Diavik Waste Rock Project: Mineralogical Investigation of Sulfide Mineral Weathering Products in Low-sulfide Waste Rock from an Operational Stockpile in the Arctic

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ABSTRACT
The weathering of sulfide minerals in waste rock at mine sites can generate acidity and contribute sulfate, metals and other trace constituents to drainage. This study examines sulfide-mineral weathering in waste rock from the Diavik Diamond Mine, located 300 km northeast of Yellowknife, Northwest Territories, Canada. Samples of drill cuttings from drill holes installed in the operational waste-rock stockpile were mounted in thin sections and analyzed to discern weathering and oxidation products and patterns. Mineralogical investigations using optical and scanning electron microscopes were conducted to identify the sulfide-mineral assemblages and their oxidation products, and to locate mineral grains for further characterization using synchrotron-based techniques. The Advanced Photon Source at Argonne National Laboratory was used to obtain μ-XRF element distribution maps and μ-XRD patterns along transects of sulfide grains. The complementary nature of these techniques allows for a more rigorous investigation of the weathering processes within the sparse sulfide mineral assemblage at Diavik.

Key Words: sulfide oxidation, weathering, mineralogy, synchrotron XAS, permafrost, low-sulfide

INTRODUCTION
Mining activities in northern climates have seen a steady increase in recent years. As operations in the North continue to follow this trend, further study into the effects of subaerial waste-rock storage under permafrost conditions will be valuable to current and future mines. A laboratory and field-based study, which is currently being conducted at the Diavik Diamond Mine (Diavik), examines the physical and geochemical responses of low sulfide waste rock stored in the continuous permafrost region. Characterizing early-stage mineralogical conditions of waste rock and the effect of permafrost formation on sulfide mineral oxidation can assist in evaluating the extent of weathering that may proceed in the upper freeze/thaw active zone in waste rock piles, and the quality of drainage that may be released to the surrounding environment. This paper describes a component of the mineralogical studies conducted on samples of waste rock collected from the large-scale waste rock pile, as part of the Diavik Waste Rock Research Project.

Diavik is located 300 km northeast of Yellowknife, Northwest Territories, Canada on a 20 km^2 island in the oligotrophic lake Lac de Gras. The ore deposits are three kimberlite pipes hosted in Achaean country rock, which is primarily composed of granite and granite pegmatite. Biotite schist occurs as xenoliths within the granite and hosts the majority of the sulfide minerals. Diabase also occurs in minor amounts as dykes that crosscut the site (Jambor 1997, Smith 2009). During mining operations, the waste rock is segregated based on sulfur content and stored in designated areas of the waste dump. The waste-rock pile is expected to reach up to 120 Mt at the time of mine closure. The waste rock designations are:

- Type I: < 0.04 wt % S
- Type II: 0.04-0.08 wt % S
- Type III: > 0.08 wt % S

Type I waste rock is composed almost exclusively of granite and is considered non-acid generating. Any trace sulfides in the granite are generally small grains of pyrite. Type II waste rock contains small amounts of biotite schist contributing to the sulfide content, and Type III contains biotite schist in greater amounts, which brings the overall sulfide content above 0.08 wt % S. The primary sulfide mineral in Type III Waste rock is pyrrhotite present in the biotite schist.

For this study, mineralogical samples were taken at various depths from drill holes installed in the Type III portion of the stockpile (Figure 1). These samples were studied to determine the extent and nature of weathering reactions occurring in the sulfide mineral assemblage as a result of blasting and exposure to subaerial weathering. Because the sulfide content of the waste rock at Diavik is very low, advanced techniques, including scanning electron microscopy (SEM) and synchrotron-based analyses, will be used to determine the composition of reaction products on the sulfide grains.

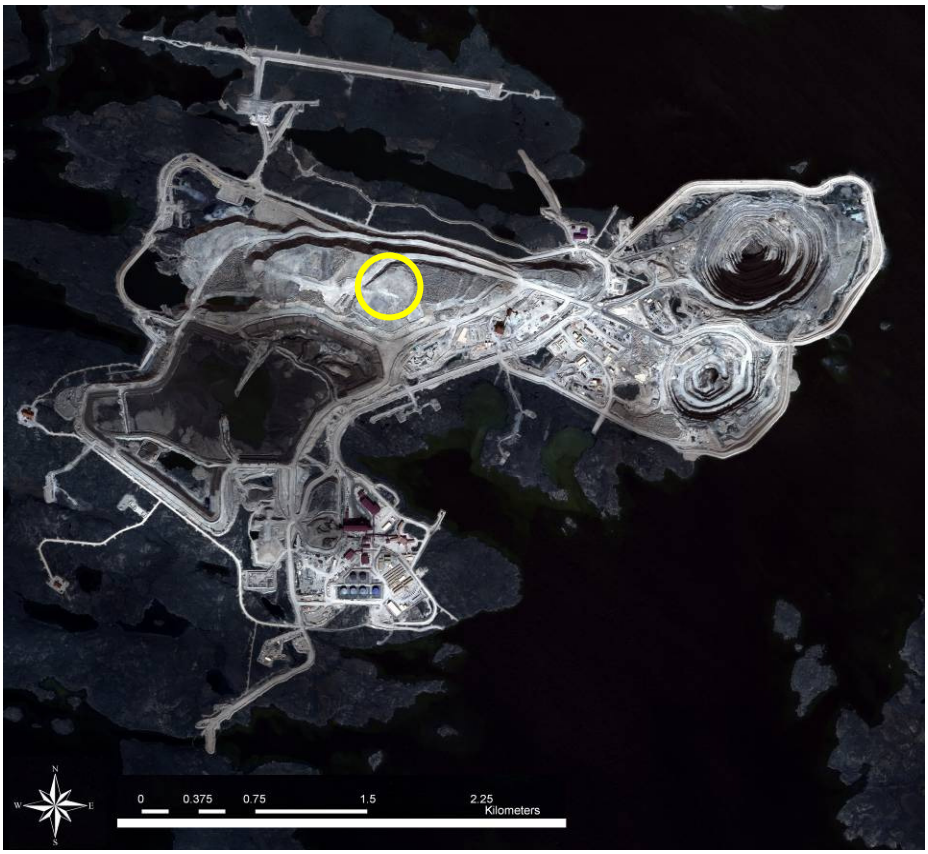

Figure 1: Location of drill holes on the operational waste-rock stockpile at Diavik (circled).

METHODS

Sample collection and preparation

Samples for mineralogical analysis were collected from three 8-inch diameter drill holes installed in the operational waste-rock pile in May of 2010. The holes drilled were approximately 30-40 m in depth and were located approximately 200 m from the outer edge of the waste rock stockpile. All three of the drill holes were installed and instrumented for further characterization of the pile. Instruments installed in each drill hole include gas sampling ports, permeability measurement devices and unsaturated zone water samplers at various depth intervals. The centre stock supporting the instrumentation in one drill hole allows for insertion of a thermal conductivity measurement probe, and in another provides support for

microbiological culture sampling. As the first borehole was drilled, cuttings were sampled at 4 m depth intervals to a maximum depth of 32 m. Cuttings samples from 32-40 m in depth were collected in the same manner from the third borehole, which was the only one of the three that reached the maximum target depth. All samples were split using a riffle-splitter into sample sizes of less than 60 mL, which were appropriate for mounting in thin section (ASTM 2003). Samples from every second depth interval were prepared in thin section by Vancouver Petrographics in Langley, British Columbia. Three polished thin sections were prepared for each selected depth interval without the use of water in polishing to prevent possible loss of oxidation products of the sulfide assemblage or dissolution of soluble secondary mineral phases. In addition, one removable thin section per selected depth interval (approximately 100 µm thick) was prepared to facilitate synchrotron-based analysis in both transmission and fluorescence modes.

Microscopy

Before using synchrotron-based techniques, all of the polished thin sections were examined for general mineralogical trends and sulfide-mineral characterization by optical microscopy. Optical investigation was also used to locate and identify sulfides exhibiting visible reaction rims that would be appropriate for analysis by synchrotron-based techniques, including micro-X-ray fluorescence (µ-XRF) mapping and micro-X-ray diffraction (µ-XRD). Grains of interest were subjected to further characterization with a variable-pressure scanning electron microscope (SEM) at CANMET in Ottawa, Ontario. The SEM was used to collect back-scatter electron (BSE) images of mineral grains, energy dispersive X-ray spectra (EDX) of minerals, coatings and surrounding features and EDX element maps.

Synchrotron analysis

All synchrotron analysis was conducted at GSECARS beamline 13-BM-D at the Advanced Photon Source (APS), Argonne National Laboratory, Argonne, Illinois. High resolution µ-XRF element maps of individual sulfide grains, and corresponding µ-XRD patterns along transects of these grains, were obtained from the removable thin sections. These sections were removed from their slides and placed between layers of Kapton® tape before mounting on the instrument stage at the beamline.

The incident beam energy used to collect the µ-XRD patterns was refined to 21 keV (0.59040Å) with a sample to detector distance of approximately 500 mm. This allowed patterns to be collected to a 2è angle of approximately 27°; a range that prevents defocusing of the spectra (He 2003). Powdered CeO_2 was used to calibrate the incident beam wavelength, sample-to-detector distance, tilt angle and rotation. The resulting Debye–Scherrer pattern were processed with the fitting program Fit2D™ (Hammersley, et al. 1996, Hammersley 1998) to generate a one-dimensional 2θ plot simulating powder diffraction results. These final patterns were then analyzed using the Materials Data Inc. (MDI) commercial software Jade and the International Centre for Diffraction Data (ICDD) database.

MINERALOGICAL RESULTS

Optical analysis

Optical analysis of the drill-hole thin sections showed an overall sulfide-mineral assemblage consistent in abundance and composition with the previous studies conducted on the Diavik waste rock (Jambor 1997, Blowes and Lodgson 1998). In general, pyrrhotite grains were more abundant than pyrite and much larger in size. As well, pyrrhotite had more frequent indications of weathering than pyrite, indicating the more reactive nature of pyrrhotite. Based on sulfur concentrations averaged over the whole depth, the waste rock at the drilling location generally falls into the designation of Type II to Type III. The presence of higher concentrations of pyrrhotite is consistent with this waste-rock type as pyrrhotite is associated with the biotite schist found in the Type II and Type III designations.

Pyrite grains within the samples were generally quite small (20-50 µm), and exhibited very little weathering compared to the pyrrhotite grains (Figure 2). These grains were often identified based on their

euhedral shape and distinct edges. Due to their small size and low relative abundance, they were examined optically and using SEM, but not using synchrotron-based techniques. Pyrite was also seen as veinlets grown along the basal cleavage of biotite (Figure 3). In some cases, these veinlets showed evidence of alteration and were further investigated using the SEM, however their location and narrow alteration features made them inappropriate for analysis by synchrotron-based techniques.

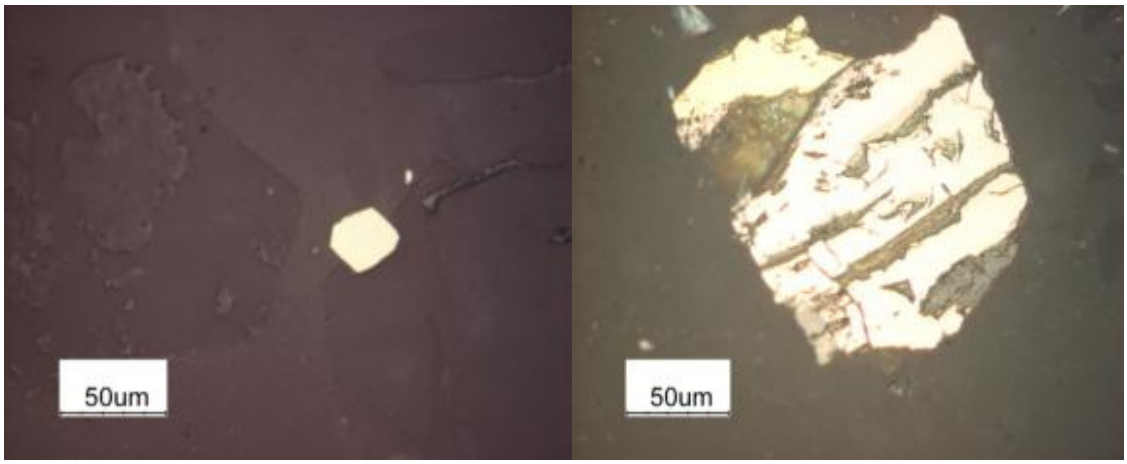

Figure 2: Characteristic small, unaltered pyrite grains (left) contrasted with the larger pyrrhotite grains (right) showing parallel alteration patterns, both under reflected light. This sulfide mineral grain size and the extent of sulfide oxidation are typical of characteristics observed throughout the drill hole.

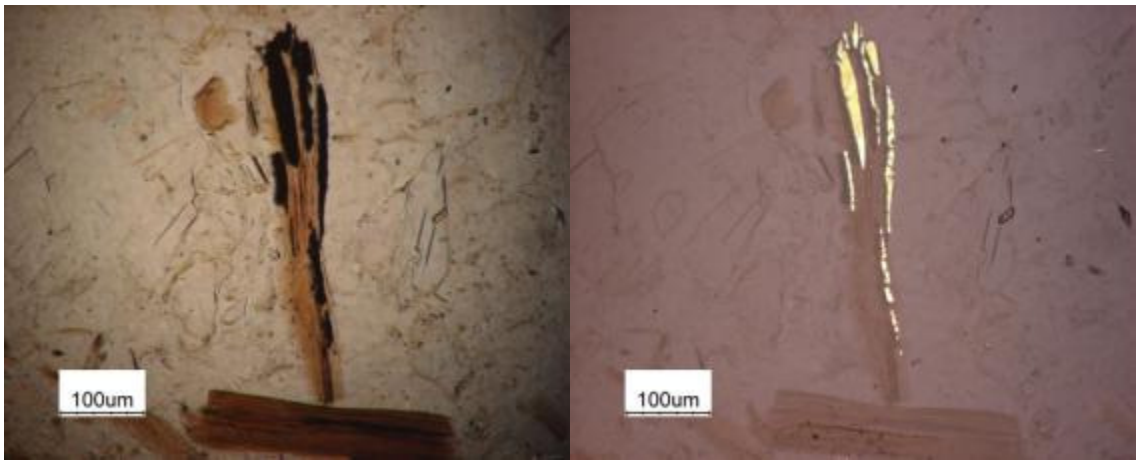

Figure 3: Pyrite growth along basal cleavage of biotite. Under plane polarized light (left) and reflected light (right).

Many of the pyrrhotite grains examined illustrated that there were varying degrees of mineral alteration along the depth of the drill holes and within each thin section. Distinct and well developed zonation of altered sulfide minerals did not follow a discernable pattern. Previous mineralogical analysis of the waste rock at Diavik shows that fresh samples contain sulfide minerals that do not exhibit extensive alteration, however exposure to atmospheric conditions quickly causes oxidation of the pyrrhotite (Jambor 1997). As a waste rock pile matures in a permafrost environment, the rate of sulfide mineral oxidation would be expected to slow as permafrost develops at depth. Additionally, oxidation would be anticipated to

continue seasonally in the upper freeze/thaw active zone. However, because the majority of the waste rock in which the borehole was drilled was dumped in a short period of time, the lack of major differences in oxidation between sample depths is not unexpected.

SEM observations

SEM analysis of the thin sections was effective in determining relative elemental compositions of the sulfide minerals and the reaction products that were seen along grain edges and in fractures extending into grains (Figure 4). In this example, the pyrrhotite has developed cracks seen across the face of the grain exposed in the thin section, which may be a result of oxidation reactions followed by subsequent desiccation (Pratt, et al. 1994). Closer examination of the cracks shows that oxidation has continued after this stage. The elemental maps obtained from the SEM-EDX spectra show that the concentration of iron across the grain extends into many of the fractured areas; however the sulfur is less abundant. This may be an indication of iron (oxy)hydroxide formation occurring in the voids as the pyrrhotite weathers. The silica map corresponds spatially to maps of aluminum and potassium and shows that some of the voids, especially where iron concentrations are lower, have increased concentrations of these elements. Many of the mineral grains in both the sulfide assemblage and matrix granite exhibited rims rich in aluminum and silica, often associated with iron in the rims associated with pyrite and pyrrhotite. The aluminum, silica and potassium present in reaction rims may be an accumulation of elements scavenged from concurrent weathering of micaceous minerals.

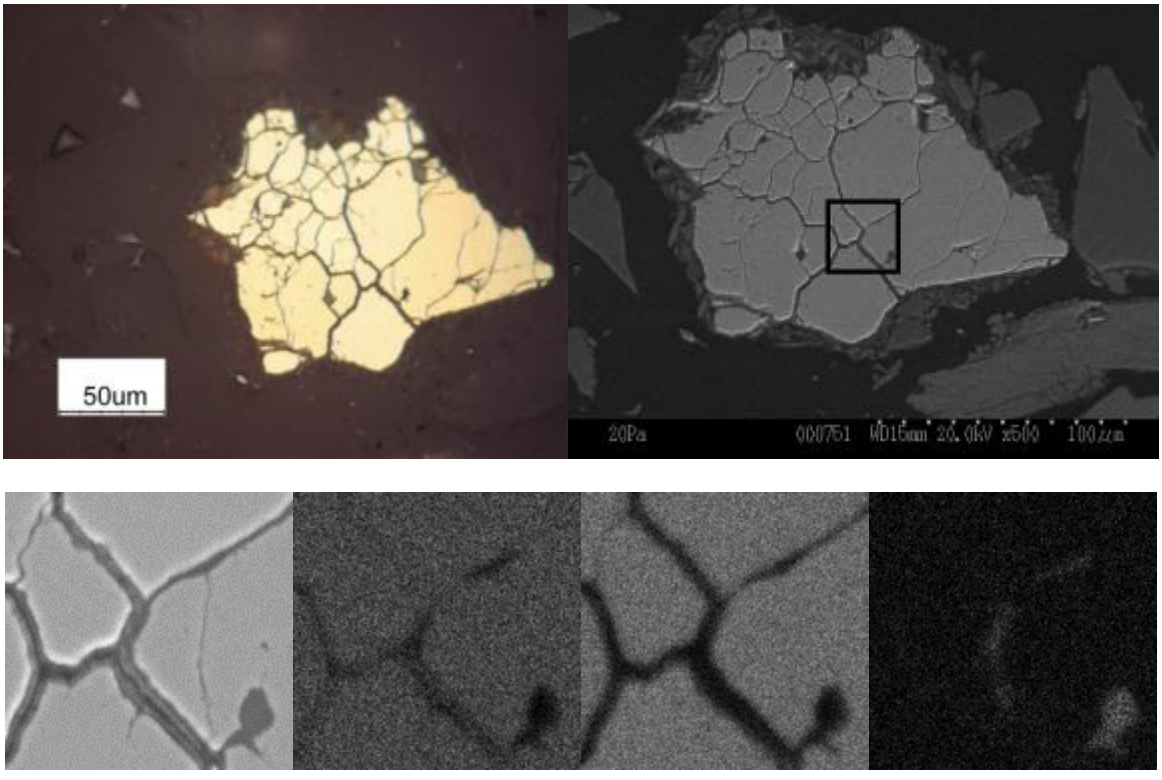

Figure 4: Top images show the same weathered pyrrhotite grain under reflected light (left) and the back-scatter image from SEM (right). Lower images are the SEM-EDX element maps of the highlighted area on the larger SEM back-scatter image. Areas with lighter shading indicate higher concentrations of each element analyzed.

Synchrotron results

Before collecting μ-XRD patterns from weathered sulfide grains in the drill hole samples, high-resolution μ-XRF element distribution maps were analyzed to discern specifically the distribution of iron, nickel, copper or zinc within a grain, and delineate the locations along which a μ-XRD transect could be measured (Figure 5).

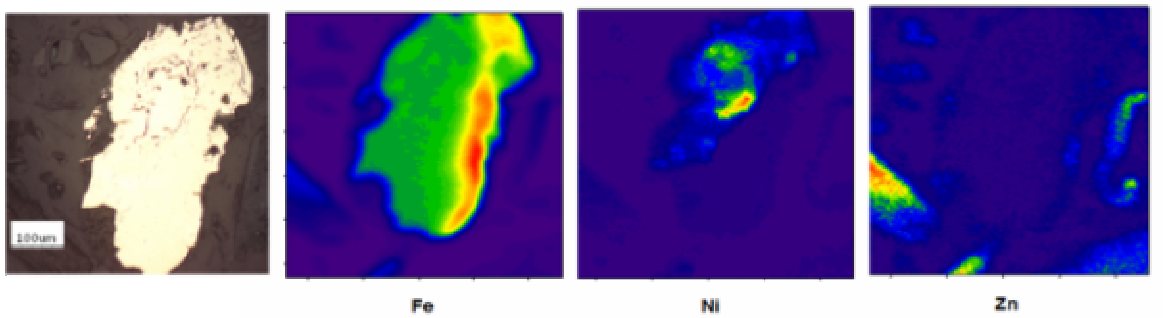

Figure 5: Sulfide grain from 16-20 m drill hole depth in reflected light, and corresponding μ-XRF elemental distribution maps for Fe, Ni, and Zn obtained at APS.

Six μ-XRD transects were collected across different grains from the drill hole over the course of the beamtime at APS in November 2010. Transects were chosen to cross locations with elements of interest and areas that showed evidence of oxidation. The size of the incident beam was small enough to allow very close examination of the changes in the elemental composition of the sulfide mineral grains. In some cases, the resultant patterns contained intensity variations in the Debye-Scherrer rings which made them difficult to analyze. The locations analyzed in these cases likely did not contain sufficient material in randomly oriented crystallites to produce a definitive X-ray diffraction pattern (He 2003).

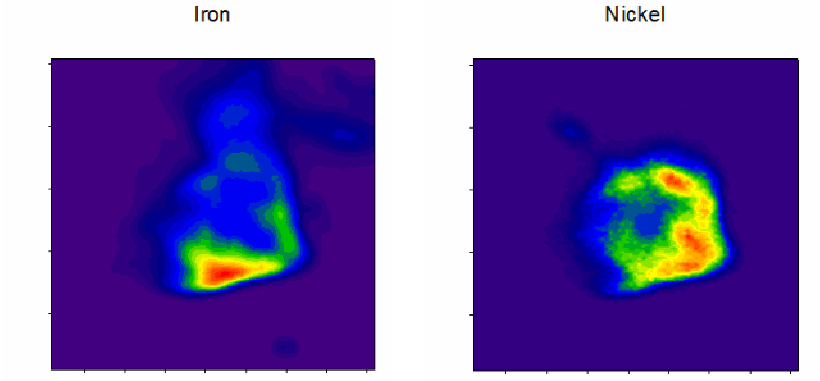

Figure 6: Iron and nickel μ-XRF elemental maps used to determine the location of the grain edges and best location for a transect of μ-XRD patterns to be gathered.

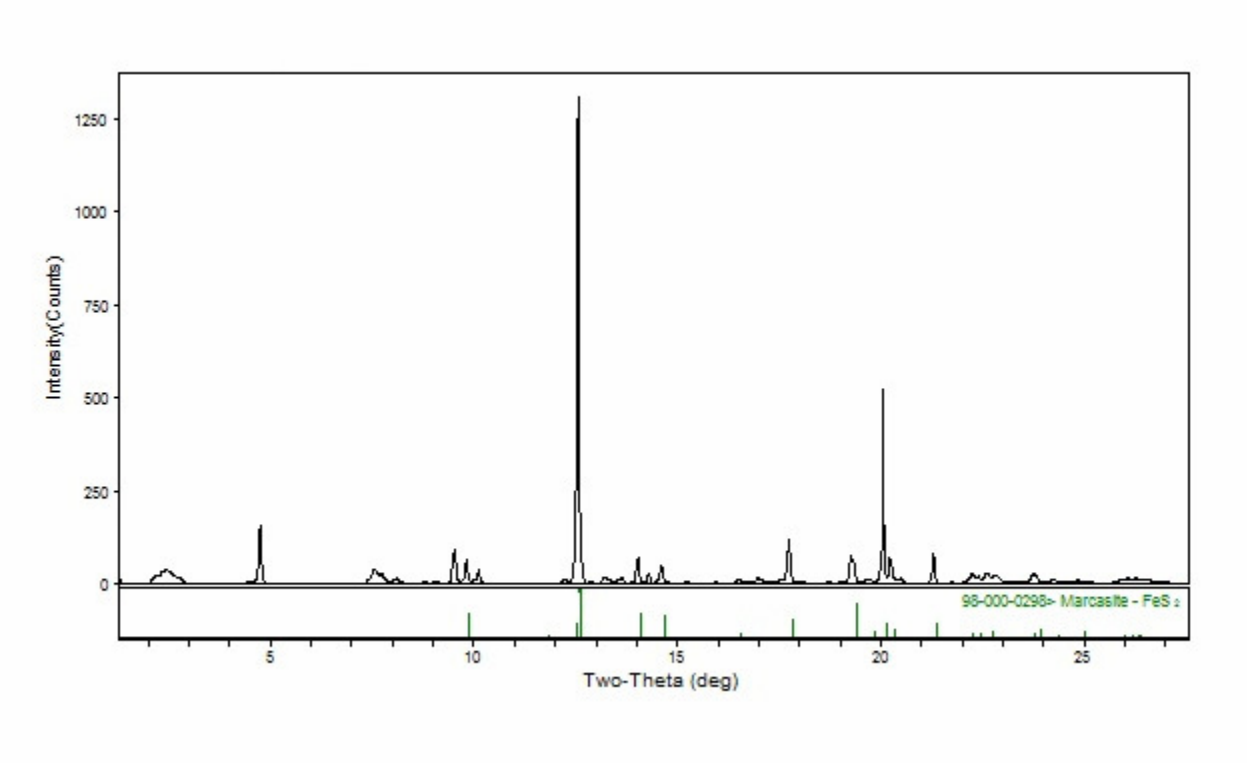

Figure 7: μ-XRD pattern analysis with MDI Jade software showing presence of marcasite. A reference pattern for marcasite is shown below the sample pattern. This pattern is from a μ-XRD spectrum collected near the edge of the above sulfide grain.

One of the transects that yielded readily interpretable results (clearly delineated Debye-Scherrer patterns) was from a weathered grain at the 24-28m depth interval of the first drill hole. The outer edges of the sulfide grain can been seen in the iron and nickel μ-XRF element maps (Figure 6), which were then used to determine the most suitable location to take μ-XRD patterns, and gain the most information about the outer coatings of the grains. Several of the spectra along the edge of the grain revealed the presence of marcasite (Figure 7), which is an indicator of early-stage oxidation of pyrrhotite (Blowes and Jambor 1990). It should be noted that the resultant 2θ plots often do not follow the intensity trends in the pattern peak heights that would be expected in powder diffraction samples. This can often occur in samples which do not contain a reasonable distribution of randomly oriented crystals (He 2003). Although analysis can often be difficult, the synchrotron results presented have been successful in the identification of early stage pyrrhotite oxidation products.

CONCLUSIONS

The combination of petrographic, SEM and synchrotron-based mineralogical investigations provide an excellent complement for characterization of the weathering products of sulfide minerals. In the case of the Diavik waste rock with its low sulfur content, these methods allow for an in-depth analysis of the composition of the sparse sulfide mineral assemblage and investigation of early-stage oxidation products. The waste rock sampled from this borehole location at Diavik has experienced oxidative conditions sufficient to cause the formation of oxidation products on the outer rims of some sulfide grains. Continued use of these methods to study samples from the waste-rock stockpile will help determine weathering trends in low sulfide waste rock stored subaerially in a permafrost region.

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Acronyms

µ-XRF	Micro-X-ray fluorescence
µ-XRD	Micro-X-ray diffraction
SEM-EDX	Scanning electron microscope – energy dispersive X-ray
ICDD	International Centre for Diffraction Data check
BSE	Back-scatter electron image