Petrographic, Geochronology, and Geochemical Analyses of the Ox Frame Andesite and Biotite Quartz Diorite, Sierrita Mine, Arizona

by

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Abstract

The Freeport-McMoRan Copper & Gold Company Sierrita Mine is located in the Sierrita Mountain Range, approximately 30 miles south of Tucson, Arizona. Two rock types, the Ox Frame Andesite and the Biotite Quartz Diorite (BQD), are two of the seven hosts to mineralization at the mine. The andesite is a problem rock type that causes the mill throughput to slow down and there is concern that the geochemically similar BQD will also contribute to throughput issues. Petrography, Whole Rock Geochemistry, XRD/CEC analyses, and Geochronology were applied to gain further knowledge about the cause of the throughput issues and increase knowledge of the mining district. The research and analyses performed on these rock types led to the conclusion that chlorite, potassium feldspar, kaolinite, and the lack of biotite are the minerals contained in these rock types that cause the throughput issues at Sierrita.

Introduction

Igneous-hosted magmatic hydrothermal deposits like porphyry copper systems are the most significant producers of copper worldwide, they also produce substantial amounts of Mo, Au, Re and minor amount of Pb, Zn and Ag (Sillitoe, 2010). Knowledge about many aspects of porphyry copper deposits has broadened immensely over the past several decades and especially since the mid-1960s (Titley and Beane, 1981). Porphyry deposits are characterized by their large tonnages and relatively low ore grades and, geologically, for the disseminated character of their ore minerals that occur both in narrow, closely spaced veins and within hydrothermally altered rock (Seedorff et al, 2005). The Sierrita Porphyry Cu-Mo deposit is located physiographically in the Basin and Range province of the Western United States (Fig. 1). More specifically, the deposit is positioned in southern Arizona in the Sierrita Mountains approximately 30 miles south of Tucson in the Pima Mining District (Fig. 2). Included in this district are the Sierrita-
Esperanza (Sierrita), Mission-Pima, Twin-Buttes and San Xavier Porphyry Cu-(Mo) deposits (Stavast, 2006). The Sierrita deposit occurs on the eastern flank of the Sierrita Mountains and contains source and host rocks of Jurassic to Tertiary age (Titley, 1982).

It has been hypothesized that recent milling issues at the Sierrita mine could have geologic origins. The Ox Frame andesite, a host rock with significant potassic alteration, is one of the problem rock types and has had difficulties with mill throughput in tons per hour (TPH). It is speculated that the Biotite Quartz Diorite (BQD) will also have issues with throughput because of mineralogic similarities that are shared with the Ox Frame andesite. During mine processing, throughput is a term used to express the expected time in hours it will take for tons of rock to grind to the target size in a ball mill. Mill throughput ranges from good throughput at 315 to 300 tons per hour (TPH), to bad throughput from less than 300 TPH to 250 TPH, to really bad throughput, which is anything less than 250 TPH. Recently, Sierrita has created a group of people that bring both milling expertise and mining knowledge together who work as a team to help improve production. It was suggested to look geologically at the Ox Frame andesite and the BQD to determine the cause of the milling problem or to eliminate geologic reasons for the TPH issues. The purpose of this study is to utilize petrographic and geochemical analyses to a) determine if there are any mineralogic and/or textural relationships between mill throughput and the Ox Frame andesite, b) compare any relationships found between the Ox Frame andesite and the BQD for potential indicators of future TPH behavior for the BQD, and c) date the Ox Frame andesite and the BQD with U/Pb geochronology to set better constraints on rock unit boundaries. Geochronology will also allow for a time-space comparison with the Mission-Pima deposit.

The hypothesis is that geologic characteristics of the Ox Frame andesite are the reason for mill throughput issues. Determining unique qualities of the andesite related to throughput could
lead to a resolution with milling. In addition, correlating these qualities to the BQD could ultimately lead to the ability to resolve any throughput issues that may arise with BQD as well. Systematically studying the petrography and geochemistry can potentially uncover key variables for answering the milling question. Geochronology will define where the Ox Frame andesite and the BQD reside within the pit and make it possible to discuss geological history in relation to another deposit within the same district.

**Background**

**Sierrita Deposit Geology**

The source of mineralizing magma at the Sierrita mine is interpreted as the Ruby Star granodiorite batholith (Preece and Beane, 1982). There are four cupolas that are sources of mineralization; the Ruby Star granodiorite (GD), the Esperanza quartz monzonite porphyry (QMP), the West Sierrita quartz monzonite porphyry, and the North Sierrita granite porphyry. The North Sierrita granite porphyry is the last pulse of mineralization, the most evolved magma, and is barren. Host rocks to this mineralization include the Ox Frame rhyolite and andesite, Harris Ranch quartz monzonite, BQD, Ruby Star GD, Esperanza QMP, and the West Sierrita QMP. The style of mineralization is that of a porphyry Copper-Molybdenum system, copper as the principal mineral and moly as a by-product from milling. In the hypogene environment, the type of mineralization is predominantly Cu-Mo veining. Early in the history of the mine, the supergene environment on the Esperanza side was mostly eroded and what had not been eroded was mined away. The principal ore-forming minerals are chalcopyrite and molybdenite, with trace amounts of bornite. Cu-oxides consist of chrysocolla, cuprite, azurite, and malachite, but occur only minimally, as do Fe-oxides such as hematite, jarosite, and goethite. The dominant alteration styles are potassic and phyllic, which can be seen at different levels of abundance and
are overprinted by one another. Propylitic alteration is peripheral and argillic alteration can be seen as clays along structures and in the leach cap.

**Ox Frame Andesite and Biotite Quartz Diorite (BQD)**

The Ox Frame andesite is one of multiple units in a volcanic package of Jurassic age, which are the oldest rock units of stratigraphic importance (Fig. 3). The Ox Frame andesite is the middle member in a succession that ranges from rhyolite to andesite tuffs. The lithology of this extrusive unit is an aphanitic to porphyritic rock that varies from black to green in color, and where porphyritic small phenocrysts of plagioclase are visible. Typical alteration of the Ox Frame andesite is seen in the chloritization of biotites and the sericitization of feldspar minerals.

The BQD is much younger than the Ox Frame andesite, having been dated by Cooper, 1971, at 67 Ma (Fig. 3). This late Cretaceous rock unit also has an aphanitic and porphyritic phase. The porphyritic phase contains phenocrysts of plagioclase and black blebs of biotite and magnetite. Phyllically altered, the BQD has quartz-pyrite-sericite (q-s-p) veining and chloritization of pyroxenes, biotites and hornblende.

**Analytical Methods**

Drill core was selected from the Ox Frame andesite based on historic logs and bench maps of mill throughput. Historically, drill holes in pushback eighty-three (PB-83) have been logged as both andesite and diorite; therefore, it was necessary to view the core holes macroscopically to ensure proper identification of rock types in PB-83. Once verification of rock type was made, the Ox Frame andesite was sampled for petrographic analysis, U/Pb age dating, whole rock geochemistry, and x-ray diffraction/cation exchange capacity analysis. Twelve samples were collected; three for each of the throughput ranges (JL1-907, JL3-939A, JL6-960, JL7-746A, JL8-2406C, JL10-1393, JL11-2317, JL13-936, JL14-940A), totaling 9
samples for petrographic examination and geochemical analyses, and three (JL3-939A, JL3-939B, JL4-2132A) for age dating.

The BQD on the western side of the pit in PB-31 has little to no mill throughput data and was sampled based upon textural differences only. Generally, the BQD has two phases, a fine-grained phase and coarse-grained phase, which were used as the basis for the textural differences of the samples. Again, using historic logs, three core holes of interest containing both textures were sampled for U/Pb age dating, petrographic analysis, whole rock geochemistry, and XRD/CEC analysis. Eight samples were collected; five samples (JL18-2449, JL19-2443, JL20-2402A, JL20-2402B, JL20-2402C) for petrographic and geochemical analyses, and three (JL18-2449, JL20-2402A, JL20-2402C) for age dating.

**Petrographic Analysis**

Samples collected from the Ox Frame andesite and the BQD were sent to Quality Thin Sections of Tucson, Arizona, for the preparation of polished thin sections. Samples of the Ox Frame andesite were selected based upon the different throughputs to determine if any mineralogical and/or textural relationships are observable among the Ox Frame andesite and the different throughputs. The BQD was sampled, based upon textural differences, to compare any mineralogical and/or textural similarities or differences with the Ox Frame andesite that would predict possible throughput problems of the BQD in the mills. Observations for all slides were made based on composition, mineralogy, alteration, and abundance.

**Whole Rock Geochemistry**

Whole rock geochemistry samples were sent to Actlabs Inc. in Ancaster, Ontario, for WRA+trace 4Litho analysis (Fig. 4). Whole rock sampling was done to compare ideal andesite and diorite chemistries with andesite and diorite from the Sierrita mine to determine the varying
levels of alteration and to run correlations with different throughputs to find possible contributors to throughput behavior. Ternary diagrams were made using Igpet2001, an igneous petrography tool used to analyze data. Three different diagrams were constructed; Quartz-orthoclase-plagioclase, Iron-alkali-magnesium, and an Alkali-lime. For each diagram data was reported using weight percents. ModAn, a normative calculating program, was used to calculate mineral percents for the QKP diagram.

**XRD/CEC Analyses**

XRD/CEC analyses were conducted by the Safford Technology Center of Freeport McMoRan Copper & Gold (Fig. 5). The analyses identify qualitative weight percent of minerals in a rock. The weight percent minerals from XRD/CEC were compared to thin section observations as well as correlated with throughput in order to identify minerals relationships. Histograms and correlations were constructed from the raw results using Microsoft Excel.

**Geochronology**

U/Pb age dating was carried out at the Arizona Laserchron Center, Department of Geosciences, University of Arizona, with the permission of Professor George Gehrels and under the guidance of Percival Gou and Nicky Giesler. The age dating was done on the Ox Frame andesite because it has never before been dated in this manner. The BQD was dated to determine if the fine-grained phase was the andesite fingering over from PB-83 into PB-31 or if the BQD does, in fact, have two phases. This information will enable mine geologists to set better rock unit constraints within the pit boundaries.
Results

Petrography

Nine Ox Frame andesite thin sections were examined to identify mineralogy, alteration, and any significant relationships that may exist between distinctive throughput ranges (Fig. 6). These ranges are grouped based upon good throughput, anything equal to or greater than 300 TPH, bad throughput, anything between 300 and 250, and bad throughput, which is anything equal to or below 250 TPH. Andesite is an intermediate volcanic rock with a typical mineralogy consisting of plagioclase, pyroxene, and hornblende. When looked at petrographically these samples are aphanitic and possibly devitrified, making it difficult to distinguish the original mineral composition. However, what minerals could be identified show the mineralogy of the samples taken from the Ox Frame andesite is not that of a typical andesite. There are only trace amounts of plagioclase left and no visible pyroxene or hornblende. On all of the slides, the andesite has been pervasively altered by potassic alteration. The levels of potassium feldspar, quartz, and biotite vary throughout the nine samples. Potassium feldspar and quartz are hard to differentiate, but distinct K-feldspar envelopes and quartz veins can be observed. The majority of biotite in these slides is seen as secondary with a shreddy texture as the result of alteration. It occurs from trace to abundant amounts and can be observed altering to chlorite from trace to abundant amounts. Sericite and clay are also difficult to distinguish from one another and occur throughout the slides, generally in moderate levels. There was no correlation in these slides between any particular ranges of throughput to any specific mineral. One slide, in particular, showed pervasive chlorite alteration, while another showed abundant shreddy biotite, covering 85% of the slide. No other slides had these properties and both of these slides occurred in the same throughput range. Accessory minerals, including calcite and anhydrite, occurred mainly in
veins. Apatite and zircons were disseminated and all of the accessory minerals were observed in all the slides.

Five BQD samples were studied petrographically to establish similarities or differences with characteristics found in the Ox Frame andesite. Diorite is an intermediate intrusive rock with mineralogy consisting of plagioclase, hornblende, pyroxene, and biotite. All slides were either aphanitic or porphyritic in texture and showed phenocrysts of all the principal minerals. Moderate amounts of plagioclase phenocrysts with albite twinning were visible in the different diorite textures. Pyroxenes and hornblende were also present, but abundantly altered to chlorite. Primary biotite occurred and contained magnetite in minor to moderate amounts. The magnetite stripped iron from the biotite, which was evident by a lack of color where the biotite and magnetite were in contact. The BQD had visible phenocrysts of all the prevailing minerals in both the aphanitic phase and the porphyritic phase. Alteration in these samples was minor and dominated by propylitic alteration indicated by the presence of the minerals chlorite and epidote. Across the five thin sections were variable amounts of phyllic alteration recognized as quartz-pyrite-sericite veining. Additionally, clay and sericite were observed in trace to minor amounts, mainly along fractures. Accessory minerals seen in the Ox Frame andesite were the same in the BQD with the addition of trace amounts of rutile.

**Whole Rock Geochemistry**

The textbook ternary diagram for quartz, K-feldspar, and plagioclase (QKP), plots typical andesite and diorite at the plagioclase corner of the diagram, with only minor amounts of quartz and orthoclase plotted (Fig. 7). The nine Sierrita Ox Frame andesite samples were separated by throughput for the purpose of identifying mineral trends, and then plotted on a QKP diagram along with the five BQD samples. Bad throughput samples revealed lower k-feldspar
values than higher throughput samples. Moderate throughputs have increased values of K-feldspar and quartz compared to the other throughput ranges. Samples with good throughput have increased K-feldspar, and BQD samples have increased quartz. All Ox Frame andesite and BQD samples plot outside of traditional ternary diagram positions for andesite and diorite.

The 14 samples were also plotted on an AFM diagram to determine where the samples fall on the calc-alkaline and tholeiitic trends (Fig. 8). All samples fall just above the calc-alkaline trend line ranging from 70-45% Na2O+K2O. Samples of andesite with good to moderates throughputs have more sodium and potassium and less MgO and Fe+Mg; bad throughput and BQD samples having less sodium and potassium, and more iron and magnesium.

Finally, the samples were plotted on an alkali-lime diagram, making it possible to report K2O/CaO ratios (Fig. 9). In general, the Ox Frame andesite has larger ratios than the BQD. There are two samples, one with bad throughput data and a BQD sample that plot with low K2O/CaO ratios.

**XRD/CEC Analyses**

Examination of all 14 rock samples was done with the goal of finding contributors to mineralogic relationships that would support the petrographic analysis and lead to the discovery of throughput issues with both the Ox Frame andesite and the BQD. Pie charts were made for the purpose of comparing mineral content between rock types (Fig. 10 and 11). Comparing typical andesite with Ox Frame samples showed that significant potassic alteration had occurred due to the presence of quartz, potassium feldspar, and biotite, three minerals not in the original composition of an andesite. Second, a comparison of the Ox Frame with the BQD demonstrated the differences in the amounts of minerals such as quartz, potassium feldspar, chlorite,
amphibole, and kaolinite, as well as minor accessory minerals. Similarities can be observed in the pie charts between biotite, plagioclase, and sericite.

Correlations were determined for XRD mineral weight percents of the Ox Frame andesite and mill throughput. When compared to throughput, positive correlations were found for chlorite, potassium feldspar, and kaolinite, and a negative correlation for biotite (Fig. 12). Next, histograms were used to compare these correlations with BQD samples to examine the existence of similarities between the amounts of different minerals. Chlorite ranged from 2-9% for andesite and 0-5% for BQD (Fig. 13). Kaolinite ranged from 0-1% for andesite and BQD (Fig. 14). Potassium feldspar ranged from 0-25% for andesite and between 5-10% for BQD (Fig. 15). And biotite ranged from 0-25% in the andesite and from 0-10% in the BQD (Fig. 16).

**Geochronology**

Three samples of the Ox Frame andesite were collected based on historic logs conducted from previous drilling programs. Despite having been macroscopically verified as Ox Frame andesite, samples that had been previously logged as diorite and andesite were gathered to have a broader range of rock unit variability. Three samples of BQD were collected based on textural differences, sampling core that was both aphanitic, resembling the Ox Frame andesite, and porphyritic, representing the more traditional diorite found within the pit, were sampled. During preparation of samples, it was discovered that the Ox Frame andesite (all samples from PB-83) yielded few zircons, whereas the BQD samples, both aphanitic and porphyritic, yielded abundant zircons. Six samples were analyzed with five samples yielding dates. Geochronology of the Ox Frame andesite revealed an age of 175 Ma and the BQD dated at 71 Ma.
Discussion

Petrography

This report has three objectives; the examination and correlation of the Ox Frame andesite and different throughput ranges, the comparison of petrographic observations found in the andesite with the BQD, and the U/Pb dating of both units. The rock descriptions of the Ox Frame andesite and the BQD have previously been discussed by many authors (West and Aiken, 1982, Cooper, 1971, Lootens, 1965, Spencer et al., 2003, Ferguson et al., 2003). Inspection of these rock units microscopically allows for an understanding of the distinctive mineralogy of the andesite and diorite at this mine for the purpose of identifying indicators to milling issues. The Ox Frame andesite and fine-grained BQD appear very similar to each other when observed macroscopically, making it difficult for mine geologists to distinguish the two. The andesite occurs on the eastern and southern side of the Esperanza pit and the BQD occurs on the western side of the Sierrita pit. By dating the texturally similar units, as well as all textural variations within the two units, restrictions can be set within the pit pertaining to where these units may intrude upon one another.

Ox Frame andesite samples had a wide spectrum of mineral characteristics making each sample unique. The most noticeable characteristic of these slides was the lack of phenocrysts. Lootens, 1965, notes devitrification in the volcanic units from an original glassy groundmass. These microcrystalline rocks have been significantly potassically altered. It has been suggested that chlorite is a source of the problem for mill TPH, after a strong correlation between the mineral and TPH was found from mill feed XRD data. In the research for this paper, there were no similarities observed petrographically from slide to slide that could relate chlorite or any other mineral to the TPH. Having not found observerable mineral relationships in the Ox Frame
andesite that correlated with throughput made it impossible to consider the BQD for petrographic comparison with the Ox Frame in terms of throughput relationships. Contrasting thin sections of Ox Frame andesite with BQD revealed very different mineralogy and textural relationships, which could be used to distinguish the two rock types. The remaining uncertainties about how the rocks will perform in the milling process are most likely a combination of the alteration that contributed to the presence of these minerals in an andesite, and devitrification, which made it impossible to make mineral determinations microscopically.

**XRD/CEC Analyses**

Four mineral correlations were established between the Ox Frame andesite and the different throughput ranges. XRD/CEC correlations found that as chlorite increases, throughput increases. This is in contrast to preliminary conclusions from the mine. The same relationship was also identified with potassium feldspar and kaolinite. A decrease in biotite was found to relate to an increase in throughput. In order to attain ideal throughput, rock types in question need to be potassically altered and, at the same time chloritized so that the biotite content is being lowered. Reactions of these hydrothermal alteration processes are

\[
NaAlSi_3O_8 + K^+ = KAlSi_3O_8 + Na^+,
\]

and

\[
2KFe_3AlSi_3O_10(OH)_2 + Cu^+ + 2H_2S + O_2 + H^+ = Fe_5Al_2Si_3O_10(OH)_8 + CuFeS_2 + 2K^+ + 6SiO_2 + \frac{1}{2}H_2O \quad \text{(Beane, 1982)}.
\]

The positive correlations indicate that as alteration of the rock increases, throughput increases, but only when biotite is substantially being altered to chlorite, which decreases the amount of biotite present in the rock and also supports the negative correlation. Samples that are potassically altered and significantly chloritized should show optimal throughput.

Looking at the same minerals in the BQD that had correlations with throughput in the Ox Frame andesite it was determined the chlorite, kaolinite, K-feldspar decrease and the biotite
constant remains the same. The lack of K-feldspar in the BQD suggests that this lithology does not have the strong potassic alteration that the Ox Frame andesite exhibits. However, the biotite has remained in the rock. Based upon the correlation of biotite versus throughput in the andesite it can be assumed that with constant or increased value of biotite, throughput will decrease. These observations support the hypothesis that the BQD will experience equal to more extreme throughput issues than the Ox Frame andesite.

**Whole Rock Geochemistry**

A further impetus has developed from the need to answer economic questions about the nature and relationships of “productive” and “non-productive” porphyries in specific copper provinces (Titley and Beane, 1981). This paper on porphyry copper deposits has quartz-orthoclase-plagioclase, alkali-lime, and AFM ternary diagrams that include rock suites from the western United States. Among other deposits, the three ternary diagrams show where a typical deposit with rocks of similar composition from Arizona would plot. These diagrams were used to check the accuracy of the analysis performed on Sierrita samples. The Sierrita samples plot in the same area of the diagrams as other porphyry deposits of this area. This demonstrates that the data for the Ox Frame andesite and the BQD samples is correct when compared to other rocks from the western US, and the samples can be classified as calc-alkaline in nature.

The quartz-K-feldspar-plagioclase (ab+an) diagram reveals significant alteration of the samples. Similar to rocks plotted in Beane, 1982, the alteration of the Ox Frame andesite samples reflect a potassic alteration characterized by a conversion of original amphiboles, pyroxenes and plagioclases to K-feldspar and biotite. The BQD samples have increasing SiO₂, in comparison to a traditional diorite, and no K-feldspar. This diagram supports the conclusion from the petrographic analysis that found increased amounts of k-feldspar and quartz seen as
alteration products in the Ox Frame andesite. This data also supports the XRD/CEC results as wall. All three analyses show increased K-feldspar in the andesite and from the correlations concluded that with increasing amount of k-feldspar, kaolinite and chlorite throughput increases. In contrast, the BQD has essentially no K-feldspar, therefore giving way to the correlation that throughput will decrease compared to the Ox Frame andesite.

The alkali-lime diagram reflects slightly greater amounts of K₂O than Na₂O in the Ox Frame andesite with no distinct separation by throughput, and also reflects increased CaO values in the BQD. Propylitic alteration, characterized by calcite, epidote, and chlorite (Beane, 1982), is the most dominant alteration process found in the BQD. Petrographic work showed pervasive chlorite as well as calcite, epidote, and chlorite salvages along quartz-pyrite veins.

The Sierrita samples of Ox Frame andesite and BQD are similar to suites examined by Titley and Beane, and have K₂O/Na₂O ratios extending them into the ranges of composition of a great number of rock suites of western and southwestern North America that have high K values (Titley and Beane, 1981). Good to moderate throughput samples cluster in the alkali portion of the AFM diagram, while BQD and one bad throughput sample, with pervasive shreddy biotite, plot closer to the iron-magnesium apex. XRD/CEC correlations suggest that an increase in biotite would support a decrease in throughput and can also be deduced from this diagram.

**Geochronology**

Previous studies have dated the majority of the units in the district (Stavast, 2006; Herrmann, 2001; Jensen, 1998). Stavast (2006) gives a record of deposition for the Pima District, noting the protracted evolution. The Ox Frame andesite is the middle member of the extrusive sequence (called the Ox Frame Volcanics), occurring as a mass, bordering the Sierrita pit on the south and as pods within the rhyolite welded tuff at Esperanza (West and Aiken, 1982). The BQD is a
northwest trending, irregularly shaped pluton that extends as a wedge into the north Sierrita pit with numerous marginal dikes. The BQD was also present in the western half and north-central part of the Esperanza mine (West and Aiken, 1982). Present mine configuration has converged the Sierrita pit and the Esperanza pit into one. The distribution of the Ox Frame is on the northeastern side, whereas the BQD is on the western side as shown by previous geologists.

The continual growth of the Sierrita mine has allowed for the rearrangement of rock unit boundaries. The visual similarities of the Ox Frame andesite and the BQD has made it difficult to distinguish the units from one another throughout the mine’s life. The U/Pb dating of Ox Frame andesite samples reveal an age of 175 Ma taken from samples that had formerly been logged as both andesite and diorite in PB-83 (Fig. 17 and 18). It can now be concluded that all rocks in this pushback are andesite. The BQD samples collected in PB-31 have generated ages of 71 Ma for all textural differences, allowing for the determination that both the aphanitic and coarse-grained phases of the BQD, are, in fact, BQD and not andesite extending over to this area (Fig. 19, 20, and 21). The implication from the geochronology of these rocks has assisted in the mining process by extending the knowledge of rock unit boundaries for the purpose of predicting which rock types will be sent to the mill.

Comparison

The Pima mining district occurs in a faulted complex of sedimentary, volcanic, and plutonic rocks that lies along the eastern pediment surface of the Sierrita Mountains (Titley, 1982). The Sierrita-Esperanza copper-molybdenum deposit is associated with a Laramide-aged, porphyritic facies of a large north-northwest trending granodiorite batholith. Over time, extensive, high-angle faulting and folding occurred throughout the range (West and Aiken, 1983). The Mission ore body transpires in an overturned sequence of Upper Paleozoic strata,
which lie in fault contact with subjacent granitic rocks. In the mine area, one mass of quartz monzonite porphyry (QMP) occurs and radiometric age dates of about 58 m.y. from the San Xavier mine have been correlated to this mass (Jansen, 1983). Dating mechanisms completed for each deposit aid in the classification, characterization, and differentiation of host, source, and alteration assemblages.

A time space diagram was created on the basis of time versus distance for the purpose of examining the ages of events for both deposits and to permit for a comparison between the deposits histories. The diagram was constructed using quadrangle maps of the district (Richard et al, 2003; Ferguson et al, 2003; Spencer et al, 2003; Johnson et al, 2003), focusing on the Sierrita-Esperanza porphyry center (Fig. 22). Ages for rock units of Ox Frame andesite and BQD were compiled from data collected for this report, as well as other ages from Aiken and Baugh (2007), and Ferguson et al (2003). There are two dates for the Harris Ranch QMP, of which the older (~190 Ma) was selected because its sample location is closest to the area from which the diagram was constructed. The distribution of temperature and alteration surrounding igneous events, and path and sources of fluids related to these events were also considered. The determination of the placement of general alteration packages were assigned using Figure 1 in S.E. Jerome (1966), in which there is a discussion of typical copper porphyry geologic events. Alteration assemblages include K-silicate localized within and extruding out of the top of the pluton, quartz-pyrite-sericite that extends slightly further on both sides of the pluton and surrounds the K-silicate, argillic that encompasses an even broader area further from the source and around the quartz-pyrite-sericite, and, finally, propylitic, which is the most distal to the source and found on the flanks on either side of the pluton. Temperature and fluid flow information for pluton related porphyry copper deposits was gathered from Norton (1983), on
which the cooling history of this kind of system is elaborated. For the first 10,000 years, the initial temperature of the pluton is < 800 C and surrounding host rocks are ~200 C for up to 1 km away from the intrusion. Temperatures on the diagram reflect the emplacement of the pluton, not the temperatures at which hydrothermal alteration occurs. For details pertaining to alteration temperatures, refer to Beane (1983). A magma chamber cools the outside first, hardening the exterior, giving the plutons their triangular shape in the diagram, initially reducing the fluid flow. As the fluid builds in the interior of the chamber, it bursts through the top of the intrusion in the form of fractures. This release leads to cooling and the process restarts. Fluid flow from host rocks moves in the direction of the pluton (Norton, 1983). The main assumption for all variables used to make alteration halos, fluid flow paths, and temperature isotherms is that the Sierrita deposit is an ideal system.

It has been suggested that the Mission area represents a faulted upper portion of the Twin Buttes area, having moved relatively northward 10 km on a flat decollement structure, the San Xavier fault (Einaudi, 1983). The environment, as a whole, is so typical of porphyry copper deposits in the Cordilleran region that the occurrence of the commercial ore bodies within silicated sediments instead of within the porphyry itself should offer no detraction from the classification of the Mission ore deposit as a “porphyry copper” (Kinnison, 1966). Einaudi (1983) explains that the Mission ore body is genetically related to the quartz monzonite porphyry stock exposed to the west, with weak potassic and sericitic alteration. The temperature ranges for skarn evolution associated with porphyry copper deposits are 900-700 C close to the source to 350-200 C at the most distal portion where sericite and argillic alteration, as well as meteoric waters can be observed in intrusive rocks and silica-pyrite replacement in sedimentary rocks (Einaudi, 1983).
Consideration of the geologic events surrounding the placement of the Sierrita-Esperanza and Mission deposits permits an interpretation of the details of temperature, alteration, and fluid flow, but for the purpose of reporting new data, this time space diagram is most useful to show the relationship between previously dated rock units and the new ages found. Although for decades, employees of the mines and researchers working in this area have assumed new information, advancing technology with regard to laser chronology has granted more precision and application for use within the mining industry. The new dates for the Ox Frame andesite (175Ma) and the BQD (71Ma) support the conclusions previously made for the area and in relation to the Mission mine. It appears that sequences of events reported by many authors are correct, noting key timing variables, such as the mineralizing intrusions that correlate to the Mission intrusion. Among the issues that remain unclear are why the Harris Ranch QMP is not a mineralizing system and whether or not the Mission intrusion is in fact a cupola or extension of the Ruby Star Granodiorite batholith or a solo event. San Xavier fault is post-mineralization and supports the Mission deposits as part of the Twin Buttes deposit and, more broadly, a part of the Sierrita-Esperanza deposit. A better understanding of the timing of the fault and reasons for the overturned strata are needed to interpret timing of events at the Mission mine.

**Summary**

The Ox Frame andesite and the BQD are significant contributors to mill ore at the Sierrita mine. Petrographic analysis allowed for an in-depth examination of the Ox Frame andesite and BQD mineralogically, from which it can be concluded that significant alteration affects the Ox Frame, and that there is a lack of mineralogical similarities between these two rock units. Geochemical data, including XRD/CEC and whole rock analysis, support each other and indicate alteration minerals, such as chlorite, K-feldspar, kaolinite, and biotite, are perhaps the reason for
the milling issues. Correlations show the positive relationship between chlorite, k-feldspar, and kaolinite, and the negative relationship between biotite with throughput in the Ox Frame andesite. Histograms were then constructed to compare these mineralogical relationships that were found in the Ox Frame to the BQD. The histograms showed decreasing amounts of the positive correlation minerals that were found to have increasing throughput effects on the Ox Frame, and a constant amount of the negative mineral that is correlated to decreasing throughput. Whole Rock analyses support the XRD/CEC finding by demonstrating the alteration processes present in the rock samples. Ternary diagrams distinctly show significant amount of K2O in Ox Frame samples and substantial amounts of Fe and Me in the BQD samples. From these analyses it can be concluded that K-feldspar, kaolinite, chlorite, and biotite contribute to throughput in the Ox Frame andesite and are seen as potassic alteration. In the BQD the lack of K-feldspar and the present of biotite are the contributing factors. The use of geochronology to date the rock units set strong boundaries on the present positions of each rock type. Considering this new information on a wide scale has allowed for a brief time space synthesis that permits for reevaluation of geologic events and geographic positions of district deposits. Although the district has been study profusely, reuse of geologic techniques for alternate purposes expands the scope of their variability and new insight to geologic reasons for mining problems. This paper has provided a geologic approach to a milling issue. By compiling this information with metallurgic and plant research there is potential for solving this issue and propelling the processing at this mine and others in to the next big discovery.
References


Figure Captions

Fig. 1. The Basin and Range of the Western United States. Modified from Parsons (1995).

Fig. 2. Location map of the Sierrita-Esperanza ore body from Jensen (1998), the deposit is situated in Green Valley, Arizona, approximately 30 miles south of Tucson, Arizona.

Fig. 3. Modified after Jensen (1998) basic map of Sierrita-Esperanza geology. Triassic volcanics include the Ox Frame andesite.

Fig. 4. Raw Whole Rock Geochemistry from Actlabs Inc. Used to make ternary diagram showing alteration.

Fig. 5. Raw XRD/CEC data used to construct histograms and run correlations for the Ox Frame andesite and the BQD.

Fig. 6. Summary of Petrographic observations for all Ox Frame andesite and BQD samples.

Fig. 7. Quartz-orthoclase-plagioclase diagram: red circles are bad TPH (below 250), green triangles are the moderate TPH (300-250), blue squares are good TPH (315-300). BQD is represented by black plus signs.

Fig 8. alkali-iron-magnesium (AFM) diagram. See figure 7 for description of symbols.

Fig 9. Alkali-lime diagram. See figure 7 for description of symbols.

Fig. 10. Pie chart depicting average mineral content of the 9 Ox Frame andesite samples. Note the absence of the two principal minerals, pyroxene and hornblende, which are typically found in andesite.

Fig. 11. Pie Chart depicting average mineral content of the 5 BQD samples. Note the difference in mineral composition between the Ox Frame andesite and the BQD.

Fig 12. Scatter plot for the Ox Frame andesite showing positive correlations between chlorite, potassium feldspar, and kaolinite with throughput. In addition, a negative correlation is observed between biotite and throughput.

Fig 13. Histogram of chlorite by rock type for Ox Frame andesite and BQD, showing relationships between mineral content for each sample and the rock type associated with the sample. A decreased amount of potassium feldspar is a potential indicator for a decrease in throughput.

Fig. 14. Histogram of kaolinite by rock type for Ox Frame andesite and BQD, showing relationships between mineral content for each sample and the rock type associated with the sample. A decreased amount of potassium feldspar is a potential indicator for a decrease in throughput.
Fig. 15. Histogram of potassium feldspar by rock type for Ox Frame andesite and BQD, showing relationships between mineral content for each sample and the rock type associated with the sample. A decreased amount of potassium feldspar is a potential indicator for a decrease in throughput.

Fig. 16. Histogram of biotite by rock type for Ox Frame andesite and BQD, showing relationships between mineral content for each sample and the rock type associated with the sample. A decreased amount of biotite is a potential indicator for an increase in throughput.

Fig. 17-18. Age Pick graphs for Ox Frame andesite samples JL3-939B (177.2 Ma) and JL4-2132A (175.43 Ma), both sample completed with 95% confidence.

Fig. 19-21. Age Pick graphs for Biotite Quartz Diorite samples JL18-2449 (71.50 Ma), JL20-2402A (71.98), and JL20-2402C (71.53), all samples complete with a 95% confidence.

Fig. 22. Time Space Diagram from quadrangle map that include the Pima mining district.
## Analysis Table

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### XRD-CEC Mineralogy of Petrographic Samples from Sierra, Wt%  

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**Notes:**

Minerals reported below 2 or 3 wt% cannot generally be positively identified by XRD alone. In most cases there are only one or two peaks above background for these minerals. These peaks are assigned to the common minerals that have peaks in that area. In some cases identified minerals are strongly overlapped by other major minerals (especially anhydrite and pyrrhotite in these samples). There is a strong overlap of calcite on chalcopyrite so no chalcopyrite was reported but small amounts are likely present.
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<td>first bio then bio to chi: about 50-50: bio; 1:2 micron sizes to 10 microns for both bio and chi pervasive chi ranging from 1-10 microns (of chi present about 5% is still what used to be shidry</td>
<td>No visible pyroxene</td>
<td>sericite altering feldspar</td>
</tr>
<tr>
<td>JL10-1383</td>
<td>355</td>
<td>Ox And</td>
<td>no plagioclase all k-feldspar (birds feet look)</td>
<td></td>
<td>No visible pyroxene</td>
<td>pervasive sericite replacing K-feldspar; enplegion and crosscutting veins</td>
</tr>
<tr>
<td>JL8-2405C</td>
<td>380-384</td>
<td>Ox And</td>
<td>big k-feldspar phases carlsbad twinning (trace albite)</td>
<td>bio crowding mag grains, veining and disse, chi is replacing the biotite trace en minor amounts, about 10% of the bio have been replaced</td>
<td>No visible pyroxene</td>
<td>cpo veining; sericite en on fracture</td>
</tr>
<tr>
<td>JL6-960</td>
<td>285</td>
<td>Ox And</td>
<td>k-spar and plag present (albite and carlsbad twinning)</td>
<td>abundant amounts of shidry bio and trace original bio, trace chi replacing bio; bio present in veins: 65 to 5 bio to chi ratio</td>
<td>No visible pyroxene</td>
<td>sericite is abundant in some areas of the slide and minor everywhere else, clay on fractures (siltites)</td>
</tr>
<tr>
<td>JL11-2317</td>
<td>275</td>
<td>Ox And</td>
<td>no plagioclase all k-feldspar (birds feet look); potassic env</td>
<td></td>
<td>No visible pyroxene</td>
<td>sericite is abundant, sericite in veins; replacing feldspar</td>
</tr>
<tr>
<td>JL1-907</td>
<td>200</td>
<td>Ox And</td>
<td>no plagioclase all k-feldspar (birds feet look)</td>
<td>abundant fine-grained bio 1:2 microns in size; chlorite 1-10 microns in size, can be seen replacing feldspar (drawing and pic)</td>
<td>No visible pyroxene</td>
<td>sericite abundant and clay</td>
</tr>
<tr>
<td>JL3-339A</td>
<td>275-280</td>
<td>Ox And</td>
<td>big k-feldspar phases carlsbad twinning (maybe trace albite)</td>
<td>Biotite pervasive secondary; shidry; 75% of the slide is HT bio; no bio to chi; chi does alter feldspars; colors of bio and chi are faint, light brown and green</td>
<td>No visible pyroxene</td>
<td>trace sericite in feldspar grains</td>
</tr>
<tr>
<td>JL14-840A</td>
<td>270</td>
<td>Ox And</td>
<td>no plagioclase all k-feldspar (no twinning)</td>
<td>tiny baidotes 1-5 microns in size, shidry; abundant HT (flowing through the slide)-dissminated, chi is larger can be seen diss as 1-10 microns in size and in veins from 10-20 microns in size (nice drawing)</td>
<td>No visible pyroxene</td>
<td>abundant clay across slide; ser in veins</td>
</tr>
<tr>
<td>JL12-1326</td>
<td>3-259</td>
<td>Ox And</td>
<td>no plagioclase all k-feldspar (no twinning)</td>
<td>Original bio (5-12 microns) occurring in veins and secondary biotite (1-5 microns) diss throughout; both can be seen altered by chi; HT bio and original bio has each converted to chi -50/60.</td>
<td>No visible pyroxene</td>
<td>slide dusted with red clay and brown sericite</td>
</tr>
<tr>
<td>JL19-2441</td>
<td>BQD</td>
<td>BQD</td>
<td>abundant plagioclase (albite twinning)</td>
<td>difficult to distinguish baid from chi, cleavages are not common and greens are irregular; primary bio and bio altering to chi; may be a bit of bio veining (hard to distinguish)</td>
<td>30-80% microns pyroxenes; Swiss cheese looking, equigranular</td>
<td>sericite altering plagioclase grains, light to dark almost black spots, minor part of alteration</td>
</tr>
<tr>
<td>JL18-2449</td>
<td>BQD</td>
<td>BQD</td>
<td>spar</td>
<td>bio is being altered to chlorite</td>
<td>to the biotites; moderate sericite replacing k-feldspar</td>
<td></td>
</tr>
<tr>
<td>JL20-2402B</td>
<td>BQD</td>
<td>BQD</td>
<td>trace remanence of plagioclase and k-spar</td>
<td>biotite replaced by chlorite and sericite. It is hard to distinguish chlorite from hornblende in this slide because of the pervasive sericite</td>
<td>hornblende being replaced by sericite</td>
<td>pervasive; abundant sericite replacing bio px hbl. feld. map</td>
</tr>
<tr>
<td>JL20-2402A</td>
<td>BQD</td>
<td>BQD</td>
<td>plagioclase (albite twinning), k-spar (carlsbad twinning); there is an 40/60 ratio of plag altered to k-spar</td>
<td>same biotite convert to chlorite; px being replaced by hbl-bio-chl blebs (pic)</td>
<td>Pyroxene equal in size to the biotites; px being replaced by hbl trace sericite; sericite om and ser-clay fracture marking the boundary between the minor sericite side of the slide and the trace sericite side of the slide</td>
<td></td>
</tr>
<tr>
<td>JL20-2402C</td>
<td>BQD</td>
<td>BQD</td>
<td>ser side: feldspar altered by ser (albite twinning still present); unser side: plagioclase albite twinning</td>
<td>ser side: chi replacing px (drawing); unser side: bio replacing px (pic). Total description from slide, px being replaced by bio or chi, original bio and shidry bio replacing px; chi replacing bio and px</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

34
Average Percent Minerals in Ox Frame Andesite

- Plagioclase: 38%
- K-feldspar: 15%
- Quartz: 18%
- Chlorite: 5%
- Sericite: 4%
- Biotite: 9%
- Koolinite: 1%
- Calcite: 2%
- Anhydrite: 1%
- Pyrite: 1%
- Swelling Clay (CEC): 2%
% K-feldspar by Rock Type

Number of Samples (n=14)

% K-feldspar from XRD

And
BOD
Mean = 175.43 ± 0.99 [0.56%] 95% conf. 
Wtd by data-pt errs only, 0 of 15 rej. 
MSWD = 0.66, probability = 0.81
Mean = 177.2±1.5 [0.86%] 95% conf.
Wtd by data-pt errs only, 0 of 14 rej.
MSWD = 1.01, probability = 0.44
Mean = 71.50±0.76 [1.1%] 95% conf. Wtd by data-pt errs only, 0 of 22 rej. MS/WD = 0.85, probability = 0.89
Mean = 71.53±0.67 [0.94%] 95% conf.
Wtd by data-pt errs only, 0 of 22 rej.
MSWD = 0.72, probability = 0.81
Mean = 71.98±0.56 [0.78%] 95% conf.
Wtd by data-pt errs only, 0 of 24 rej.
MSWD = 0.63, probability = 0.91
Time Space Diagram from Geologic maps of Samaniego Peak, Twin Buttes, Batamote Hills, and Esperanza Mill 7 1/2' Quadrangles, Pima County, Arizona