

Geochemistry of surface water in alpine catchments in central Colorado, USA: An example of sampling scale versus detail

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ABSTRACT: The U.S. Geological Survey is conducting a study of surface-water quality in the Rocky Mountains of central Colorado. Sampled media include stream water, sediment, and biofilm coatings on streambed rocks. At selected sites, aquatic macroinvertebrates are being collected. This paper focuses on the stream-water chemistry. The dominant regional feature affecting water quality in central Colorado is the Colorado Mineral Belt (CMB), a northeast-trending zone hosting many polymetallic vein and replacement and porphyry Mo deposits that were mined from the mid-1800's to the present. The influence of the CMB is seen in lower surface-water pH (<5), and higher concentrations of SO_4^{2-} (>100 mg/L) and siderophile and chalcophile metals such as Fe (>1 mg/L), Cu (>0.01 mg/L), Zn (>0.1 mg/L), and Cd (>0.001 mg/L). At local scales, effects of individual rock units on water chemistry are subtle but discernible, as shown primarily by concentrations of major lithophile elements or ratios between them.

1 INTRODUCTION

1.1 Study area

The study area encompasses approximately 55,000 km² in central Colorado (fig. 1), which includes most of the Precambrian core of the Rocky Mountains. Major lithologic groups include granitic and granodioritic intrusive rocks, metasedimentary and metavolcanic rocks, and sedimentary rocks from Pennsylvanian to Cretaceous age. Between 2004 and 2006, more than 300 samples were collected from approximately 250 unique sites (the remainder are repeat sample sites within and between years).

The sample sites are at high altitude, ranging from 1,800 to 3,560 meters above sea level. Climate of the study area is temperate continental, with generally more than 50 cm of precipitation per year, especially at higher altitudes. Much of this precipitation occurs as snow in winter or as rain primarily between June and August. Vegetation ranges from deciduous cover at lower altitudes and in riparian zones, to conifer forests, and at the highest altitudes, open tundra.

The Colorado Mineral Belt (CMB) is shown in Figure 1 as the dashed line trending northeastward through the middle of the study area. Hundreds of historical mines occur within the CMB, and many of them produce acidic metal-rich drainage. The CMB is also an area of high background concentrations of dissolved metals that are liberated by the weathering of pyrite and other sulfide minerals.

1.2 Objectives

The main objective of this study was to carry out a sampling program to evaluate regional environmental geochemistry in the context of catchment lithology. Within this framework, a second objective was to evaluate metal mobility and bioavailability in areas impacted by historical mining, or in areas with high background concentrations of certain toxic trace metals, such as Fe, Zn, Cu, and Cd. Catchment basins with relatively simple, homogeneous headwater lithology were given highest priority for sampling, given access to sites and geographic distribution. Most of the sites are located on land administered by the state or the US government.

For the entire study area, the average sample density is about 1 per 220 km², but as seen in Figure 1, the samples are not homogeneously distributed because of our sampling objectives. With the sampling design, weighted to represent the major bedrock lithologies found in central Colorado, one hypothesis is that areas receiving sparse sample coverage may be represented by other proxy sites with similar lithology and greater sample density (cf. Miller, 2002). This hypothesis may be tested by detailed examination of sections of our study area with greater sample density, to see whether lithologic variations are reflected in stream-water chemistry.

An important aspect of this study is to determine what level of interpretations may be made at various

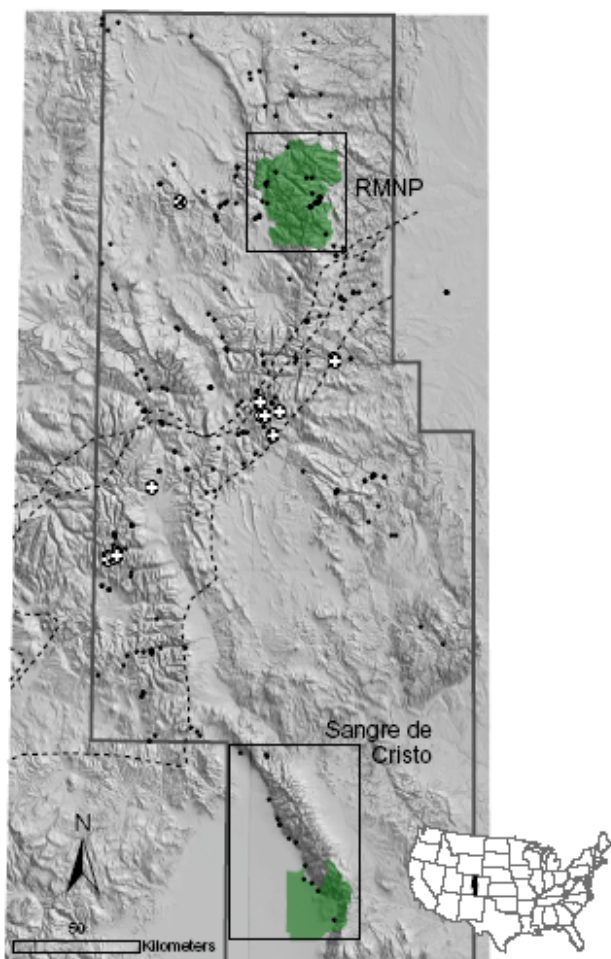


Figure 1. Outline of the study area within central Colorado, USA, shown by the heavy gray line. The northern boundary of the study is the border with the state of Wyoming, and the southern boundary is the border with New Mexico. Inset map at lower right shows the study area in black within the continental US. The dashed line is the outline of the Colorado Mineral Belt. The areas in boxes (RMNP and Sangre de Cristo) are discussed in detail later in this paper. Samples with pH > 5 are shown with a small dot; a white cross denotes pH < 5.0.

spatial densities of sampling. For example, certain geochemical features should be observable at the regional scale (100's of km), taking the full data set into view. Of equal interest is the more detailed scale (10's of km or less). This paper contrasts these spatial scales and shows interpretations possible at each.

2 METHODS

2.1 Field sampling

Sampling was conducted in late Spring to early Autumn in 2004 to 2006. Field sampling methods are described in detail in Fey et al. (2007). At each sample site, the parameters measured on-site included pH, temperature, conductance, and discharge. Water samples were collected and preserved in the field for later analysis. Separate samples were collected for analysis of alkalinity, organic carbon, and Fe^{II}. In each year, approximately 15% of samples were for quality assurance, including field blanks

and site duplicates. In 2005 and 2006, several sites from previous months or years were resampled to evaluate short-term (monthly to annual) variability.

2.2 Laboratory and numerical methods

Samples were returned to the USGS laboratories in Denver, Colorado for thorough chemical analysis. Cations were analyzed by both ICP-MS and ICP-AES, anions by ion chromatography, and alkalinity was measured by standard-acid titration to pH 4.5 (Taggart, 2002). Fe^{II} was analyzed using the method of To et al. (1999).

To check the quality of the data, several steps were taken. An average of 20% of samples each year were either field duplicates or field blanks. All analytical results were run through the PHREEQC program (Parkhurst & Appelo, 1999) to check for charge balance and to calculate saturation-index values for minerals. In most cases, charge imbalance was within $\pm 15\%$.

3 RESULTS

3.1 Regional results- scales of 100's of km

Streams within the CMB have a number of chemical differences from those outside the CMB. For example, Figure 1 shows the regional variation in pH of stream waters throughout the study area; with one exception, all samples with pH < 5 occurred within the CMB.

Similar results were obtained for Fe, Cu, Zn, and Cd; the highest (and in many cases, the only detectable) concentrations of these elements were observed within the CMB. For example for Cd, the only samples measuring above the detection limit of 0.02 $\mu\text{g/L}$ were within the CMB, where the highest concentration was just over 500 $\mu\text{g/L}$. Zn and Cd are strongly correlated ($r^2 = 0.99$) in the stream waters, which suggests that they have a common source, such as dissolution of sphalerite (ZnS), a common mineral in the CMB deposits. In this data set, the dissolved Cd/Zn ratio suggests that sphalerite from the CMB contains approximately 0.5% Cd, within the range of Cd substitution in sphalerite worldwide as reported by Piatak et al. (2004).

Stream waters within the CMB have generally higher concentrations of sulfate (>25 mg/L), as well as alkaline earth elements. As a result, saturation indices of gypsum, celestite, and barite are generally greater within the CMB. Gypsum and celestite were undersaturated in all samples, but to a lesser degree than in the rest of the study area. Barite was near saturation or slightly supersaturated in many samples within the CMB.

Concentrations of large-ion lithophile elements such as U should be related to source and weathering rates. In this study, U concentrations were greatest in the CMB, for both reasons. Mineral deposits within



Figure 2. Mg/Ca ratios in the RMNP area, represented by 20 sample sites in an area of approximately 1,100 km². Bedrock within the shaded area is Early Proterozoic metasedimentary rocks; the white areas are dominated by Middle Proterozoic granitic rocks. Small symbols denote Mg/Ca molar ratios <0.5.

the CMB and the felsic intrusive rocks that produced them commonly are enriched in U (Sims, 1963) and the more aggressive weathering environment produced by the weathering of sulfide minerals leads to greater solubility and less adsorption of U within the CMB (Wanty et al., 1998).

3.2 Local results- Rocky Mountain National Park

Rocky Mountain National Park (RMNP) has almost no history of mining, and water from the area was typically low in total dissolved solids, usually <20 mg/L. The geology of RMNP is characterized by mostly Middle Proterozoic granitic rocks on the east, which contain quartz, oligoclase, microcline, and biotite. The dominant lithology on the west side of the park is Early Proterozoic metasedimentary rocks that vary in composition and mineral assemblage, but generally contain quartz, feldspars, and biotite (Braddock & Cole, 1990).

Streams with catchment lithology dominated by granites generally have lower pH, alkalinity, and Mg/Ca ratios. The differences are subtle and significant overlap occurs, as seen in Figure 2. Saturation indices for calcite follow a similar trend, with lower values of SI in watersheds underlain by granite (fig. 3). The sampling program was not conducted for the purpose of “zooming in” to this level of detail. Nevertheless, the differences that are observed follow

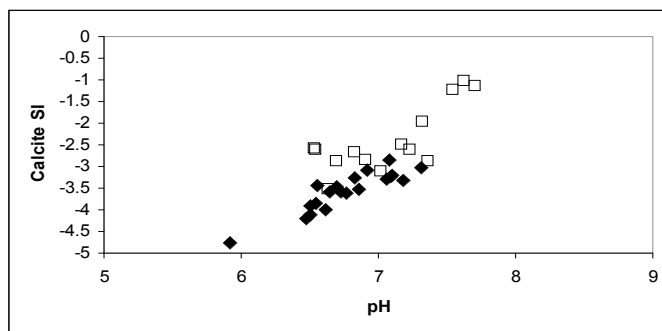


Figure 3. pH and calcite saturation indices in the samples from the RMNP area. Solid diamonds are samples from granitic watersheds, open squares from metamorphic watersheds.

differences in dominant lithology.

3.3 Local results- the Sangre de Cristo range

The Sangre de Cristo Mountains in southern Colorado comprise Paleozoic arkosic sand- and siltstones, Early and Middle Proterozoic granitic rocks and Early Proterozoic metasedimentary and meta-volcanic rocks (fig. 4). Streams draining the west side of the range encounter some or all of these rock types along their flow paths. Total dissolved solids were as high as 340 mg/L, but most streams have TDS <100 mg/L. Hence, the differences in stream chemistry are subtle but discernible. As seen in Figure 4, Mg/Ca ratios in Sangre de Cristo streams are generally higher in streams draining sandstone and metamorphic rock than from watersheds underlain by granite. This result is similar to that found in RMNP, but more subtle, owing either to the mixed lithologies of these catchment basins or to the fact that there is less chemical contrast between the lithologic groups. The RMNP streams exhibit systematic differences in other properties but no pronounced differences are seen for the streams in the Sangre de Cristo Mountains.

4 CONCLUSIONS

A regional geochemical study undertaken in central Colorado, USA, examined the effects of bedrock lithology on stream-water chemistry. Numerous historical abandoned mines occur within the study area, which superimpose chemical effects other than those attributable to lithologic variations. Within the Colorado Mineral Belt, stream pH values are generally lower, and concentrations of sulfate and many chalcophile trace elements are higher, due to the weathering of sulfide minerals such as pyrite and sphalerite that were exposed during mining. At a scale of 100's of kilometers, the effect of the CMB is seen clearly regardless of variations in bedrock lithology. Weathering of sulfide minerals produces a dominant chemical signature. This effect is due to

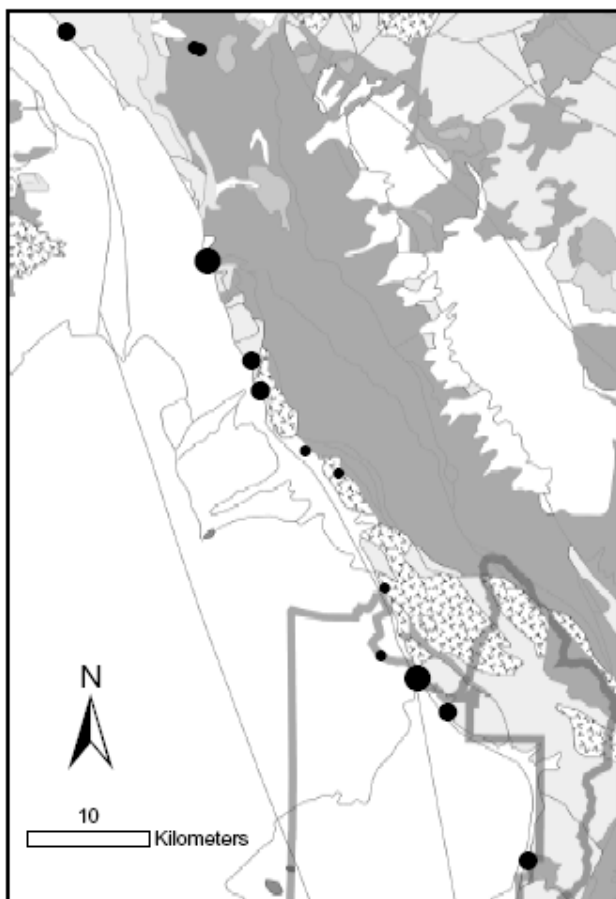


Figure 4. Mg/Ca ratios in the Sangre de Cristo range front. Sample sites represent streams draining from NE to SW. The shaded line in the SE corner of the map shows the outline of Great Sand Dunes National Park. White areas are Quaternary deposits, the stippled areas contain Middle Proterozoic granites, the light-shaded areas contain Early Proterozoic metamorphic rocks, and the darker shaded areas contain predominantly arkosic sandstones and conglomerates. Small dots represent Mg/Ca molar ratios <0.25 , medium-sized dots represent Mg/Ca ratios between 0.25 and 0.4, and the largest dots are for Mg/Ca ratios >0.4 .

the greater reactivity of sulfide minerals in the weathering environment as opposed to silicate and carbonate minerals, which are chiefly responsible for the chemical signatures of various lithologies away from mineralized areas.

At local scales of 10's of km, stream-water chemistry variations are subtle but discernible. Away from mineralized or mined areas, these variations can be attributed to differences in bedrock lithology and are primarily observed in either the concentrations of the lithophile elements or ratios between them. For example, ratios of Mg/Ca tend to be higher in streams draining arkosic sandstone and metasedimentary rocks when compared with granite and granodiorite.

With an average sample density of 1 per 220 km², the most obvious feature is related to the CMB, a large mineralized zone that contains highly reactive sulfide minerals exposed at the surface. Historical mining has resulted in rapid chemical weathering at

disturbed sites. Dissolution of chalcophile elements leads to greater concentrations of Fe, Cu, Zn, and Cd in streams in the CMB. However, large-ion lithophile elements such as U also are enriched in streams within the CMB— a result of both greater U concentrations in those rocks and a more aggressive weathering environment produced by low-pH water from sulfide-mineral weathering.

Future work will examine the role of bedrock lithology in greater detail, especially considering the relative weathering rates of mineralized versus non-mineralized rocks. Comparison between stream sediment and water chemistry also should aid this interpretation. The samples collected in this study also will allow us to evaluate bioavailability of metals, as measured by uptake by either biofilm coating rocks or by the metal concentrations found in aquatic macroinvertebrates.

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