

## DEHYDRATION AND CRYSTALLIZATION REACTIONS OF SECONDARY SULFATE MINERALS FOUND IN MINE WASTE: *IN SITU* POWDER-DIFFRACTION EXPERIMENTS

RONALD C. PETERSON<sup>§</sup> AND ALAN H. GRANT

*Department of Geological Sciences and Geological Engineering, Queen's University, Kingston, Ontario K7L 3N6, Canada*

### ABSTRACT

A sample stage and a control system have been developed to vary the humidity and temperature of the atmosphere surrounding a powder sample during an X-ray-diffraction experiment. The use of this stage and a position-sensitive detector creates the opportunity to conduct experiments that determine the stability fields and reaction mechanisms of related sulfates of different states of hydration, such as melanterite, siderotil and rozenite. The sample is dusted onto a zero-background plate, and this small amount of dispersed sample ensures maximum interaction among all of the crystallites of the sample and the atmosphere. Determination of the phase boundary for the dehydration of melanterite to rozenite is compared to that determined by Chou *et al.* (2002). The rate of dehydration of cuprian melanterite to cuprian siderotil is shown to depend on the relative humidity in the chamber, which is consistent with a diffusion-controlled process. Rozenite is observed to form by very rapid dehydration of cuprian melanterite. The crystallization of melanterite from liquid under controlled humidity is demonstrated.

*Keywords:* powder X-ray diffraction, melanterite, siderotil, rozenite, relative humidity, dehydration.

### SOMMAIRE

Nous avons développé une platine et un système de contrôle de l'humidité et la température de l'atmosphère entourant un échantillon de poudre au cours d'une expérience utilisant la diffraction X. L'utilisation de cette platine avec un détecteur sensible à la position crée la possibilité d'effectuer des expériences visant à déterminer les champs de stabilité et les mécanismes de réaction de sulfates semblables différant dans leurs degrés d'hydratation, tels mélanterite, sidérotile et rozenite. L'échantillon pulvérisé est répandu sur une plaquette dépourvue d'un bruit de fond; la faible proportion d'échantillon dispersé assure une interaction maximale entre tous les cristallites de l'échantillon et l'atmosphère. Une détermination des champs de stabilité lors de la déshydratation de la mélanterite à la rozenite est comparée avec ceux qu'ont déterminé Chou *et al.* (2002). Le taux de déshydratation de la mélanterite cuprifère au sidérotile cuprifère dépendrait de l'humidité relative dans la chambre de réaction, ce qui concorde avec un processus régi par la diffusion. La rozenite se forme par déshydratation très rapide de la mélanterite cuprifère. Nous démontrons la cristallisation de la mélanterite à partir d'un liquide sous conditions d'humidité contrôlée.

(Traduit par la Rédaction)

*Mots-clés:* diffraction X sur poudre, mélanterite, sidérotile, rozenite, humidité relative, déshydratation.

### INTRODUCTION

Minerals that form in, on, or near sulfide-bearing mine-waste that has been exposed to air and water are generally very reactive. Throughout the year and even from day to day, these minerals react to small changes in temperature or humidity. Most commonly, these reactions involve dehydration or hydration, but oxidation, dissolution or deliquescence also are observed.

Field observations of the mineral assemblages and the extrinsic conditions of their occurrence form the basis for understanding the relationships in these complex multicomponent systems and how the mine

waste evolves over time (Alpers *et al.* 1994, Jambor *et al.* 2000). The assemblage of minerals related by hydration and dehydration that may be observed at a site depends on 1) the temperature, as influenced by the season and whether or not the material is shaded from direct sunlight, and 2) humidity, as influenced by current climatic conditions, nearby flow of surface water, and local changes in airflow over the material. The oxidation of sulfide is an exothermic process, and this heat may modify the conditions within the mine waste.

The ability to study the details of these relationships is compromised because the materials commonly changes while being transported back to the labora-

<sup>§</sup> E-mail address: peterson@geol.queensu.ca

tory for further analytical work. The minerals react in response to the changes in conditions induced by sampling and storage in the sample container, and soon no longer resemble the original material. If the method of collection does not duplicate and maintain the conditions at the time of collection, the samples will begin to change, and the experiments done in the laboratory will measure the properties of a different material than what was collected. It is common practice to immerse the materials in mineral oil in an attempt to arrest or slow the hydration, dehydration or oxidation reactions, which begin as soon as the material is collected, but this approach limits further analysis by some techniques.

The experimental approach presented here enables studies of the effect of changing temperature or relative humidity on material of known composition. The experimental design also creates the opportunity to study mineral reactions in "real time" if used in conjunction with a position-sensitive detector. Reactions may be studied by diffraction measurements made in rapid succession as the reaction proceeds. By adding the dimension of time to the experiment, rates of reaction may be measured with the aim of understanding the mechanisms by which these phases dehydrate and hydrate.

#### APPARATUS AND APPROACH

The chamber that encloses the sample is a modified Anton Paar THC<sup>TM</sup> chamber. The base and lid of the chamber have a water jacket through which water flows at a constant temperature (Fig. 1). As supplied by the manufacturer, the chamber has a resistance-heated fixed sample-holder and a thermocouple sensor that provides data to control the power supply of the resistance heater. The sample holder provided by Anton-Parr has been removed because the heating from below and the thickness of the sample do not allow the study of rapid and reversible dehydration-hydration reactions. There are complications created by the sample holder supplied: 1) changes in sample volume on dehydration or hydration displace the surface from the parafocusing plane of the diffractometer, and 2) a reaction crust commonly forms on the surface, and it limits reaction. The thick sample causes a humidity gradient to form from the surface inward. The X-ray-diffraction experiment measures diffracted intensity from material on the surface but also through this reacting layer, complicating the interpretation of the response of the material to changing conditions. To overcome these problems, a sample stage was constructed where the sample is placed on a spinning zero-background plate cut from a single crystal of Si. A small amount of powdered sample is sprinkled on the surface of the plate (Fig. 1b), which ensures maximum exposure of each grain of the powdered sample to the atmosphere of the chamber. The spinning motion increases the number of crystallites capable of satisfying the Bragg condition for diffraction. The incident

and diffracted X-rays pass through a Kapton<sup>TM</sup> foil, and the sample surface remains horizontal during the experiment. All measurements were made with a Philips X'Pert<sup>TM</sup> Pro  $\theta$ - $\theta$  diffractometer and an X'Celerator<sup>TM</sup> position-sensitive detector using CoK $\alpha$  (Fe) radiation (45 kV, 40 mA).

The temperature of the chamber is controlled by a flow of constant-temperature water pumped from a Fisher Isotemp<sup>TM</sup> water bath. The set-points, ramps and soaks of the temperature cycles are controlled by the PID (proportional-integral-derivative) controller of the water bath, which is in turn controlled and monitored through a serial cable by a personal computer and a Visual Basic<sup>TM</sup> program. The temperature-control system has the ability to maintain a constant temperature from room temperature up to 80°C. The temperature of the sample inside the chamber is constant to  $\pm 0.5^\circ\text{C}$ . Temperatures below room temperature may be obtained using a refrigerated water bath.

The relative humidity of the atmosphere in the chamber is controlled by mixing a stream of dry gas and a stream of saturated gas in a proportion to give the desired partial pressure of water vapor (Fig. 2). The humidity is monitored by an Edgetech Dewprime DF<sup>TM</sup> chilled-mirror hygrometer connected to a personal computer through a serial line. The chilled mirror hygrometer senses the change in laser reflectance off an electronically cooled mirror as it fogs or clears. The temperature of the mirror is determined by a thermocouple connected directly to the mirror surface. Given the temperature of the dew point of the gas mixture and the temperature of the gas in the chamber, it is possible to calculate the relative humidity of the gas. These calculations are done using Humidity Calculator software (ver. 2.1, Mitchell Instruments), which is based on the work of Sonntag (1990). The relative humidity is defined as the ratio of the partial pressure to saturation vapor pressure of H<sub>2</sub>O at a given temperature. Relative humidity is used here as a measure of the activity of water in the atmosphere, to allow direct comparison with previous work. The accuracy of the relative humidity measurement was tested by replacing the sample stage with a beaker containing a solution saturated with NaCl and allowing the atmosphere in the chamber to equilibrate with this liquid. Accurate relative humidities over various salt-saturated solutions as a function of temperature were provided by Greenspan (1977). The measured and predicted relative humidity differed by less than 1.5% relative humidity.

In practice, dehydration-hydration reactions are studied by setting the mixture of dry gas and saturated gas to yield a constant partial pressure of water vapor. The temperature of the experiment is then controlled by varying the temperature of the water bath. The computer control of the temperature bath allows convenient automatic control, but changing gas mixtures requires manual adjustment of the flow meters. The relative humidity in the chamber is a function of both

the gas mixture and the temperature of the system. All of the gas lines must be isothermal with the sample chamber to prevent condensation along the supply lines. This is accomplished by mixing the gas streams within the water bath and surrounding the gas-supply line to the sample chamber with the same temperature-controlled water that fills the jacket that surrounds the sample chamber. The use of Swagelok™ fittings allow coaxial flow of gases through a tube surrounded by a

water-filled tube. The Philips diffractometer system (PreFix™) enables sample stages to be conveniently interchanged with minimal error in repositioning. The sample chamber may be removed from the goniometer without interrupting the constant environmental conditions and set aside in the diffractometer housing for longer term equilibration experiments while allowing a standard sample-stage to be used for routine diffractometer use.

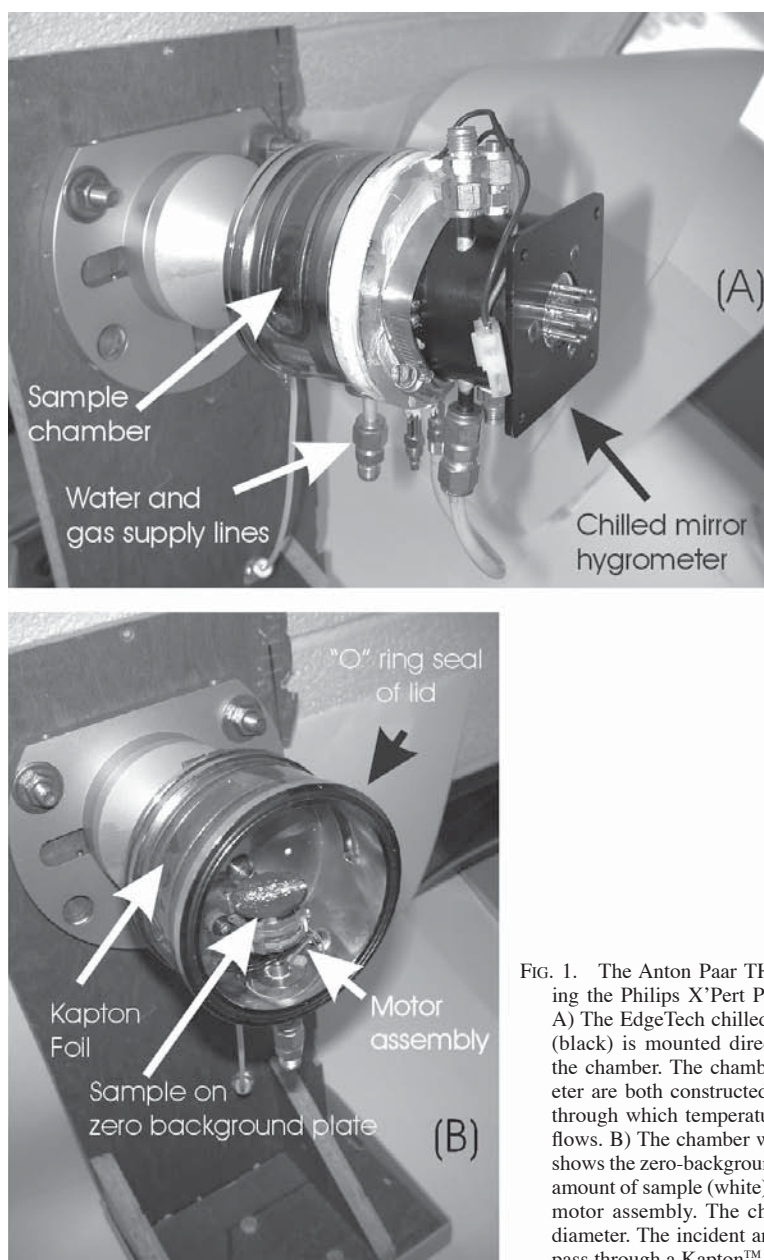


FIG. 1. The Anton Paar THC chamber including the Philips X'Pert PRO™ stage mount. A) The EdgeTech chilled-mirror hygrometer (black) is mounted directly onto the lid of the chamber. The chamber and the hygrometer are both constructed with water jackets through which temperature-controlled water flows. B) The chamber with the lid removed shows the zero-background plate with a small amount of sample (white), and the underlying motor assembly. The chamber is 10 cm in diameter. The incident and diffracted X-rays pass through a Kapton™ foil.

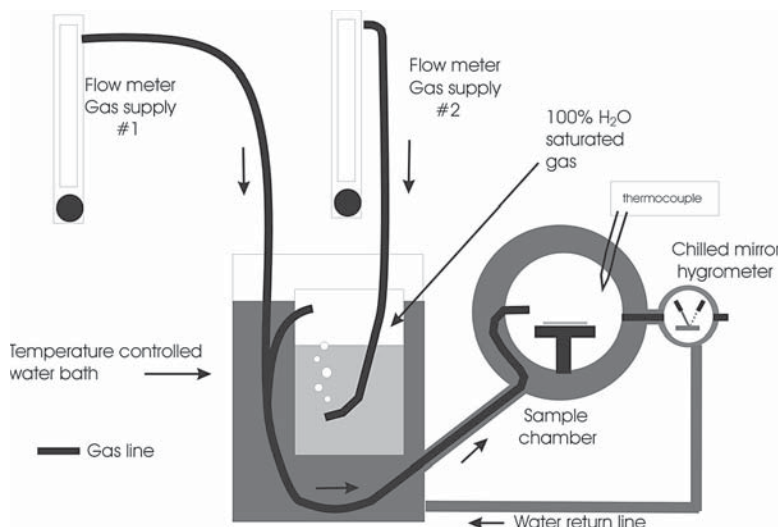


FIG. 2. Schematic diagram of experiment configuration. Gas-flow meter #2 regulates the flow of nitrogen gas that is bubbled through water to create 100% H<sub>2</sub>O saturated gas. Gas-flow meter #1 regulates the flow of a dry nitrogen that is mixed with the 100% H<sub>2</sub>O saturated nitrogen, in proportions to give the desired partial pressure of water vapor. The gas mixing takes place within the constant temperature bath. The gas of the desired humidity travels to the sample chamber in a tube surrounded by water of constant temperature from the water bath. This water also flows through the jacket of the sample chamber and maintains a constant temperature at the sample. The chilled-mirror hygrometer, also surrounded by water of constant temperature, measures the humidity of the gas as it exits the chamber. The temperature of the sample is measured with an independent thermocouple. A VisualBasic™ program controls the temperature of the water bath, including rate of change and soak periods. The program also monitors the relative humidity as determined by the chilled-mirror hygrometer and the temperature measured by an independent thermocouple.

## APPLICATIONS

### *Determination of the stability fields of different hydrates*

The phase relationship between melanterite FeSO<sub>4</sub>•7H<sub>2</sub>O and rozenite FeSO<sub>4</sub>•4H<sub>2</sub>O has been investigated previously by Chou *et al.* (2002), who determined the phase boundary by a series of weight-loss and weight-gain measurements of a melanterite–rozenite mixture under controlled temperature and relative humidity. The samples were placed into closed chambers over different salt-saturated solutions that generate known relative humidity at a specific temperature. The work of Chou *et al.* (2002) provides an accurate determination of the reaction boundary and is an ideal reference in an evaluation of the performance of the design of the diffractometer chamber. In this study, saturated salt solutions were not used to control the relative humidity in the diffractometer chamber because over time, the salts migrate through the system and

coat the chilled mirror of the hygrometer. The mixing of an H<sub>2</sub>O-saturated and a dry gas stream also allows a continuous range of relative humidity rather than the specific relative humidities corresponding to specific salt-saturated solutions.

Melanterite in which small amounts of Cu replace Fe will dehydrate to siderotil, FeSO<sub>4</sub>•5H<sub>2</sub>O. Copper is required to stabilize the siderotil structure over that of the rozenite, FeSO<sub>4</sub>•4H<sub>2</sub>O (Jambor & Traill 1963), but the minimum amount of Cu substitution required to stabilize siderotil is unknown. A fine powder, consisting of a mixture of a cuprian melanterite and cuprian siderotil with a metal ratio of Cu/(Cu + Fe) = 0.17, was created by partially dehydrating a homogeneous sample of melanterite. A small amount of this powder was dusted onto a zero background plate and placed in the sample chamber at 39.3°C. Figure 3 shows a series of diffraction measurements made at 15-minute intervals. From the beginning of the experiment until time A (Fig. 3), the relative humidity in the chamber was 68.9%. Under this relative humidity, cuprian melanterite is not

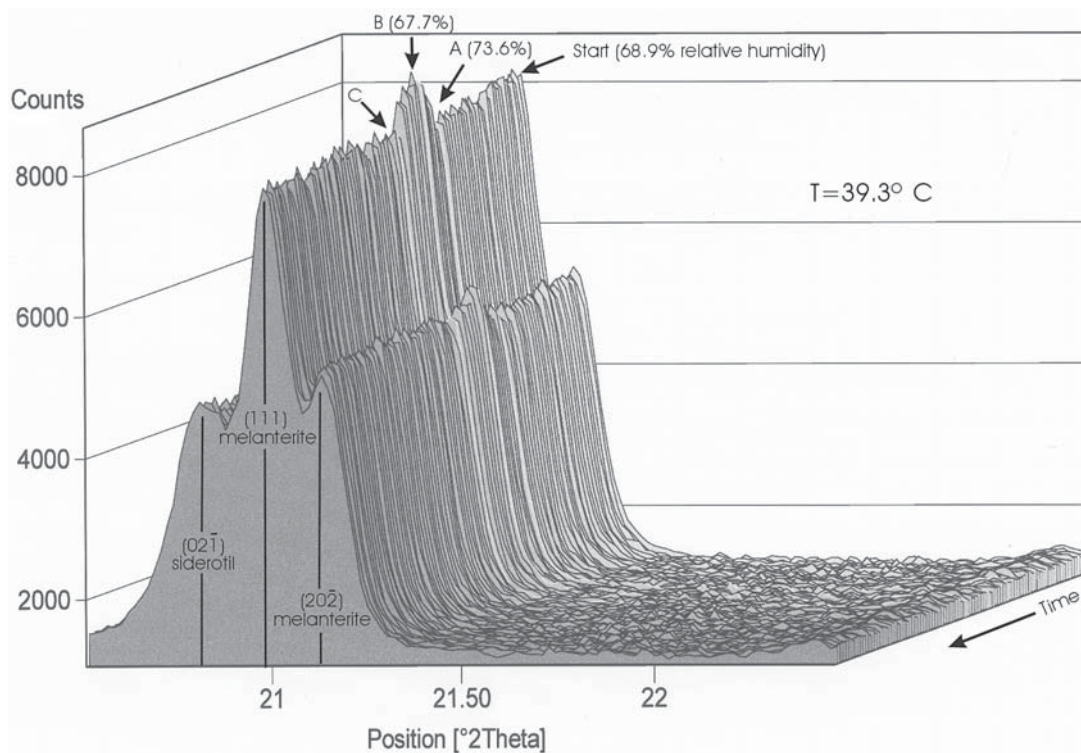


FIG. 3. The intensity of the major X-ray-diffraction peaks (111) and (202) for cuprian melanterite increases as the melanterite forms through hydration of cuprian siderotil and decreases as cuprian melanterite dehydrates to cuprian siderotil. The heights of the diffraction peaks at 20.95° and 21.12° are directly related to the amount of cuprian melanterite in the sample. In this experiment, a cuprian melanterite – cuprian siderotil mixture with composition  $(\text{Fe}_{0.83}\text{Cu}_{0.17})\text{SO}_4 \cdot x\text{H}_2\text{O}$  was studied at 39.3°C. Scans were 15 minutes apart, with the earliest scans at the back of the figure. Initially, at 68.9% relative humidity, the intensity of the cuprian melanterite peak was very slowly decreasing as cuprian melanterite dehydrated to cuprian siderotil. At time A, the relative humidity was changed to 73.6%, and immediately the intensity of the cuprian melanterite peaks began to increase. After 105 minutes (time B), the relative humidity was returned to a value close to the initial value (67.7%), and the cuprian melanterite that had just formed dehydrated back to cuprian siderotil. At time C, no change was made to the humidity in the chamber, but this abrupt slowing in the dehydration rate occurs because all of the “new” cuprian melanterite that had formed in the previous three hours had dehydrated back to cuprian siderotil, and the intensity of the peak returned to a value close to that observed before the humidity was changed. The intensity of the cuprian melanterite peak then resumed its slow decline as cuprian melanterite present in the starting material continued to dehydrate to cuprian siderotil.

stable relative to cuprian siderotil, and the melanterite peaks showed a very slow decrease in intensity. The intensity of the diffraction peaks reflects the abundance of the phase. At time A, the mixture of dry and saturated gas was adjusted, and the relative humidity in the chamber changed to 73.6%. As a result, the intensity of the cuprian melanterite peak immediately began to increase (between A and B) as cuprian siderotil was hydrated to form cuprian melanterite. After 105 minutes (time B), the gas mixture was adjusted to create a relative humidity of 67.7%, and the intensity of the cuprian melanterite peak returned to a value, at time C, close to that exhibited prior to increasing the humidity at time A. The change of the intensity of the cuprian

melanterite peaks corresponds directly to the change in intensity of the cuprian siderotil peaks elsewhere in the diffraction pattern.

In Figure 4, we present the rozenite–melanterite reaction boundary given by Chou *et al.* (2002) and the results of our diffraction experiments for the melanterite–rozenite and the cuprian melanterite – cuprian siderotil reactions of the present study. The determination of the melanterite–rozenite phase boundary by X-ray diffraction closely matches the curve presented by Chou *et al.* (2002). At 40.7°C, Chou *et al.* (2002) predicted the equilibrium between rozenite and melanterite to occur at a relative humidity of 72.5%. In the present study, the boundary between the field

of melanterite (no Cu) and rozenite was found to be 71%. The boundary between cuprian melanterite and cuprian siderotil was found to occur between 67.5 and 70.5% relative humidity at 39.3°C. At this temperature, the relative humidity at which cuprian melanterite dehydrates to cuprian siderotil is similar to the relative humidity where melanterite dehydrates to rozenite. At 40°C, the Cu content of melanterite dictates that the lower hydrate, resulting from the dehydration of cuprian melanterite, is cuprian siderotil, but the presence of Cu has very little effect on the relative humidity at which this dehydration occurs.

The experiments of Chou *et al.* (2002) are simple in design and rely on accurate measurement of mass change of samples that have reacted under very well characterized conditions of humidity and temperature. In comparison, the diffractometer experiments presented in this study are more prone to experimental uncertainty with respect to temperature and relative humidity, but provide phase identity and crystallographic information as well as details of the reaction over a very short time-interval. Both techniques have an important role to play in mapping the phase relationships in these systems.

#### Reaction-rate studies

The dehydration rate of cuprian melanterite to cuprian siderotil depends on the relative humidity in the chamber. Figure 5 illustrates the continued dehydration experiment of the cuprian melanterite described in Figure 3. The heights of the diffraction peaks at 20.95° 2θ and 21.12° 2θ are directly related to the amount of cuprian melanterite in the sample. At time C, the humidity in the chamber (67.7%) is slightly lower than the equilibrium value where cuprian melanterite and cuprian siderotil are in equilibrium (Fig. 4), and cuprian melanterite is slowly dehydrating to form cuprian siderotil, as indicated by a gradual decrease in the intensity of the most intense diffraction-peak. Between time C and time D, 14 hours elapsed, and the amount of cuprian melanterite decreased slowly. At time D, the relative humidity of the chamber was manually decreased to 65%, and a slight increase in the dehydration rate of cuprian melanterite is observed between time D and time E (7 hours elapsed time). At time E, the humidity was further reduced to 59%, and the rate of dehydration of cuprian melanterite increased significantly, as seen

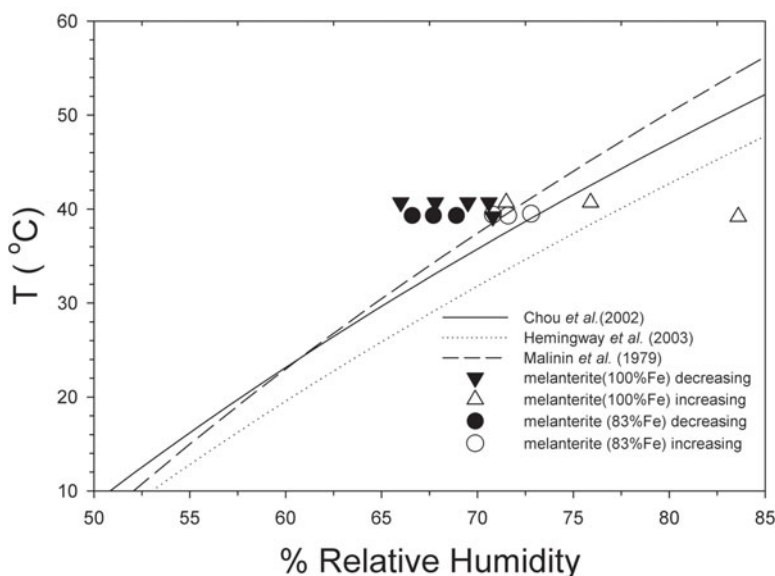


FIG. 4. The phase boundary between the field of stability of melanterite,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , and rozenite,  $\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$ , as described by Chou *et al.* (2002), Malinin *et al.* (1979) and Hemingway *et al.* (2002). Experimental observations of the melanterite (100%Fe) – rozenite transition are indicated by triangles. Experimental observations of the cuprian melanterite – cuprian siderotil transition are indicated by circles. The determination of whether melanterite was increasing or decreasing is based on the change in maximum intensity of the (111) peak of melanterite. There is excellent agreement with the melanterite–rozenite phase boundary at 40.7°C at 71% relative humidity and the values predicted by Malinin *et al.* (1979) (RH 71.9%) and Chou *et al.* (2002) (RH 72.5%). There is no observable difference in the phase boundary near 40°C with that between (100% Fe) melanterite and rozenite and that between cuprian melanterite and cuprian siderotil.

by the more rapid decline in the intensity of the cuprian melanterite peak with time. The relative humidity in the chamber remained at 59% for 17 hours between time E and time F. The rate of dehydration of cuprian melanterite slowed considerably over this period of constant humidity, as seen by a slowing in the rate of change of the intensity of the diffraction peak with time. At time F, the relative humidity is further reduced to 47.8%. Between time F and time G, once again the dehydration rate increased relative to the dehydration rate just before the relative humidity was changed at time F, and then the rate of dehydration slowed with time at this constant relative humidity. At time G, the relative humidity was further decreased to 42%. Two effects are observed in this experiment: 1) the rate of dehydration of melanterite is dependent on the relative humidity in the chamber; 2) at a constant relative humidity, the dehydration rate slows with time.

In a model where the dehydration–hydration reaction is limited by the diffusion of water vapor in or out of the

sample, the rate of reaction is dependent on the concentration gradient according to Fick's law. According to this law, the mass of a solute crossing a unit area per unit time in a given direction is proportional to the gradient of solute concentration in that direction. For a one-dimensional process, it can be stated as:

$$q = -D (\partial C / \partial x) \quad (1),$$

where  $q$  is the mass flux of solute,  $D$  is the diffusion coefficient,  $C$  the mass concentration of diffusing solute, and  $x$ , the direction coordinate. The negative sign indicates that transport is from high to low concentrations. At atmospheric concentrations of  $H_2O$  close to the equilibrium conditions at which cuprian melanterite and cuprian siderotil coexist, the gradient between the surface of the dehydrating cuprian melanterite through the mantle of cuprian siderotil to the atmosphere is small. The rate of diffusion of water vapor away from

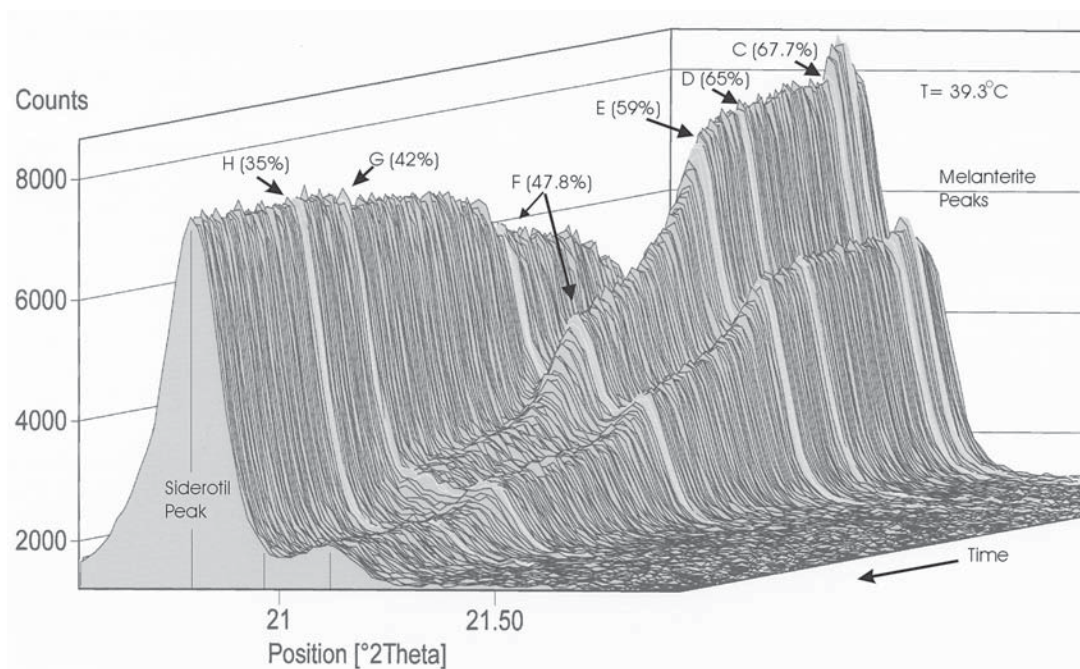


FIG. 5. A continuation of the experiment described in Figure 3. The earliest experiments are at the back of the figure. The relative humidity in the chamber was set at the times indicated by arrows. The humidity in the chamber remained constant between these times. The rate of dehydration of cuprian melanterite changes in response to this change of concentration of  $H_2O$  of the atmosphere. Data were collected at 15-minute intervals. At time D, the humidity was decreased slightly from 67.7% to 65%, and there was a slight increase in dehydration rate of cuprian melanterite. At time E, the humidity was set to 59% and left for 8 hours. Between time E and time F, the rate of dehydration is seen to be high initially and then to slow, as indicated by the rate of change in the heights of the cuprian melanterite peaks. This is attributed to increase length of the diffusion path as the thickness of the cuprian siderotil layer around the cuprian melanterite grains increase. At time F, the relative humidity is further reduced, and the rate of dehydration again increases owing to this decrease in atmospheric concentration of  $H_2O$  in the chamber. Once again, this rate slows as the path length for diffusion increases. By time H, all of the cuprian melanterite has dehydrated to cuprian siderotil.

cuprian melanterite, and therefore the rate of dehydration, is low. As the relative humidity in the chamber is decreased farther below the value where cuprian melanterite is stable, the concentration gradient through the boundary layer increases, and therefore the rates of diffusion and dehydration increase. The slowing of the dehydration rate between time E and time F, as indicated by the slowing of the rate of decrease of the intensity of the cuprian melanterite peaks, is consistent with a diffusion-limited dehydration of melanterite. During this time, the chamber is at a constant humidity, the length of diffusion path through the mantle of siderotil increases, and the rate of dehydration slows. At time F, at which point the humidity in the chamber is once again decreased, and therefore the diffusion gradient is increased, the diffusion of water vapor out of the sample increases, and the rate of dehydration of cuprian melanterite increases. As dehydration proceeds, the path length necessary for water vapor to escape from the cuprian melanterite through the mantle of cuprian siderotil increases. A simple decrease in dehydration rate with time could be attributed to a decrease of the surface area of the materials as the melanterite grains become smaller, but this does not explain the repeated increase in dehydration rate each time the humidity is lowered. A process whose rate is only controlled by surface area will not be dependent on the relative humidity.

Figure 3 illustrates the dehydration behavior, which also supports the hypothesis of a diffusion-controlled model. The starting material was a large crystal of synthetic cuprian melanterite (Bodurtha 1995) that was ground by hand with a mortar and pestle and allowed to partially dehydrate during the preparation of the experiment. At the beginning of the experiment, prior to time A, there is a small decrease in the amount of cuprian melanterite with time, as this material continues to dehydrate to cuprian siderotil. At time A, the humidity is increased slightly by adjusting the gas mixture, and cuprian melanterite begins to form at the expense of cuprian siderotil, as indicated by the increase in the height of melanterite peaks. The formation of this "new" cuprian melanterite takes place by hydrating fine-grained cuprian siderotil exposed directly to the atmosphere in the chamber. The diffusion paths are quite short, and the rate of hydration, quite rapid. After 90 minutes (time B), the humidity in the chamber was set close to the original value prior to A, at which cuprian melanterite is not stable. The "new" cuprian melanterite that had just formed at the expense of cuprian siderotil dehydrated back to cuprian siderotil. At time C, all of the "new" cuprian melanterite that had formed since time A had once again become cuprian siderotil, and the rate of dehydration of cuprian melanterite decreased abruptly. Further conversion of cuprian melanterite required long diffusion-paths to the original cuprian melanterite of the starting material,

which was covered with a mantle of siderotil. With this hypothesis, we assume that movement of water vapor through the sample takes place by diffusion through a homogeneous solid. There is a significant decrease in volume on dehydration from melanterite to siderotil, and water vapor may also leave the sample through cracks in the material created by this shrinkage. This shrinkage would decrease the effective path-length for diffusion, as melanterite surfaces are continuously exposed directly to the atmosphere. This proposal does not explain the reduction in rate of dehydration with time. It is possible that the mechanical effects of dehydration have an effect the dehydration behavior, but current experimental observations are explained by a simple diffusion-limited process.

#### *Non-equilibrium dehydration*

During one of the experiments using the cuprian melanterite, the chamber was opened to the atmosphere while the sample was warm (40°C) to repair the motor assembly. This resulted in a very abrupt drop in the relative humidity over the sample, and the material dried very quickly. When the chamber was resealed, and diffraction resumed, the sample was unexpectedly seen to contain a mixture of rozenite and siderotil (Fig. 6). The dehydration to rozenite of material with this composition had not been previously observed. When the chamber was resealed, the humidity increased to 57.5%, and there was no change in the amount of either phase over a four-hour period. The humidity in the chamber was increased to 76% at time A, as indicated by the white scan in Figure 6. The rozenite quickly disappeared (best seen at X in the figure) by hydrating to siderotil (best seen as the increase in intensity of the siderotil peaks near Y in the figure), and the siderotil subsequently hydrated to melanterite. At time B, the sample was then exposed to conditions of low humidity (68%), and melanterite began to dehydrate, but the rozenite did not reappear. The existence of rozenite with 17 mol.% Cu may be the result of the flash drying experienced by the sample when the chamber was abruptly opened. We do not know the composition of the rozenite, but the starting material was a large optically clear single crystal of synthetic cuprian melanterite; it is unlikely that two phases of different composition could form during such a rapid dehydration. There is no increase in peak widths of the melanterite, which would indicate the formation of a Cu-free melanterite with different unit-cell dimensions.

The formation of rozenite may be related to the requirement that Cu and Fe are ordered between two metal sites in siderotil, whereas there is only one metal site in rozenite. As cuprian melanterite breaks down under conditions of low humidity, the copper and iron atoms must be distributed over the two metal sites in siderotil. Peterson *et al.* (2003) found that Cu preferen-



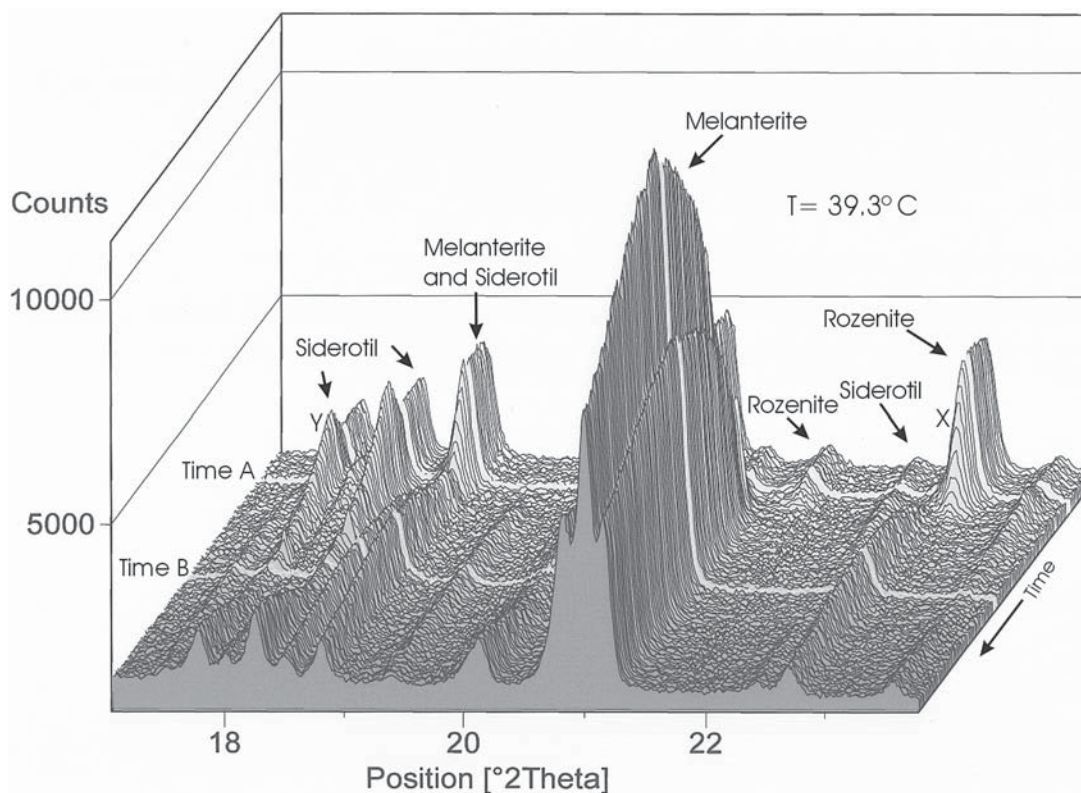


FIG. 6. The sample chamber was opened briefly to the atmosphere of the laboratory, for motor adjustment while the sample was at 40°C. The cuprian siderotil – cuprian melanterite mixture, while still warm, was exposed to much drier laboratory air (~30% relative humidity) and dried very quickly. After the lid was resealed, the sample was observed to contain only diffraction peaks due to siderotil and unexpected rozenite. The first scans were made soon after the chamber was resealed. No peaks for cuprian melanterite were observed. The humidity in the chamber equilibrated to 57.5% relative humidity and remained at this value until time A, indicated by the first white scan. At this point, the humidity was increased to 76%. The rozenite disappeared quickly (seen best at X), and the siderotil peak intensities increased briefly at the expense of the hydrating rozenite (seen best at Y). The siderotil peaks then began to decrease in intensity as melanterite formed. Some time later, at time B indicated by the second white scan, the humidity was decreased to 68%, and siderotil began to increase again, but rozenite did not reappear over this 56-hour period.

tially occupies the M1 site in siderotil. Under very rapid dehydration, however, the ability to order these cations may be reduced, which may be the reason why rozenite (with only one metal site) forms. In future work, we will use the Rietveld technique to determine the site occupancies of these rapidly dehydrated materials, in order to explore this hypothesis further.

#### *Crystallization from a solution*

In Figure 7, we present the results of an experiment in which we studied the crystallization of melanterite from a solution. Diffraction data were measured at four-minute intervals for a  $\text{FeSO}_4$  solution that has soaked a Kimwipe™ that was attached to the zero-background

plate. The soaked Kimwipe™ is used rather than placing only liquid on the zero background plate to avoid the formation of droplets owing to the surface tension of the liquid. The droplets cause the material being studied to be significantly above the parafocusing plane of the diffractometer. Also, if the liquid alone is allowed to evaporate, the solids form on the outer edge of the liquid and then move toward the center of the droplet as the liquid evaporates, whereas the Kimwipe™, evaporation takes place more evenly over the entire surface of the sample holder. The Kimwipe™ contributes very little to the background aside from a broad peak at  $26^\circ 2\theta$  and a weak peak at  $31^\circ 2\theta$  (Fig. 7).

The apparatus creates the possibility of experiments where evaporation and subsequent crystallization can

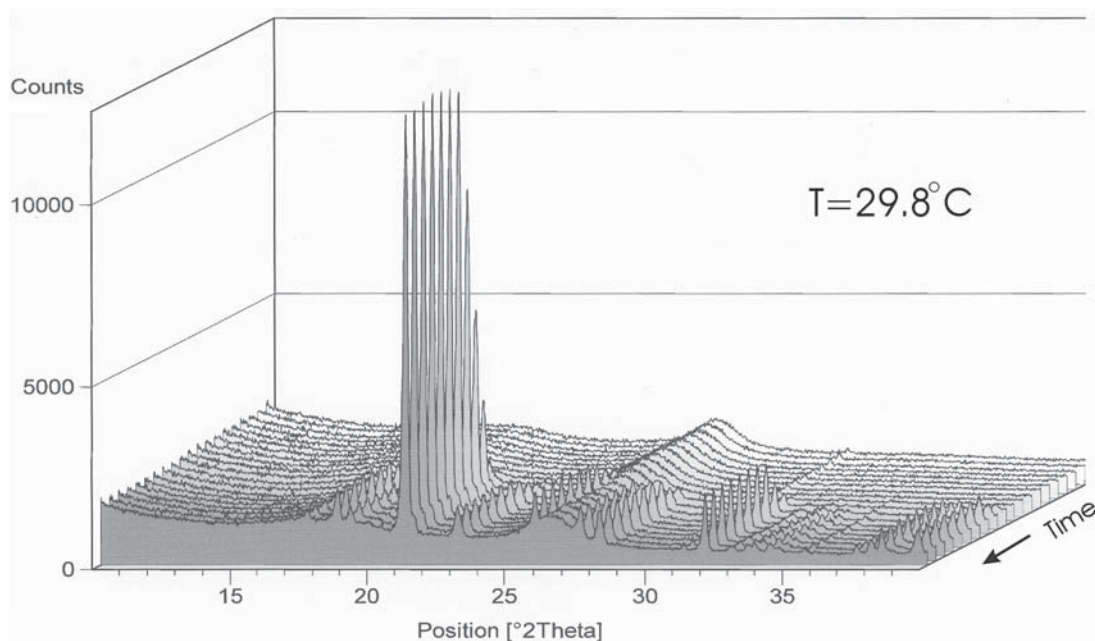


FIG. 7. Crystallization of melanterite from solution. The  $\text{FeSO}_4$  solution was soaked into a Kimwipe™ on a zero-background plate. A broad peak at about  $26^\circ 2\theta$  is due to the Kimwipe™. Data were collected at four-minute intervals.

take place under different relative humidities and under different partial pressures of oxygen. The use of a spinning zero-background plate helps overcome the influence of the large size of crystallites of melanterite that occurred during this crystallization experiment. It is also possible to use a zero-background plate that has been machined with a rim so that it may hold a mineral-liquid slurry in order to study reactions as the material changes in response to acidity of the solution, atmosphere conditions or temperature.

#### CONCLUSIONS

The ability to study the dehydration-hydration reactions in sulfate minerals in a controlled environment creates the opportunity to determine the subtle factors that control them. In mine wastes, these reactions are observed, but are complicated by 1) variations of chemical composition, 2) knowledge of the precise temperature and humidities over the previous several hours, and 3) the inability to return the material to the laboratory without significant changes in the mineralogy. With diffraction studies using materials of known composition, exposed to carefully controlled atmospheres, it is possible to remove these uncertainties and to allow isolation of particular details of these reactions.

The experiments presented here demonstrate that 1) the rate of dehydration of melanterite slows with

time, and 2) the rate of dehydration of melanterite is dependent on the relative humidity of the atmosphere. These two observations are consistent with a dehydration process that is limited by a diffusion process. The rate of diffusion of water vapor, and therefore the rate of dehydration, are proportional to the length of the diffusion path and to the concentration gradient. In experiments in which humidity is maintained at a constant value, the dehydration of melanterite to siderotil slows as the distance that the water vapor must diffuse through the mantle of siderotil increases. When the humidity in the chamber is decreased, the gradient through this boundary layer increases, and the rate of dehydration increases, but again slows as the length of the diffusion path increases as more siderotil forms.

The creation of rozenite from a cuprian melanterite that has been very rapidly dried and then rehydrated illustrates what may be learned from measurements made over short time-periods. The demonstration of the monitoring of the crystallization of melanterite from solution illustrates the applicability of this technique to the study of the formation of sulfate minerals from solutions.

#### ACKNOWLEDGEMENTS

The authors thank I-Ming Chou for generously supplying details of his experimental results and

reviewing the manuscript, J.E. Dutrizac for a helpful review, and D. Paktunc and R.F. Martin for editorial assistance. The research was funded by an NSERC discovery grant.

## REFERENCES

- ALPERS, C.N., BLOWES, D.W., NORDSTROM, D.K. & JAMBOR, J.L. (1994): Secondary minerals and acid-mine water chemistry. *In* The Environmental Geochemistry of Sulfide Mine-Wastes (J.L. Jambor & D.W. Blowes, eds.). *Mineral. Assoc. Can., Short Course Vol. 22*, 247-270.
- BODURTHA, P. (1995): A *Geochemical-Mineralogical Study of Melanterite FeSO<sub>4</sub>•7H<sub>2</sub>O*. H.BSc. thesis, Queen's University, Kingston, Canada.
- CHOU, I-MING, SEAL, R.R. II & HEMINGWAY, B.S. (2002): Determination of melanterite-rozenite and chalcantite-bonattite equilibria by humidity measurements at 0.01 MPa. *Am. Mineral.* **87**, 108-114.
- GREENSPAN, L. (1977): Humidity fixed points of binary saturated aqueous solutions. *J. Res. Nat. Bur. Standards A. Phys. Chem.* **B1A**, 89-96.
- HEMINGWAY, B.S., SEAL, R.R., II & CHOU, I-MING (2002): Thermodynamic data for modeling acid mine drainage problems. I. Selected soluble iron-sulfate minerals. *U.S. Geol. Surv., Open File Rep.* **02-161**.
- JAMBOR, J.L., NORDSTROM, D.K. & ALPERS, C.N. (2000): Metal-sulfate salts from sulfide oxidation. *In* Sulfate Minerals – Crystallography, Geochemistry and Environmental Significance (C.N. Alpers, J.L. Jambor & D.K. Nordstrom, eds.). *Rev. Mineral. Geochem.* **40**, 303-350.
- \_\_\_\_\_ & TRAILL, R.J. (1963): On rozenite and siderotil. *Can. Mineral.* **7**, 751-763.
- MALININ, A.A., DRAKIN, S.I. & ANKUDIMOV, A.G. (1979): Equilibrium dehydration pressures of salt crystal hydrates. *Russ. J. Phys. Chem.* **53**, 755 (translated from *Zh. Fizicheskoi Khim.* **53**, 1332-1333).
- PETERSON, R.C., ROEDER, P.L. & ZHANG, Y. (2003): The atomic structure of siderotil (Fe,Cu)SO<sub>4</sub>•5H<sub>2</sub>O. *Can. Mineral.* **41**, 671-676.
- SONNTAG, D. (1990): Important new values of the physical constants of 1986, vapor pressure formulations based on the ITS-90, and psychrometer formulae. *Z. Meteorol.* **40**, 340-344.

*Received October 19, 2003, revised manuscript accepted July 9, 2005.*