

WHAT'S WEATHERING? MINERALOGY AND FIELD LEACH STUDIES IN MINE WASTE, LEADVILLE AND MONTEZUMA MINING DISTRICTS, COLORADO¹

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Abstract. Weathering is important in the development of rock fabrics that control porosity in mine-waste materials, and in turn, porosity affects metal transport through and from mine-waste piles into watersheds. Mine-waste piles are dynamic physical and chemical systems as evidenced by remnant Fe-oxide boxwork structures after sulfide minerals, development of alteration rinds and etch pits on grains, and precipitation of secondary minerals under low temperature conditions. These microscale changes in the mine-waste materials are the result of partial to total dissolution of sulfide and other minerals.

Mine-waste materials from the Dinero, Lower Chatauqua, and Saints John sites, Leadville and Montezuma mining districts, Colorado, exhibit rock fabrics that indicate that weathering products, e.g., Fe oxyhydroxides, jarosite, and clays, have been transported in suspension through the waste piles and deposited in voids and as coatings on rock fragments. Microscale characterization of weathered, partially dissolved minerals lends insight into the source of leachable metals in these mine-waste sites. Mineralogic studies show that galena in the Lower Chatauqua waste is enriched in Ag. Qualitative and semiquantitative microanalysis of weathered, altered galena grains from all three sites show that the Ag-bearing galena is more susceptible to dissolution. It is not surprising, then, that solutions experimentally leached from Lower Chatauqua waste are higher in Pb (2310 ppb) compared to leachates from the Dinero (31 ppb) and Saints John (1360 ppb) wastes.

The mobility of metals is increased at acidic pH. Using the USGS Field Leach Test protocol, leachate derived from the Dinero waste has a pH of 3 and high concentrations of Al (443 ppb), Fe (441 ppb), and Zn (7970 ppb). Leachate from Sts. John tailings has a pH about 4 and high concentrations of Mn (1520 ppb), Zn (2240 ppb), and Pb (1360 ppb). Leachate from the Lower Chatauqua waste has an intermediate pH of 5, but in addition to the high Pb level already mentioned, it contains high levels of K (1.9 ppm), Mn (6720 ppb), and Zn (1550 ppb). The high concentration of metals, despite the intermediate pH of the leachate, may be explained by acidic microenvironments that exist at the surfaces of sulfide minerals, where sulfur- and iron-oxidizing microbes may flourish. It is at the reactive mineral-oxygen-water interface where metals are released and low-pH sulfate precipitates such as jarosite-beudantite form.

Additional Key Words: dissolution, jarosite, anglesite, microlamination, leachate

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Introduction

Gold and base-metal mining in the late 1800's and early 1900's in the Leadville and Montezuma districts of Colorado left extensive waste piles, containing lead, zinc, copper, and iron sulfides (Figs. 1, 2). Weathering of the sulfide minerals has generated acid mine drainage and released metals at toxic levels to surface waters and stream sediments (Upper Arkansas Watershed Council, 2001; Bureau of Land Management, Colorado, 2003). The mining districts are located in mountainous terrain at altitudes greater than 10,000 feet; therefore, mine-waste material is situated on steep slopes and (or) in drainages subject to rapid stream flow. Because of the steep topography, mining was conducted through adits (Ritter, 1908), many of which remain open and drain into local watersheds (Walton-Day et al., 2005). Because of acidity and (or) high metal content, drainage from the mine-waste piles, tailings, and open adits have a negative impact on downstream aquatic biota (Bureau of Land Management, Colorado, 2003).

Our objectives were to: (1) identify the mineralogic source of the metals in solution, whether from the weathering of primary sulfide minerals, or the dissolution of secondary mineral precipitates, or both, and (2) to relate the leachate results of the U.S. Geological Survey Field Leach Test to minerals that exhibited dissolution textures (Hageman and Briggs, 2000; Diehl et al., 2005). Dissolution textures in sulfide and other minerals are evidence for the transport of metals in solution from the mine-waste pile.

Geological Setting

The Leadville and Montezuma districts are located near timberline, at approximately 10,500 to 11,000 feet in altitude, in areas of Precambrian schist, gneiss, and granite (Lovering, 1935; Singewald, 1955) (Fig. 1). The schist and gneiss of the Rocky Mountain physiographic province may be correlated with the Early Proterozoic to Precambrian Swandyke Hornblende Gneiss and the Idaho Springs Formation of the Front Range of Colorado, and the granite may be correlated with the Middle Proterozoic to Precambrian Silver Plume granite (Singewald, 1955). Unaltered host rock is resistant to weathering and forms a steep topography (Fig. 2). During the Late Cretaceous Laramide Orogeny, the region was highly deformed by orthogonal fault sets and the emplacement of veins. The granite bodies were highly altered during ore mineralization; feldspars were partially to totally altered to fine-grained potassic sericitic clays. Rock fragments of manganese carbonate occur in veins with galena, pyrite, chalcopyrite, and Ag-sulfide minerals. Barite is a common accessory mineral.

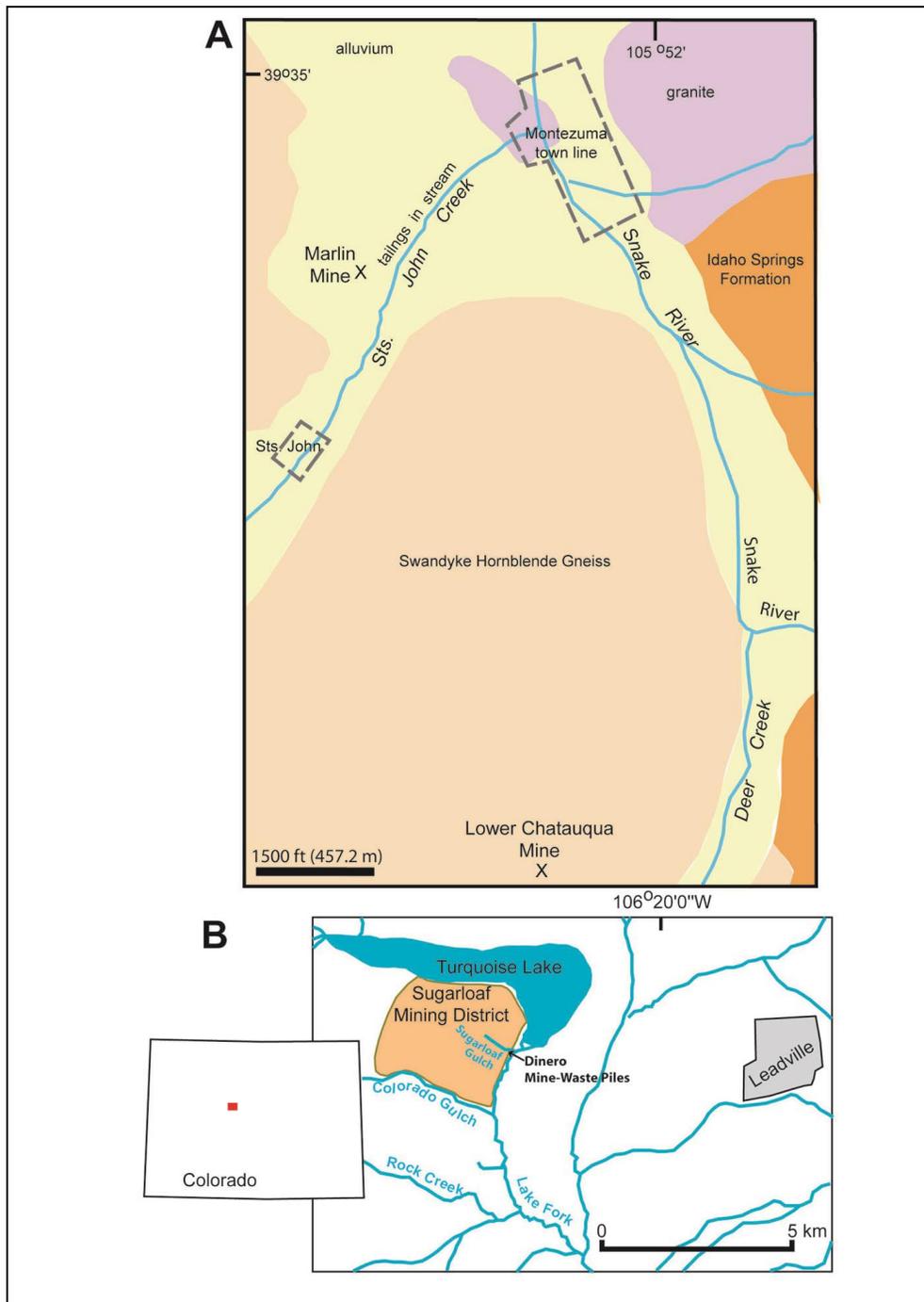


Figure 1. **A.** Location map and geology of the Sts. John tailings and Lower Chataqua mine-waste sites, Summit Co., Colorado.

B. Location map, Dinero mine-waste site, Lake Co., Colorado.

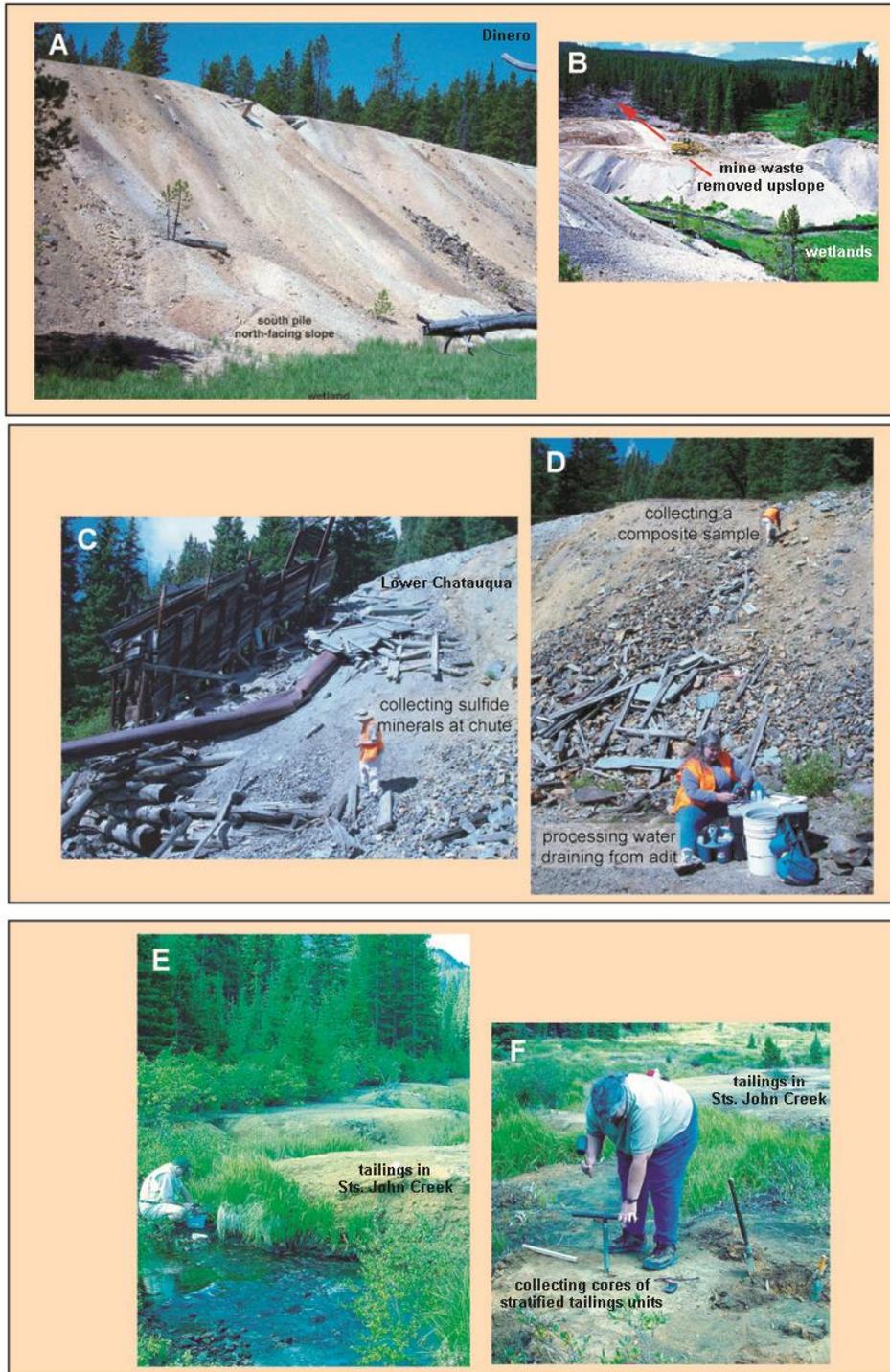


Figure 2. Sample sites. **A. B.** Dinero mine-waste piles, Leadville district, Colorado. Mine waste piles were removed upslope from the wetlands in 2003. **C. D.** Lower Chatauqua mine-waste pile, Montezuma district, Colorado. **E. F.** Tailings in Sts. John Creek, Montezuma district, Colorado.

Methods

The USGS Field Leach Test protocol was used to leach composite mine-waste samples from the Dinero and Lower Chatauqua mine-waste piles and the Sts. John mine tailings (Hageman and Briggs, 2000; Smith et al., 2000; Smith et al., 2002; U.S. Geological Survey, 2005). The Sts. John tailings sediments were collected from a wetland, downstream from a mill site in the historic town of Sts. John. Therefore, the tailings are composed of various types of ore from around the region that were processed at the Sts. John mill. Complete details of the non-grid sampling technique and the leaching procedure are fully described in Hageman and Briggs (2000). A representative sample was collected of all lithologies in the waste piles and tailings by compositing a minimum of 30 increments of surficial (upper 15 cm) mine-waste material in a random manner. Coarse material (approximately ≥ 3 cm) was discarded during collection. All increments were put into a 5-gallon plastic bucket and mixed to create a composite sample of the various lithologies. The mine-waste composite was then air dried and sieved to pass a 2 mm stainless steel screen. The < 2 -mm fraction was saved for leaching and microscopic analysis, and all material larger than 2 mm was discarded. To leach the sample, 50 g of < 10 mesh (< 2 mm) mine-waste composite sample was weighed into a 1-L plastic bottle. One liter of deionized water was added slowly so that no dust was lost. The bottle was capped and vigorously hand shaken for 5 minutes. The contents were then allowed to settle for ~ 10 minutes. After settling, sub-samples of the leachate were measured for pH and specific conductance (SpC). A portion of leachate was filtered using a 60 cc syringe and a $0.45 \mu\text{m}$ pore-size nitrocellulose syringe filter. The filtrate was preserved and analyzed in the lab for 44 elements, using inductively coupled plasma-mass spectrometry (ICP-MS) (Table 1; Briggs, 2002; Lamothe et al., 2002).

In addition to geochemical analysis, selected samples were examined in reflected light microscopy and with a Cambridge 250 Mark 2 scanning electron microscope (SEM), equipped with an energy-dispersive X-ray (EDX) detector to determine basic mineralogy, analyze structural and textural features, and for qualitative analysis of trace-element content and distribution in sulfide minerals. (Note: Mention of trade names or commercial products is for descriptive purposes only and does not imply endorsement by the U.S. Government.)

Filtered ($0.45 \mu\text{m}$), acidified samples of efflorescent salts from the Dinero waste site were analyzed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES). Efflorescent salt samples were also analyzed by X-ray diffraction (XRD). XRD patterns were collected on a Scintag X-1 theta-theta diffractometer.

Results and Discussion

Leachate Chemistry

The mobility of most metals is increased at low pH. Therefore, the high metal concentration of Al, Fe, and Zn from the Dinero site is predictable because leachate from a composite mine-waste sample recorded a pH of 3.3 (Table 1; Fig. 3). However, the high Pb, K, and Mn from the Lower Chatauqua site, where the leachate pH is 5, requires explanation (Table 1). Studies at the microscopic scale suggest the presence of acidic microenvironments on mineral surfaces and dissolution enhanced by microbial activity.

All mine-waste and tailings sampling sites contained galena and sphalerite. However, Zn is in greater concentration in the leachate from the Dinero site; Pb is in greater concentration in leachates from the Lower Chatauqua and Sts. John waste sites (Fig. 3).

Mn in leachate is elevated at all sites. Mn carbonate, a common gangue mineral in the ores of mining districts, is soluble at low pH.

Table 1. Results of the U.S. Geological survey Field Leach T (20:1 water/rock ratio); ppb = parts per billion; bdl = below detection limit.

Sample Locality	pH	Spc ($\mu\text{S/cm}$)	Al	As	Ba	Cd	Cu	Fe	K	Mn	Ni	Pb	Zn
Dinero	3.30	845	443	2	91	50	49	441	880	1250	8	31	7970
Lower Chatauqua	5.03	197	3	bdl	116	9	22	bdl	1900	6720	13	2310	1550
Sts. John	3.55	170	52	1	130	9	30	bdl	630	1520	3	1360	2240

Hydrologic Setting, Grain Size, Mineralogy of Mine-Waste Piles and Tailings

Dinero Mine-Waste. Mine waste from the Dinero mine was situated in highly porous, saturated sediments, composed of outwash gravels from eroded unconsolidated glacial moraine material and alluvium at the mouth of Sugarloaf Gulch that drained into the Lake Fork of the Arkansas River (Fig. 1). The north and south Dinero mine-waste piles were relocated upslope in 2003 and revegetated by grasses, wheat, and clover (Diehl et al., 2005).

Grain sizes of the waste material range from boulder-sized rock fragments down to very fine-grained matrix material. Characteristic rock fragments are composed of quartz, sericitized feldspars, muscovite, manganese carbonate, and sulfide and iron-oxide minerals. Rock fragments are enclosed in a fine-grained matrix of potassic clays, iron oxides, and other rock fragments of variable size. Because the particle size of the waste-rock material was highly heterogeneous, the mine waste was porous, and therefore, open to the infiltration of precipitation and oxygen. The mine-waste piles were a composite of different rock types with surficial weathering features that included brown iron-oxide streaks, grayish zones with sulfide material, black manganoan streaks, and white areas of soluble salts (e.g., gypsum, starkeyite) (Fig. 2A, 2B).

Lower Chatauqua Mine-Waste. The Lower Chatauqua mine-waste pile is itself unvegetated but is located on a steep slope covered by pine and spruce (Fig. 2C, 2D). The mine is located in the Swandyke Hornblende Gneiss. Run-off from the mine-waste drains into Deer Creek, thence to the Snake River (Fig. 1). The mine-waste pile is heterogeneous in grain size and composition; coarse-grained to boulder-size rock fragments that contain sulfide material is concentrated at the old ore chute and atop the mine-waste pile adjacent to the open adit. Coarse- to boulder-size rock fragments of biotite and hornblende gneiss are abundant. Rock fragments of pegmatite and breccia cemented by carbonate and quartz are common. Galena commonly occurs in quartz-

cemented rock fragments of breccia. Pyrite typically occurs in rock fragments of intrusive porphyry rock.

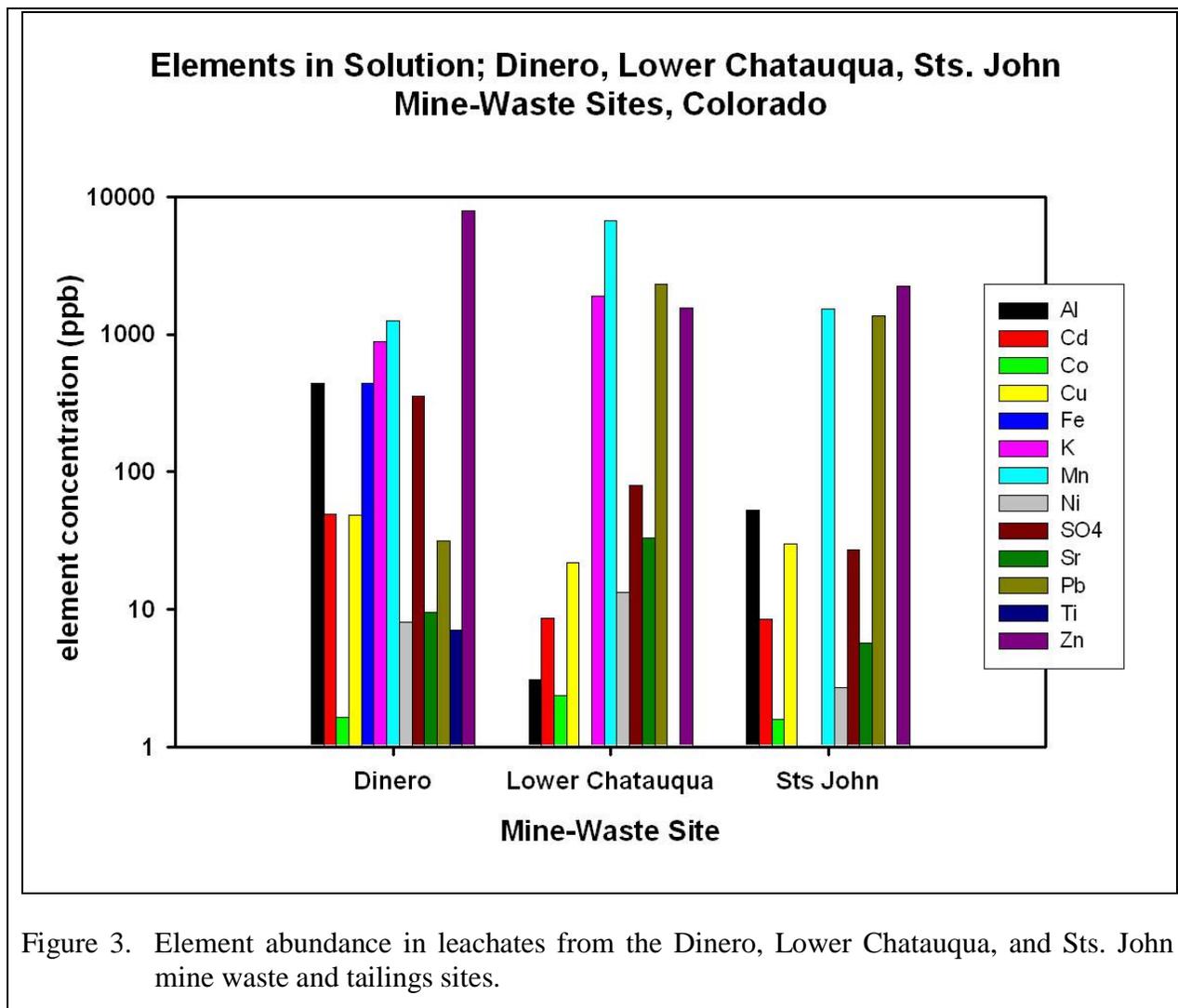


Figure 3. Element abundance in leachates from the Dinero, Lower Chatauqua, and Sts. John mine waste and tailings sites.

Sts. John Tailings. Tailings from the Sts. John mining district were deposited in alluvium and sediments along stream channels (Figs. 1, 2). Several mine-waste piles that contain boulder-sized material abut Sts. John Creek, some of which protrude into the creek. These mine-waste piles host weathered sulfide minerals, and therefore are also sources of metals during precipitation events. Tailings in Sts. John Creek are deeply incised by rapid stream flow and partially overgrown by willow and alder (Fig. 2E, 2F).

Stream sediments in Sts. John creek largely consist of sand-size mine tailings (sulfide minerals, Fe-Mg minerals, micas, barite), and quartz grains. The tailings are well sorted and stratified. We cored and dug pits to examine the stratification of the tailings deposits. Typically, the top 0-10 cm is silt to coarse sand, dark black to dark red-brown. From 10-18 cm in depth, the silt to sand size layer is oxidized, red-brown to pale red brown. From 18-30 cm, the layer is silt,

gray to light gray, well sorted and cross bedded. Below 30 cm, sand-size to coarse-grained material is black and rich in sulfide and ferromagnesian minerals.

Weathering Products

Weathering induces fragmentation in the rock particles. Rock fragments break down along grain boundaries and transgranular fractures that are lined with iron oxides and other secondary minerals. Based on our observations of large rock fragments with debris and secondary mineral-coated fractures, freezing and thawing at altitude may be a major contributor to the breakdown of the larger boulder-sized rock fragments.

Weathering and vertical transport of material within the Dinero and Lower Chatauqua waste piles was evidenced by clay coatings or clay drapes on mineral grains and rock fragments, and by geopetal fabrics (features that demonstrate vertical orientation), such as fine-grained minerals that partially fill dissolution voids, or amorphous material that has settled out of suspension into distinct chemical layers. Matrix material is largely composed of jarosite, potassic clays, amorphous iron oxides and silica; rock fragments are commonly coated by amorphous iron-oxide material (Fig. 4).

Dissolution of Minerals. At all the waste sites, minerals such as pyrite (FeS_2), chalcopyrite (CuFeS_2), sphalerite $[(\text{Zn}, \text{Fe})\text{S}]$, galena (PbS), and ilmenite (FeTiO_3) show partial to total dissolution (Fig. 4). Nonetheless, the existence of sulfide mineral grains is commonly inferred on the basis of iron-oxide boxwork skeletal remnants and euhedral outlines of voids (Fig. 4). Minerals are the source of trace elements. For example, sulfide minerals such as pyrite commonly host arsenic; galena frequently contains Ag; sphalerite has substituted Cd; and jarosite $[\text{KFe}^{3+}_3(\text{SO}_4)_2(\text{OH})_6]$ commonly contains Pb, Ag, Cu, or Zn constituents. Trace-element content may increase the solubility of a mineral by substitution of elements, such as As for S in pyrite, or Ag for Pb in galena (Savage et al., 2000; Diehl et al., 2003). Element substitution changes electrical properties of the minerals and may distort the lattice structures (Lehner and Savage, 2004).

Microbial Activity. Scanning electron photomicrographs of sulfide minerals collected from the surface of the Dinero and Lower Chatauqua mine-waste piles show etch pits that are consistent with features obtained in laboratory studies of etch pits and dissolution textures formed on mineral surfaces by sulfur-oxidizing microorganisms (Edwards et al., 2000) (Fig. 5) Dissolution of the mineral surface proceeds as etch pits join together. Secondary sulfate precipitates fill the etch pits and coalesce into layers (Fig. 5).

A common by-product of the microbial alteration of sphalerite is elemental sulfur (Edwards et al., 2000; Stanton, 2005). Scanning electron photomicrographs of sphalerite show well-formed, very fine-grained, elemental sulfur as a surface alteration mineral of sphalerite (Fig. 6).

Pyrite exhibited euhedral dissolution pits consistent with features observed on the surfaces of sulfide minerals by activity of sulfur-oxidizing organisms under laboratory conditions (Fig. 7; Edwards et al., 2000). The pitted pyrite from the Lower Chatauqua mine exhibited coatings of jarosite. Jarosite forms at $\leq \text{pH } 3$, yet the leachate of the composite mine waste yielded a pH of 5. This demonstrates that acidic microenvironments exist on the surfaces of sulfide grains, which enable low-pH sulfate precipitates to form.

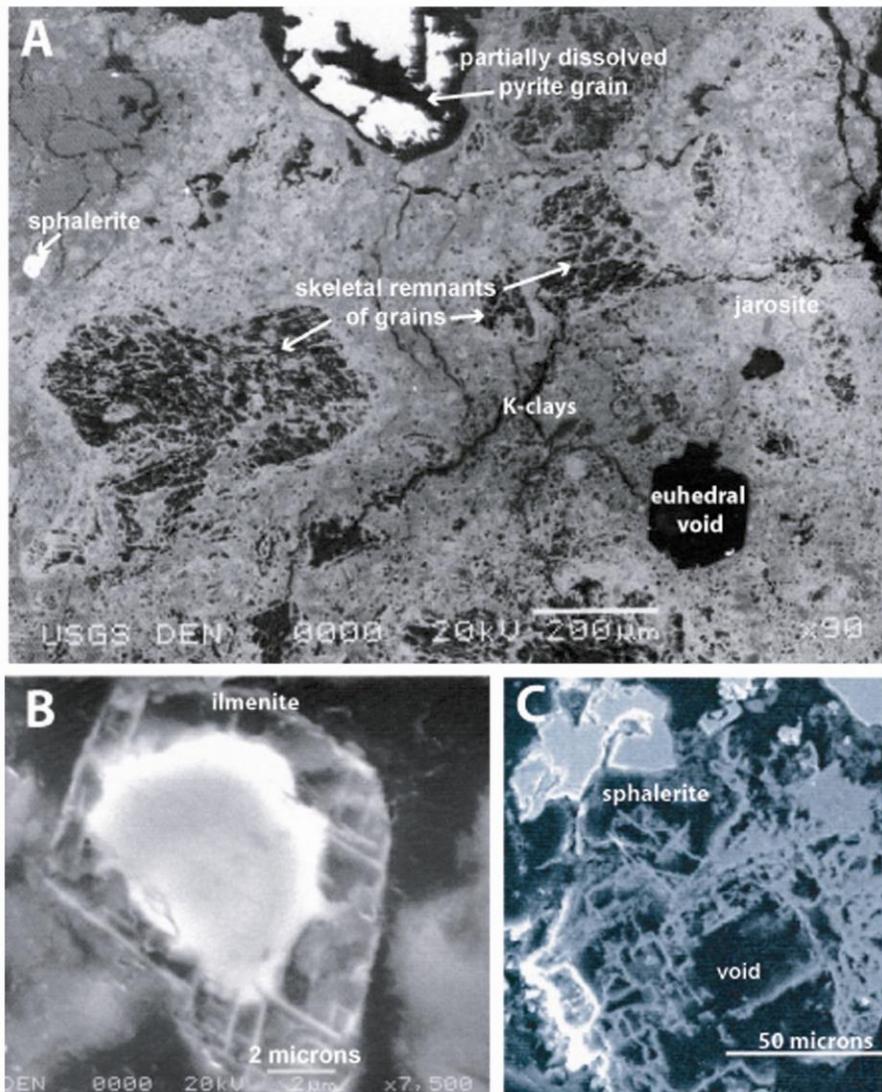


Figure 4. Sulfide and oxide minerals undergo dissolution, commonly leaving only boxwork skeletons, which are ambiguous as to their original mineralogy, Dinero site. **A.** Scanning electron photomicrograph of thin section of mine-waste sample, showing euhedral voids left by the total dissolution of grains, Fe-oxide skeletal remnants of grains, and partial dissolution of a pyrite grain. **B.** Scanning electron photomicrograph of partially dissolved grain of ilmenite, FeTiO_2 . Remnant alteration rims around grains have been described as “atoll-type” textures by Jambor (2003). **C.** Scanning electron photomicrograph of partially dissolved grain of sphalerite, showing remnant sphalerite and Fe oxide boxwork.

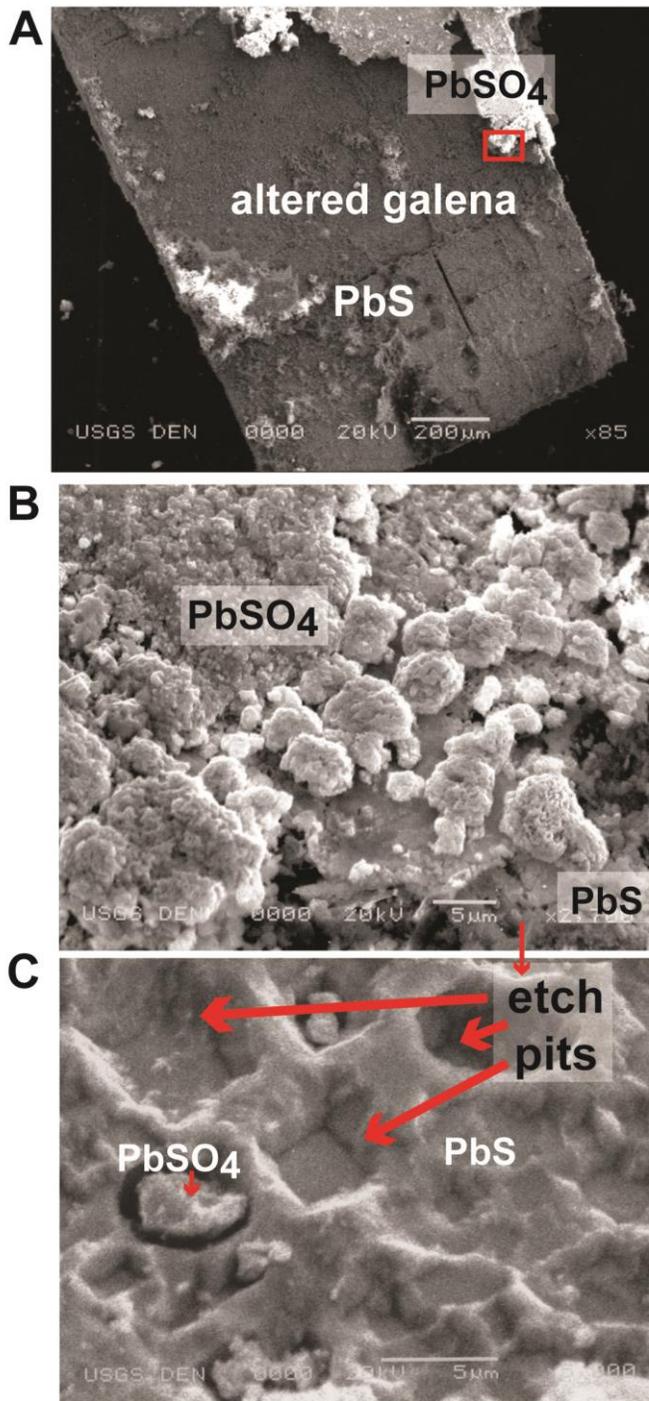


Figure 5. **A.** Scanning electron photomicrograph of altered galena grain from Lower Chatauqua mine-waste pile. Red rectangle is area depicted in **B.** **B.** Bulbous clusters of PbSO₄ coalesce into to form alteration layers around galena grain. **C.** Etch pits develop as PbSO₄ precipitates.

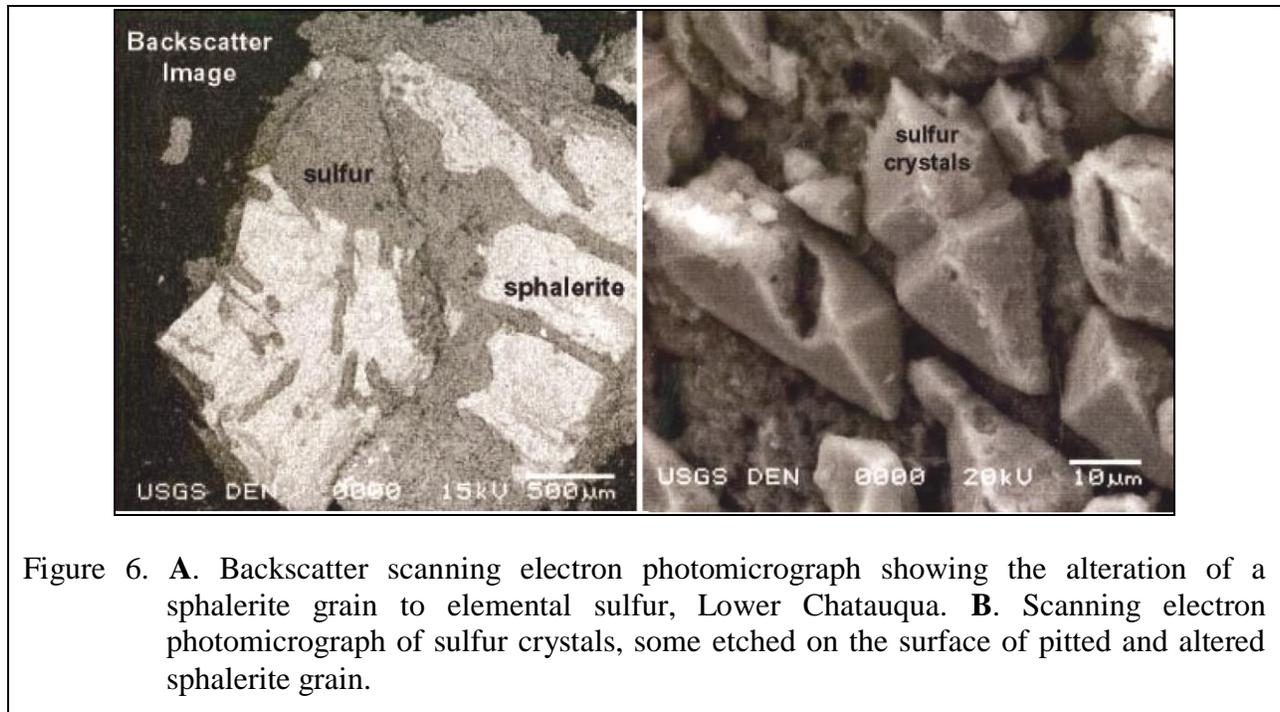


Figure 6. **A.** Backscatter scanning electron photomicrograph showing the alteration of a sphalerite grain to elemental sulfur, Lower Chatauqua. **B.** Scanning electron photomicrograph of sulfur crystals, some etched on the surface of pitted and altered sphalerite grain.

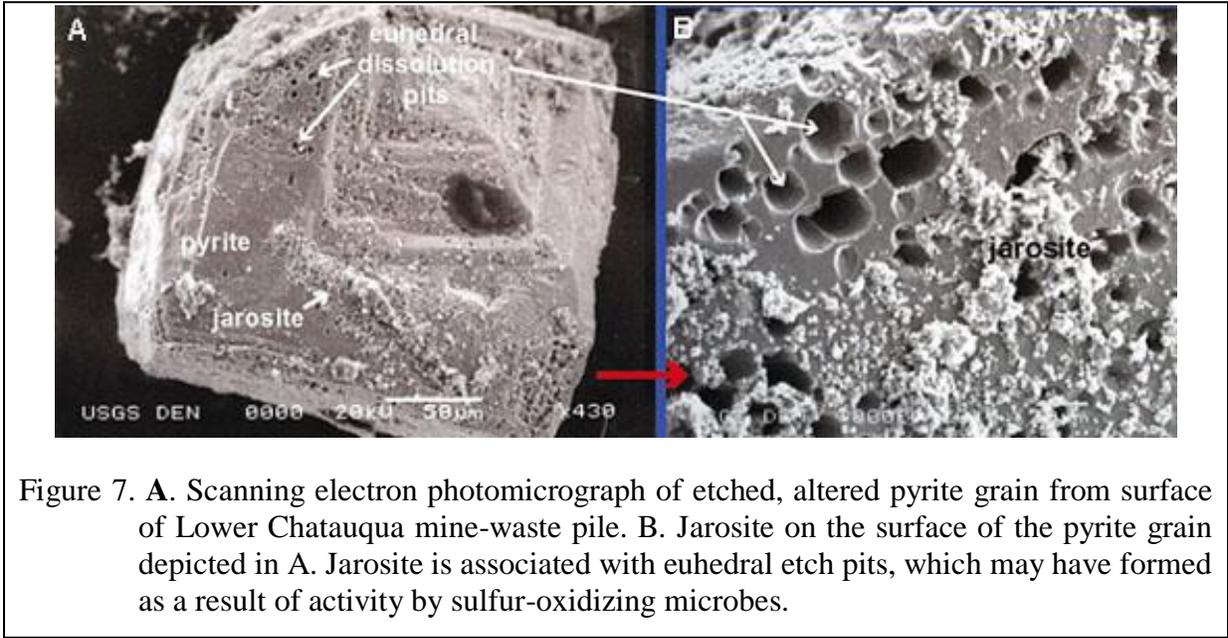


Figure 7. **A.** Scanning electron photomicrograph of etched, altered pyrite grain from surface of Lower Chatauqua mine-waste pile. **B.** Jarosite on the surface of the pyrite grain depicted in A. Jarosite is associated with euhedral etch pits, which may have formed as a result of activity by sulfur-oxidizing microbes.

Formation of Secondary Minerals. Potassium jarosite was the common jarosite phase, but Na-, Pb- and Ag-bearing jarosite, and beudantite $[PbFe_3[(OH)_6|SO_4|AsO_4]]$ were also present (Fig. 8). Jarosite is commonly less than 2 μm in diameter. Grain-size clusters of submicron K- and Pb-jarosite suggest total replacement, or pseudomorphing, of sulfide minerals by these secondary sulfate minerals (Fig. 8B).

Potassium jarosite is commonly present between cleavage planes in altered exfoliated muscovite (Fig. 8). Low-pH fluids can attack minerals such as biotite and muscovite, releasing K^+ , which is used to form K-jarosite. This demonstrates that acidic fluids produced by the weathering of the sulfide minerals can dissolve primary silicate minerals.

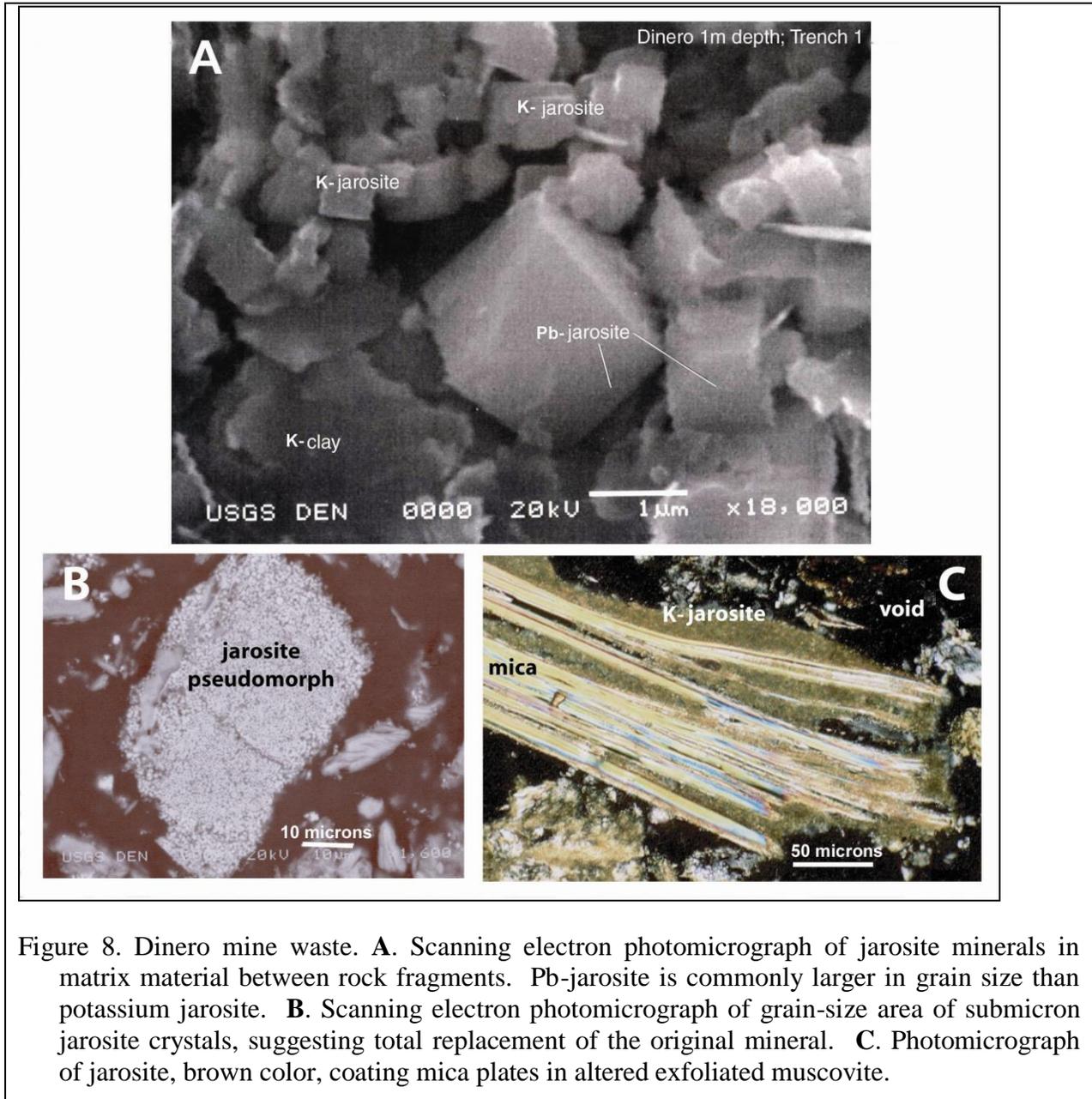


Figure 8. Dinero mine waste. **A.** Scanning electron photomicrograph of jarosite minerals in matrix material between rock fragments. Pb-jarosite is commonly larger in grain size than potassium jarosite. **B.** Scanning electron photomicrograph of grain-size area of submicron jarosite crystals, suggesting total replacement of the original mineral. **C.** Photomicrograph of jarosite, brown color, coating mica plates in altered exfoliated muscovite.

Sulfide minerals such as galena (PbS) exhibited alteration rims (Fig. 9). The fine-grained porous anglesite ($PbSO_4$) alteration rinds showed partial to total dissolution, suggesting that the weathering of the galena to anglesite, and dissolution of anglesite, was a primary source for aqueous Pb^{2+} . Figure 9B shows dissolution embayments at the interface between the galena

grain and the fine-grained porous anglesite. Note the penetration of the duller gray anglesite alteration product into the brighter light gray galena grain (Fig. 9B); this is a reaction/alteration zone. The reaction rim of anglesite does not function as a protective barrier against fluid infiltration because the anglesite is very fine grained (i.e., reactive) and has a porous texture.

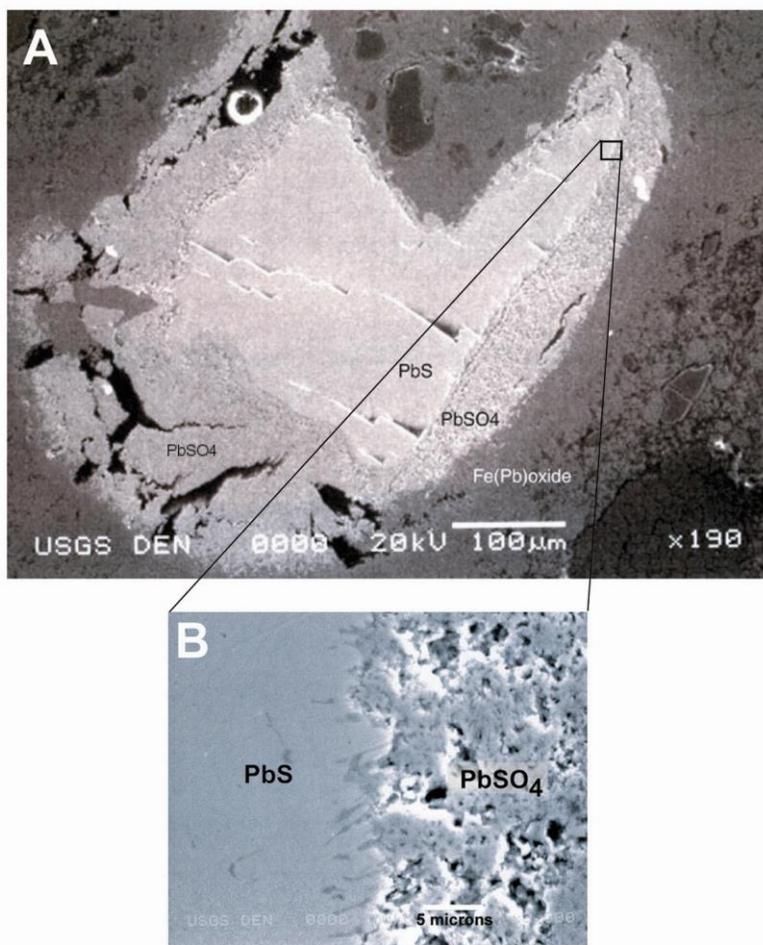


Figure 9. Dinero mine waste. **A.** Scanning electron photomicrograph of galena with an alteration rim of anglesite. Black square is area shown in **B.** **B.** Close-up scanning electron photomicrograph of the altered interface between galena and anglesite.

Element distribution maps show that galena in the Lower Chatauqua mine waste is commonly enriched in Ag (Fig. 10), whereas argentiferous galena was not observed in the Dinero mine waste. The alteration rim of anglesite (PbSO_4) in Fig. 9B shows partial dissolution. We believe that the trace-element rich galena is more susceptible to dissolution, and therefore, leachates from the Lower Chatauqua site have a high concentration of Pb. Formation of anglesite is important because it is much more soluble than galena, and this directly confirms why Pb is in such high concentration in the Lower Chatauqua mine-waste pile.

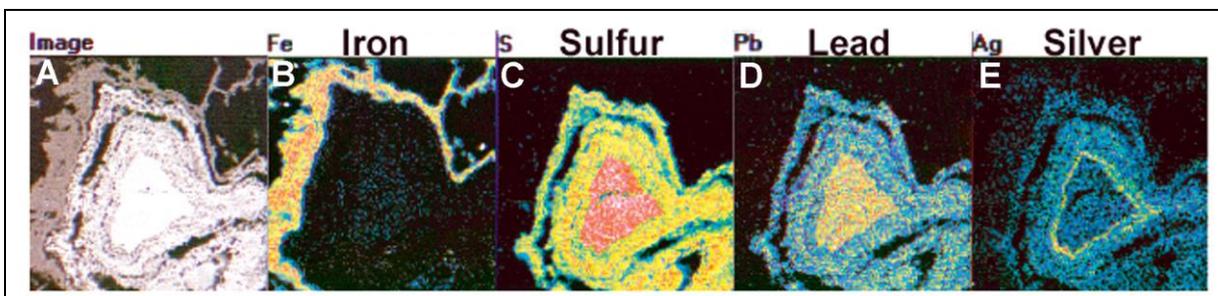


Figure 10. Galena, Lower Chatauqua mine waste. **A.** Backscatter photomicrograph of galena grain (center bright area) with alteration rinds of anglesite and Fe oxide. **B.** SEM element map showing Fe oxide coating around anglesite rind. **C.** SEM element map showing distribution of S in galena and the anglesite alteration rind. **D.** SEM element map showing distribution of Pb. **E.** SEM element map showing distribution of Ag within the galena grain and anglesite alteration rind. Note: Warm yellow to red colors indicate relatively higher concentration of an element; cool blue colors indicate relatively lower concentration.

Grain size as well its trace element content appears to control the solubility of a sulfide mineral. Figure 11 shows scanning electron photomicrographs of galena grains, all collected in a surface composite sample from the Lower Chatauqua mine-waste pile. The galena grains are in various stages of alteration, although the grains have likely spent the same residence time in the mine-waste pile. Large grains of galena that do not contain trace metals are intact, whereas Ag-bearing galena grains have undergone partial dissolution and have formed alteration rinds of anglesite. Mineralization commonly occurs in multiple stages in structurally disrupted rock, so the galena grains are likely from many stages of sulfide mineralization; each stage having its own trace-element characteristics. Therefore, we observe a range of weathering textures.

Soluble Salts. Water-soluble salts, formed by evaporation of acidic metal-bearing solutions, were collected from a seep on the remediated south Dinero waste pile and at the edges of a remediation pond below the open Dinero adit. These white, metal-sulfate minerals formed crusts on waste material and vegetation. X-ray analysis shows the presence of starkeyite ($MgSO_4 \cdot 4H_2O$), gunningite ($(Zn, Mn) SO_4 \cdot H_2O$), and gypsum ($CaSO_4$). ICP-AES analysis shows that metals such as Cd, Co, and Ni are stored in the soluble salts (Table 2). Because they dissolve rapidly, these efflorescent salts are a source of acid and metals during every rain event.

Table 2. Selected element concentration results of ICP-AES analysis of efflorescent salts, Dinero waste site.

Sample Locality (Dinero)	Al (%)	Cd (ppm)	Co (ppm)	Cu (ppm)	Fe (%)	K (%)	Mn (%)	Ni (ppm)	Pb (ppm)	Zn (ppm)	SO ₄ %
Seep in waste repository	0.065	350	340	12	0.009	0.448	5.8	400	0	238000	57
Remediation Pond	0.110	61	290	27	0.024	0.165	1.7	340	0	233000	45

Infiltration of Fluids and Transport of Material

Amorphous Iron- Sulfate, Oxide, and Oxyhydroxide Material. Scanning electron photomicrographs show amorphous iron-sulfate and iron-oxyhydroxide material coating rock fragments and filling voids in weathered mine waste as microlaminated sedimentary deposits (Fig. 12). The microlaminated textures are important indicators that this amorphous material was flushed through the mine waste during wetting events and deposited out of suspension during periods of dryness. The microlaminated void-fill material exhibits sedimentary features, such as cross beds and soft sediment slump structures (Fig. 12). Iron oxyhydroxides adsorb and retain metals, as evidenced by the Pb-rich bright white layers coating the voids. This again is evidence that iron-bearing solutions generated from pyrite weathering precipitated in voids after primary weathering of pyrite occurred.

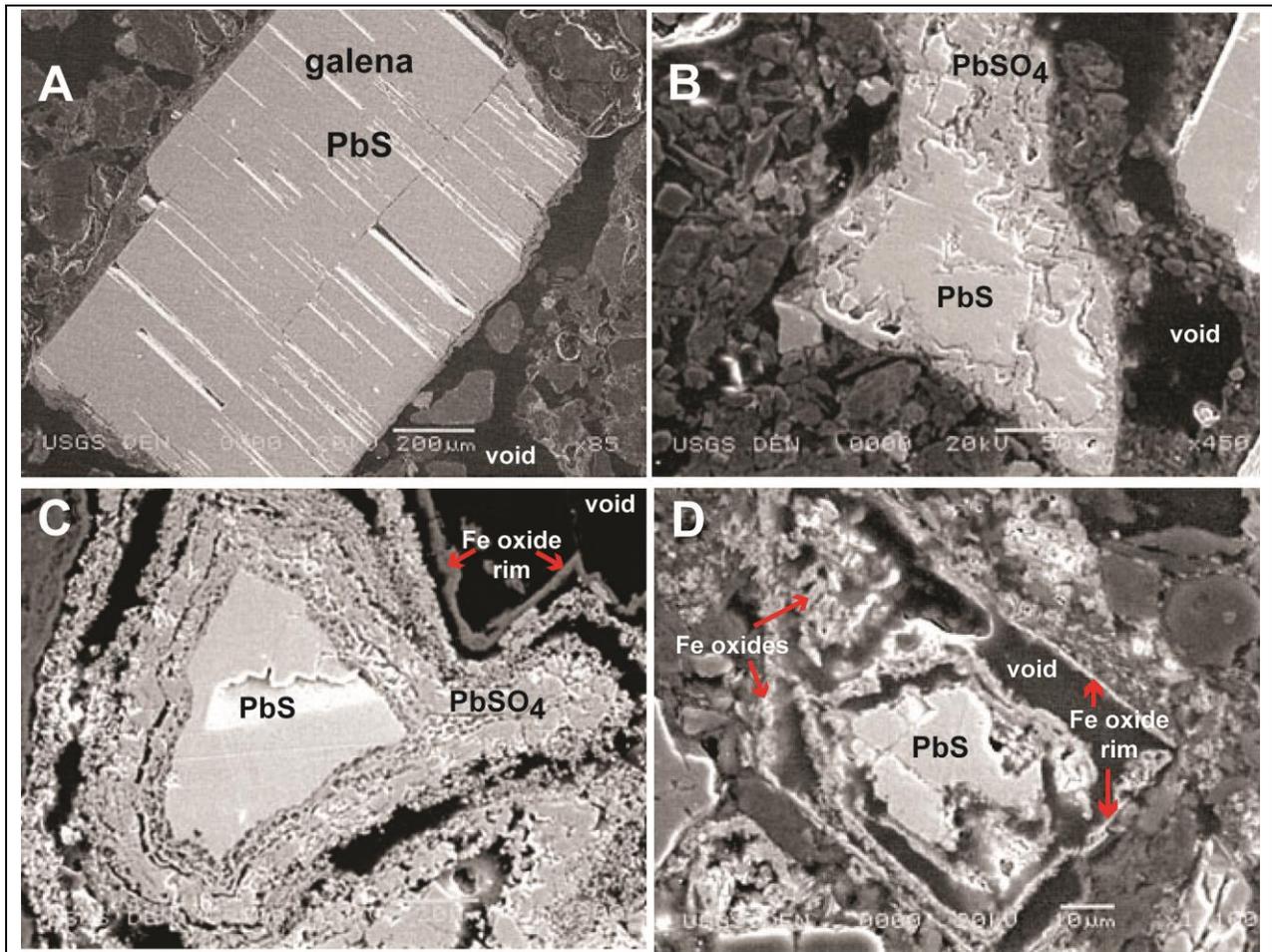


Figure 11. Galena, Lower Chatauqua mine waste. **A.** Large galena grain, 600 microns in length, no Ag content, showing minor alteration along crystallographic planes. **B.** Ag-bearing galena, 100 microns in length, with PbSO₄ alteration. **C.** Ag-bearing grain (depicted in Fig. 10A), with partially dissolved PbSO₄ rind. **D.** PbSO₄ alteration rim has totally dissolved, leaving Fe oxides.

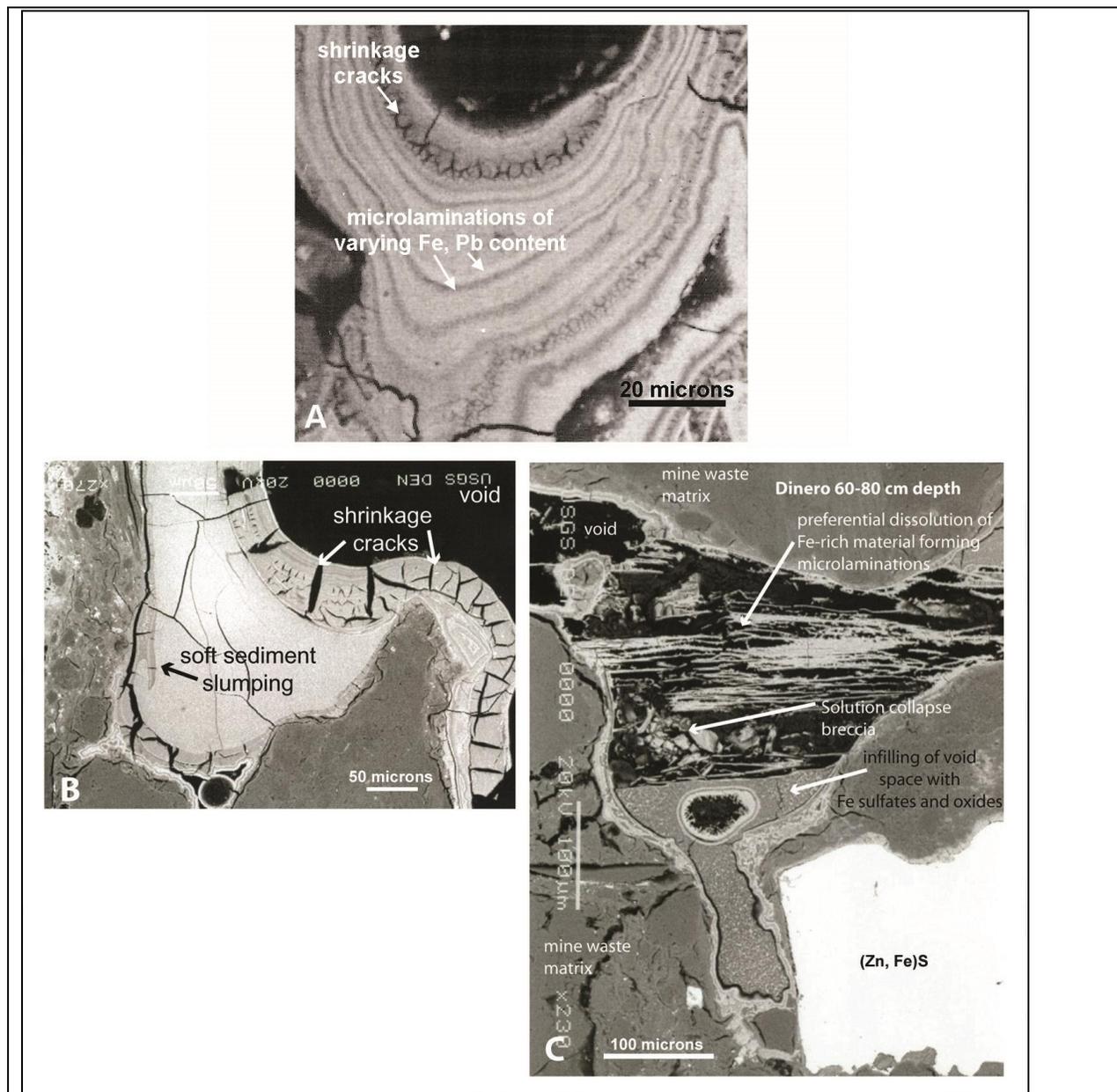


Figure 12. **A.** Scanning electron photomicrograph of amorphous Fe- oxyhydroxides and sulfates lining a void, Lower Chatauqua. Microlaminations exhibit a sedimentary, geopetal texture in the void. **B.** Scanning electron photomicrograph showing several generations of void fill, recorded by the difference in brightness in each microlayer, Dinero. Bright, central nonlaminated area of photo is more Fe rich. Soft sediment deformation structure is evident. **C.** Scanning electron photomicrograph showing preferential dissolution of a Fe-rich amorphous void filling, Dinero. Sphalerite, lower right corner, has a thin Fe-oxide alteration rim.

The light and dark microlaminations indicate fluctuations in metal content during deposition. Figure 12C shows partial dissolution of a brighter, more iron-rich void-fill phase, and the accumulation of a microscale solution-collapse breccia, atop a less soluble, less iron-rich oxide phase. Dissolution of the amorphous iron sulfate and oxyhydroxide material demonstrates that it is not a stable cementing material between rock fragments. Cementing material is transient, and its dissolution contributes to the instability of the mine-waste pile.

Amorphous Mn-Oxyhydroxide Material. Amorphous Mn oxyhydroxide is a common aqueous precipitate in the Sts. John tailings and occurs as coatings on stream sediment grains, as a cement around fresh-water diatoms and shell material, and replacement of cellular plant material (Fig. 13). Manganese oxides and oxyhydroxides may be produced by bacterial action (Robbins et al., 1999). Mn oxyhydroxides are capable of absorbing metals, and these Mn precipitates host Ba, Cu, Pb and other trace metals (Fuller et al., 2005).

Summary

This study has shown the following important pieces of evidence concerning the relation between the weathering of a waste-rock pile and what is observed in solutions leached from that pile:

1. Sulfide minerals such as pyrite, galena, and sphalerite were observed at various stages of weathering, ranging from intact to partially dissolved Fe-oxide remnants to total removal of the mineral into solution. These remnant Fe-oxide boxwork structures and grain-sized euhedral voids are evidence that solutions, developed within the waste-rock piles, attacked primary sulfide and silicate minerals. Weathering of the mine-waste minerals, especially the processes of dissolution, increases permeability in the mine waste pile, and therefore, increases fluid and oxygen access, which in turn can accelerate the rate of dissolution at the mineral-water interface.
2. The presence of microlaminated iron-sulfate and iron-oxide/oxyhydroxide material, which forms oriented geopetal textures in voids, is evidence for the transport of material in suspension or solution through well-connected porous channelways in the mine-waste pile. Shrinkage cracks and partial dissolution of the amorphous laminae attest to periods of wetting and drying within the mine waste; dissolution of this void-filling material shows that any cement formed is easily dissolved during a precipitation event.

Previous research on samples collected from trenches dug into the Dinero mine-waste pile revealed that no internal laterally consistent layering existed in the mine waste that would inhibit the vertical transport of fluids and very fine-grained clays and secondary minerals (Diehl et al., 2005). The development of microlaminated material in the voids of mine-waste piles is similar to illuvial accumulations of clays and other materials in voids and fractures in soils. Amorphous iron sulfate and oxide materials were abundant, and dissolution of these solids was probably the source of iron in the Dinero leachate.

Although we could not examine the Lower Chatauqua waste pile in the 3-dimensional manner in which we studied the Dinero, we suspect that similar transport processes exist in these small high-altitude waste piles. This is based on similar textures such as microlaminated, amorphous Fe-oxyhydroxide void-filling material, and jarosite and clay coatings on grains, found in the Lower Chatauqua waste pile in near-surface material. Iron oxyhydroxides coat stream sediments at the mouth of the Dinero and Lower Chatauqua adits. In addition, at the

reclaimed Dinero site, Fe oxyhydroxides form heavy coatings on bottom sediments of downstream remediation ponds.

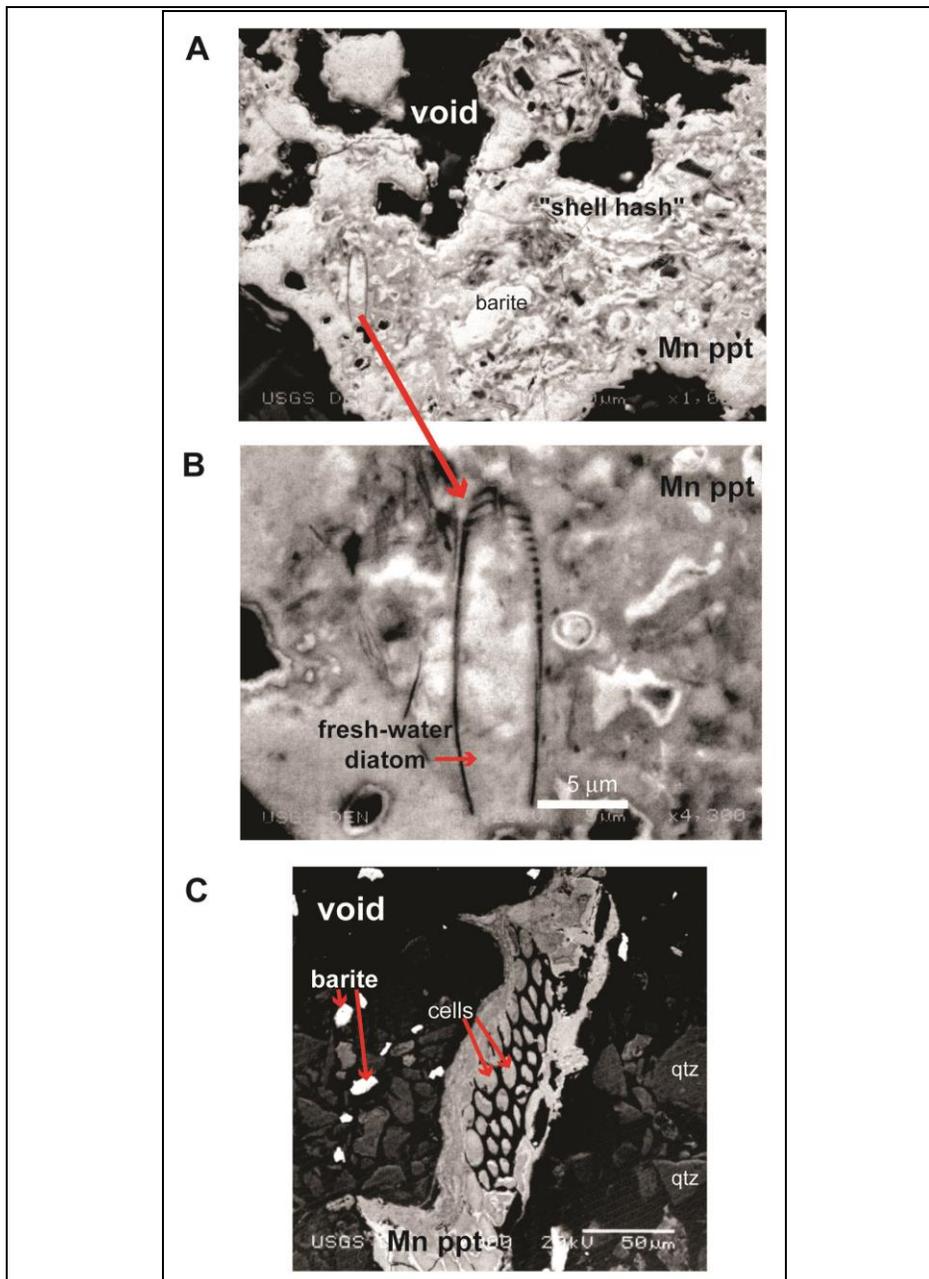


Figure 13. **A.** Mn oxyhydroxides (Mn ppt) coat organic material in Sts. John Creek. **B.** Close-up of fresh-water diatom encased in Mn-oxide cement. **C.** Mn-oxide/oxyhydroxide replacement of cellular material.

3. The formation of anglesite and efflorescent salts are evidence that the primary sulfides and silicates weather into sulfates and oxides that are much more soluble. Water-soluble sulfates form mineral crusts at seeps in the reclaimed Dinero mine waste and around the edges of remediation ponds below the adit. These efflorescent salts are primarily Zn, Mn sulfates, which also store metals such as Cd, Co, and Ni. These salts readily go into solution during precipitation events, adding metals to the Lake Fork River, and therefore, a concern for continued monitoring. As shown in the leachates developed from the mine-waste composites, concentrations of metals in the USGS Field Leach Test are a direct result of weathering of secondary sulfates.

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