CHARACTERIZATION OF WEATHERING OF MINE ROCK PILES: EXAMPLE FROM THE QUESTA MINE, NEW MEXICO, USA

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ABSTRACT
The Questa mine (Chevron Mining Inc. or CMI, formerly Molycorp, Inc.), a porphyry molybdenum deposit in New Mexico, USA, constructed nine mine waste rock piles between 1969 and 1982. The evidence for weathering in the Goathill North (GHN) rock pile includes some combination of: 1) color changes, 2) bulk texture changes, 3) mineralogy changes, 4) mineral texture changes, and 5) grain texture changes. Clay minerals are abundant and varied in the Questa rock piles, but five lines of evidence suggest that clays are predominantly from the pre-mining hydrothermal alteration: 1) fresh or lightly tarnished pyrite surrounded by clay minerals, 2) similar types and abundance of clay minerals in the unweathered drill core and rock pile samples from GHN, 3) similar chemical compositions for the clays from unweathered drill core vs. weathered GHN rock pile, 4) textural association between clay and other minerals, and 5) oxygen and hydrogen isotopic analysis. Predominant weathering reactions in the GHN rock pile are oxidation of pyrite, dissolution of carbonate, and formation of sulfate minerals (gypsum, jarosite, and soluble, efflorescent salts). Waters from the Questa rock piles yield SO₄ (up to 19,000 ppm) and Al (up to 1690 ppm), indicating major sulfide and subordinate silicate dissolution.

Key words: Mo porphyry deposit, oxidation, hydrothermal alteration

INTRODUCTION
Chevron Mining Inc. (CMI, formerly Molycorp, Inc.) currently produces molybdenum from the underground Questa mine in north-central New Mexico, USA (Fig. 1). During the period of open-pit mining at the mine from 1969 to 1982, approximately 317.5 million metric tons of overburden rock was removed and deposited onto mountain slopes and into tributary valleys forming nine rock piles surrounding the open pit (Fig. 1). In this paper, we describe the primary Questa rock-pile lithologies and investigate pre-mining hydrothermal alteration and post-mining weathering.

Rock piles, the preferred term by some in the metal mining industry today, refer to man-made structures consisting of piles of non-ore overburden material that had to be removed in order to extract ore. Traditionally, rock-pile material was discarded in the most efficient and least costly manner possible by dumping as close to the open pit as possible to limit haulage costs.

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Alteration is a general term describing the changes in mineralogy, texture, and chemistry of a rock as a result of a change in the physical, thermal, and chemical environment in the presence of water, steam, or gas, including those changes produced by weathering (Henley and Ellis, 1983; Reed, 1997; Neuendorf et al., 2005). Weathering is the set of physical and chemical changes, up to and including disintegration of rock by physical, chemical, and/or biological processes occurring at or near the earth's surface that result in reductions of grain size, changes in cohesion or cementation, and change in mineralogical composition (modified from Neuendorf et al., 2005). Hydrothermal alteration is the change in original composition of in-situ rock by hydrothermal (warm to hot) solutions during mineralization. In this study, hydrothermal alteration refers to pre-mining conditions.

SITE DESCRIPTION
The climate at the Questa mine is semi-arid with 51.8 cm/yr of precipitation and alpine. The mine is on southward facing slopes at elevations of 2290-3280 m. The rock piles are mostly unsaturated, although seeps of acidic water occur at the base of some rock piles. The geology and mining history of the Questa-Red River area is complex (Meyer and Leonardson, 1990; Ludington et al., 2005; McLemore, 2008). The Questa rock piles were constructed using standard mining practices at the time, primarily by haul-truck end-dumping in high, single lifts (URS Corporation, 2003). The sequence of construction was typically from the top down. End dumping generally results in the segregation of materials with finer-grained material at the top and coarser-grained material at the base.

The Goathill North (GHN) rock pile contained approximately 10.6 million metric tons of hydrothermally-altered rock material (URS Corporation, 2003) before it was reclaimed. The rock pile was constructed (1969-1974) by end-dumping material in a gully on a mountain slope. CMI stabilized the rock pile by redistributing material from the top portion of both areas to the bottom of the pile (Norwest Corporation, 2004). During progressive down-cutting of the top of GHN (regrading), trenches were constructed to examine, map, and sample the internal geology of the rock pile. The depositional layers locally are at, or near, the angle of repose (36-38° as measured) and subparallel to the original slope angle. Detailed geologic mapping and sampling revealed that these layers could be defined as mappable geologic units in the rock pile based on
grain size, color, texture, stratigraphic position, and other physical properties (Fig. 2). Units were correlated between benches and to opposite sides of each trench. Several units were correlated down slope through the excavated trenches and to units in the drill holes through the rock pile (McLemore et al., 2008).

Figure 2. Conceptual layered geological model of Goathill North (GHN) rock pile as interpreted from surface mapping, detailed geologic cross sections, trenches, drill holes, construction method and observations during reclamation of GHN (McLemore et al., 2006a, b, 2008). Detailed analyses were from trench LFG-006.

SAMPLING AND ANALYTICAL METHODS

Standardized protocols for sampling and laboratory analysis were followed (summarized in McLemore and Frey, 2008; available upon request). Typically at each site, a select, or bulk sample of rock or other solid material was collected in separate bags or buckets for petrographic study and laboratory analyses. Location information, sample type, and field petrographic descriptions were recorded. Two different types of solid samples were collected for this report: 1) rock-pile material including a fine-grained matrix of clay- to sand-sized particles (<1 mm) and gravel, cobble, and boulder fragments of mixtures of different lithologies and hydrothermal alteration assemblages, and 2) unweathered drill core of the open-pit deposit before mining. Samples for chemical analyses were crushed in jaw crushers, pulverized by disc grinders to a particle size of <35 µm, homogenized, and sent to the laboratories for analyses (McLemore and Frey, 2008).

Petrographic analyses (mineralogy, lithology, type of hydrothermal alteration) were performed on both the fine-grained matrix and rock fragments using a binocular microscope. The analyses were supplemented by thin section analysis, microprobe, and X-ray diffraction (XRD) analysis. The major clay mineral groups were identified using standard clay separation techniques and XRD analyses of the clay mineral separate on an oriented glass slide (Hall, 2004; Moore and Reynolds, 1989). This method does not liberate or measure the amount of clay minerals within the rock fragments. The concentrations of major and trace elements, except S, SO₄, C, LOI (loss on ignition), and F were obtained by X-ray fluorescence (XRF) spectroscopy. F concentrations were determined by fusion and single-element electrode and LOI concentrations were determined by gravimetric methods. Total S and C were determined by Leco Furnace or XRF, and SO₄ was determined by sulfate-sulfur-carbonate leach. S as sulfide was determined by subtracting SO₄ from the total S. Quantitative mineralogy was determined using a modified ModAn (Paktunc, 2001) technique along with petrographic observations (including an estimated modal analysis), electron microprobe analysis, clay mineral analysis, and the whole-rock chemistry of the sample (McLemore et al., 2009).
Water samples were collected from seeps at the toe of Goathill North (GHN) rock pile before reclamation and from a seep in trench LFG-021 from the colluvium/bedrock during reclamation of GHN, stored in plastic bottles, transported to the laboratory within 24 hrs, and filtered in the laboratory before analysis. Water analyses were completed by the NMBGMR Chemistry Laboratory following EPA methods and Standard Methods for the Examination of Water and Waste Water as described in McLemore and Frey (2008).

Precision was monitored by multiple analyses of sample duplicates and internal standards. In general, analyses obtained from the different laboratories and methods are in agreement with values of certified standards; precision is excellent between multiple analyses. The overall analytical error of the Questa samples is generally within ±5%.

DESCRIPTION OF HYDROTHERMAL ALTERATION AT QUESTA
The hydrothermal alteration at Questa is similar to most Climax-type porphyry molybdenum systems (Molling, 1989; Ludington et al., 2005). Prior research has identified seven types of hydrothermal alteration assemblages in the rock piles (Molling, 1989; Reed, 1997). These include: propylitic (chlorite, calcite, pyrite, albite, and epidote), argillic (chlorite, smectite, kaolinite, calcite, epidote, quartz, and pyrite), potassic (replacement of primary minerals by K-feldspar and potassium-bearing micas, illite, and sericite + fluorite, quartz, and molybdenite), QSP (quartz-sericite-pyrite), magnetite veining, silicification (replacement by fine-grained quartz), and post-mineral carbonate-fluorite veins (locally with anhydrite). Post-mining weathering of rock-pile material is superimposed on pre-mining hydrothermal alteration. Some examples of hydrothermal alteration types are shown in Figure 3.

CHEMICAL WEATHERING OF THE QUESTA ROCK PILES
Evidence for chemical weathering in the Questa rock piles includes field and petrographic observations and geochemical data (McLemore et al., 2008). Effects due to post-mining weathering can be difficult to distinguish from pre-mining hydrothermal alteration, because some of the same minerals are formed during both processes. Mineral coatings, rims, efflorescent salts, cementation, and newly precipitated minerals are most likely indicative of post-mining weathering, whereas pervasive replacement of silicate minerals are most likely a result of pre-mining hydrothermal alteration (Harris et al., 2003). Not all weathered samples exhibit all of these features listed above, and some show dissolution features. In many samples, the fine-grained soil matrix is weathered, while the interiors of rock fragments (even within weathered rock-pile material), exhibit little or no indication of weathering.

Samples obtained across bench 9 (trench LFG-006, Fig. 2) were examined in detail for indications of weathering as a function of proximity to the outer parts of the rock pile. Figure 4 is a cross section of bench 9 showing the stratigraphy and location of samples. An example of several geological units within bench 9 is shown in Figure 5, and these units are described in more detail in McLemore et al. (2008).

Weathering intensity varies spatially; in general, decreasing from the outer edge of the GHN rock pile to its interior and increasing toward the base of the rock pile where water and oxygen are available to dissolve pyrite and calcite to form gypsum, jarosite, soluble efflorescent salts, and iron oxide/hydroxide minerals. This hypothesis is supported in part by an observed color change from darker browns and grays in the
interior of the rock pile to yellow to white to light gray in the outer oxidized units (Figs. 5 and 6). This color change is observed primarily within the fine-grained matrix material. Rock fragments surrounded by the fine-grained matrix typically appear unweathered except along fractures and their outer edges. Thin yellow to orange, oxidized or “burnt” layers also are found within the interior of GHN, where water and/or air flow have interacted with the rock-pile material.

Figure 3. Backscatter scanning electron microprobe (BSE) images of pre-mining hydrothermally-altered samples. (a) QSP (Quartz-Sericite-Pyrite)-altered sample showing pyrite, illite/sercite and quartz, (b) propylitically-altered andesite containing epidote and chlorite replacing a feldspar phenocryst, (c) QSP-overprinting of propylitically-altered andesite sample containing pyrite, illite/sercite (groundmass) and chlorite, (d) jarosite replacing pyrite and vein filling in a QSP-altered sample. Scale bars at the bottom of the photo.

Figure 4. Geologic cross section of bench 9, trench LFG-006, located in Figure 2. Samples used for petrographic and chemical analysis were obtained at approximately 5 ft intervals. Description of geologic units is in McLemore et al. (2008). Figure 5 shows part of the bench.
Figure 5. Contact between units I, J and N in trench LFG-006, GHN. Weathering increased towards the interior of GHN.

Figure 6. A) Sample GHN-VTM-194 from Unit I (outer GHN), with predominant pale yellow color, subprismoidal to subdiscoidal and angular to subrounded shape; B) Sample GHN-VTM-197, Unit N with predominant light olive brown color, subprismoidal to subdiscoidal and angular to subrounded shape; C) Sample GHN-VTM-212- from interior Unit O, with predominant dark grayish brown color, subprismoidal to subdiscoidal and angular to subrounded shape. All samples are from bench 9. All fields of view are 6 mm.

Petrographic and geochemical analyses suggest higher abundances of jarosite, gypsum, Fe oxide minerals and soluble efflorescent salts (locally as cementing minerals), and lower abundances (to absence) of calcite, pyrite, and epidote in samples from the outer parts of the rock pile as compared to the interior (see representative diagrams in Fig. 7, plus image of epidote alteration in Fig. 9). The chemical composition of waters from the Questa rock piles (i.e., seeps and runoff waters from the rock piles), contain high amounts of SO$_4$ (up to 19,000 ppm) and Al (up to 1690 ppm) and are low pH (2-4), implying that sulfide and silicate dissolution is occurring within the rock piles. Paste pH, which is interpreted as correlating with degree of weathering, is generally lower in samples from the outer parts of the rock pile (<5) as compared to samples from the interior (>5; McLemore et al., 2008). Furthermore, chemical classification as potential acid-forming materials using acid base accounting methods also indicate that the outer parts of the rock pile are more weathered then the interior (Tachie-Menson, 2006). These color, geochemical, and mineralogical factors are all consistent with an increased level of weathering in the outer parts of the rock pile as compared to the interior.

Gypsum, iron oxides and jarosite are all mineralogical phases that, based on their textures, are precipitating in the rock pile as a result of weathering in the ~40 years since deposition; pyrite and calcite are dissolving. Cracks or fractures within rock fragments
can be filled with gypsum, jarosite, or iron oxides. Delicate iron oxides and feathery gypsum crystals, locally associated with jarosite (Fig. 8) are interpreted to form by weathering, rather than hydrothermal alteration, because it is unlikely that these delicate features could be preserved after blasting, haulage, and dumping required to form the rock piles. Stable isotopic analyses also support a weathering origin for some gypsum (Campbell and Lueth, 2008). Cementation at the formation of the rock piles was zero, so any cementation documented in the rock piles is the result of weathering (Fig. 8). In contrast, alteration of feldspars, characterized by the presence of illite and chlorite along the cleavage planes and within the cores, is interpreted to be hydrothermal (Fig. 3).

Figure 7. Variations in gypsum + jarosite, and SO\(_4\) in weight percent across bench 9, GHN. More weathered samples (units I, J, N) on the outside of the rock pile (left side of diagram) have slightly higher concentrations of gypsum + jarosite than samples from the interior. See McLemore et al. (2008, fig. 43, table 20) for geologic section and units.

Figure 8. Backscatter scanning electron microprobe (BSE) showing a) delicate gypsum blades with intergrown jarosite cement (bright phase) and b) feathery blades in adhered soil matrix.

Pyrite oxidation generates acid, which can cause alteration of other mineral phases, driving weathering processes within the rock piles. Pyrite within the Questa rock pile shows a wide range in degree of alteration from no apparent alteration (or light tarnish) to significantly altered grains, often with eroded or dissolved edges or oxidized rims (Fig.
Oxidized grains typically show leaching of S and deposition of amorphous Si +/- Al resulting in goethite rims (Heizler et al., 2007). While some of these textures could be the result of hydrothermal processes, the presence of delicate skeletal crystals or variable alteration within the same sample (i.e. grains along edges of rock fragments or within veins more oxidized than interior grains), are indicative of weathering phenomena.

Several lines of evidence support the conclusion that the majority of clay minerals in the GHN rock pile are forming not as the result of chemical precipitation under low pH during weathering over the last 25-40 years, but were formed during hydrothermal alteration of the host lithologies prior to excavation and emplacement (Donahue et al., 2009). Drill core samples collected within unweathered pre-mining host-rock material and samples from GHN have similar types and abundances of clay mineral groups based on XRD and electron microprobe analysis (Donahue et al., 2009). Backscatter electron images (BSE) of drill core samples of pre-mining host rock show primary igneous minerals being replaced by clay minerals, supporting a hydrothermal origin for the clays. Clay minerals in both the fine-grained soil matrix and the matrix of rock fragments have similar clay mineral chemical compositions, suggesting liberation of pre-existing clay minerals into the matrix during mining and emplacement. In addition, contacts between sand- and clay-size particles within the rock-pile samples are sharp and do not indicate the in-situ formation of the clay minerals.

The presence of fresh or lightly tarnished pyrite surrounded by clay minerals further suggests a hydrothermal origin. The process of weathering-related clay mineral formation would likely have resulted in pervasive pyrite oxidation (Heizler et al., 2007; McLemore et al., 2008). Stable isotope analyses of hydrogen and oxygen of clay mineral separates from rocks throughout the area also show that, to the limit of analytical detection, all clay minerals are hydrothermal in origin, with minimum temperatures of formation >100°C, which are greater than the temperatures observed in the Questa rock piles (Graf, 2008; McLemore et al., 2008; Donahue et al, 2009). Although no petrographic, mineralogic, or isotopic evidence for the formation of new clay minerals by chemical weathering in either the rock piles or in the natural analog materials was observed, clay minerals could form in the rock pile in the future if chemical conditions (mainly pH) in the pile change.

**CONCLUSIONS**

The geochemical characteristics of rock samples are important indicators of weathering, and must be well understood before weathering indices are applied to a geological system (Duzgoren-Aydin et al., 2002). In the Questa rock-pile and analog materials, dissolution of pyrite, calcite, and to a lesser extent some combination of chlorite, illite, feldspars, smectite, and other silicate minerals by acidic pore waters are the predominant chemical reactions that result in 1) the precipitation of gypsum, jarosite, soluble efflorescent salts, and iron oxide/hydroxide minerals, and 2) the geochemical signature of acidic water seeping from the rock piles. Oxygen and water are available at or near the surface and base of the rock pile, in local permeable strata within the rock pile, and along cracks and crevasses cutting across the strata. Weathering occurs in the Questa rock piles where water and oxygen are available to dissolve pyrite and calcite to form gypsum, jarosite, soluble efflorescent salts and iron oxide/hydroxide minerals. The majority, if not all of the clay minerals were formed by hydrothermal alteration of the rocks before mining.
rather than being the result of chemical precipitation in the rock pile under low pH during weathering over the last 25-40 years.

Figure 9. Backscatter scanning electron microprobe (BSE) showing a) A “clean” or unaltered pyrite cube; b) Skeletal pyrite crystals in soil matrix; c) Variably altered pyrite crystals. Intensity of alteration increases with distance from the edge of rock fragment; d) A partially dissolved epidote phenocryst with associated apatite. Figures b through d are indicative of post-mining weathering.

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