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Geochemistry of surface water in alpine catchments in central Colorado, USA: Resolving host-rock effects at different spatial scales

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ABSTRACT

The US Geological Survey is conducting a study of surface-water quality in the Rocky Mountains of central Colorado, an area of approximately 55,000 km^2. Using new and existing geologic maps, the more than 200 rock formations represented in the area were arranged into 17 groups based on lithologic similarity. The dominant regional geologic feature affecting water quality in central Colorado is the Colorado mineral belt (CMB), a NE-trending zone hosting many polymetallic vein or replacement deposits, and porphyry Mo deposits, many of which have been mined historically. The influence of the CMB is seen in lower surface-water pH (<5), and higher concentrations of SO_4^{2-} (>100 mg/L) and chalcophile metals such as Cu (>10 μg/L), Zn (>100 μg/L), and Cd (>1 μg/L) relative to surface water outside the CMB. Not all streams within the CMB have been affected by mineralization, as there are numerous catchments within the CMB that have no mineralization or alteration exposed at the surface. At the regional-scale, and away from sites affected by mineralization, hydrothermal alteration, or mining, the effects of lithology on water quality can be distinguished using geochemical reaction modeling and principal components analysis. At local scales (100 s of km^2), effects of individual rock units on water chemistry are subtle but discernible, as shown by variations in concentrations of major lithophile elements or ratios between them. These results demonstrate the usefulness of regional geochemical sampling of surface waters and process-based interpretations incorporating geologic and geochemical understanding to establish geochemical baselines.

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1. Introduction

1.1. Objectives

As part of a regional reconnaissance of central Colorado, USA (Fig. 1) that included geologic mapping and map compilation, resource evaluation, and regional-scale environmental sampling, the relationship between stream water chemistry and catchment lithology has been studied. The main objective of the study was to carry out a sampling program to evaluate regional environmental geochemistry in the context of catchment lithology. Part of this study was to evaluate metal mobility in areas impacted by historical mining, or in areas with high natural background concentrations of potentially toxic trace metals, such as Zn, Cu and Cd. Catchment basins with relatively uniform, homogeneous headwater lithologies were given highest priority for study. Representative geographic distribution and access were important constraints, and most of the sites are located on land administered by the State of Colorado or the US Government.

The average sample density for the entire study area is about 1 per 220 km^2, but the samples are not uniformly distributed (Fig. 1) because of the geologic-based sampling objectives and constraints related to land access. The sampling design was weighted to represent the major bedrock lithologies found in central Colorado, with or without the overprinting of mining or hydrothermal alteration. It was hypothesized that areas with sparse sample coverage may be represented by other proxy sites with similar lithology and greater sample density (Wanty et al., 1991; Miller, 2002). This hypothesis may be tested by detailed examination of areas with greater sample density to see whether lithologic variations are reflected in stream water chemistry. The approach is to sort the data into lithologic groups and analyze similarities and differences between those groups. Principal components analysis (PCA), a commonly used type of factor analysis, was applied to further evaluate chemical similarities and differences within the data set because this statistical approach enables the grouping of variables depending on covariation of chemical characteristics.

An important aspect of this study is to determine what level of interpretations can be made at various spatial scales and densities of sampling. Certain geochemical features should be observable at the regional scale (100 s of km), taking the full data set into view.

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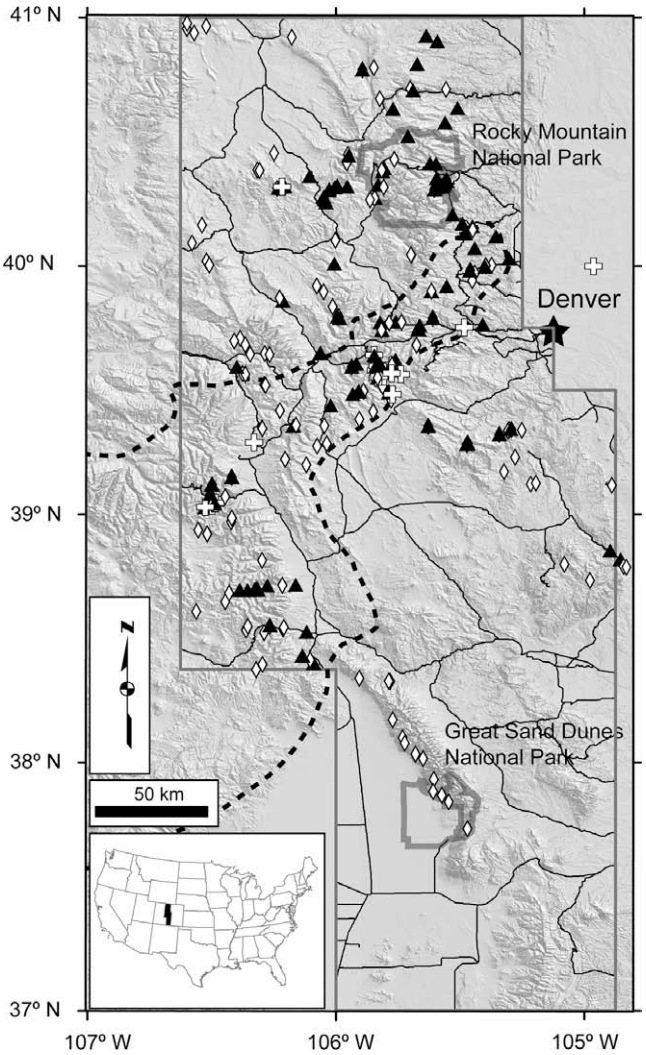

Fig. 1. Base map of study area showing sample sites in central Colorado, USA. The different symbols denote pH values: white plus sign for pH < 5, black triangle for pH between 5 and 7, and white diamond for pH > 7. The dashed line shows the outline of the Colorado mineral belt.

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, using geochemical reaction modeling, geographic information system (GIS) methods, and PCA.

1.2. Study area

The study area encompasses the central portion of Colorado, from the New Mexico border on the south to the Wyoming border on the north (Fig. 1). This area of approximately 55,000 km^2 includes most of the Rocky Mountains in Colorado and represents about 20% of the land area of Colorado. Between 2004 and 2007, 341 samples were collected from 229 unique sites; the total includes repeat samples within and between years, and 13 field blanks.

The sample sites in this study are at high altitude, ranging from 1800 to 3560 m above sea level. The 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 (Mutel and Emerick, 1992). Soils within the study area are thin (rarely greater than 10 cm) to non-existent, the latter occurring in areas dominated by bedrock outcrops. Thicker (up to 1 m or more) immature soils, as well as unconsolidated overburden, occur intermixed at lower elevations and along streams (Soil Survey Staff, 1999).

The Early Proterozoic basement of the study area is composed of metamorphosed and deformed 1.75–1.73-Ga island-arc volcanic rocks in the south-central part of the area (Bickford et al., 1989a; Van Schmus et al., 1993). These rocks are intruded by intermediate-composition plutonic rocks of similar age (Reed et al., 1987). Throughout much of the rest of the area the basement is composed of 1.73–1.71-Ga metasedimentary rocks shed from the Archean Wyoming craton to the north or from retreating arc complexes to the SE. Plutonic rocks of 1.72–1.68-Ga intrude all the older rocks across the area. Middle Proterozoic plutonic rocks (1.44–1.39-Ga) of intermediate to felsic composition are abundant throughout the area (Anderson, 1983). The 1.1-Ga Pikes Peak batholith is the youngest and largest of all Proterozoic granitic rocks (Barker et al., 1975; Smith et al., 1999).

Paleozoic carbonate sedimentary rocks formed a thin cover (less than 2 km) on the basement from Cambrian to Pennsylvanian time (DeVoto, 1990). Late Cambrian plutonic rocks and carbonatite were emplaced in the south-central part of the area related to rifting of the continental margin to the SE in Oklahoma (Bickford et al., 1989b). In Pennsylvanian and Permian time, parts of the area covered by Paleozoic formations were uplifted and the sedimentary cover and basement materials were shed into adjacent basins, creating locally thick accumulations (3–4 km) of conglomerate and red beds (Lindsey et al., 1986). The region stabilized during the remainder of Mesozoic time as marine shale and limestone were deposited in seaways across the area (thickest sequences 3 km). In latest Cretaceous time, the region was deformed by the Laramide Orogeny which created monoclinal uplifts and adjacent depositional basins (Dickinson and Snyder, 1978).

From Cretaceous to early Tertiary time plutons ranging from mafic to intermediate composition intruded the basement and created sills and laccoliths in the Paleozoic and Mesozoic strata (Simmons and Hedge, 1978). Hydrothermal alteration is associated with some of these plutons, and some contain mineral deposits of base and precious metals that were exploited beginning in the mid-1800s (Sims et al., 1963; Rice et al., 1985). This superposition of Precambrian basement structures with Cretaceous–Tertiary magmatism and concurrent hydrothermal mineralization defines the Colorado mineral belt (CMB; Fig. 1; Tweto and Sims, 1963; Wilson and Sims, 2003). Most of the deposits in the CMB (Fig. 1) are base- and precious-metal veins. Volcanoes erupted and formed calderas across the southern part of the study area during middle Tertiary time and formed large volcanic fields such as those in the San Juan Mountains to the SW of the study area (Steven and Lipman, 1976). Large base-metal deposits in the west-central part of the study area are of this general age (Loughlin and Koschmann, 1935; Beaty et al., 1990). Emplacement of silica-undersaturated subvolcanic rocks led to the formation of some large Au deposits in the east-central part of the study area late in the eruption of these volcanic centers (Lindgren and Ransome, 1906; Kelley and Ludington, 2001). Plutons of predominantly felsic composition were emplaced during middle Tertiary time and formed large porphyry Mo deposits (Mutschler et al., 1981).

During late Tertiary time, much of the area was disrupted by extensional faulting related to development of the Rio Grande Rift. Block-faulted mountain ranges and basins were created. Pleistocene glaciation sculpted the modern valleys and mountain peaks. Quaternary deposits blanket the modern valleys.

The nearly 200 mapped geologic units were grouped together into 17 discrete lithologic units characterized by common rock

type and chemistry, or in the case of sedimentary rock units, by their depositional environment and composition rather than by age of the rocks. In addition to composition and mode of origin, sedimentary rock units were sorted into carbonate-rich versus carbonate-poor units to distinguish possible effects of acid neutralization if mines were found in the catchment. A brief description of some of the lithologic groups is presented in Table 1; Church et al. (in press) provide more detailed descriptions of each lithologic group. Of the 229 unique catchments sampled, 145 have at least 50% of their area covered by one lithologic group.

Within the study area, the total area occupied by the CMB is about 10,000 km^2 – slightly less than 20% of the area. Thousands of historical mines and prospects occur within the CMB. Many of these historical mines produce acidic metal-rich drainage. Most of these mines exploited polymetallic veins of limited extent, producing Au, Ag, Zn, Pb, and Cu (Lovering and Goddard, 1950; Pearson, 1980). Weathering of abundant pyrite and other sulfide minerals in the waste-rock piles is the primary source of acidity, metals and SO_4^{2-} in surface water (Plumlee et al., 1995). The CMB is also an area of high natural background concentrations of dissolved metals that are mobilized by the weathering of pyrite and other sulfide minerals from hydrothermally altered and mineralized rocks. Most of the acidic drainages (pH < 5) sampled in this study resulted from impacts of historical mines, although many natural acid drainages exist. About half of the samples were collected within the CMB, but not all of those samples are from catchments that were affected by historical mining or hydrothermal alteration.

Table 1
List of lithologic groups found in the study area. Although 17 distinct groups were found in the area, only 9 were represented by the 145 samples with more than 50% of their catchment area within a particular lithologic group. The number of samples in the last column denotes this 50% cutoff. Brief descriptions are given here for the lithologic groups that are represented by at least one sample; more detailed descriptions for all the lithologic groups can be found in Church et al. (in press).

Group name	Description	Number of samples
(1) Volcanic-intermediate to mafic	Volcanic rocks of intermediate to andesitic to basaltic composition. Minerals include pyroxenes, amphiboles, plagioclase, biotite, olivine, etc.	1
(2) Volcanic-unsaturated rocks	Volcanic rocks of intermediate composition, which are silica undersaturated, including latite-andesites and phonolite. Minerals include plagioclase, pyroxenes, amphiboles, alkali feldspars, biotite, etc.	3
(5) Plutonic-intermediate	Plutonic (coarse-grained) rocks, including those of diorite, granodiorite, and monzonite composition. Minerals include plagioclase, alkali feldspars, biotite, amphiboles, quartz, etc.	20
(6) Plutonic-felsic	Plutonic (coarse-grained) rocks of alkali granite to granodiorite composition. Minerals include plagioclase, alkali feldspars, quartz, biotite, etc.	28
(7) Plutonic-Pikes Peak Granite	Plutonic (coarse-grained) rocks of the 1.0 Ga Pikes Peak batholith. This is a coarse-grained alkali granite with local pegmatites. It is distinguished from the plutonic-felsic group by its high halogen content and its weathering behavior, tending to weather to coarse gruss. Minerals include quartz, feldspars, biotite, muscovite and minor fluorite.	21
(8) Metamorphic-pelitic to siliceous	Metasedimentary rocks including gneiss, schist, quartzite, and migmatite. Minerals include plagioclase, quartz, biotite, muscovite, etc.	39
(9) Metamorphic-intermediate to mafic	Amphibolite schist and gneiss, and calc-silicate gneiss. Minerals include plagioclase, amphiboles, epidote, garnet, biotite, etc.	17
(10) Sedimentary-carbonate	Carbonate rocks of marine origin. Minerals include calcite, dolomite, quartz, ankerite, clays, and organic materials.	2
(12) Sedimentary-clastic, non-carbonate	Mixed siltstone, shale sandstone, etc. Minerals include quartz, feldspars, clays, organic materials and minor carbonates.	1
(13) Sedimentary-evaporite and red beds	Sedimentary rock containing gypsum and anhydrite in a matrix of quartz, clays, carbonates, and feldspars.	1
(14) Sedimentary-shale and sandstone	Sedimentary rock, predominantly siltstone and shale, with minor sandstone. Similar mineral assemblage to the clastic, non-carbonate group.	22
(14a) Sedimentary-Minturn formation	Compositionally similar to the sandstone/shale group, but distinguished by stream waters having greater total dissolved solids, pH, and low alkali metal concentrations.	9

Previous studies have characterized the effects of historical mining on Colorado streams, and found varying severity of effects due to mining and natural processes. Wentz (1974) conducted an extensive study of Colorado streams and estimated that more than 700 km of Colorado streams were adversely affected by either mining or weathering of mineralized and hydrothermally altered areas. The decision to classify a stream as "affected" was based either on pH (<6), or if high concentrations of Cu (>20 μg/L), Zn (>70 μg /L), Ag (>1 μg/L), or Pb (>10 μg/L) were found. These values were chosen based on stream criteria for fish or other aquatic life that were established at the time of that report. Following this reconnaissance study, Moran and Wentz (1974) chose 17 impacted areas for more detailed investigation, showing that the degree of impact was greater proximal to the historical mines that had acidic or metal-rich drainage and that processes such as dilution, precipitation, and adsorption contribute to reduced metal concentrations and loads downstream. In this study, primarily first and second order streams were sampled, close to many mining and natural acid rock drainage sources. Samples from mined and unmined-mineralized catchments presented in this paper should reflect similar water quality effects as reported for upstream samples by Moran and Wentz (1974).

Miller (2001, 2002) examined the evolution of stream chemistry in first-order streams in southwestern Colorado as a function of lithology. Miller avoided catchments containing historical mines, so that a "pure" lithologic effect on water chemistry could be observed. Although the catchments sampled by Miller were geologically complex, simple relationships between water quality and lithology were obtained by collecting samples at high altitude in small catchments. These samples included springs emanating from well-defined outcrops and streams high in drainage basins. From this work, Miller (2002) constructed maps relating headwater lithology to predicted ranges of water chemistry parameters such as pH, total dissolved solids, and acid neutralizing capacity in catchments. Miller's work showed that although water chemistry in streams or springs draining each lithologic group had relatively well-constrained compositional ranges in terms of these major parameters, there was considerable overlap in water composition between the lithologic groups, and distinct lithologic signatures thus may be difficult to define.

2. Methods

2.1. Field sampling

Sampling was conducted in late spring to early autumn in 2004–2007, after spring runoff had subsided and base-flow conditions prevailed. Field sampling methods are described in detail in Fey et al. (2007). At each sample site, pH, water temperature,

specific conductance, and stream discharge were measured (Wood, 1981; Rantz 1982a, 1982b; Wilde and Radtke, 1998; Wilde et al. 1998). The pH meter/electrode combination was calibrated at the beginning of each sampling day with at least 3 standard buffers (pH 4.01, 6.86, and 9.18 at 25 °C). Buffers were checked periodically throughout each sampling day to check for drift. The pH meter was recalibrated if the buffer did not measure within ±0.05 pH units of the accepted value. Water samples were collected and preserved in the field for later analysis. One aliquot was filtered through a 0.45-μm filter and acidified with ultrapure HNO_3 to a pH of ~1 for cation analysis. A similar unfiltered aliquot was collected for analysis of total dissolved and suspended cations. A filtered, unacidified aliquot was collected for anion analyses. Separate aliquots were collected for analysis of alkalinity (unfiltered, unacidified), dissolved organic C (DOC; 1 μm glass–fiber filtered, HCl acidified to pH ~1, stored in amber glass bottle), and Fe^{II} (0.45 μm filtered, HCl acidified to pH ~1, stored in amber bottle). Unacidified samples were stored refrigerated and the acidified samples were stored at room temperature.

Field blanks were prepared by analyzing doubly-deionized water that was brought from the lab to the field, and treated as a sample at a field site. A similar set of field blank samples was collected as for regular samples. Results of analyses of the field blanks were generally below detection, although one blank showed some contamination, particularly for Fe. Field duplicate samples collected the same day as the suspect field blank showed good reproducibility, usually within ±10%. In most cases, reproducibility was within ±10%, although errors increased if elements were present near their detection limits.

2.2. Laboratory and numerical methods

Samples were analyzed at the USGS laboratories in Denver, Colorado. Cations were analyzed by both inductively coupled plasma-mass spectrometry (ICP-MS) and ICP- atomic emission spectroscopy (ICP-AES), anions were determined by ion chromatography, and alkalinity was measured on unfiltered samples that had been refrigerated from the time of sample collection, by standard-acid titration to pH 4.5 (Taggart, 2002). $Iron^{II}$ concentrations were determined using the colorimetric method of To et al. (1999).

To check the quality of the data, 10% of samples each year were either field duplicates (two samples collected at the same time) or field blanks. In 2005, 2006 and 2007, several sites from previous months or years were resampled to evaluate short-term (monthly to annual) variability. In addition, all analytical results were run through the PHREEQC program (Parkhurst and Appelo, 1999) to calculate charge balance and saturation-index values for minerals. In most cases, charge balance was within ±10%.

When looking for similarities and differences among variables in large geochemical datasets, statistical analysis such as PCA can be useful. This statistical method examines the variability within the data and interrelationships among independent parameters (Jolliffe, 2002). Principal components, or factors, represent a set of new, transformed orthogonal reference axes that are linear combinations of the original variables. The first principal component (PC1 or factor 1) is oriented along the direction of the greatest variance in the data, and the second principal component (PC2) is orthogonal to PC1 and is oriented to show the next greatest amount of variance in the data. Depending on how strongly correlated the variables are, more principal components can be generated, and each are orthogonal to the previous (Davis, 1986). In general, 3 or 4 principal components will explain a large percentage of the variance for the type of data presented here. Factor loadings quantify how the original variables are associated with each factor. The principal component score is the projection of each sample onto the principal component axis and is a useful way to compare samples. The statistical software package SYSTAT® (version 8.0) was used to do the PCA.

The data analysis presented here includes water chemistry results for the subset of the sampled catchments that had at least 50% of their area in one lithologic group ($n = 119$). The number of samples used in the PCA analysis is less than the total number of catchments with >50% lithology (145) because duplicate samples from the same stream site were eliminated from the data set. Sixteen chemical parameters (H^+, alkalinity, Cl, F, SO_4, DOC, Al, Ca, Fe, K, Mg, Mn, Na, SiO_2, Sr, and Ba) were included because they represent a wide range in chemical properties and, in most cases, their concentrations were above the detection limit. If the concentration was below the detection limit, 0.5 times the detection limit was used. For most variables this occurred in less than 5% of the samples. One exception was Fe, for which 44% of the samples were below the detection limit. To carry out this multivariate analysis, the chemical data were converted to mmol/L and then log-transformed, a procedure that maximizes the linear relations among solutes that result from stoichiometric chemical reactions. One additional constraint was that samples with pH < 6.0 were not included because one objective was to evaluate lithologic controls of water chemistry without the influence of mineralized or hydrothermally altered rock. Samples with pH < 6.0 may have some effects of sulfide weathering, while pH < 5 are almost certainly affected by sulfide weathering. Including these samples in the PCA would slant the results towards the effects of sulfide weathering, masking the more subtle lithologic effects.

3. Results and discussion

3.1. Regional results – the Colorado mineral belt

The CMB crosses the central part of the study area in a general trend from SW to NW. Many streams within the CMB have chemical differences from those outside the CMB. For example, the regional variation in pH of stream water throughout the study area (Fig. 1) shows that, with one exception, all samples with pH < 5 occurred within the CMB. Not all catchments within the CMB have stream water that exhibits the effects of mining or mineralization/hydrothermal alteration, but those streams that are affected by mineral deposits lie almost exclusively within the CMB.

The highest, and in some cases, the only detectable, concentrations of many trace metals were observed in streams within the historically mined catchments in the CMB. For example, the only samples with Cd concentrations above the detection limit (0.02 μg/L) were within the CMB, where the highest concentration was just over 500 μg/L. For Cu, all samples with concentrations >90th percentile (>140 μg/L) were from catchments within the CMB. Concentration distributions of other important metals in the polymetallic veins (Pb, Zn, Al, Mn, U) show similar differences for areas within and outside of the CMB (Table 2). Simpson et al. (1993) found similar relationships between metals and historically mined areas in the UK. In the present study, Fe is a notable exception to this pattern, with virtually indistinguishable medians between CMB and non-CMB samples. This result is due to the large percentage of analytical results that were below detection (44% of samples had <20 μg/L Fe) and the ubiquity of Fe in the environment. However, the samples with the highest Fe concentrations occurred within the CMB. Similar patterns of trace-metal concentrations in CMB versus non-CMB samples were observed by Wentz (1974).

Dissolved Zn and Cd are strongly correlated in the stream water (Fig. 2), which suggests that they have a common source, such as dissolution of sphalerite (ZnS), a common mineral in the CMB deposits. Cadmium can substitute for Zn in the sphalerite crystal

Table 2
Median concentrations of selected elements in stream water from catchments within and outside of the Colorado mineral belt. Detection limits are provided in the units of each column heading. The row titled "% below DL" gives the percent of samples whose values were below the analytical detection limit for each element.

	pH	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	K (mg/L)	SO_4 (mg/L)	Fe (μg/L)	Cu (μg/L)	Zn (μg/L)	U (μg/L)	Sr (μg/L)
Inside mineral belt	6.89	14.5	2.9	1.4	0.59	16.6	43	0.7	8.7	0.62	74.6
Outside mineral belt	7.10	7.2	1.4	2.1	0.58	4.0	45	<0.5	0.9	0.17	34.2
Detection limit		0.2	0.1	.01	0.1	0.08	20	0.5	0.5	0.1	0.5
(%) Below DL		0	0	0	0	0	34	58	10	21	0

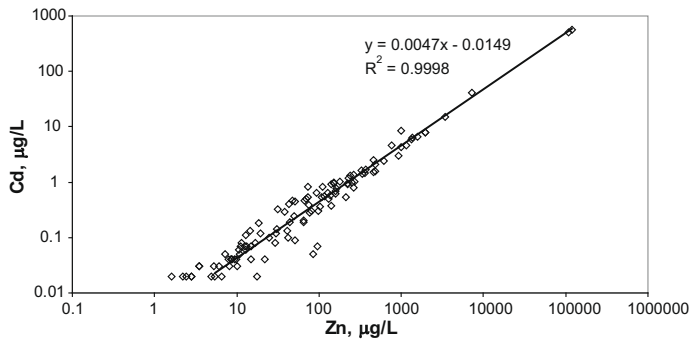

Fig. 2. Dissolved Zn and Cd in stream waters of the central Colorado study area.

lattice, so sphalerite regularly contains small percentages of Cd (cf. Stoiber, 1940; O'Day et al., 1998; Carroll et al., 1998). In this data set, the dissolved Cd/Zn ratio, determined from the slope of the best-fit line in Fig. 2, suggests that approximately 0.3% of Zn sites in sphalerite from the CMB are occupied by Cd. This value is within the range of Cd substitution in sphalerite worldwide as reported by Piatak et al. (2004), and similar to ratios observed in Colorado and New Mexico sphalerites by Manning et al. (2007) and Plumlee et al. (2005). There is no observed spatial variation in Cd:Zn ratio.

The waters from many streams within the CMB have concentrations exceeding the 80th percentile for SO_4^{2-} (>25 mg/L), and alkaline earth elements (Mg > 5 mg/L, Ca > 19 mg/L, Sr > 140 μg/L, and Ba > 40 μg/L). As a result, saturation indices of gypsum, celestite and barite are generally greater for stream waters within the CMB. Gypsum and celestite were undersaturated in all samples, but closer to equilibrium within the CMB than in the rest of the study area. Barite was near saturation or slightly supersaturated in many streams that were sampled in the CMB.

Concentrations of large-ion lithophile elements such as U typically are controlled by source and weathering rates, as well as pH. In this study, dissolved U concentrations in stream waters were greatest in the CMB. Mineral deposits within the CMB and associated felsic intrusive rocks commonly are enriched in U (Sims, 1963) and the more aggressive acidic weathering environment produced by the weathering of sulfide minerals leads to greater solubility and less adsorption of U in historically mined catchments (Simpson et al., 1993; Wanty et al., 1998).

3.2. Regional results – effects of catchment lithology on water chemistry away from the CMB

One of the goals of this project was to characterize stream water chemistry based on catchment headwater lithology, similar to the earlier work of Miller (2002). As described above, lithologic groups were derived from regional-scale geologic maps, and overlain on a 10-m digital elevation model using GIS software. Catchment boundaries for each sample point were derived using the Arc Hydro tool set (Maidment, 2002). This layering of catchment boundaries with lithologic maps allowed the quantitative determination of the outcrop surface area of each lithologic group within each catchment.

A ternary plot of alkali metals and alkaline earths (Fig. 3) shows samples from unmined, unmineralized catchments for which more than 50% of the catchment area occurred within a single lithologic group. Some stream water data from individual lithologic groups fall within relatively restricted areas on the plot, as demonstrated by the groups for Pikes Peak Granite (Table 1, group 7), Minturn Formation (group 14a), and intermediate-composition plutonic rocks (group 5). Other groups, such as metamorphic rocks (group 8), felsic plutons (group 6), and non-carbonate-bearing sedimentary rocks (group 12), cover nearly the full range of observed compositions. For the groups that plot within relatively narrow fields (Fig. 3), there is still overlap with the chemistry of waters draining other lithologies. The two points in Fig. 3 that represent carbonate sediment were collected from the same site in two consecutive years, so they are not considered to represent all carbonate-dominated catchments. These samples contain almost equal amounts of Ca and Mg, and very low alkali metals, consistent with the fact that they drain dolomite-rich Paleozoic carbonate rocks (Olson, 1983).

Water chemistry from some of the lithologic groups shown in Fig. 3 varies over a wide range of compositions. Groups 6, 8, 12, 13, and 14 are among these overlapping groups. These lithologic groups represent a large number of individual geologic formations that comprise somewhat broader compositional ranges and were mapped more on the basis of age, texture, mode of emplacement, or basin of deposition. Thus, these rocks were grouped together on the basis of other geologic criteria than mineral/chemical composition. These groups span a wide range of mineral proportions and bulk chemical compositions, thus the relatively wide range of water compositions. The overlap among these groups may be explained by the fact that in many cases, the parent rocks for the sedimentary groups (12, 13, and 14) are the plutonic and metamorphic rocks (groups 6 and 8).

The tightness of the clusters of water data from catchments underlain by the lithologic groups in Fig. 3 reflects the relatively limited compositional variation of the rocks comprising each lithologic group. The Pikes Peak Granite (group 7) covers a large geographic area in Colorado, but it varies little in composition (Barker et al.,

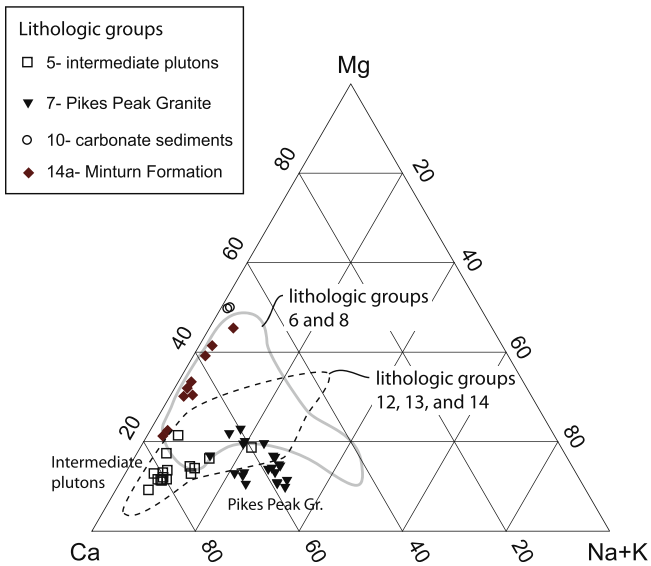

Fig. 3. Ternary plot showing relative proportions of equivalents of Ca, Mg, and Na + K in stream waters whose catchments are underlain by >50% of one lithologic group. The gray line includes all water data from streams underlain by metamorphic rocks of group 8 (Table 1) and felsic plutons (group 6). The dashed line includes all water data from streams underlain by non-carbonate sediment-dominated rock (groups 12, 13, and 14) except the Minturn Formation (group 14a).

1975). The Minturn Formation (group 14a) has a water-chemical signature reflecting dissolution of gypsum or carbonate minerals such as dolomite or calcite. Waters draining catchments underlain by plutons of intermediate composition (lithologic group 5) have high proportions of Ca relative to alkali metals, reflecting the effects of dissolution of minerals such as amphibole, feldspar and calcite.

Waters in catchments underlain by lithologic groups 6, 7, 8, and 14a have other distinguishing chemical characteristics in addition to the alkali metal and alkaline earth concentrations (Table 3). Waters in catchments underlain by Pikes Peak Granite (group 7) have consistently higher concentrations of F^-, Cl^-, and silica, but generally lower specific conductance (total dissolved solids), than waters draining other lithologic groups. Surface waters from catchments underlain by Minturn Formation (group 14a) have higher specific conductance, pH values commonly greater than 8, and generally higher concentrations of SO_4^{2-}, alkalinity, Ca and Mg, in good agreement with the results of Miller (2001). Streams draining catchments underlain by metamorphic and plutonic rocks of felsic composition (groups 6 and 8) have lower specific conductance, but variable concentrations of alkali metals and alkaline earths (Table 3).

The samples collected in this study have some similarities to samples collected elsewhere in the world, as shown in Fig. 4. According to Gibbs (1970), rivers may have an assemblage of dissolved load that reflects dominant effects of precipitation, rock weathering, or evaporation in dry regions as TDS increases. Most of the samples collected in this study are in the area of "rock dominance" (Gibbs, 1970), which is consistent with the semiarid climate of Colorado. Three samples, all from sites located within the CMB, are unusual. These samples have some of the lowest pH values measured during the study (pH < 3) and plot close to the ordinate (high proportion of Ca relative to Na) in Fig. 4 with TDS >1000 mg/L. These three samples have concentrations of Fe that are great enough that Fe is a significant contributor to the total dissolved cation load in these streams, and SO_4^{2-} is the dominant anion. All three of these streams contain a substantial amount of acid mine drainage, therefore sulfide weathering is contributing the greatest abundance of dissolved solids. The high proportion of Ca relative to Na, a property of rock-dominated weathering of Gibbs (1970), is likely due to the rapid weathering of Ca-bearing feldspars and carbonates. Thus, extremely acidic stream waters derived from sulfide weathering are chemically different from typical worldwide river waters.

PCA provides insight into the relative similarities and differences among samples by reducing the number of observed variables in a large geochemical data set such as this one (Jolliffe, 2002). Four principal components, or factors, account for 71% of the total variance, with factor 1 (F1) accounting for 29% of the total variance. High positive component loadings (0.65–0.90) in F1 in-

Table 3
Values for selected chemical constituents of stream waters found in catchments dominated by various lithologies (i.e., >50% of catchment area in one lithologic group). The three values in each cell correspond to the minimum, median and maximum (median in bold-face type). Shaded cells call attention to variables that are empirically different from the overall populations, either because the range is significantly different, or the distribution follows a different pattern than the overall population of samples. Alkalinity is given as mg/L $CaCO_3$.

Group name	Conductance (μS/cm)	pH	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	K (mg/L)	Alkalinity (mg/L)	SO_4^{2-} (mg/L)	Cl (mg/L)	F (mg/L)	SiO_2 (mg/L)
(5) Plutonic-intermediate	49	5.35	6.9	0.91	0.94	0.25	2.9	2.8	<0.0	<0.08	4
	95	**6.97**	**14.**	**1.4**	**1.4**	**0.52**	**27**	**17**	**1.2**	**0.16**	**6.7**
	155	7.97	24.	2.5	2.7	0.8	46	49	2.4	0.35	13.
(6) Plutonic-felsic	24	5.18	2.2	0.44	0.48	0.2	11.	1.8	<0.08	<0.08	2.8
	46	**7.1**	**5.1**	**1.2**	**2.3**	**0.5**	**26.**	**2.7**	**1.4**	**0.24**	**9.7**
	168	7.97	20.	6.0	6.5	1.4	70.	14	7	0.5	20.
(7) Pikes Peak granite	33	6.24	3.1	.34	1.5	.58	7.4	2.9	.17	0.33	9.4
	70	**7.36**	**8.9**	**1.4**	**3.8**	**1.3**	**23**	**6.0**	**1.7**	**2.1**	**15.**
	210	8.21	38.	6.2	7.8	3.3	100	17	13.	4	22
(8) Metamorphic-pelitic to siliceous	13	5.49	1.4	0.2	0.4	0.2	4.8	2.0	<0.08	<0.08	1.5
	49	**6.93**	**4.7**	**1.3**	**1.6**	**0.5**	**17.**	**4.3**	**1.3**	**0.2**	**5.9**
	172	7.98	18.	6.4	9.2	1.4	51.	58	9.5	0.8	15.
(9) Metamorphic-intermediate to mafic	48	6.14	4.4	1.1	0.6	0.5	19.	1.1	<0.08	<0.08	**8.2**
	93	**7.29**	**12.**	**2.8**	**1.4**	**0.6**	**34.**	**5.0**	**1.3**	**0.2**	5.0
	222	7.92	34.	9.3	36.	17.	98.	24	2.8	0.5	17.
(14) Sedimentary-shale and sandstone	68	5.05	5.8	1.2	1.0	0.4	9.2	3	1.1	0.1	3.4
	93	**6.81**	**12.**	**2.1**	**3.7**	**0.6**	**34.**	**6.5**	**1.3**	**0.4**	**10.**
	372	7.83	54.	4.9	6.2	1.1	58.	140	2.7	0.9	30.
(14a) Sedimentary-Minturn Fm.	210	7.93	29.	6.7	1.2	0.7	110	5.0	0.5	<0.08	5.3
	259	**8.03**	**39.**	**13.**	**1.4**	**0.8**	**130**	**17.**	**1.5**	**<0.08**	**5.9**
	467	8.53	65.	18.	3.1	2.8	140	120	2.6	0.3	9.8

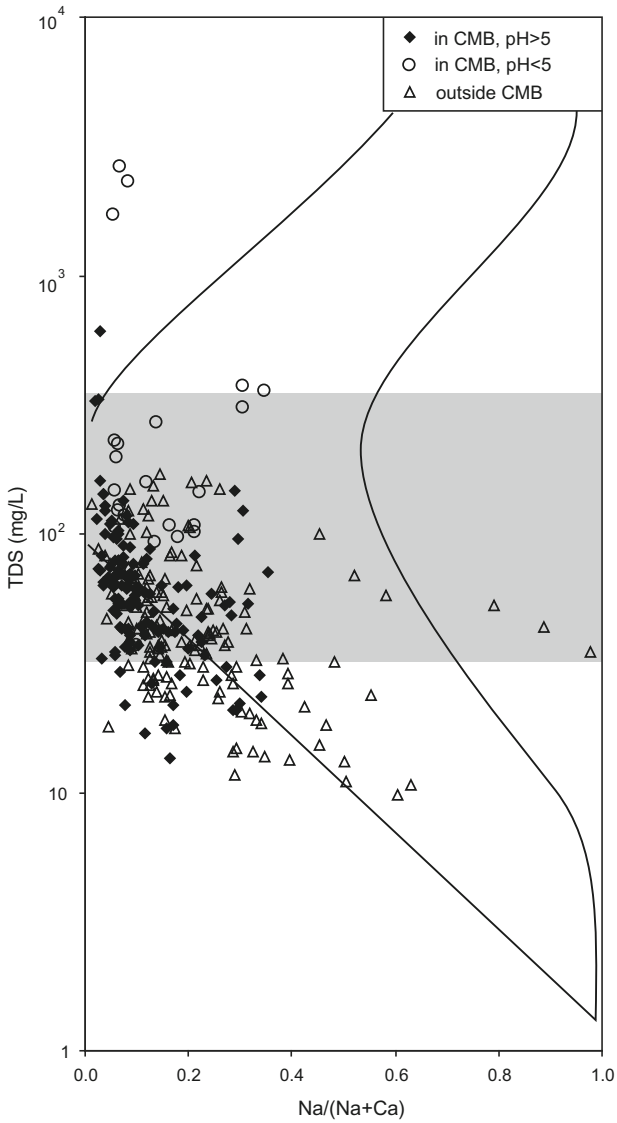

Fig. 4. Weight ratios of Na, Ca, and TDS in all samples from this study. The basis for this plot comes from Gibbs (1970). The boomerang-shaped field was identified by Gibbs as including most major river waters in the world. The gray shaded area was proposed by Gibbs to reflect weathering dominated by rocks in the catchment area. TDS values below the shaded area were proposed by Gibbs to reflect precipitation dominance, and TDS values above the shaded area are dominated by evaporation and mineral precipitation.

clude Ca, Mg, Sr, Ba, K and SO_4 and moderate negative loading (−0.38) of H^+ ion. Factor 2 (21% of the variance), is associated with positive loading of Al, Mn, SiO_2, F and Na (0.61–0.74 component loadings) and negative loading of alkalinity (−0.53). Factor 3 (11% of the variance), is dominated by Fe and DOC (0.58 and 0.57 component loadings). Factor 4 (9% of the variance), is dominated by SO_4 (0.54 component loading).

Fig. 5 shows the principal component scores of PC1 and PC2 for each sample, coded by lithologic group. As discussed previously, there is considerable overlap in water chemistry between many of the lithologic groups. In PC1 and PC2 space, groups 5, 6, 8, 9, and 14 tend to overlap. Two groups that form relatively unique fields are group 14a (waters from catchments that are underlain by Minturn Formation) and group 7 (stream waters draining Pikes Peak Granite). Surface waters in the group 14a catchments plot in the lower right field in Fig. 4, which is dominated by relatively high Ca, Ba, Mg, and alkalinity. Surface waters in the group 7 catchments plot along the upper portion of Fig. 5, which indicates a strong association with PC2. These waters, which drain the Pikes Peak Granite, tend to have relatively high concentrations of F, SiO_2, and Al (Table 3), which are three of the elements that are strongly associated with PC2.

The inset plot in Fig. 5 displays the component loadings for PC1 and PC2. Alkalinity, Ca, Mg, and Ba plot together in the lower right quadrant and Fe, Al, and H^+ plot in the upper left quadrant. The inverse correlation of these groups of constituents is consistent with known weathering and aqueous geochemical processes. Carbonate-bearing rocks are likely to produce water with relatively high Ca concentrations and alkalinity and high pH values, whereas waters with high H^+ concentration, i.e., low pH, tend to be relatively enriched in Fe and Al.

Miller (2002) was able to distinguish stream water chemistry from a number of headwater lithologies in central Colorado. Some important differences between this study and that of Miller (2002) are: (1) the samples for this study were collected at lower elevations within the catchments and therefore it was more difficult to quantify the geochemical signature of individual lithologic groups; (2) the larger area of the current study required that a greater number of geologic formations be grouped together, introducing greater variability into the lithologic groups as compared to those used by Miller (2002); (3) this study sampled only stream waters, whereas Miller (2002) sampled both streams and springs; and (4) Miller (2002) avoided catchments that included historical mines or mineralized/hydrothermally altered rocks, which would be expected to have abnormally high concentrations of many constituents. For these reasons, in this study the assignment of catchment areas to specific lithologic groups is less specific, and more overlap of water chemistry occurs between lithologic groups.

3.3. Local results – Rocky Mountain National Park

Rocky Mountain National Park (RMNP) has a limited history of human disturbance. Small-scale mining occurred in two watersheds, which were not sampled in this study, prior to the area being reserved as a national park in 1915 (Reamer, 2006; Anonymous, 2008). These mines have almost no lasting environmental impact (Burghardt et al., 2008). The land management philosophy of the US National Park Service is to maintain the land in as close to a primitive, undisturbed condition as possible, while allowing public access via a minimum of roads and encouraging non-motorized land use (walking, horseback riding, etc.). The geology of RMNP is characterized by mostly Middle Proterozoic granitic rocks of the Silver Plume Granite on the east side (group 6 in Table 1), which contain quartz, oligoclase, microcline and biotite (Fig. 6). The dominant lithology on the west side of the park is Early Proterozoic metasedimentary rocks (group 8 in Table 1) that vary in composition and mineral assemblage, but which are generally more mafic in composition and contain feldspars, quartz, biotite and muscovite (Braddock and Cole, 1990).

Stream waters from within RMNP commonly were low in total dissolved solids, with median specific conductance (SpC) of 20 microsiemens/cm (μS/cm), approximately one-fourth of the median SpC for all samples outside RMNP. Streams with catchment lithology dominated by granitic rocks generally have lower pH, total dissolved solids, alkalinity, and Mg and Ca concentrations than the waters in catchments dominated by metamorphic rocks. Fig. 6 shows the relative proportions and total concentrations of Ca, Mg, Na and K in stream waters from RMNP. The shading of each pie diagram is arranged so that Ca, Mg, Na and K appear as increasingly dark shades of gray. As seen in the figure, the pie diagrams on the east side of the park are generally darker and smaller, indicating a greater relative proportion of alkali metals, but with generally lower total dissolved solid concentrations. The differences are subtle and some overlap occurs, as seen in Fig. 6.

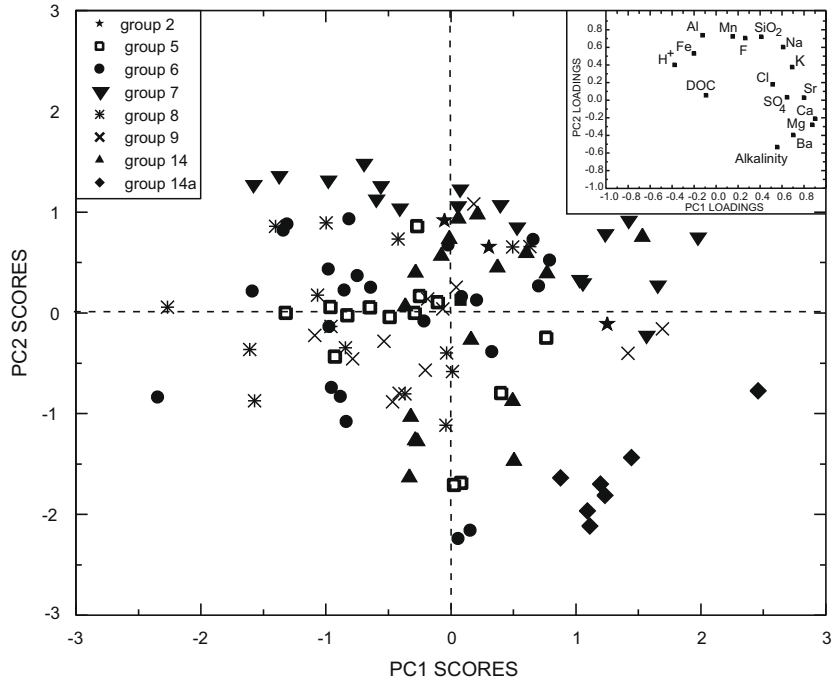

Fig. 5. Principal component scores for unique samples whose catchments are underlain by at least 50% of one lithologic group. Inset figure shows PC loadings for various chemical constituents projected onto the PC1 and PC2 axes. The lithologic group numbers in the legend correspond to the numbers in Table 1.

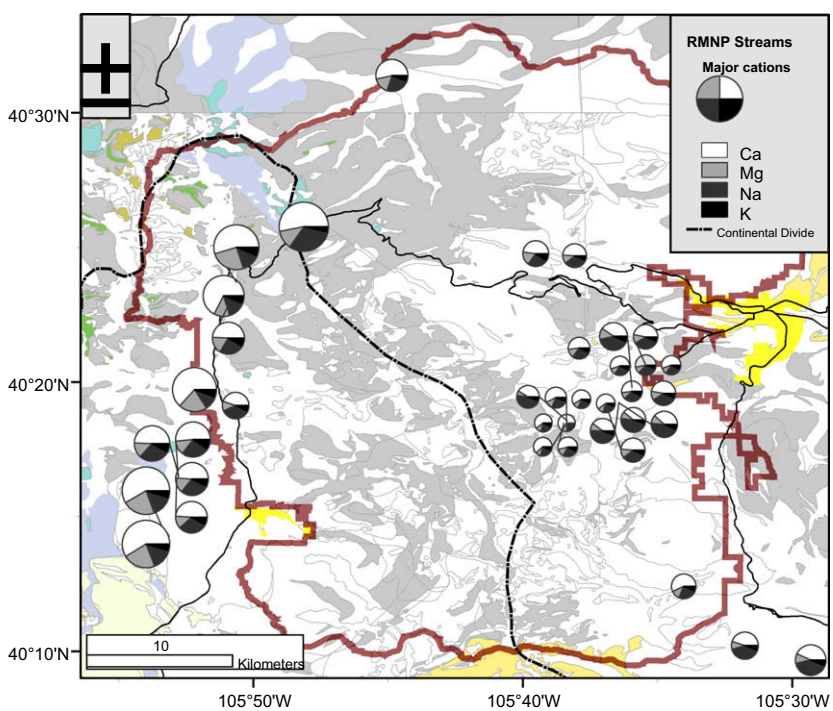

Fig. 6. Relative amounts of dissolved Ca, Mg, Na and K, in mg/L, in waters collected from 30 sample sites in an area of approximately 1100 km^2 in RMNP. Early Proterozoic metasedimentary rock crops out in the shaded areas and Middle Proterozoic granitic rock crops out in the white areas. The size of each symbol is proportional to the total mass/L of the four elements. The width of this map corresponds to approximately 40 km.

Saturation indices for calcite versus total dissolved solids (TDS) follow a positive trend, with lower values of both properties in catchments underlain by granite (Fig. 7). In this example, there is a fairly clear break between the two lithologies at calcite SI = −3, with almost all catchments underlain by metamorphic rocks having SI > −3, and catchments underlain by granitic rocks less than that threshold. The calculation of calcite SI incorporates pH, alkalinity and alkaline earth element concentrations of stream waters. Thus the SI provides a simultaneous measure of several parameters and may be a more effective way to discern lithologic effects on water quality.

Silica concentrations in streams of RMNP are generally greater in catchments on the west side of the park, where the finer-grained, metamorphic rocks predominate. This relationship is

demonstrated by chalcedony saturation indices, which are generally greater in the waters from catchments underlain by metamorphic rocks (Fig. 8), and which approach or slightly exceed saturation levels with respect to chalcedony. Chalcedony may or may not be the solid that controls silica concentrations in these waters, but the general relationship is illustrated by this calculated parameter. Although the granitic rocks on the east side of RMNP have a greater silica concentration (Braddock and Cole, 1990), they are not as good a source of dissolved silica, for a variety of reasons: (1) quartz in the granites is less soluble than the silica-bearing mafic minerals; (2) the kinetics of silica dissolution are faster for the mafic minerals; and (3) the grain size of the metamorphic minerals is generally smaller, thus the specific surface area is greater (cf. Harden, 1988; Cehrs, 1991; White et al., 1996; Harmon and Lyons, 2007).

The fact that the stream waters in RMNP are dilute relative to all samples collected indicates that not much weathering of rocks is needed to produce the observed element concentrations. Still, there are consistent differences in stream water chemistry between streams draining catchments underlain predominantly by granitic or metamorphic rocks. These differences are understandable based on the mineralogic and petrologic differences between the two major rock types.

The scale specificity of any interpretations of reconnaissance data depends heavily on the scales at which the component data are collected. The regional reconnaissance data are readily interpreted in the context of geologic data at the 1:100,000 scale, but more detailed geologic mapping would be required if the spatial scale of geochemical sampling was more dense.

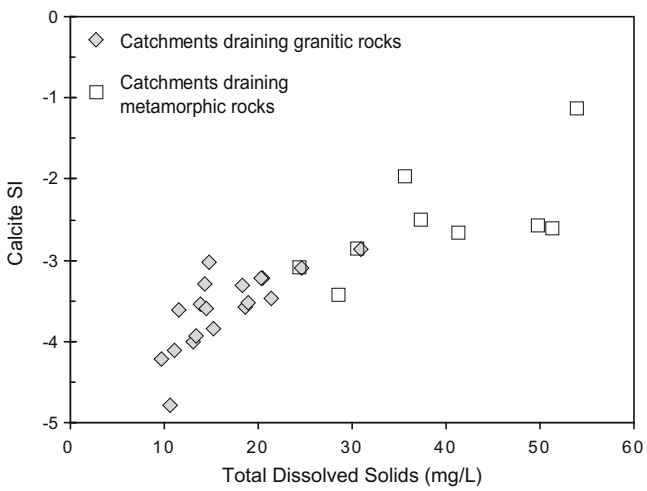

Fig. 7. Calcite saturation indices and total dissolved solids in samples from the RMNP area. Diamonds represent samples collected from catchments underlain by granitic rocks, squares represent samples collected from catchments underlain by metamorphic rocks.

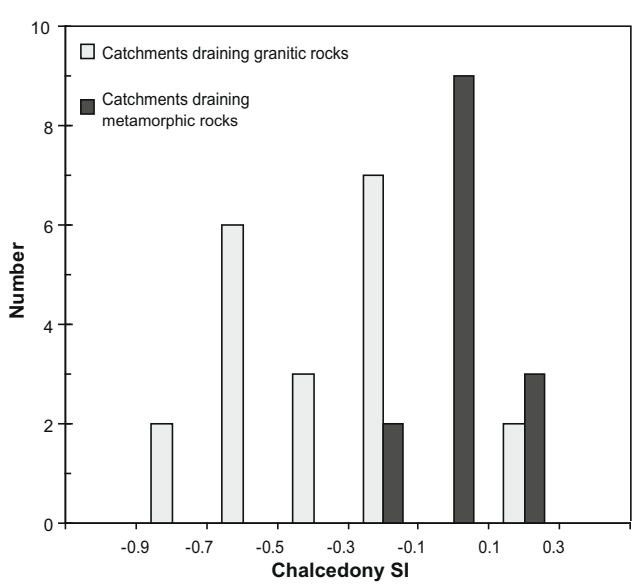

Fig. 8. Histogram of chalcedony saturation indices for stream waters in RMNP.

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 attributable to human disturbance rather than lithologic variations. Within the Colorado mineral belt, stream pH values are generally lower, and concentrations of SO_4^{2-} and many chalcophile trace elements, including Cu, Zn and Cd, are higher, due to the weathering of sulfide minerals such as pyrite, sphalerite and chalcopyrite that were exposed during historical prospecting and mining activities. At a scale of 100 s of kilometers (average sample density of 1/220 km^2), the geochemical 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 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. Nevertheless, streams that are affected by rapid sulfide weathering also exhibit the effects of more rapid weathering of major rock-forming minerals. Large-ion lithophile elements, such as U, also are enriched in streams within the CMB, which is 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.

At the same regional-scale, and at local scales of 10 s of km, lithologic effects on water chemistry are seen for some catchments that have no mining history and that lack mineralized or hydrothermally altered rocks. Using GIS mapping and modeling methods to overlay a lithologic map on a map of catchment boundaries allows the calculation of proportion of catchment area underlain by each lithologic group. A comparison of catchments with >50% of their area covered by a single lithologic group shows that for most lithologic groups, there is a wide range of water chemical compositions, with considerable overlap between many of the groups. This wide range and overlap occurs because of mineralogic and geochemical similarities between these lithologic groups. A few of the lithologic groups are more tightly constrained from a mineralogic/geochemical viewpoint, and the waters draining these rock types have less chemical variability as well. These distinct chemical signatures can be attributed to differences in bedrock lithology and are primarily observed in either the concentrations of lithophile elements or ratios between them. For example, in the study area, ratios of Mg/Ca tend to be higher in streams draining catchments underlain by metavolcanic and metasedimentary rocks when compared with those underlain by granitic and intermediate composition plutonic rocks.

Reconnaissance geochemical studies facilitate a broad understanding of a region, and may allow for a limited capability to predict aspects of stream water chemistry in catchments that have not been sampled. The best cases in which to gain such a predictive capability are for catchments dominated by lithologies that have

a limited range of chemical and mineralogic compositions. In most cases, such lithologies result in stream waters of similarly limited compositional variability. As demonstrated in this study, regional variations in surface water quality attributable to lithologic variations help to establish regional geochemical baselines for water-resource evaluation and for comparison to future sampling.

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