

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

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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 $\delta^{18}\text{O}_{\text{SO}_4^{2-}}$) can provide insight into the processes that formed the sulfate. In some geologic settings, $\delta^{18}\text{O}_{\text{SO}_4^{2-}}$ data can reflect the mineralogy of the dissolved-sulfate source. The $\delta^{18}\text{O}_{\text{SO}_4^{2-}}$ data also can determine whether sulfate reduction has occurred in the water. The analytical measurement of $\delta^{18}\text{O}_{\text{SO}_4^{2-}}$ 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-

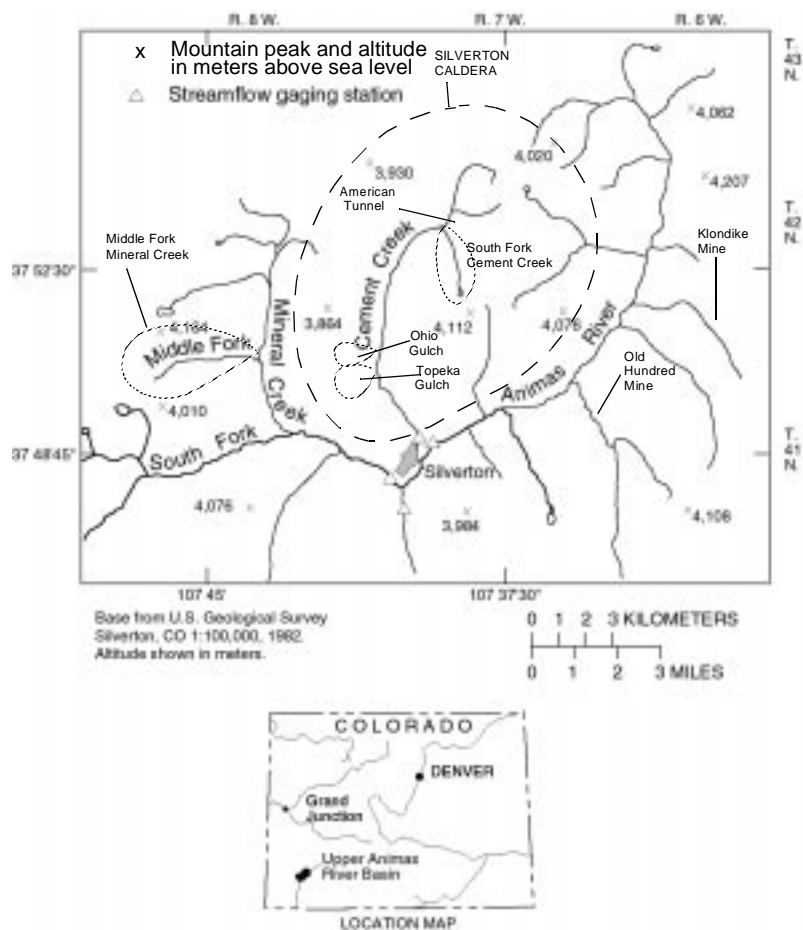
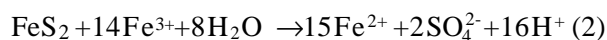
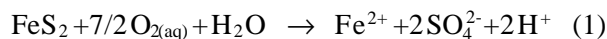


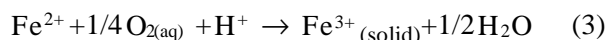
Figure 1. Upper Animas Watershed and locations of study areas.

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):



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:



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