

Environmental Effects of Hydrothermal Alteration and Historical Mining on Water and Sediment Quality in Central Colorado

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Abstract

The U.S. Geological Survey conducted an environmental assessment of 198 catchments in a 54,000-km² area of central Colorado, much of which is on Federal land. The Colorado Mineral Belt, a northeast-trending zone of historical base- and precious-metal mining, cuts diagonally across the study area. The investigation was intended to test the hypothesis that degraded water and sediment quality are restricted to catchments in which historical mining has occurred. Water, streambed sediment, and aquatic insects were collected from (1) catchments underlain by single lithogeochemical units, some of which were hydrothermally altered, that had not been prospected or mined; (2) catchments that contained evidence of prospecting, most of which contain hydrothermally altered rock, but no historical mining; and (3) catchments, all of which contain hydrothermally altered rock, where historical but now inactive mines occur. Geochemical data determined from catchments that did not contain hydrothermal alteration or historical mines met water quality criteria and sediment quality guidelines. Base-metal concentrations from these types of catchments showed small geochemical variations that reflect host lithology. Hydrothermal alteration and

mineralization typically are associated with igneous rocks that have intruded older bedrock in a catchment. This alteration was regionally mapped and characterized primarily through the analysis of remote sensing data acquired by the ASTER satellite sensor. Base-metal concentrations among unaltered rock types showed small geochemical variations that reflect host lithology. Base-metal concentrations were elevated in sediment from catchments underlain by hydrothermally altered rock. Classification of catchments on the basis of mineral deposit types proved to be an efficient and accurate method for discriminating catchments that have degraded water and sediment quality. Only about 4.5 percent of the study area has been affected by historical mining, whereas a larger part of the study area is underlain by hydrothermally altered rock that has weathered to produce water and sediment with naturally elevated geochemical baselines.

Keywords: geochemistry, sediment, water, toxicity, aquatic life, mining, hydrothermal alteration

Introduction

A geoenvironmental assessment of central Colorado was conducted on a 54,000-km² area in the central Rocky Mountains (Figure 1). The study area covers the central portion of Colorado, from the New Mexico border on the south to the Wyoming border on the north, and represents about 20 percent of the land area of Colorado. The Colorado Mineral Belt (Tweto and Simms 1963), an area of extensive historical base- and precious-metal mining, cuts diagonally across the study area. The study area contains two National Parks: Rocky Mountain National Park established in 1908 and Great Sand Dunes National Park, formerly a National Monument (1932), established in 2004. Both areas have been set

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aside and isolated from mineral entry since their establishment. Sample sites in this study are at high altitude, ranging from 1,800 to 3,560 meters 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 during June through 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). Federal land management agencies are required to manage their lands for protection and improvement of the aquatic and riparian habitat. The primary objective of the study described in this paper is to evaluate the effects of hydrothermal alteration and historical mining on the water and sediment quality in the study area.

Study Design

Samples of water and unconsolidated sediment were collected from shallow riffle reaches (<0.5-m depth) from 198 small 1st- and 2nd-order streams in central Colorado. The catchments were selected on the basis of public access, physiography, and geology. Catchments sampled in the study area are primarily on public land and have similar gradients, riparian vegetative canopy, and size (median size is 14.75 km², although one catchment is nearly 200 km² in area). To determine the background lithologic metal contribution, water and streambed sediment samples were collected from catchments that were underlain, as much as possible, by a single lithogeochemical unit (i.e., rocks of similar geochemistry and mode of formation) and that had not been prospected or mined. To determine the metal contribution from hydrothermally altered catchments, additional sample sites were located in catchments that contain historical prospects. Finally, to determine the contribution from historical mining activities, samples were collected from catchments that contain inactive mines. A subset of these catchments was sampled for aquatic macroinvertebrates to determine the population, distribution, and body burden of base metals (Schmidt et al., this volume). Catchments are classified on the basis of disturbance by historical mining. Catchments containing no evidence of historical prospecting (as shown by land disturbance) are classified as unmined or unimpacted (background); those containing prospects, whether or

not those prospects were for base and precious metals or for some other commodity, are classified as prospected; and those catchments containing mines (defined as a site where there is a public record of production of a commodity) are classified as mined. Areas that contain hydrothermal mineralization are color-coded by mineral deposit type (Table 1) on Figure 1.

Methods

Sites from background (undisturbed or unmined) catchments were generally sampled only once during the study. Filtered and unfiltered water samples were analyzed using both inductively coupled plasma–atomic emission spectrometry (ICP-AES) and inductively coupled plasma–mass spectrometry (ICP-MS). Sediments were prepared using total digestion and EPA 3050B leach procedures. Analyses were done using both ICP-AES and ICP-MS. A few duplicate samples of all media were collected at randomly selected sites at the same time to evaluate sampling and analytical reproducibility. Results from duplicate samples were averaged. Replicate samples were collected at the same site in different years. About 20 percent of the sites were replicate sites sampled in one or more field seasons. Samples from catchments containing historical mines and prospects were collected several times during the course of the study. Because previous work has shown that the sediment geochemistry, in particular, is dominated by the colloidal sediment component and that the amount of colloids varies depending on both the time of year and seasonal fluctuations in rainfall (Fey et al. 2002, Church et al. 2007), each sample was treated as a separate observation to determine a range of element concentrations from these disturbed catchments. Both filtered (0.45 µm) and unfiltered water and fine (<177 µm) sediment samples collected from 198 catchments over a 4-yr period (2003–2007) constitute the data set discussed in this paper.

The catchments were classified by disturbance and by hydrothermal alteration type (Figure 2). State (M.A. Sares, 2008, U.S. Forest Service Abandoned Mine Land Inventory, CO, Colorado Geological Survey, unpublished report) and Federal (USGS Mineral Resource Data System, <http://tin.er.usgs.gov/mrds/>, accessed August 2008) databases were used to determine disturbance by mining. The term mine, for the purposes of

Table 1. Characteristics of the principal hydrothermal mineral deposit types found in central Colorado

[Metals, minerals, and alteration types are listed in approximate order of abundance]

Deposit type	Frequency¹	Metals	Major ore minerals	Minor ore minerals	Gangue minerals	Alteration type and style
Polymetallic veins	73	Ag, Au, Pb, Zn, Cu	pyrite, galena, sphalerite, tetrahedrite, chalcopryrite	argentite, ruby silver	quartz, calcite, siderite, dolomite	argillization, sericitization, silification, propylitization
Porphyry Mo or Cu-Mo	20	Mo, Cu, Sn, W	molybdenite, chalcopryrite, pyrite	hebnerrite, cassiterite	quartz, fluorite, sericite, topaz	silicification, sericitization, potassium feldspar, propylitization
Polymetallic replacement and skarn	9	Ag, Pb, Zn, Cu	galena, sphalerite, tetrahedrite, pyrite	chalcopryrite, pyrrhotite	dolomite, barite, siderite, fluorite	regional dolomitization, local silicification
Fluorite veins	4	F	fluorite	base metal sulfides, pyrite	quartz, calcite, barite, manganese oxide	argillization, sericitization, silification
Tungsten veins	--	W	ferberite	pyrite, sphalerite, tetrahedrite, scheelite	quartz, calcite, siderite, barite	silicification, argillization, sericitization, potassium feldspar, propylitization
Uranium veins	3	U, Th, V	uraninite, torbernite, coffinite	base-metal sulfides, pyrite	calcite, ankerite, quartz	argillization, sericitization
Stratabound Cu-Zn	1	Cu, Zn	chalcopryrite, sphalerite, pyrrhotite, pyrite, gahnite	galena, arsenopyrite	amphiboles, chlorite, garnet, sillimanite, epidote, anthophyllite, pyroxene	argillization (metamorphosed to high temperature aluminosilicate minerals)
Alkaline Au-telluride veins	--	Au, Ag, Te	gold, silver, and base metal telluride minerals, native gold	pyrite	quartz, chalcedony, fluorite, calcite, dolomite, hematite, apatite	argillization, silicification, sericitization, potassium feldspar, biotitization

¹Frequency is the intersection of sampled watersheds with mineral deposit types.

production, is restricted, i.e., there must be publically available data indicating that a commodity from the mine site was produced. All other disturbances, such as adits, shafts, and prospect pits, were classified as prospects.

Hydrothermal alteration was mapped and characterized across the study area primarily using mineral maps derived from analysis of Advance Spaceborne Thermal Emission and Reflection Radiometer (ASTER) remote-sensing data. Such maps were supplemented and verified by published

alteration data at local scales (generally from dissertations and wilderness studies) and more detailed mineral maps generated from Airborne Visible/Infrared Imaging Spectrometer (AVIRIS) data. Hydrothermal alteration identified using the ASTER data was classified into types (advanced argillic, argillic \pm ferric iron, quartz-sericite-pyrite (QSP), and propylitic) on the basis of spectrally identified mineral assemblages. For example, the QSP alteration type was characterized by the occurrence of ferric iron + sericite \pm kaolinite and is referred to in Table 1 by the process terms

seritication and silicification with pyrite. In like manner, the term propylitization refers to the propylitic alteration mineral assemblage, the term dolomitization refers to the conversion of limestone to dolomite, the terms biotization and potassic alteration refer to adding potassium by hydrothermal alteration process to form potassium-bearing minerals such a biotite and potassium feldspar in the hydrothermal alteration suite, and so forth. Several minerals that are associated with alteration may also occur in unaltered sedimentary and metamorphic rocks. Hydrothermally altered areas were differentiated from unaltered areas by applying a 3-km buffer around intrusions and by excluding specific lithogeochemical units that contain abundant muscovite (e.g., shales and metapelites) and (or) carbonate minerals (limestones and dolomites). The mapping of hydrothermal alteration using remote sensing data is possible only where the ground is not covered by vegetation. Some catchments that have no evidence of historical mining activity (Figure 2) are, nevertheless, hydrothermally altered.

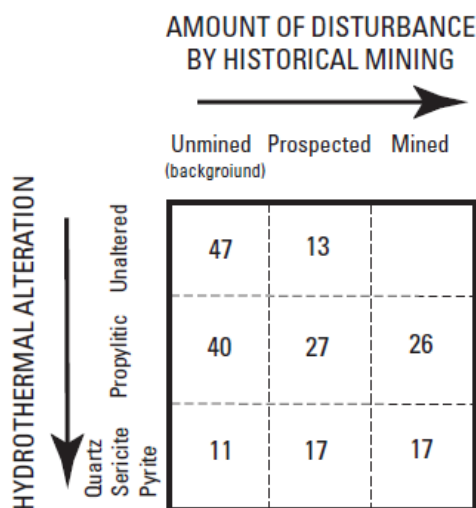


Figure 2. Diagram showing the distribution of samples classified on the basis of hydrothermal alteration and disturbance by historical mining.

Environmental Effects of Hydrothermal Alteration and Historical Mining

Water data

Weathering of pyrite (FeS_2) to release ferrous iron (Fe^{+2}) and sulfate (SO_4^{-2}) is the basic geochemical reaction generally indicative of the presence of

hydrothermal alteration (Plumlee 1999). The oxidation of ferrous to ferric iron (Fe^{+3}) results in a lowering of the pH in surface water. Values of pH ranged between 2.8 and 8.6 (median = 6.99, $n = 262$). Water samples that have low pH have high concentrations of sulfate, which is directly correlated with specific conductance (range of specific conductance is 13–3,000, median = 79.6; Figure 3).

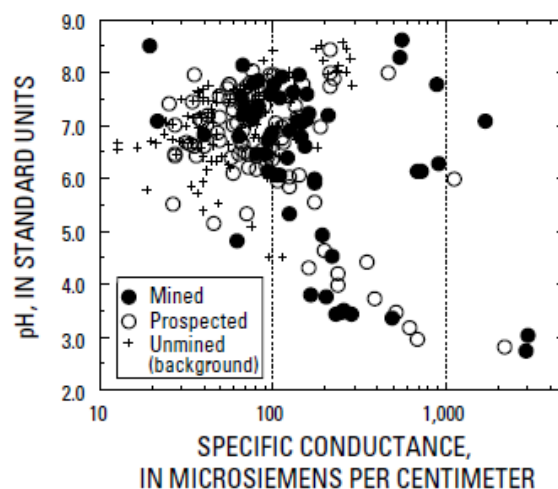


Figure 3. Plot of the relationship of specific conductance to pH in water, by disturbance class.

All samples with low pH and high conductivity are from streams in either prospected or mined catchments; however, the converse is not true. Not all catchments that have been prospected or that contain inactive mines have water that has a low pH or high conductivity (i.e., high concentrations of sulfate). Furthermore, samples from background catchments containing some marine sediment rocks contain evaporate sequences and have high concentrations of sulfate caused by the dissolution of gypsum (Wanty et al. 2009). Metal concentrations in both unfiltered and filtered water samples ($0.45\mu\text{m}$) were analyzed by ICP-MS and ICP-AES to determine metal and sulfate concentrations. Low concentrations of SO_4^{-2} were determined by ion chromatography where the concentrations were below the detection limit (DL) for SO_4^{-2} by ICP-AES. The distributions of base metals (cadmium, Cd; copper, Cu; lead, Pb; and zinc, Zn) and SO_4^{-2} , classified by disturbance, are shown in Figure 4. Dissolved concentrations for the bulk of the background samples for Cd, Cu, and Pb are below the limit of detection by ICP-MS (DL = 0.02, 0.5, and 0.05 $\mu\text{g/L}$, respectively). Concentrations of dissolved Cu and Pb are also censored for some of the prospected catchments

and for most of the background (unmined) catchments. Concentrations of Zn are partially censored (DL = 0.5 $\mu\text{g/L}$) for catchments from both the background and prospected classes. Concentrations of all the base metals (Cd, Cu, Pb, and Zn) and SO_4^{-2} are elevated in water

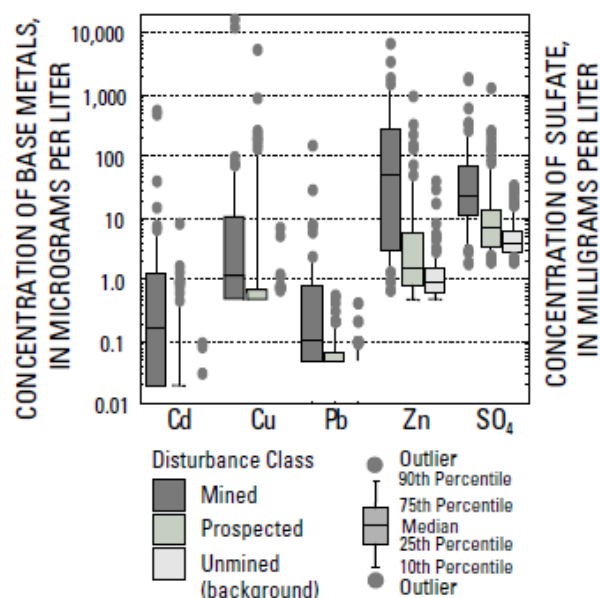


Figure 4. Box plot of the distribution of dissolved base-metal concentrations (cadmium, Cd; copper, Cu; lead, Pb; and zinc, Zn) and sulfate (SO_4^{-2}) in water, by disturbance class (Figure 2).

from catchments containing prospects relative to those from background (unmined) catchments. Likewise, concentrations of both base metals and SO_4^{-2} are elevated in water from catchments containing mines relative to those containing prospects. However, only water samples from mined catchments had significant concentrations of metals (iron, Fe; aluminum, Al; Cd; Cu; Pb; and Zn) that were transported as suspended colloids (Kimball et al. 1995).

Sediment data

Sediment geochemical data (Figure 5) show that there are two very distinct groups of samples and that these groups are not clearly defined on the basis of known disturbance by historical mining. Most, but not all, of the sediment data in the geochemical background (unmined) group plot within the general cluster at the lower left (Figure 5) and have low concentrations of total iron and leachable sulfate. Most, although not all, of the sediment samples from mined catchments and

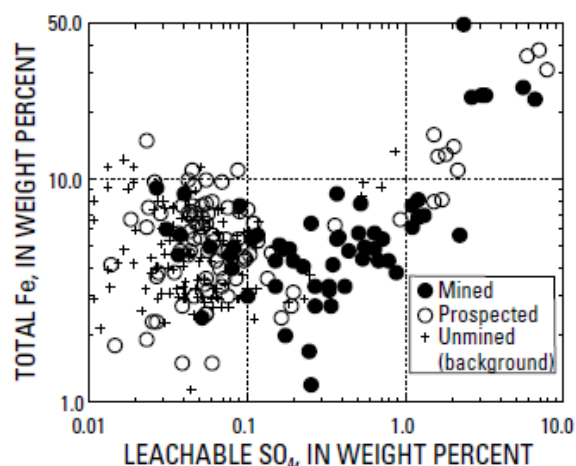


Figure 5. Plot of the concentration of total iron (Fe) and leachable sulfate (SO_4) in sediment, by disturbance class. Two distinct populations are readily apparent. Data from sediment from mined catchments plot largely in the linear array, whereas data from the background population plot in a cluster in the lower left of the figure. Disturbance by historical mining is shown to not be a good descriptor of the geochemical data.

many sediment samples from prospected catchments plot in the linear array of data that show good correlation of increasing total iron with leachable sulfate concentrations that increase and correlate diagonally across the diagram to the upper right corner (Figure 5). In the background group, some of the rocks are from catchments underlain by marine shale that contains gypsum (Wanty et al. 2009). They plot in the low-iron, high-sulfate group. Likewise, those samples from mined catchments that have a low-iron, high-sulfate signature (Figure 5) indicate that disturbance by historical mining has not changed the background lithogeochemical signature; i.e., they cause little geochemical change in the sediment geochemistry of the catchment. Finally, the fact that some sediment data from the background catchments plot along the high-iron, high-sulfate trend indicates that not all sites of hydrothermal alteration had been explored by prospectors in the past. These unexplored catchments have sediment and water that contain elevated metals and acidity resulting from weathering of altered rock and are unrelated to historical mining.

The major-element geochemistry of the sites varies by hydrothermal alteration type. In comparison with the background catchments, hydrothermal alteration generally resulted in lower median concentrations of

sodium, potassium, and calcium in sediment (data not shown). Median Fe concentration in sediment from mined catchments is somewhat higher and the range of Fe concentrations is larger than that from sediment in background catchments. Concentrations of base metals (Cd, Cu, Pb, and Zn), and of barium (Ba), manganese (Mn), and sulfate are indicative of sulfide mineralization. Figure 6 summarizes the geochemical differences in sediment geochemistry among catchments by disturbance and hydrothermal alteration. The effects of hydrothermal alteration are shown in each panel (Figure 6), whereas the effects of disturbance by historical mining (Figure 2) are shown by comparing the differences between classes in different panels.

There is little difference between the geochemistry of sediment from unmined background and propylitic-altered catchments and sediment from those catchments that are unmined and unexplored that contain some QSP alteration (Figure 6A). At the scale of the catchments sampled, the ASTER-derived mineral maps showed that QSP-altered areas are always smaller (usually on the order of 1 km² or less) than the total catchment area. Furthermore, the QSP-altered areas are surrounded by areas of propylitic alteration. Our attempt to rank the amount of QSP alteration relative to propylitic-altered and unaltered areas within the catchments was not useful in further describing the data. Median concentrations of Mn and Pb in sediment from propylitic-altered catchments are lower than that in sediment from either background or QSP-altered, unmined catchments. In contrast, the median concentration of SO₄⁻² in sediment from QSP-altered catchments is somewhat higher. The ranges of metal concentrations in sediment, as shown by the 25th and 75th percentiles in the QSP-altered, unmined catchments, always have a larger spread than the other two hydrothermal alteration classes. Median concentrations of Cd, Pb, Mn, and Zn are near crustal abundance in unaltered rocks, whereas Cu is lower and Ba higher than crustal abundance values (Fortescue 1992).

The presence of prospects in catchments on sediment geochemistry, regardless of the presence of propylitic hydrothermal alteration, does not substantially affect the median concentrations or ranges of the geochemical data. Median values of all constituents in sediment (Figure 6B) from prospected catchments are very similar to those from the unaltered, unmined catchments

(Figure 6A). Relative to the sediment geochemical data from background catchments, median concentrations of Ba, Mn, Cd, Pb, and Zn show little variation among the three hydrothermal alteration classes. Essentially, the only major difference is that the 75th percentile of the copper and sulfate sediment data in QSP-altered, prospected catchments (Figure 6B) is higher than that in QSP-altered, unmined catchments (Figure 6A). The 75th percentile for both Cu and SO₄⁻² in sediment from catchments containing both prospects and some QSP alteration exceeds the maximum concentration in sediment from the background catchments.

In catchments where historical mining has occurred, the disturbance of hydrothermally altered rock by mining appears to have resulted in substantial release of metals and sulfate (Figure 6C). Although catchments have been mined, some degraded water and sediment quality results from weathering of exposed hydrothermally altered rock. Relative to background sediment data, the median concentrations of Ba, Mn, and SO₄⁻² in sediment from mined catchments increase in sediment from propylitic-altered catchments and are even more elevated in sediment from catchments containing some QSP-altered rock. Furthermore, the range of concentrations of these three constituents in sediment in both classes of hydrothermally altered rock is much greater than the ranges of concentrations in background catchments. Median concentrations of Mn, SO₄⁻², and all four of the base metals in sediment from disturbed catchments are greater than the 75th percentile for sediment from background catchments. For the metals Cd, Cu, and Pb, the median concentrations in sediment from disturbed catchments for both classes of hydrothermal alteration exceed the maximum concentration in sediment from the background catchments. Median concentrations of Zn in sediment from mined, QSP-altered catchments likewise exceed the maximum in background sediment concentrations, whereas median Zn concentrations in sediment from propylitic-altered, mined catchments is within the range of sediment data from background Zn concentrations but is still strongly enriched.

Comparison of Geochemical Data from Hydrothermal Alteration and Disturbance Class with Sediment Quality Guidelines

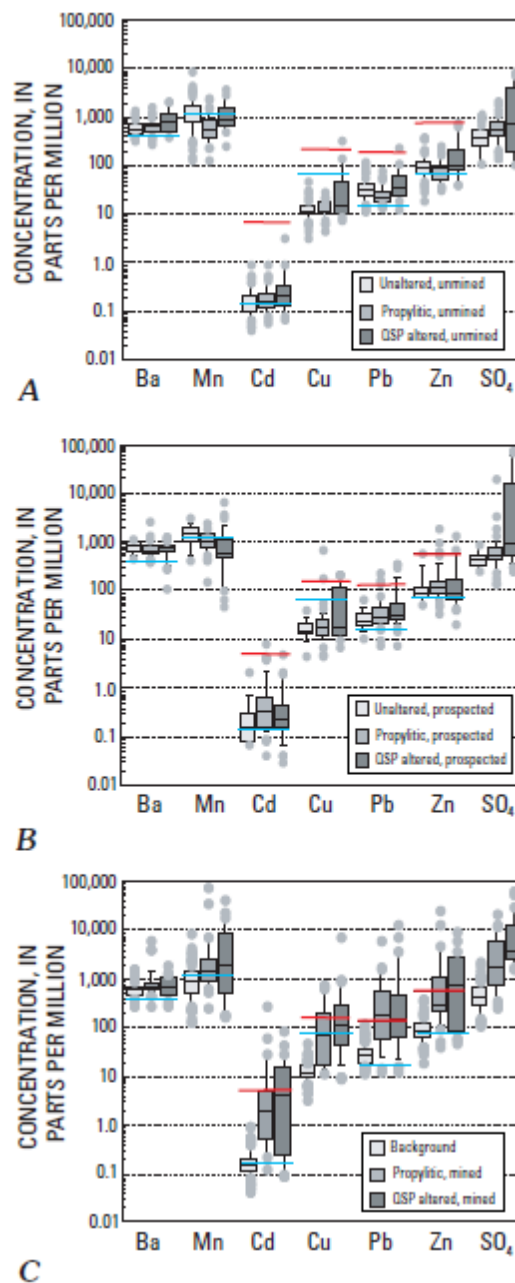
The consensus probable effects concentration sediment quality guidelines (PEC-SQG; Macdonald et al. 2000) for Cd, Cu, Pb, and Zn are shown on Figure 6. These

guidelines represent the concentration in sediment above which these elements have been shown to have significant toxicity effects on sensitive aquatic life. Rarely do the observed concentrations in sediment from QSP-altered rock in background catchments exceed the PEC-SQG (Figure 6A). However, in catchments where historical prospecting has occurred (Figure 6B), the concentrations of all four metals in a few catchments exceed the PEC-SQG. In mined, propylitic-altered and QSP-altered catchments, the PEC-SQG concentrations of the base metals are often less than the 75th percentile and, in some cases, approach the median value (Figure 6C). The PEC-SQG concentrations of Cd in sediment from these catchments are at the 75th percentile in propylitic-altered catchments and approach the median value in sediment from QSP-altered catchments. The PEC-SQG concentrations of Cu in sediment from these catchments are less than the 75th percentile for both hydrothermal alteration groups. The PEC-SQG concentrations of Pb in sediment are likewise lower than the median value for both groups. And the PEC-SQG concentrations of Zn in sediment are less than the 75th percentile for propylitic-altered catchments and less than the median value for sediment from QSP-altered catchments. Historical mining can be implicated for some of the poor water and sediment quality in the study area; however, it is erroneous to assume that all degraded water and sediment quality is the result of historical mining. Some degraded water and sediment quality results from the weathering of exposed hydrothermally altered rock (Church et al. 2007) that is undisturbed by human activity (Figure 6A).

Figure 6. Box plots of total barium (Ba), manganese (Mn), cadmium (Cd), copper (Cu), lead (Pb), zinc (Zn), and leachable sulfate (SO_4) in sediment.

A. Geochemical data in sediment from background catchments versus catchments containing propylitic and quartz-sericite-pyrite (QSP) altered rock with no mines or prospects. These data correspond to the left-hand column in Figure 2.

B. Geochemical data in sediment from prospected background catchments in relation to sediment data from prospected catchments with propylitic alteration and sediment data from prospected catchments containing some QSP-altered rock. These data correspond to the center column in Figure 2.



C. Geochemical sediment data from unmined background catchments (both unaltered and propylitic alteration) in relation to sediment data from mined catchments containing either propylitic altered or QSP-altered rock. These data correspond to the right-hand column in Figure 2. The red lines indicate metal concentrations in sediment that are potentially toxic to aquatic life (probable effects concentration, sediment quality guidelines; Macdonald et al. 2000). Blue lines are the crustal abundance concentrations (Fortescue 1992).

Mineral Deposit Data

The mineral deposits in the study area were classified by mineral deposit type (Cox and Singer 1986). Areas of hydrothermal mineralization are shown in Figure 1. Table 1 shows the characteristics of these mineral deposits, including exploited metals, gangue mineralogy, and hydrothermal alteration type. The catchments were reclassified according to their intersection with the mineralized areas. Development of the specific deposit type areas utilized data from the disturbance classes discussed previously but did not rely on the hydrothermal alteration data developed from the AVIRIS and ASTER data. The polymetallic vein type of deposits has the highest frequency of occurrence in sampled catchments (Table 1). Polymetallic veins may constitute a surface expression of and overlie many larger mineral deposit types (Cox 1986 a and b; Ludington 1986; Cox and Singer 1986) that occur within the study area. These polymetallic vein deposits were the target of historical mining at the turn of the twentieth century in Colorado (e.g., Henderson 1926). The numerical and areal abundance of polymetallic vein deposits reflect the exploration history and the level of erosion and exposure in the study area. Porphyry molybdenum (Mo) and Cu-Mo deposits are known in the study area, but only the porphyry Mo deposits at Climax and Henderson have been exploited. Polymetallic replacement and skarn deposits have also been exploited in the western and southwestern part of the study area. The catchments containing uranium vein deposits and fluorite vein deposits were sampled in only a few catchments (Table 1). The stratabound Cu-Zn deposits occur mostly in dry, low-lying terrane that was privately owned and was generally not accessible for sampling. The one catchment that contained a stratabound Cu-Zn deposit that was sampled was lumped with the polymetallic replacement deposits in plotting of the sediment geochemical data (Figure 7). The total area of the mineralized zones is 2,426 km² or 4.5 percent of the study area.

Evaluation of Water and Sediment Quality Data with Mineral Deposit Types

Sediment geochemical data for Cd, Cu, Pb, Zn, and SO₄ categorized by mineral deposit type are presented in Figure 7. The sediment geochemistry from catchments containing base-metal-rich polymetallic veins, porphyry Mo and Cu-Mo deposits, and polymetallic replacement and skarn deposits clearly outline the areas of high base-

metal concentrations. The fluorite and uranium vein deposits do not contribute substantial base metals to sediment in catchments that contain them. In fact, stream sediment from these catchments do not differ significantly from sediment from unmined, background catchments. Mineral deposit type is a better discriminator for elevated base-metal concentrations in the environment than disturbance or hydrothermal alteration. The base-metal distributions (Figure 7), because they are not separated by disturbance class, have a larger range than those shown in Figure 6 but would show similar patterns of metal enrichment if subdivided by disturbance class. High concentrations in the base-metal distributions in Figure 7 represent the sediment geochemistry from mined catchments (Figure 6). The base metals Cd, Cu, Pb, and Zn are enriched in sediment from catchments that contain polymetallic vein, polymetallic replacement, and skarn-type mineral deposits, whereas copper is generally more enriched in sediment from catchments that contain porphyry Cu-Mo and Mo, polymetallic replacement, and skarn-type mineral deposits relative to catchments containing other mineral deposit types. Elevated concentrations of SO₄⁻² in sediment are interpreted to reflect the high abundance of pyrite in the hydrothermal alteration halo of the porphyry mineral deposits (Ludington 1986, Cox 1986b).

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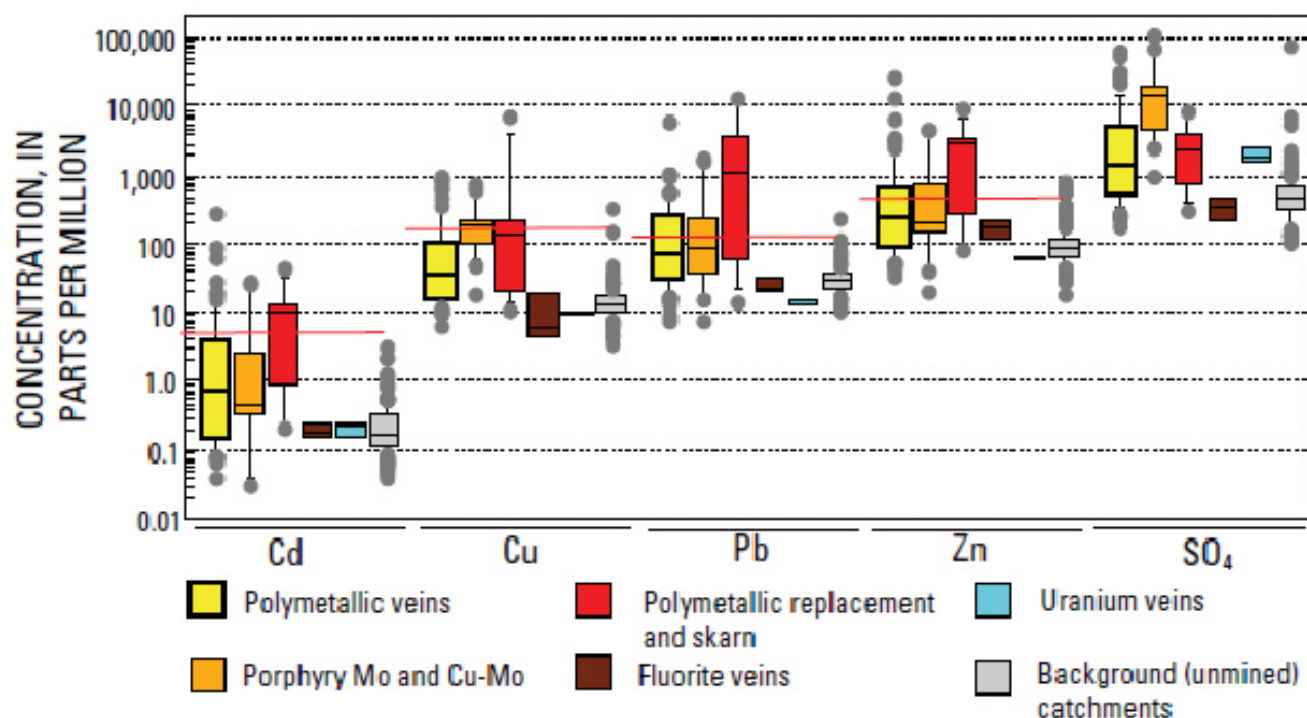


Figure 7. Box plots of total concentration data for cadmium (Cd), copper (Cu), lead (Pb), zinc (Zn), and sulfate (SO₄) in sediment from catchments containing different types of mineral deposits (Table 1). The red lines indicate metal concentrations in sediment that are potentially toxic to aquatic life (probable effects concentration, sediment quality guidelines; Macdonald et al. 2000).

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