



Naturally acidic surface and ground waters draining porphyry-related mineralized areas of the Southern Rocky Mountains, Colorado and New Mexico

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ABSTRACT

Acidic, metal-rich waters produced by the oxidative weathering and resulting leaching of major and trace elements from pyritic rocks can adversely affect water quality in receiving streams and riparian ecosystems. Five study areas in the southern Rocky Mountains with naturally acidic waters associated with porphyry mineralization were studied to document variations in water chemistry and processes that control the chemical variations. Study areas include the Upper Animas River watershed, East Alpine Gulch, Mount Emmons, and Handcart Gulch in Colorado and the Red River in New Mexico. Although host-rock lithologies in all these areas range from Precambrian gneisses to Cretaceous sedimentary units to Tertiary volcanic complexes, the mineralization is Tertiary in age and associated with intermediate to felsic composition, porphyritic plutons. Pyrite is ubiquitous, ranging from ~1 to >5 vol.%. Springs and headwater streams have pH values as low as 2.6, SO₄ up to 3700 mg/L and high dissolved metal concentrations (for example: Fe up to 400 mg/L; Cu up to 3.5 mg/L; and Zn up to 14.4 mg/L). Intensity of hydrothermal alteration and presence of sulfides are the primary controls of water chemistry of these naturally acidic waters. Subbasins underlain by intensely hydrothermally altered lithologies are poorly vegetated and quite susceptible to storm-induced surface runoff. Within the Red River study area, results from a storm runoff study documented downstream changes in river chemistry: pH decreased from 7.80 to 4.83, alkalinity decreased from 49.4 to <1 mg/L, SO₄ increased from 162 to 314 mg/L, dissolved Fe increased from 0.011 to 0.596 mg/L, and dissolved Zn increased from 0.056 to 0.607 mg/L. Compared to mine drainage in the same study areas, the chemistry of naturally acidic waters tends to overlap but not reach the extreme concentrations of metals and acidity as some mine waters. The chemistry of waters draining these mineralized but unmined areas can be used to estimate premining conditions at sites with similar geologic and hydrologic conditions. For example, the US Geological Survey was asked to estimate premining ground-water chemistry at the Questa Mo mine, and the proximal analog approach was used because a mineralized but unmined area was located adjacent to the mine property. By comparing and contrasting water chemistry from different porphyry mineralized areas, this study not only documents the range in concentrations of constituents of interest but also provides insight into the primary controls of water chemistry.

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1. Introduction

Acidic, metal-rich waters produced by the weathering of pyritic rocks can adversely affect water quality and riparian ecosystems because acidic waters that result from pyrite oxidation also leach major and trace elements from host rocks and discharge into receiving streams. Upon entering streams, the chemistry of the water changes due to dilution and in-stream chemical reactions (Chapman et al., 1983; McKnight and Bencala, 1990; Kimball et al., 2002; Runkel and Kimball, 2002). In many metal mining districts, natural-acid drainage substantially affected water quality

prior to mining; as a result, establishing restoration goals in these districts is difficult because of the occurrence of both natural and mining-related sources of metals and acidity (Runnells et al., 1992; Alpers and Nordstrom, 2000).

In mineralized settings, acid waters are produced by sulfide oxidation in the near-surface weathering environment. Pyrite can occur as fine-grained disseminated crystals within a host rock or as veins, both with or without other metal sulfides. Pyrite oxidation results in the production and release of H₂SO₄, and at least some of the Fe remains in solution. The acidic water can react with other minerals in the rock to leach major elements such as Al, Ca, Mg, Na, and K, and trace elements such as Zn and Cu; the resultant water chemistry is controlled by a complex interplay of mineralogical, chemical, and hydrological factors along the flow path.

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Porphyry mineralized areas are characterized by the presence of intrusions that are porphyritic in texture and genetically associated with the mineralizing event. These intrusive rocks tend to be intermediate to felsic in composition and host Cu and (or) Mo mineralization. Hydrothermal alteration is commonly most intense near the porphyry and decreases in intensity outward into the rocks surrounding the intrusion. A typical alteration sequence grades outward from a relatively high temperature potassic zone with a mineral assemblage of K feldspar, biotite, and quartz to progressively more distal zones of quartz–sericite, quartz–kaolinite, and propylitic (chlorite–epidote–albite–calcite) alteration zones (Lowell and Guilbert, 1970). Typically, pyrite is present in all of the alteration zones and within the intrusive rocks, but tends to be most abundant in the quartz–sericite alteration (resulting in the more common name quartz–sericite–pyrite [QSP] for this alteration zone).

Within the southern Rocky Mountains, headwater catchments characterized by acidic, metalliferous waters that are relatively unaffected by human activity are ideally suited to constrain geochemical processes that control the surface- and ground-water chemistry associated with near surface acid weathering, as well as to estimate premining conditions in heavily mined areas of similar geology. Five areas (Table 1) that have a range in geologic and geographic characteristics were chosen for this study (Fig. 1). Two common features of the study areas are each area contains (1) porphyritic intrusions that are genetically related to the mineralization and (2) disseminated pyrite in the country rock that produces acidic waters. To minimize the effect of in-stream processes and dilution, water samples were collected from seeps, springs, headwater streams, and ground-water wells. The objectives of this study were to determine the factors that control the chemistry of natural waters draining porphyry mineralized areas and compare these waters to mine drainage in the same study areas. An example of the utilization of a mineralized, but un-mined area to estimate premining ground-water chemistry is the US Geological Survey (USGS) baseline study at Questa, a porphyry Mo deposit in northern New Mexico within the Red River study area. Establishing realistic remediation goals at hardrock mining sites is essential, but at historically mined areas is quite difficult because no water chemistry data were determined prior to mining. Quantifying the range in water chemistry of naturally acidic waters and determining the processes that control the variation in chemistry provide constraints for premining water quality in similar hydrogeochemical settings.

2. Study sites

2.1. Upper Animas River watershed

The Animas River watershed within the San Juan Mountains of Colorado (Fig. 1) is the largest and most complex of the study areas,

covering 380 km² with a range in elevation from 3000 to 4000 m. Mean annual precipitation in this rugged, mountainous terrain ranges from about 60 to 100 cm/a. Although Precambrian-age amphibolites, schists, and gneisses, as well as Paleozoic and Mesozoic sedimentary rocks, crop out in the southern portion of the watershed, water sampling primarily focused on the upper watershed which is underlain by intermediate to felsic composition volcanic and plutonic units associated with the Tertiary-age San Juan and Silverton calderas.

Multiple hydrothermal alteration and mineralization events spanning a 17 Ma history from about 27 Ma to 10 Ma are the culmination of a complex cycle of volcano-tectonic events that have affected the region (Lipman et al., 1976; Bove et al., 2001). The first episode of hydrothermal alteration, a pre-ore propylitization event defined by Burbank (1960), formed during the cooling of the San Juan caldera volcanic fill; the intracaldera lava flows cooled, degassed, and released large quantities of CO₂. This event altered the primary mineral assemblage of the lava flows, and formed an alteration assemblage that includes calcite, epidote, and chlorite (Burbank, 1960). Three discrete mineralizing events postdated the initial regional propylitization. The earliest event occurring between 26 and 25 Ma, was related to emplacement of monzonitic intrusions, and consists of low-grade Mo–Cu–porphyry mineralization (Ringrose, 1982; Bove et al., 2001). The central part of this zoned system is composed of bleached, quartz–stockwork-veined, quartz–sericite–pyrite altered, intrusive, and volcanic rocks, and hosts the exposed Mo–Cu mineralized rock (McCusker, 1982). Disseminated sulfides in this zone consist mainly of pyrite, lesser chalcocopyrite, and traces of molybdenite and bornite, and the sulfides comprise as much as 5 vol.% of the host rock (McCusker, 1982). Progressively outward from the locus of mineralization, zones of weak sericite–pyrite and propylitically altered igneous and volcanoclastic rocks, respectively, form the periphery of the hydrothermally altered and mineralized porphyry system.

An acid sulfate system, associated with the emplacement of coarsely porphyritic dacite intrusions, formed at 23 Ma and hosts the Red Mountain mining district. This acid sulfate mineralization is often characterized by breccia-pipe and fault-hosted vein ore with abundant Cu–As–Sb-rich minerals such as enargite and tetrahedrite–tennantite, in addition to Cu ores of chalcocite, bornite, and covellite (Burbank et al., 1972). Gangue minerals include barite, calcite, and fluorite.

The third episode of mineralization formed post 18-Ma and is closely associated with the emplacement of high-silica alkali rhyolite intrusions (Lipman et al., 1973; Bartos, 1993). Mineral deposits formed during this episode consist of polymetallic, Cu–Pb–Zn base- and precious-metal veins that were deposited along caldera-related fractures and faults (Casadevall and Ohmoto, 1977). Unlike the pervasive areas of alteration that are associated with both

Table 1
Location information and selected chemistry of dissolved constituents for porphyry mineralized study areas.

Study area	Upper Animas River		East Alpine Gulch	Mount Emmons		Handcart Gulch	Red River
State	CO		CO	CO		CO	NM
Latitude	37.81°		37.98°	38.88°		39.518°	37.70°
Longitude	–107.67°		–107.35°	–107.05°		–105.82°	–105.45°
Group	Natural	Mining affected	Natural	Natural	Mining affected	Natural	Natural
Number of sites	109	75	19	37	6	34	32
pH range	2.58–8.02	2.35–7.77	3.15–7.83	2.93–8.03	2.90–6.09	2.69–6.77	2.60–7.71
pH-median	4.5	5.7	6.6	6.4	3.5	3.7	3.9
Constituent, mg/L							
SO ₄ range	1.0–1300	45–2720	6.6–323	3.8–130	20–328	31–1010	119–3700
SO ₄ -median	120	310	55	21	280	160	1400
Zn range	<0.02–14.4	<0.001–228	<0.01–0.210	<0.001–6.1	1.7–65	0.03–0.59	<0.001–12.8
Zn-median	0.026	0.62	<0.01	0.53	40.	0.13	2.2
Cu range	<0.001–0.37	<0.001–98.6	<0.01	<0.001–0.478	0.048–2.0	<0.001–23.0	<0.001–3.5
Cu-median	0.004	0.006	<0.01	0.004	0.690	0.14	0.065

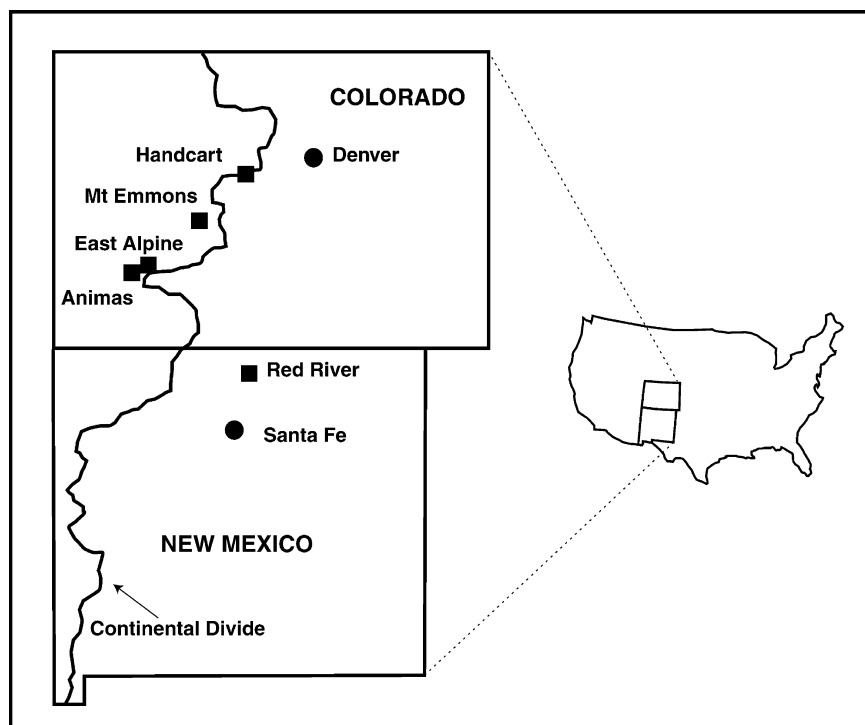


Fig. 1. Map showing locations of the study areas.

the porphyry Mo–Cu mineralization and acid–sulfate mineralization systems that commonly affect entire mountain blocks, the style of post-18 Ma alteration tends to be focused adjacent to veins and vein structures.

Surface water samples were collected from natural springs, headwater streams, mining-affected areas, and draining mines. Complete water chemistry is reported in Mast et al. (2000). A ranking system, based on field observations and literature reviews, was devised to evaluate the potential for effects of upgradient mining activity on the sampling site (Mast et al., 2007). The ranking system consisted of four categories ranging from category I (no evidence of upgradient mining activity) to category IV (direct discharges from mine sites). If a site appeared unaffected, but not unequivocally, the site was ranked category II. Conversely, sites that were not directly affected, but had upgradient mining activity that likely affected the water quality, were ranked as category III. An example of a category I site is a headwater stream or spring upgradient from any man-made disturbances. An example of a category II site is a spring along a valley side that has several dry prospect pits upgradient from it. An example of a category III site would be a stream or spring with an upgradient adit and mine waste pile but no direct discharge or signs of direct discharge. A category IV site would have obvious direct effects from mining upgradient or upstream from the site. Categories I and II sites within porphyry mineralized portions of the study area were used as background sites (109 sites). Water samples from 75 draining mines were collected, and in this manuscript, selected constituents are compared to the background sites.

2.2. East Alpine Gulch

East Alpine Gulch, elevation 3000–3900 m, lies within the San Juan Mountains approximately 15 km east of the Animas River watershed (Fig. 1) and receives similar amounts of precipitation. It is a headwater catchment near Lake City, Colorado that drains the west side of a porphyry mineralized system. The headwaters of East Al-

pine Gulch host the Red Mountain alunite deposit, which is believed to be the upper level of a weakly mineralized, Cu and Mo porphyry system (Bove and Hon, 1990). Mineralization is associated with Tertiary-age, dacitic, and quartz monzonitic porphyry intrusions, but overall base-metal sulfide abundances are quite low (Bove and Hon, 1990). Hydrothermal alteration assemblages at the surface consist of a quartz–alunite core that grades outward to a kaolinite–sericite zone and then outward to a propylitic zone with smectite (Bove and Hon, 1990). Nineteen surface water samples were collected from springs and headwater streams within East Alpine Gulch. No mining activity has occurred within the study area except a few exploration holes drilled near the upper part of the gulch.

2.3. Mount Emmons

Mount Emmons is located 5 km NW of Crested Butte, Colorado. The range in elevation of the study area is 2750–3775 m, and the mean annual precipitation is 80 cm. The study area is comprised of a thick package of Cretaceous to Tertiary sedimentary rocks of marine, marginal marine, and fluviolacustrine origin (the Mesaverde and Wasatch Formations) that were intruded by two Mo-bearing porphyritic granite stocks about 16–18 Ma. Stockwork Mo mineralization is centered around the stocks (Mount Emmons and Redwell deposits), which are believed to be connected at depth. In Redwell basin, one stock is overlain by a rhyolitic breccia pipe that formed by release of magmatic gases and fluids from the magma that crystallized to form the stock (Sharp, 1978). Previous geological and geochemical studies of the Mount Emmons/Redwell basin area have suggested that the deposit is of the Climax type (Sharp, 1978), which is characterized by highly evolved granite intrusions enriched in trace elements, including Ba, Cs, F, Li, Mo, Nb, Sn, Ta, Ti, Th, U, W, Zr, and the light rare earth elements (Mutschler et al., 1981).

Outward from the stocks base- and precious-metal vein-type deposits, mined historically for Ag, Pb, and Zn, occur along

north-striking extensional faults (Berger et al., 2001). Hydrothermal alteration, also centered around the stocks, consists of a potassic core that grades outward into a phyllic zone (quartz–sericite), and then a propylitic zone (Thomas and Galey, 1982).

The hydrogeochemical studies have focused primarily on the Redwell basin, a glaciated cirque that receives snowmelt-derived drainage from natural springs and mine effluent. The basin is named for a natural, Fe-rich, acidic spring that is surrounded by a Fe-oxide apron. Carbon-14 age determinations of organic material in the Fe-oxide spring deposits document that this spring has been active for at least the past 2.8 ka (Fall, 1997).

This alpine region receives an average of 6 m of annual snowfall between November and April. Stream flow originates primarily as snow melt either directly as runoff or indirectly as ground-water flow. Thirty-seven springs and headwater streams were sampled and summary statistics are reported in Verplanck et al. (2004). For comparison, six samples from draining mines were collected.

2.4. Handcart Gulch

Handcart Gulch, an alpine watershed located along the continental divide in the southeastern portion of the Montezuma mining district of the central Colorado Rocky Mountain Front Range, contains an un-mined, porphyry-related molybdenite exploration target (Fig. 1). The study area within Handcart Gulch is located in the upper 2–3 km of the watershed, encompassing approximately 4.7 km² and ranging in elevation from 3300 to 3815 m. Precipitation in Handcart Gulch averages 35 cm/a. The bedrock geology consists of Precambrian gneisses, schists, amphibolites and granites that have been intruded by a series of Tertiary-age stocks and veins. The largest and most-well studied stock in the district is the Montezuma stock, which is dominantly porphyritic quartz monzonite in composition but ranges to granite aplite (Neuerburg et al., 1974). The surface geology of Handcart Gulch was mapped by Lovering (1935) and primarily consists of quartz–biotite–sillimanite schists and gneisses as well as hornblende gneisses. Small quartz monzonite porphyries crop out. Along the valley floor much of the stream bed lies in ferricrete, Fe-oxide cemented alluvial and colluvial deposits. Within the study area, intense hydrothermal alteration is associated with the porphyry intrusions. Most of the lithologies in the upper portion of the watershed have been overprinted by quartz–sericite–pyrite alteration. Less common are exposures of propylitically-altered lithologies.

Groundwater samples were collected from three deep exploration drillholes, at least 455 m below the surface, located on or near the continental divide, and 9 shallow wells (3–52 m) located along the Handcart Gulch trunk stream. Twenty-two surface inflows (tributaries, springs, and seeps) were sampled along the upper 2-km reach of the Handcart Gulch trunk stream. Locations and water chemistry for the ground- and surface-water samples are reported in Verplanck et al. (2007).

2.5. Red River, New Mexico

The Red River, New Mexico, study area lies along the southern edge of the Questa caldera, and is the southern extent of the Oligocene Latir volcanic field (Lipman and Reed, 1989; Meyer and Leonardson, 1990). The topography is steep, rising rapidly from the valley floor at an altitude of about 2270 m to ridge crests with altitudes exceeding 3200 m, and the average annual precipitation is 52 cm. The geology of the basin consists of Proterozoic crystalline basement, primarily gneisses and intermediate-composition plutonic rocks that have been intruded by and are overlain by intermediate to felsic volcanic units associated with the Latir volcanic field. Subsequent to formation of the Questa caldera at about 25.7 Ma, these units were intruded by high-silica, porphyritic gra-

nitic stocks at 24.1 to 24.6 Ma (Czamanski et al., 1990). These stocks are believed to be the sources of the hydrothermal fluids that formed the Questa Mo deposit and caused the extensive hydrothermal alteration both on the Questa mine site and observed elsewhere in other parts of the study area (Leonardson et al., 1983; Czamanski et al., 1990; Meyer, 1991). Hydrothermal activity associated with the Questa caldera is believed to have caused regional propylitization, which altered mafic mineral phases to chlorite, epidote and calcite. These propylitized rocks and other slightly younger lithologies were subsequently altered again, and more intensely, during the hydrothermal activity associated with the granitic stocks. Hydrothermally altered areas are characterized by pyrite mineralization and associated alteration mineral assemblages, including quartz–sericite–pyrite and pyrite–kaolinite (Meyer and Leonardson, 1990; Ludington et al., 2004). Surface weathering (supergene alteration) has, in part, transformed these mineral assemblages to Fe oxides, gypsum, and clay minerals (Meyer and Leonardson, 1990; Ludington et al., 2004). These areas, referred to as erosional “scar areas”, contain incompetent bedrock and sparse vegetation and consequently have high erosion rates. A more detailed discussion of the geology, alteration, and weathering processes is presented in Ludington et al. (2004), Plumlee et al. (2005). Water chemistry from 21 wells and 11 headwater streams and springs are reported in Naus et al. (2005), Nordstrom et al. (2005), Verplanck et al. (2006).

3. Methods

3.1. Sampling procedures

On-site measurements of pH, specific conductance, and temperature were obtained. At each site, the pH electrode was calibrated using two buffers that bracketed the measured pH and that had been thermally equilibrated with the water sample. Water-chemistry samples consisted of (1) an unfiltered, acidified sample preserved with HNO₃ for total recoverable cations, (2) a filtered, unacidified sample for anion determinations and alkalinity, (3) a filtered, acidified sample preserved with HNO₃ for dissolved cation determinations, and at selected sites, and (4) a filtered sample, acidified with HCl, for Fe redox determinations. Filtration, primarily using 0.45 μm pore size syringe or canister filters, and acidification was done at the sampling sites. Anion subsamples were collected in acid washed, polyethylene bottles that had been soaked overnight in distilled water. Cation and Fe redox subsamples were collected in acid washed, polyethylene bottles that had been rinsed 3 times with distilled water. Constituent concentrations measured in filtered subsamples are called “dissolved”, and constituent concentrations in unfiltered subsamples are called “total recoverable”.

3.2. Analytical procedures

Major cations (Ca, Mg, K, and Na) and SiO₂ for both total recoverable and dissolved samples were determined by inductively-coupled plasma atomic-emission spectroscopy (ICP-AES) (Briggs, 2002). Minor and trace elements for total recoverable and dissolved samples were analyzed with an inductively-coupled plasma mass spectrometer (ICP-MS) using a method developed by the USGS (Meier et al., 1994; Lamothe et al., 2002). Concentrations of major anions (Cl⁻, F⁻, NO₃⁻, and SO₄²⁻) were determined by ion chromatography (Brinton et al., 1995). Alkalinity (as HCO₃⁻) was determined using an autotitrator and standardized H₂SO₄ (Barringer and Johnsson, 1989). Samples were diluted as necessary to bring the analyte concentration within the optimal range of the method. Fe(II) redox species and total Fe, in filtered, HCl-acidified samples, were determined using a modification of the FerroZine™ colorimetric method (Stookey, 1970; To et al., 1999).

4. Results

4.1. Sulfate and pH variations

Ground and surface waters from the five study areas that are unaffected by mining range in pH from 2.6 to 8.0 and in SO_4 concentration from 1.0 to 3700 mg/L (Fig. 2). The lowest pH and highest SO_4 waters drain the most intensely hydrothermally altered areas examined in this study, the scar areas within the Red River study area. However, ground waters tend to be less acidic than surface waters in the Red River study area. Samples from the Mount Emmons study area have relatively low SO_4 concentrations, ranging from 3.8 to 130 mg/L with a median value of 21 mg/L, even though the pH ranges from 2.93 to 8.03. Sulfate and pH are negatively correlated in ground and surface waters from Handcart Gulch but poorly correlated in waters from the Upper Animas and Red River study areas.

4.2. Copper and zinc variation

Similar to SO_4 concentrations, dissolved Cu and Zn concentrations are quite variable, and, with the exception of one Animas and one Handcart Gulch site, the Red River study area waters have the highest concentrations (Figs. 3 and 4). Handcart Gulch samples also have elevated Cu concentrations but not Zn concentrations. In contrast, Mount Emmons samples tend to be enriched in Zn but not Cu. The Cu and Zn concentrations in the Upper Animas study area samples are quite variable with a few samples having elevated Zn concentrations. The East Alpine Gulch samples have relatively low concentrations of both Zn and Cu, especially Cu which was below the analytical detection limit in all the samples.

4.3. Storm run-off results

Pathways for acidic, metal-rich water to be transported to lower parts of watersheds include surface- and ground-water flow and storm-induced runoff. In the Red River study area, the downstream effects of a late-summer rain event that produced surface runoff from the hydrothermally-altered scar areas were investigated. These areas, located in the lower portion of the watershed (Fig. 5), are characterized by incompetent bedrock and sparse vegetation such that they are quite susceptible to storm events. The

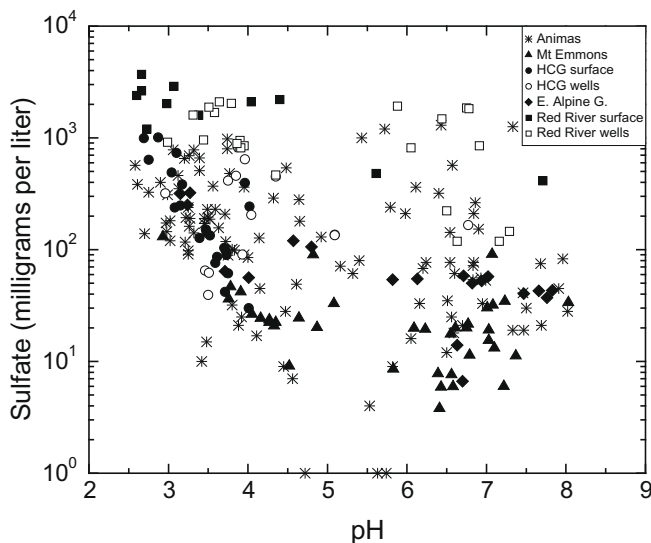


Fig. 2. Variation in pH and dissolved SO_4 concentration of ground and surface waters from 5 porphyry mineralized areas. HCG – Handcart Gulch.

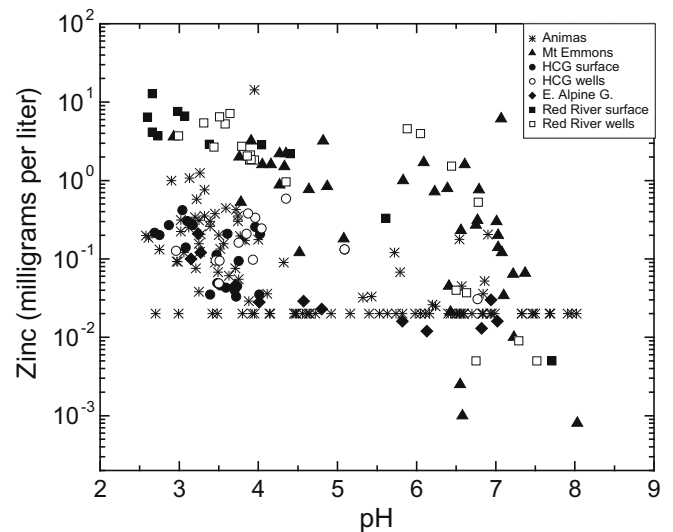


Fig. 3. Variation in pH and dissolved Zn concentration of ground and surface waters from 5 porphyry mineralized areas. HCG – Handcart Gulch. Detection limit for Animas samples was 0.02 mg/L consequently some Animas samples form a line at 0.02 mg/L.

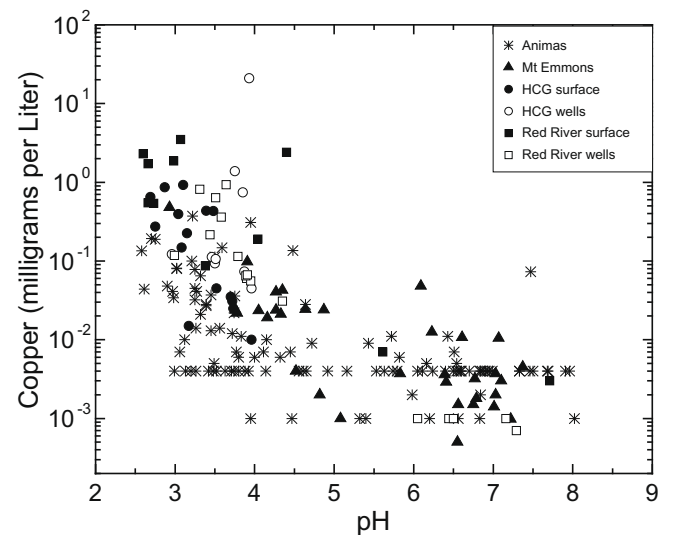


Fig. 4. Variation in pH and dissolved Cu concentration of ground and surface waters from 5 porphyry mineralized areas. HCG – Handcart Gulch. East Alpine Gulch samples not shown because all were below the detection limit of 0.01 mg/L. During the study, the detection limit for Animas samples changed from 0.004 to 0.001 mg/L consequently some Animas samples form lines at 0.004 and 0.001 mg/L.

upper portions of the watershed are primarily underlain by Proterozoic metamorphic and sedimentary units, including limestones, and propylitically-altered Tertiary andesites (Lipman and Reed, 1989). Thus the Red River water upstream of the scar areas is circumneutral, Ca-HCO_3 composition, and relatively low in trace metals (Verplanck et al., 2006). During most of the year, the acidic, metal-rich, surface water flows from the scar areas but enters the alluvium and goes underground prior to reaching the Red River. Downstream from the scar areas and the Questa Mo mine, the Red River remains circumneutral but SO_4^{2-} and HCO_3^- are the dominant anions.

Rivers draining the southern Rocky Mountains typically have their peak flows during spring snowmelt, and flow derived from summer or fall rainstorm events are episodic and not usually as

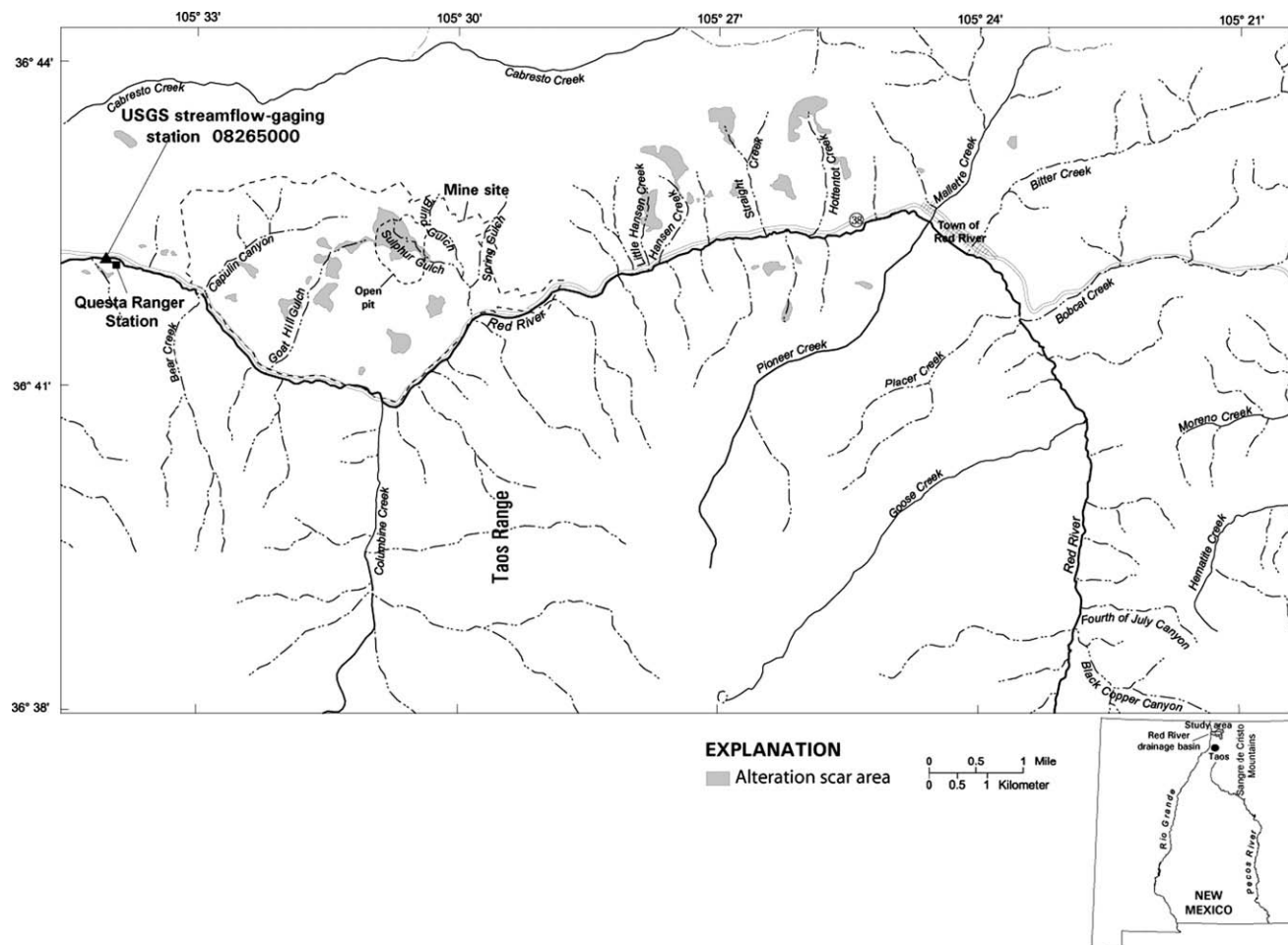


Fig. 5. Simplified Red River watershed map. Overall flow direction for the Red River is from right to left in this figure.

great (Ingersoll, 2000). During September 2002, a storm event which produced the peak discharge for the year was investigated. The year 2002 was one of the driest on record, and Red River discharge reflected the low seasonal snow pack with only a minor increase in discharge during the spring snow-melt period. During the storm-runoff study, three water samples were collected at the Questa Ranger Station gage (Fig. 5): the first sample on September 17, 6 h before the rainstorm began, the second sample on September 18 shortly after the peak discharge and about 14 h after the rainstorm began, and the third sample on September 19, during the falling limb of the hydrograph (Fig. 6A). Instantaneous discharge at the USGS Questa Ranger Station gage increased from 0.23 to 2.9 m³/s (8 to 102 ft³/s; Fig. 6A), and the river water changed from clear to quite turbid. From the first to the second sample, pH decreased from 7.80 to 4.83, alkalinity decreased from 49.4 to <1 mg/L, SO₄ increased from 162 to 314 mg/L, dissolved Fe increased from 0.011 to 0.596 mg/L, dissolved Al increased from 0.189 to 2.88 mg/L, and dissolved Zn increased from 56 to 607 µg/L (Fig. 6B). The second sample contained predominantly particulate Fe (99%) and Al (85%), but the fraction of particulate Fe and Al decreased in the third sample (58% and 13%, respectively).

During the storm, acid runoff from the scars flowed over the debris fans at the base of the scar areas and entered the Red River, causing it to become acidic and change from clear to highly turbid (Fig. 7). A sample of scar runoff was collected on September 18. The water was acidic (pH of 3.01) and high in dissolved constituents (SO₄ = 1530, Fe = 48.8, Al = 54.4, and Zn = 3.76 mg/L).

To investigate the source of the turbidity, the material trapped on the filter membranes from the Red River samples and the scar sample was collected, dried, and analyzed by X-ray diffraction. The material trapped on the filter from the Questa Ranger Station gage sample collected on September 17 prior to the storm was pale yellow, relatively small in volume, and consisted of amorphous material, quartz, kaolinite and mica. The trapped material from the two Questa Ranger Station gage samples collected on September 18 and 19 during the storm was pale yellow and consisted of smectite, mica, kaolinite, quartz, chlorite, amorphous material and jarosite. The material trapped on the scar area runoff sample filter was pale yellow and consisted of smectite, mica, kaolinite, quartz, chlorite, amorphous material and jarosite, similar to the particulate material at the Questa Ranger Station gage collected during the storm. This mineralogy documents that much of the turbidity in the lower Red River during the storm event is derived from runoff from the scar areas. Furthermore, the mineralogy of the material trapped on the scar area runoff sample filter is generally similar to the surficial material within the Straight Creek scar (Plumlee et al., 2005).

5. Discussion

5.1. Water–rock interactions

In porphyry mineralized areas, bedrock is overprinted by hydrothermal alteration, which varies in intensity depending on proximity to the intrusion and location of hydrothermal fluid flow paths.

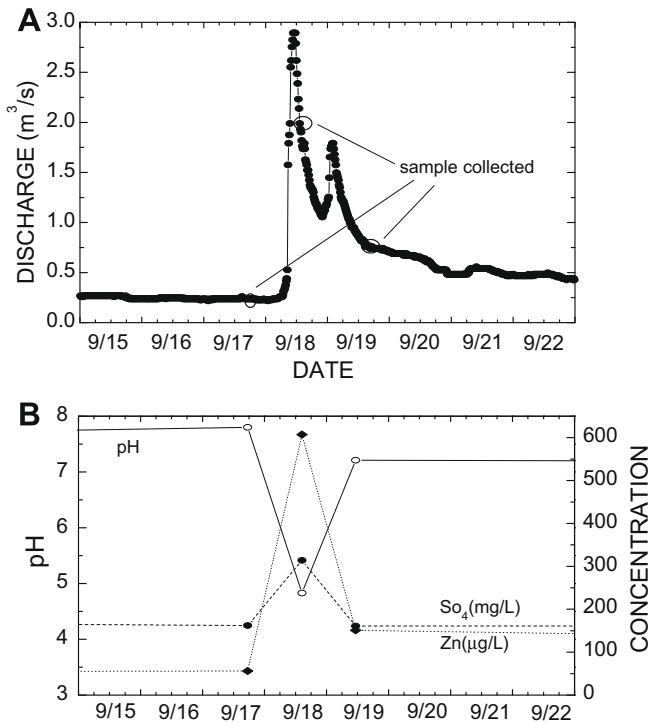


Fig. 6. (A) Instantaneous discharge of the Red River measured at the USGS streamflow-gaging station at the Questa Ranger Station from September 15–22, 2002. (B) Variation of pH and dissolved SO_4 and Zn concentrations during the Red River storm study.

To evaluate the significance of the intensity of hydrothermal alteration on water chemistry in porphyry mineralized areas, water sampling sites in the Upper Animas River study area were categorized by the dominant alteration type up-gradient of the site. Four alteration assemblages were utilized: propylitic, propylitic with veins, weak sericitic, and quartz–sericite–pyrite (QSP). If more than one alteration assemblage comprised a substantial amount of up-gradient area, the site was classified as 'mixed'. Because of presence of veins within some of the propylitically altered areas, this

alteration assemblage was divided into two groups. Veins consist of quartz and may contain sulfides including pyrite, chalcopyrite, sphalerite, galena, and tetrahedrite or tennantite (Burbank and Luedke, 1969).

Headwater streams and springs draining propylitically altered rock generally had higher median values of pH and alkalinity and lower median values of SO_4 , Fe, and Zn than water draining other alteration assemblages (Fig. 8). Propylitically altered rock contains calcite, as well as chlorite and epidote, which weather to produce circumneutral water. Zinc and SO_4 concentrations in waters draining propylitically altered areas that contain veins (PROPV) are commonly higher than waters from propylitically altered areas without veins.

In contrast to propylitically altered rock, QSP altered rock in the Upper Animas study area produces water that is acidic and metal-rich (Fig. 8), reflecting an abundance of pyrite and a lack of acid-neutralizing minerals (Mast et al., 2007). Similarly, within the Red River study area the most acidic waters emanate as surface waters from QSP altered rocks within the scar areas. Quartz–sericite–pyrite altered rocks within the Red River study area also contain vein-related calcite in quantities high enough to prevent shallow ground water from becoming quite as acidic as the surface waters (Plumlee et al., 2005). In the Upper Animas study area, QSP altered bedrock tends to be located within or adjacent to base-metal mineralized areas such that water draining from QSP altered areas has relatively high concentrations of base metals (for example Zn; Fig. 8E). Weak sericitic (WS) altered bedrock tends to produce water with intermediate compositions between that derived from propylitic or quartz–sericite–pyrite altered bedrock (Fig. 8).

5.2. Sulfate and pH variations

In porphyry mineralized areas the primary source of acidity is the weathering of disseminated pyrite. Oxidation of pyrite not only produces acidity but also S. If this process is the only source of dissolved SO_4 , then pH and SO_4 should be negatively correlated in the waters that drain these areas, as in the case of the Handcart Gulch waters (Fig. 2). Sulfate and pH are poorly correlated in waters from the Red River and Upper Animas study areas, which suggests that there is another source of SO_4 . To evaluate if dissolution of gypsum, a mineral phase known to occur in the Red River and Upper Animas



Fig. 7. Photographs of the Red River from the USGS streamflow-gaging station at the Questa Ranger Station looking upstream in August 2002 (left side) and September 18, 2002 (right side).

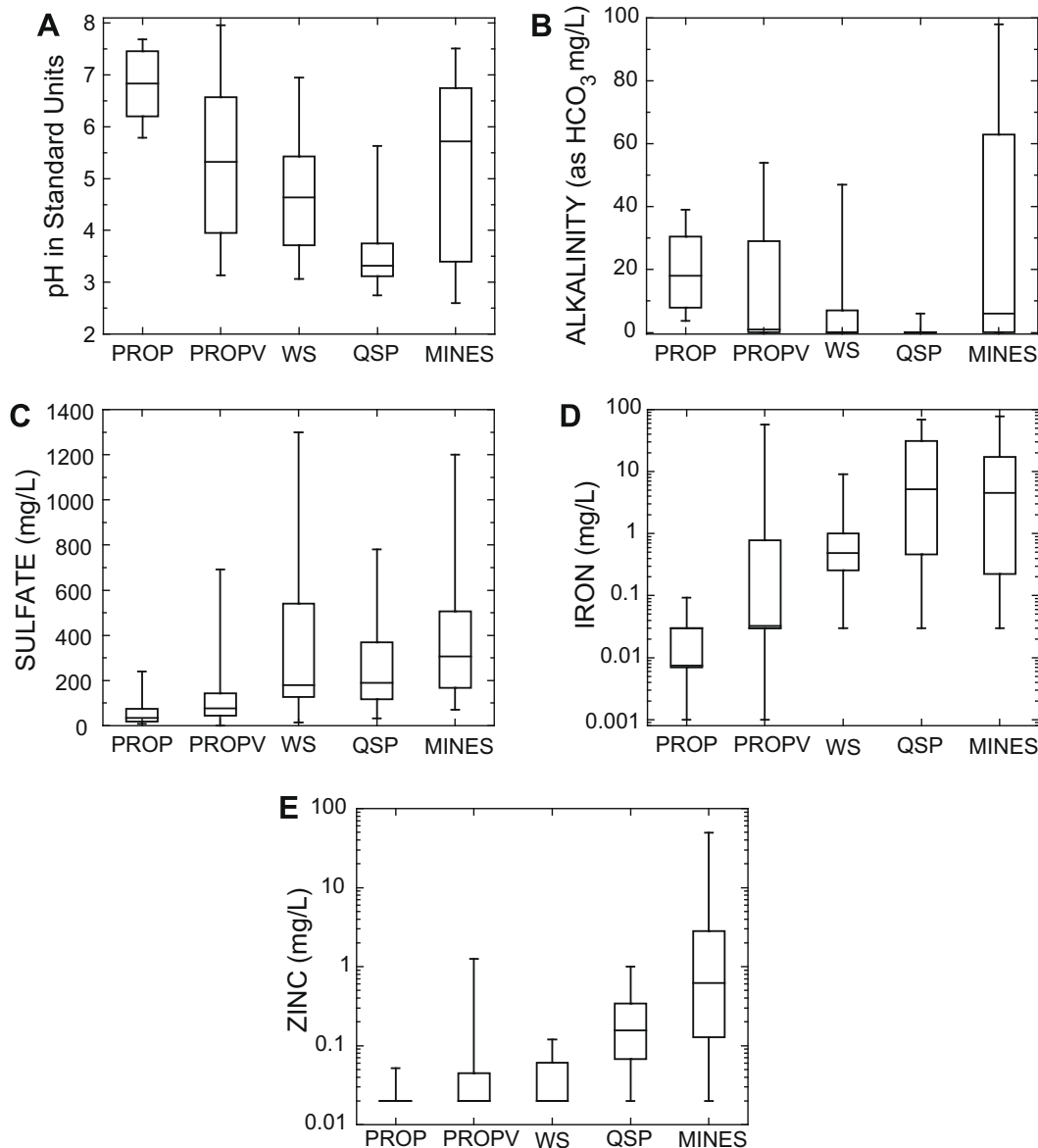


Fig. 8. Box plots displaying pH, alkalinity and dissolved SO₄, Fe and Zn concentrations in surface waters draining different alteration assemblages and mined areas in porphyry mineralized localities in the Upper Animas River watershed study area. PROP – propylitic ($n = 23$); PROPV – propylitic with veins ($n = 12$); WS – weak sericitic ($n = 17$), and QSP–quartz–sericite–pyrite ($n = 30$); and MINE – mine drainage ($n = 75$). Box plot displays median concentration (line), 25th and 75th percentile (box), and 5th and 95th percentile (whisker).

River study areas, is the additional source of SO₄, the molar concentration of Ca and SO₄ were graphed (Fig. 9A and B). The Ca:SO₄ 1:1 line in Fig. 9 represents the stoichiometric dissolution of gypsum. The field above the line requires addition of Ca from a mineral phase with little or no SO₄ such as calcite, calcic plagioclase, hornblende or epidote, and the field below the line requires an additional SO₄ source without Ca such as pyrite or other sulfide minerals. Many of the samples from the Red River and Upper Animas study areas plot on or near the gypsum dissolution line suggesting that this is the additional source of SO₄. Primary anhydrite is common in altered rocks at Questa, and secondary gypsum formed by evaporation of acid waters is common in the weathered Red River scar area rocks (Ludington et al., 2004; Plumlee et al., 2005). A recent stable isotopic study (³⁴S and ¹⁸O) of dissolved SO₄ in the Upper Animas River watershed, demonstrated that dissolution of pyrite and gypsum contribute to the SO₄ loading (Nordstrom et al., 2007). In contrast, most of the Handcart Gulch

study area samples plot well below the line (Fig. 9C), consistent with pyrite being the dominant source of SO₄ in this area.

5.3. Copper and zinc sources

In acid waters, the geochemical behavior of Zn is quite different than that of Cu. Zinc tends to remain in solution up to a pH of approximately 7.5, and Cu tends to partition from the aqueous phase to the solid phase in waters with a pH above approximately 4 (Dzombak and Morel, 1990; Smith and Huyck, 1999). This behavior is displayed in this comprehensive data set. Zinc concentrations do not covary with pH (Fig. 3), but Cu concentrations decrease markedly as pH increases above 4 (Fig. 4).

The relative enrichments in Cu and Zn in these waters appear to be primarily related to mineralogy of sulfides present. At the Red River study area detailed examination of rock faces and drill cores document the presence of sphalerite and chalcopyrite either as dis-

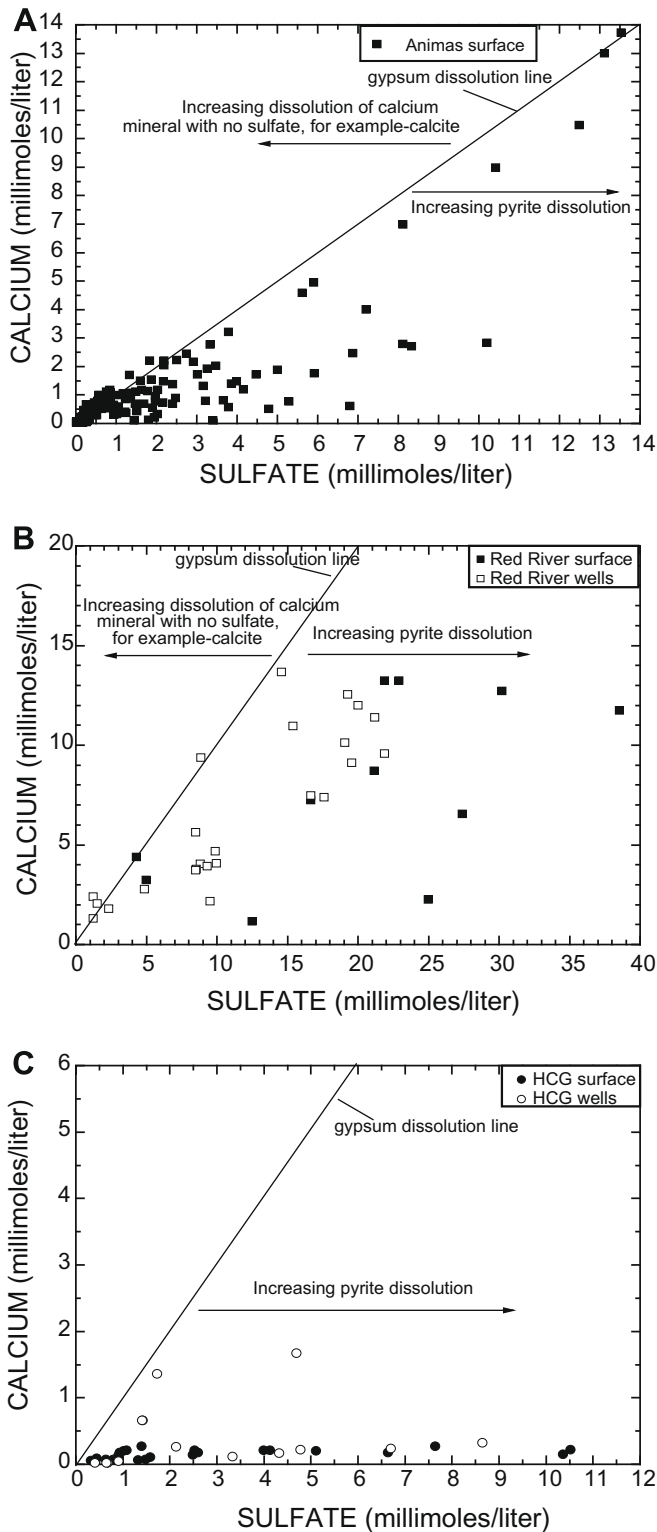


Fig. 9. Molar variation of dissolved Ca and SO_4 concentrations of natural waters from porphyry mineralized areas in the Upper Animas River study area (A), Red River study area (B), and Handcart Gulch study area (C).

crete blebs within pyrite or as fine crystals or blebs within altered rocks or veinlets (Plumlee et al., 2005). These observations are consistent with elevated Cu and Zn in waters from this study area. Drill cores from the Handcart Gulch contain minor amounts of Cu sulfides in the form of chalcopyrite in quartz veinlets and as secondary sulfides including chalcocite, covellite, and bornite, but only

rare observations of sphalerite. Again, this is consistent with the relatively high concentration of Cu in the Handcart waters. Base-metal veins at the peripheries of the Mount Emmons porphyries were mined for Pb, Zn, and Ag but not Cu. Many of the non mining-impacted waters from the Mount Emmons area reflect this elevated background concentration of Zn. The Lake City porphyry system (East Alpine Gulch area) lacks base-metal sulfides (Bove and Hon, 1990), which is reflected in the waters with relatively low concentrations of both Cu and Zn (Table 1). The wide-range in Cu and Zn concentrations in water samples from the Upper Animas study area is not surprising because of the occurrence of both Cu and Zn mineralization and the large sample population.

5.4. Comparison with mine drainage

Within the Upper Animas and Mount Emmons study areas, water draining from abandoned mines also contributes to the metal loading of the watersheds. Mine drainage was collected from 75 sites in the Upper Animas River watershed and six sites in the Mount Emmons study area. The size of abandoned mines in these study areas is quite variable. Some draining adits likely only have minor underground workings, because the volume of waste rock produced is on the order of tens to hundreds of cubic meters, and other mines have relatively large waste-rock piles and well-documented records of ore production. Thus, some mining operations intersected extensive sulfide-rich zones and others likely did not.

Comparing naturally acidic and mine drainage sites in the Upper Animas, overall the mine drainage sites produce waters with similar variations in pH, SO_4 , and Fe concentrations (Fig. 8A, C, and D) but display significant differences at the extremes (Table 1). The highest SO_4 concentration for the naturally acidic waters is 1300 mg/L; in contrast, the highest concentration for the mine drainage is 2720 mg/L. Similarly, the highest dissolved Fe concentration for the naturally acidic waters is 117 mg/L; and the highest concentration for the mine drainage is 685 mg/L. Only three natural sites had dissolved Fe concentrations >60 mg/L but 10 mine drainage samples were >60 mg/L. The lowest pH value of the naturally acidic waters is 2.58, and the lowest pH value for mine drainage is 2.35.

For the Upper Animas data set, dissolved Zn concentrations are greater for mine waters than for naturally acidic waters (Fig. 8). The median and maximum dissolved Zn values for the mine sites are 0.62 and 228 mg/L, respectively, and for the natural sites are 0.026 and 14.4 mg/L, respectively (Table 1). Fig. 10 displays the variation in dissolved Zn and Cu for all the sites in the Upper Animas and the Mount Emmons study areas. In both study areas the maximum dissolved concentration of these metals in the mine waters is substantially greater than the maximum concentration in the naturally acidic waters. Detailed work along Cement Creek, a major drainage in the Upper Animas River watershed, determined that water draining mined areas had higher Cu and Zn concentrations than unmined areas (Kimball et al., 2002). Plumlee (1999) compiled dissolved metal concentration data from mined and unmined mineralized areas in the western USA and observed a similar trend with mine waters tending to have greater concentrations of metals than waters draining naturally acidic areas.

Many of the mine waters overlap in composition with the naturally acidic waters which is not surprising because some of the mine sites were simply small adits that never produced ore and were not enriched in base-metals. Ore-producing mines make up the subset of samples with substantially greater concentrations of Cu and Zn consistent with the known occurrence of Cu and Zn sulfides. The mine-water samples with lower pH and greater Fe concentrations than the naturally acidic waters are also from larger, ore-producing mines. The more extreme chemistry of these

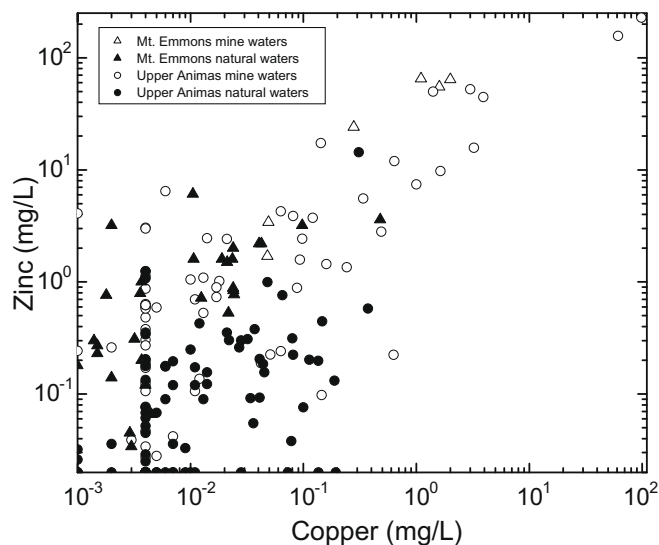


Fig. 10. Comparison of dissolved Zn and Cu concentration of surface waters from mines and natural springs and headwater streams in porphyry mineralized areas in the Upper Animas River and Mount Emmons study area.

waters likely is caused by increased pyrite oxidation in the mining environment due to a greater mass of pyrite available to oxidize and/or greater rates of pyrite oxidation in the mining environment.

5.5. Estimation of premining water chemistry

Documenting the range in compositions of waters draining naturally acidic, porphyry mineralized areas and determining the processes that control the chemical variations have important implications for stream ecologists and land managers. One challenge for mine-site reclamation is determining the environmental conditions of the site prior to mining because for many sites, no systematic water-quality data were collected prior to the onset of mining. In or adjacent to each of the five study areas described here, active or historical hard-rock mining has occurred. Mineralized, but un-mined, areas located in the vicinity of mined areas can be used as natural analogues for estimating premining conditions if they have similar characteristic such as geology, hydrology, and climate (Alpers and Nordstrom, 2000).

In 2001 the USGS was asked by the New Mexico Environment Department to estimate pre-mining ground-water quality at the Molycorp Inc.'s Questa Mo mine in the Red River Valley near Questa, New Mexico. The State of New Mexico requires that ground-water quality standards be met on closure by active mines unless it can be shown that potential contaminant concentrations were higher than the standards before mining. No ground water at the mine site had been chemically analyzed before mining, and to the authors' knowledge no third party had attempted a study to infer premining ground-water quality at any active mine site. The key to the determination of pre-mining ground-water quality at the Questa mine site was to study the geological, hydrological, and geochemical processes at a proximal analog site that had not been disturbed by mining. An overview of this work is presented here, and a series of reports on specific studies as well as the final report (Nordstrom, 2007) provide a more detailed description of the study.

To compliment the detailed study at the proximal analog site, a broader scale study was undertaken to document that the proximal analogue site was an adequate representation of the premining condition as well as to better understand the watershed scale ground water system. The primary tasks of this study were two synoptic surveys of the Red River (the discharge terminus for

ground waters) (Kimball et al., 2006), reactive-transport modeling of the river (Ball et al., 2005), a water budget for the valley (Naus et al., 2006), environmental geology and mineralogy of the mine site and erosional scar areas (Ludington et al., 2004; Plumlee et al., 2005), AVIRIS mapping of the valley (Livo and Clark, 2002), structural geology of the valley pertaining to ground-water flow (Caine, 2006), leaching studies of both natural and waste rock material (Smith et al., 2006), compilations of historical records of surface- and ground-water chemistry (LoVetere et al., 2004; Maest et al., 2004) and a geomorphological analysis of the valley (Vincent, 2006). The project was both detailed and broad in scope because of the complexities of the geology and water chemistry and because the potential for legal contention was high and necessitated a thorough scientific approach.

The proximal analog site, the Straight Creek drainage (Fig. 5), was subject to several detailed studies aimed at determining the range in ground-water chemistry and elucidating ground-water processes that control the chemistry and flow. Studies included electrical surveys (Lucius et al., 2001); high-resolution seismic surveys (Powers and Burton, 2006); ground-water dating with $^3\text{H}/\text{He}$ (Naus et al., 2005); water budget (McAda and Naus, 2006); ground-water hydrology and geochemistry (Naus et al., 2005); and comparisons of mineralogy and lithology to that of the mine site (Plumlee et al., 2005). Straight Creek lies only 4 km to the east of the mine site boundary, has similar climatic conditions with nearly the same elevation, slope, aspect, topography, rock types and alteration zones, and has similar geomorphological features.

Eleven wells were installed and monitored, surface-water drainage was monitored, and two existing wells were monitored in the Straight Creek catchment. The contact between the Straight Creek debris fan and bedrock was outlined with high-resolution seismic profiles that were modeled tomographically (Powers and Burton, 2006). The bottom of the debris fan lies on a highly irregular surface, and ground water in the debris fan is acidic with pH values of 3–4, and carries high concentrations of dissolved SO_4 and metals. In the underlying bedrock, the ground water has neutral pH, and most trace element concentrations are low, except for Fe and Mn together with SO_4 (Naus et al., 2005).

The Straight Creek debris fan is fed primarily by Straight Creek surface water of low pH (2.5–3) derived from the weathering of QSP-altered bedrock with a high pyrite content (up to 10%) (Plumlee et al., 2005; Verplanck et al., 2006). This surface water contains only oxidized Fe, but after it infiltrates the fan, it becomes reduced with the removal of some Cu and the addition of SiO_2 and Na. This ground water is diluted to a half of its original concentration from canyon seepage adjacent to the debris fan and from mixing with Red River alluvial ground water at the toe of the debris fan. Dilution of acid debris fan ground waters by circumneutral Red River alluvial ground water results in the removal of some Al and SiO_2 from the most diluted waters (at a pH near 4). Also, most dissolved constituents in these debris fan ground waters are diluted proportionally with SO_4 , as shown by significant linear correlations with SO_4 (Naus et al., 2005). Exceptions include Ba, which is limited by barite solubility and Sr, which appears to be derived from carbonate mineral dissolution. These same linear correlations hold for most elements in other catchments containing naturally acidic ground water.

These trends provided a constraint on mineral weathering under acidic conditions. Mineral solubility controls are effective in limiting the concentrations of many constituents, and these controls are manifested in two ways, by the common-ion effect and with plots of saturation indices. Because the alluvial ground water in the debris fan is acidic and the bedrock ground water below the debris fan is circumneutral, the importance of solubility limits can differ depending on the type of ground water. Solubility limits for calcite, siderite, rhodochrosite and fluorite are reached at circum-

neutral pH values. Solubility limits for hydrous ferric-oxide phase (HFO) are reached at pH values of 2.5 and higher. Solubility limits for Al are reached at pH values of 4 and higher for ground water and 5 or higher for surface water. Gypsum and barite solubilities are independent of pH. Ferric iron is limited by the solubility of an HFO. In the circumneutral bedrock ground water, Fe(II) is limited by the solubility of siderite and Mn is limited by the solubility of rhodochrosite. Aluminum and SiO₂ are limited by the solubility of amorphous Al(OH)₃, a hydrous aluminosilicate colloid or clay, and amorphous SiO₂, depending on pH and concentration. Calcium is limited by the solubility of gypsum or calcite depending on pH. Magnesium concentrations approach dolomite solubility saturation for a few waters. Fluoride is limited by the solubility of fluorite. Barium is limited by the solubility of barite.

The metal–SO₄ correlation trends for acidic ground waters at Straight Creek generally agreed well with data from ground waters in other catchments unaffected by mining activities and provided a framework to delineate ranges of various element concentrations for each catchment on the mine site where no solubility control exists. The geochemical constraints that define solute concentrations were applied separately to bedrock and alluvial aquifers and, in one case, had to be applied to different parts of the catchment because of hydrothermal alteration and mineralization that changes substantially with location within the catchment. Exceptions to the correlation trends were noted for Be, F⁻, and Mn because examples were found where the pH is too low (about 6.0) for any solubility control.

The results demonstrate that natural conditions in the Red River Valley can exceed the State of New Mexico's ground-water quality standards. Magnesium, Fe, F⁻, and SO₄²⁻ commonly exceeded standards by a factor of 10 or more. Manganese can exceed the standards by as much as 250 times. The high Mn concentrations are caused by the common occurrence and high solubility limits for rhodochrosite and manganiferous calcite in acidic water. The high natural concentrations of other constituents are caused by the particular geological and hydrological conditions that exist in the Red River Valley. Extensive hydrothermal alteration has enriched the rocks in pyrite, sphalerite, chalcocopyrite, calcite, rhodochrosite, fluorite and illite; in addition to the Fe, Zn, Cu, S, and Mn that are major components of these minerals, the alteration and mineralization has also led to enriched concentrations of Co, Ni, Cd, Be, and Cr in these rocks. Cobalt and Ni are primarily found in pyrite, Cd in sphalerite, Be in illite and Cr in chlorite (Plumlee et al., 2005).

A carefully planned study that includes all the relevant aspects of geology, hydrology and geochemistry, and focuses on the processes that produce the observed ground-water chemistry can elucidate the most important controls on ground-water chemistry. This knowledge can then be applied to a very similar terrain where ground-water chemistry was not monitored before large-scale mining began. Through such efforts, "background" concentrations can be inferred to provide valuable information for establishing regulatory goals.

6. Conclusions

Five watersheds which produce naturally acidic drainage from porphyry mineralized systems were investigated to determine the range in ground- and surface-water chemistry and understand the processes that control the chemistry variations. Comparing results from watersheds with different characteristics provides constraints on the key variables that control water quality in mineralized but unmined rocks.

Porphyry mineralized areas are characterized by the presence of intrusions that are porphyritic in texture and genetically associated with the mineralizing event and by an outward decrease in hydrothermal alteration intensity. Extensive work in the Upper

Animas River study area documents that intensity of hydrothermal alteration plays a major role in the water chemistry. Although pyrite is ubiquitous, streams and springs draining propylitically altered rock on the distal portions of the mineralized areas had higher pH and alkalinity and lower concentrations of SO₄ and metals than water draining other alteration assemblages (Fig. 8A and B). This is consistent with the presence of calcite, chlorite and epidote in the propylitic zone, which neutralize acid produced by pyrite oxidation. In contrast, quartz–sericite–pyrite altered rocks produced the most acidic waters, pH as low as 2.58.

The mineralogy of sulfides present is another fundamental control on water chemistry. For example, variable Cu and Zn concentrations, in part, result from the variability of sulfide minerals within and between the different study areas. Water samples from the Red River area are elevated in both Cu and Zn, consistent with the presence of Cu and Zn sulfides observed in both outcrop and drill core. In contrast, elevated Cu concentrations, but not high Zn concentrations, are found in waters from Handcart Gulch where Cu sulfides but not Zn sulfides are prevalent in drill core.

Other minerals also play important roles in controlling the chemistry of water draining these areas. For example, variable SO₄ concentrations in part result from oxidation of pyrite, which results in a negative correlation between pH and SO₄ in water, such as at Handcart Gulch (Fig. 8). In some areas (e.g., Red River and Upper Animas), elevated SO₄ concentrations result from both pyrite oxidation and from dissolution of primary anhydrite and secondary gypsum from the mineralized rocks, resulting in a poor correlation between SO₄ and pH (Fig. 9).

This comprehensive data set provides insight into premining baseline water chemistry in porphyry mineralized systems with similar geologic and climatological characteristics. Comparison of natural waters and mine drainage in the Upper Animas and Mount Emmons study areas shows that the mine waters overlap the range in pH, SO₄, Fe, Zn, and Cu, but have more extreme concentrations of these species than natural waters. The more extreme chemistry of mine waters may result from a number of factors including (1) ore deposits are mined because they tend to be richer in metals than surrounding areas; (2) pyrite oxidation is increased in the mining environment due to a greater mass of pyrite available to oxidize and/or greater rates of pyrite oxidation in the mining environment which tend to lead to higher concentrations of Fe and SO₄ and more acidity; and (3) with increasing acidity, more metals can be leached.

Detailed work at the Red River site provided regulators with estimates of premining ground-water quality at an active mine site. The results demonstrate that ground-water quality standards in the State of New Mexico locally are exceeded naturally in the Red River Valley. Standards are commonly exceeded by tenfold for Mg, Fe, F⁻, and SO₄²⁻. Manganese exceeds the standards by as much as 250 times.

An important, and generally less-well studied, aspect of the weathering of intensely-altered areas is the episodic flux of acidic, metal-rich water and suspended material during storm events. Results from the storm-event study at the Red River area documented that acidic, sediment-rich surface run-off from hydrothermally-altered subbasins can adversely affect water quality several kilometers downstream.

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