



A method for quantitative pyrite abundance in mine rock piles by powder X-ray diffraction and Rietveld refinement

Erik J. Oerter^{a,*}, George H. Brimhall Jr.^a, Jennifer Redmond^a, Bruce Walker^b

^a Department of Earth and Planetary Science, University of California, Berkeley, 307 McCone Hall, Berkeley, CA 94720-4767, USA

^b MolyCorp, Inc., P.O. Box 469, Questa, NM 87556-0469, USA

Received 20 March 2007; accepted 8 August 2007

Editorial handling by B. Kimball

Available online 24 August 2007

Abstract

The abundance of pyrite and other sulfide minerals in mine rock piles is a potentially significant factor in terms of the geochemical and geomechanical evolution of the dumps as oxidation produces acid solutions that drive hydrolysis reactions. A technique is presented here that supports the quantitative determination of pyrite abundance in mine rock dumps by heavy liquid mineral separation to concentrate pyrite for powder X-ray diffraction and then Rietveld method refinement of the diffraction data on a large number of samples using commonly available laboratory equipment. In order to improve and constrain the accuracy of XRD results, binary (pyrite-quartz) and 6-part mineral mixtures (pyrite and rock-forming andesite minerals) spanning a wide range of pyrite concentrations were prepared gravimetrically and run as standards. These standards were then used to minimize errors in pyrite abundance data by constraining key input parameters in the Rietveld refinement. A new polynomial relationship was derived between diffracting crystallite size and the Brindley microabsorption correction input size. This method provides a means to determine uncertainties in pyrite abundance, whereas conventional Rietveld refinement techniques done without the use of standards yield only statistical measures of the least-squares fit, rather than absolute uncertainties in mineral constituent weight percentages. The technique was applied to a number of mine rock pile samples and the uncertainty in the results determined by applying the relationship derived from the 6-part gravimetric standards to the results of the Brindley corrected Rietveld refinements. Uncertainties determined by this method are found to be on the order of $\pm 10\%$ for samples with pyrite content greater than ~ 10 wt% and $\pm 30\%$ for samples with pyrite content less than 10 wt%. In order to evaluate the technique's improvement upon traditional visual mineral abundance estimation the quantitative results are compared to manual volumetric estimates.

© 2007 Elsevier Ltd. All rights reserved.

1. Introduction

The mining industry is beginning to appreciate that sulfide-bearing mine rock dumps are among the most chemically reactive rocks known on earth and that their long-term environmental management

* Corresponding author. Present address: Colorado Geological Survey, 1313 Sherman Street, Room 715, Denver, CO 80203, USA. Tel.: +1 303 990 1499.

E-mail address: eoerter@hotmail.com (E.J. Oerter).

poses unprecedented challenges and significant costs. This growing awareness of the environmental sensitivity of mine rock piles is complicated by the fact that these rock piles have often been emplaced over a long time period with variable source rocks, while few records were kept, and before concern about their stability developed. Hence, the data relevant to mine rock pile behavior, especially in terms of geomechanical stability and acid production, is scant at best in some mines facing closure, or in those requiring a closure plan in order to keep operating. This paucity of available data on sulfide mineral abundance motivates the development of a new quantitative strategy for mine rock pile characterization required for modeling their long-term geochemical evolution and geotechnical stability. Specifically, pyrite abundance, distribution, and grain size (surface area) in combination with O₂ availability influence to first order both the rate and duration of acid generation by bacterially catalyzed surface oxidation and resultant hydrolysis reactions that affect other minerals in the rock piles, especially silicates and carbonates. The resultant chemical weathering reactions in certain rock types, especially aluminous silicates like feldspars, can yield clays and other minerals, that can cause mechanical and hydrological changes in the physical behavior of the mine rock piles and thus be relevant to geotechnical stability over long (hundred-year) time scales.

As in natural supergene leaching and enrichment systems, it is the exposure of pyrite to bacterially catalyzed oxidation in the air-filled voids in the unsaturated zone of the rock pile that drives the creation of H₂SO₄ and the weathering of rocks under near surface conditions. Acid interacts with rock minerals by hydrolysis (reaction with H⁺ ion) to produce acid rock drainage solutes and secondary minerals such as clays and gypsum formed in situ or along the flow path. Therefore, in supporting geochemical modeling, it is essential to accurately characterize the pyrite content of the mine rock piles and its spatial distribution, specifically in relation to minerals that absorb and buffer acidity.

Mine rock piles in general pose several problems when evaluating and quantifying their mineralogical composition. The manner in which the dumps were emplaced is a complicating factor, in that successive dumping events may have been separated by a considerable length of time, allowing oxidation and weathering to occur at the dump surface. This weathered surface is then covered by subsequent

dumping events and a horizon that may be considerably different from the surrounding material is included in the growing pile. The rock fragments comprising the pile are of varying size as a result of blasting and can range from boulders to rock dust, greatly influencing the rate at which weathering and alteration reactions take place by means of increasing the effective surface area available for reaction.

The model was developed and applied to mine rock piles at the porphyry Mo mine at Questa, New Mexico, and has wide application to many other existing mine rock piles worldwide including porphyry Cu and massive sulfide deposits. The Questa Mo mine, owned and operated by MolyCorp, Inc., is located in the Sangre de Cristo Mountains in Taos County, northern New Mexico, USA, at an elevation of 2400–2900 m. From 1965–1982, large-scale open pit mining produced over 330 million tons of mine rock, which was end-dumped into various steep-sided valleys adjacent to the open pit. Accordingly, these mine rock piles typically exist at angle of repose and have long slope lengths (up to 600 m) with depths from 30 to 110 m (Lefebvre et al., 2002; Shaw et al., 2002). In general, the rocks hosting this Climax-type porphyry Mo deposit and composing the mine rock piles consist primarily of mid-Tertiary, hydrothermally altered (mostly propylitized) Latir andesite porphyry flows and associated volcanoclastic sandstone with a significant volume of rhyolite dikes and hydrothermally altered (quartz-sericite-pyrite) Amalia welded tuff. The economic mineralization from the open pit consists of high grade (>0.2% by weight) hydrothermally deposited molybdenite (MoS₂). Associated with the hydrothermal mineralization processes are pyrite veinlets and disseminations with an average pyrite abundance of 3.5% by volume (Shaw et al., 2002; Wels et al., 2003).

The goal of this study is to develop a method that supports accurate and rapid quantification of mineralogy, especially pyrite, in mine rock piles. The level of accuracy and the degree to which these results are reliable (i.e. uncertainties), are extremely important in regards to providing meaningful inputs for geochemical modeling, and so the technique must both minimize error and provide for a reliable assessment of these uncertainties. In order to be practical, the analysis strategy must be both accurate and fast as an enormous number of samples are required to adequately characterize the heterogeneous nature of these large mine rock piles.

2. Methodology

2.1. Mineral mixture standards

Standard mineral mixtures were prepared to assess the accuracy and precision of the analysis scheme with simple binary (2-part) mineral mixtures of varying amounts of quartz and pyrite, and also a set of 6-part mixtures intended to simulate the altered andesite that is characteristic of the Questa site. All standard mineral materials are from the research grade series of Ward's Natural Science Supply. The binary mixtures consist of quartz from Minas Gerais, Brazil and pyrite from Huanzala, Peru. Five to six replicates each were prepared in 1% increments over a span of 1–10 wt% pyrite, in 5% increments over the span of 10–50 wt% pyrite (including a 12.5 wt%), and in 10% increments over the 50–99 wt% span, for a total of 134 binary standards.

The 6-part mineral mixtures are composed of the same Brazilian quartz and Peruvian pyrite, as well as andesine plagioclase from Virginia (USA), orthoclase from India, montmorillonite from Arizona (USA), and kaolinite from New Mexico (USA). The silicate minerals were mixed in the following gravimetric proportions to simulate a slightly altered synthetic andesite: 2 parts andesine, 1 part each of quartz and orthoclase, and 1/3 part each of montmorillonite and kaolinite. The synthetic andesite was combined with pyrite in 1% increments over the span of 1–5 wt% pyrite; 2.5% increments over the 5–15 wt% pyrite span; 5% increments over the 15–50 wt% pyrite; and 10% increments over the 50–99 wt% pyrite, for a total of 138 standards. The binary and 6-part mineral materials were crushed to the same size by the same method as unknown samples from the mine rock dumps.

2.2. Mine rock pile samples

Samples of mine rock pile material in this study originate in several different mine rock piles and were collected from drill cores as well as sampling trenches cut into the rock piles. Thus, the sample inventory varies widely with respect to composition and texture. Following initial field collection, samples are crushed to ~7 mm size in a jaw crusher. This material is then pulverized by a disc crusher down to a 100 mesh passing size (0.15 mm). The sample material is then placed onto a large sheet of plastic coated butcher paper and homogenized

by lifting on opposing sides of the paper and rolling the sample over itself in a random variety of directions (Saheurs et al., 1993). A small sample split is then taken by cross-sampling the homogenized material with a channel sampler.

2.3. Heavy liquid mineral separation of mine rock pile samples

While the Mo ores at the Questa site are relatively enriched in pyrite, abundance of pyrite in the dump material varies tremendously and is often too sparse in bulk samples for accurate quantification by XRD. XRD analysis is therefore preceded by concentration of the dense mineral fraction including pyrite by heavy liquid separation so that the artificial concentrations in the separate are well above the detection limit of the XRD instrument used. Lithium polytungstate heavy liquid provides a suitable separation medium and offers the safest handling characteristics of the available heavy liquids. Differential gravitational settling is accelerated by the use of a centrifuge to increase the effective gravitational forces acting on the grains, causing sinking of grains denser than the heavy liquid, and buoyancy of the grains less dense than the liquid. Within the context of this study, a heavy liquid separation technique is employed that increases both the total heavy mineral fraction recovered as well as the precision (reproducibility) of the technique in regards to the hundreds of samples needed to accurately characterize rock pile materials.

After selecting approximately 5 g of rock pulp which has been processed and split-sampled by the method outlined previously, a magnet is run through the sample in order to remove any scrap Fe fragments derived from the pulverizing plates. The mass of the sample is then recorded and added to a 50 mL centrifuge bottle with 5 mL of lithium polytungstate heavy liquid with a density of at least 2.85 g/cm³. The centrifuge bottles are capped and shaken vigorously to wet the mineral grain surfaces, and then filled with heavy liquid to the 45 mL line and again shaken. An even number of centrifuge bottles are centrifuged at 2000 rpm for 5 min. After this first separation, the floating cake of gangue minerals is broken up. This is a key step as it increases the recovery and precision (reproducibility) of dense minerals by releasing them from the lighter mineral fraction trapped during the initial phase of centrifugation. The centrifuge bottle is then

centrifuged at 2000 rpm, after which the gangue cake is broken up again. The light fraction is extracted from the tube by using an inflatable low pressure bulb isolator developed for this study (Fig. 1) to physically isolate the heavy fraction while the light fraction is poured off. After the light fraction is removed, the bulb is deflated and the heavy fraction is then poured into a rotary vacuum apparatus (Brimhall and Vigus, 1985) which facilitates the complete recovery of the heavy fraction by filtering the heavy liquid through Millipore glass fiber

10 μm filters with vacuum assist. This separate is then removed from the filter apparatus, washed with distilled water onto a watch glass, and dried on a hotplate, after which the dry mass of the heavy mineral separate is recorded to the same precision as the bulk sample. Neither the binary nor the 6-part mineral standard mixtures were subjected to heavy liquid separation as these standards are intended to cover a broad range of pyrite concentration both above and below the probable detection limit of the XRD instrument.

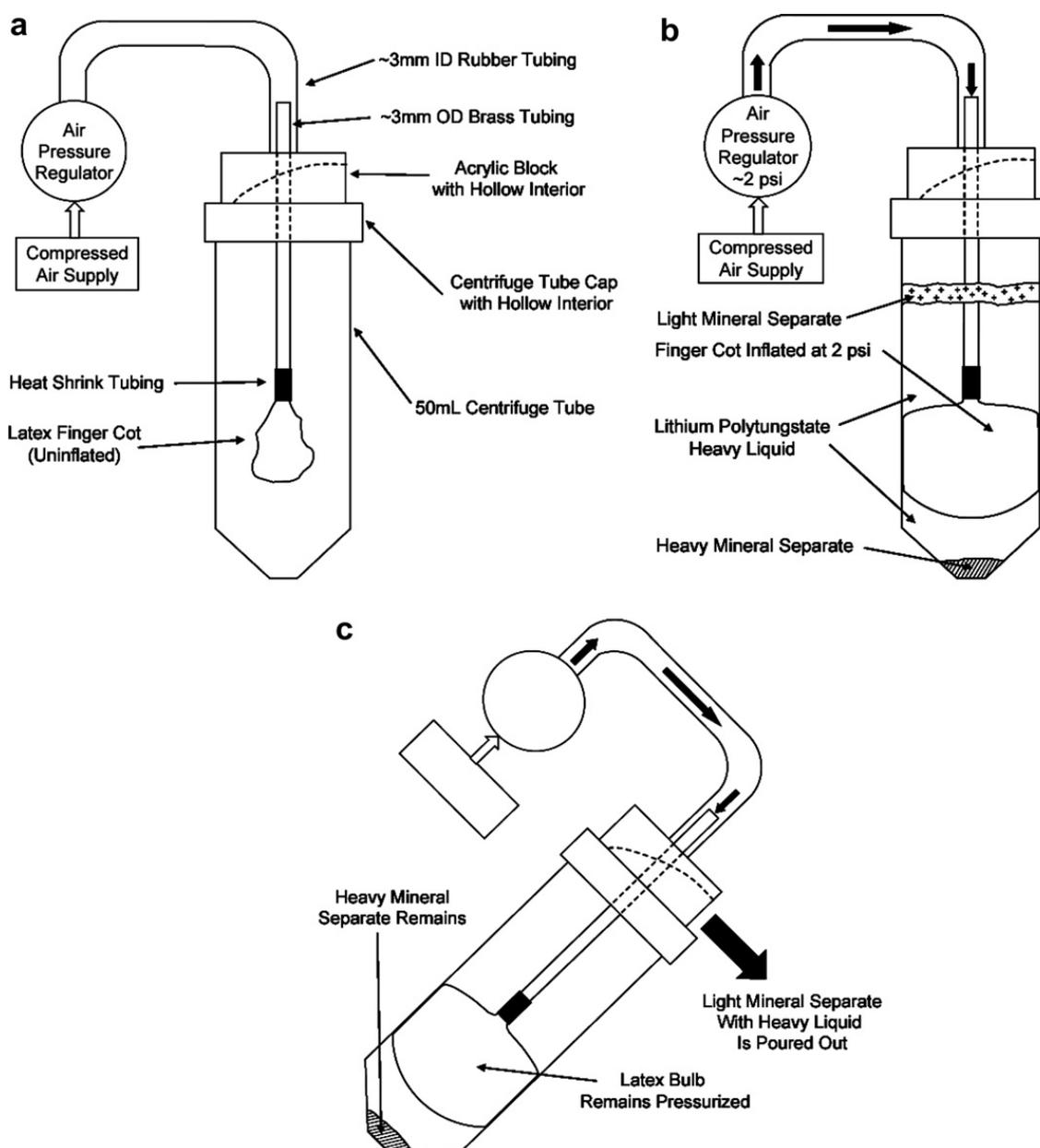


Fig. 1. (a) Schematic drawing of the Inflatable Bulb Mineral Isolator. (b) After centrifuging, the bulb is inflated to allow the dense, heavy mineral separate to be isolated from the light fraction, (c) Which is then poured off into a filter flask to facilitate heavy liquid recovery and washing of the recovered grains with distilled water.

2.4. XRD sample preparation

After heavy liquid separation of ~5 g mine rock pile material, typically 0.1–0.6 g of the heavy mineral fraction remains. The heavy mineral separate consists largely of minerals with a density greater than 2.85 g/cm³, although some less dense minerals are inevitably present as well, due to interlocking of lighter mineral grains with heavy minerals not liberated by grinding. This separated dense mineral fraction has the desired advantage for XRD analysis in that pyrite is enriched relative to the original natural sample. However, it also has disadvantages, in particular, very large differences in mineral density (pyrite versus inevitably included gangue minerals), and a small sample volume.

The heavy mineral concentrate is wet ground in acetone by hand in an agate mortar and pestle until the operator is satisfied that no more mineral crystals are felt and heard to be cracking and the grind becomes consistent in terms of texture and acoustic emissions. This grinding procedure is the single greatest source of variability in this sample preparation scheme, as it relies on a human element of perception as to when the grinding is complete. In order to minimize this effect, the same operator ground nearly all of the samples in this study. The use of mechanized milling equipment such as a McCrone micronizing mill is precluded in this application by the time required for each sample to be ground as well as by the small amount of separated heavy mineral fraction material available.

Given the properties of heavy liquid separates, preparation of uniform powder grain mounts of the samples is difficult. A traditional front, side or rear packed powder mount (Buhrke et al., 1998; Jenkins and Snyder, 1996; Klug and Alexander, 1974) is not appropriate because of the small available sample volume. A smear mount (Buhrke et al., 1998; Klug and Alexander, 1974) is also inappropriate due to the differences in densities between the constituent minerals. This effect is manifested in the formation of a settling column whenever the sample is suspended in a low viscosity fluid such as acetone or water during the smear mount preparation. This settling leads to an under representation of the mineral of interest, pyrite with a density of 5 g/cm³, at the diffracting surface of the sample. The use of zero background plates made of quartz cut off the diffraction axis is precluded by the large number required for efficient sample throughput,

as well as a desire to archive each sample for future reanalysis.

A common method of quickly producing a random-powder mount is to sprinkle the powder onto a slide or sample holder coated with a viscous material. Common high viscosity materials typically chosen include Vaseline, machine oil, and silicone grease. The sprinkle mount has the disadvantage of producing a quasi-monolayer of diffracting material that may not yield reliable diffraction intensities, while having the advantage of not producing any diffraction peak shifts due to sample height displacement (Bish and Reynolds, 1989).

The method employed in this study uses 0.2 g of hand ground heavy mineral separate mixed with approximately 0.15 g of Dow Corning silicone high vacuum grease, which is then sufficiently homogenized into a paste by hand mixing. The relative proportions of sample material and grease were chosen based on available sample volume as well as specific sample holder dimensions, with the goal of producing the highest sample to grease ratio that will still allow the paste to be worked consistently. A round glass slide ~1 mm thick is placed into the front-loading Al sample holder, which serves as a spacer to accommodate the excess depth of the sample holder cavity. This leaves a gap of 0.16 mm between the top of the glass slide and the rim of the sample holder. The sample and grease paste is loaded into the sample holder by using a commonly available spatula or putty knife whose edge has been ground to a straight, even edge. A wiping motion serves to spread the sample paste into the holder, leaving the sample mount exactly even with the rim of the sample holder. The resulting mount has a volume of approximately 85 mm³ of the grease-sample paste.

This technique allows small amounts of sample to be reliably analyzed with materials commonly available with a high degree of reproducibility and to do so efficiently so that a large number of samples can be processed. Variations in mineralogical composition homogeneity within the sample volume are minimized as the viscosity of the grease is high enough to prevent differential gravitational settling of the minerals present. There is no sample height displacement effect because the sample height is fixed at the same height as the rim of the sample holder. Preferred orientation effects are also minimized as the sample is suspended in the grease in a random manner. This method also allows for the easy removal of the prepared sample and subsequent long-term archiving. Disadvantages are

present in this method, most significantly through the introduction of increased background levels from the grease (Bish and Reynolds, 1989). Reduced overall diffraction intensities may also be realized with this method, because of sample dilution in the grease matrix.

2.5. Data acquisition

XRD data were collected on a GBC Scientific Equipment MMA (Mini Materials Analyzer) automated Bragg–Brentano diffractometer with a 3° incident Soller slit, 2° divergence slit, 1° scatter slit, and 0.3° receiving slit, as well as a Xe proportional detector fitted with a graphite monochromator and a 10 sample autochanger stage. Scans were conducted from 4° to 100° 2θ, at 2.0°/min, with a step increment of 0.02° 2θ, using Cu Kα radiation generated at 45 kV and 40 mA. These settings reflect the best compromise between data quality and data collection time, in accordance with our stated goals of accuracy and high throughput. The software Visual-XRD v2.81 software by GBC Scientific was used to run the diffractometer and collect the raw X-ray data for each sample. All samples were scanned while spinning to decrease preferred orientation effects and to improve diffracting particle statistics (Klug and Alexander, 1974).

2.6. Quantitative analysis by Rietveld refinement

X-ray powder diffraction (XRD) has been a widely applied method of determining the quantitative mineralogical composition of materials for almost 70 year (Clark and Reynolds, 1936). Traditional methods for quantitative determination largely consist of the addition of a known quantity of a standard reference material and then assessment of the intensity of diffraction peaks relative to those of the standard (Chipera and Bish, 2002; Klug and Alexander, 1974; Srodon et al., 2001). However, these reference intensity ratio (RIR) methods suffer from several limitations, including effects caused by variations in mineral crystallinity, preferred orientation in the sample mount and differential absorption of X-rays by minerals in the mixture, as well as problems with broad or overlapping diffraction peaks, and the requirement that standard data be obtained for every phase present in the mineral mixture (Bish and Post, 1993).

Inherent in the RIR methods is a data reduction in the creation of a set of integrated intensities of

resolved diffraction peaks into intensity lines. By utilizing the whole dataset obtained from an XRD scan, considerably more information is available for mineral quantification. The Rietveld (1969) method is a least squares regression originally applied to refinement of crystal structures based on the full neutron-diffraction profile and later modified for use on XRD data by numerous authors (Bish and Howard, 1988; Taylor, 1991; Young et al., 1977). The Rietveld method calculates a synthetic diffraction pattern based on mineral candidates' crystallographic data and then uses a least squares refinement to calculate a "best fit" scale factor for each mineral, which when added together yields the best model fit to the observed diffraction pattern using the relationship enumerated by Hill and Howard (1987):

$$W_p = S_p(ZMV)_p / \sum_i S_i(ZMV)_i \quad (1)$$

where W_p is the weight fraction of phase p in a mixture of i phases, S is the Rietveld scale factor, Z is the number of formula units per unit cell, M is the mass of the formula unit and V is the unit-cell volume. This relationship is valid for crystalline phases without preferred orientation of mineral grains, and having similar degrees of microabsorption of X-rays amongst phases.

In practice, these conditions are difficult to meet across the wide variety of lithology and mineralogy present in mine rock pile material. Samples containing minerals possessing distinct crystal habit and which cannot be presented to the X-ray beam in a truly random fashion despite careful sample preparation, i.e. phyllosilicates, can still be quantified accurately with the inclusion of the intensity-conserving March function during Rietveld refinement (Dollase, 1986).

Microabsorption contrast is a more difficult problem, especially in regards to mineral quantification. First described by Brindley (1945), in terms of a binary mixture composed of minerals A (high linear absorption) and B (low linear absorption), microabsorption occurs when large crystallites of phase A lie above or below crystallites of phase B . Since the incident beam may spend a disproportionate amount of time inside an A -crystallite, it will not be absorbed as if it passed through a medium having the average mass absorption coefficient of the mixture. Instead, if it spends more time in an A -crystallite, it will act as if it had been absorbed by

a material with a mass absorption closer to that of pure *A* (Jenkins and Snyder, 1996). The net effect on quantification is that the wt% of mineral *A* will be overestimated and *B* will be underestimated.

Linear absorption coefficients representative of X-ray absorption per cm of mineral are computed as the product of the elemental mass absorption coefficients (International Tables for X-ray Crystallography, 1962) weighted by their stoichiometric weight fraction and then normalized by the mineral's density. In the case of a simple binary quartz–pyrite system, the linear absorption coefficient for pyrite is 1018 cm⁻¹ and 93 cm⁻¹ for quartz with Cu K α radiation, yielding a ratio of ~11 to 1.

The traditional solutions for minimizing absorption contrast effects are to either irradiate the sample with a different X-ray source or to reduce the powdered sample's particle size to the order of 1 μ m wherein absorption contrast effects are minimized. By changing the source of X-rays to one that produces a shorter wavelength or “harder” radiation, the linear absorption coefficient for each element changes, and thus it is possible to select the radiation source that is most appropriate for the specific analysis. This approach does not address a specific goal of this study which is to develop a technique that will be applicable in a wide variety of analytical settings, because Cu anode X-ray tubes are by far the most prevalent source of radiation used in XRD instrumentation. Reducing the particle size to <1 μ m does not satisfy this study's goal of accessibility and throughput because it requires specialized and expensive micronising equipment as well as a per sample processing time on the order of hours, instead of minutes. Very fine grinding of this sort also presents problems because of the wide range in hardness of the minerals present in mine rock pile material. This hardness contrast will tend to manifest in the harder grains overgrinding the softer phases and producing crystallographic strain which, in turn will effect diffraction peak shape (Jenkins and Snyder, 1996; Klug and Alexander, 1974).

The effects of absorption contrast between phases can be corrected by applying a particle absorption factor τ_p , given by:

$$\tau_p = \frac{1}{V_p} \int_0^{A_p} \exp[-(\mu_p - \bar{\mu})x] dV_p \quad (2)$$

where V_i is the particle volume of phase *p*, μ_p is the linear absorption coefficient for phase *p* and $\bar{\mu}$ is the mean linear absorption coefficient of the solid ma-

trix (Brindley, 1945). Brindley gives τ_p as a function of $(\mu_p - \bar{\mu})R$, where R is the effective particle radius. Since $(\mu_p - \bar{\mu})$ is readily computed knowing either the approximate or exact composition of the matrix, the only unknown quantity in applying the correction is the particle size for a specific phase, R (Taylor and Matulis, 1991). Thus, according to Brindley theory, Eq. (1) becomes:

$$W_p = S_p(ZMV)_p / \left[\sum_i (S_i(ZMV)_i / \tau_i) \tau_p \right] \quad (3)$$

All X-ray diffraction data were refined with SIROQUANT v2.5 by CSIRO of Australia (Taylor, 1991; Taylor and Clapp, 1992) running on a PC personal computer at ~2 GHz. In most cases, including all standards, the following refinement scheme was employed, only occasionally omitting a parameter due to minor phase abundances which cause parameter instability and program stops. Anomalous dispersion corrections were applied to all crystallographic structure data (Sietronics, 1989). Parameters which were refined include scale factors, instrument zero correction, background polynomial coefficients and line halfwidths. Preferred orientation was refined in instances of minerals with anisotropic habit. Line profile shape was treated as Pearson VII and line profile asymmetry was refined. Unit cell parameters, atomic positions, shape, extinction, and temperature factors were not refined in order to reduce the total number of degrees of freedom between the accuracy analyses conducted with gravimetric standards of component phases likely to be mineralogically different from the phases present in the Questa rock dumps. Within the context of the goals of this study, which are focused on abundance and distribution of pyrite in mine rock dumps, refinement of the individual phase crystallographic parameters invokes a level of complexity incompatible with this study's stated goals. The Brindley microabsorption correction (Brindley, 1945; Taylor and Matulis, 1991) was applied to every analysis.

2.7. Direct optical measurement of particle size

There are several particle size measurement techniques which will produce an overall particle size distribution including sieving, laser diffraction, and electron microscopy. However, these methods do not discriminate between various mineral phases present. The microabsorption contrast between pyr-

ite and silicate minerals is sufficient so that a particle size for the Brindley correction parameter for each phase is required. Optical microscopy in reflected light allows a direct measure of the physical particle size as well as a differentiation between opaque minerals (sulfides) and translucent minerals (silicates). The samples were prepared for optical analysis using an acrylic disc of 25 mm diameter with a 15 mm thickness and a 4 mm hole originating on the edge of the disc equidistant from both disc faces and extending 20 mm through the center of the disc towards the opposite edge. This hole is filled with petrographic epoxy, and the mineral mixture (after being ground by the method previously outlined) is mixed into the epoxy. The disc is set on edge and the mineral particles are allowed to settle in accordance with Stokes law, that is, by density and size. After the epoxy has cured, half of the disc is machined off, creating a cross-section of the grain settling column. This surface is then polished with diamond paste, and final polishing is done using CaCO_3 to give the silicates better contrast against the epoxy which has a similar index of refraction to that of the silicate minerals. The grain mount is then viewed under reflected light in a petrographic microscope. Digital images are captured spanning the full settling column as a whole (i.e. tiled images, from bottom to top). These images are then processed digitally into a classification of either sulfides or silicates and measurements are computed of each grain present in each image.

In order to interpret the resultant particle size distribution in terms of a median particle size with respect to mineralogy, a stereological correction is necessary. It is a well-known phenomenon that a plane slicing a system of randomly spaced spheres will produce a distribution of sections of those spheres that underestimates the true median diameter of the spheres because the plane will only rarely intersect the center of each sphere. A number of stereological corrections are available, with the Saltykov area analysis being the most appropriate for the present application (Underwood, 1981). The Saltykov (1967) analysis normalizes the size distribution by the ratio of each particle's area to the maximum particle area present and then weights the contribution of each size interval of the distribution to the total number of particles per volume. One caveat to this method (and most stereological corrections) is that it is based on a system composed of spheres, of which fractured mineral grains may only be a crude approximation. However, to move

beyond this assumption would invoke an impractical level of mathematical complexity and it is therefore not used in this technique.

3. Results and discussion

3.1. Effects of microabsorption

In Rietveld refinement of the binary quartz–pyrite standard mixtures, the effects of microabsorption contrast becomes immediately apparent in that systematic over or under calculation of pyrite wt% is found by varying the Brindley correction parameter from 1 μm to 10 μm and 20 μm (Fig. 2a). This particle size effect is manifested in a shift in the magnitude and sign of the relative % error at the 3 different Brindley size parameter inputs (Fig. 2b). Relative % error is calculated as:

$$\left(\frac{\%Py_{\text{calc}} - \%Py_{\text{known}}}{\%Py_{\text{known}}} \right) \times 100 = \%Error \quad (4)$$

where $\%Py_{\text{calc}}$ is the wt% of pyrite as calculated by Rietveld refinement and $\%Py_{\text{known}}$ is the known wt% of pyrite in the mineral standard. This illustrates the value in analyzing standards of known composition because the statistical measures of the goodness of fit of the refinement are exactly the same throughout the three refinements done with 1 μm , 10 μm and 20 μm Brindley particle size. Without the outside check provided by the gravimetric standards, the accuracy of the refinement is essentially unknown, even though the final input parameters and their standard deviations are well known.

Standard deviations of the refinement parameters reported by the Rietveld software are often interpreted as a direct indication of the uncertainty in the true quantitative values of the phases present in a sample. Instead, these statistical measures are reflective of the likely uncertainty within the Rietveld least-squares refinement itself. That is, they are indicative of the precision of the least-squares regression, rather than the accuracy of the results of the refinement. Prince (1993) suggests that the ratio of the calculated residual factor to the statistically expected residual factor, also known as χ^2 , can be a correction factor. In this instance, the estimated standard deviation of the refinement parameter is multiplied by χ^2 to find the true standard deviation of that parameter. This invokes the assumption that the lack in model fit is due entirely to a uniform over-weighting of all data points. This use of χ^2 as a correction factor has no statistical basis, in that

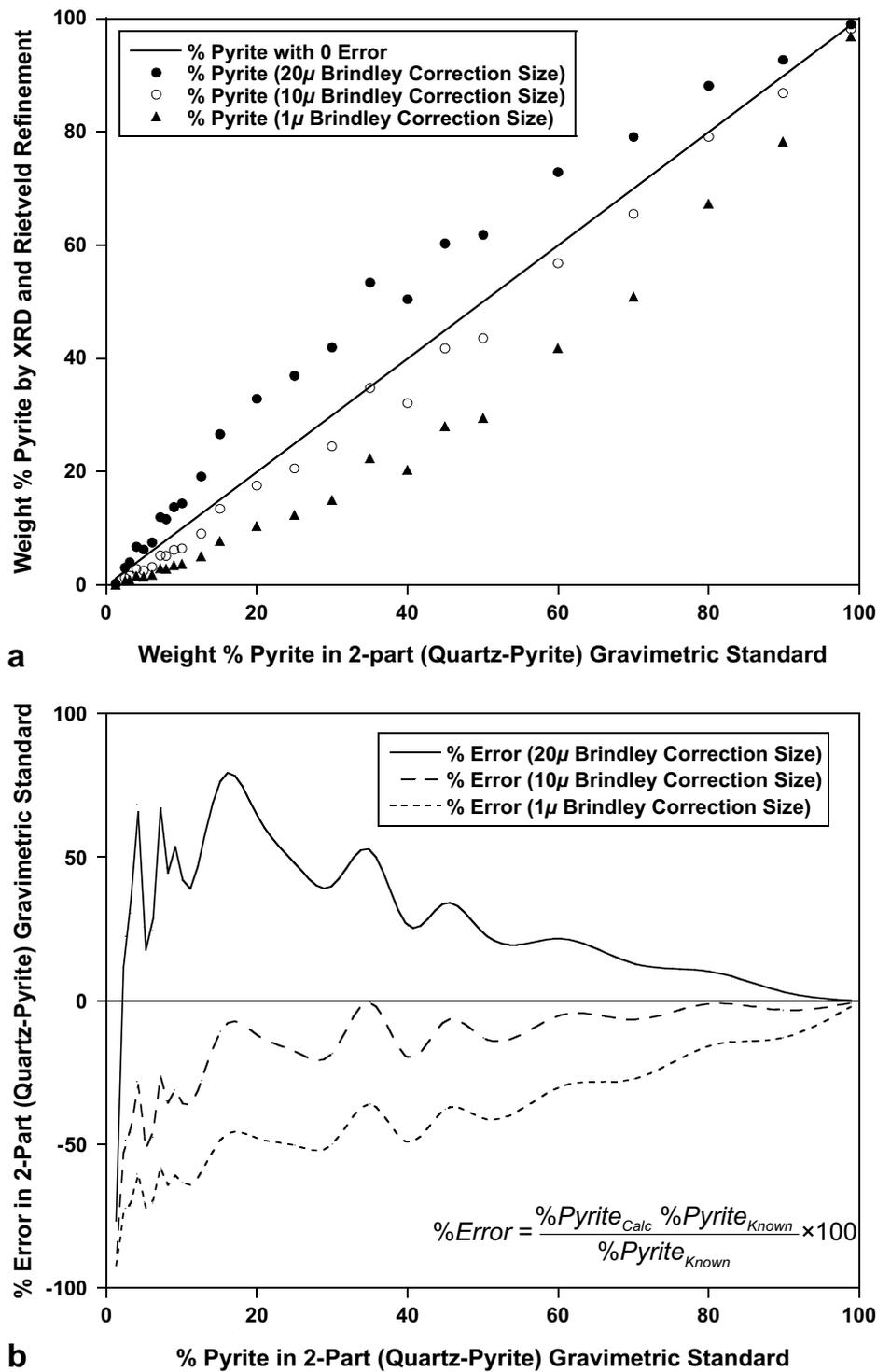


Fig. 2. (a) Comparison of pyrite wt% calculated by Rietveld refinement with Brindley absorption contrast correction size set to 1 μm, 10 μm and 20 μm for both quartz and pyrite plotted against the true gravimetric proportions of pyrite. (b) Comparison of the % error of the pyrite abundance determined by Rietveld refinement with 1 μm, 10 μm, 20 μm Brindley sizes. All analyses were conducted on the median sample replicate (i.e. 3rd of 5 sample replicates).

defects in the model may or may not be correlated with parameters included in the model, with the result that the estimated values may be more or less precise estimates of the ‘true’ value and may or may

not be systematically biased (Prince, 1993). In this study, all refinements were considered complete when the χ^2 factor was less than 3. In most cases, the χ^2 factor was less than 2, indicating a very good

fit of the calculated diffraction pattern to that of the observed pattern.

3.2. Results of direct optical measure of particle size

For the binary quartz–pyrite system, 10 standards at compositional intervals of approximately 10% pyrite content were examined. In all, 27,754 grains were measured, which would have been an intractable number under manual optical counting methods. For the 6-part system, 3 standards were analyzed and 7026 grains were measured. As seen in Fig. 3a, the optically determined mean particle size of both quartz and pyrite are compositionally independent in the binary standards. This suggests that the manual grinding in the sample preparation technique is not affected by the relative abundance of quartz and pyrite in the mineral standards. Pyrite particle sizes show considerable scatter over the range of prepared standards from 1 to 99 wt% pyrite, while quartz particle size is more centered around 7 μm .

3.3. Diffracting crystallite size calculated by peak broadening

According to Bragg's law, X-ray scattering from crystallographic planes (hkl) at spacing intervals of a multiple of the incident radiation wavelength (λ) will be out of phase and will not produce diffraction in what is termed *Bragg extinction*. However, when diffracting crystallite size becomes small enough (~ 1000 Å), there may not be enough crystallographic planes to effectively cancel out all X-ray scattering and consequently, the diffraction peak broadens, where the peak begins to show intensity at a lower 2θ and ends at a higher 2θ than the Bragg angle (Jenkins and Snyder, 1996). This diffraction line broadening effect can be calculated from the diffraction data by means of the Scherrer equation (Scherrer, 1918):

$$L = \frac{K\lambda}{(B_i - b) \cos \theta} \quad (5)$$

where L is the mean crystallite thickness in Å, λ is the incident radiation wavelength in Å, B_i is the observed line width measured at full width at half maximum in degrees 2θ , b is the line width associated with instrumental broadening in degrees 2θ , and K is the *shape factor* relating crystallite shape and the manner in which B and L are defined. In practice, K is effectively approximated by unity (Jenkins and Snyder, 1996; Klug and Alexander, 1974).

When the diffracting crystallite size is calculated from diffraction peak broadening by means of the Scherrer equation (Eq. (5)), a compositionally dependent trend in pyrite Scherrer size is realized (Fig. 3b), wherein at low pyrite concentrations the diffracting crystallite size of pyrite is small and at high pyrite concentrations, Scherrer size is large. The converse is true of the quartz Scherrer size.

3.4. Aggregation factor

The crystallite size given by the Scherrer equation can be thought of as the ultimate diffracting crystallite size; whereas the Brindley correction particle size can be thought of as conceptually analogous to an aggregate of these diffracting crystallites, more akin to the actual particle size of mineral grains in the XRD sample mount. By establishing the relationship of the Scherrer size to the Brindley size, an *aggregation factor* may be found that is useful in converting easily measured Scherrer size (by peak broadening) to more useful, but harder to measure, Brindley size which is an input parameter in the Rietveld refinement routine. This *aggregation factor* is defined as the ratio between the optically determined “aggregate” particle size and the calculated Scherrer crystallite size; or the number that when multiplied by the Scherrer size will yield the “aggregate of diffracting crystallites” size, or the Brindley size. Matulis and Taylor (1994) have explored this relationship and offer a general aggregation factor of 50. However, this factor has not been determined rigorously on a wide range of compositions, nor for systems containing pyrite where the linear absorption effect must be treated rigorously.

The wide variation in optically determined particle size yields a pyrite aggregation factor that is similarly variable and which has no compositionally dependant trend, whereas the quartz aggregation factor is more consistent across a wide range of compositions (Fig. 4a). Given the lack of a distinct compositional trend in both pyrite and quartz aggregation factors, the mean value across the range of compositions was chosen for both mineral's aggregation factors. However, when aggregation factors for both quartz and pyrite are applied to Scherrer size to determine an appropriate Brindley size input, the relative % error is not centered on or symmetric about zero (Fig. 4b).

By fixing one of the two Brindley sizes, the possible combinations of input parameters drop from practically infinite to a more tractable number. As

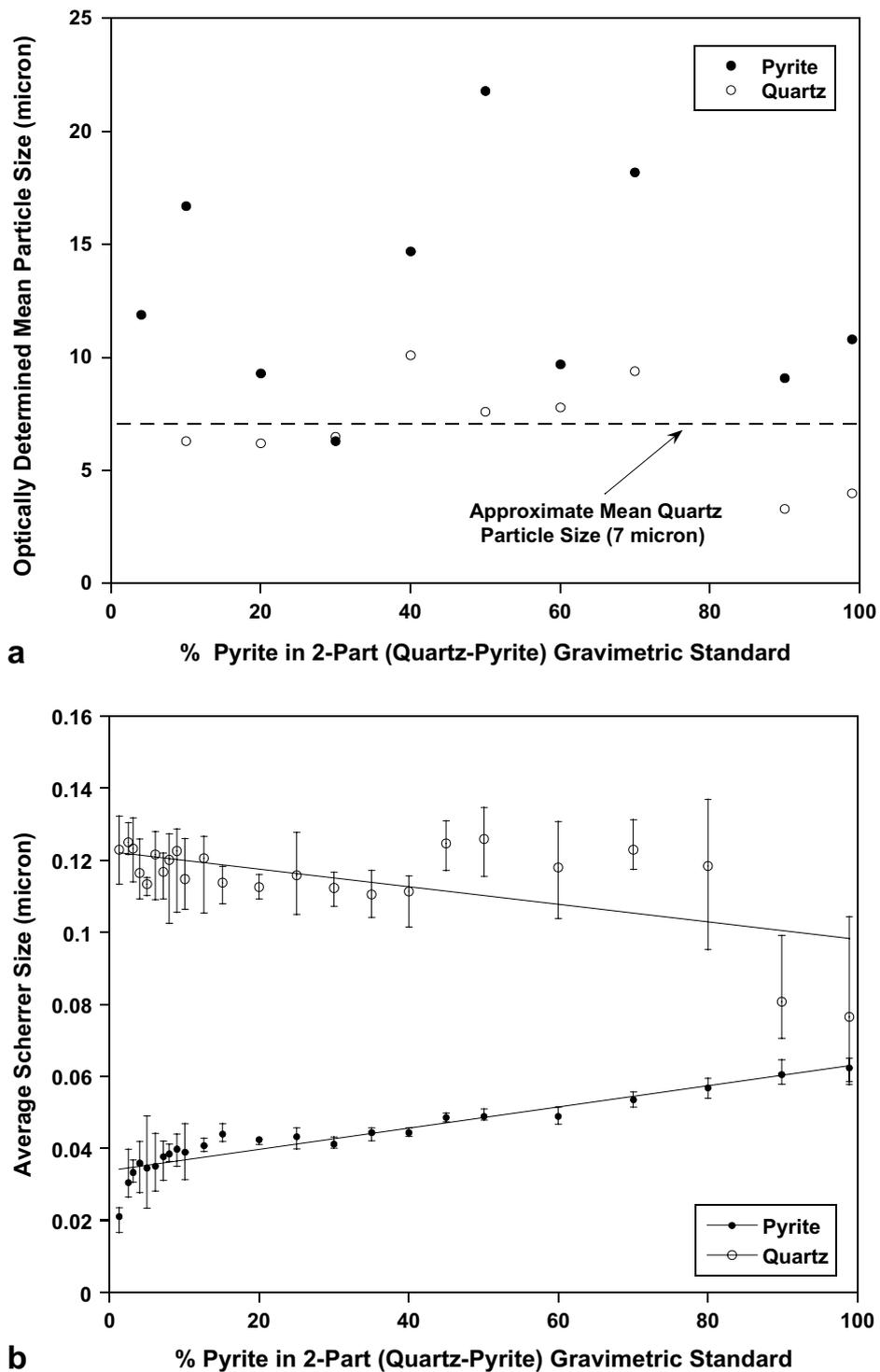


Fig. 3. (a) Stereologically corrected, optically determined mean particle sizes for quartz and pyrite in the binary mineral mixtures. (b) Scherrer diffracting crystallite sizes calculated based on peak broadening effects plotted against composition. Error bars represent the range of values calculated from sample replicates at each compositional interval.

seen in Fig. 3b, the Scherrer size of pyrite and quartz become most similar at the pyrite rich end of the compositional spectrum, where quartz is found to have the most similar size to that of pyrite

(~90 wt% pyrite). By applying the aggregation factor for quartz to this Scherrer size, the quartz Brindley size is fixed at 6 μm. The Scherrer size for the 99 wt% pyrite sample is suspect, however, considering

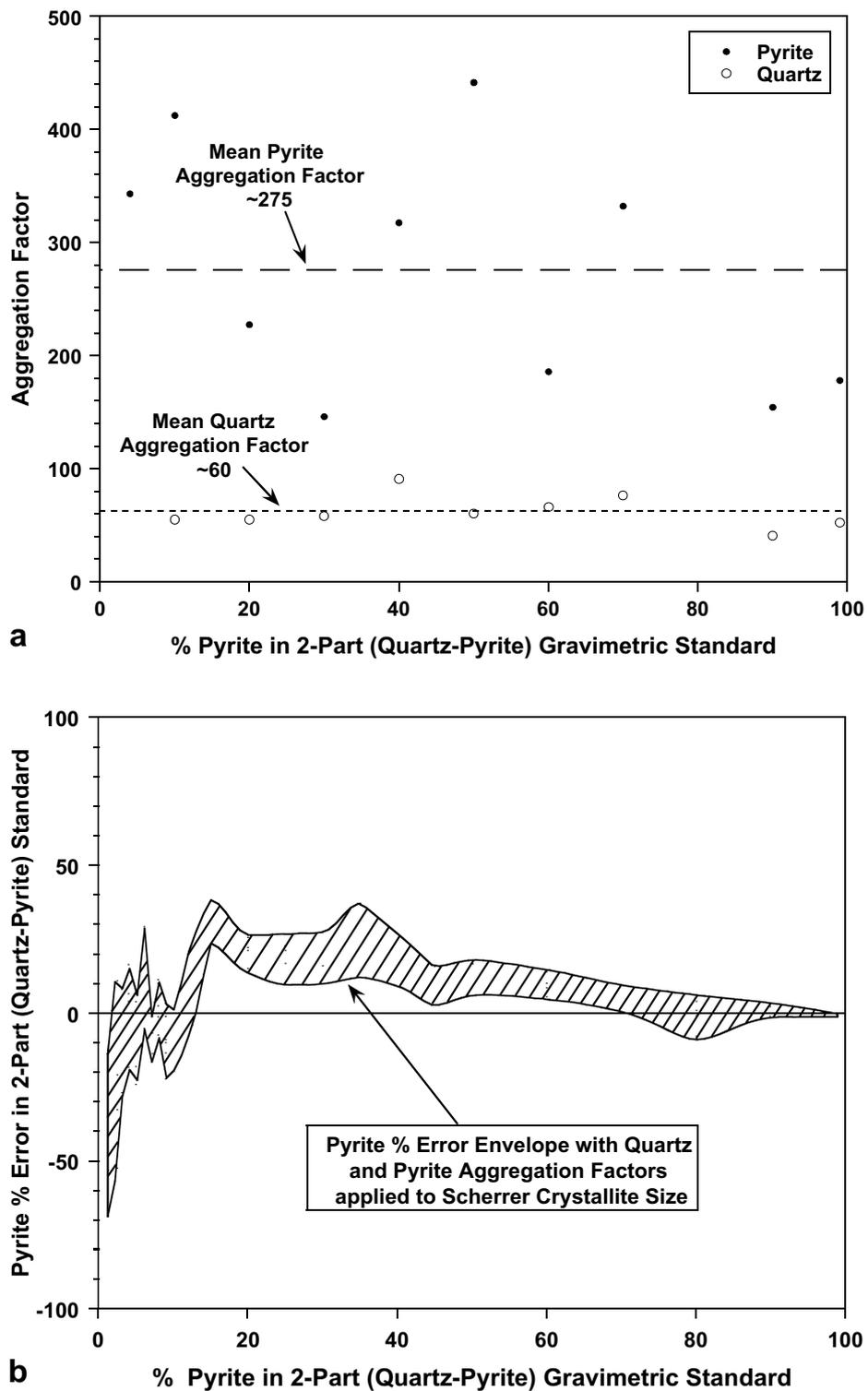


Fig. 4. (a) Aggregation factors for quartz and pyrite specific to the binary mineral mixtures. (b) Error envelope of pyrite wt% after Rietveld refinement when aggregation factors for both quartz and pyrite are applied to determine the Brindley absorption contrast correction input parameter size for binary standards.

that the limit of detection for quartz may be much higher than 1%, and thus the Scherrer size calculation may not be accurate.

An appropriate pyrite Brindley size that yields the most reliable results with the quartz Brindley size fixed at 6 μm is found by performing successive

iterations of Rietveld refinement while varying the pyrite Brindley size, in order to find the Brindley size that will give the true quantitative values

(Fig. 5a). At the pyrite rich and poor ends of the compositional spectrum, a wide range of pyrite Brindley sizes will yield good results, as denoted

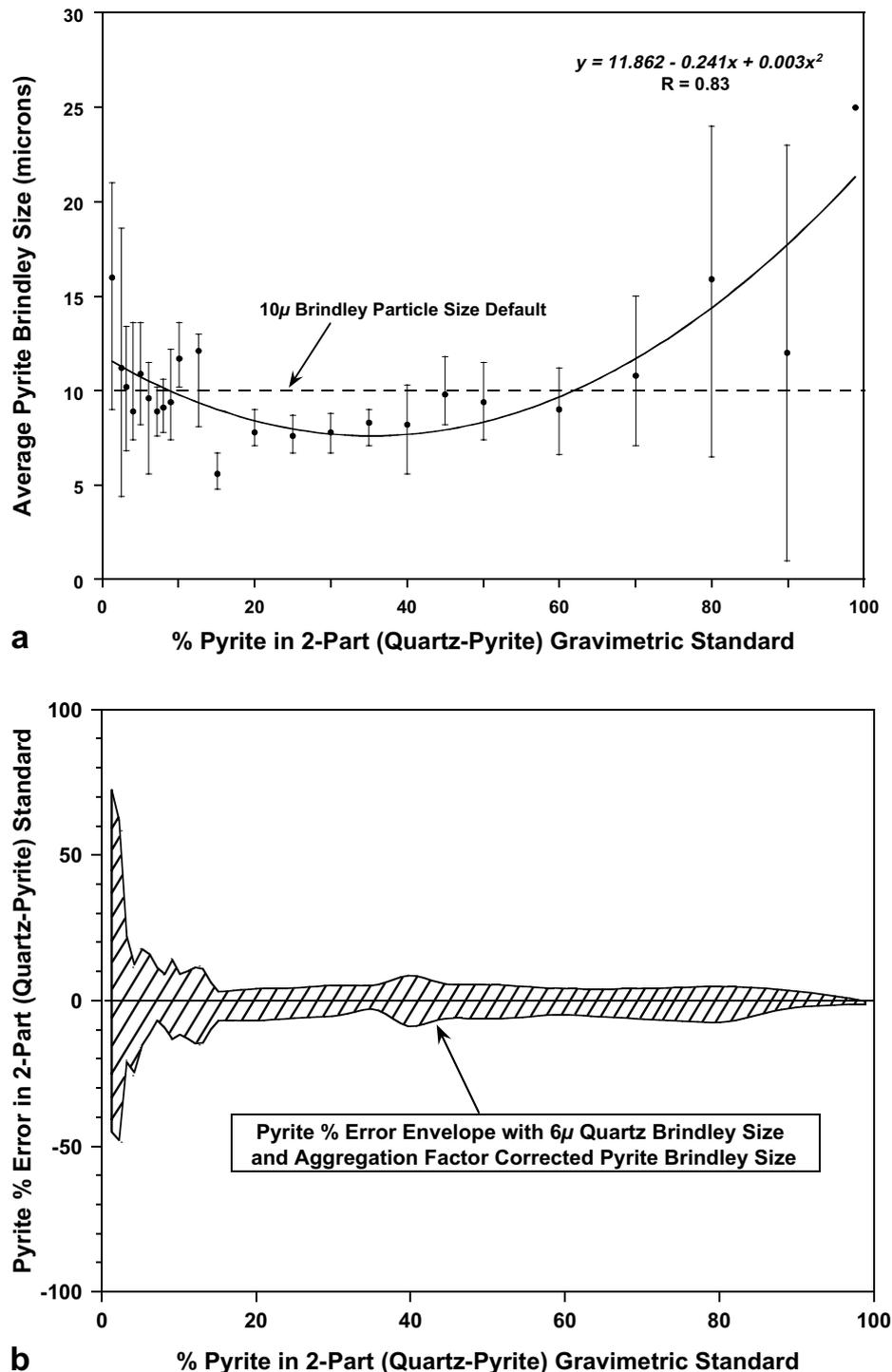


Fig. 5. (a) The average pyrite Brindley size required to minimize relative pyrite error in Rietveld refinement of the binary mineral mixtures with quartz Brindley size fixed at 6 µm is depicted by the solid markers. The error bars represent the range of values that will allow for error minimization over the set of sample replicates at each composition interval. There are no error bars for the 99% pyrite sample because the Brindley size required for error minimization is outside the range of allowable input parameters. Note that a constant 10 µm pyrite Brindley size only gives good quantitative results at ~10% pyrite and ~60% pyrite. (b) The error envelope for Rietveld refinement of the binary mineral mixtures with a quartz Brindley size fixed at 6 µm and a compositionally dependant pyrite Brindley size as determined by the trend depicted in (a).

by the error bars in Fig. 5a. This result is most likely due to the absence of microabsorption contrast in samples approaching that of pure pyrite and pure quartz. That is, the $(\mu_p - \bar{\mu})$ term in Eq. (2) approaches zero in the nearly pure end members. A function for the compositionally dependant pyrite Brindley size is found by fitting a second order polynomial to the mean of the pyrite Brindley sizes required for accurate quantification at each composition interval. This function is more appropriate than a constant value straight line fit, which would also fall inside the range of appropriate pyrite Brindley sizes, because the mean of 5 or 6 values represents the center of a Gaussian distribution of appropriate pyrite Brindley sizes. That is, if more standards were analyzed at each composition interval, the appropriate Brindley sizes would cluster around this mean value, with relatively few at extreme values. When this compositionally variable pyrite Brindley size is applied to the quantification of the binary quartz–pyrite system, the error envelope is found to be centered on and symmetric around zero (Fig. 5b), which represents a significant improvement in systematic error as compared to using arbitrary “default” values for the Brindley absorption contrast correction, especially at pyrite concentrations less than 20 wt% (Fig. 6).

As a more realistic application of this technique, the same rationale and methodology applied to the binary standards is invoked for the 6-part system of standards. In this case, because the optically determined particle size for the silicates in the 6-part system were comparable and within the maximum and minimum bounds of the binary system, a similar Brindley size of 6 μm was chosen as the reference value for all 5 silicate minerals. This assumption is likely valid for quartz, andesine and orthoclase, but probably less correct in the case of the clay minerals montmorillonite and kaolinite with their anisotropic habit. With this fixed silicate Brindley size, the appropriate pyrite Brindley size was found in the aforementioned manner (Fig. 7a) and the resultant error envelope is shown in Fig. 7b. When compared to the error envelope of the binary standards, the uncertainties are similar to those of the binaries by approximately a factor of 2 (Fig. 8). This attains a major goal of this study: a rigorous determination and minimization of the uncertainties of this analysis technique by means of both simple binary mineral mixtures as well as more realistic 6-part standards.

3.5. Application of technique to unknowns

In order to apply the appropriate Brindley corrected Rietveld refinement to a sample of unknown

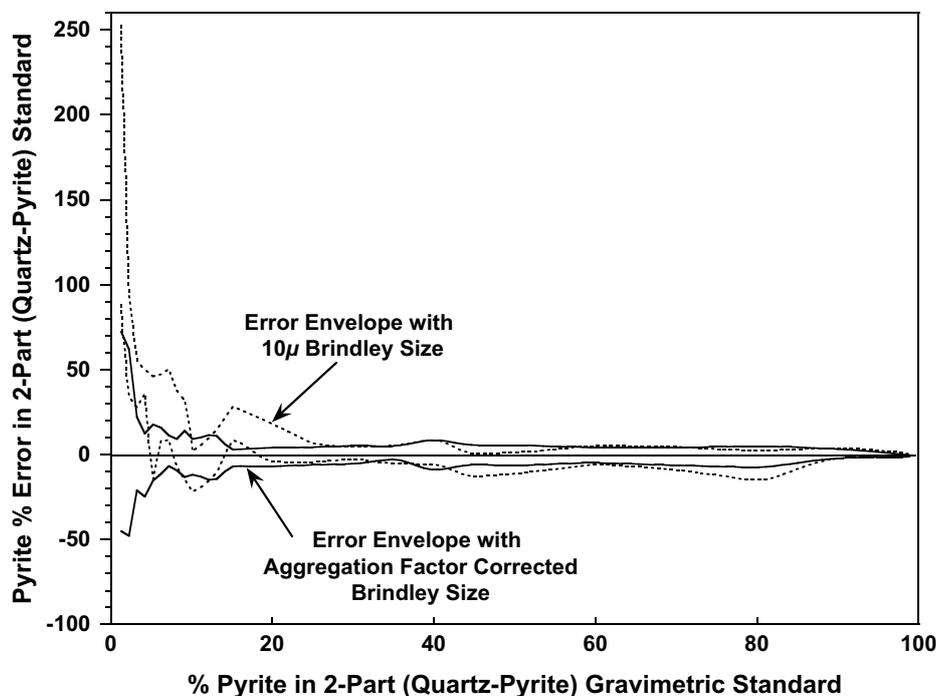


Fig. 6. Comparison of the error envelopes produced by Rietveld refinement of the binary mineral mixtures with a default Brindley size of 10 μm for both quartz and pyrite, and the quantification results obtained by the use of an aggregation factor for quartz Brindley size and the error minimization Brindley size function for pyrite.

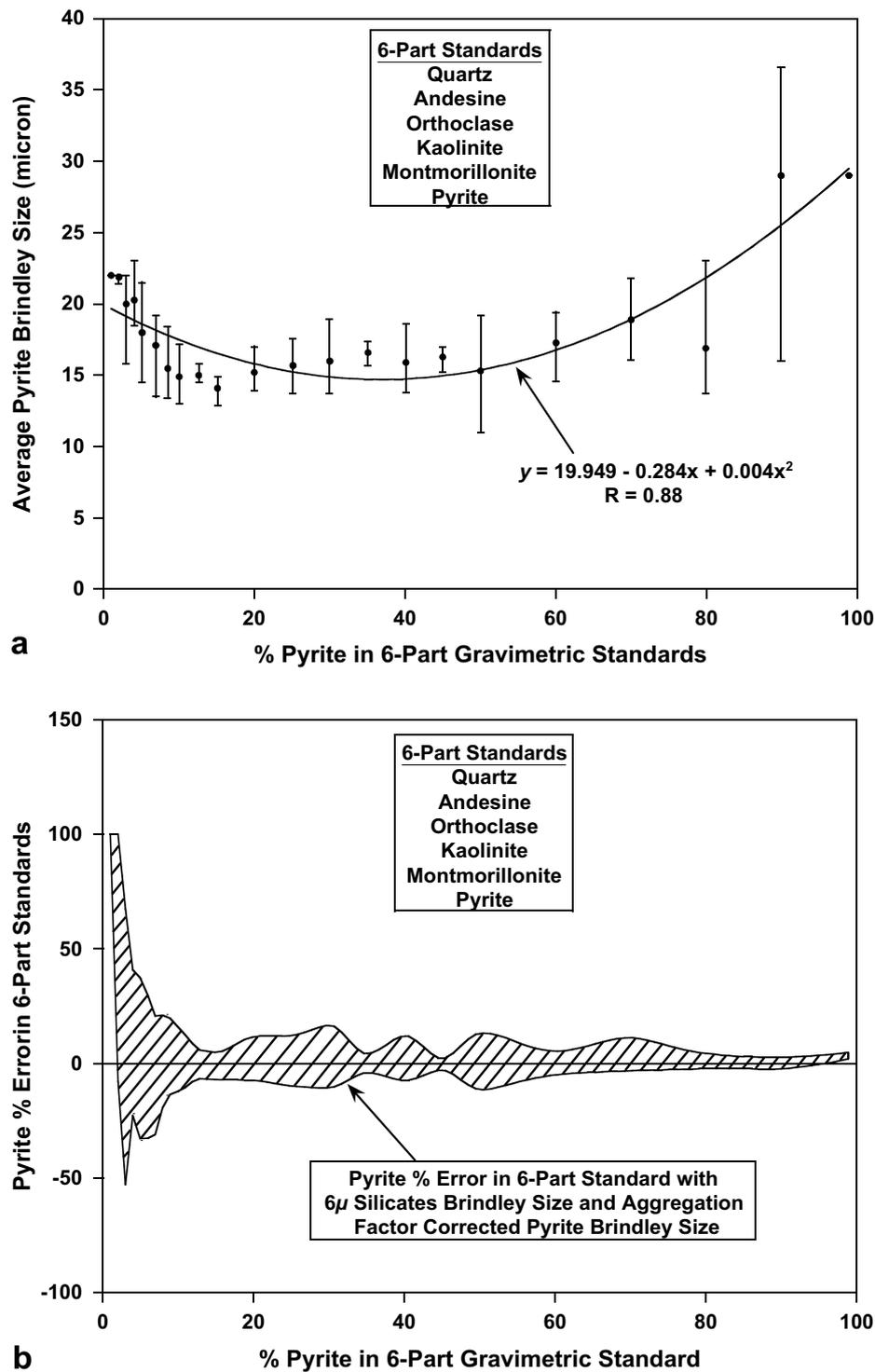


Fig. 7. (a) The average Brindley size required to minimize relative pyrite error in Rietveld refinement of the 6-part mineral mixtures (quartz, andesine, orthoclase, kaolinite, montmorillonite, pyrite) with a silicate Brindley size fixed at 6 μm is depicted by the solid markers. The error bars represent the range of values that will allow for error minimization over the set of sample replicates at each composition interval. The fitted curve represents the trend to be used for pyrite Brindley particle size in conjunction with a silicate Brindley size of 6 μm . There are no error bars for the 1 wt% and 99 wt% pyrite sample because the Brindley size required for error minimization is outside the range of allowable input parameters. (b) The error envelope for Rietveld refinement of the 6-part mineral mixtures with a silicate Brindley size fixed at 6 μm and a compositionally dependant pyrite Brindley size as determined by the trend depicted in (a).

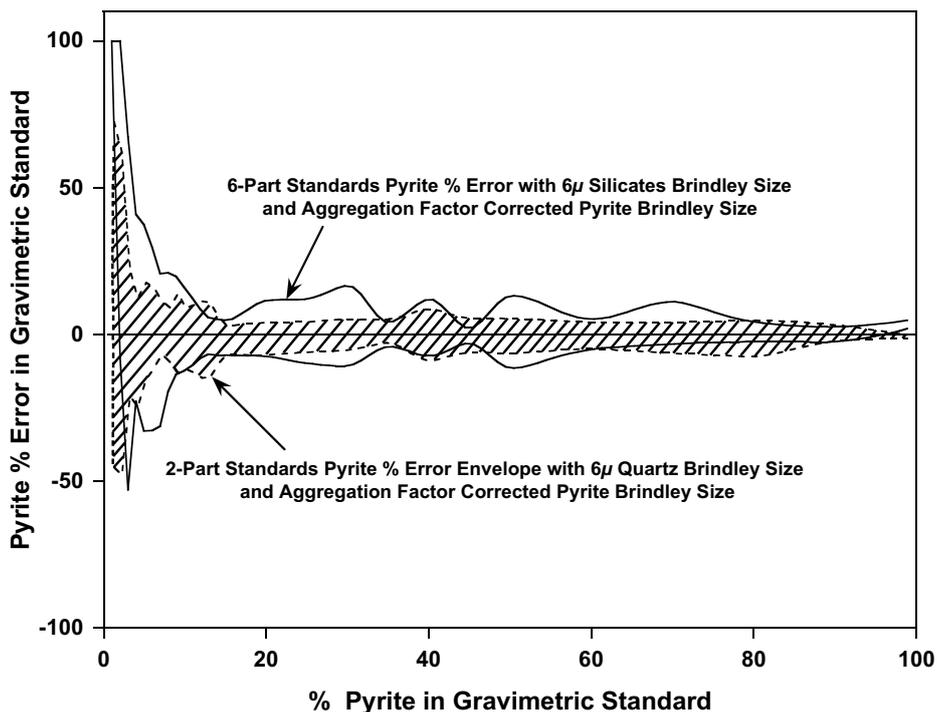


Fig. 8. Comparison of the error envelopes produced by Rietveld refinement of the 2-part and 6-part mineral mixtures obtained by the use of a 6 µm silicate Brindley size and the aggregation factor corrected Brindley size function for pyrite.

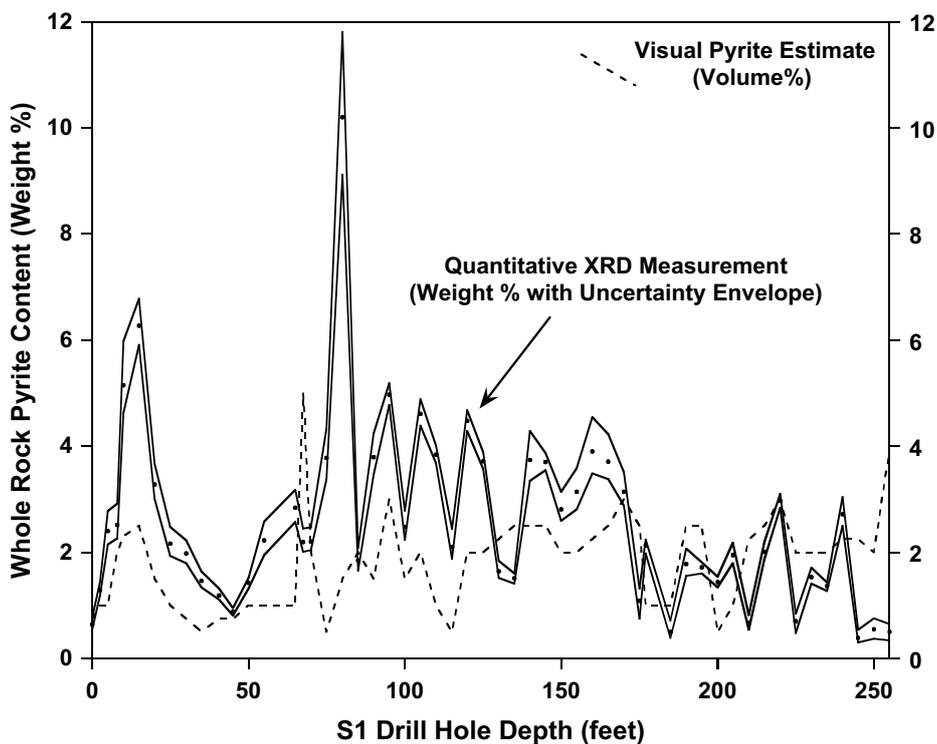


Fig. 9. Calculated pyrite wt% on a whole rock basis for samples from drill hole S1 at the Questa mine site in New Mexico with an uncertainty envelope as calculated by the method outlined in this paper compared to a visual estimate of volumetric pyrite content. The dashed line is a visual volumetric estimation of pyrite at the Questa site from sonic drill core.

composition, a refinement is first done with a Brindley particle size input of 10 µm for all minerals. This gives pyrite abundance to within ~5% and provides

a composition on which to assign appropriate Brindley correction sizes as determined by the 6-part standards and the method outlined. Another

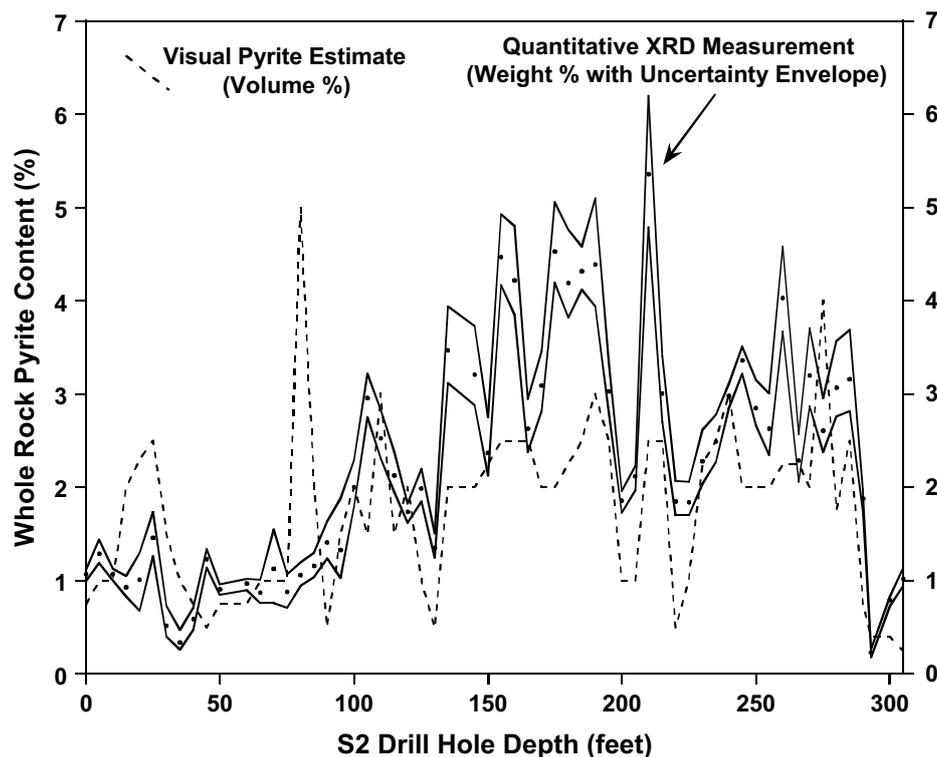


Fig. 10. Calculated pyrite wt% on a whole rock basis for samples from drill hole S2 at the Questa mine site in New Mexico with an uncertainty envelope as calculated by the method outlined in this paper compared to a visual estimate of volumetric pyrite content. The dashed line is a visual volumetric estimation of pyrite at the Questa site from sonic drill core.

Rietveld refinement is then conducted with this compositionally dependant Brindley input size. The quantification result of this refinement is then assigned an uncertainty based on that found from the 6-part standards at that particular composition interval. This heavy mineral fraction wt% is then multiplied by the ratio of heavy mineral fraction to whole rock source material yielding a whole rock wt% pyrite figure.

Figs. 9 and 10 present the pyrite abundances found in samples originating from drill holes in two separate rock piles at the Questa site and their uncertainties. As a further check of the accuracy of the method, Figs. 9 and 10 compare the whole rock wt% pyrite results to a visual estimation of volumetric pyrite. Overall trends in pyrite abundance are similar between the traditional visual estimation and the quantitative XRD measurement, with systematic differences largely due to the density of pyrite, which at 5 g/cm^3 will tend to underestimate visual volumetric abundance relative to the gravimetric abundance. Comparing these two methods helps to illustrate the utility of this quantitative XRD technique, in that many samples can be processed efficiently and a quantitative value can be

assigned to a sample with known uncertainty limits, whereas traditional visual techniques provide only a volumetric estimation with no assessment of the uncertainty of that estimate.

4. Conclusions

Within the context of mine rock pile characterization, quantitative mineralogical analysis by XRD and Rietveld refinement is a powerful and readily employable technique. Advantages to this technique include a straightforward sample preparation scheme with a high sample throughput in a laboratory setting that is relatively common. Rietveld method based quantitative XRD analysis is often described as a standardless method, in that no mineral standard diffraction data are collected and used in the quantitative analysis. This avoids problems associated with obtaining mineral standard materials that are similar to and prepared in the same way as the unknown samples. However, without use of standards, the absolute accuracy of the results cannot be ascertained. A good idea of the precision of the model is found by examining the uncertainty estimates (standard deviations)

provided by the least-squares regression, but this uncertainty reflects a statistical measure based solely on the refinement input parameters. In effect, while an XRD user can derive quantitative results, the accuracy of the results in relation to measured, compositionally known samples are unconstrained. Given the 14 input parameters in the Rietveld method, a reasonable concern can be raised in quantitative XRD by the Rietveld method about how so many parameters can yield unambiguous results without use of standards.

In order to constrain the uncertainties associated with quantitative results, it is necessary to analyze a set of gravimetrically prepared mineral mixtures. This independent check of the analysis scheme allows the parameters, which can cause significant errors to be adjusted appropriately, especially with respect to sample composition. A very significant factor in the context of mine rock pile material is microabsorption contrast between minerals. The effects of microabsorption contrast are well described in the literature, but in practice are commonly ignored due to the difficulty in compensating for them. The Brindley correction is effective when an appropriate input particle size is found by independent means. Commonly applied arbitrary “default” values are shown to be a major source of error. Here a method for determining an appropriate Brindley correction input that is based on empirically derived data from a set of standards with a known gravimetric composition has been developed. By establishing a relationship between Scherrer size and Brindley size in the form of an aggregation factor, a useful tool has been created allowing for the appropriate selection of an input parameter that has a substantial benefit in increasing the accuracy of results.

Simple binary standards of quartz and pyrite are representative of the general mineralogy present in the mine rock dumps to a first order approximation. Six-part mineral mixtures are a better approximation of the mine rock dump material, and serve to more realistically constrain the error associated with a quantitative result. In this study, errors for the 6-part standards are approximately twice those of the binary standards, suggesting that the diffraction analyst can choose an appropriate level of standard mineral mixture complexity based on the needs of the specific analysis situation. This establishes the usefulness of incorporating at least a set of binary standards into any Rietveld based quantitative XRD analysis, especially when pyrite or a signifi-

cant microabsorption contrast is involved. Considering the relative ease of incorporating a set of standards into an analysis scheme, the use of standards as an independent assessment of uncertainty levels is recommended even in situations where absorption contrast is minimal.

In the context of the stated goals of this study, which are to provide a reliable and efficient method to quantitatively assess the abundance of sulfides in mine rock pile material, the method has proven to be practical. Not only does the technique present a method that allows for processing and analysis of many hundreds of samples, but it also provides a means with which to evaluate the accuracy and precision of those results. When attempting to model the geochemistry and geotechnical evolution of these sorts of rock piles, this minimization and constraining of uncertainty is crucial when assessing the reliability of any type of modeling.

Acknowledgements

This work was funded by a grant from Molycorp, Inc., as part of its Questa Mine Rock Pile Weathering and Stability Project as well as various UC-Berkeley fellowships, most notably the Charles Meyer Fellowship. The authors thank M. Logsdon of Geochimica, Inc. for helpful proposal reviews, T. Chatwin of the University of Utah for project administration, K. Donahue and numerous others from New Mexico Tech for sample collection, processing and shipment, T. Teague of UC-Berkeley for shop and lab expertise, C. Kelaart of CSIRO for SIROQUANT expertise and advice, J. Krauss of Analytical X-ray Instrument Sales for technical support, and A. Vanegas of UC-Berkeley for computer support. The authors also thank two anonymous reviewers for helpful comments.

References

- Bish, D.L., Howard, S.A., 1988. Quantitative phase analysis using the Rietveld method. *J. Appl. Crystallogr.* 21, 86–91.
- Bish, D.L., Post, J.E., 1993. Quantitative mineralogical analysis using the Rietveld full-pattern method fitting. *Am. Mineral.* 78, 932–940.
- Bish, D.L., Reynolds, R.C.J., 1989. Sample preparation for X-ray diffraction. In: Bish, D.L., Post, J.E. (Eds.), *Modern Powder Diffractometry. Reviews in Mineralogy*. Mineralogical Society of America, Washington, DC.
- Brimhall, G.H., Vigus, L.J., 1985. Rotary Support for Vacuum Filtration Apparatus. The Regents of University California, Berkeley, CA.

- Brindley, G.W., 1945. The effect of grain or particle size on X-ray reflections from mixed powders and alloys, considered in relation to the quantitative determination of crystalline substances by X-ray methods. *Philos. Mag.* 36, 347–369.
- Buhrke, V.E., Jenkins, R., Smith, L. (Eds.), 1998. *A Practical Guide to the Preparation of Specimens for X-ray Fluorescence and X-ray Diffraction Analysis*. Wiley-VCH, New York.
- Chiperă, S.J., Bish, D.L., 2002. FULLPAT: a full-pattern quantitative analysis program for X-ray powder diffraction using measured and calculated patterns. *J. Appl. Crystallogr.* 35, 744–749.
- Clark, G.L., Reynolds, D.H., 1936. Quantitative analysis of mine dusts – an X-ray diffraction method. *Ind. Eng. Chem. – Anal. Ed.* 8, 36–42.
- Dollase, W.A., 1986. Correction of intensities for preferred orientation in powder diffractometry: application of the March model. *J. Appl. Crystallogr.* 19, 267–272.
- Hill, R.J., Howard, C.J., 1987. Quantitative phase analysis from neutron powder diffraction data using the Rietveld method. *J. Appl. Crystallogr.* 20, 467–474.
- International Tables for X-ray Crystallography, 1962. *International Tables for X-ray Crystallography*. Kynoch Press, Birmingham.
- Jenkins, R., Snyder, R.L., 1996. *Introduction to X-ray powder diffraction*, Chemical Analysis, vol. 138. Wiley, New York.
- Klug, H.P., Alexander, L.E., 1974. *X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials*. Wiley, New York.
- Lefebvre, R., Lamontagne, A., Wels, C., Robertson, A.M., 2002. ARD production and water vapor transport at the Questa Mine, Tailings and Mine Waste. In: *Proceedings of the 9th International Conference on Tailings and Mine Waste, Tailings and Mine Waste'02*, Balkeema, Rotterdam, pp. 479–488.
- Matulis, C.E., Taylor, J.C., 1994. Absorption Contrast Corrections in Rietveld XRD Phase Quantification. Sietronics Pty Limited, Canberra, Australia.
- Prince, E., 1993. Mathematical aspects of Rietveld refinement. In: Young, R.A. (Ed.), *The Rietveld Method*. Oxford University Press, New York, pp. 43–54.
- Rietveld, H.M., 1969. A profile refinement method for nuclear and magnetic structures. *J. Appl. Crystallogr.* 2, 65–71.
- Saheurs, J.-P.G., Wilson, W.P., Sherwood, W.G., 1993. Sample preparation. In: Riddle, C. (Ed.), *Analysis of Geological Materials*. Marcel Dekker, New York, pp. 65–122.
- Saltykov, S.A. (Ed.), 1967. *The Determination of the Size Distribution of Particles in an Opaque Material from a Measurement of the Size Distribution of Their Sections*. Proceedings of the 2nd International Congress for Stereology. Springer, New York.
- Scherrer, P., 1918. Estimation of the size and internal structure of colloidal particles by means of roentgen. *Nachr. Ges. Wiss. Gottingen Math. Phys. Kl.* 2, 96–100.
- Shaw, S.C., Wels, C., Robertson, A.M., Lorinczi, G., 2002. Physical and geochemical characterization of mine rock piles at the Questa mine, new mexico: an overview, tailings and mine waste. In: *Proceedings of the 9th International Conference on Tailings and Mine Waste, Tailings and Mine Waste'02*, Balkeema, Rotterdam, pp. 447–458.
- Sietronics, P.L., 1989. The Effect of Anomalous Dispersion on the Rietveld Quantification of Minerals Containing Iron. Sietronics Pty Limited, Canberra, Australia.
- Srodon, J., Drits, V.A., McCarty, D.K., Hsieh, J.C.C., Eberl, D.D., 2001. Quantitative X-ray diffraction analysis of clay-bearing rocks from random preparations. *Clays Clay Min.* 49, 514–528.
- Taylor, J.C., 1991. Computer programs for standardless quantitative analysis of minerals using the full powder diffraction profile. *Powder Diffr.* 6, 2–9.
- Taylor, J.C., Clapp, R.A., 1992. New features and advanced applications of SIROQUANT: a personal computer XRD full profile quantitative analysis software package. *Adv. X-ray Anal.* 35, 49–55.
- Taylor, J.C., Matulis, C.E., 1991. Absorption contrast effects in the quantitative XRD analysis of powders by full multiphase profile refinement. *J. Appl. Crystallogr.* 24, 14–17.
- Underwood, E.E., 1981. *Quantitative Stereology*. Addison-Wesley, Reading, MA.
- Wels, C., Lefebvre, R., Robertson, A.M., 2003. An Overview of Prediction and Control of Air Flow in Acid-Generating Waste Rock Dumps. Robertson GeoConsultants Inc..
- Young, R.A., Mackie, P.E., von Dreele, R.B., 1977. Application of the pattern-fitting structure-refinement method to X-ray powder diffraction patterns. *J. Appl. Crystallogr.* 10, 262–269.