Proceedings of the 12th International Symposium on Applied Isotope Geochemistry (AIG-12)

Strontium isotopic systematics of mineralized and background water samples, Montezuma Mining District, Colorado

Philip L. Verplanck[a], Robert L. Runkel[a]

[a]U.S. Geological Survey, Denver Federal Center, Denver, Colorado, USA 80225

Abstract

Surface and groundwater samples within the Montezuma mining district were sampled to evaluate the use of strontium isotopic compositions as signatures of different water types. Waters draining Precambrian metamorphic units had distinctly higher $^{87}Sr/^{86}Sr$ values (0.72893 to 0.73833) than waters draining Tertiary-age plutonic rocks (0.71064 and 0.71114). Waters draining mine workings along Tertiary-age mineralized veins in Precambrian metamorphic units had isotopic compositions between these two endmembers such that Sr isotopic composition could not be used as a unique signature of mining-related waters.

Introduction

An understanding of the hydrogeologic framework of an alpine region that receives acidic, metal-rich drainage is important for water-management decision making. Many of these regions in the western United States are quite complex because of geologic, metallogenic, and anthropogenic effects. This study evaluates the use of strontium isotopic systematics to constrain groundwater flow in a mineralized watershed, the Montezuma mining district, Colorado (Fig. 1). This district was one of the primary silver producers in Colorado from approximately 1870 to 1895. Mineralization is associated with Tertiary-age magmatism that intruded Precambrian hornblende gneisses and schist (Neuerburg and Botinelly, 1972). Within the study area, stream chemistry is affected by drainage from numerous abandoned mines and by acidic, metal-rich seeps and springs.

The strontium isotopic composition of groundwater reflects the isotopic composition of the rocks that it has passed through. The water strontium isotopic composition is controlled by water-rock interactions including dissolution of minerals and exchange reactions. Moreover, the strontium isotopic composition of waters is not altered by fractionation or precipitation. These characteristics make strontium a potential tracer for identifying groundwater flow paths and unraveling mixing of groundwaters assuming lithologic units have an isotopic contrast.

We chose to utilize this technique in the Montezuma mining district because of the potential for significant isotopic contrasts between waters interacting with Precambrian metamorphic units and Tertiary-age plutonic rocks and associated mineralization. Radioactive decay of ^{87}Rb produces ^{87}Sr such that older rocks and rocks with high Rb/Sr have higher $^{87}Sr/^{86}Sr$ values. The objective of the study was to evaluate the use of strontium isotopic compositions of groundwaters as a geochemical tracer. Specifically, we wanted to evaluate whether the strontium isotopic composition could be used to differentiate between natural springs and mine drainage and whether the isotopic compositions of mixed waters could be used to determine mixing ratios from source lithologies.

Setting

The study area lies within the Montezuma mining district, a precious and base metal mining district in the Colorado Front Range (Fig. 1). The Continental Divide cuts through the southeast portion of the mining district such that water within the district flows to the east and west. Elevation varies from approximately 3200 to 4000 meters. As a result of Pleistocene glaciation, valleys tend to be broad and U-shaped with steep headwalls approaching ridge lines. Mean annual precipitation is 75-85 cm with 55-80% falling as snow. The study area includes portions of Peru Creek and its tributaries, all within the Snake River watershed.

Bedrock geology consists of Precambrian gneisses, schists, and amphibolites that have been intruded by Tertiary felsic plutons. The largest body, the Montezuma stock, primarily consists of porphyritic quartz monzonite dated at ~40 Ma. The Montezuma stock and associated intrusions are responsible for most of the mineralization in the Montezuma mining district (Lovering, 1935). This mining district was one of the primary silver producers in Colorado from approximately 1870 to 1895. Production of lead, zinc, copper, and gold also occurred from the late 1800s to mid 1900s. Most of the mining centered along narrow, 10 centimeters to 1 meter wide, polymetallic veins that primarily occur along the margins of the Montezuma stock. The veins consist of quartz with minor manganese carbonates and barite, pyrite, galena, and subordinate sphalerite, chalcopyrite, and tennantite (Lovering, 1935). Hydrothermal alteration occurs adjacent to the quartz veins, along the margin of the Montezuma stock, and along zones of increased permeability within the surrounding Precambrian gneisses and schist. The intensity of alteration is variable, but fine-grained disseminated pyrite is common throughout. Within Cinnamon Gulch, a tributary to Peru Creek and location of a detailed study, a zone of more intense alteration and pyritization occurs along the Montezuma shear, a ~200 m wide, northeast-trending shear zone (Neuerburg and Botinelly, 1972).

Within the study area, numerous abandoned mines and naturally acidic springs contribute metals and acidity to receiving streams. Previous studies in the southern Rocky Mountains have demonstrated that hydrothermal alteration can play an important control on surface-water chemistry (Mast et al., 2007; Verplanck et al., 2009; Neubert et al., 2011). In general, waters draining more intensely altered areas (quartz-sericite-pyrite) have low pH values (pH 3-4) with moderate concentrations of dissolved metals. When compared to waters draining abandoned mines with similar acidic pH values, the dissolved copper and zinc concentrations tend to be lower in the natural waters (Verplanck et al., 2009).

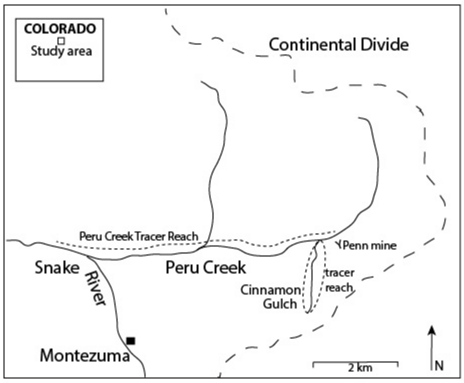

Fig. 1. Map displaying study area. Along Peru Creek, the Montezuma stock crops out at the Cinnamon Gulch confluence. Precambrian metamorphic rocks crop out upstream of there.

Methods

Samples for major, trace, and isotopic compositions were field filtered through 0.45 micrometer-pore-size filters and acidified with ultrapure nitric acid to a pH value of <2. Strontium isotopic compositions of water samples were determined using a Finnigan MAT 261, six-collector solid source mass spectrometer at the University of Colorado, Boulder or using a Nu Instruments HR® MC-ICP-MS at the U.S. Geological Survey, Denver. Sample sites include draining adits, springs, and alpine streams.

As part of a larger study to quantify metal loading in the Peru Creek watershed, two tracer experiments were conducted. A conservative tracer was injected into the stream and samples were collected downstream for chemical analysis. Streamflow at each site was quantified by tracer dilution (see Runkel et al., 2013, for details). One tracer study focused on a 6.5 km reach along the main stem of Peru Creek from immediately upstream of the Pennsylvania mine, a significant metal loader in the middle of the watershed, to the confluence with the Snake River. The second tracer was along Cinnamon Gulch, a tributary to Peru Creek.

Results

As a first order test of the use of Sr isotopic systematics to identify signatures of water-rock interaction in the study area, a suite of five samples from headwater catchments were analyzed. Sample sites were selected that occurred in unimpacted, monolithologic catchments. Three samples that drained Precambrian metasedimentary units had $^{87}Sr/^{86}Sr$ values of 0.72893, 0.73022, and 0.73833 (Fig. 2). The two samples with the lower isotopic compositions were located just west of the Montezuma stock near where mineralized veins crop out. Of note, the dissolved zinc and sulfate concentrations were slightly elevated compared to the third sample which was away from any associated mineralization. Two samples from small catchments within the Montezuma stock had $^{87}Sr/^{86}Sr$ values of 0.71064 and 0.71114. One sample was from an unaltered catchment while the other drained an area of the stock of quartz-sericite-pyrite alteration. Two additional samples were collected from small catchments that contained both Precambrian metasedimentary units and Montezuma stock, $^{87}Sr/^{86}Sr$ values of 0.72191 and 0.72484.

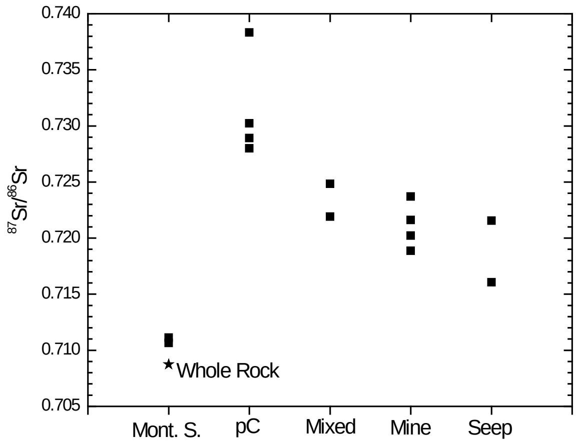

Fig. 2. Graph displaying Sr isotopic compositions of water samples and one whole-rock sample. Mont. S.: Montezuma stock, pC: Precambrian metasedimentary, Mixed: mixed lithologies.

The Sr isotopic composition of a set of samples from the Peru Creek tracer study were analyzed to gain insight into variations in Sr within the watershed and to assess the conservative nature of dissolved Sr. For each stream sample, we have discharge data by tracer dilution such that we can evaluate relative changes in the mass of Sr downstream to test if Sr behaves conservatively, that is to say, remains as a dissolved phase and is not removed from solution by precipitation, adsorption, or exchange. The Sr loading profile displays a steady, downstream increase in mass and overall conservative behavior. We selected a subset of samples for Sr isotopic determinations. Along the study reach, the $^{87}Sr/^{86}Sr$ values systematically decreased from 0.72801 to 0.72087. Upstream of the study reach, the bedrock geology is primarily Precambrian metasedimentary units with minor Tertiary age dikes and veins. Within the study reach, much of the geology includes the Montezuma stock. Sampled inflows to Peru Creek tend to have $^{87}Sr/^{86}Sr$ values between the endmembers identified above (~0.7190 to 0.7273).

A second study reach, Cinnamon Gulch, was sampled to evaluate $^{87}Sr/^{86}Sr$ as a tracer of mining-affected groundwater. Waters from four draining adits and two seeps were collected. The mine drainage was acidic, pH 3.4-3.7, with elevated Fe, Cu, Zn, and Pb. The $^{87}Sr/^{86}Sr$ values included 0.71886 from the mine input at the head of Cinnamon Gulch and within an area where the bedrock was mapped as the Montezuma stock. The $^{87}Sr/^{86}Sr$ values for three other draining adits farther downstream were 0.72023, 0.72161, and 0.72371. These small mines are along narrow mineralized veins within the shear zone in the Precambrian metasedimentary mass adjacent to the Montezuma stock (~200 m). One natural spring upgradient of mining impacts, and closer to the Montezuma stock proper was 0.71606, and another seep downgradient of the three draining adits was 0.72155.

Discussion

This study was undertaken because of the likely Sr isotopic contrast between waters draining Precambrian metasedimentary and Tertiary magmatic units. Little isotopic data are available for the bedrock lithologies. Stein (1985) published a whole-rock $^{87}Sr/^{86}Sr_m$ for the Montezuma stock of 0.70874. No data are available for Precambrian units, but because of the age (~1.7 Ga) and amount of rubidium present, the Sr isotopic composition should be substantially higher than that of the Montezuma stock. Another complicating factor is that the isotopic composition of groundwater flowing through a rock will reflect the most easily dissolved mineral phase or exchangeable Sr, not the whole-rock isotopic composition. We chose to sample small monolithic catchments to constrain the Sr isotopic composition in groundwater in these units. The Sr isotopic composition of groundwater emanating from Precambrian metasedimentary units (0.72893 to 0.73833) was substantially higher than from the Montezuma stock (0.71064 and 0.71114). Waters from areas of mixed lithologies were intermediate between these endmembers (0.72191 and 0.72484). Conservative behavior of Sr in these waters was confirmed by the Peru Creek tracer.

One important question within the watershed is: what are the relative contributions of metals to receiving streams from mine drainage and natural acid springs? This has important ramifications for setting cleanup standards. Because the mineralization in the Montezuma mining district is genetically related to Tertiary magmatism, we wanted to test if the Sr isotopic composition of mine drainage would reflect a Montezuma stock signature and could be used to fingerprint mine drainage occurring outside of the Montezuma stock. Whole-rock (0.70874) and our monolithic catchment (0.71064 and 0.71114) Sr isotopic data suggest that groundwater associated with the Montezuma stock would have an isotopic composition <0.712. Four mine drainage samples from adits that were driven along Montezuma stock-related veins had isotopic compositions ranging from 0.71886 to 0.72371. These values lie between the stock signature (<0.712) and the Precambrian signature (~0.728 and 0.738), and are similar to the isotopic composition of surface waters draining mixed lithologic catchments (0.72191 and 0.72484). One reason for the mixed signature may be that the adits tend to be 1 to 2 meters in width and the actual veins are generally only tens of centimeters in width such that although the mineralization was the focus of the mine, much of the disturbed rock was Precambrian. Furthermore, these adits were driven in veins within a shear zone in the Precambrian metamorphic lithologies.

Summary

The Peru Creek tracer results provide strong evidence that Sr can be used as a conservative tracer in surface waters. Overall, as shown by the samples from monolithic catchments, Sr isotopic composition is a valuable tracer of major lithologies in the study area. The large isotopic difference between Precambrian and Tertiary age units is the key to having more radiogenic Sr in groundwaters associated with the Precambrian units. In this study we could not use the Sr isotopic composition of mine waters as a unique signature because the isotopic ratios are intermediate between the two endmembers. Although the mineralization is from Montezuma stock-related magmatism, the mine workings include both Tertiary and Precambrian lithologies.

Disclaimer

References

Lovering TS, 1935. Geology and ore deposits of the Montezuma quadrangle, Colorado. US Geol Surv Prof Pap 178.

Mast, MA, Verplanck, PL, Wright, WG, Bove, DJ, 2007. Characterization of background water quality in the Upper Animas River watershed. In: Church, SE, von Guerard, P, Finger, SE (Eds.), Integrated investigations of environmental effects of historical mining in the Animas River watershed, San Juan County, Colorado. US Geol. Surv. Prof. Paper 1651. 347–386.

Neubert, JT, Kurtz, JP, Bove, DJ, Sares, MA, 2011. Natural acid rock drainage associated with hydrothermally altered terrain in Colorado. Colorado Geological Survey Bulletins B-54, 112 p.

Neuerburg, GT, Botinelly T, 1972. Map showing geologic and structural controls of ore deposits, Montezuma District, Central Colorado. US Geol Surv Misc Geol Invest Map I-750.

Runkel, RL, Walton-Day, K, Kimball, BA, Verplanck, PL, Nimick, DA, 2013. Estimating instream constituent loads using replicate synoptic sampling, Peru Creek, Colorado. J. Hydrol. 489. 26-41.

Stein HJ, 1985. A lead, strontium, and sulfur isotope study of Laramide-Tertiary intrusions and mineralization in the Colorado mineral belt with emphasis on Climax type porphyry molybdenum systems plus a summary of other newly acquired isotopic and rare earth element data. PhD Thesis, Univ N Carolina, Chapel Hill, 500 p.

Verplanck, PL, Nordstrom, DK, Bove, DJ, Plumlee, GS, Runkel, RL, 2009. Naturally acidic surface and ground waters draining porphyry-related mineralized areas of the southern Rocky Mountains, Colorado and New Mexico. Appl. Geochem, 24, 255–267.