Oxygen Isotopes of Dissolved Sulfate as a Tool to Distinguish Natural and Mining-Related Dissolved Constituents

By Winfield G. Wright and D. Kirk Nordstrom

ABSTRACT

Natural and mining-related dissolved-constituent concentrations need to be distinguished in a watershed affected by abandoned mines to prioritize subbasins for remediation and to assist with the establishment of water-quality standards. The oxygen isotopes of dissolved sulfate can be used to distinguish between natural and mining-related sources of dissolved constituents. Several methods employing the oxygen isotopes of dissolved sulfate can be used to determine the relative amounts of natural and mining-related dissolved constituents in water: (1) the isotope-dilution equation for simple mixing zones (two sources and one receiving stream); (2) the isotope mass-balance equation for streams receiving dissolved sulfate from multiple geologic sources; and (3) graphical relations and the mathematical solution of simultaneous equations in a watershed approach. Using the different methods for data collected during low flow, about 71 to 75 percent of the dissolved-constituent concentrations are from natural sources in selected subbasins of the upper Animas watershed.

NATURAL AND MINING-RELATED CONCENTRATIONS OF DISSOLVED CONSTITUENTS

Natural and mining-related concentrations of dissolved constituents need to be distinguished in watersheds affected by abandoned mines in order to prioritize subbasins for remediation and to assist with the establishment of water-quality standards. The typical method for distinguishing between natural and mining-related sources of dissolved constituents is a mass-balance approach, in which all mines and natural streams are sampled synoptically (a snapshot in time), and a mass balance is obtained for a conservative constituent (such as dissolved sulfate or zinc). However, in the mountainous Upper Animas Watershed (fig. 1), this can be a monumental task subject to errors, and theoretically conservative constituents might not be truly conservative. Oxygen isotopes of dissolved sulfate can be used to distinguish natural and mining-related sources on a watershed basis, and the results can be used to verify mass-balance calculations of natural and mining-related dissolved constituents. When used in mass-balance calculations, oxygen isotopes of dissolved sulfate can provide very accurate estimates of natural and mining-related dissolved constituents.

THEORETICAL DESCRIPTION OF THE OXYGEN ISOTOPES OF DISSOLVED SULFATE

Data for the oxygen isotopes of dissolved sulfate (symbol $\delta^{18}O_{SO_4^{2-}}$) can provide insight into the processes that formed the sulfate. In some geologic settings, $\delta^{18}O_{SO_4^{2-}}$ data can reflect the mineralogy of the dissolved-sulfate source. The $\delta^{18}O_{SO_4^{2-}}$ data also can determine whether sulfate reduction has occurred in the water. The analytical measurement of $\delta^{18}O_{SO_4^{2-}}$ is more precise than other hydrologic parameters (such as discharge and analytical determination of inorganic constituents), and could be useful for quantitative calculations.

In sulfide-mineralized geologic regions that have been mined, such as the Upper Animas Watershed (fig. 1), the oxidation of sulfide minerals produces dissolved sulfate (symbol SO_4^{2-}) in natural springs and in mine drainage. These oxidation pro-
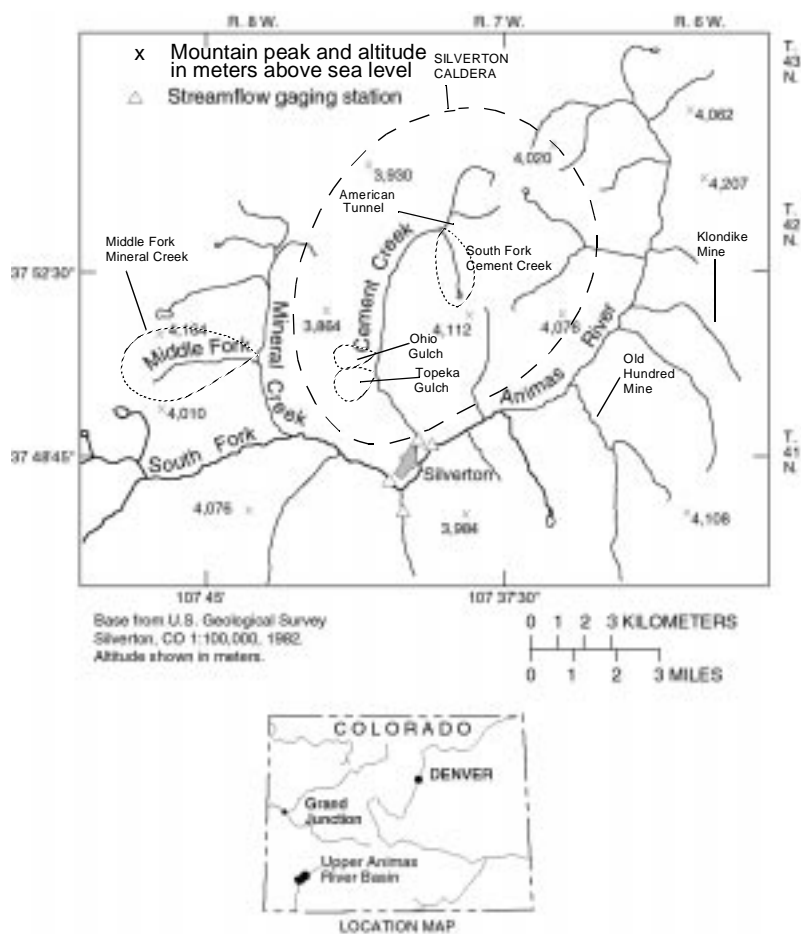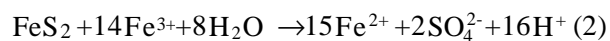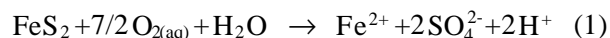
Figure 1. Upper Animas Watershed and locations of study areas.

cesses involve oxygen that has an isotope composition indicative of the reaction mechanism. Oxygen in the dissolved sulfate has two possible sources-- dissolved oxygen (symbol $O_{2(aq)}$ for oxygen in the aqueous phase) and oxygen in the water molecule (symbol H_2O). Oxygen isotopes of dissolved sulfate are expressed in per mil (or parts per thousand) relative to the Vienna Standard Mean Ocean Water (VSMOW) on a scale that is normalized such that the $\delta^{18}O$ of the Standard Light Arctic Precipitation (SLAP) water is -55.5 per mil exactly. Precision of $\delta^{18}O_{SO_4^{2-}}$ measurements is ± 0.2 per mil.

Numerous studies of sulfide-mineral oxidation have been conducted in the last two decades. Of particular interest are those studies conducted under conditions similar to environments producing acid mine drainage. The following reactions commonly are used to represent the overall oxidation processes of pyrite (symbol FeS_2):
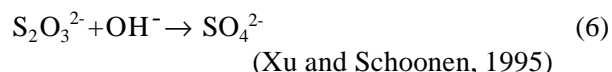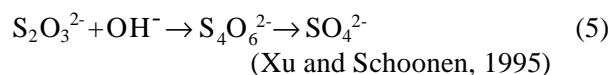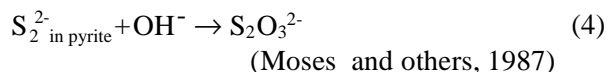
$$FeS_2 + 7/2\,O_{2(aq)} + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \quad (1)$$

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

Reaction (1) is limited by the availability of dissolved oxygen and reaction (2) is limited by the oxidation rate of Fe^{2+} to Fe^{3+}. The ferrous iron (Fe^{2+}) produced from reactions 1 and 2 is subsequently oxidized further to produce ferric iron (symbol Fe^{3+}), which can precipitate as iron oxyhydroxide:

$$Fe^{2+} + 1/4\,O_{2(aq)} + H^+ \rightarrow Fe^{3+}_{(solid)} + 1/2\,H_2O \quad (3)$$
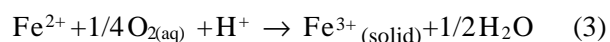
Sulfur oxyanions, such as thiosulfate ($S_2O_3^{2-}$), polythionate ($S_nO_6^{2-}$), and sulfite (SO_3^{2-}) are sulfur compounds intermediate to the oxidation pathway of FeS_2 to SO_4^{2-}. The oxidation of sulfur oxyanions can occur quickly, and the

resulting SO_4^{2-} may acquire oxygen via exchange with H_2O (Van Stempvoort and Krouse, 1994). Oxidation of sulfur and sulfur oxyanions may proceed as follows:

$$S_2^{2-}_{\text{ in pyrite}} + OH^- \rightarrow S_2O_3^{2-} \qquad (4)$$
$$\text{(Moses and others, 1987)}$$

$$S_2O_3^{2-} + OH^- \rightarrow S_4O_6^{2-} \rightarrow SO_4^{2-} \qquad (5)$$
$$\text{(Xu and Schoonen, 1995)}$$

$$S_2O_3^{2-} + OH^- \rightarrow SO_4^{2-} \qquad (6)$$
$$\text{(Xu and Schoonen, 1995)}$$

The oxygen molecules (whether in $O_{2(aq)}$ or in H_2O) that are involved in reactions (1)-(6) can, except during sulfate reduction, retain the original isotopic composition of the source of the oxygen. The oxygen isotope composition of H_2O (symbol $\delta^{18}O_{H_2O}$) varies with the altitude of the precipitation that deposited the water on the Earth's surface and with other processes such as evaporation, transpiration, and latitude. For the Upper Animas Watershed, $\delta^{18}O_{H_2O}$ averages about -15.9 per mil. The oxygen-isotope composition of atmospheric oxygen that dissolves in water (symbol $\delta^{18}O_{O_{2(aq)}}$) has the value of +23 per mil (Horibe and others, 1973). Graphically relating $\delta^{18}O_{SO_4^{2-}}$ data to dissolved SO_4^{2-} data can indicate the geochemical mechanisms involved with the formation of the dissolved SO_4^{2-}.

The isotopic composition of $\delta^{18}O_{SO_4^{2-}}$ that results from the reactions can indicate whether the dissolved sulfate is from natural or mining-related sources. If reaction (1) is the predominant reaction pathway, the resulting $\delta^{18}O_{SO_4^{2-}}$ might consist of a greater percentage of the $\delta^{18}O_{O_{2(aq)}}$ composition, as compared with the $\delta^{18}O_{H_2O}$ composition. If reaction (2) is the predominant oxidation pathway, aqueous ferric iron ($Fe^{3+}_{(aq)}$), rather than $O_{2(aq)}$, is the primary agent responsible for oxidation of pyrite in acid conditions. All of the reactions (1)-(6) are mediated by bacteria in the environment; however, mining accelerates the weathering processes through both exposure of fresh minerals to oxygen and increased populations of sulfide-mineral oxidizing bacteria (Taylor and others, 1984). In accelerated weathering environments, reactions (4), (5), and (6) might occur very quickly; consequently, the resulting $\delta^{18}O_{SO_4^{2-}}$ might consist of a greater percentage of the $\delta^{18}O_{H_2O}$ composition, as

compared to the $\delta^{18}O_{O_{2(aq)}}$ composition, because of oxygen exchange between H_2O and SO_4^{2-}.

Effects on $\delta^{18}O_{SO_4^{2-}}$ values might be caused by the relative distribution of different sulfur minerals in different rock types. The dissolution of anhydrite, gypsum, barite, and alunite affect the $\delta^{18}O_{SO_4^{2-}}$ compositions. Two samples of vein gypsum collected from a mine dump pile in the Cement Creek subbasin of the Upper Animas Watershed had $\delta^{18}O_{SO_4^{2-}}$ values of +9 and +10 per mil. In a geochemical environment dominated by pyrite oxidation, dissolution of gypsum imparts a mixture of the two processes on the resulting $\delta^{18}O_{SO_4^{2-}}$ compositions.

Microbially-mediated reduction of SO_4^{2-} to sulfide (symbol H_2S, which can be present in the dissolved or gaseous phases) can result in substantial enrichments of sulfur isotopes (symbol $\delta^{34}S_{SO_4^{2-}}$) and $\delta^{18}O_{SO_4^{2-}}$ in residual SO_4^{2-}. The lighter ^{32}S molecule in SO_4^{2-} is preferentially utilized over the ^{34}S molecule by microbes, which enriches (or makes more positive) the $\delta^{34}S_{SO_4^{2-}}$ composition of the remaining SO_4^{2-}. Likewise, the lighter ^{16}O molecule is preferentially utilized over the ^{18}O molecule by microbes, which enriches (or makes more positive) the resulting $\delta^{18}O_{SO_4^{2-}}$. In addition, in geochemically-reducing conditions, the oxygen molecule in $O_{2(aq)}$ and in H_2O become parallel electron acceptors during dissimilatory reduction of SO_4^{2-}; hence both $\delta^{18}O_{O_{2(aq)}}$ and $\delta^{18}O_{H_2O}$ may become enriched isotopically, whereby further FeS_2 oxidation by these isotopically-enriched oxygen molecules produces isotopically enriched $\delta^{18}O_{SO_4^{2-}}$ (C. Kendall, U.S. Geological Survey, written commun., 1997). Several collapsed mines in the Upper Animas Watershed show indications of SO_4^{2-} reduction: zero $O_{2(aq)}$, smell of H_2S gas, and isotopically heavy $\delta^{34}S_{SO_4^{2-}}$ and $\delta^{18}O_{SO_4^{2-}}$ compositions. There is, however, some debate concerning the electron donors available for SO_4^{2-} reduction. Mold on wood timbers in the abandoned mines may provide sufficiently labile organic matter for SO_4^{2-} reduction; however, this hypothesis has not been tested.

OXYGEN ISOTOPES OF DISSOLVED-SULFATE DATA FROM THE UPPER ANIMAS WATERSHED, SOUTH-WESTERN COLORADO

The Upper Animas Watershed has complex geology related to the approximately 28 million-year-old Silverton Caldera (fig. 1) and placement of intracaldera lavas. Regional propylitic alteration introduced sulfur as sulfide minerals which are present in veins and disseminated throughout the rocks in varying proportions. Late-stage hydrothermal mineralization is typified by quartz vein filling accompanied by chalcopyrite, pyrite, galena, gold, rhodonite, silver, and sphalerite. Vein gypsum and barite also were introduced by late-stage hydrothermal venting. Copper-molybdenum porphyry complexes and acid-sulfate hydrothermal alteration systems also are present in the region.

Water-quality samples were collected during low flow from natural springs, draining mines, and streams in the Middle Fork Mineral Creek, South Fork Cement Creek, Ohio Gulch, and Topeka Gulch subbasins (fig. 1), as well as from the Klondike Mine, the Old Hundred Mine, and the American Tunnel (fig. 1). Graphically relating $\delta^{18}O_{SO_4^{2-}}$ to $\delta^{34}S_{SO_4^{2-}}$ indicates water from natural springs and mine drainage plot parallel (fig. 2). When comparing natural springs to mine drainage in figure 2, there is an isotopic shift to the left (decrease in oxygen isotope values) from natural springs to mine drainage. This might be explained by the incorpo-
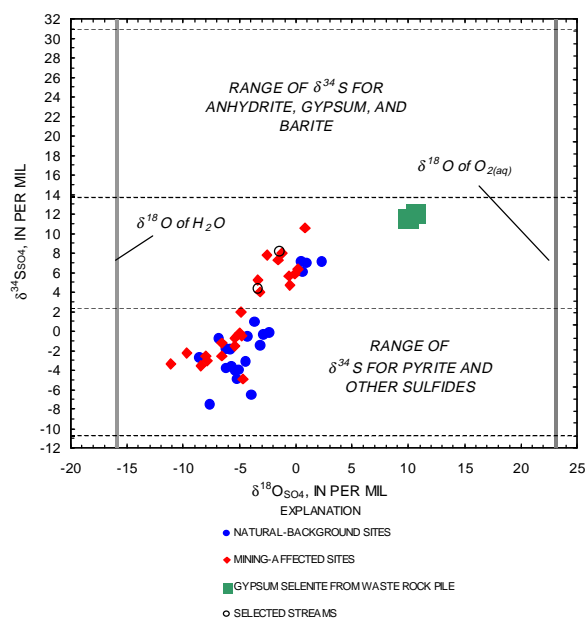
ration of a greater percentage of $\delta^{18}O_{H_2O}$ in $\delta^{18}O_{SO_4^{2-}}$ possibly because of bacterially-mediated sulfide oxidation. For the purposes of this report, this isotopic shift is called the kinetic shift. Also shown on figure 2 are the solid- and aqueous-phase endmembers that are incorporated into the oxygen and sulfur isotopic compositions (Casadevall and Ohmoto, 1977; Horibe and others, 1973). When relating all $\delta^{18}O_{SO_4^{2-}}$ data to dissolved SO_4^{2-} and dissolved-calcium concentrations, the importance of gypsum to $\delta^{18}O_{SO_4^{2-}}$ compositions is evident (fig. 3). Data points that have lower dissolved-calcium concentrations and lighter $\delta^{18}O_{SO_4^{2-}}$ compositions represent the sulfide-oxidation region (fig. 3); data points that have lower dissolved-calcium concentrations and heavier $\delta^{18}O_{SO_4^{2-}}$ compositions represent the sulfate-reduction region (sulfate reduction that occurs in collapsed, anoxic mines) (fig. 3); and data points that have higher dissolved-calcium concentrations represent a mixture of sulfide oxidation and gypsum dissolution (fig. 3).
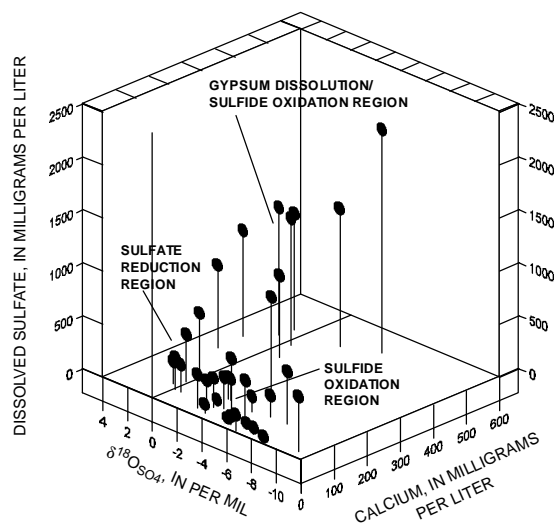

Figure 2. Oxygen isotopes of sulfate related to sulfur isotopes of sulfate in water from springs and mines in the upper Animas watershed during low flow.

Figure 3. Oxygen isotopes of sulfate related to dissolved sulfate and dissolved calcium in water from ground-water sites (springs and mines) during low-flow.

Graphically relating $\delta^{18}O_{SO_4^{2-}}$ to SO_4^{2-} can help distinguish natural from mining-related dissolved sulfate. Figure 4 shows data from ground-water samples collected during low flow in the Cement Creek subbasin (rock types from the center of the caldera). The isotopically heavier $\delta^{18}O_{SO_4^{2-}}$ compositions probably are affected by gypsum dissolution or SO_4^{2-} reduction, or both. When compar-

ing natural springs to mine drainage in figure 4, the isotopic shift is evident in the data. To illustrate the kinetic shift, three pairs of spring/mine combinations (a-a', b-b', and c-c') are shown on figure 4 where the springs and mines are situated in similar rock types. There is a shift to the left and up on figure 4 from the springs to the mines. A t-test of the paired data indicated that the kinetic shift is significant ($p \leq 0.3$, $r^2 = 0.78$). The kinetic shift is a result of the mining-related acceleration of weathering processes. The data point for Cement Creek at the mouth of the subbasin, an amalgamation of all water types in the Cement Creek subbasin, plots in the middle of all data points.
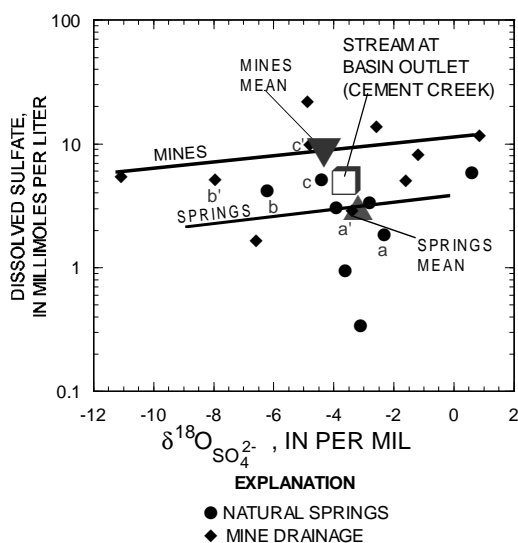

Figure 4. Oxygen isotopes of sulfate related to dissolved sulfate in water from springs and mines in the Cement Creek subbasin during low-flow.

Total-dissolved metals concentrations (Cd, Cu, Co, Fe, Ni, Pb, and Zn) are related to oxygen and sulfur isotopes of sulfate in figure 5. Increased dissolved-metal concentrations in mine drainage are shown in figure 5, which are caused by (1) location of mines along mineralized ore deposits, and (2) acceleration of sulfide-metal oxidation in mines, which creates higher dissolved-metal concentrations in mine drainage compared to natural springs. The kinetic shift (lighter oxygen-isotope compositions in mine drainage) also is evident in the data (fig. 5). This may be caused by the incorporation of a greater proportion of $\delta^{18}O_{H_2O}$ in $\delta^{18}O_{SO_4^{2-}}$ during oxidation of sulfur oxyanions. Some of the mine-drainage samples that plot among the spring

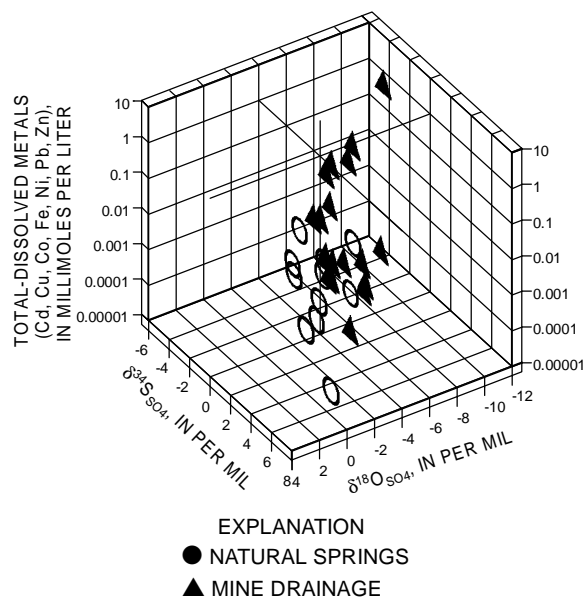samples have similar water-quality characteristics as natural springs.

Figure 5. Oxygen isotopes of sulfate related to sulfur isotopes of sulfate and total-dissolved metals in water from springs and mines in the upper Animas watershed during low flow.

USES OF THE OXYGEN ISOTOPES OF DISSOLVED SULFATE

A typical method for distinguishing between natural and mining-related dissolved constituents in a subbasin is to collect water-quality samples, measure discharges, and perform loading mass-balance calculations, in which all mines and natural sources are accounted for. This effort can be a monumental task. The method described in this paper uses the oxygen isotopes of dissolved sulfate in a watershed approach so that all water sources (natural and mining-related) do not need to be sampled, only a representative sampling of the different site types is needed. Current work in the Upper Animas Watershed is, however, using the traditional mass-balance approach to distinguish natural and mining-related dissolved constituents, and the isotope method will be used to verify the mass-balance approach.

The oxygen isotopes of dissolved sulfate also can be used to perform mass-balance calculations. The error associated with analysis of water samples for the $\delta^{18}O_{SO_4^{2-}}$ isotopes is ± 0.1 per mil; therefore, the mass-balance calculations will have great

accuracy using isotopes. Also, in a geologically heterogeneous subbasin, it is possible to determine the source of the dissolved sulfate using $\delta^{18}O_{SO_4^{2-}}$ data.

The following example describes the use of oxygen isotopes of dissolved sulfate in a simple mixing problem to determine how much sulfate came from a particular mine. The sites and conditions of a location in Topeka Gulch are described as follows:

Topeka Gulch (fig. 1):

TOPEKA8=Natural alpine stream upstream from mine; $\delta^{18}O_{SO_4^{2-}}$ = -6.8 per mil.
TOPEKA9=Large draining mine; $\delta^{18}O_{SO_4^{2-}}$ = 0.83 per mil.
TOPEKA10=Mining-affected stream downstream from mine; $\delta^{18}O_{SO_4^{2-}}$ = 0.3 per mil.

To determine the percent of dissolved sulfate that comes from the TOPEKA9 mine, the isotope-dilution equation can be used (Shearer & Kohl 1993):

Isotope-dilution equation:

$$\text{Percent TOPEKA9} = \frac{(\delta^{18}O_{TOPEKA8} - \delta^{18}O_{TOPEKA10})}{(\delta^{18}O_{TOPEKA8} - \delta^{18}O_{TOPEKA9})} \times 100 \quad (7)$$

$$= [(-6.8) - (0.3)/(-6.8) - (0.83)] \times 100$$

$$= 93 \text{ percent of the dissolved sulfate came from the mine.}$$

In this simple example, the isotope-dilution equation calculated that 93 percent of the dissolved sulfate came from the mine at TOPEKA9. The discharge of the stream and the mine are needed to perform a typical sulfate mass balance, and errors are inherent in the discharge and sulfate measurements. When the isotope-dilution equation was used, discharges were not needed, which eliminated the errors in streamflow-discharge measurements and in sulfate analyses.

An example using oxygen isotopes of dissolved sulfate in multiple geologic settings can be applied in the Middle Fork Mineral Creek subbasin (fig. 1). About one-half of the subbasin consists of chlorite-epidote-calcite dominated intracaldera lavas, and one-half of the subbasin consists of rocks altered by a copper-molybdenum porphyry complex. An isotope mass balance is obtained so that natural and mining-related sources balance at the mouth of the subbasin.

Isotope mass-balance equation:

$$\delta QC_{\text{natural}} + \delta QC_{\text{mining-related}} = \delta QC_{\text{Middle Fork at mouth}} \quad (8)$$

where

δ is $\delta^{18}O_{SO_4^{2-}}$, in per mil,
Q is discharge at the site, in cubic feet per second, and
C is dissolved-sulfate concentration, in mg/L.

The known value is $\delta QC_{\text{Middle Fork at mouth}}$, and $\delta_{\text{Middle Fork at mouth}} = 0.0$ per mil.

All of the mines in the Middle Fork Mineral Creek subbasin were sampled during low-flow conditions. Values of $\delta^{18}O_{SO_4^{2-}}$ for the mines ranged from -5.8 to +0.2. Using isotope mass balance, the flow-weighted average $\delta^{18}O_{SO_4^{2-}}$ composition for the mining-related water in the subbasin was calculated as: $\delta_{\text{mining-related}} = -0.76$ per mil, which is an amalgamation of $\delta^{18}O_{SO_4^{2-}}$ compositions from mining-related sources.

Because two of the three values in equation (8) are known, the remaining unknown can be calculated: $\delta_{\text{natural}} = +0.32$ per mil, which is an amalgamation of $\delta^{18}O_{SO_4^{2-}}$ compositions from natural sources in the subbasin. Because this composition is weighted towards the positive side, and there is gypsum and barite in the copper-molybdenum porphyry complex (contributing heavy $\delta^{18}O_{SO_4^{2-}}$ compositions), much of the SO_4^{2-} concentration at the mouth of the Middle Fork Mineral Creek subbasin probably comes from the porphyry complex. The isotope-dilution equation now can be used to determine the percent of mining-related dissolved sulfate that discharges from the mouth of the Middle Fork Mineral Creek: Mining-related sulfate = 29 percent; therefore, natural sulfate = 71 percent.

The percent of natural and mining-related dissolved zinc also can be determined using the $\delta^{18}O_{SO_4^{2-}}$ data and the solution of simultaneous equations. By determining the geometric means of the natural and mining-related data, the result is two end members and a receiving stream, and the proportion of the two end members in the Cement Creek sample can be solved using simultaneous equations. Solution of the simultaneous equations for the Cement Creek data indicate 75 percent of the

dissolved zinc in Cement Creek comes from natural springs and 25 percent of the dissolved zinc comes from mine drainage during low-flow. This estimate might vary during snowmelt-runoff periods.

A t-test of the $\delta^{18}O_{SO_4^{2-}}$ means for the simultaneous equations solution indicates the differences in the natural and mining-related means are significant to the $p \leq 0.4$ level. A t-test of the dissolved-zinc means indicates the natural and mining-related means are significant to the $p \leq 0.3$ level. Hence, there is a 60 to 70 percent confidence that the means are significantly different, and this confidence must be considered in the interpretation of the simultaneous equations results.

SUMMARY AND CONCLUSIONS

The oxygen isotopes of dissolved sulfate ($\delta^{18}O_{SO_4^{2-}}$) are a useful diagnostic tool to describe the geochemical processes that incorporate dissolved sulfate into water from sulfide-mineral oxidation and from gypsum dissolution. The percentage of natural and mining-related sources of dissolved constituents can be determined using $\delta^{18}O_{SO_4^{2-}}$ data in a watershed approach. Using the isotope dilution equation in simple mixing zones near a mine site, accurate estimates of the percentage of natural and mining-related dissolved sulfate can be determined, and discharge measurements are not needed for the calculation. Using the isotope mass-balance method in a heterogeneous geologic setting, $\delta^{18}O_{SO_4^{2-}}$ data indicated that 71 percent of the dissolved sulfate in the Middle Fork Mineral Creek subbasin came from natural sources and 29 percent came from mining-related sources. Using the graphical method and solution of simultaneous equations in a watershed approach, $\delta^{18}O_{SO_4^{2-}}$ data indicated that 75 percent of the dissolved zinc in the Cement Creek subbasin came from natural sources.

REFERENCES

Casadevall, T.J., and Ohmoto, H., 1977, Sunnyside Mine, Eureka Mining District, San Juan County, Colorado-- Geochemistry of gold and base metal ore deposition in a volcanic environment: Economic Geology, v. 72, p. 1285-1320.

Horibe, Y., Shigehara, K., and Takakuwa, Y., 1973, Isotope separation factor of carbon dioxide-water system and isotopic composition of atmospheric oxygen: J. Geophys. Res., v. 78 n. 15, p. 2625-2629.

Moses, C.O., Nordstrom, D.K., Herman, J.S., and Mills, A.L., 1987, Aqueous pyrite oxidation by dissolved oxygen and by ferric iron: Geochim. et Cosmochim. Acta, v. 51, p. 1561-1571.

Shearer, G., and Kohl, D.H., 1993, Natural abundance of nitrogen-15 isotopes--Fractional contribution of two sources to a common sink and use of isotope discrimination, in Knowles, R., and T.H. Blackburn, eds., Nitrogen isotope techniques: San Diego, Calif., Academic Press, Inc., p. 89-125.

Taylor, B.E., Wheeler, M.C., and Nordstrom, D.K., 1984, Stable isotope geochemistry of acid mine drainage--Experimental oxidation of pyrite: Geochim. et Cosmochim. Acta. v. 48, p. 2669-2678.

Van Stempvoort, D.R., and Krouse, H.R., 1994, Controls of $\delta^{18}O$ in sulfate--Review of experimental data and application to specific environments, in Alpers, C.N., and Blowes, D.W., eds., Environmental geochemistry of sulfide oxidation: Washington, D.C., American Chemical Society, Symposium Series 550, p. 446-480.

Xu, Y., and Schoonen, M.A.A., 1995, The stability of thiosulfate in the presence of pyrite in low-temperature aqueous solutions: Geochim. et Cosmochim. Acta, v. 59, p. 4605-4623.

AUTHOR INFORMATION

Winfield G. Wright
U.S. Geological Survey
Water Resources Division
Durango, Colorado 81301
(wgwright@usgs.gov)

D. Kirk Nordstrom
U.S. Geological Survey
Water Resources Division
National Research Program
Boulder, Colorado 80303
(dkn@usgs.gov)