18}O_w$, for decreasing contributions by reaction [3], and increasing contributions by reaction [5]. These lines were calculated on the basis of the isotopic balance equation

$$[7] \quad \delta^{18}O_s = R(\delta^{18}O_w + \epsilon_w) + (1 - R)[0.875(\delta^{18}O_a + \epsilon_a) + 0.125(\delta^{18}O_w + \epsilon_w)]$$

in which R is the fraction of SO_4^{2-} produced by reaction [3]. It should be noted that the lines are not parallel. The slopes of individual lines are equal to $0.875R + 0.125$ and range from 1.0 for $R = 1.0$, to 0.125 for $R = 0.0$. The lines converge and intersect at the point where $\delta^{18}O_w = +10.0‰$ and $\delta^{18}O_s = +12.6‰$.

The convergence of the lines in Fig. 1 means that at lower latitudes, where $\delta^{18}O_w$ values are less negative, it is more difficult to differentiate contributions from individual reactions than at higher latitudes, where $\delta^{18}O_w$ values can be lower than $-30‰$. Figure 1 also suggests that oxidation of FeS_2 in contact with water having a $\delta^{18}O_w$ value of $+10.0‰$ should produce sulfate with a $\delta^{18}O_s$ value equal to $+12.6‰$, independent of the relative contributions by reactions [3] and [5]. It should be possible to verify this point experimentally. Additional experiments may be required to check on the validity of the values used for ϵ_a and ϵ_w as well as on the validity of the assumption that the stoichiometry of reaction [5] applies, or whether the overall approach is too simplified.

The position of the Paint Pots data in Fig. 1 suggests that reaction [3] accounts for 68–71% of the sulfate produced at the Paint Pots and that *T. ferrooxidans* or similar bacteria likely contribute to the oxidation process.

At least a portion of the ferrous iron produced by reactions [3] and [5] is discharged with the groundwater. Upon contact with the atmosphere, oxidation of the ferrous iron and subsequent hydrolysis lead to precipitation of $Fe(OH)_3$ and increasing acidity of the water. In the presence of sulfate and Na^+, some of the ferric hydroxide may be converted to even less soluble natrojarosite.

Mineralogical analyses of the materials of the Ochre Beds (Table 3) show that some portions of the deposit consist entirely of goethite, whereas jarosite is present locally.

The Golden Deposit

The discharge at this site is a Mg–Na–Ca–SO_4 water. The [Mg]/[Ca] ratio in this water (3.87) cannot be derived from dissolution of dolomite. This high ratio, in combination with the high [Na]/[Cl] ratio, suggests that a unit with large cation-exchange capacity, such as shale, has been encountered by this water. These observations, in combination with the high iron and sulfate concentrations, lead to the suggestion that the water discharged at the Golden Deposit derives its geochemical character from extensive contact with pyrite-bearing marine shales of Cretaceous age that are widespread in the Great Bear Basin (Yorath and Cook 1981). The low concentrations of other metals in the water discharged at the Golden Deposit suggest that pyrite is the predominant sulfide mineral present in the shales.

Negative $\delta^{34}S$ values and $\delta^{18}O$ values close to zero (Table 2) both indicate that the sulfates of the Golden Deposit are not derived from marine sulfates, which in this area have $\delta^{34}S$ values between $+15.1$ and $+32.6‰$ and $\delta^{18}O$ values between $+12.0$ and $+17.1‰$ (van Everdingen *et al.* 1982). Both parameters support the conclusion that the sulfates are derived from oxidation of sulfides that are strongly depleted in ^{34}S.

The differences between the $\delta^{18}O_w$ and $\delta^{18}O_s$ values for the Golden Deposit samples (Fig. 1) are somewhat greater than those found for the Paint Pots samples. Using Lloyd's (1967) values for ϵ_w and ϵ_a we find that 44–49% of the sulfate oxygen may be supplied by the water (O_w). Using the ϵ_w and ϵ_a values derived from Taylor *et al.* (1984*a*), we find also that 44–49% of the sulfate oxygen was likely derived from O_w. According to Fig. 1, reaction [3] accounted for between 36 and 42% of the sulfate produced, indicating that *Thiobacillus ferrooxidans* was involved, accompanied by a supply of oxygen-carrying water or possibly occasional exposure to the atmosphere.

It is likely that the flow system discharging at the Golden Deposit is recharged on a low ridge extending northward from the St. Charles Rapids on Great Bear River. Sinkholes that would allow recharge have been observed in Lower and Middle Devonian outcrops on this ridge about 10 km west of the deposit (van Everdingen 1981). Some of the sulfate in the water might thus be derived from Lower Devonian Bear Rock Formation evaporites, with $\delta^{18}O$ values between $+14.0$ and $+17.1‰$ (van Everdingen *et al.* 1982). In that case, the proportion of H_2O oxygen in the portion of the sulfate derived from pyrite oxidation could be somewhat higher than indicated above. At the same time, the $\delta^{34}S$ value for the sulfur source would have to be more negative than the $\delta^{34}S$ value of $-22.8‰$ for the dissolved sulfate.

The mineralogical analyses for the Golden Deposit (Table 3) show that natrojarosite, $NaFe_3(SO_4)_2 \cdot (OH)_6$, forms a major component of the deposit, as a result of the high Na^+ content of the discharge. The remainder of the Fe content of the deposit occurs as goethite. Much of the natrojarosite appears to have been leached out of the crust of the deposit.

The Engineer Creek tributary

The acidic discharge at kilometre 181 along the Dempster Highway is a Mg–Fe–SO_4 water. Its [Mg]/[Ca] ratio of 15.3 cannot be explained by dissolution of dolomite but likely reflects cation exchange with shales. The high [SO_4]/[Ca] and [Mg]/[Ca] ratios, combined with the high Fe concentration and the significant Zn and Ni contents, lead to the conclusion that the geochemical character of the water is established during flow through black shales of the Upper Devonian Canol Formation (or possibly the Lower Devonian Michell Formation) mapped by Norris (1979*b*). The metal content of the water could be derived from subsurface oxidation of pyrite (possibly Ni-bearing pyrrhotite) and sphalerite. Significant U and F concentrations have been found in water samples from the same source by Jonasson and Goodfellow (1976).

The negative $\delta^{34}S$ values and the $\delta^{18}O$ values close to zero (Table 2) both support the above interpretation. As in the case of the Golden Deposit, the source sulfides would have to be strongly depleted with respect to ^{34}S. The differences between the $\delta^{18}O_w$ and $\delta^{18}O_s$ values for the acidic tributary of Engineer Creek are somewhat larger than those found for the Golden Deposit (Fig. 1).

Again using Lloyd's (1967) values for ϵ_w and ϵ_a, we find that 39–42% of the sulfate oxygen may have been supplied by the water (O_w). Using the values for ϵ_w and ϵ_a from Taylor *et al.* (1984*a*), we find that 37–41% of the sulfate oxygen may have been derived from O_w, indicating that reaction [3] accounted for only 28–32% of the sulfate produced (Fig. 1). These low values in turn would indicate involvement of *Thiobacillus ferrooxidans*, accompanied by a supply of oxygenated water, or occasional exposure to the atmosphere.

The mineralogical analysis for the Engineer Creek ochre deposit (Table 3) shows that goethite and limonite constitute the bulk of the minerals precipitated from the acidic water; some jarosite is also present. The deposit is contaminated with silicates contributed by erosion of shale exposures.

Conclusions

High [SO_4]/[Ca] and [Na]/[Cl] ratios in the acidic groundwater discharges investigated in this study rule out marine evaporites as the source for their sulfate contents. The strong acidity and the high heavy-metal contents suggest that oxidation of pyrite (and possibly other sulfides) is primarily responsible for the high concentrations of sulfate in these waters.

The $\delta^{34}S$ values of the dissolved sulfate, in combination with the [Mg]/[Ca] ratios, suggest that the chemical compositions of the waters from the Paint Pots, the Engineer Creek tributary, and the Golden Deposit are controlled by oxidation of sulfides in Cambrian carbonates, in pyrite-bearing Devonian shales, and in pyritiferous Cretaceous shales, respectively.

The $\delta^{18}O$ values of the dissolved and precipitated sulfates reveal that the proportion of sulfate oxygen derived from water molecules ranges from about 74% in the Paint Pots to between 37 and 49% in the Engineer Creek tributary and at the Golden Deposit.

These percentages suggest that *Thiobacillus ferrooxidans* (or similar bacteria) play a role in the sulfide oxidation at all three sites. The water moving through the shales in the latter two cases would have to carry dissolved oxygen, which in turn would require either that the oxidation take place at a shallow depth or that the water flow relatively rapidly through fractured rock (or possibly solution channels) before it reaches the shales.

The data in Fig. 1 show that there is no direct correlation between $\delta^{18}O_s$ and $\delta^{18}O_w$ in groundwaters that have been involved in subsurface oxidation of sulfides. The results of the experiments by Taylor *et al.* (1984*b*) help to explain why this direct correlation, expected by Schwarcz and Cortecci (1974), is not found

Determination of $\delta^{18}O_s$ values for dissolved sulfates in groundwater discharge may provide an additional tool in the exploration for metal sulfides, particulary in areas where $\delta^{18}O_w$ values are strongly negative.

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