Alpersite (Mg,Cu)SO$_4$·7H$_2$O, a new mineral of the melanterite group, and cuprian pentahydrite: Their occurrence within mine waste

RONALD C. PETERSON,[1,*] JANE M. HAMMARSTROM,[2] AND ROBERT R. SEAL II[2]

[1]Department of Geological Sciences and Geological Engineering, Queen's University, Kingston, Ontario K7L 3N6, Canada
[2]United States Geological Survey, 954 National Center, Reston, Virginia 20192, U.S.A.

ABSTRACT

Alpersite, Mg$_{0.58}$Cu$_{0.37}$Zn$_{0.02}$Mn$_{0.02}$Fe$_{0.01}$SO$_4$·7H$_2$O, a new mineral species with direct relevance to reactions in mine waste, occurs in a mineralogically zoned assemblage in sheltered areas at the abandoned Big Mike mine in central Nevada at a relative humidity of 65% and T = 4 °C. Blue alpersite, which is isostructural with melanterite (FeSO$_4$·7H$_2$O), is overlain by a light blue to white layer dominated by pickeringite, alunogen, and epsomite. X-ray diffraction data (Mo$K\alpha$ radiation) from a single crystal of alpersite were refined in $P2_1/c$, resulting in wR = 0.05 and cell dimensions a = 14.166(4), b = 6.534(2), c = 10.838(3) Å, β = 105.922(6)°, Z = 4. Site-occupancy refinement, constrained to be consistent with the compositional data, showed Mg to occupy the M1 site and Cu the M2 site. The octahedral distortion of M2 is consistent with 72% Cu occupancy when compared with the site-distortion data of substituted melanterite.

Cuprian pentahydrite, with the formula (Mg$_{0.49}$Cu$_{0.41}$Mn$_{0.08}$Zn$_{0.02}$)SO$_4$·5H$_2$O, was collected from an efflorescent rim on a depression that had held water in a large waste-rock area near Miami, Arizona. After dissolution of the efflorescence in de-ionized water, and evaporation of the supernatant liquid, alpersite precipitated and quickly dehydrated to cuprian pentahydrite. These observations are consistent with previous experimental studies of the system MgSO$_4$-CuSO$_4$-H$_2$O. It is suspected that alpersite and cuprian pentahydrite are widespread in mine wastes that contain Cu-bearing sulfides, but in which solubilized Fe^{2+} is not available for melanterite crystallization because of oxidation to Fe^{3+} in surface waters of near-neutral pH. Alpersite has likely been overlooked in the past because of the close similarity of its physical properties to those of melanterite and chalcanthite. Alpersite is named after Charles N. Alpers, geochemist with the United States Geological Survey, who has made significant contributions to our understanding of the mineralogical controls of mine-water geochemistry.

Keywords: Alpersite, pentahydrite, crystal structure, environmental mineralogy, new minerals, XRD data, sulfate mineralogy, chalcanthite, Rietveld refinement, acid mine waste

INTRODUCTION

Secondary sulfate minerals, which occur in sulfide mine waste, play a large role in determining the composition of the effluent that flows from mined areas. Secondary minerals are commonly fine grained and are often mixed with other minerals with which they may, or may not, be in equilibrium. An understanding of the phase relationships and dehydration mechanisms of these sulfate-mineral mixtures is important in determining how the mine waste interacts with the local environment. It is important that we quantify the details of chemical variations, atomic structure, physical properties, and phase relationships of these minerals to understand the processes by which mine waste matures with time and reacts to changes in temperature and (or) humidity. This paper describes the occurrence of alpersite, (Mg$_{0.58}$Cu$_{0.37}$Zn$_{0.02}$Mn$_{0.02}$Fe$_{0.01}$)SO$_4$·7H$_2$O, from central Nevada, and alpersite and cuprian pentahydrite (Mg$_{0.49}$Cu$_{0.41}$Mn$_{0.08}$Zn$_{0.02}$)SO$_4$·5H$_2$O from Miami, Arizona. Alpersite is isostructural with melanterite (FeSO$_4$·7H$_2$O), and cuprian pentahydrite is isostructural with siderotil [(Fe,Cu)SO$_4$·5H$_2$O], but both alpersite and penta-

hydrite have Mg as the dominant cationic species. We suspected that alpersite may have been overlooked because it is similar in color and other physical properties to chalcanthite (CuSO$_4$·5H$_2$O) and cuprian melanterite.

OCCURRENCE

The Big Mike mine, located on the south side of Panther Canyon, on the west flank of the north end of the Tobin Range in sec. 23, T. 31 N, R. 39 E in Pershing County, north-central Nevada (latitude 40° 32' 32"N, longitude 117° 33' 25" W), was discovered in the 1930s and production began in 1967. The mine exploited a massive sulfide deposit that occurs in the late Devonian to early Mississippian Havallah sequence (Rye et al. 1984). Ore minerals include chalcopyrite, bornite, and digenite in the massive sulfide zone, and tenorite and cuprite in the oxide zone. In addition to the high-grade sulfide ore, lower-grade mixed oxide and sulfide ores were mined and stockpiled for hydrometallurgical leaching. By 1970, 2.9 Mt of overburden and 90 000 t of ore averaging 10.5% Cu had been mined from an open pit. From 1970 until 1978, a leaching facility treated 270 000 t of low-grade ore from the dumps and the periphery of the pit (Rye et al. 1984). The hydrometallurgical process involved addition

* E-mail: peterson@geol.queensu.ca

of sulfuric acid to the surface of the leach piles, and collection of pregnant leach solution at the base of the piles. The collected solution was reacted with scrap steel to produce an impure Cu cement (Biswas and Davenport 1976).

Alpersite

Efflorescent sulfate minerals were observed in several settings at the Big Mike mine in June, 1999 and November, 2000 (Fig. 1). These sulfates formed crusts on mine waste adjacent to a small pond at the bottom of the Big Mike open pit. Pit sulfates ranged from dark blue through pale blue, yellow, green, and white, and include chalcanthite, siderotil, melanterite, pickeringite, alunogen, and gypsum. The abandoned Cu-leach operation is several hundred meters from the open pit. A 25 cm thick band of color-zoned efflo-rescent sulfates was present under a concrete berm along the base of a leached ore pile during both site visits. The base of the zoned sulfate sequence consisted of deep blue, very wet crystals of alp-ersite. Alpersite was overlain by progressively drier layers of pale blue, white, and yellowish green sulfates that include pickeringite, epsomite, alunogen, and halotrichite. The yellowish sulfates in the outermost layer were the only minerals found to contain any Fe, as detected by energy-dispersion spectra obtained using a scanning electron microscope. Similar blue to yellow color-zoned sulfate sequences were also observed to fill a length of PVC pipe 25 cm in diameter, and as an upward growth on a vertical concrete wall that formed part of the leach infrastructure.

At the time of the November site visit, the temperature was 4 °C and the measured relative humidity was 65%. At this tem-perature and relative humidity, melanterite and chalcanthite are stable relative to less hydrous Fe- and Cu-sulfate hydrate minerals, assuming ideal compositions (Chou et al. 2002). Average monthly temperatures in the region range from 6 to 34 °C; the region is semi-arid with an average monthly precipitation of less than 2.5 cm. During the June site visit, alpersite was observed growing from puddles near the base of the pile. In November the surfaces of the puddles were frozen. Water from one of the puddles was evaporated in the laboratory and precipitated bright blue crystals

FIGURE 1. Alpersite at the Big Mike mine, Nevada, occurs as a bright blue efflorescence associated with pickeringite [$MgAl_2(SO_4)_4 \cdot 22H_2O$], alunogen [$Al_2(SO_4)_3 \cdot 17H_2O$], and epsomite $MgSO_4 \cdot 7H_2O$. Pickeringite and alunogen (white and yellow) occur on top of a matte of alpersite (blue) adjacent to a concrete wall. The black end of the pen is 5 cm long.

of chalcanthite in the bottom of the dish. Pale blue to white mate-rial composed of alpersite, siderotil, gypsum, pickeringite, and alunogen grew along the sides of the dish. Sediment lining the bottom of the puddle was composed of quartz, mica, chlorite, albite, goethite, and hematite. The sediment contained 7 wt% Fe, 1.6 wt% Mg, and 8800 ppm Cu. Similarly, a bulk sample of the leach-pad material shows that the mine waste is Fe-rich (19.4 wt% Fe, 1.38 wt% Mg, with 1540 ppm Cu). The bulk sample was a 30-increment (stainless steel trowel scoops) composite of <2 mm surface material that weighed about 1 kg. The material was split by cone-and-quarter methods and a sub-sample (about 100 g) was submitted for grinding and analysis. During an industrial leach process, pH is adjusted to depress Fe precipitation and promote Cu precipitation. The solubility of Fe in solution is strongly con-trolled by the pH. Effluent that flows from mine waste typically precipitates large amounts of hydrous iron oxides when the pH is raised to near neutral values. Therefore, the composition of a particular solution depends in part on the average composition of the waste but also to a large extent on the conditions the fluid experienced as it interacted with the mine waste and any second-ary minerals that may have formed. Jarosite-rich mud lines some puddles at the mine site, but no jarosite was detected in the zoned sulfate samples containing alpersite.

Cuprian pentahydrite

In February 2002, a sample containing cuprian pentahydrite was collected at a large area of mine waste northeast of the townsite of Miami, Arizona. The sample was a brownish white efflorescent crust that outlined the edge of a small depression that had once contained water. The X-ray diffraction pattern of the crust also contained peaks attributable to quartz, hematite, jarosite (both indicating the presence of Fe^{3+}), muscovite, and a 7 Å phyllosilicate.

There is no evidence that heap leaching or any other metal extraction process has taken place in the area. There are no nearby buildings, foundations, or other structures associated with the mining activities.

RELATED MINERAL SPECIES

Melanterite is commonly found where water has interacted with sulfide mine tailings and evaporated at relatively high humidity conditions (Frau 2000; Peterson 2003a). Melanterite is readily soluble in water. Melanterite that contains only Fe dehydrates to rozenite ($FeSO_4 \cdot 4H_2O$) when left in low-humidity conditions at room temperature (Chou et al. 2002). The most common metals that substitute for Fe in melanterite are Cu and Zn. When Cu is the dominant metal, the mineral is boothite ($CuSO_4 \cdot 7H_2O$). A recent occurrence of boothite was described by Leverett et al. (2004). Boothite has been synthesized recently, but only crystals with compositions whose amount of Cu is slightly greater than that of Fe were observed (Anderson et al. 2002). Melanterite with small amounts of Cu dehydrates to siderotil, which is isostructural with chalcanthite (Jambor and Traill 1963; Peterson 2003b). When Zn is the dominant metal, the mineral is zinc-melanterite.

Palache et al. (1951) used the name "pisanite" ($(Fe,Cu)SO_4 \cdot 7H_2O$) to describe the range of compositions of the Fe-dominant monoclinic heptahydrate with Cu/(Fe + Cu + Mg + etc.) greater than 17 at% Cu. Palache et al. (1951) used the name

"kirovite" $(Fe,Mg)SO_4·7H_2O$ to describe the range of composi-
tions of the Fe-dominant monoclinic heptahydrate with Mg/(Fe +
Cu + Mg + etc.) greater than 17 at% Mg. Minerals within either
of these compositional ranges are properly named melanterite
under the currently recognized nomenclature (Mandarino and
Back, 2004). Alpersite is defined as the Mg-dominant monoclinic
heptahydrate. The location of the Mg atom within the crystal
structure is not specified by the definition. The preference of
any Cu atom for the M2 site is observed and may stabilize the
alpersite structure, but the presence or location of Cu is not part
of the species definition of alpersite.

Palache et al. (1951) reported that monoclinic crystals with
composition $(Cu,Mg)SO_4·7H_2O$ were obtained by the evapo-
ration of water obtained by dissolving a bluish green crust
found on the lava of an 1872 eruption at Vesuvius. The name
"cupromagnesite" was given to this material. This procedure is
identical to that which was used here to produce alpersite from
the efflorescent material collected at Miami, Arizona. Palache
et al. (1951), Gaines et al. (1997), and Jambor et al. (2000) and
references therein provide complete descriptions of the previous
studies of the melanterite group of minerals.

Milton and Johnston (1938) observed cuprian pentahydrite
occurring with pickeringite on mine timbers in the Com-
stock Lode, Nevada, and determined the composition to be
$(Mg_{0.67}Cu_{0.33})SO_4·5H_2O$. Keller (1908) (in Palache et al. 1951) de-
scribed cuprian pentahydrite, which occurred with chalcanthite,
to have the formula $[Mg_{0.56}(Cu,Zn)_{0.42}]SO_4·5H_2O$.

Epsomite, $MgSO_4·7H_2O$, is orthorhombic and can include
only very small amounts of substitution for Mg by Fe or Cu.
Natural occurrences of kieserite $MgSO_4·H_2O$ and pentahydrite
$MgSO_4·5H_2O$ have been previously described (Palache et al.
1951). Kieserite is the most common Mg sulfate mineral in salt
deposits worldwide, and has been observed to be stable in the
system $MgCl_2$-Na_2SO_4-$NaCl$-H_2O (Braitsch 1971). Pentahy-
drite has been reported from several localities, among which
are The Geysers, Sonoma Co., California, (Gaines et al.1997)
and brine pools in the shore zone of the Gulf of Karas Bugas
(Sedelnikow 1958). Fleischer (1951) recognized pentahydrite,
and its cuprian and zincian varieties, as a valid mineral species.
Baur and Rolin (1972) obtained crystals of $MgSO_4·5H_2O$ for
diffraction experiments from a solution acidified by the addition
of H_2SO_4. These crystals were unstable in air and were coated
with epoxy resin to limit dehydration during the diffraction
experiment.

PREVIOUS SYNTHETIC STUDIES

The secondary sulfates found at the two mine sites described
here contain only low amounts of metals other than Mg and Cu.
The relevant phase system is therefore $MgSO_4$-$CuSO_4$-H_2O,
which has been studied experimentally by Minguzzi (1948) and
Balarew and Karaivanova (1976). Figure 2 summarizes the work
of Minguzzi (1948) and shows that at 30 °C in the presence of a
solution, three different solids can exist: epsomite ($MgSO_4·7H_2O$,
orthorhombic), chalcanthite ($CuSO_4·5H_2O$, triclinic), and alpersite
$[(Mg,Cu)SO_4·7H_2O$, monoclinic]. The particular solids that coex-
ist with solution depend on the bulk composition. There are two
compositional gaps between the coexisting solid sulfates. One gap,
denoted by B in Figure 2, is between epsomite and alpersite, and

the other gap, denoted by A in Figure 2, is between alpersite and
chalcanthite. The range of substitution among these three minerals
is limited. In experiments conducted at 30 °C (Minguzzi 1948),
chalcanthite incorporates up to 8 wt% solid-solution Mg (Fig. 2)
whereas Cu uptake by epsomite is only 3 wt%. Minguzzi (1948)
did not observe boothite, or any of the lower hydrates in this
system, in equilibrium with solution at 30 °C.

According to Lallemant et al. (1974) the only solids that exist in
equilibrium with solution in the $MgSO_4$-H_2O system between 0 and
100 °C are starkeyite $MgSO_4·4H_2O$, hexahydrite $MgSO_4·6H_2O$,
and epsomite $MgSO_4·7H_2O$. Smits and Mazee (1928) and Linke
(1965 and references therein) reported stable $MgSO_4·H_2O$ above
70 °C. Additional hydrates of $MgSO_4$ that have been synthesized
in the system $MgSO_4$-H_2O-H_2SO_4 are (1) kieserite $MgSO_4·H_2O$,
(2) $MgSO_4·1.25$–$2H_2O$, (3) $MgSO_4·3H_2O$, and (4) pentahydrite
$MgSO_4·5H_2O$ (Hodenberg and Kuhn 1967).

PHYSICAL PROPERTIES

Alpersite from the Big Mike mine (Nevada) is turquoise
in color. The collected material consists of equant euhedral
crystals as large as 0.3 mm across. The observed crystal forms
in order of development are {110},{001}, {010}, and {101}. A
good {001} cleavage was observed. The streak is white and the
luster is vitreous. The hardness is 2½ and alpersite is brittle with
an uneven fracture. Optical measurements were made at 25 °C
with sodium light using a Supper spindle stage. The program
EXCALIBR (Bloss 1981) was used to analyze extinction data.
Refractive indices are $α = 1.462$, $β = 1.465$, and $γ = 1.469$, $2V_{meas}$
$= 79.8(7)°$, $2V_{calc} = 82°$), $r > v$ weak. The calculated density is
1.820 g/cm^3. The Gladstone–Dale compatibility index 1–(Kp/Kc)
(Mandarino 1981) is 0.0168, which is categorized as superior.
Fine needles of pickeringite occur within the alpersite. Holotype
material has been deposited at the Canadian Museum of Nature
(specimen number CNMNC 83921). The sample is stored in a
sealed container to avoid dehydration.

CHEMICAL ANALYSIS

Alpersite

The average electron-microprobe analysis of alpersite from the Big Mike
locality is presented in Table 1. The microprobe, a JEOL JXA-8900 instrument, is
equipped with 5 wavelength-dispersion spectrometers, and was operated at 12 kV
with a beam current of 20 nA. Standards included anhydrite for S, chalcopyrite for
Cu, and a variety of silicate and carbonate mineral standards for other elements. The
presence of a small amount of Al in the analysis is likely the result of contamina-
tion due to the close association of alunogen and pickeringite with alpersite at this
locality. The composition of alpersite from the Big Mike mine is plotted on the
ternary diagram of Minguzzi (1948) (Fig. 2).

Thermogravimetric analysis (Fig. 3) of alpersite was completed using a Mettler
SDTA851 thermogravimetric analyzer. Simultaneous evolved-gas analysis with
a Balzers quadrupole mass spectrometer verified that the low-temperature mass
losses represent evolved water and the high-temperature mass losses reflect SO_2.
Upon heating from 25 to 400 °C at a rate of 10 °C per minute in an atmosphere
of flowing Ar, the sample lost 50.8 wt% of the initial sample mass (24.6 mg) due
to dehydration. The sample was dehydrating as the experiment was initiated (note
that the starting mass is less than 100%) and lost weight in three discrete pulses.
The sample lost 45 wt% by 120 °C, and an additional 6 wt% was lost between 120
and 340 °C. This cumulative loss of 50.8 wt% is close to the 48.08 wt% loss that
would be expected for the dehydration of alpersite to anhydrous sulfate. Between
600 and 950 °C an additional 28 wt% decrease occurred, which is attributed to loss
of sulfur species. The residue after heating consisted of cuprite, tenorite, and peri-
clase. The mass-loss for chalcanthite, using reagent-grade crystalline $CuSO_4·5H_2O$,
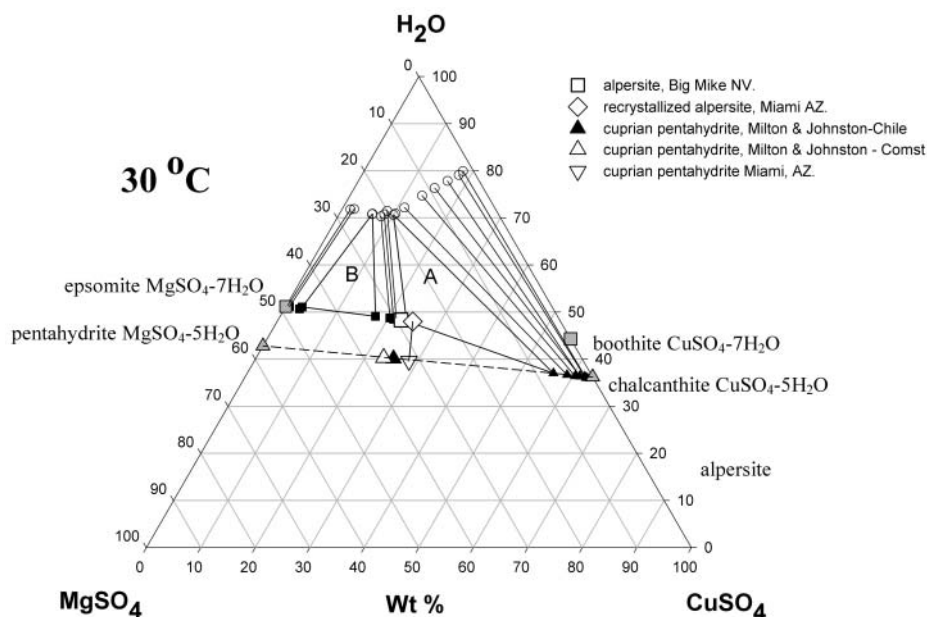was also determined under the same operating conditions. The low-temperature

FIGURE 2. The phase diagram MgSO$_4$-CuSO$_4$-H$_2$O at 30 °C determined by Minguzzi (1948) and modified from I-M. Chou (pers. comm. 2003). Minerals with 7H$_2$O are indicated by a square or diamond. Minerals with 5H$_2$O are indicated by triangles. Solutions are indicated by open circles. Tie lines connect solution compositions, from experiment, in equilibrium with the solids (small squares or diamonds). The composition of alpersite from the Big Mike mine (large open square) and the alpersite which crystallized from the solution obtained from the Miami material (large open diamond) are shown to fall very close to the compositions observed to be stable in the experimental system (small black squares). Alpersite is in equilibrium with solution and chalcanthite (CuSO$_4$·5H$_2$O) (field marked A) or with solution and epsomite (field marked B). The composition of cuprian pentahydrite from Miami (Arizona) is connected by a line to the composition of the alpersite recrystallized from solution. The cuprian pentahydrite observed by Milton and Johnston (1938) falls on the dashed line from pentahydrite (MgSO$_4$·5H$_2$O) to chalcanthite. These minerals most likely represent the dehydration product of alpersite. The experimental data show only limited substitution along the alpersite-epsomite join.

loss of 35.9 wt% is in excellent agreement with the water content of 36.07 wt% predicted from stoichiometry.

Cuprian pentahydrite

The efflorescent sample from Miami, Arizona, was placed in de-ionized water and shaken vigorously. The mixture was allowed to settle and the resulting fluid was a blue-green color. A portion of the decanted solution was submitted to Analytical Services, Queen's University for ICP-AES analysis. The remainder of the solution was allowed to evaporate and the resulting powder X-ray diffraction data of the precipitate match those of pentahydrite. A small amount of gypsum, as determined by powder diffraction, is also present. The results of the fluid analysis are presented in Table 1, and the composition of the resulting solid, (Mg$_{0.49}$Cu$_{0.41}$Mn$_{0.08}$Zn$_{0.02}$)SO$_4$·5H$_2$O (assuming a pentahydrate), is plotted in Figure 2.

The compositions of alpersite from the Big Mike mine and of alpersite crystallized from the supernatant liquid derived by washing the efflorescence from the Miami (Arizona) site are plotted in Figure 2. The compositions of both solids plot very close to the synthetic (Mg,Cu)SO$_4$·7H$_2$O that Minguzzi (1948) observed to be in equilibrium with a solution and chalcanthite.

POWDER X-RAY DIFFRACTION STUDIES

Sulfate minerals were first identified by powder X-ray diffraction (XRD, Cu$K\alpha$) using a Scintag X1 automated powder diffractometer equipped with a Peltier detector. Samples were prepared as smear mounts on zero-background quartz plates, using toluene as a binder or smearing the wet sulfate minerals directly on the plate. Hand-picked sulfate minerals were also examined using a JEOL JSM-840 scanning electron microscope (SEM) equipped with a backscattered-electron (BSE) detector, a secondary electron (SE) detector, and a PGT X-ray energy-dispersion system (EDS). A semi-quantitative, standardless software package was used to estimate atomic proportions of elements in the sulfate minerals to verify and refine XRD identifications. Alpersite was initially identified as a melanterite-group mineral by XRD; SEM analysis showed that material contained Cu and Mg rather than the Fe expected for melanterite. A Gandolfi pattern of the blue material confirmed that the

TABLE 1. Chemical analysis of alpersite

	Big Mike mine NV	Big Mike NV	Big Mike NV	Miami AZ.
	microprobe	ICP-MS	ICP-AES	ICP/AES
	Apfu*†	Apfu†‡	Apfu†‡	Apfu§†
SiO$_2$	(0.01)	na	na	na
Al$_2$O$_3$	(0.11)	(0.07)	(0.06)	(0.00)
FeO	0.01	0.01	0.00	0.00
MnO	0.02	0.02	0.02	0.08
MgO	0.58	0.57	0.58	0.49
CuO	0.37	0.38	0.38	0.41
ZnO	0.02	0.02	0.02	0.02
CaO	(0.00)	(0.01)	(0.00)	(0.02)
Na$_2$O	(0.00)	(0.00)	(0.00)	(0.01)
K$_2$O	(0.00)	(0.00)	(0.00)	(0.00)
SO$_3$	1.02			

* Electron probe microanalysis (average of 37 analyses).
† Formula calculated assuming the sum of Mg and transition metals equals one. Si, Al, Ca, Na, and K are assumed to be contaminants.
‡ Splits of the same digestion (1 g of salt in 100 mL deionized water).
§ ICP-AES performed by the Analytical Services Unit, Queen's University; formulae calculated assuming 1 sulfur atom per formula unit.

unit cell is consistent with a melanterite-group mineral (Howard Evans, written comm., 2000). Heating in an oven at 100 °C for 24 h yielded material that produced an XRD pattern consistent with that of poitevinite (Cu,Fe)SO$_4$·H$_2$O.

ATOMIC STRUCTURE REFINEMENT

Alpersite

Alpersite from the Big Mike mine gives a powder diffraction pattern similar to that of melanterite (Table 2). A single-crystal fragment was extracted and mounted in a capillary, filled with mineral oil, to limit dehydration. Single-crystal X-ray diffraction data (Mo$K\alpha$) were obtained with a Bruker AXS diffractometer;

4430 reflections were collected, which sorted to 2298 unique reflections with an agreement factor of $R = 0.04$ in space group $P2_1/c$. Initial atomic positions for non-hydrogen atoms were taken from the structure of melanterite (Peterson 2003a). Scattering curves for neutral atoms were taken from *International Tables for X-ray Crystallography* (Iber and Hamilton 1974). Least-squares refinement, using XTAL (Hall et al. 1992) and including anisotropic temperature factors and site-occupancy factors, and assuming only Cu and Mg to be present, resulted in a wR of 0.05. The cell dimensions are given in Table 3, atomic coordinates in Table 4, thermal parameters in Table 5, and bond lengths and angles in Table 6. Calculated and observed structure factors are deposited as supplementary information and may also be obtained from the authors upon request.

Alpersite precipitated from a supernatant solution

The blue-green solution obtained by washing the efflorescence collected at Miami (Arizona) was allowed to evaporate and alpersite crystallized from solution. Using the same methods as were used for the alpersite from the Big Mike mine, 6776 reflections were collected, which sorted to 2254 unique reflections with an internal agreement of $R = 0.04$ and refined to w$R = 0.08$. The results are given in Tables 3–6.

Rietveld refinement

The alpersite from the Big Mike mine and alpersite obtained by crystallization of solution obtained from Miami, Arizona, dehydrates to cuprian pentahydrite if left at ambient conditions (21 °C and R.H. = 46%). Several grams of finely ground material of each sample were left to dry. In approximately a week, the material had fully transformed to cuprian pentahydrite. Powder-diffraction data were collected from 6° to 100° 2Θ (Fe filtered Co$K\alpha$ radiation) from a backpacked sample using a Philips X'pert theta-theta diffractometer and X'celerator position-sensitive detector. The data were refined with the Rietveld program X'pert Plus. Starting parameters were taken from Peterson et al. (2003). The unit-cell data are presented in Table 7, atomic coordinates and thermal parameters in Table 8, and bond lengths and angles in Table 9.

DISCUSSION

Alpersite belongs to the melanterite group of minerals ($M^{2+}SO_4 \cdot 7H_2O$, monoclinic) and is defined as the Mg-dominant species. Alpersite from the Big Mike mine also contains Cu^{+2}. The Cu distorts the octahedral coordination in a tetragonal "square-planar" fashion in which the four equatorial bonds are approximately equal in length and are much shorter than the apical bonds (Strens 1966). The octahedron is stabilized if the two apical coordinating oxygen atoms are displaced away from the Cu^{2+} atom with a d^9 electronic configuration. In the melanterite and siderotil structures, the octahedra are very regular if they contain Fe or Mg, but become increasingly distorted with Cu substitution. This distortion can be simply quantified by deter-
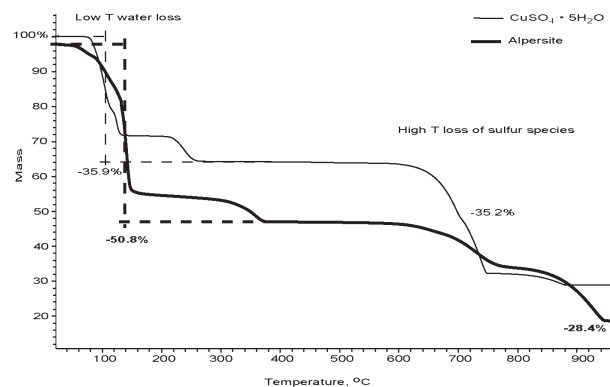
mining the variance of the octahedral bond lengths. The variance is low if no Cu is present, and increases as Cu substitutes into the site. This effect has been described by Peterson (2003a) and is demonstrated in Figure 4. The observed distortion for alpersite from the Big Mike mine and for the re-precipitated material from Miami demonstrates that Cu preferentially occupies the M2 site. The amount of Cu predicted from the distortion, as well as the amount determined by site refinement, matches the measured chemical composition. The distortion of octahedra in melanterite-group minerals directly reflects Cu^{2+} substitution because each octahedron shares no oxygen atoms with other octahedra or tetrahedra, and the distortions are not constrained by polyhedral linkages stronger than those involving hydrogen bonding. It is possible that alpersite with no Cu could be found. The site occupancies of the alpersite described here are driven by the strong preference of Cu to occupy M2; consequently, nothing can be predicted about the site occupancies of an alpersite sample that does not contain Cu.

Alpersite is isostructural with melanterite and, most likely, with boothite ($CuSO_4 \cdot 7H_2O$, monoclinic). Leverett et al. (2004) described boothite with the composition $Cu_{0.86}Mg_{0.072}Zn_{0.055}Mn_{0.010}Co_{0.003}SO_4 \cdot 7H_2O$ from Burraga, New South Wales, Australia. The atomic structure has not been determined but the cell dimensions (Table 3) of boothite are very close to those of alpersite. The ex-
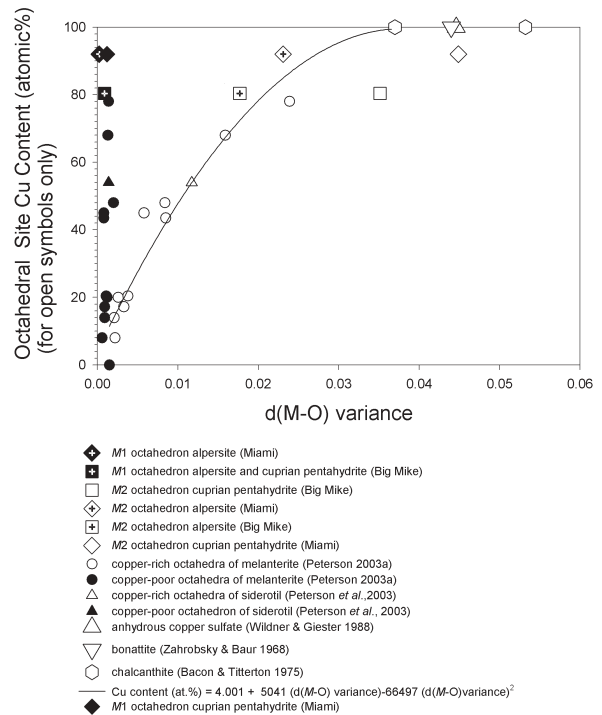

FIGURE 3. Thermogravimetric analysis of alpersite from the Big Mike mine, Nevada, (bold line). A mass-loss pattern for nominal chalcanthite, using reagent-grade crystalline $CuSO_4 \cdot 5H_2O$ and collected under the same operating conditions, is shown for reference (thin line).

FIGURE 4. Octahedral bond-length variation in alpersite and other $MSO_4 \cdot xH_2O$ minerals. The square and diamond symbols containing a cross indicate the octahedral variance of the M2 site for the two alpersite structures refined in this study. All the Cu determined by chemical analysis is assumed to occupy the M2 site. The curve is a least-squares fit of the Cu content of the M2 site as a function of the M2 bond-length variance ($R^2 = 0.95$). The M1 bond-length variance for all of the structures are very low and are plotted as solid symbols. The M1 site-variance data are plotted using the Cu content of the M2 site to allow comparison, but no Cu occupies this site.

TABLE 2. Powder diffraction data for alpersite, Big Mike mine, Nevada

I_{rel}	d_{obs}	d_{calc}	h k l	h k l
30	13.386	13.413	1 0 0	
9	6.782	6.762	2 0 0	
21	5.853	5.849	1 1 0	
136	5.498	5.495	0 1 $\bar{1}$,	0 1 1
91	5.343	5.343	1 0 $\bar{2}$	
1000	4.850	4.854	1 1 1	
139	4.792	4.798	2 0 $\bar{2}$	
51	4.510	4.520	3 0 0	
158	4.439	4.442	1 0 2	
119	4.126	4.131	1 1 $\bar{2}$	
65	3.997	3.998	2 1 1,	3 0 $\bar{2}$
381	3.779	3.778	3 1 $\bar{1}$,	
150	3.663	3.671	1 1 2,	2 0 2
30	3.394	3.395	4 0 0	
149	3.254	3.253	0 2 0,	3 1 1
66	3.145	3.145	1 1 $\bar{3}$	
37	3.102	3.102	4 1 $\bar{1}$	
137	3.078	3.078	2 1 $\bar{3}$,	1 2 $\bar{1}$
77	3.015	3.022	3 0 2,	4 1 0
37	2.939	2.934	4 1 $\bar{2}$	
8	2.874	2.876	3 1 $\bar{3}$	
55	2.781	2.782	1 2 $\bar{2}$	
64	2.742	2.742	3 1 2	
143	2.721	2.720	4 1 1	
63	2.687	2.686	1 0 $\bar{4}$	
86	2.642	2.644	3 2 0	
74	2.627	2.628	1 2 2	
42	2.607	2.609	4 1 $\bar{3}$,	0 0 4
46	2.584	2.577	3 0 $\bar{4}$	
45	2.523	2.524	5 1 $\bar{2}$,	4 0 2
18	2.507	2.509	5 1 0	
22	2.470	2.469	3 2 1	
53	2.429	2.427	1 0 4	
55	2.397	2.397	3 1 $\bar{4}$,	4 2 $\bar{1}$
37	2.369	2.371	0 2 $\bar{3}$,	0 2 3
26	2.322	2.325	6 0 $\bar{2}$,	4 2 $\bar{2}$

I_{rel}	d_{obs}	d_{calc}	h k l	h k l
19	2.310	2.309	5 1 1	
2	2.276	2.267	6 0 0	
27	2.212	2.205	5 0 $\bar{4}$	
20	2.188	2.190	6 1 $\bar{2}$	
8	2.142	2.136	5 2 $\bar{1}$	
16	2.119	2.119	1 3 $\bar{1}$	
27	2.084	2.083	1 3 1	
20	2.035	2.035	1 1 $\bar{5}$	
35	2.014	2.014	1 3 $\bar{2}$	
47	2.004	2.004	4 2 2,	6 0 $\bar{4}$
127	1.971	1.968	3 3 $\bar{1}$	
8	1.943	1.944	7 0 0	
8	1.935	1.937	4 2 $\bar{4}$	
24	1.921	1.924	7 1 $\bar{1}$	
17	1.894	1.894	6 2 $\bar{2}$	
33	1.886	1.888	1 1 5	
29	1.860	1.862	6 2 0,	7 1 $\bar{3}$
113	1.841	1.840	2 2 4	
28	1.824	1.824	5 1 3	

Notes: Co$K\alpha$ (Fe) back-packed sample; a = 14.1831(6), b = 6.5312(3), c = 10.8193(5) Å, β = 106.005(3)°. I_{obs} and d_{obs} determined by profile fit (X'Pert plus). Cell dimensions, d_{calc}, and indexing based on Rietveld refinement.

TABLE 3. Cell dimensions of $M^{2+}SO_4 \cdot 7H_2O$

	melanterite* (Peterson 2003a)	alpersite* Big Mike, NV	alpersite (syn)* Miami, AZ	boothite† (Leverett et al. 2004)
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a (Å)	14.071(6)	14.166(4)	14.189(5)	14.190(10)
b (Å)	6.505(2)	6.534(2)	6.547(2)	6.537(2)
c (Å)	10.958(3)	10.838(3)	10.830(4)	10.825(6)
$\beta°$	105.69(1)	105.922(6)	105.872(8)	106.02(5)
V (Å³)	965.7(6)	964.6(9)	967(1)	965

* Determined by least-squares refinement of single-crystal diffraction data.
† Determined by least-squares refinement of powder-diffraction data.

TABLE 4. Atomic coordinates of alpersite from the Big Mike mine NV (BM) and from Miami AZ (MIAM)

Atom	Locality	X	Y	Z	Mg/(Cu + Mg) (%)
M1	BM	0.	0.	0.	0.964(3)
	MIAM	0.	0.	0.	0.845(5)
M2	BM	.5	.5	0.	0.402(3)
	MIAM	.5	.5	0.	0.265(4)
S	BM	.22874(8)	.4693(2)	.1744(1)	
	MIAM	.22865(9)	.4672(2)	.1741(1)	
O1	BM	.2019(2)	.4718(5)	.0327(3)	
	MIAM	.2017(2)	.4691(5)	.0321(3)	
O2	BM	.1440(2)	.5424(5)	.2159(3)	
	MIAM	.1444(2)	.5431(5)	.2181(4)	
O3	BM	.3142(2)	.6036(5)	.2245(3)	
	MIAM	.3152(2)	.6028(5)	.2240(4)	
O4	BM	.2533(2)	.2582(5)	.2230(3)	
	MIAM	.2538(3)	.2569(5)	.2221(4)	
Ow5	BM	.1053(2)	.3750(6)	.4255(4)	
	MIAM	.1057(3)	.3789(6)	.4256(4)	
Ow6	BM	.1043(2)	.9561(5)	.1765(3)	
	MIAM	.1047(3)	.9562(5)	.1773(4)	
Ow7	BM	.0273(2)	.7908(5)	.4297(3)	
	MIAM	.0286(3)	.7911(5)	.4300(4)	
Ow8	BM	.4810(2)	.4535(5)	.1751(3)	
	MIAM	.4814(2)	.4530(5)	.1737(3)	
Ow9	BM	.4309(2)	.2692(5)	.4419(3)	
	MIAM	.4294(2)	.2645(5)	.4391(4)	
Ow10	BM	.3491(2)	.8418(5)	.4400(3)	
	MIAM	.3480(3)	.8390(5)	.4413(4)	
Ow11	BM	.3666(2)	.0073(5)	.1123(3)	
	MIAM	.3682(2)	.0085(5)	.1131(3)	

periments of Minguzzi (1948) for the system $MgSO_4$-$CuSO_4$-H_2O showed that alpersite coexists with chalcanthite and solution, but not with boothite at 30 °C.

The relationship of alpersite to minerals in the $MgSO_4$-$CuSO_4$-H_2O system is shown in Figure 2. The composition of alpersite falls along the line that joins epsomite and boothite. Experimental studies have indicated that a compositional gap exists between alpersite and boothite and between alpersite and chalcanthite at 30 °C in equilibrium with solution. Epsomite is the Mg-dominant orthorhombic heptahydrate and has a different crystal structure than alpersite. The Mg/Mg + Cu ratio of the alpersite and cuprian pentahydrite observed in this study fall near, but not on, the mid-point in the chalcanthite-pentahydrite series. Minguzzi (1948) showed that solid solution between chalcanthite and alpersite, and between chalcanthite and epsomite, is limited (Fig. 2). An independent measure of the chemical composition of

TABLE 5. Anisotropic displacement parameters (Å²) for alpersite from the Big Mike mine, Nevada (BM), and from Miami Arizona (MIAM)

Site	Sample	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
M1	MIAM	3.1(1)	3.1(1)	3.3(1)	−.32(9)	.93(8)	−.2(1)
	BM	2.7(1)	2.4(1)	3.5(1)	−.3(1)	1.0(1)	−.4(1)
M2	MIAM	3.10(6)	3.48(8)	2.41(6)	−.49(5)	.55(4)	−.18(5)
	BM	2.9(7)	3.00(7)	2.47(7)	−.44(6)	.64(5)	−.19(6)
S	MIAM	3.27(7)	3.81(9)	3.23(8)	.05(6)	.88(6)	−.10(7)
	BM	3.07(7)	3.10(7)	3.63(8)	.06(6)	1.02(6)	−.03(7)
O1	MIAM	5.0(2)	4.7(2)	3.0(2)	−.8(2)	.5(2)	−.3(2)
	BM	4.9(2)	4.6(2)	3.0(2)	−.7(2)	.8(2)	−.1(2)
O2	MIAM	4.0(2)	5.9(3)	6.2(3)	2.1(2)	2.5(2)	1.3(2)
	BM	4.8(2)	5.0(2)	5.9(2)	1.5(2)	3.3(2)	1.2(2)
O3	MIAM	4.5(2)	5.9(3)	4.3(3)	−1.8(2)	1.2(2)	−1.0(2)
	BM	4.7(2)	4.4(2)	5.0(3)	−1.8(2)	.9(2)	−1.1(2)
O4	MIAM	6.1(2)	2.7(2)	4.6(3)	.8(2)	1.0(2)	.5(2)
	BM	5.0(2)	3.6(2)	5.5(3)	.8(2)	.9(2)	.7(2)
Ow5	MIAM	6.5(3)	7.0(3)	6.2(3)	3.8(2)	3.4(2)	2.2(2)
	BM	6.7(3)	6.3(3)	6.4(3)	3.0(2)	3.7(2)	2.4(2)
Ow6	MIAM	4.6(2)	4.8(3)	5.2(3)	.1(2)	.2(2)	.5(2)
	BM	5.1(2)	4.3(2)	4.6(2)	.4(2)	.3(2)	.3(2)
Ow7	MIAM	5.5(2)	3.5(2)	5.3(3)	−.4(2)	1.4(2)	.5(2)
	BM	4.5(2)	3.4(2)	5.0(2)	−.3(2)	1.1(2)	.8(2)
Ow8	MIAM	4.9(2)	4.6(2)	3.8(2)	−.5(2)	1.2(2)	.3(2)
	BM	4.3(2)	4.8(2)	3.6(2)	−.4(2)	1.3(2)	.1(2)
Ow9	MIAM	5.0(3)	4.6(2)	3.9(2)	.73(2)	1.1(2)	.5(2)
	BM	4.9(2)	4.0(2)	4.3(2)	.7(2)	.7(2)	.7(2)
Ow10	MIAM	4.3(2)	5.6(3)	4.7(3)	.1(2)	.8(2)	−.6(2)
	BM	5.1(2)	5.3(2)	4.5(3)	.8(2)	.6(2)	−.7(2)
Ow11	MIAM	4.6(2)	3.9(2)	4.6(2)	−.2(2)	.8(2)	.3(2)
	BM	4.9(2)	3.6(2)	4.9(2)	.1(2)	.8(2)	.4(2)

Notes: $U = \{\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]\} \times 10^2$.

TABLE 6. Bond lengths (angstroms) and angles (°) for alpersite

	Big Mike, NV	Miami, AZ	Angle	Big Mike, NV	Miami, AZ
M1-Ow5(×2)	2.051(4)	2.046(5)	Ow5-M1-Ow6	89.6(1)	90.1(1)
M1-Ow6(×2)	2.091(3)	2.101(3)	Ow5-M1-Ow7	89.5(1)	88.6(1)
M1-Ow7(×2)	2.122(3)	2.131(4)	Ow5-M1-Ow6	90.4(1)	89.9(2)
Average	2.088	2.093	Ow5-M1-Ow7	90.5(1)	91.5(2)
Variance	0.0008	0.0012	Ow6-M1-Ow7	87.0(1)	92.7(1)
			Ow6-M1-Ow7	93.1(1)	87.3(1)
M2-Ow8(×2)	2.012(3)	1.994(4)	Ow8-M2-Ow9	90.9(1)	90.4(1)
M2-Ow9(×2)	2.028(3)	2.019(3)	Ow8-M2-Ow10	91.1(1)	91.4(1)
M2-Ow10(×2)	2.302(3)	2.328(4)	Ow8-M2-Ow9	89.1(1)	89.7(2)
Average	2.114	2.114	Ow8-M2-Ow10	88.9(1)	88.6(1)
Variance	0.0177	0.0231	Ow9-M2-Ow10	88.3(1)	87.6(1)
			Ow9-M2-Ow10	91.7(1)	92.4(1)
S-O1	1.477(3)	1.480(4)	O1-S-O2	108.4(2)	109.2(2)
S-O2	1.473(4)	1.488(4)	O1-S-O3	109.1(2)	109.0(2)
S-O3	1.472(4)	1.491(4)	O1-S-O4	110.4(2)	110.0(2)
S-O4	1.484(3)	1.481(4)	O2-S-O3	110.5(2)	109.8(2)
Average	1.477	1.485	O2-S-O4	108.9(2)	109.6(2)
			O3-S-O4	109.5(2)	109.3(2)

Notes: Variance = average of the squared deviation of each bond length from the mean bond length.

alpersite was completed by least-squares refinement of the site occupancies of the octahedral sites in alpersite. The content of each octahedral site was constrained such that the site is fully occupied. A Mg/(Mg + Cu) ratio of 0.56 for alpersite from Miami (Arizona) determined by site refinement agrees well with a ratio of 0.49 determined by chemical analysis (Table1). The site refinement of alpersite from the Big Mike mine gave a ratio of Mg/(Mg + Cu) = 0.68, which is higher than the ratio Mg/(Mg + Cu + Zn + Mn + Fe) = 0.58 obtained by chemical analysis. The maximum Mg/(Mg + Cu) ratio observed by Minguzzi (1948) is 0.72 (Fig. 2)

Cuprian pentahydrite, the dehydration product of alpersite, belongs to the chalcanthite group of minerals ($M^{2+}SO_4 \cdot 5H_2O$, triclinic). The composition is intermediate between chalcanthite and pentahydrite, which are isostructural. Rietveld refinement of powder-diffraction data of the occupancy of the two symmetrically distinct octahedral sites shows that Cu is ordered at the M2 site (Table 8). It could be argued that $Mg_{0.5}Cu_{0.5}SO_4 \cdot 5H_2O$ is an ordered member of the pentahydrite - chalcanthite series and deserves a distinct mineral name. The cuprian pentahydrite is separated from chalcanthite and pentahydrite by a compositional gap, but this apparent gap may only be a reflection of the gap that exists in the heptahydrates, from which cuprian pentahydrite commonly forms by dehydration (Fig. 2). However, in their study of the $CuSO_4$-$MgSO_4$-H_2O system at 60 °C Balarew and Karaivanova (1976) observed a compositional gap between $MgSO_4 \cdot 6H_2O$ and $(Mg,Cu)SO_4 \cdot 5H_2O$, as well as a gap between $(Mg,Cu)SO_4 \cdot 5H_2O$ and $CuSO_4 \cdot 5H_2O$. Use of the name cuprian pentahydrite or magnesian chalcanthite, as was suggested by Fleischer (1951) to describe the minerals of intermediate composition in this isostructural series, allows a clear description without the additional complexity of defining a new mineral species.

Milton and Johnston (1938) observed a cuprian pentahydrite from Comstock, Nevada, and determined the composition to be $(Mg_{0.67}Cu_{0.33})SO_4 \cdot 5H_2O$. Keller (1908) (in Palache et al. 1951) described a sulfate, which occurred with chalcanthite, to have the formula $Mg_{0.64}Cu_{0.35}Mn_{0.01} SO_4 \cdot 5H_2O$. These compositions are plotted on the $MgSO_4$-$CuSO_4$-H_2O phase diagram (Fig. 2). The Mg/(Mg + Cu) ratio of both of these minerals suggests that they formed by crystallizing from a liquid as alpersite, which subsequently dehydrated to cuprian pentahydrite. This is also the case for cuprian pentahydrite from Miami (Arizona), which likely formed by dehydration of alpersite that crystallized as an efflorescence, in contact with fluid, at the edge of the depression on the surface of mine waste. Melanterite-group minerals readily incorporate Fe^{2+}, but none of the collected alpersite or cuprian pentahydrite contains significant Fe. The absence of Fe in these samples indicates that no Fe^{2+} was available from solution during crystallization.

One scenario that would result in the formation of alpersite in mine waste involves the dissolution of melanterite. If melanterite

TABLE 7. Cell dimensions for $M^{+2}SO_4 \cdot 5H_2O$

	Cuprian pentahydrite Big Mike, NV	Cuprian pentahydrite Miami, AZ	Siderotil Iron Mtn, CA (Peterson et al. 2003)	Pentahydrite (Baur and Rolin 1972)	Chalcanthite (Bacon and Titterton 1975)
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	6.2490(3)	6.2470(3)	6.292(5)	6.314(5)	6.141
b (Å)	10.5846(4)	10.5995(4)	10.632(8)	10.57(2)	10.736
c (Å)	6.0384(2)	6.0395(2)	6.072(5)	6.030(6)	5.986
α (°)	82.461(2)	82.530(2)	82.63(1)	81.1(2)	82.26
β (°)	109.433(2)	109.408(2)	110.02(1)	109.8(2)	107.43
γ (°)	104.805(2)	104.794(2)	105.19(1)	105.08(5)	102.66
V (Å³)	363.7	364.2	368.0	364.4	366.4

with significant and roughly equal amounts Mg and Cu is dissolved in distilled water in the laboratory, within 24 h all of the Fe is precipitated as a ferric hydroxide. If the resulting solution is allowed to evaporate, a heptahydrate sulfate crystallizes. If Mg is in excess relative to Cu, epsomite will form with alpersite. If Cu is significantly in excess relative to Mg, chalcanthite forms with alpersite.

Melanterite forms in acidic mine waters and is stable in contact with air with a relative humidity of greater than 60% at 20 °C (Chou et al. 2002). Most mine sites go through seasonal variations in the amount of water available to interact with the waste. After a dry period, if the melanterite or melanterite dehydration products are exposed to rain water, they dissolve and the Fe^{2+} oxidizes to Fe^{3+}, thereupon precipitating as the hydrous iron oxides that are observed lining the stream beds at many mine sites. If this type of solution accumulates and subsequently evaporates, alpersite may form. In many cases, however, high flow rates and dilution prevent precipitation. It is possible that the Miami occurrence of the dehydration product of alpersite resulted because such a fluid accumulated in a depression and formed alpersite as the solution evaporated. Other scenarios would also result in alpersite crystallization, but all must involve a mechanism whereby minimal Fe^{2+} exists in solution; otherwise, Fe^{2+} will be incorporated into the crystal structure and melanterite, not alpersite, will be more likely to crystallize.

Alpersite and cuprian pentahydrite are likely common under surface conditions where Cu and Mg exist in solution and Fe has been oxidized to the ferric state. Such conditions exist in many Cu mining areas around the world and these minerals may play a significant role in controlling the seasonal variation of the composition of the aqueous effluents, which flow from these mine sites. Alpersite may have been overlooked because it could easily be mistaken for chalcanthite or melanterite, both of which can occur as blue vitreous material or a fine-grained efflorescence. Cuprian pentahydrite may be mistakenly identified as siderotil, as both occur as white or lightly colored crusts. Proper identification requires careful X-ray diffraction measurements and chemical analysis.

The presence of cuprian pentahydrite and not the monohydrate in the hot and arid conditions at Miami (Arizona) indicates that the dehydration behavior in the Cu-Mg system is similar to that in the Fe-Cu system, wherein siderotil [$(Fe,Cu)SO_4·5H_2O$] and not szomolnokite ($FeSO_4·H_2O$) is observed under such conditions. An experimental study to determine the dependence of dehydration behavior on composition is in progress (Peterson 2003b).

New species designation

Initially, we questioned the designation of alpersite as a new mineral species, as it was first observed in a mine-waste setting where it may have formed because of the unique chemistry created by the heap-leach activity of the mine. If this were the only evidence of the existence of alpersite, then we would not have put the mineral forward as a candidate for new species designation. However the presence of the alpersite dehydration product, cuprian pentahydrite, at several different localities, and the ability to recrystallize these dehydration products to alpersite

TABLE 8. Atomic coordinates of cuprian pentahydrite from Big Mike mine, Nevada, (BM) and from Miami, Arizona, (MIAM)

Atom	Locality	X	Y	Z	U(iso) ($Å^2 × 10^2$)	Site occupancy (Mg)/(Cu + Mg)
M1	BM	0	0	0	4.9(2)	0.2(7)
	MIAM	0	0	0	5.6(2)	0.1(8)
M2	BM	.5	.5	0	4.8(3)	0.7(6)
	MIAM	.5	.5	0	3.7(2)	0.7(6)
S	BM	.0363(7)	.2884(4)	.6392(7)	3.6(3)	
	MIAM	.0368(8)	.2935(4)	.6402(7)	3.9(2)	
O1	BM	.910(1)	.1601(9)	.669(1)	3.7(1)	
	MIAM	.911(1)	.1662(9)	.666(1)	3.7(1)	
O2	BM	.261(2)	.3232(7)	.842(2)	3.7(1)	
	MIAM	.263(2)	.3227(8)	.847(2)	3.7(1)	
O3	BM	.872(1)	.3715(8)	.638(1)	3.7(1)	
	MIAM	.872(1)	.3720(8)	.639(1)	3.7(1)	
O4	BM	.051(1)	.2981(7)	.408(1)	3.7(1)	
	MIAM	.053(1)	.2958(8)	.411(1)	3.7(1)	
Ow5	BM	.820(1)	.0683(7)	.173(1)	3.7(1)	
	MIAM	.821(1)	.0687(7)	.178(1)	3.7(1)	
Ow6	BM	.314(1)	.1172(8)	.174(2)	3.7(1)	
	MIAM	.312(1)	.1161(8)	.173(2)	3.7(1)	
Ow7	BM	.530(1)	.5959(6)	.672(1)	3.7(1)	
	MIAM	.535(1)	.5917(7)	.671(2)	3.7(1)	
Ow8	BM	.232(1)	.5913(7)	.981(1)	3.7(1)	
	MIAM	.230(1)	.5917(7)	.988(1)	3.7(1)	
Ow9	BM	.453(1)	.1276(7)	.648(2)	3.7(1)	
	MIAM	.446(2)	.1289(8)	.647(2)	3.7(1)	

TABLE 9. Bond lengths (Å) and angles (°) of pentahydrite

Bond	Pentahydrite (Baur and Rolin 1972)	Cuprian pentahydrite Big Mike mine, NV	Cuprian pentahydrite Miami, AZ	Angle	Big Mike, NV	Miami, AZ
M1-O1(×2)	2.091(5)	2.457(8)	2.511(8)	Ow5-M1-Ow6	93.1(4)	92.8(5)
M1-Ow5(×2)	2.059(5)	2.066(9)	2.088(10)	Ow5-M1-Ow6	86.9(4)	87.2(4)
M1-Ow6(×2)	2.049(5)	2.053(7)	2.039(7)	Ow5-M1-O1	91.6(5)	91.7(5)
Average	2.064	2.192	2.213	Ow6-M1-O1	85.8(4)	86.6(4)
Variance	0.00030	.03514	.04490	Ow6-M1-O1	94.2(4)	93.4(4)
				Ow5-M1-O1	88.4(4)	88.3(4)
M2-O2(×2)	2.097(5)	2.175(8)	2.167(8)	Ow8-M2-Ow7	89.0(5)	86.3(5)
M2-Ow7(×2)	2.046(5)	2.150(9)	2.153(9)	Ow8-M2-Ow7	91.0(5)	93.7(5)
M2-Ow8(×2)	2.038(5)	2.103(9)	2.130(9)	Ow8-M2-O2	86.1(4)	85.6(4)
Average	2.053	2.143	2.150	Ow7-M2-O2	94.7(5)	94.8(5)
Variance	.00071	.00089	.00023	Ow7-M2-O2	85.3(4)	85.2(4)
				Ow8-M2-O2	93.9(5)	94.4(5)
S-O1	1.471(5)	1.408(9)	1.396(9)	O3-S-O1	103(1)	102.20(2)
S-O2	1.477(5)	1.524(9)	1.537(9)	O3-S-O2	109.82(8)	112.2(2)
S-O3	1.462(5)	1.510(11)	1.475(11)	O3-S-O4	106.89(9)	109.8(2)
S-O4	1.467(2)	1.420(9)	1.418(9)	O1-S-O2	111.90(4)	110.22(4)
Average	1.469	1.466	1.456	O1-S-O4	105(1)	102(1)
				O2-S-O4	118.5(2)	118.6(2)

Note: Variance = average of the squared deviation of each bond length from the mean bond length.

under high-humidity conditions, indicate that alpersite forms in nature and then dehydrates to cuprian pentahydrite. Alpersite is isostructural with minerals of the melanterite group, it has a chemical composition which involves elements that are common in areas where sulfide ore has oxidized, and synthetic studies have shown that conditions for the formation of alpersite can be expected in near-surface mine-waste settings.

Alpersite is named after Charles N. Alpers (b. 1958), geochemist with the United States Geological Survey, who has made significant contributions to our understanding of the mineralogical controls of mine-water geochemistry (Alpers et al. 1989, 1994a, 1994b, 2000; Alpers and Nordstrom 1999; Nordstrom and Alpers 1999a, 1999b; Nordstrom et al. 2000; Jamieson et al. 2005).

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