ORIGINS OF CLAY MINERALS IN THE MOLYCORP MINE GOATHILL NORTH ROCK PILE, QUESTA, NM

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Abstract

There are three principle lines of evidence that indicate the clay minerals found in the Goathill North (GHN) rock pile at the Molycorp mine are predominantly a product of hydrothermal alteration, not weathering. The unweathered drill core and samples from GHN have similar chemical compositions for the hydrothermal alteration clays in drill-core samples and clays found in the rock pile. Textural evidence gathered from petrographic and microprobe examination also suggests a hydrothermal origin for clay minerals.

Purpose

Rock piles, the preferred term by many in the metal mining industry today, refer to the man-made structures consisting of piles of non-ore material that had to be removed in order to extract ore. This material, referred to in older literature as mine waste, mine soils, overburden, subore, or proto-ore, does not include the tailings material, which consists of non-ore material remaining after milling. Stability of rock piles has become a concern at many mines in North America, because mines are typically required to develop and implement a mine closure plan and before bonding is released, long-term stability of these and other structures must be assured. Understanding how clay minerals form and the rate of clay mineral formation in the rock pile is important in order to determine if clay minerals will form as a result of weathering in the near- or long-term future. A critical increase in the amount of clay minerals within the rock pile could decrease the slope stability due to the effect of clays on hydrologic characteristics of the rock pile.

The purpose of the Molycorp weathering study is to assess conditions and processes occurring in the rock piles, especially related to the physical and chemical weathering of rock-pile materials at Molycorp's Questa mine in Taos County, NM (Fig. 1). Weathering is the disintegration of rock by physical, chemical, and/or biological processes, at or near the surface that results in reduction of grain size, change in cohesion or cementation, and change in mineralogical composition. For the purpose of this study, weathering refers to the changes in the rock-pile material after emplacement. A key component of this investigation is to estimate changes in these materials, if any, that have occurred since construction of the rock piles, and subsequently develop a model to extrapolate changes that could occur in the future. As a result, it could be possible to determine the effect of weathering on the geotechnical behavior of the rock piles as a function of time. The current approach is to test the geotechnical behavior of samples across a range of weathering intensities that are characterized by petrology, mineralogy, and chemistry for samples collected from the existing rock piles and elsewhere in the Questa-Red River area. As part of this study, type and composition of clay minerals were examined to determine the origin of the clay minerals.

Description of site

The Questa molybdenum mine is located on the western slope of the Taos Range of the Sangre de Cristo Mountains in northern New Mexico (Fig. 1). The mine is on southward facing slopes and is bounded on the south by the Red River and on the north by mountain divides. The geology and mining history of the area is complex and are described by others (Carpenter, 1968; Clark, 1968; Lipman and Reed, 1989; Meyer and Leonardson, 1990; Czamanske et al., 1990; Roberts et al., 1990; Meyer, 1991; Meyer and Foland, 1991; Robertson GeoConsultants, Inc. 2000a, b; Ross et al., 2002; Rowe, 2005).

The mine began production in 1919 from underground workings. Open-pit removal of overburden began in 1964; ore production from the open pit began in 1965 and ended in 1982, at which time approximately 73.5 million tons of ore with an average grade of 0.185% MoS2 had been processed (Schilling, 1960, 1990; Ross et al., 2002; McLemore and Mullen, 2004). The elevation of these rock piles ranges from 2301 to 3020 m. Underground mining resumed in 1982 using block-caving mining methods to extract the deeper molybdenum ore. During the open-pit period of mining, approximately 317.5 million metric tons of overburden rock was excavated and end-dumped onto mountain slopes and into tributary valleys, thereby forming the rock piles examined in this study (URS Corporation, 2000).

The Goathill North (GHN) rock pile is one of nine rock piles created during open-pit mining and contained approximately 10.6 million metric tons of overburden material with slopes similar to the original topography. GHN was divided into two areas: a stable area and an unstable area (Fig. 2). The unstable area had slid down slope since its construction. Molycorp stabilized this rock pile by removing material from the top portion of both areas to the bottom of the pile (Norwest Corporation, 2003). This regrading decreased the slope, reduced the load, and created a buttress.

Figure 1. Location of Molycorp Questa mine, northern Taos County, New Mexico.
to prevent movement of the rock pile. During the progressive down-cutting of the top of the stable portion of GHN (regrading), trenches were constructed to examine, map, and sample the internal geology of the rock pile (McLemore et al., 2005, 2006a, b).

Prior studies (McLemore et al., 2005, 2006a, b) found that the outer portion of the GHN rock-pile material can be described generally as hydrothermally altered rock fragments that were subsequently exposed to surface conditions and oxidized to moderately weathered with a considerable amount of clay minerals within the matrix and rock fragments. Weathering (oxidation) decreased from the outer edge of the rock pile to its interior and then increased toward the base of the rock pile. The inner portion of the GHN rock pile is slightly weathered and also contains clay minerals. The GHN rock pile is stratified, and the strata can be mapped and correlated down slope through the rock pile.

Figure 2. GHN before regrading, looking east. The dashed line indicates the boundary between the stable and unstable portion of GHN, the solid line is the approximate location of the trenches constructed during the fall of 2004 and spring of 2005.

Rock fragment lithology is generally consistent within each mapped unit and correlates well with bulk mineralogy and chemistry of each unit. Field and laboratory analyses indicated the GHN rock pile consisted primarily of hydrothermally-altered andesite and rhyolite (Amalia Tuff) rock fragments. Unaltered rhyolite (Amalia Tuff) is a gray to reddish brown welded ignimbrite (ash flow tuff) that typically contains 10-20% phenocrysts of alkali feldspar (albite-orthoclase) and quartz with sparse ferrohedenbergite, fayolite, and sodic amphibole. The unaltered coarsely porphyritic andesite contains plagioclase, quartz with sparse ferrohedenbergite, fayolite, and sodic amphibole. Contains 10-20% phenocrysts of alkali feldspar (albite-orthoclase) and quartz with sparse ferrohedenbergite, fayolite, and sodic amphibole. The unaltered coarsely porphyritic andesite contains plagioclase, quartz with sparse ferrohedenbergite, fayolite, and sodic amphibole.

Procedures

Field sampling and laboratory procedures are described in McLemore et al. (2005, 2006a, b) and project SOP (standard operating procedures) reports. Three types of samples were analyzed for this study. Samples of the fine-grained matrix material (i.e. soil-like) of the GHN rock pile were collected during excavation of the trenches during reclamation (McLemore et al., 2006a, b). Samples of drill core of the open pit deposit drilled before the open-pit deposit was mined were collected to represent the deposit before weathering in the rock pile. In addition, a sample of andesite and adjacent soil were collected from Fourth of July Canyon near Red River as representative of a less hydrothermally-altered andesite.

Clay mineral identification of major clay-mineral groups was performed using standard clay separation techniques and X-ray diffraction (XRD) analyses of the clay-mineral separate on an oriented glass slide (Hall, 2004; Moore and Reynolds, 1989). The semi-quantitative method used at the New Mexico Bureau of Mines and Mineral resources indicates the presence and estimates the amounts of the clay-mineral groups illite, smectite, kaolinite, chloride, and mixed layer illite-smectite (I/S) in parts per ten. It does not differentiate between specific clay-mineral species.

Samples were mixed with deionized water to suspend the clay minerals in solution. If the sample flocculated, it was rinsed with de-ionized water up to 5 times and a deflocculant sodium hexametaphosphate was added (Moore and Reynolds, 1997). Clay slides were allowed to air-dry and were then analyzed using XRD techniques. The clay slides are run on the XRD from 2° to 45° 2-theta for 3 runs, oriented, glycolated and heated. The clay-mineral relative abundances are determined using a set of equations to calculate the abundances of the five main clay types (kaolinite, illite, chloride, smectite, and I/S) using the first, second, and third order peak heights (intensities) (Hall, 2004). The clay-mineral relative abundances are reported in parts per ten instead of percentages due to the lack of precision using the peak height equation method.

Samples were prepared for microprobe analysis by placing a split of the sample in a one-inch round sample disk, vacuum impregnating with epoxy, and polished with a series of grit polishing cloths. Electron microprobe backscattered electron (BSE) imaging and quantitative analysis were performed using a Cameca SX-100 electron microprobe at New Mexico Tech. The quantitative analyses were accomplished using a 15 kV accelerating voltage and 10 nA beam current. The beam was broadened to between 20 and 25 microns in order to be able to determine average abundances of clay mineral areas. Analyses were carried out for 9 major elements, plus S, F and Cl. The microprobe can not analyze for structural water held in the clay minerals resulting in low total element weight percentages for the clay minerals (Table 1). Quantitative analyses were accomplished using a 15 kV accelerating voltage and 10 nA beam current. The beam was broadened to between 20 and 25 microns in order to be able to determine average abundances of clay mineral areas. Analyses were carried out for 9 major elements, plus S, F and Cl. The microprobe can not analyze for structural water held in the clay minerals resulting in low total element weight percentages for the clay minerals (Table 1). Count times were 20 seconds for all elements except S and Cl (40 seconds) and F (60 seconds). Standard ZAF matrix correction techniques were used. Analytical precision was determined based on replicate analyses of standard reference materials with similar composition to unknowns (Table 1).

Results and Discussion

Clay types and abundances

Clay-mineral analyses of the GHN rock pile revealed the presence of five phyllosilicate minerals groups: chlorite, illite, smectite, and kaolinite, and mixed layered illite-smectite (I/S) clay minerals. Twenty-one rock-pile samples along a single bench (bench 9) of an excavated trench (LFG-006) in GHN were analyzed for relative abundances of clay minerals (Fig. 3, 4). The samples were channel composites collected along approximate 5-ft-long horizontal slots using a rock hammer to chip material from bench walls into a sample bag. Samples were collected within each defined unit and did not cross unit boundaries. The inner units of the rock pile are darker in color and contain more abundant chlorite and smectite. The outer units of the rock pile are yellow to orange in color and contain more kaolinite and I/S clay minerals. Very few samples from the GHN rock pile contain abundant kaolinite. Soil petrographic analyses for lithology and alteration types from bench 9 were compared to the relative clay-
mineral types and abundances determined by XRD for the same samples on bench 9 (Fig. 3, 4). The results indicate the relative abundances of the clay minerals are most likely controlled by the pre-mining host-rock lithology and hydrothermal alteration. Samples with higher percentages of propylitically-altered andesite typically have higher amounts of chlorite, while samples with higher percentages of quartz-sericite-pyrite (QSP)-altered rhyolite (Amalia Tuff) have higher amounts of illite and smectite (Fig. 3, 4). Similar results were found by PIMA spectroscopy and XRD Rietveld analyses by PetraScience Consultants Inc. (2002) on samples from the front rock piles.

Drill-core samples represent material that has never been subjected to surface weathering. These samples were crushed and analyzed to identify the clay-mineral types within the bedrock presumably without the effects of weathering. The results indicate that for each major lithology (ryolite and andesite), the same clay minerals are present in the rock-pile samples as are present in the pre-mining drill-core samples. The clay minerals within a propylitically-altered andesite drill-core sample (PIT-KMD-0008) are mostly illite, chlorite, and I/S mixed-layer clay minerals (Fig. 5). The andesite, both propylitic- and QSP-altered drill-core samples, contains each of the four main clay minerals and random mixed-layer I/S clay minerals. The QSP-altered rhyolite drill-core samples only contain illite and minor amounts of kaolinite.

Figure 3. The relative clay-mineral abundances of chlorite, illite and smectite (kaolinite and I/S clays shown in Figure 4) for bench 9 samples shown in parts per ten. The major host-rock lithologies and hydrothermal-alteration type (prop = propylitic, QSP = quartz-sericite-pyrite) are from petrographic descriptions of the rock fragments within the fine-grained matrix from samples along bench 9. Sample numbers are located in the scaled figure representing bench 9, and correspond to each UTM easting. The outer edge of the rock pile is on the left (NW) and the bench cuts into the interior of the rock pile as you move across to the right 9NE. A geologic sketch is in McLemore et al. (2005, 2006a, b).

Two less-altered andesite samples (one rock and one weathered soil adjacent to the rock outcrop) were taken from Fourth of July Canyon area outside of the mine site to determine the effects of weathering on an andesite that was not subjected to high degrees of hydrothermal alteration. The XRD diffractograms (Fig. 6a, b) show the rock and soil clay minerals found in this sample. The rock sample only contains smectite and not any other major clay-mineral types. The soil sample contains both smectite and I/S clay minerals. This suggests a less-altered (hydrothermal) but weathered andesite would most likely produce smectite and mixed layer clay minerals. The presence of chlorite and illite within the rock-pile samples further suggests that these clay minerals are predominantly due to hydrothermal alteration.

Figure 4. The relative clay-mineral abundances of kaolinite and random mixed-layer I/S (chlorite, illite, and smectite shown in Figure 3) clay minerals for bench 9 samples shown in parts per ten. The major host-rock lithologies and hydrothermal alteration type (prop = propylitic, QSP = quartz-sericite-pyrite) are from petrographic descriptions of rock fragments within the fine-grained matrix from samples along bench 9. Sample numbers are located in the scaled figure representing bench 9 and correspond to each UTM easting. The outer edge of the rock pile is on the left (NW) and the bench cuts into the interior of the rock pile as you move across to the right 9NE. A geologic sketch is in McLemore et al. (2005, 2006a, b).

Figure 5. X-ray diffractogram of drill-core sample PIT-KMD-0008 showing the presence of illite, chlorite, and I/S clay minerals with other minerals such as gypsum and quartz. Kaolinite and smectite are not major clay-mineral types within this sample.

The shape of the clay XRD peaks gives another indication of the origins of the clay minerals. The smectite peak of less-altered andesite sample has a narrower peak than the smectite peak of the weathered soil (Fig. 6a, b). The broadening of the X-ray diffraction peak in the weathered soil is due to disordering of the clay-mineral structure shown as a wide base on the smectite peak (Fig. 6b), ascribed to weathering of the rock (Moore and Reynolds, 1997). Samples from the
outer and inner portions of GHN rock pile both have narrow clay XRD peaks, suggesting that weathering of the clay minerals is minor (Fig. 7a, b).

**Clay-mineral chemistry**

Geochemical analysis of the clay minerals by microprobe analysis indicates the majority of the clay minerals are chlorite and illite (Table 1). These are characteristic minerals of hydrothermal alteration at Questa (Molling, 1989; Meyer, 1991).

![Figure 6. X-ray diffractograms of a less-altered andesite sample from Fourth of July Canyon showing the presence of only smectite for the rock (A) and weathered soil sample (B).](image)

The chemical compositions of clay minerals as analyzed by electron microprobe vary widely (Fig. 8). One reason for this variation is the intimate intermixture of clay minerals in the samples and the different hydrothermal-alteration intensities and stages. Isolated areas of end-member clay minerals, including chlorite, random mixed-layer I/S, smectite, and kaolinite were identified (Table 1). The Al₂O₃ concentrations are lower than idealized alumina concentrations for end-member clay minerals (39.55% Al₂O₃ for kaolinite as per Deere et al., 1966) and could be related to interstratified kaolinite-smectite clay minerals with Mg substituting for Al in the clay-mineral structure (Dudek et al., 2006). These clay minerals typically form from different stages of hydrothermal alteration, and the presence of both minerals in single samples may be the result of multiple hydrothermal events. Chlorite, a Fe- and Mg-bearing clay, is mainly found in the andesitic rock samples. This may be related to hydrothermal alteration of Fe- and Mg-bearing silicate phases. The lack of these phases in the rhyolite (Amalia Tuff) can explain the relatively low abundance of chlorite in this rock type. Within the fine-grained matrix of GHN rock-pile samples, illite and chlorite also are the most common clay phases observed, but areas of kaolinite and smectite (most similar in composition to montmorillonite) were observed.

![Figure 7. X-ray diffractograms of clay samples from bench 9 trench LFG-006 showing the sharp x-ray peaks for clay minerals from the weathered exterior of the rock pile (GHN-VTM-0196, a) and the interior of the rock pile (GHN-VTM-0211, b).](image)

Similar mineral-chemical compositions between drill core and GHN clay samples (Fig. 8, 9) were observed (Fig. 8 and 9). Many of the clay-mineral chemical analyses represent a mixture of clay-mineral phases. The clay minerals are not discrete areas of one clay-mineral type. On these diagrams, the high Si, low Fe points represent more illitic compositions, whereas the low Si, higher Fe compositions are chloritic. The points in between represent combinations of the two phases that could not be distinguished separately due to the width of the microprobe beam. The presence of a number of analyses with very low Si and very high Fe contents on the geochemical diagrams also illustrate the presence of amorphous Fe-oxide phases mixed with the clay minerals or due to leaching of the clay minerals during weathering of the GHN rock pile. Due to the very fine-grain size of the clay minerals and Fe-bearing phases, many analyses include combinations of both.

When examining the clay-mineral chemistries for all microprobe samples, there is no clear distinction between samples within the GHN rock-pile and drill-core samples. The graphs show the clay-mineral chemistries overlap, while the spread in the data for the on the graphs reinforces the suggestion that multiple clay-mineral phases are present (Fig. 8, 9). The drill-core samples have never been exposed to surface weathering processes therefore; hydrothermal alteration is the most likely process for forming the clay minerals in the drill core. The similar chemical compositions observed for rock-pile and drill-core samples suggest clay minerals have the same origin. The minor differences between chemical compositions of some clay minerals within the drill-core and GHN rock-pile samples could be explained by subsequent leaching of the GHN clay minerals during weathering.

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Clay-mineral textures

Backscattered electron imaging of drill-core samples indicate that clay minerals have replaced primary igneous phenocrysts (Fig. 10), as would be expected during hydrothermal alteration. The clay minerals within a propyltically altered andesite drill-core sample (PIT-KMD-0007) are mostly contained within the silicate phenocrysts and not as clay veins or pockets.

This also is true for samples from the GHN rock pile, in which clay minerals are typically found replacing phenocrysts throughout the rock fragment. Most primary mafic silicates in the rock fragments are completely replaced by clay minerals, and many feldspar crystals are selectively replaced. Clay minerals are found in spatial association with other phases, such as epidote, that are a product of hydrothermal alteration. Clay minerals are not found to form along fractures in the rock fragments, or along the edges of rock fragments that were exposed to weathering within the GHN rock pile.

Table 1. Representative clay-mineral chemistries determined by electron microprobe analysis.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>P2O5</th>
<th>SiO2</th>
<th>SO2</th>
<th>TiO2</th>
<th>Al2O3</th>
<th>MgO</th>
<th>CaO</th>
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<tr>
<td>GHN-NWD-0008-20</td>
<td>0.00</td>
<td>30.90</td>
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<td>0.01</td>
<td>16.42</td>
<td>15.96</td>
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<td>GHN-NWD-0017-13</td>
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<td>27.76</td>
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<td>0.00</td>
<td>16.26</td>
<td>18.21</td>
<td>0.11</td>
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<tr>
<td>illicic clay</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>GHN-NWD-0021-14</td>
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<td>26.44</td>
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<td>0.25</td>
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<tr>
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<td>0.00</td>
<td>0.07</td>
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<td>1.57</td>
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<td>kaolinite clay</td>
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<td></td>
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<td></td>
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<td>0.05</td>
<td>23.79</td>
<td>2.09</td>
<td>1.42</td>
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Notes: Geochemical quantities are in weight %. Analytical precision, based on replicate analyses of standard reference materials of similar composition to the unknowns, are as follows (all in wt.%): P2O5±0.02, SiO2±0.47, SO2±0.01, TiO2±0.03, Al2O3±0.12, MgO±0.07, CaO±0.02, MnO±0.06, FeO±0.06, Na2O±0.55, K2O±0.27, Cl±0.07.

Figure 8. Electron microprobe analyses of clay-mineral-rich locations in rock and fine-grained matrix samples. The open circles are clay mineral analyses from drill-core samples, blue diamonds are clay mineral analyses of the GHN rock-pile samples.

Figure 9. Electron microprobe analyses of clay-mineral-rich locations of drill-core rock and rock-pile samples. The open circles are clay mineral analyses from drill-core samples, blue diamonds are clay mineral analyses of the GHN rock-pile samples.

Figure 10. Back-scattered electron image of a drill-core sample PIT-KMD-0007 showing clay minerals contained within a feldspar phenocryst. Clays are represented by the rough-appearing areas of the sample surface.
Based on electron microprobe analysis, clay minerals are present in the fine-grained matrix component of all GHN rock-pile samples, as well as in many rock fragments from the GHN rock-pile material. The fine-grained matrix component of GHN samples contains a clay-mineral matrix surrounding rock and mineral fragments. Large relict igneous feldspar phenocrysts crystals within the rock fragments contain isolated pockets of clay minerals and the groundwork of rock fragments also contains pockets of clay minerals. Fresh or slightly tarnished pyrite cubes are locally surrounded by clay minerals (Fig. 11, 12).

An important aspect of the textural investigation is that the contacts between the rock/mineral grains and the clay matrix are very sharp, as would be expected during hydrothermal alteration but not weathering. In these samples, there is no indication of in-situ breakdown of rock or mineral grains to form clay minerals, but rather the clay minerals appear to have infiltrated between the rock/mineral fragments. A possible genesis of these clay minerals is that they were transported/dumping process, and filtered from those broken fragments into their current location.

![Back-scattered electron image of a fine-grained matrix of sample GHN-NWD-0019 showing the abundant clay minerals surrounding rock clasts and mineral grains.](image1)

A possible explanation for the texture of the clay minerals in the matrix is that they were either transported via water or crept through by differential pressure or compaction. The moisture content of the rock pile does not seem to lend itself to the transport of clay minerals by water, although local layers within the rock pile likely were saturated and allowed water transport (Shannon, 2006). The most plausible explanation is the clay minerals were physically moved and squeezed from pressure within the pile or during the placement and compaction of the material in the rock pile.

**Conclusions**

There are three principal lines of evidence that the clay minerals in GHN rock pile are predominantly formed from the hydrothermal alteration of the host lithologies prior to excavation and emplacement into the GHN rock pile and not formed by weathering of silicate minerals:

- the unweathered drill core and samples from GHN rock pile have similar types and abundances of clay mineral groups based on XRD analyses
- chemical analyses from electron microprobe analysis reveal similar chemical compositions for the clay minerals from the two environments (unweathered drill core vs. weathered GHN rock-pile material)
- textural evidence gathered from electron microprobe examination suggests that the clay minerals did not form in situ.

Other observations that suggest the clay minerals are not the result of silicate mineral weathering is the presence of fresh or lightly tarnished pyrite cubes surrounded by clay minerals. The mechanical grain-size reduction from mining activities can release the clay minerals contained within the silicate phenocrysts resulting in more “free clay” within the rock piles. Physical weathering in the rock pile, can cause the rock clasts to break apart releasing more hydrothermal clay minerals into the matrix as well as creating clay-size fraction material of minerals such as quartz and feldspar. There is no conclusive evidence to suggest there are abundant clay minerals forming today in the GHN rock pile from the weathering of feldspars or other minerals in the rock pile since its emplacement. Some of the reasons for the lack of clay-mineral formation as a result of silicate mineral weathering process could be 1) little or no oxidation within the interior of the GHN rock pile, 2) low amounts of water within the GHN rock pile (average moisture contents less than 15%, Shannon, 2006), and 3) relatively short time that the GHN rock pile has been in place. Several studies indicate the silicate minerals will weather to clay minerals at a much slower rate than pyrite and calcite will weather (Gleisner, 2005; Gleisner et al., 2003; Salmon, 2003). The buffering capacity from carbonate minerals in the system will decrease the rate of weathering of silicate minerals by neutralizing sulfuric acids produced from the oxidation of pyrite.

The evidence from the techniques used in this study suggests the clay minerals in GHN are the result of hydrothermal alteration; however clay minerals could be produced from weathering of silicate minerals in quantities that are not detectable with the technology available for this study. The abundance of clay minerals resulting from the weathering of silicate minerals will increase as the amount of time the rock pile is exposed to weathering increases.
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