SOURCES OF ACID AND METALS FROM THE WEATHERING OF THE DINERO WASTE PILE, LAKE FORK WATERSHED, LEADVILLE, COLORADO[1]

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Abstract. Two trenches were dug into the south Dinero mine-waste pile near Leadville, Colorado, to study the weathering of rock fragments and the mineralogic sources of metal contaminants in the surrounding wetland and Lake Fork Watershed. Water seeping from the base of the south Dinero waste-rock pile was pH 2.9, whereas leachate from a composite sample of the rock waste was pH 3.3. The waste pile was mostly devoid of vegetation, open to infiltration of precipitation, and saturated at the base because of placement in the wetland. The south mine-waste pile is composed of poorly sorted material, ranging from boulder-size to fine-grained rock fragments. The trenches showed both matrix-supported and clast-supported zones, with faint horizontal color banding, suggesting zonation of Fe oxides. Secondary minerals such as jarosite and gypsum occurred throughout the depth of the trenches. Infiltration of water and transport of dissolved material through the pile is evidenced by optically continuous secondary mineral deposits that fill or line voids. Iron-sulfate material exhibits microlaminations with shrinkage cracking and preferential dissolution of microlayers that evidence drying and wetting events. In addition to fluids, submicron-sized to very fine-grained particles such as jarosite are transported through channel ways in the pile. Rock fragments are coated with a mixture of clay, jarosite, and manganese oxides. Dissolution of minerals is a primary source of metals. Skeletal remnants of grains, outlined by Fe-oxide minerals, are common. Potassium jarosite is the most abundant jarosite phase, but Pb- and Ag-bearing jarosite are common. Grain-sized clusters of jarosite suggest that entire sulfide grains were replaced by very fine-grained jarosite crystals. The waste piles were removed from the wetland and reclaimed upslope in 2003. This was an opportunity to test methods to identify sources of acid and metals and metal transport processes within a waste pile.

A series of entrapment ponds, lined with limestone rip rap, was created where the mine waste was once situated. A flooded adit discharges low-pH metal-bearing waters into the ponds. A white (Zn, Mn)-sulfate precipitate was observed in 2003 around the edges of the most distal pond.

Key Words: mine waste, dissolution, jarosite, anglesite, microlamination, leachate

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Introduction

Acid mine drainage from abandoned mine adits in the Sugarloaf Mining District flows into the Lake Fork of the Arkansas River (Fig. 1). Because of acidity and high metal content, drainage from the open adits has a negative impact on downstream wetland and riparian habitats. The Colorado Unified Watershed Assessment determined that the Upper Arkansas River was in need of restoration because the Arkansas River does not meet water-quality standards for potentially toxic metals in the Lake Fork confluence (Upper Arkansas Watershed Council, 2001; Bureau of Land Management, Colorado, 2003). Elements of concern that are at toxic levels to aquatic life in the Lake Fork are Cd, Pb, and Zn.

The Sugarloaf Mining District was mined for Ag, Au, Pb, and Zn from the 1880's until 1949 (Singewald, 1955). There are many abandoned mines in the district, but this study focuses on the weathering of the mine-waste piles from the Dinero mine. The Dinero adit drains into Sugarloaf Gulch, which flows into the Lake Fork, then to the Arkansas River (Walton-Day et al, 2004; Fig. 1). Sugarloaf Gulch was identified as a major source of metal loading to the Lake Fork; Mn, Zn, and Cd exceed aquatic life criteria at this site (Upper Arkansas Watershed Council, 2001; Bureau of Land Management, Colorado, 2003). The Dinero mine-waste piles, located in a grassy wetland, had active seeps and were identified as a significant contributor of metals to the Lake Fork Watershed. Although the wetlands exhibited a diverse plant community, there was evidence of chronic toxicity to the plant life (Upper Arkansas Watershed Council, 2001). In addition, there was no evidence of aquatic life directly below the Dinero mine-waste site.

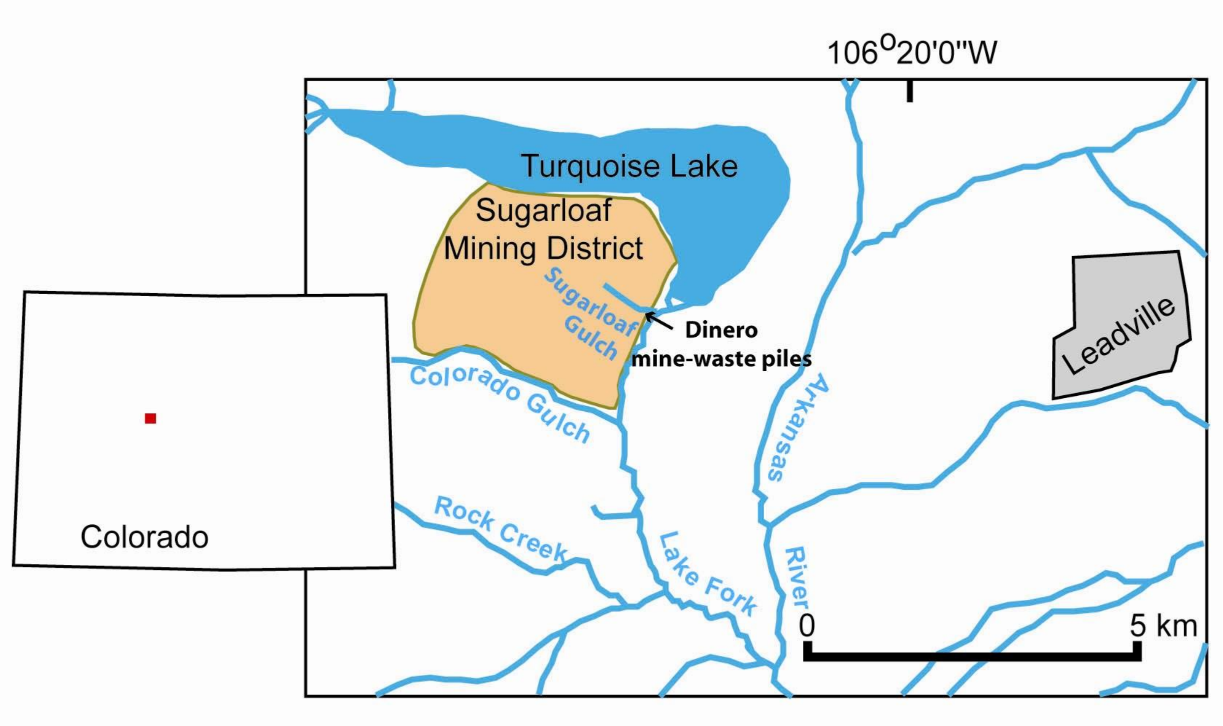

Figure 1. Location map showing the outline of the Sugarloaf Mining District, streams that drain the area, and Turquoise lake in Lake County, Colorado.

Two piles of waste-rock material from the Dinero mine, designated the north and south piles, were dumped directly into a grassy wetland (Fig. 2). In 2003 the mine-waste piles were removed upslope to remediate the wetland and decrease the concentrations of metals entering the watershed. During the removal of the mine waste, we were afforded the opportunity to study the south waste pile in three dimensions in a 2 m-deep trench dug by a backhoe. One goal was to document the influence of internal sedimentary features on metal transport in the waste pile. Previous hydrologic research on waste piles suggested that internal layering of fine to coarse particles controlled the infiltration of precipitation and the lateral channeling of water (Hawkins and Aljoe, 1990, 1991). Another objective was to 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.

General Geology

The Sugarloaf Mining District is located at approximately 10,000 to 10,500 feet altitude, in an area of schist, gneiss, and granite (Singewald, 1955). The schist and gneiss may be correlated with the Early Proterozoic to Precambrian 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). The host rock is resistant to weathering and forms a steep topography. During the Late Cretaceous Laramide Orogeny, the area comprising the Sugarloaf Mining District was highly deformed by veins and orthogonal fault sets, trending north-northwest and east-northeast. The host granite was highly altered during ore mineralization; feldspars are partially to totally altered to fine-grained potassic sericitic clays. Manganoan carbonate occurs locally in veins with pyrite, chalcopyrite, and Ag-sulfide minerals.

The wetlands are situated in outwash gravel from eroded unconsolidated glacial moraine material and alluvium from Sugarloaf Gulch. The mine waste from the Dinero mine was deposited at the mouth of Sugarloaf Gulch atop the highly porous sediments.

Methods

The USGS Field Leach Test was used in the collection and analysis of a composite mine-waste sample of the south Dinero waste pile (Hageman and Briggs, 2000; Smith et al., 2000; Smith et al., 2002). Complete details of both the non-grid sampling technique and the leaching procedure are fully described in Hageman and Briggs (2000). A composite sample was gathered from all lithologies in the waste pile by collecting a minimum of 30 increments of surficial mine-waste material in a completely 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 lithologic sample. 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 microscope analysis, and all material larger than 2 mm was discarded. To leach the sample, 50 g of <10 mesh (<2mm) mine-waste composite sample was weighed into a 1-L plastic bottle. Approximately 1-L 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. A portion of leachate was syringe filtered through a 0.45 μm pore-size nitrocellulose syringe filter. The filtrate was later analyzed in the lab, using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) (Briggs, 2002; Lamothe et al., 2002) (Table 1). Note:

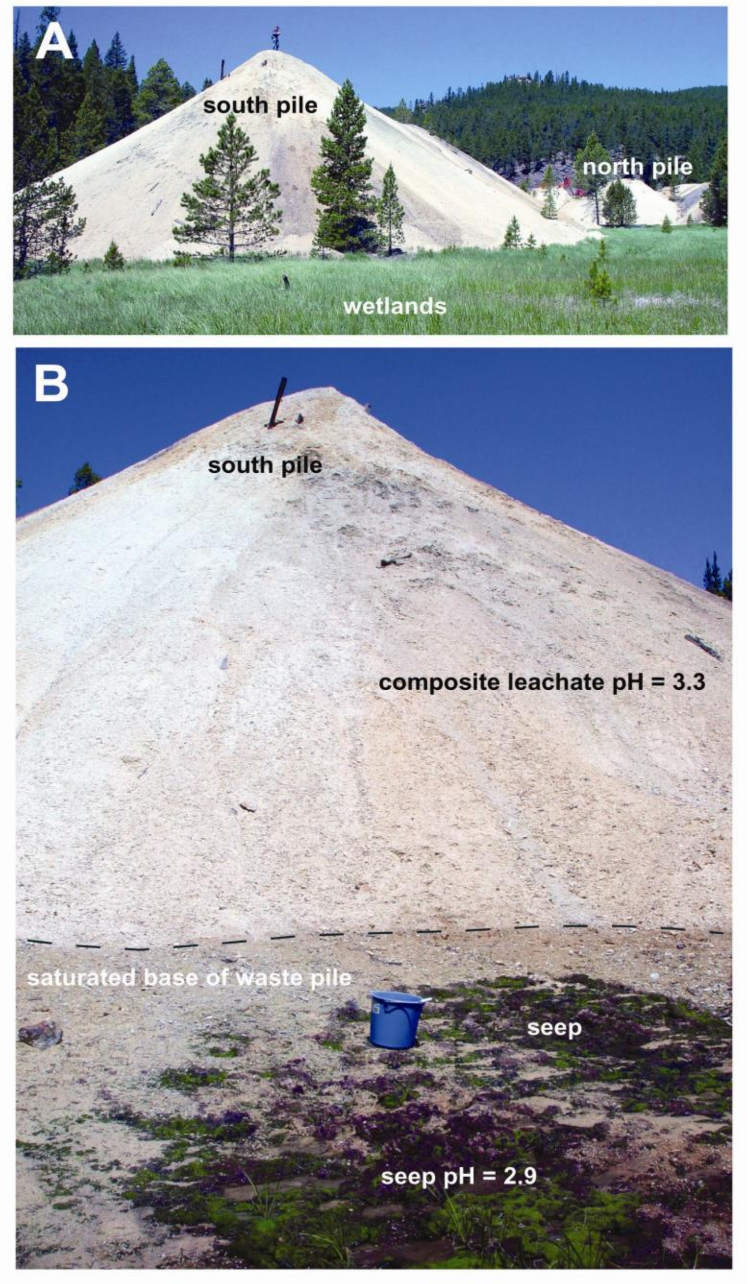

Figure 2. A. North and south Dinero mine-waste piles in grassy wetlands. B. Because the south waste pile was located in wetlands, the base of the pile was saturated (dark brown horizontal line). Several seeps of low pH water drained from the base of the waste pile.

In addition to geochemical analysis, the petrographic microscope and scanning electron microscope were used to conduct basic mineralogic and textural studies of the weathered mine-waste material.

Results and Discussion

Geology of Constituents of the South Mine-Waste Pile

The waste pile was composed of boulder-sized rock fragments down to very fine-grained matrix material. Because the waste-rock piles are highly heterogeneous in particle size, the mine waste is porous, open to the infiltration of precipitation and oxygen. The mine-waste pile was a composite of different rock types and surficial weathering features; there were brown iron-oxide streaks, grayish zones with sulfidic material, black manganoan streaks, and white areas of soluble salts (e.g., gypsum, zinc efflorescent minerals; Fig. 2A).

Two trenches exposed clast-supported layers and matrix-supported layers. Distinct zoning was evident in trench 2, with a gray reduced zone at the base of the trench, and brown oxidized zones toward the surface (Fig. 3). Color and particle-size zonation suggested that horizontal layers with different physical properties could act as a barrier to infiltration and induce lateral flow; however, the mine-waste material was uniformly damp throughout the depth of the trench. In addition, secondary minerals, such as jarosite, occurred in all samples collected through the depth of the trench. These features indicate that the mine-waste pile was porous with well-connected channelways.

Characteristic rock fragments were 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.

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. 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 waste pile is 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. 4A).

Dissolution of Minerals. Minerals such as pyrite (FeS_2), chalcopyrite ($CuFeS_2$), sphalerite [(Zn, Fe)S], galena (PbS), and ilmenite ($FeTiO_3$) show partial to total dissolution (Fig. 4). The existence of mineral grains is commonly inferred on the basis of iron-oxide boxwork skeletal remnants and euhedral outlines of voids (Fig. 4A). Minerals are the source of trace elements. For example, sulfide minerals such as pyrite commonly host arsenic; galena frequently contains Ag; sphalerite has Cd; and jarosite commonly contains Pb, Ag, Cu, or Zn constituents. Trace element content may increase the solubility of a mineral by substitution of elements, such as arsenic for sulfur in pyrite, or silver for lead 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).

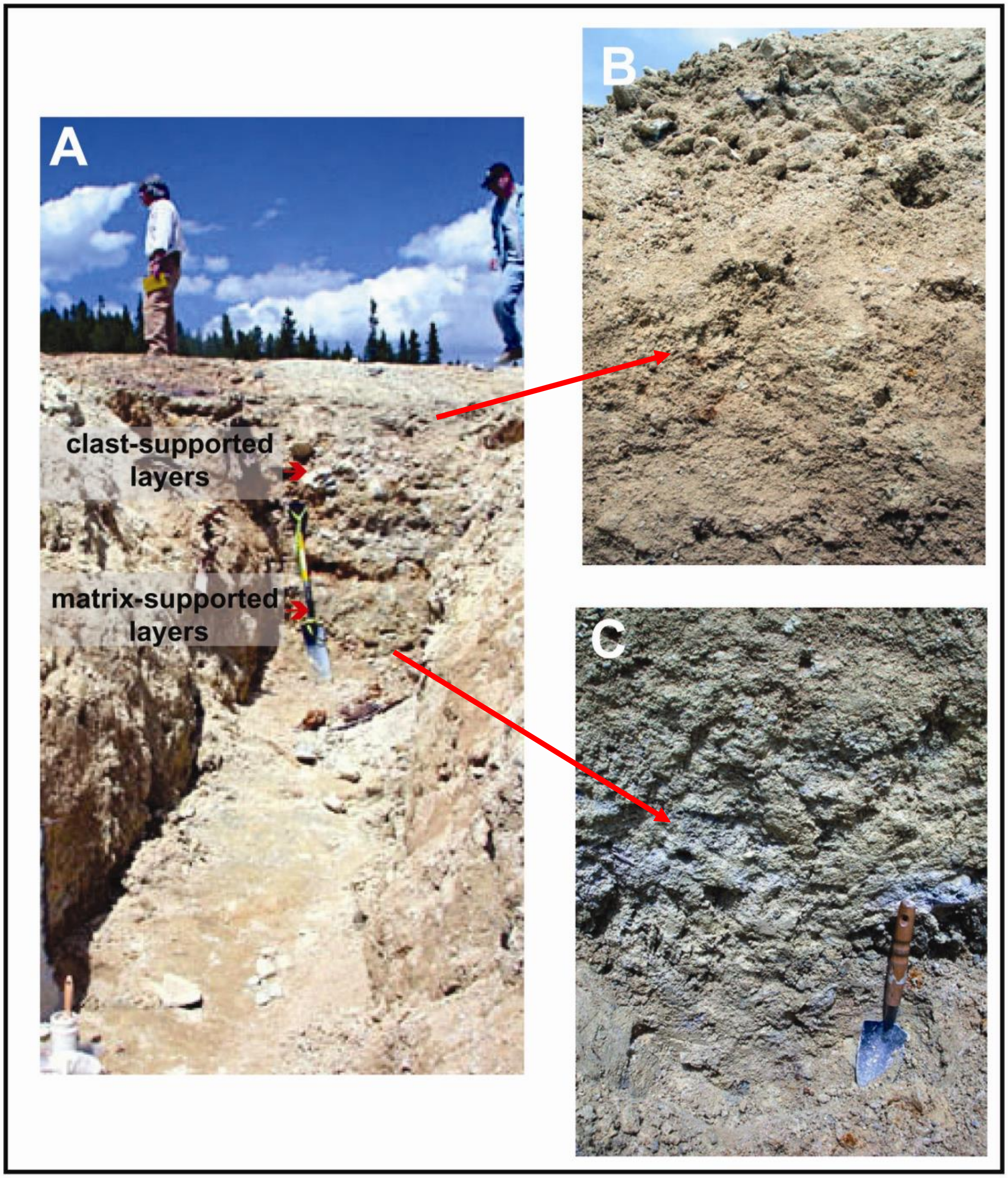

Figure 3. A. 2-m deep trench in south waste pile, exposing clast-and matrix-supported layers. B. Brown oxidized top 0.5 m of trench. C. Discontinuous gray layers near the base of the trench. The trowel for scale in c also serves as a scale for photo B.

Formation of Secondary Minerals. Potassium jarosite was the common jarosite phase, but Na-jarosite and Pb- and Ag-bearing jarosite were also present (Fig. 5). 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. 5B).

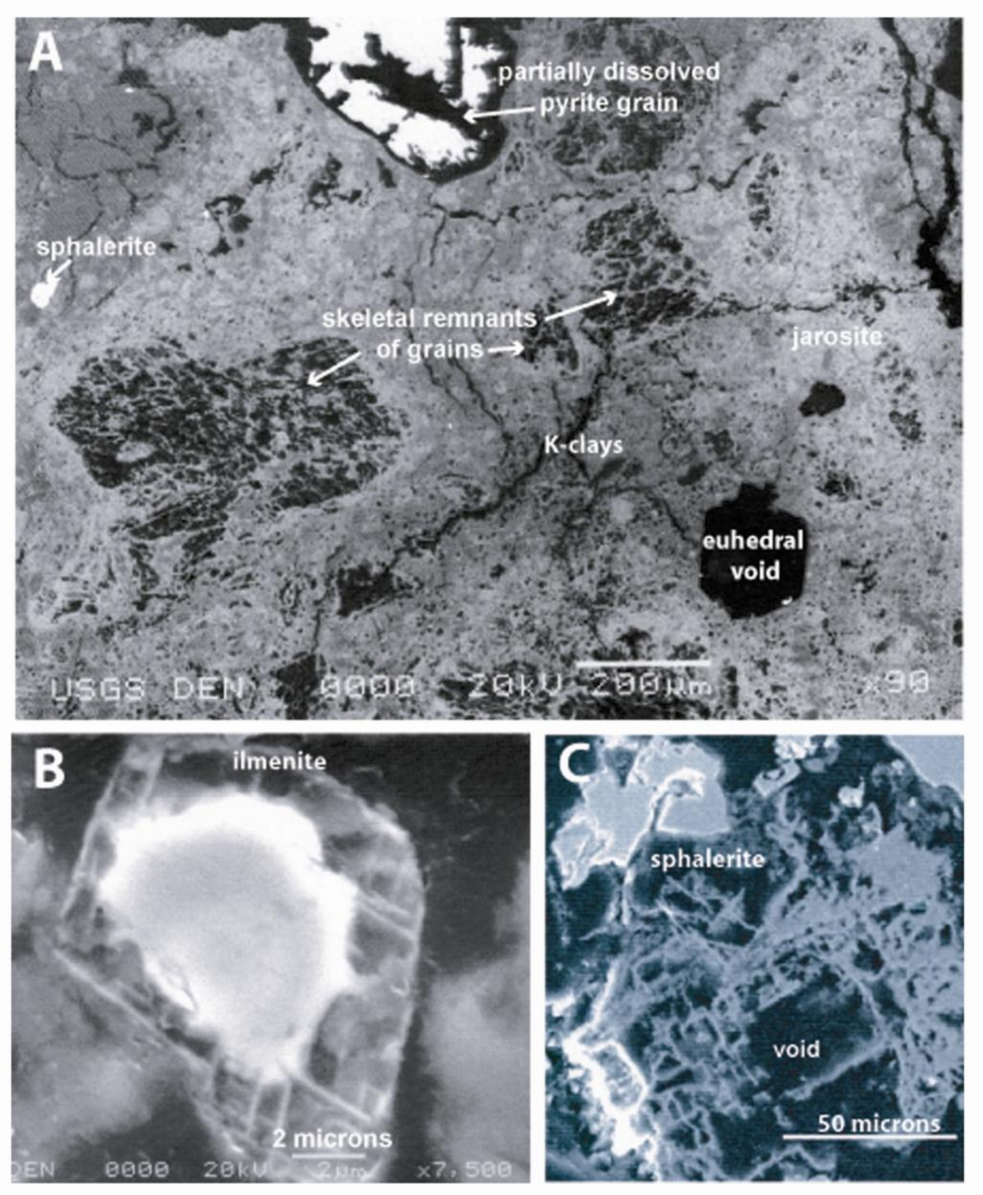

Figure 4. Sulfide and oxide minerals undergo dissolution, commonly leaving only boxwork skeletons, which are ambiguous as to their original mineralogy. A. Scanning electron photomicrograph of mine-waste sample, showing euhedral voids left by the total dissolution of grains, Fe-oxide skeletal remnants of grains, and partial dissolution of a sulfide mineral, pyrite. B. Scanning electron photomicrograph of partially dissolved grain of ilmenite, FeTiO2. Such remnant structures have been described as “atoll-type” textures by Jambor (2003). C. Scanning electron photomicrograph of partially dissolved grain of sphalerite.

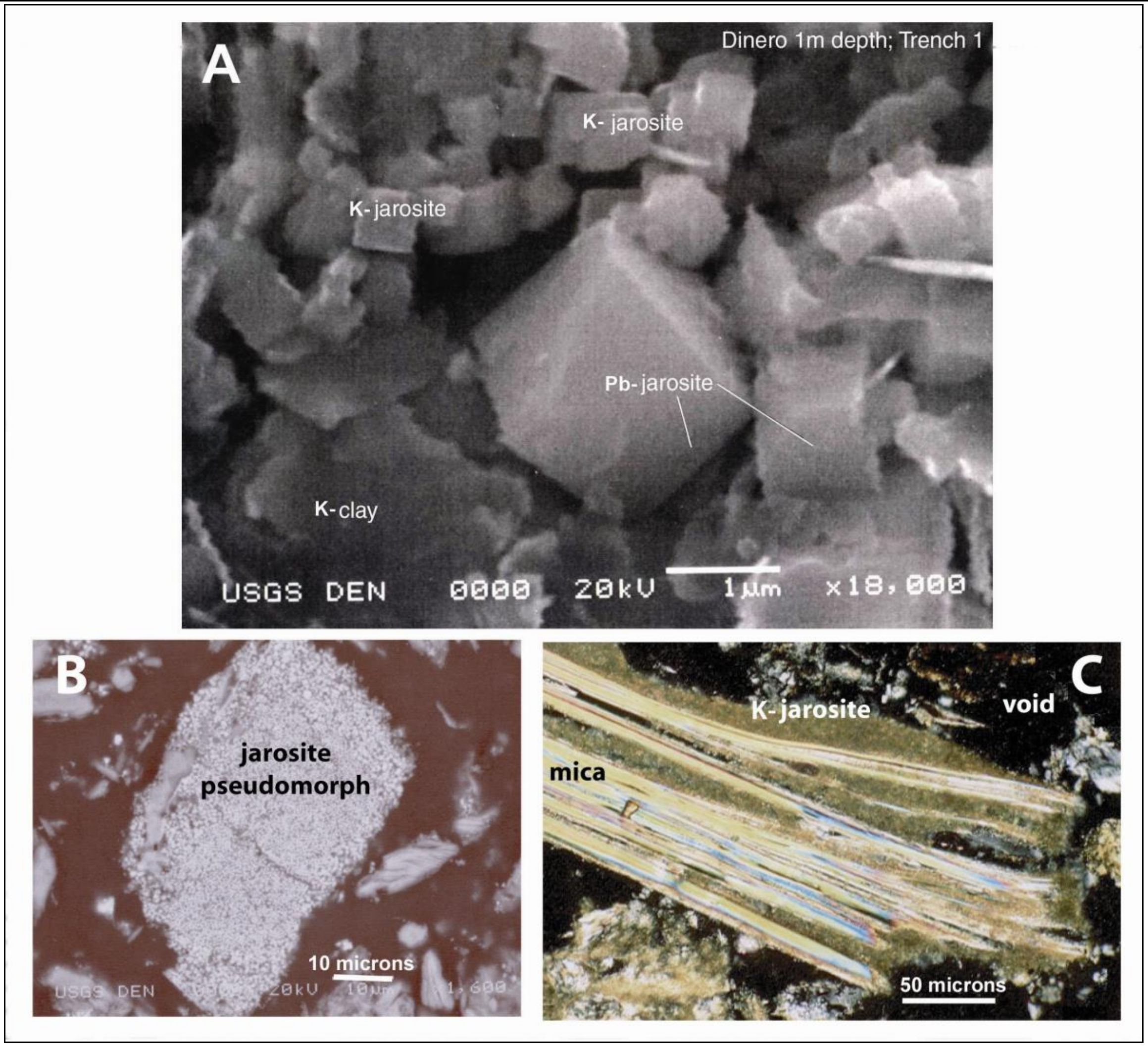

Figure 5. A. Scanning electron photomicrograph of jarosite minerals in matrix material between rock fragments. Pb-jarosite is commonly larger in grain size than potassium jarosite. B. Scanning electron photomicrograph of grain-size area of submicron jarosite crystals, suggesting total replacement of the original mineral. C. Photomicrograph of jarosite, brown color, coating mica plates in altered exfoliated muscovite.

Potassium jarosite commonly occurred between cleavage planes in altered exfoliated muscovite (Fig. 5C). Low-pH fluids can attack minerals such as biotite and muscovite, releasing K^+, which is used to form K-jarosite.

Sulfide minerals, such as galena (PbS), exhibited alteration rims (Fig. 6). 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 6B 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. 6B); 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.

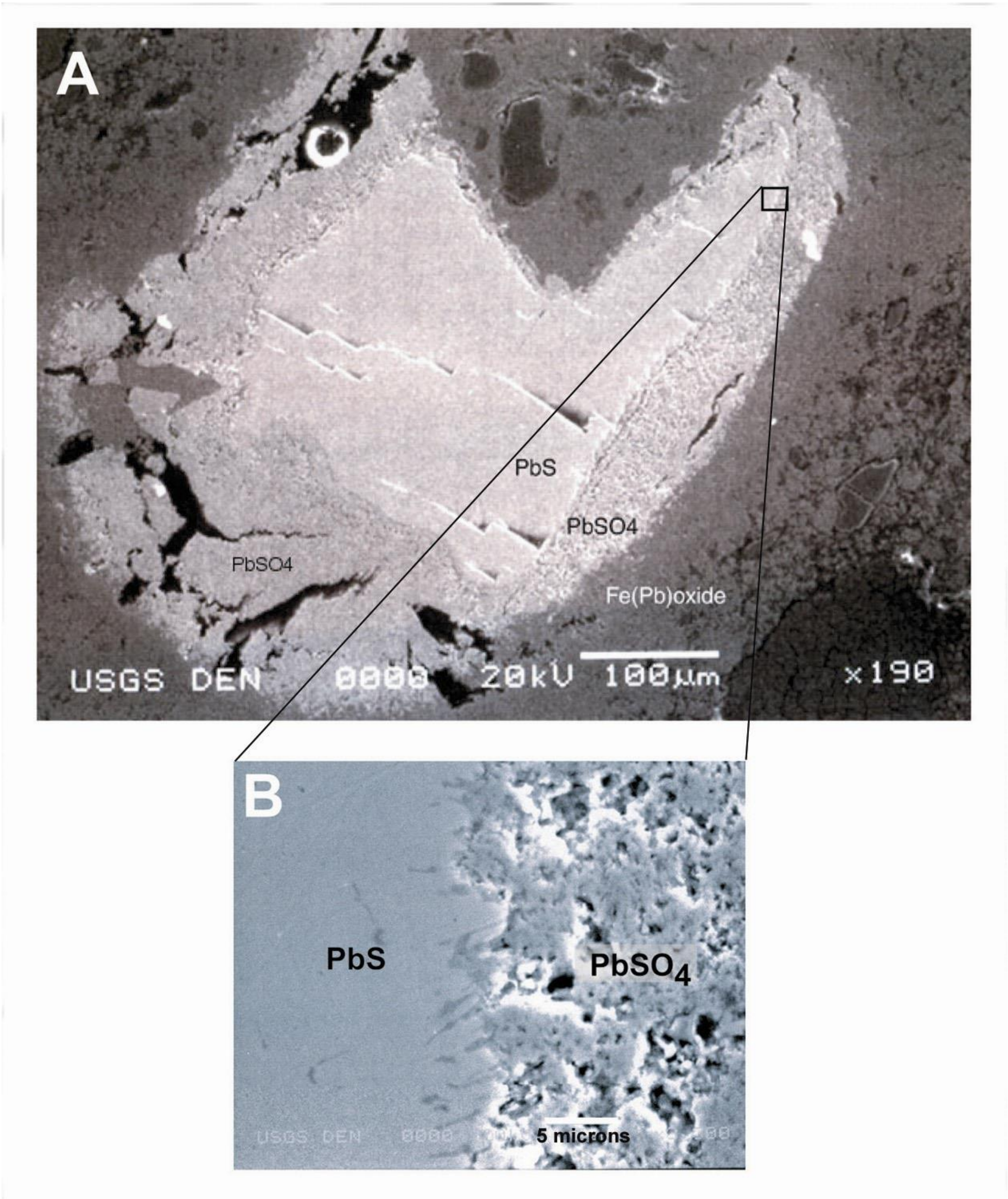

Figure 6. A. Scanning electron photomicrograph of galena with an alteration rim of anglesite. Black square is area shown in B. B. Close-up scanning electron photomicrograph of the altered interface between galena and anglesite.

<u>Amorphous Iron Sulfate, Oxide, and Oxyhydroxide Material.</u> 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. 7). The microlaminated textures are important indicators that this 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. 7B). Iron oxyhydroxides attract metals, as evidenced by the Pb-rich bright white layers coating the voids in Fig. 7A and 7B.

The light and dark microlaminations indicate fluctuations in metal content during deposition. Fig. 7C 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.

Leachate Chemistry

Table 1. Selected element concentration results of U.S. Geological Survey Field Leach Test (Hageman and Briggs, 2000) on the Dinero mine-waste composite.

Element	Al	As	Ba	Be	Cd	Ce	Cu	Fe	Mn	Ni	Pb	Zn
Concentration (ppb)	443	2	91	0.2	50	5	50	441	1250	8	31	7970

Elements detected in the leachate chemistry reflect those primary and secondary minerals that have undergone alteration and dissolution. Zn and Mn are elevated in the leachate solution, and these two metals are prominent in efflorescent precipitates [$(Mg, Mn, Zn)SO_4 \cdot 7H_2O$] around the edges of the remediation ponds (Fig. 8).

Summary

The mine-waste pile was a dynamic physical and chemical system. The presence of moisture and precipitation/deposition of K- and Pb-jarosite throughout the depth of the mine-waste pile indicates that continuous chemical reactions were taking place under low pH (<3) conditions. Sulfide minerals such as pyrite, galena, and sphalerite were observed at various stages of weathering, ranging from intact to partially dissolved remnants to total removal of the mineral into solution, the latter based on the evidence of remnant boxwork structures composed of iron-oxides. Weathering of the mine-waste constituents, especially the process 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.

The microlaminated iron sulfate and iron oxyhydroxide material that forms oriented geopetal textures in voids is evidence for the transport of material in suspension or solution through porous channel ways in the mine-waste pile. Shrinkage cracks and partial dissolution of laminae attest to periods of wetting and drying within the mine waste. Amorphous iron sulfate and oxide material were abundant, and dissolution of this material was probably the source of iron in the leachate. Iron oxyhydroxides coat stream sediments at the mouth of the adit and form heavy coatings on bottom sediments of downstream remediation ponds.

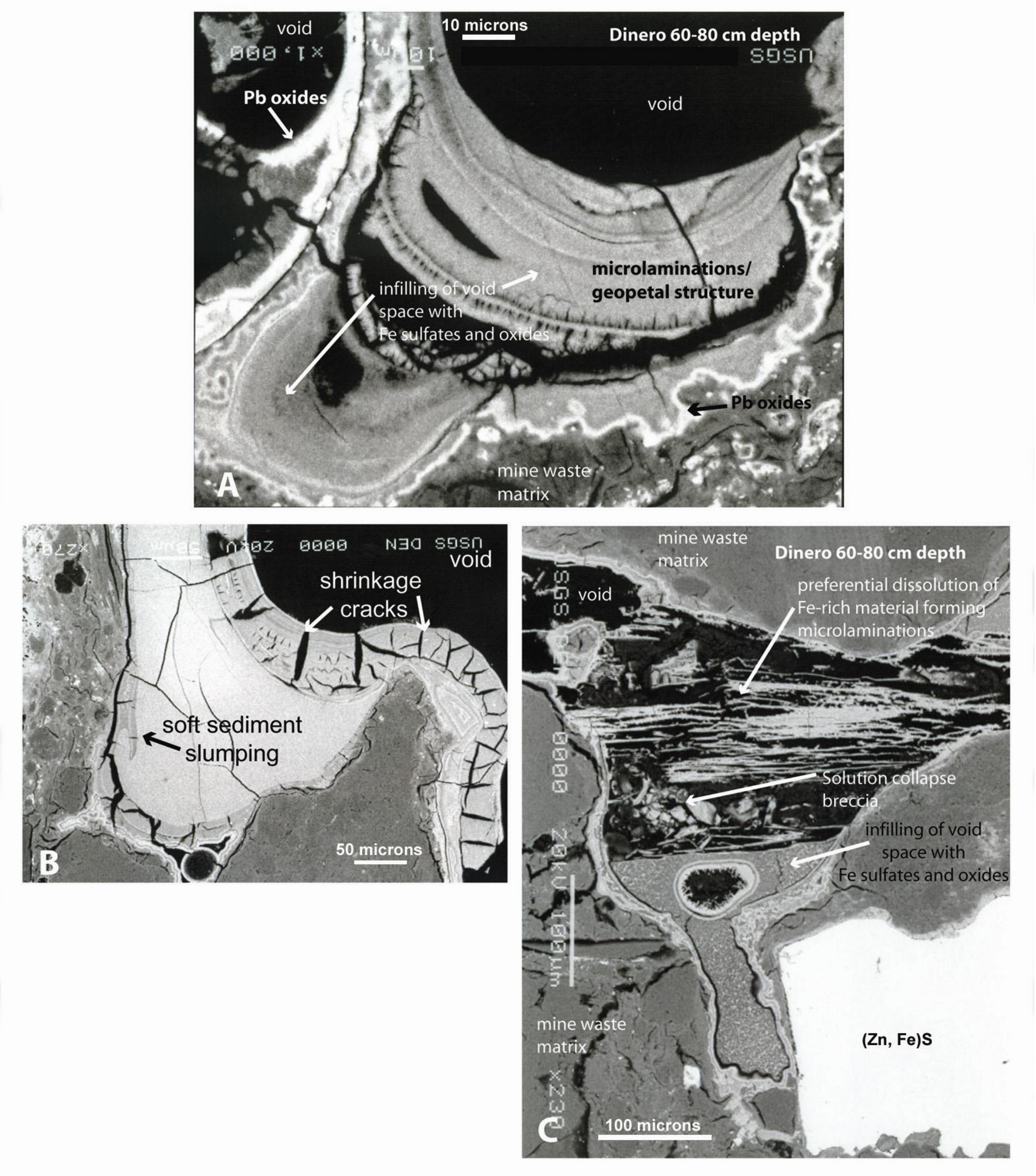

Figure 7. A. Scanning electron photomicrograph of amorphous Fe-oxides and sulfates lining a void. Microlaminations exhibit geopetal and cross-bedding textures. Bright void-lining material is Pb-rich Fe oxide. B. Scanning electron photomicrograph showing several generations of void fill, recorded by the difference in brightness. 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. Sphalerite, lower right corner, has a thin alteration rim.

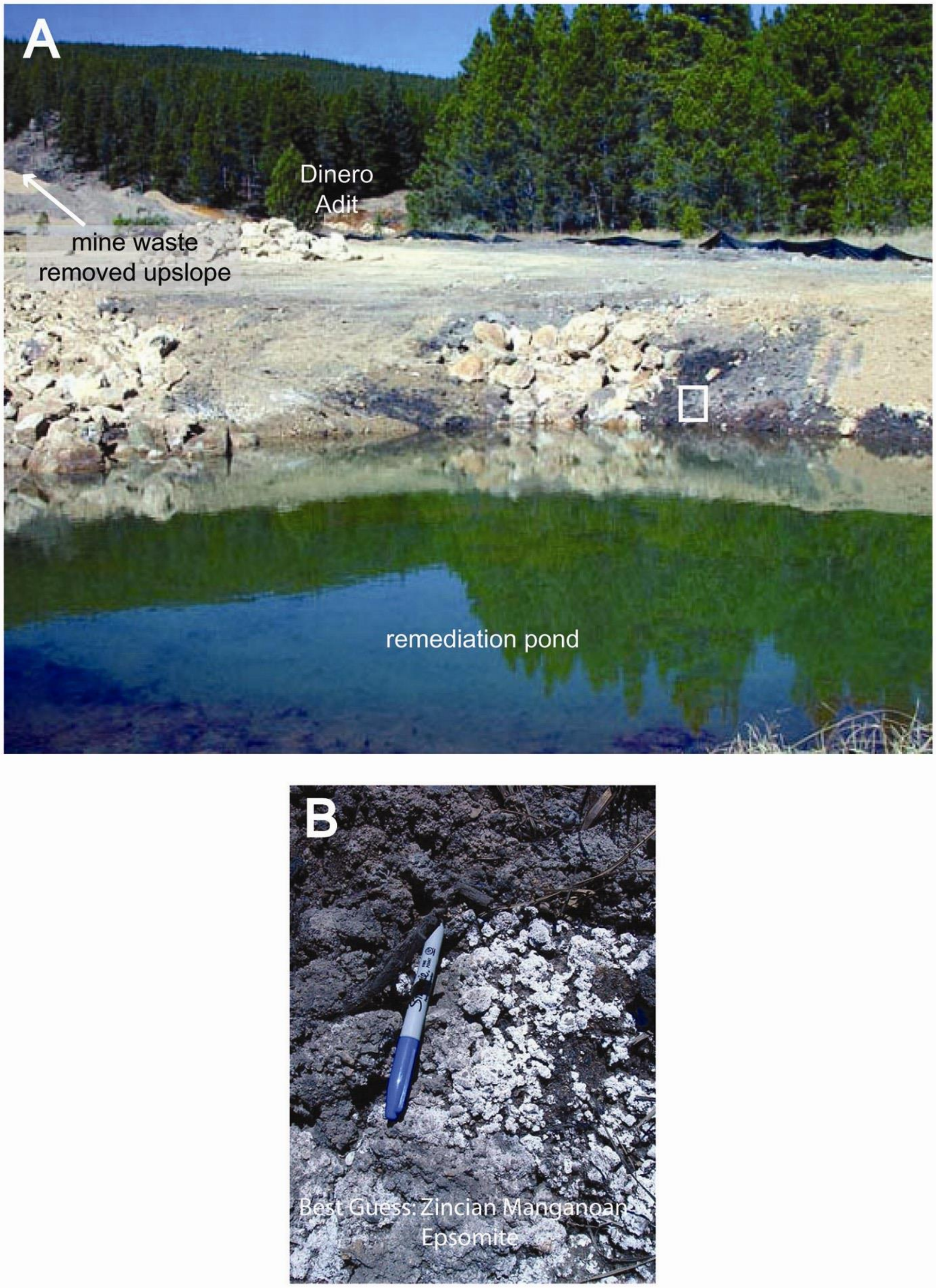

Figure 8. A. Photo of remediation pond, 2003, after the removal of the north and south mine waste piles. Coarse-sized rocks and boulders are carbonate rock. White square is area depicted in 8B. B. Close up photo of efflorescent Zn and Mn salts precipitated at edge of pond.

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. Microlaminated material displays optical continuity and a strong textural and color contrast with adjacent matrix material, attesting to their transport and deposition out of suspension. Clay coatings and clay drapes on mineral grains also demonstrate the transport and deposition of fine-grained material through a porous, permeable mine-waste pile.

The dissolution of minerals in the mine-waste pile reflects the trace elements detected in the U.S. Geological Survey Field Leach Test; therefore, primary mineralogy in weathered mine waste can be inferred from leachate results. Mn and Zn, which were enriched in the composite leachate sample, made an appearance in efflorescent precipitates at the edges of the remedial ponds. There are two possibilities for the source of the secondary precipitates. One is that despite the removal of the mine-waste piles upslope from the wetlands, these metals may still be present in waters draining from the open Dinero adit. The second possibility is that a reclaimed mine-waste site may take several years to show a positive recovery from metal contamination. Sulfide or sulfate minerals were exposed during the removal of the mine waste, and these minerals are now oxidizing. Secondary sulfate minerals at the edges of the remediation ponds may precipitate under evaporating conditions, but these minerals may represent a finite source of metals as they dissolve during runoff events.

In 2005, Colorado Division of Minerals and Geology personnel will focus their studies inside the Dinero adit and attempt to identify the sources of clean and contaminated waters and where these waters mix. They will continue to monitor water quality from the adit and remediation ponds.

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