

Variations in Copper and Zinc Isotopes in Surface- and Groundwater of a Mineralized Area in Handcart Gulch, Central Colorado, USA

Richard B. Wanty, Andrew H. Manning, Philip L. Verplanck, Jonathan S. Caine, Laurie S. Balistrieri
U.S. Geological Survey, MS 963 Denver Federal Center, Denver, CO 80225 USA
rwanty@usgs.gov

Abstract

Handcart Gulch is an alpine watershed that drains mineralized and hydrothermally altered rocks. The stream water is naturally acidic, with pH values between 3 and 4 most of the year, and high concentrations of metals and sulfate, typical of streams draining rocks rich in sulfide minerals such as pyrite. Samples of stream water were collected along a 1.5-km reach of the stream, and groundwater was collected from 5 shallow (<50m) wells along the same reach of the stream and from 2 deep (>150m) wells located higher up in the watershed. Copper concentrations ranged from <0.5 $\mu\text{g/L}$ to >17,000 $\mu\text{g/L}$ and $\delta^{65}\text{Cu}$ values ranged from -0.1‰ to +7.05‰ relative to SRM-976. Zinc concentrations ranged from 35 to 360 $\mu\text{g/L}$ and values of $\delta^{66}\text{Zn}$ ranged from -0.21 to +0.46 ‰ relative to the JMC-07349L *de facto* standard. Because of the low stream pH values, adsorption of either Cu or Zn is minimized in the stream, so both elements should approximate conservative behavior. If that is the case, variations in both concentrations and isotopic ratios of Cu and Zn should be controlled by inputs from stream and groundwater sources, as opposed to being affected by in-stream processes. Both the concentrations and isotopic compositions of Cu and Zn in stream- and groundwater change approximately 800 meters downstream from our uppermost stream sample point, possibly reflecting a different style of bedrock mineralization or alteration that may be associated with a concealed mineralized zone in the rock.

Study Area

Handcart Gulch is in central Colorado on the eastern side of the Continental Divide approximately 75 km southwest of Denver. The watershed geology includes complexly folded and fractured Proterozoic metamorphic rocks intruded by Tertiary porphyrys overlain by Quaternary rock glaciers, ferricretes, colluvium, and thin soils. Elevations range from 2900 to approximately 4000 m above sea level. The upper part of the Handcart watershed has had no past mining activity, but the stream draining the watershed has low pH (~3.5) and high concentrations of metals and sulfate. As a result, some exploration for mineral deposits has been conducted in the watershed and possible areas of interest have been identified based on geochemical and geophysical prospecting. Average annual temperature, as indicated by groundwater temperatures, is ~3°C and average precipitation is >600 mm/yr, mostly in the form of snow in winter, and late-summer rains. From 2001-2005, a number of boreholes were drilled in the watershed for mineral exploration and/or research purposes. Several of the boreholes have now been converted to monitoring wells for research use. Figure 1 shows the study area with the locations of the wells and sample sites, as well as a possible zone of interest for future mineral-deposit prospecting which was roughly delineated by geophysical surveys performed by a privately held company.

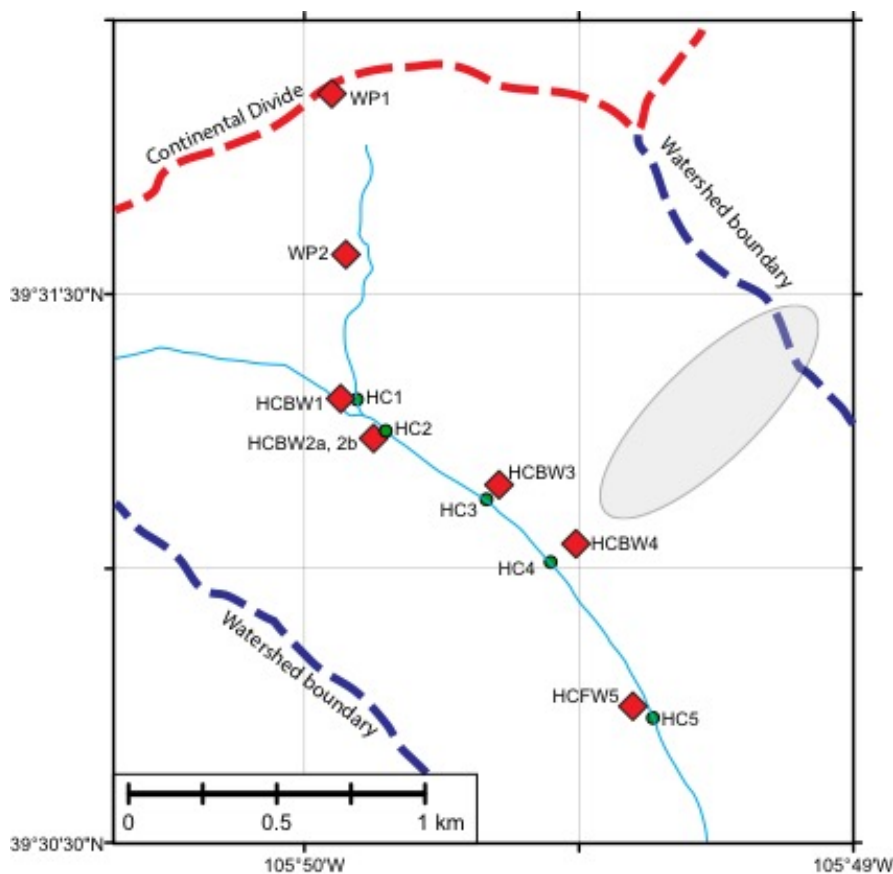


Figure 1. The Handcart Gulch study area. Circles denote surface water sample sites, diamonds represent wells. The gray ellipse is an area identified as containing a possible mineral deposit.

Methods

Samples were collected following established methods. Field measurements of pH were made following a 3-point buffer calibration (pH 1.68, 4.01, and 6.86 NIST buffers). Samples for later analyses were stored in pre-cleaned low-density polyethylene bottles. Samples for cation and metal isotope determinations were filtered through a 0.45 μm filter and acidified to pH~1 with concentrated HNO_3 . Samples for anion analyses were similarly filtered and kept on ice until returning to the lab, where they were refrigerated until analysis. Anion analyses were performed by ion chromatography, and cation analyses were performed by quadrupole ICP-MS. Samples for isotope analyses were separated according to the ion exchange methods of Borrok et al. (2007) and Pribil et al. (2010) into three discrete fractions (Cu, Zn, or Fe). Cu and Zn isotopes were determined on a Nu Instruments HR multicollector ICP-MS using the standard-sample-standard bracketing method. Precision of the isotopic analyses, as determined by multiple replicate analyses of samples and standards, was better than $\pm 0.1\text{‰}$ (2σ).

Results and Discussion

Wells HCBW1, HCBW2, HCBW3, and HCFW5, along Handcart Creek, are all artesian. Well HCBW4 is slightly uphill from the creek. Thus, samples collected from these wells represent groundwater as it is about to discharge into the stream. Concentrations of Cu in streamwater increase downstream as groundwater with greater Cu concentration enters the stream (Fig. 2). Copper entering the stream near HC3 is isotopically very heavy, and thus the $\delta^{65}\text{Cu}$ value for the stream increases from HC1 to HC3. Lighter Cu entering the stream between HC4 and HC5 likely reflects a different source of Cu and causes a decrease in $\delta^{65}\text{Cu}$ values of stream water. This different source, with a value of -0.1‰ , could reflect dissolution of primary sulfide minerals (Mathur et al., 2009) in a subsurface deposit. Similarly, Zn concentrations in the stream increase from HC1 to HC3 in

response to the greater concentrations of Zn entering the stream, as indicated by well-water Zn concentrations (Fig. 3). Zinc-isotope values do not change appreciably within the reach of stream studied. However, it is interesting to note the slight drop in $\delta^{66}\text{Zn}$ in the stream at HC4, probably in response to the much lighter Zn in well HCBW4, which again may be attributed to a changing source of Zn. Concentrations of dissolved Al, Fe, Mn, Ni, SO_4^{2-} , and U follow very similar profiles to that of Zn in stream- and groundwater, and are likely the result of discharge of low-pH, metal-rich groundwater to the stream between sites HC3 and HC4. The pH values of the groundwater are consistently below 4, and combined with the high concentrations of metals and SO_4^{2-} , indicate that oxygen is being replenished to the groundwater as it is being consumed in reactions with sulfide-bearing minerals. A likely mechanism for the oxygen replenishment is sulfide oxidation occurring within a deep unsaturated zone within mountain ridges, with further contributions from large seasonal fluctuations in the groundwater table level (Manning et al., 2013). Using a simple conceptual model in PHREEQEC (Parkhurst and Appelo, 1999), we calculated that without oxygen replenishment, the lowest pH attainable would be ~ 4 , but concentrations of metals and SO_4^{2-} would be much lower than we observed in both stream- and groundwater. Thus, we conclude that deep unsaturated zones and an active water table at high elevation, combined with the presence of sulfide-bearing minerals in the rocks, lead to the water-chemical properties we observe in Handcart Creek. The combination of concentrations and metal isotope ratios helps constrain areas of interest for mineral-deposit exploration.

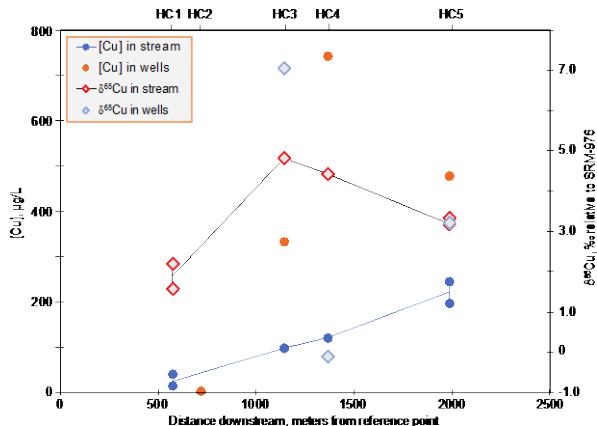


Figure 2. Concentrations and isotope ratios of Cu in streamwater and wells in Handcart Creek.

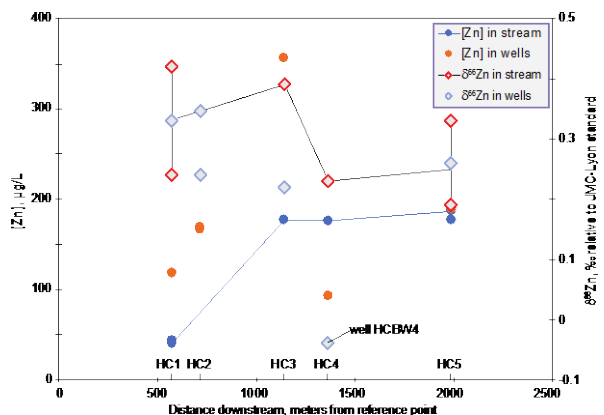


Figure 3. Concentrations and isotope ratios of Zn in streamwater and wells in Handcart Creek.

Summary

Handcart Gulch, in central Colorado, USA, is drained by a stream that is naturally acidic and metal rich. Although no mining has taken place in the watershed, it has been the subject of mineral exploration efforts, including drilling of several deep boreholes within the watershed. Chemistry of groundwater in those wells, and in new wells drilled by the USGS for research purposes, reveals inputs of metals that can be attributed to oxidative weathering of primary mineralized or hydrothermally altered zones in the area. To the extent that the well samples represent discharging groundwaters, effects on stream chemistry can be seen along a 2-km transect of stream. Inputs of greater metal concentrations with variable isotopic ratios lead to changes in bulk stream chemistry, and help to identify the location of a possibly mineralized zone in the mountain watershed.

Future work to be done in the area includes more detailed sampling of the stream, springs, and shallow wells, in addition to chemical and isotopic characterization of solid samples (core and cuttings) that were collected during drilling of the research wells.

References

- Borrok, D.M., Wanty, R.B., Ridley, W.I., Wolf, R., Lamothe, P.J., Adams, M., 2007. Separation of copper, iron, and zinc from complex aqueous solutions for isotopic measurement. *Chemical Geology*, 242, pp. 400-414.
- Manning, A.H., Verplanck, P.L., Caine, J.S., Todd, A.S., 2013. Links between climate change, water-table depth, and water chemistry in a mineralized mountain watershed. *Applied Geochemistry* 37, 64-78.
- Mathur, R., Titley, S., Barra, F., Brantley, S., Wilson, M., Phillips, A., Munizaga, F., Makshev, V., Vervoort, J., Hart, G., 2009. Exploration potential of Cu isotope fractionation in porphyry copper deposits. *Journal of Geochemical Exploration* 102, 1-6.
- Parkhurst, D.L., Appelo, C.A.J., 1999. User's guide to PHREEQC (version 2) – a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. U.S. Geol. Surv. Water-Resources Investigations Report 99-4259.
- Pribil, M., Wanty, R.B., Ridley, W.I., Borrok, D.M., 2010 Influence of sulfur-bearing polyatomic species on high precision measurements of Cu isotopic composition. *Chemical Geology* 272, 49-54.