

DRA-3. CHARACTERIZATION OF THE CLAY MINERALOGY WITHIN THE ROCK PILES ON THE MOLYCORP QUESTA MINE SITE

K. Donahue, N. Dunbar, L. Heizler, V.T. McLemore, and A. Campbell, April 24, 2007, revised March 30, 2009 (reviewed by G.S. Austin, G. Robinson, Art Rose)

1. STATEMENT OF THE PROBLEM

Will clay minerals form as a result of weathering in the near- or long-term future and how will any changes in clay content or mineralogy affect the long-term stability of the rock pile? Understanding the origin of clay minerals is important because the potential generation of clay minerals by weathering processes could result in a decrease in slope stability.

2. PREVIOUS WORK

Donahue et al. (2007, 2008, 2009) discuss the origins of the clay minerals from the Goathill North (GHN) rock pile. PetraScience Consultants Inc. (2002) identified clay minerals in 32 samples from the mine site using short wave infrared spectral analyses. URS Corporation (2003) determined the clay mineral composition expected to precipitate from the dissolution of feldspars based on rinse-water chemistry of mine rock-pile materials. Lueth (2008) presents a survey of the literature and concludes that the clays found at Questa are hydrothermal in origin.

3. TECHNICAL APPROACH

- Literature review of techniques, interpretation of XRD results, and articles related to the origins of clay minerals in different environments, with emphasis on mine rock piles.
- Several different types of samples were collected (SOP 5, 9) and analyzed for clay mineralogy:
 - Rock-pile material that included both the soil matrix and rock fragments of mixtures of different lithologies and alteration assemblages
 - Samples collected from the surface and from test pits throughout the rock piles
 - Samples of the rock-pile material collected from trenches in GHN (5 ft channel or composite of selected layers)
 - Soil profiles of colluvium/weathered bedrock, alteration scar, and debris flows
 - Outcrop samples of unweathered (or least weathered) igneous rocks representative of the mined rock (overburden) (includes all predominant lithologies and alteration assemblages at various hydrothermal alteration and weathering intensities)
 - Sections of drill-core samples of the mined rock (overburden) and ore deposit before mining
 - Splits of drill cuttings from holes drilled into the rock piles and underlying colluvium/bedrock
- Selected samples were analyzed using X-ray diffraction (SOP 29, Hall, 2004; Moore and Reynolds, 1987, 1997), electron microprobe techniques (SOP 26), and stable isotope analysis (SOP 25). The XRD patterns are in the project data repository. Descriptions by electron microprobe are in the Access database (eprobe form) and photographs are in the project data repository. The stable isotope analyses are in the project Access database and Graf (2008).

- Geochemical modeling was performed using the water chemistry data from GHN to calculate the stability of clay minerals in contact with waters from GHN (DRA-28).

4. CONCEPTUAL MODEL(S)

- The Questa rock piles were constructed primarily by haul-truck end-dumping in high, single lifts, which involved the dumping of rock over the edge of the hill slopes and resulting pile crests (URS Corporation, 2003; McLemore et al., 2006; McLemore and the Questa Rock Pile Weathering and Stability Team, 2008). The GHN rock pile is stratified and consists of heterogeneous and locally alternating layers and lenses of coarse and fine rock pile material that increase in grain-size down slope (DRA-6, fig. 2).
- The mechanical liberation of the hydrothermally-altered rocks by mining activities along with subsequent physical weathering processes (i.e. freeze-thaw, thermal expansion, rebound, see DRA-27) can release hydrothermal clay minerals contained within the mined rock to form some of the fine-grained matrix of the rock-pile material. This liberation occurred during blasting, haulage, and end-dumping, in part, because the original mined rock was highly fractured before mining.
- Feldspars and other aluminosilicates are hydrolyzed by acidic pore waters, locally at temperatures of up to 70°C (DRA-7), and are dissolved via incongruent dissolution and could form new clay minerals if the geochemical conditions change.
- The alteration scars, debris flows, and colluvium/weathered bedrock in the Red River area are natural geologic analogs that can be used to predict the end products of short-term pyrite-calcite-gypsum weathering and longer-term silicate hydrolysis (DRA-19).

5. STATUS OF COMPONENT INVESTIGATION

- Electron microprobe backscatter (BSE) images of drill core samples show evidence of primary igneous minerals being replaced by pre-mining, hydrothermal clay minerals (Fig. 1a). The contacts between the sand-size rock and mineral grains within the fine-grained soil matrix are sharp and do not indicate the in-situ formation of the clay minerals into the fine-grained soil matrix (Fig. 1b, c).

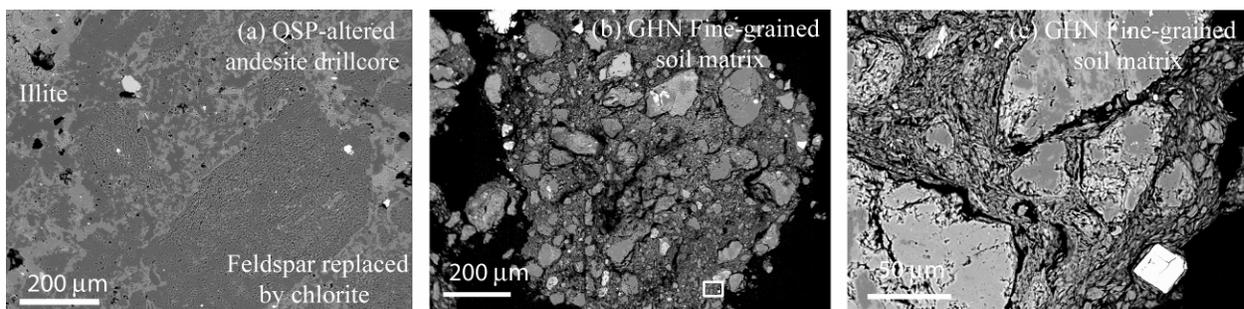


FIGURE 1. (a) Backscatter (BSE) images of QSP-altered andesite drill core, (b) fine-grained soil matrix samples from GHN rock pile, (c) the magnification of fine-grained soil matrix outlined by the white box in figure 1b.

- Samples with high relative abundances of illite and low relative abundances of chlorite tend to have higher abundances of QSP-hydrothermally altered rhyolite rock fragments (Fig. 2). Samples with higher relative abundances of chlorite tend to have higher

abundances of propylitically-altered andesite rock fragments (McLemore et al., 2008b; Donahue et al., 2008, 2009).

- Clay minerals from the fine-grained soil matrix and rock fragments of GHN samples are chemically similar to the clay minerals within the unweathered drill core (Fig. 3, 5).
- Stable isotope analyses of hydrogen and oxygen of clay mineral separates from rocks throughout the area show that, to the limit of analytical detection, all clay minerals are hydrothermal in origin, with minimum temperatures of formation $>100^{\circ}\text{C}$ (Fig. 6; DRA-17).
- Clay minerals from sample GHN-STM-0002 near the toe of GHN rock pile is similar in clay mineral composition (2% kaolinite, 0.5% chlorite, 17% illite, and 1% smectite as determined using the modified ModAn method, McLemore et al., 2009) and XRD patterns to samples obtained from unit C and I from the trenches in the upper 1/3 of the GHN rock pile.
- Clay minerals from the colluvium and native soils in the Questa mine area have similar XRD patterns as the rock pile samples. However, there is a statistically significant higher concentration of clay minerals in the colluvium and soil samples when compared to the rock-pile material (Appendix 1), which suggests that clay minerals did form by weathering in the colluvium and native soils. Although an exact age of the colluvium and native soils is unknown, they are older than the rock piles, which lie upon these materials and probably are greater in age than 1000 yrs (the upper time limit of this study). The Goat Hill debris flows was dated as 4220 ± 40 yrs (^{14}C on wood, Lueth et al., 2008).

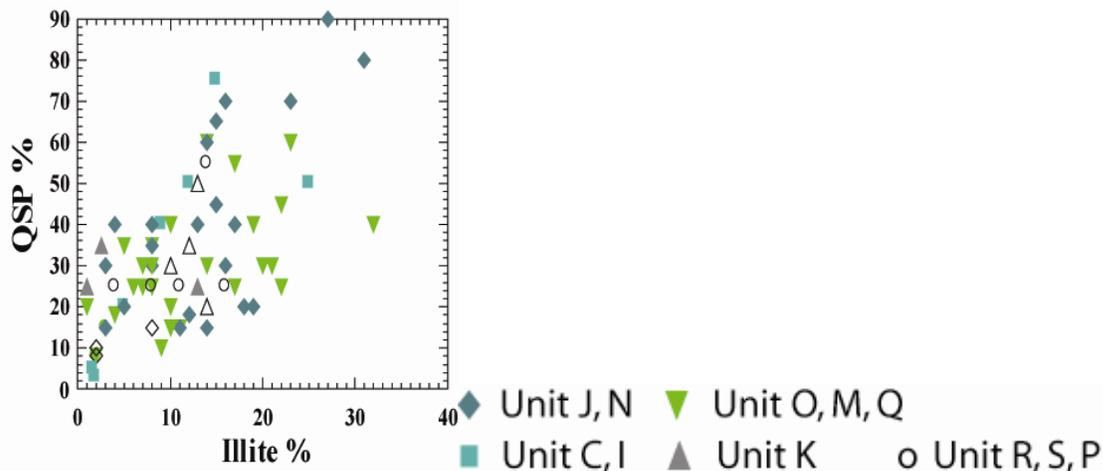


FIGURE 2. Scatter plot of QSP hydrothermal alteration versus illite within the rock fragments and soil matrix in all of GHN samples. See McLemore et al. (2008a, table 20) for description of geologic units.

Based on these investigations, the evidence strongly favors the conceptual model, i.e. that clay minerals observed in the Questa materials are derived from mechanical liberation of pre-existing hydrothermal clays from fractured rock during mining activities and subsequent physical weathering. There is no petrographic, mineralogic, or isotopic evidence for formation of significant amounts of new clay minerals by chemical weathering in either the rock piles or in the natural analog materials.

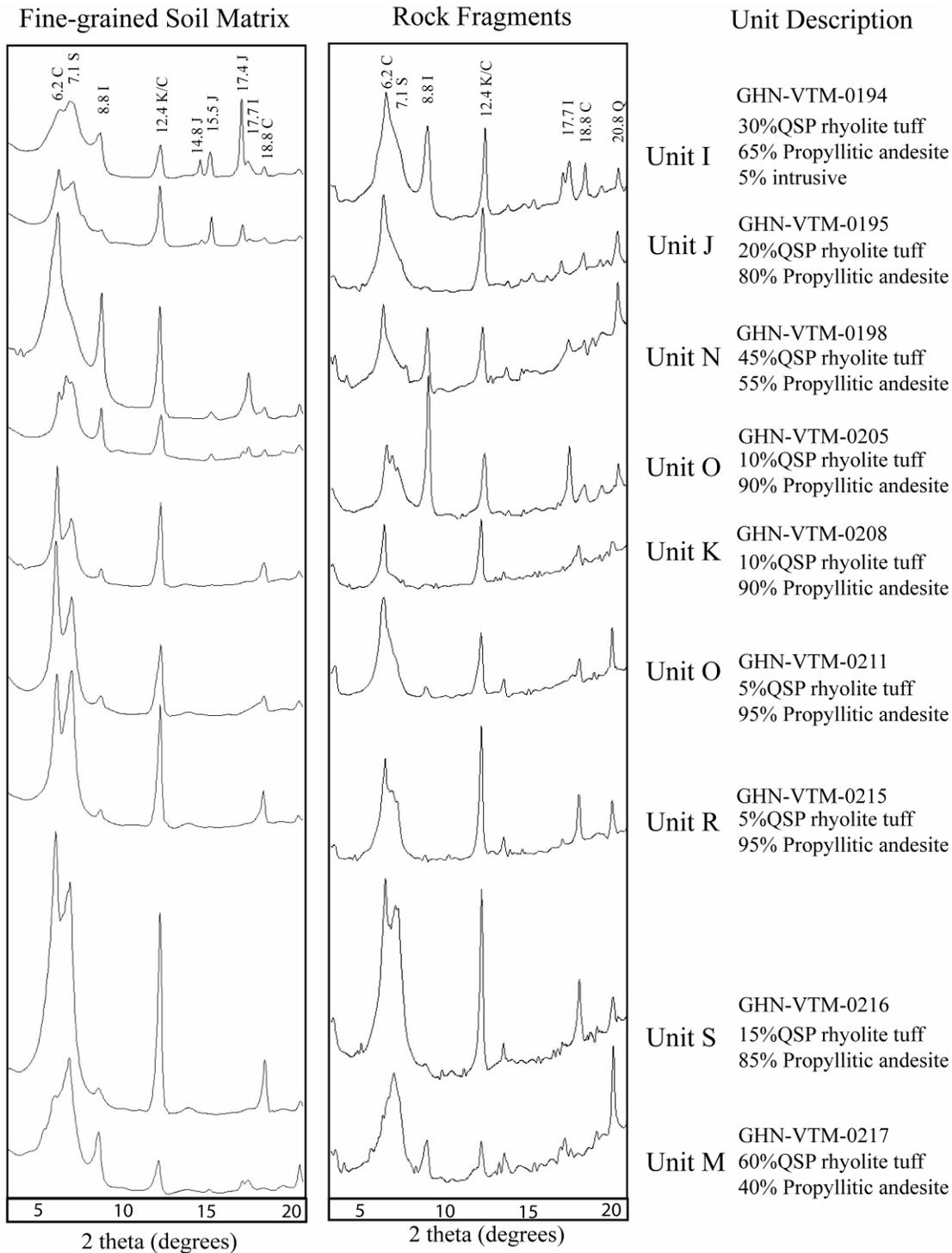


FIGURE 3. X-ray diffraction results of fine-grained soil matrix and rock fragment samples from bench 9 trench LFG-006 in the GHN rock pile. Unit descriptions include the rock fragment lithology and predominate hydrothermal-alteration mineral assemblage, estimated visually using a binocular microscope. I = illite, C = Chlorite, S = Smectite, K = Kaolinite, J = Jarosite, Q = Quartz. See Figure 4 for location and geologic section across bench 9.

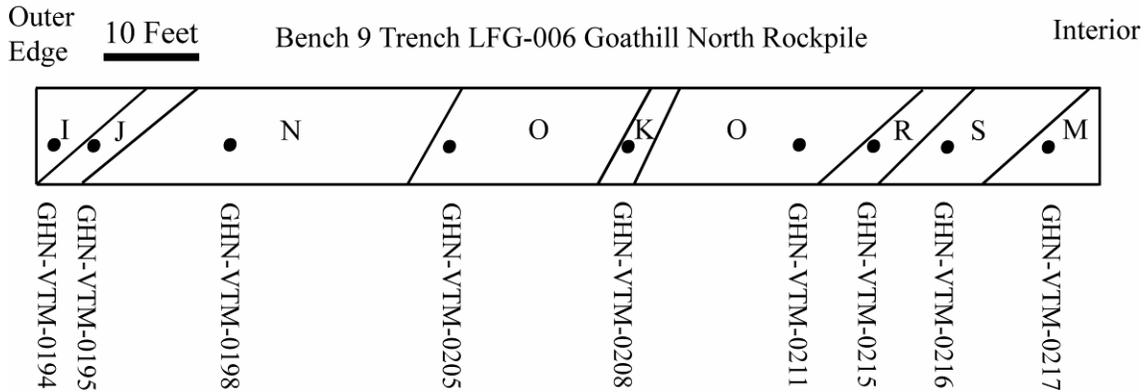
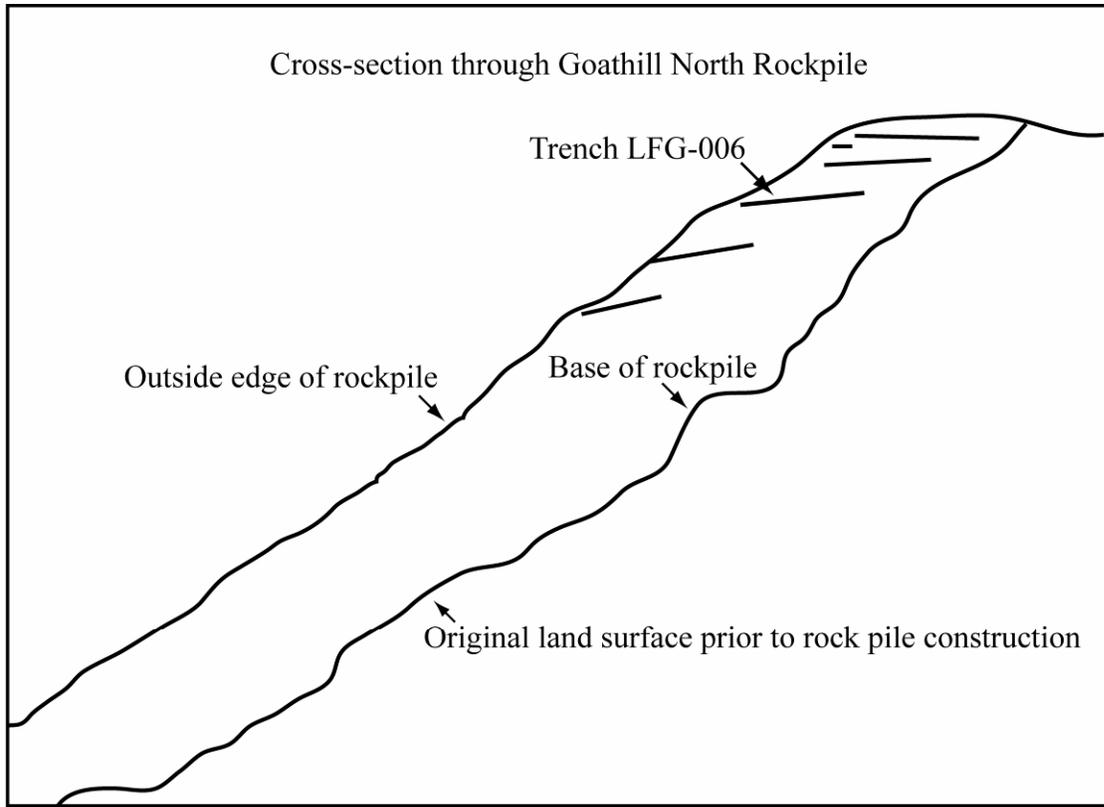


FIGURE 4. Schematic drawing of a cross section through the Goathill North rock pile along the line of the constructed trenches (McLemore et al., 2008a). The solid lines represent the location and length of the six trenches constructed in the stable portion of Goathill North. The geologic map of bench 9 from trench LFG-006 showing the sample locations and the described geologic units from the outer edge to the interior of the rock pile.

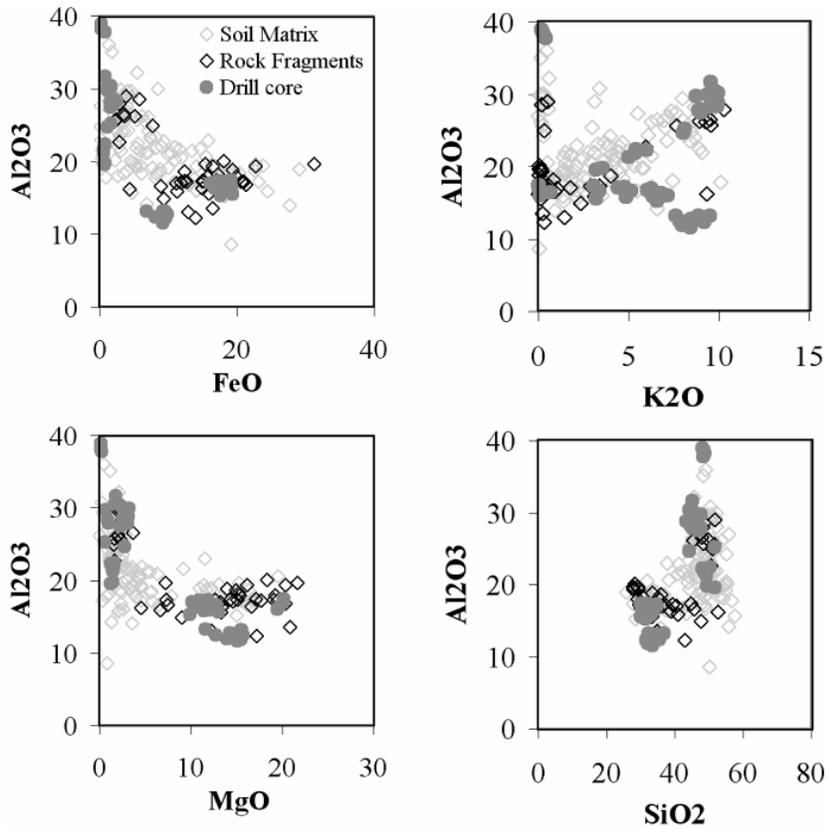


FIGURE 5. Scatter plots of mineral chemistries of clay minerals determined using quantitative electron microprobe analysis for GHN fine-grained soil matrix samples (open gray diamond), rock fragments (open black diamonds) and unweathered, drill core samples (filled gray circles).

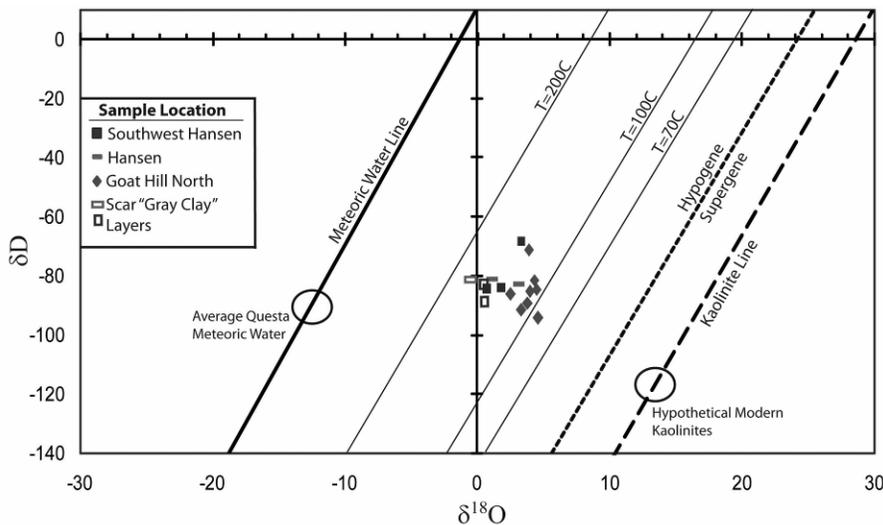


FIGURE 6. δD - $\delta^{18}O$ diagram for clay minerals from rock pile and alteration scar (Graf, 2008). The clays plot in the hypogene field, indicating an origin consistent with hydrothermal alteration. There is no isotopic evidence that clay minerals formed as a result of weathering in either the alteration scars or the rock piles.

6. RELIABILITY ANALYSIS

Drill core samples represent hydrothermally-altered rocks that have not been exposed to post-mining surface weathering. GHN rock-pile samples represent rocks that were variably hydrothermally altered, and then exposed to surface weathering since the construction of the rock piles (between 25 to 40 years). Alteration scar, debris flow, and colluvium/weathered bedrock samples represent hydrothermally-altered samples that have been weathered under surface conditions for significantly longer periods of time than the rock piles at the Questa mine. These sites serve as analogs to the Questa mine rock pile samples because they are similar in lithology, hydrothermal alteration assemblages, mineralogy, chemistry, and clay types and are affected by similar weathering processes as the rock piles (DRA-19).

Some of the technical and data uncertainties include:

- The mineralogical and petrographic techniques used for this study are not able to detect small differences in the types of clay minerals or minor changes in their mineral chemistry.
- The GHN rock-pile materials are a mixture of different lithologies and hydrothermal alteration mineral assemblages, therefore changes of mineralogy and chemistry between the outer, oxidized zone and the interior, unoxidized zones of the rock pile are a result of differences due to pre-mining composition as well as chemical weathering. These differences can be difficult to distinguish.
- Samples of the saturated toe zone were not analyzed for their clay minerals.
- The pre-treatment methods used for the clay-sized stable isotope samples are not able to remove clay-sized silicate minerals such as quartz. However, the presence of other silicate minerals was verified using the post-treatment XRD patterns. The samples for isotope analysis were not dried at high temperature and thus not all the interlayer water may have been removed from the sample. This could have a big effect on the δD values determined but not much effect on the $\delta^{18}O$. Despite the uncertainty in δD , the oxygen values still suggest that the clays were not in equilibrium with local water and thus not newly formed.

Suggested processes for resolving discrepancies in data and uncertainties include:

- The differences between the clay minerals within the matrix of rock fragments and the fine-grained soil matrix material within the rock-pile material could be an indication of in-situ weathering.
- Plots of δD - $\delta^{18}O$ against the quartz XRD peak of the sample after treatment indicate that the minor variability of the $\delta^{18}O$ is from non-clay silicate mineral contaminating the samples (Fig. 3).
- Analyze the saturated toe samples for their clay mineralogy (sample GHN-VTM-0022, GHN-STM-0010, 11).

See Appendix 2 for an alternative hypothesis on the formation of clay minerals. Although, the information in the memo is accurate, the data we have presented in this DRA and Donahue et al. (2007, 2008, 2009) indicates that, if new clays are being formed in a less acidic environment within the Questa rock piles, these new weathered clays are very minor in abundance (i.e. trace amounts less than 0.1%, below our detection limits) and will not affect the gravitational stability of the Questa rock piles. The clay minerals within the analog sites (alteration scar, debris flows) also support that only minor amounts of clays are being formed in the area over the last several hundred thousand years (DRA-19, 20, 21, 22).

7. CONCLUSIONS OF THE COMPONENT

The clay minerals within the fine-grained soil matrix of the GHN rock pile are predominantly of hydrothermal origin and are the result of the liberation from highly, fractured mined rock during mining activities and subsequent physical weathering. The majority (if not all) of the clay minerals did not form as the result of chemical precipitation in the rock pile under low pH during weathering over the last 25-40 years, but were formed by hydrothermal alteration of the rocks before mining. There are seven principal lines of evidence that the clays in GHN are predominantly from hydrothermal alteration of the host lithologies prior to excavation and emplacement into the GHN rock pile and not formed by weathering (Donahue et al., 2007, 2009):

- Electron microprobe backscatter (BSE) images of the drill core samples shows evidence of primary igneous minerals being replaced by pre-mining, hydrothermal clay minerals (Fig. 1a). The contacts between the sand-size rock fragments and mineral grains within the fine-grained soil matrix are sharp and do not indicate the in-situ formation of the clay minerals into the fine-grained soil matrix (Fig. 1b, c). There is no petrographic, mineralogic, or isotopic evidence for formation of new clay minerals by chemical weathering in either the rock piles or in the natural analog materials.
- Presence of fresh or lightly tarnished pyrite surrounded by clay minerals (Heizler et al., 2007) suggests that the clays did not form in situ because the fluid involved in clay formation would have caused pyrite oxidation.
- Clay minerals in fine-grained soil matrix and within the rock fragments of the GHN samples have similar clay mineral chemical compositions (Fig. 5).
- The unweathered drill core and samples from GHN have similar types and abundances of clay mineral groups based on XRD analyses. Chemical analyses from electron microprobe analysis of clay minerals reveal similar chemical compositions for the clays from the two environments (unweathered drill core versus weathered GHN rock-pile material, Fig. 5).
- Stable isotope analyses of hydrogen and oxygen of clay mineral separates from rocks throughout the area support the conclusion, to the limit of analytical detection, that all clay minerals are hydrothermal in origin despite the potential contamination with interlayer water (Fig. 6; DRA-17; Graf, 2008).
- Pre-mining hydrothermal clays will dissolve in a sulfuric acid environment as determined from leaching experiments on Questa clay minerals (Donahue, 2008).
- Persistence of 2M₁ illite and pyrophyllite in the alteration scars and fine-grained soil matrix of rock-pile materials indicates the hydrothermal clay minerals predominate in the fine-grained soil matrix.
- There is a statistically significant higher concentration of clay minerals within the colluvium and native soils sampled in the Questa mine area, which suggests that clay minerals did form by weathering in the colluvium and native soils. Although an exact age of the colluvium and native soils is unknown, they are older than the rock piles and probably greater than 1000 yrs (the upper time limit of this study). The mechanism of clay formation in these materials needs to be investigated further.

The possibility of a significant increase in the percent of clay minerals in the rock piles due to weathering would most likely be due to physical weathering of the rock fragments remaining in the rock-pile material or a possible change in chemical conditions that could allow for precipitation of clay minerals from pore waters. The persistence of 2M₁ illite and pyrophyllite in

the fine-grained soil matrix of alteration-scar samples indicates that hydrothermal clay minerals predominate in the fine-grained soil matrix even after a substantial duration of weathering at the surface under acidic conditions (Donahue et al., 2009).

There is some evidence that suggests the clay in the Questa rock piles have been leached or otherwise affect by weathering since emplacement in the rock piles, including 1) tritium data of clay minerals (Marston, 2009), which suggests formation of new clay minerals or replacement of existing clay minerals by modern tritium, 2) leaching of Questa clay minerals (Donahue, 2008), and 3) broadening of the clay peaks of some samples, as shown in Figure 3. The exposure to relatively low humidity coupled with moderate to high temperatures in the rock pile results in the partial dehydration of smectite clay minerals within the fine-grained soil matrix of the GHN rock pile samples. The occurrence of 1W smectite in each of the geologic units of GHN indicates that dehydration is not restricted to the exterior of the rock pile.

8. REFERENCES CITED

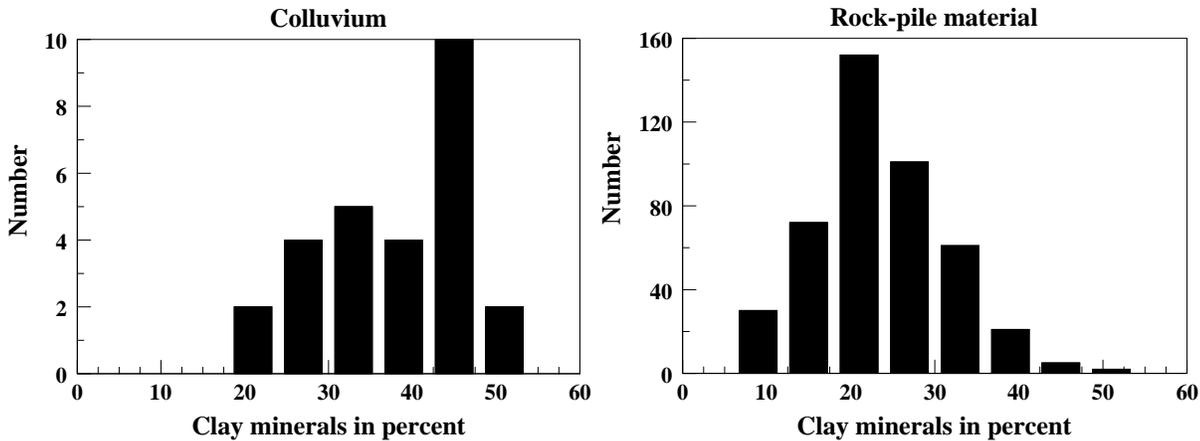
- Donahue, K.M., 2008, Clay Minerals Sulfuric Acid Leach Experiment: unpublished report to Chevron Mining Inc. 13 p.
- Donahue, K.M., Dunbar, N.W., and McLemore, V.T., 2007, Origins of clay minerals in the Molycorp Mine Goathill North Rock pile, Questa NM: Society of Mining, Metallurgy and Exploration Annual Convention, Denver, Feb. 2007, no. 07-100, 8 p.
- Donahue, K.M., Dunbar, N.W., Heizler, L., and McLemore, V.T., 2008, Origins of clay minerals in the Molycorp Mine Goathill North Rock pile, Questa NM: revised unpublished report to Molycorp.
- Donahue, K.M., Dunbar, N.W., and McLemore, V.T., 2009, Clay mineralogy of the Goathill North rock pile, Questa mine, Taos County, NM: Origins and indications of in-situ weathering: Society of Mining, Metallurgy and Exploration Annual Convention, Denver, Feb 2009.
- Graf, G.J., 2008, Mineralogical and geochemical changes associated with sulfide and silicate weathering, natural alteration scars, Taos County, New Mexico: M.S. thesis, New Mexico Institute of Mining and Technology, Socorro.
- Hall, J.S., 2004, New Mexico Bureau of Mines and Mineral Resource's Clay Laboratory Manual: Unpublished New Mexico Bureau of Geology and Mineral Resources report.
- Heizler, L., Dunbar, N., and Sweeney, D., 2007, Summary of Investigation of Tarnish on Pyrite Grains in Questa Rock Pile Samples: Unpublished report to Molycorp, Inc, Task B1.1, 3 p.
- Lueth, V.W., 2008, Clay mineral formation and stability: unpublished report to Chevron Management, Task B1
- Lueth, V.W., Campbell, A.R., Peters, L. and Samuels, K., 2008, Data report on the geochronological ($^{40}\text{Ar}/^{39}\text{Ar}$ and ^{14}C) dating of jarosite, alunite, manganese oxide, and carbon samples from the Red River area alteration scars, debris flows, and the Questa Mine, New Mexico: unpublished report to Molycorp, Inc., Task B1.2.2, 38 p.
- Marston, T.M., 2009, An evaluation of annual net infiltration to bedrock for waste rock piles near Questa, New Mexico and the development of a method for examining tritium in clay minerals: M.S. thesis, University of Utah, Salt Lake City, in preparation.
- McLemore, V.T., Ayakwah, G., Boakye, K., Campbell, A., Donahue, K., Dunbar, N., Gutierrez, L. Heizler, L., Lynn, R., Lueth, V., Osantowski, E., Phillips, E., Shannon, H., Smith, M. Tachie-Menson, S., van Dam, R., Viterbo, V.C., Walsh, P., and Wilson, G.W., 2008a,

- Characterization of Goathill North Rock Pile: revised unpublished report to Molycorp, Tasks: 1.3.3, 1.3.4, 1.4.2, 1.4.3, 1.11.1.3, 1.11.1.4, 1.11.2.3, B1.1.1, B1.3.2.
- McLemore, V.T., Donahue, K., and Sweeney, D., 2008b, Lithologic atlas for the Questa mine, Taos County, New Mexico: revised unpublished report to Molycorp (revised from appendix 2.3, May 2005 report).
- McLemore, V.T., Donahue, K.M., Phillips, E.H., Dunbar, N., Walsh, P., Guitierrez, L.A.F., Tachie-Menson, S., Shannon, H.R., Lueth, V.W., Campbell, A.R., Wilson, G.W., and Walker, B.M., 2006, Characterization of Goathill North mine rock pile, Questa molybdenum mine, Questa, New Mexico; in 7th ICARD, March 26-30, 2006, St. Louis MO: Published by American Society of Mining and Reclamation., Lexington, KY. CD-ROM, p. 1219-1249.
- McLemore, V., Sweeney, D., Dunbar, N., Heizler, L. and Phillips, E., 2009, Determining quantitative mineralogy using a combination of petrographic techniques, whole rock chemistry, and MODAN: Society of Mining, Metallurgy and Exploration Annual Convention, preprint 09-20, 19 p.
- McLemore, V.T. and the Questa Rock Pile Weathering and Stability Team, 2008, Descriptive and conceptual rock pile models: revised unpublished report to Chevron, Task B1.3.2.
- Moore, O.M. and Reynolds, R.O., Jr., 1989, X-ray diffraction and the identification and analyses of clay minerals: Oxford University Press, New York, 378 p.
- Moore, O.M. and Reynolds, R.O., Jr., 1997, X-Ray Diffraction and the Identification and Analysis of Clay Minerals, Oxford University Press, New York, 378 p.
- PetraScience Consultants Inc., 2002, PIMA Short-wave Infrared Analysis, Questa Mine Field Work: unpublished report to Molycorp, October 30, 2002.
- URS Corporation, 2003, Mine rock pile erosion and stability evaluations, Questa mine: Unpublished Report to Molycorp, Inc. Project No. 22236156.00100, 4 volumes.

9. TECHNICAL APPENDICES

- Donahue, K.M., 2008, Clay Minerals Sulfuric Acid Leach Experiment: unpublished report to Chevron Mining Inc. 13 p.
- Donahue, K.M., Dunbar, N.W., and McLemore, V.T., 2007, Origins of clay minerals in the Molycorp Mine Goathill North Rock pile, Questa NM: Society of Mining, Metallurgy and Exploration Annual Convention, Denver, Feb 2007, no. 07-100, 8 p.
- Donahue, K.M., Dunbar, N.W., Heizler, L., and McLemore, V.T., 2008, Origins of clay minerals in the Molycorp Mine Goathill North Rock pile, Questa NM: revised unpublished report to Molycorp.
- Donahue, K.M., Dunbar, N.W., and McLemore, V.T., 2009, Clay mineralogy of the Goathill North rock pile, Questa mine, Taos County, NM: Origins and indications of in-situ weathering: Society of Mining, Metallurgy and Exploration Annual Convention, Denver, Feb 2009.

APPENDIX 1. Comparison of clay minerals in the colluvium and soil to clay minerals in the rock-pile material. See DRA-3a for complete descriptive statistics and histograms.



APPENDIX 2. Memo on Formation of Clay Minerals

The recognition that low pH and other chemical concentrations in the discharge from the GHN rock pile implies instability of clay minerals (DRA 30) is a very important accomplishment of the research project. To the extent that pore fluids in a section of a rock pile have such a low pH and similar major element chemistry, the accumulation of clay in contact with such a pore fluid is essentially impossible. Any clay would tend to dissolve in such a water.

However, careful study of the detailed data indicates that some segments of the rock pile do not have pore fluids of low pH. If the pH is above about 5, clay minerals are stable. A calculation using PHREEQC shows that in GHN spring water evaluated at pH 5, several clay minerals are supersaturated (Ca-montmorillonite, Illite, K-mica and kaolinite). A similar calculation at pH 4 shows stability of Ca-montmorillonite, K-mica and kaolinite. Therefore, if the pH of pore fluids are above about 4, clay minerals can be formed and persist.

Evidence for higher pH in some units of the pile includes the following:

1. In the suite of samples collected on Bench 9, Trench LFG006, samples from units O,S and RUB have paste pH values of 5 to 8 (DRA27, Figure 4-3). This result strongly suggests that pore fluids in these units are not strongly acid, but are neutral to alkaline. Cross-sections showing all the samples in GHN tested for Paste pH show a zone of near-neutral paste pH in the middle of the GHN pile (Figure 96 in Final Trench Report). In contrast shallow units have paste pH values less than 4

2. In the same suite of samples in Trench LFG006, most of the samples below 60 ft on the traverse have positive Net Neutralization Potential (DRA27, Figure 4-8). This means that the carbonate in the samples will more than neutralize acidity from oxidation of pyrite in the sample. Most of these samples contain only traces of pyrite, but percent level calcite as well as epidote, a relatively unstable and neutralizing Ca silicate (DRA27, Fig. 4-4).

3. Humidity cell leaches of samples from the same trench have leachate pH values of 5 to 8 (DRA35C, Figure 2-1). Also, leaching tests of samples from units R,S, and M show leach pH of 5-7 (DRA26, Figure 7).

4. The only really high contents of pyrite are in surface unit I at depths of 0-5ft, with 3% pyrite; all deeper samples have <1% pyrite, and most have only 0.1%. Research conducted at Penn State shows that samples with <0.5% pyrite rarely generate acid (Brady et al., 1994).

Based on this information, we suggest that considerable acid is generated by the high pyrite contents near the surface and penetrates the top few units (C, I, N), but this acid is either consumed by the lower units or flows down the layering and does not penetrate the units in the

middle of the pile. Possibly some acid is generated in the deeper layers, related to air flow in these coarse units. This interpretation provides the possibility for clay formation and accumulation in a zone in the middle of the pile, and possibly deeper where little data exists.

A zone of clay enrichment is potentially significant because it might decrease the strength of a layer directly because of the softness and slippery quality of the clay, or it might form an aquiclude that would trap water behind and above it, allowing for increase of pore pressure.

A zone of clay enrichment might develop by in situ alteration of feldspars or other aluminosilicates, or by accumulation of clays mobilized from other units. The total amounts of hydrothermal clay (illite, chlorite, kaolinite) in the rock are very large, and if this clay was mobilized from its original host and accumulated in a limited zone, a considerable accumulation could be formed.

References

Brady, K.B.C., Perry, E.C., Beam, R.L., Bisko, D.C., Gardner, M.D., and Tarantino, J.M., 1994, Evaluation of acid-base accounting to predict quality of drainage at surface coal mines in Pennsylvania, U.S.A. U.S. Bureau of Mines Special Publication SP06A-94, p. 138-147.