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WILCOXITE $MgAl(SO_4)_2F•17H_2O$, FROM RICO, COLORADO: OCCURRENCE AND CRYSTAL STRUCTURE

R.C. PETERSON[§] AND B.R. JOY

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

ABSTRACT

Wilcoxite, $(Mg_{0.81}Mn_{0.07}Fe_{0.04}Zn_{0.04})_{\Sigma 0.96}Al_{1.01}(SO_4)_2F_{1.02}•17H_2O$, is a secondary sulfate mineral that occurs in hydrothermal systems containing significant amounts of fluorine. A sample of wilcoxite was collected from abandoned mine workings east of Rico, Dolores Co., Colorado, U.S.A., where it occurs as white, efflorescent crusts composed of small anhedral crystals within a timber crib that protected the material from direct exposure to rain and snow, but not from changes in the humidity and temperature of the atmosphere. It is remarkable that this highly hydrated mineral has remained stable under these conditions. Unit cell dimensions are *a* 6.644(1), *b* 6.749(2), and *c* 14.892(3) Å, α 79.664(4)°, β 80.113(4)°, γ 62.487(3)°, and *V* 579.6(2) $Å^3$, space group $\overline{P}$ The previously unknown crystal structure was determined from single-crystal X-ray diffraction data and consists of isolated sulfate tetrahedra, $Mg(H_2O)_6$ octahedra, and $Al(H_2O,F)_6$ octahedra connected only through hydrogen bonding involving additional water molecules. Wilcoxite has 1.5 water molecules per sulfate tetrahedron that do not participate in the formation of an $Al(H_2O,F)_6$ or $Mg(H_2O)_6$ octahedron. The water molecules held within the epsomite ($MgSO_4•7H_2O$) structure are lost if the relative humidity (RH) drops below 50% at 298 K, and hexahydrite ($MgSO_4•6H_2O$) loses water to form starkeyite ($MgSO_4•4H_2O$) at 40% RH at 298 K. The fact that wilcoxite, with such a high water content, is stable when the magnesium sulfate with which it coexists has become starkeyite indicates that water molecules are more tightly bonded within the wilcoxite structure. If epsomite crystals are warmed slightly they slowly become first translucent and then an opaque white powder, whereas wilcoxite does not dehydrate but abruptly melts when warmed. This behavior is similar to the incongruent melting of meridianiite ($MgSO_4•11H_2O$) on warming above 2 °C.

Keywords: wilcoxite, crystal structure, meridianiite, epsomite, hexahydrite, hydrogen bonding, Rico, Colorado, X-ray diffraction, infrared spectroscopy, dehydration.

INTRODUCTION

Sulfate minerals are common in many different environments on Earth. Within this group of minerals are simple anhydrous sulfates such as thenardite, Na_2SO_4, which occurs in saline lake deposits as the result of the dehydration of the hydrated sulfate mirabilite, $Na_2SO_4•10H_2O$. Sulfates often occur as a result of the oxidation of sulfide minerals through reactions with oxygen and water. The formation of melanterite, $Fe^{2+}SO_4•7H_2O$, associated with the oxidation and hydration of pyrite, is well known. Sulfate minerals often contain transition metals and are important phases that may affect the effluent from mine waste. Jarosite, $KFe_3(SO_4)_2(OH)_6$, and copiapite, $Fe^{2+}(Fe^{3+})_4(SO_4)_6(OH)_2•20H_2O$, are important sulfate minerals in such an environment. Sulfates may contain other anion groups, such as the OH^- in jarosite, but they may also contain $(CO_3)^{2-}$ [*e.g.*, rapidcreekite, $Ca_2(SO_4)(CO_3)•4H_2O$], $(PO_4)^{3-}$ (*e.g.*, woodhouseite, $CaAl_3(PO_4)(SO_4)(OH)_6$), $(AsO_4)^{3-}$ [*e.g.*, beudantite, $PbFe^{3+}{}_3(OH)_6(AsO_4)(SO_4)$], and $(NO_3)^-$ [*e.g.*, ungemachite, $K_3Na_8Fe^{3+}(SO_4)_6(NO_3)_2(H_2O)_6$]. Sulfates, such as kainite, $KMg(SO_4)Cl•3H_2O$, that form in marine evaporite deposits contain chlorine as an anion. The chlorine is often bonded to sodium or potassium, forming part of a large coordination polyhedra. This study describes a new occurrence of the mineral wilcoxite, $MgAl(SO_4)_2F•17H_2O$. Wilcoxite was first described by Williams & Cesbron (1983) from the Lone Pine mine, Catron County, New Mexico and contains fluorine as an anionic species. Zhdanov *et al.* (1993) described the occurrence of wilcoxite within oxidized cassiterite-tourmaline-quartz-polysulfide ore in northeastern Yakutia, Russia.

The incorporation of fluorine into sulfate minerals is uncommon, likely due to the low concentration of fluorine in the low-temperature aqueous environments where most sulfates form. Fluorine is found as an anion as part of the octahedron coordinating aluminum

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[§] *E-mail address:* peterson@geol.queensu.ca

in the atomic structure of wilcoxite that is described here. Fluorine is also found to coordinate aluminum in khademite, $Al(SO_4)F{\bullet}5H_2O$ (Cesbron & Bayliss 1988, Bachet *et al.* 1981). Fluorine may also combine with sulfur to form SO_3F groups, as found in reederite $Na_{15}Y_2(CO_3)_9(SO_3F)Cl$ (Grice *et al.* 1995). Reederite has been described from the Poudrette Quarry at Mont St. Hilaire, Quebec, which is known for its unusual geochemical environment (Currie *et al.* 1986, Horváth & Gault 1990). Table 1 lists those sulfate minerals that contain significant fluorine but the list does not include minerals containing fluoro-sulfate tetrahedra.

OCCURRENCE

The sample of wilcoxite was collected in October of 2009 from the side of a timber crib, used in the past to load ore, east of Rico Colorado (N37 42.023 W108 00.959) (Fig. 1). The Rico mining district is in the western San Juan Mountains of Colorado. The ores in the district are found in epithermal vein deposits, porphyry-style molybdenum deposits, and carbonate replacement deposits (Larson 1987).

Secondary sulfate minerals directly associated with wilcoxite at this locality are hexahydrite $MgSO_4{\bullet}6H_2O$, starkeyite $MgSO_4{\bullet}4H_2O$, and alunogen $Al_2(SO_4)_3{\bullet}17H_2O$. All of these minerals occur as efflorescence on the surface of waste ore found between the timbers of the crib where there is some protection from rain and snow. An X-ray powder diffraction pattern was used to identify the powder as wilcoxite (see "X-ray Diffraction Experiments" below) by comparison with the measured pattern for wilcoxite (Williams & Cesbron 1983: ICDD-PDF 35-575). The second most likely match in the ICDD-PDF database was svyazhinite, $(Mg,Mn)(Al,Fe^{3+})(SO_4)_2F{\bullet}14H_2O$ (Chesnokov *et al.* 1984) (ICDD-PDF 37-433). The formula of svyazhinite is very similar to that of wilcoxite, $MgAl(SO_4)_2F{\bullet}17H_2O$, but svyazhinite is described as having less water. The powder patterns are compared in Table 2. The most significant differences are that the 14.73 Å diffraction peak observed in the wilcoxite diffraction pattern was not observed in the diffraction pattern of svyazhinite and the diffraction peak at 6.25 Å observed for svyazhinite is not observed in the diffraction pattern of wilcoxite. However, it is clear that these minerals are

FIG. 1. Wilcoxite locality east of Rico, Colorado, October 2009. The secondary sulfates are found on the surface of waste rock contained between the wooden timbers of the crib.

TABLE 1. LIST OF SULFATE MINERALS CONTAINING FLUORINE

Anhydrous
sulphohalite, $Na_6(SO_4)_2Cl\ F$
kogarkoite, $Na_3(SO_4)F$
krasheninnikovite, $KNa_2CaMg(SO_4)_3F$
grandreefite, $Pb_2(SO_4)\ F_2$
pseudograndreefite, $Pb_6(SO_4)F_{10}$
thermessaite, $K_2Al(SO_4)F_3$
thermessaite(NH4), $(NH_4)AlSO_4F_3$
galeite, $Na_{15}(SO_4)_5\ F_4Cl$
lannonite, $HCa_4Mg_2Al_4(SO_4)_8F_9(H_2O)_{32}$
schairerite, $Na_3(SO_4)(F,Cl)$

With water
khademite, $Al(SO_4)F(H_2O)_5$
Chukhrovite-(Y,CeCa), $Ca_3YAl_2(SO_4)F_{13}(H_2O)_{12}$
cossaite, $Mg_{0.5}Al_6(SO_4)_6(HSO_4)F_6(H_2O)_{36}$
vlodavetsite, $AlCa_2(SO_4)_2F_2Cl(H_2O)_4$
uklonskovite, $NaMg(SO_4)F(H_2O)_2$
svyazhinite, $(Mg,Mn,Ca)(Al,Fe)F(SO_4)_2\ (H_2O)_{14}$
wilcoxite, $MgAl(SO_4)_2F(H_2O)_{17}$

With water and OH$^-$
creedite, $Ca_3Al_2(SO_4\ F_8(OH)_2(H_2O)_2$

With other groups (PO_4, CO_3, SiO_4)
schröckingerite, $NaCa_3((UO_2)\ (CO_3))_3\ (SO_4)\ F(H_2O)_{10}$
sulfoborite, $Mg_3(B(OH)_4)_2(SO_4)\ (OH)F$
mineevite-(Y), $Na_{25}Ba(Y_{.55}Gd_{.25}Dy_{.20})_2\ (CO_3)_{11}(HCO_3)_4(SO_4)_2F_2Cl$
meniaylovite, $Ca_4(F,SO_4,SiF_6,AlF_6)(H_2O)_{12}$
ellestadite-(F), $Ca_{10}(SiO_4)_3(SO_4)_3F_2$
martinite, $(Na,Ca)_{11}Ca_4(Si,S,B)_{14}B_2O_{40}F_2(H_2O)_4$

closely related. The relationship between svyazhinite and wilcoxite deserves further study.

CHEMICAL ANALYSIS

Chemical analysis of wilcoxite was difficult because the intimate mixture of the wilcoxite crystals with other sulfates precluded bulk chemical analysis methods. The very high water content and instability of wilcoxite under the electron beam of the microprobe required special care (see below). Chemical analysis was performed on a rough surface of an coated, 0.3 mm fragment of a single crystal of wilcoxite using a JEOL JXA-8230 electron microprobe equipped with five wavelength dispersive spectrometers. Accelerating voltage was 10 kV, and beam current measured on the Faraday cup was 10 nA. The beam was defocused to about 12 µm in order to minimize beam damage; no obvious change in the appearance of the mineral was observed in backscattered electron images collected before and after analysis. Peak and background count times for each element were 10 s each, except for fluorine, for which peak and background count times were both 20 s. A TAP diffracting crystal was used for the fluorine analysis. Standards were zinc metal (Zn), natural anhydrite (S), rhodonite (Mn), and topaz (F), and synthetic fayalite (Fe) and $MgAl_2O_4$ glass (Mg, Al). Data were treated using a ZAF correction, and the results are presented in Table 3. The mineral formula, based on 2 sulfur atoms per formula unit, is $(Mg_{0.81}Mn_{0.07}Fe_{0.04}Zn_{0.04})_{\Sigma 0.96}Al_{1.01}(SO_4)_2F_{1.02}\bullet 17H_2O$; the formula was calculated from an average of five analyses.

PHYSICAL DESCRIPTION

Wilcoxite occurs as a crust of anhedral clear crystals up to 0.3 mm in size. The crystals melt under the heat

TABLE 2. COMPARISON OF THE POWDER DIFFRACTION PATTERNS OF SVYAZHINITE AND WILCOXITE

Svyazhinite[*] (Chesnokov *et al.* 1984) *d* Å	*I* (rel)	Wilcoxite[†] (this study) *d* Å	*I* (rel)	*hkl*	Wilcoxite (Williams & Cesbron 1983) *d* Å	*I* (rel)
6.25	20	14.60	18	001	14.55	30
5.90	30	5.883	34	100	5.877	
5.68	70	5.658	100	101	5.654	90
		5.311	11	$01\bar{1}$	5.304	20
		4.992	20	112	4.978	5
4.91	100	4.921	91	$11\bar{1}$	4.908	100
		4.823	9	102	4.813	5
4.40	50	4.377	51	$01\bar{2}$	4.371	60
4.26	40					
4.15	50	4.121	40	113	4.117	40
		4.070	10	$11\bar{2}$	4.058	10
3.80	20					
3.65	20	3.649	33	004	3.654	30
3.59	10	3.576	14	$10\bar{3}$	3.575	20
		3.484	20	$1\bar{1}0$	3.482	30
3.39	40	3.379	41	121	3.384	50
3.29	30	3.280	10	210	3.278	20
		3.211	32	212	3.210	30
3.10	30	3.134	20	$1\bar{1}2$	3.141	30
		3.087	17	$21\bar{1}$	3.082	30
2.99	30	3.012	12	123	3.016	3
		2.982	34	020	2.980	40
		2.953	5	$01\bar{4}$	2.958	10
		2.918	5	005	2.918	10
2.87	20	2.873	5	221	2.874	10
2.84	50	2.833	38	$12\bar{2}$	2.834	40
2.824	50	2.828	9	202		
		2.809	27	$11\bar{4}$	2.804	40
2.759	40	2.750	12	015	2.749	20

[*] ICDD-PDF 37-443

[†] *a* 6.6682(2) Å, *b* 6.7726(2) Å, *c* 14.9104(4) Å, α 79.628(1)°, β 80.155(1)°, γ 62.488(1)°

from a microscope lamp and the resulting liquid then crystallizes to an amorphous solid. The optical properties of a single crystal of wilcoxite were measured using a Supper spindle stage. The refractive indices determined using Na light are $n_\alpha = 1.427$, $n_\beta = 1.438$ $n_\gamma = 1.439$, $2V = 51.9°$ (obs.) and compare well with those obtained by Williams & Cesbron (1983) of $n_\alpha = 1.424$, $n_\beta = 1.436$ $n_\gamma = 1.438$, $2V_\alpha = 48°$ (obs.). The Gladstone-Dale calculation (Mandarino 2007) based on these measured refractive indices and the ideal formula for wilcoxite yields $1-(k_c/k_p) = 0.027$, an excellent agreement. The density of wilcoxite was determined to be 1.57 g/cm^3 by using a Berman balance and immersing the mineral in toluene and is close to the density of 1.63 g/cm^3 calculated from the ideal formula and the unit-cell volume determined by single-crystal diffraction. A handpicked sample consisting of 0.0654 g of wilcoxite was heated to 550 °C for one hour in air in a platinum boat and lost 55.35% of its weight. This compares well with the predicted weight loss of 55.79% for the loss of H_2O and F in the ideal formula $MgAl(SO_4)_2F \cdot 17H_2O$. The residual powder gave a poor X-ray diffraction pattern that matches millosevichite $Al_2(SO_4)_3$ (ICDD-PDF30-0043). Based on the chemical analysis, weight-loss measurements, and structure determination by X-ray diffraction, the formula for the studied wilcoxite is $(Mg_{0.81}Mn_{0.07}Fe_{0.04}Zn_{0.04})_{\Sigma 0.96}Al_{1.01}(SO_4)_2F_{1.02} \cdot 17H_2O$ (Table 3).

INFRARED SPECTROSCOPY MEASUREMENT

The infrared spectrum of wilcoxite was recorded using a Nicolet Avatar 320 FTIR spectrometer with 32 scans over the range of 4000 to 400 cm^{-1} with 4 cm^{-1} resolution and is presented in Figure 2. The infrared spectrum exhibits absorption bands at 3400 and 2900 cm^{-1}. The absorption band at 3400 cm^{-1} is close to the absorption band observed for liquid water. This band is attributed to the loosely held water molecules not involved directly with cation polyhedra in wilcoxite. The absorption band at 2900 cm^{-1} is attributed to water molecules that form the coordination polyhedra of magnesium and aluminum. The band at 1100 cm^{-1} is attributed to the antisymmetric stretching mode of the SO_4 ion. The absorption band near 1640 cm^{-1} is due to a bending mode of the H_2O molecule.

TABLE 3. MICROPROBE ANALYSIS OF WILCOXITE FROM RICO, COLORADO

	wt.%	atoms per 2S
SO_3	27.09	2
Al_2O_3	8.93	1.01
MgO	5.66	0.81
FeO	0.50	0.04
MnO	0.68	0.07
ZnO	0.56	0.04
F	3.47	1.02
H_2O	53.11*	17*
Total	100.00**	

*assumed based on structure refinement

**oxide and fluorine weight percent measured by microprobe analysis have been normalized to result in a total of 100% assuming 17 water molecules per formula unit.

X-RAY DIFFRACTION EXPERIMENTS

X-ray powder diffraction data were obtained from a handpicked sample containing no detectable impurities using a Panalytical X'Pert™ Pro θ-θ diffractometer equipped with an X'Celerator™ position-sensitive detector. Cu$K\alpha$ (Ni) radiation was generated at settings of 45 kV and 40 mA to collect data over the 5 to 70° 2θ range. A pattern identification search was conducted using the X'Pert Highscore™ software. The collected pattern intensities are listed in Table 2. The diffraction powder pattern was fit by Rietveld analysis using the Panalytical program Highscore™ and the atomic coordinates obtained through single-crystal analysis (see below). The unit cell dimensions of the powdered sample and the estimated intensities presented in Table 2 were obtained from this Rietveld analysis. A 0.06 × 0.10 × 0.20 mm single-crystal fragment of the wilcoxite was selected, immersed in mineral oil to prevent dehydration, and inserted in a 0.3 mm glass capillary, which was then studied using a Bruker SMART APEX II X-ray diffractometer. The sample was cooled to 180(2) K during data collection, using a nitrogen gas Cryostream Controller 700. The atomic structure was refined using the program SHELXTL. Details of the data collection and structure refinement are listed in Table 4. Hydrogen atom positions and isotropic displacement parameters were not constrained. The occupancy of the [O,F] site was assumed to be 50:50 based on the experimentally determined chemical composition. The atomic coordinates and atomic displacement parameters are listed in Tables 5 and 6.

DESCRIPTION OF THE CRYSTAL STRUCTURE

The atomic structure of wilcoxite consists of isolated sulfate tetrahedra, $Mg(H_2O)_6$ octahedra, and $Al(H_2O,F)_6$ octahedra connected through hydrogen bonding involving water molecules (Fig. 3). The water molecules form the coordination polyhedra around magnesium (Ow7, Ow8, and Ow9) and aluminum (Ow5, Ow6, and [F,O]). Three water molecules are not directly bonded to a cation (Ow10, 11, and 12). The sulfate tetrahedral bond lengths (mean 1.476 Å) and angles (Table 7) are very close to the average observed for all sulfate minerals, 1.473 Å (Hawthorne *et al.* 2000). There is no suggestion of an S–F bond, as S–F bonds are observed to be greater than 1.478, with most being greater than 1.50 Å (Hawthorne *et al.* 2000). The octahedron formed by water molecules

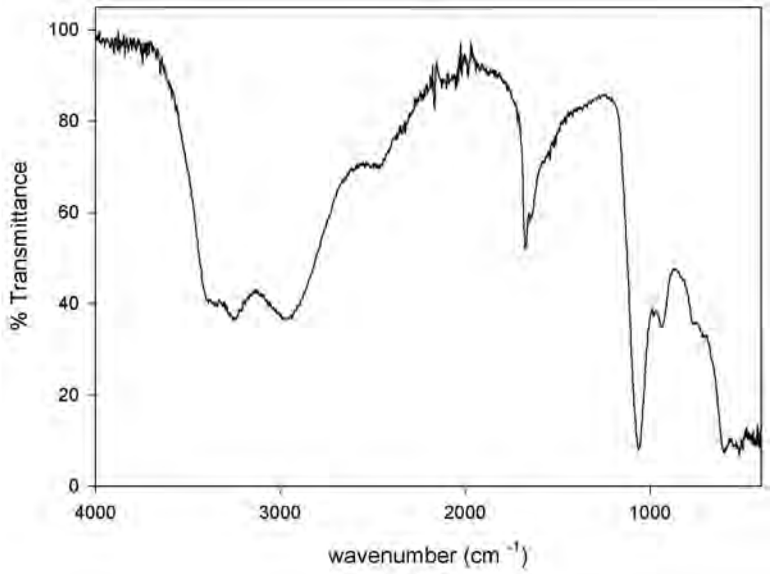

FIG. 2. Attenuated total-reflection infrared spectrum of wilcoxite. Zhdanov *et al*. (1993) also recorded the IR spectra of wilcoxite from Yakutia over the range of 2000 to 500 cm^{-1} and these measurements show similar absorption features, although at lower resolution than the present study.

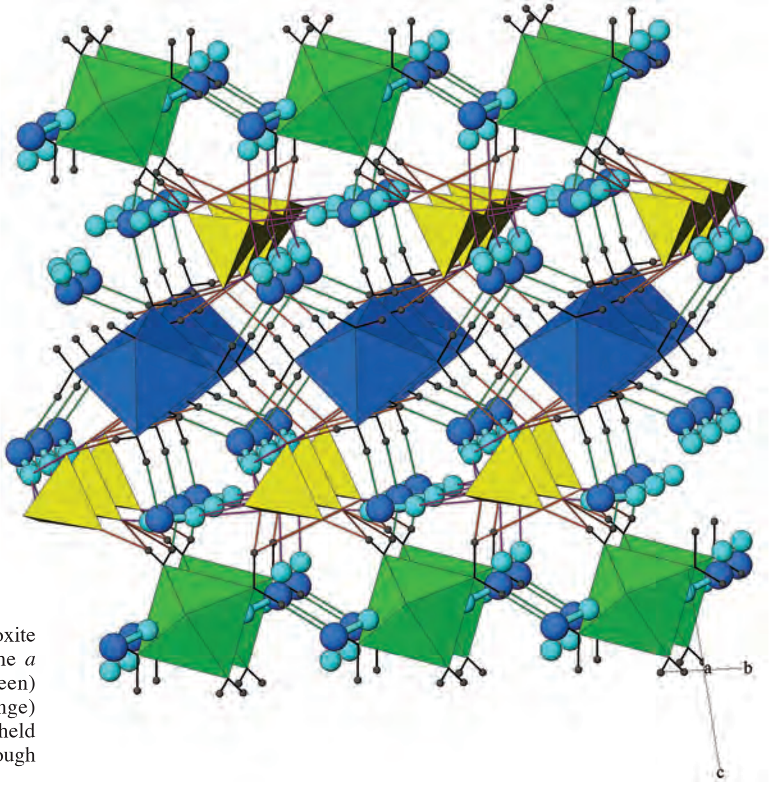

FIG. 3. The atomic structure of wilcoxite (viewed approximately along the *a* axis) consists of aluminum (green) and magnesium octahedra (orange) and sulfate tetrahedra (yellow) held together by water molecules through a network of hydrogen bonds

TABLE 4. CRYSTALLOGRAPHIC DETAILS OF THE WILCOXITE ATOMIC STRUCTURE REFINEMENT

	This work	Williams & Cesbron (1983)
a (Å)	6.644(1)	6.65
b (Å)	6.749(2)	6.77
c (Å)	14.892(3)	14.90
α (°)	79.664(4)	79.42
β (°)	80.113(4)	80.17
γ (°)	62.487(3)	62.49
V ($Å^3$)	579.6(2)	
Space group, Z	$\bar{P}$, 1	
Mo*K*α (Graphite monochromator)	0.71073 Å	
Crystal size (mm)	0.06 × 0.10 × 0.20	
θ (min)°	2.79	
θ (max)°	27.18	
Reflections measured	5022	
Total reflections used	2502	
Agreement of averaged reflections	0.038	
h, min., max.	–8,7	
k, min., max.	–8,8	
l, min., max.	–17,18	
Measurement temp. (K)	180	
R (int) (1673 $F_o > 4\sigma F_o$)	0.049	
R (int) (all reflections 2262)	0.069	
Parameters varied	203	
Highest positive difference peak (e/$Å^3$)	0.77	
Highest negative difference peak (e/$Å^3$)	–0.48	
Goodness of fit	1.057	
R all reflections	0.075	
w *R* all reflections	0.161	
$R\ I > 2\sigma_I$	0.053	
$wR\ I > 2\sigma_I$	0.144	

$w = 1 / [\sigma^2(Fo^2) + (0.0776P)^2]$, where $P = [\mathrm{Max}\ (Fo^2, 0) + 2Fc^2] / 3$

coordinating a magnesium atom has bond lengths and angles approaching that of a regular octahedron (Table 7). The octahedron that contains aluminum is formed by five water molecules and either a fluorine atom or an oxygen of the 17th water molecule. The fluorine/water site is disordered and forms the shortest Al–O bond, 1.805 Å, within the octahedron. This bond is considerably shorter than the other Al–O bonds, which have a mean length of 1.888 Å (Table 7). The observed average of the Al–F bonds in creedite is 1.812 Å, where four of the six ligands coordinating aluminum are fluorine (Giuseppetti & Tadini 1983). This bond-length argument was also used by Bachet *et al.* (1981) to locate the F atom in khademite.

TABLE 5. ATOMIC POSITIONS AND ISOTROPIC DISPLACEMENT PARAMETERS FOR WILCOXITE

Atom	*x*	*y*	*z*	U_{eq}/U_{iso}
Al	0.5	0	0.5	0.017(3)
Mg	0	0	0	0.009(4)
S	0.5883(2)	0.5499(2)	0.24406(7)	0.018(2)
O1	0.4849(6)	0.3945(5)	0.2605(2)	0.027(2)
O2	0.6124(5)	0.6242(5)	0.1453(2)	0.024(2)
O3	0.4447(5)	0.7461(5)	0.2948(2)	0.027(3)
O4	0.8173(5)	0.4338(5)	0.2784(2)	0.024(2)
(F,O)	0.2477(5)	0.9826(5)	0.4810(2)	0.032(3)
Ow5	0.6179(6)	0.7026(5)	0.5617(2)	0.025(2)
Hw51	0.705(9)	0.583(10)	0.529(4)	0.035(15)
Hw52	0.572(11)	0.680(11)	0.630(5)	0.063(19)
Ow6	0.6435(6)	0.8824(5)	0.3889(2)	0.021(3)
Hw61	0.552(11)	0.834(10)	0.358(5)	0.059(19)
Hw62	0.723(12)	0.924(12)	0.362(5)	0.06(2)
Ow7	0.2437(6)	0.9981(6)	0.0699(2)	0.028(3)
Hw71	0.399(11)	0.859(11)	0.085(4)	0.056(18)
Hw72	0.285(15)	0.094(15)	0.097(6)	0.10(3)
Ow8	0.8146(7)	0.3408(6)	0.0049(3)	0.032(3)
Hw81	0.755(9)	0.404(9)	0.047(4)	0.026(16)
Hw82	0.840(10)	0.426(11)	0.956(5)	0.057(19)
Ow9	0.1685(6)	0.0678(6)	0.8763(2)	0.029(2)
Hw91	0.222(11)	0.159(12)	0.874(5)	0.06(2)
Hw92	0.153(12)	0.046(12)	0.827(5)	0.07(2)
Ow10	0.2053(6)	0.3578(5)	0.1495(2)	0.026(2)
Hw101	0.078(11)	0.402(10)	0.192(4)	0.044(17)
Hw102	0.307(15)	0.370(14)	0.185(6)	0.09(3)
Ow11	0.1473(6)	0.6445(6)	0.5360(3)	0.025(2)
Hw111	0.161(9)	0.610(9)	0.582(4)	0.025(17)
Hw112	0.200(11)	0.805(12)	0.507(5)	0.08(2)
Ow12	0.9722(6)	0.9611(6)	0.2877(2)	0.026(2)
Hw121	0.106(9)	0.903(8)	0.294(3)	0.017(13)
Hw122	0.945(13)	0.121(14)	0.286(5)	–.021(18)

HYDROGEN BONDING

Each of the oxygen atoms that form the tetrahedron that surround sulfur act as an acceptor to hydrogen bonds from water molecules. O1 acts as an acceptor to Ow5 (Mg) and Ow10 (free, *i.e.*, not bonded to a cation) through hydrogen bonds of 1.65 and 1.84 Å. O2 accepts hydrogen bonds from three water molecules, Ow7 (Mg), Ow8 (Mg), and Ow9 (Mg) with O…H bonds of 1.78, 2.06, and 2.15 Å. O3 acts an acceptor for hydrogen bonds from O6 (Al) and Ow12 (free) with O…H bonds of 1.60 and 2.00 Å. O4 acts as an acceptor with three water molecules, Ow10 (free), Ow11 (free), and Ow12 (free) with O…H bonds of 1.92, 2.06, and 1.86 Å. There are two types of water molecules in the structure. There are five symmetrically distinct water molecules that bond directly to a cation and form the coordination polyhedra around magnesium and aluminum. Ow5 and Ow6 are bonded directly to Al, and Ow7, Ow8, and Ow9 are bonded directly to Mg. The second type of water molecules consists of three

TABLE 6. ANISOTROPIC DISPLACEMENT PARAMETERS FOR WILCOXITE

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mg	0.0114(9)	0.0083(9)	0.0091(9)	0.0000(7)	–0.0019(7)	–0.0049(8)
Al	0.0181(9)	0.0153(9)	0.0176(9)	–0.0020(7)	–0.0012(7)	–0.0068(8)
S	0.0190(6)	0.0185(6)	0.0179(5)	–0.0021(4)	–0.0030(4)	–0.0075(5)
O1	0.0348(18)	0.0298(18)	0.0226(17)	0.0000(14)	–0.0037(14)	–0.0211(16)
O2	0.0294(18)	0.0233(16)	0.0178(16)	0.0007(13)	–0.0023(13)	–0.0109(15)
O3	0.0218(17)	0.0271(17)	0.0319(18)	–0.0138(15)	–0.0020(14)	–0.0064(15)
O4	0.0182(16)	0.0251(17)	0.0245(16)	–0.0009(13)	–0.0050(13)	–0.0069(14)
(F,O)	0.0303(15)	0.0332(15)	0.0366(16)	–0.0053(13)	–0.0060(13)	–0.0155(13)
Ow5	0.0308(19)	0.0189(17)	0.0201(18)	–0.0017(14)	0.0011(14)	–0.0076(15)
Ow6	0.0238(17)	0.0222(17)	0.0207(17)	–0.0062(13)	0.0011(14)	–0.0124(15)
Ow7	0.0274(18)	0.0244(17)	0.0322(19)	–0.0023(15)	–0.0120(15)	–0.0083(16)
Ow8	0.044(2)	0.0235(19)	0.0210(19)	–0.0036(17)	–0.0011(17)	–0.0091(17)
Ow9	0.039(2)	0.033(2)	0.0229(19)	–0.0012(15)	–0.0042(15)	–0.0237(18)
Ow10	0.0295(19)	0.0262(17)	0.0249(17)	–0.0012(14)	–0.0058(15)	–0.0131(16)
Ow11	0.0318(19)	0.0203(17)	0.0217(19)	–0.0001(15)	–0.0065(15)	–0.0102(15)
Ow12	0.0182(18)	0.0279(19)	0.0304(18)	–0.0003(14)	–0.0046(14)	–0.0100(15)

TABLE 7. BOND LENGTHS (Å) AND ANGLES (°) IN WILCOXITE

Al–Ow5	1.903(2)	x2	S–O1	1.465(3)	
Al–Ow6	1.873(3)	x2	S–O2	1.473(3)	
Al–(F,O)	1.805(3)	x2	S–O3	1.476(3)	
Mean Al–O	1.860		S–O4	1.488(3)	
			Mean	1.476	
Mg–Ow7	2.063(3)	x2			
Mg–Ow8	2.055(4)	x2	O1–S–O2	110.5°	
Mg–Ow9	2.078(3)	x2	O1–S–O3	119.4°	
Mean Mg–O	2.065		O1–S–O4	119.1°	
			O2–S–O3	110.0°	
Ow7–Mg–Ow8	90.12°	x2	O2–S–O4	109.3°	
Ow7–Mg–Ow8	89.88°	x2	O3–S–O4	108.5°	
Ow7–Mg–Ow9	89.97°	x2	Mean	112.2	
Ow7–Mg–Ow9	90.03°	x2			
Ow8–Mg–Ow9	91.58°	x2	Ow5–Al–Ow6	90.7°	x2
Ow8–Mg–Ow9	88.42°	x2	Ow5–Al–Ow6	89.3°	x2
			(F,O)–Al–Ow6	89.5°	x2
			(F,O)–Al–Ow6	90.5°	x2
			Ow5–Al–Ow6	89.2°	x2
			Ow5–Al–Ow6	90.8°	x2

symmetrically unique water molecules (Fig. 4) that are bonded only by hydrogen bonds to other oxygen atoms. Ow10 and Ow12 are bonded by hydrogen bonds to the oxygen atoms of the sulfate groups. Ow11 has one hydrogen bond to an oxygen atom of a sulfate group, but the position of the second hydrogen atom of this water molecule is less well defined (Hw112, $U_{\text{iso}} = 0.08$). This hydrogen would form a bond with the [F,O] site when it is occupied by oxygen, but the site occupancy for this site is 50% fluorine and 50% oxygen.

Relationship with other minerals and stability

Wilcoxite is closely related to pickeringite $MgAl_2(SO_4)_4 \bullet 22H_2O$, meridianiite $Mg(SO_4) \bullet 11H_2O$, and epsomite $Mg(SO_4) \bullet 7H_2O$. All of these minerals consist of isolated sulfate tetrahedra and $Mg(H_2O)_6$ octahedra held together only by hydrogen bonding (Fig. 5). The tetrahedra and octahedra do not share corners or edges with each other. Wilcoxite is slightly different in that there are aluminum-containing octahedra that have the formula $Al(H_2O,F)_6$. Peterson (2011) showed that the unit cell volume of these sulfates is directly related to the amount of water molecules per sulfate group in the mineral formula. Figure 6 shows this relationship and indicates that the effective volume of the water molecule in magnesium-aluminum sulfates is 25.3 Å; this volume corresponds to an effective sphere with radius of 1.82 Å. Pickeringite has an intermediate amount of water in this series, but wilcoxite has significantly more water molecules per sulfate group than epsomite. Magnesioaubertite, (Mg,Cu) $Al(SO_4)_2Cl(H_2O)_{14}$, is chemically similar to wilcoxite but the atomic structure is different. Ginderow & Cesbron (1982) determined the atomic structure of aubertite, $AlCuCl(SO_4)_2(H_2O)_{14}$, and although the structure consists of isolated polyhedra connected by hydrogen bonds, the chlorine atoms do not coordinate a cation like the fluorine atoms do in wilcoxite.

The stability of wilcoxite as a function of temperature and relative humidity is not known. Of the samples collected at Rico, Colorado, some contain hexahydrite and others contain starkeyite coexisting with wilcoxite. The stability of both starkeyite and hexahydrite are well known from experimental studies (Chou & Seal 2003). The presence of starkeyite and hexahydrite are expected under the conditions found at Rico, Colorado, where temperatures range from an average of –11 °C in January to 14 C in July, according to the historical records of the United States National Climatic Data Center. The historical average for rainfall is 20 mm of rain-equivalent precipitation per month in the winter and 60 mm per month in the summer. The samples were protected from direct precipitation by the timber crib structure. What is unexpected is the stability of wilcoxite under the conditions where starkeyite is found to occur. Wilcoxite has 1.5 water molecules per sulfate tetrahedron that do not participate in the formation of an $Al(H_2O,F)_6$ or $Mg(H_2O)_6$ octahedron. The water molecules held within the epsomite structure are lost if the relative humidity drops below 50% at 298 K (Chou & Seal 2003). Hexahydrite loses water to form starkeyite

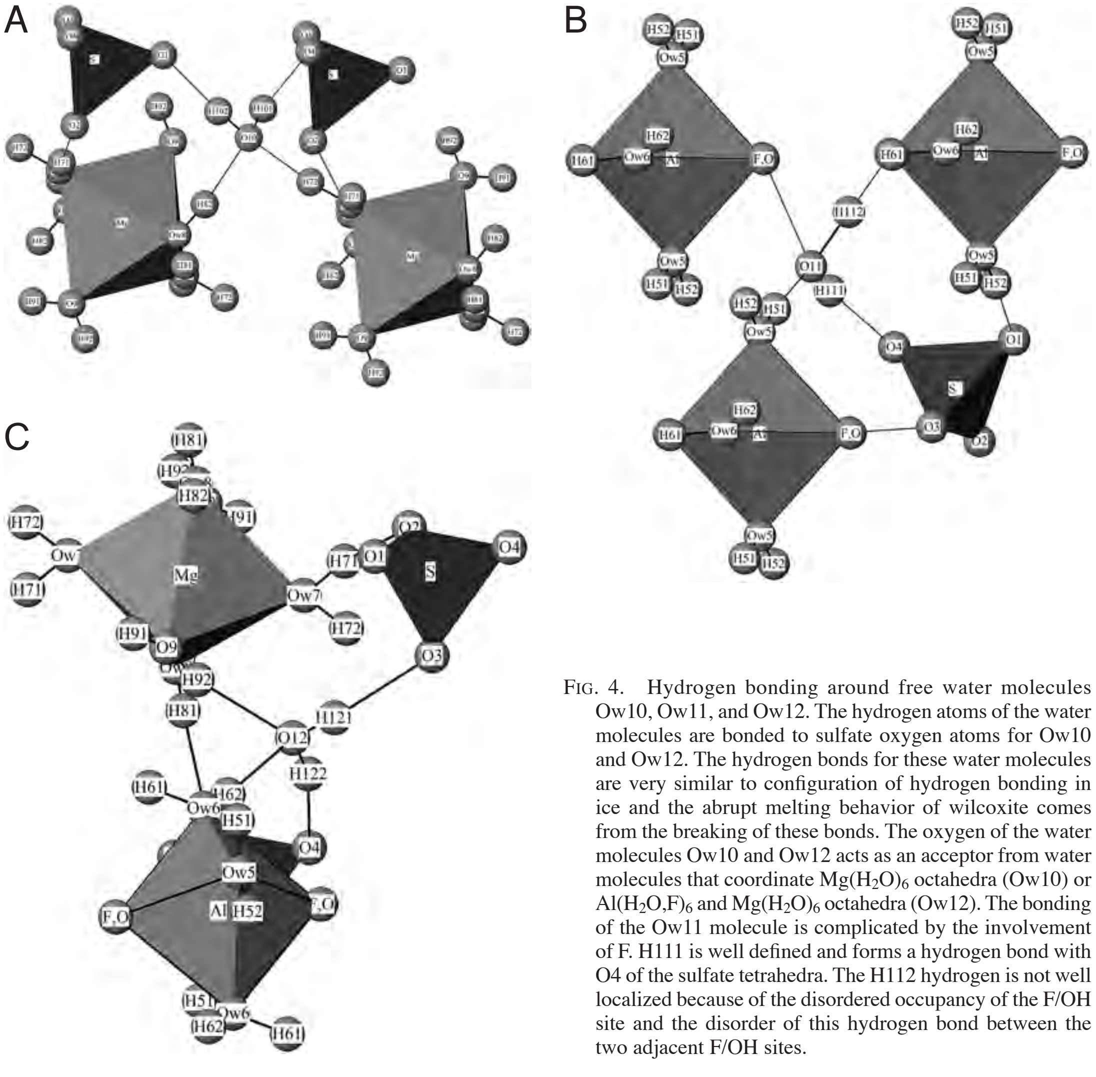

FIG. 4. Hydrogen bonding around free water molecules Ow10, Ow11, and Ow12. The hydrogen atoms of the water molecules are bonded to sulfate oxygen atoms for Ow10 and Ow12. The hydrogen bonds for these water molecules are very similar to configuration of hydrogen bonding in ice and the abrupt melting behavior of wilcoxite comes from the breaking of these bonds. The oxygen of the water molecules Ow10 and Ow12 acts as an acceptor from water molecules that coordinate $Mg(H_2O)_6$ octahedra (Ow10) or $Al(H_2O,F)_6$ and $Mg(H_2O)_6$ octahedra (Ow12). The bonding of the Ow11 molecule is complicated by the involvement of F. H111 is well defined and forms a hydrogen bond with O4 of the sulfate tetrahedra. The H112 hydrogen is not well localized because of the disordered occupancy of the F/OH site and the disorder of this hydrogen bond between the two adjacent F/OH sites.

TABLE 8. HYDROGEN BOND LENGTHS AND ANGLES IN WILCOXITE

Hydrogen atom	Donor	O–H (Å)	Acceptor	O…H (Å)	O–H…O angle (°)	
Hw51	Ow5	0.92	Ow11	1.75	175.6	2.666
Hw52	Ow5	1.02	O1	1.65	172.0	2.660
Hw61	Ow6	1.01	O3	1.60	166.8	
Hw62	Ow6	0.74	Ow12	1.92	166.8	
Hw71	Ow7	1.05	O2	1.78	161.8	2.801
Hw72	Ow7	0.98	Ow10	1.88	151.0	
Hw81	Ow8	0.77	O2	2.06	168.2	2.816
Hw82	Ow8	0.87	Ow10	1.90	162.0	
Hw91	Ow9	0.83	O2	2.15	173.0	2.990
Hw92	Ow9	0.81	Ow12	2.04	165.0	
Hw101	Ow10	0.93	O4	1.92	168.0	2.833
Hw102	Ow10	0.97	O1	1.84	175.6	2.806
Hw111	Ow11	0.69	O4	2.06	169.9	2.749
Hw112	Ow11	1.27	O,F	1.35	176.2	2.621
Hw121	Ow12	0.80	O3	2.00	173.1	2.797
Hw122	Ow12	1.00	O4	1.86	165.0	2.848

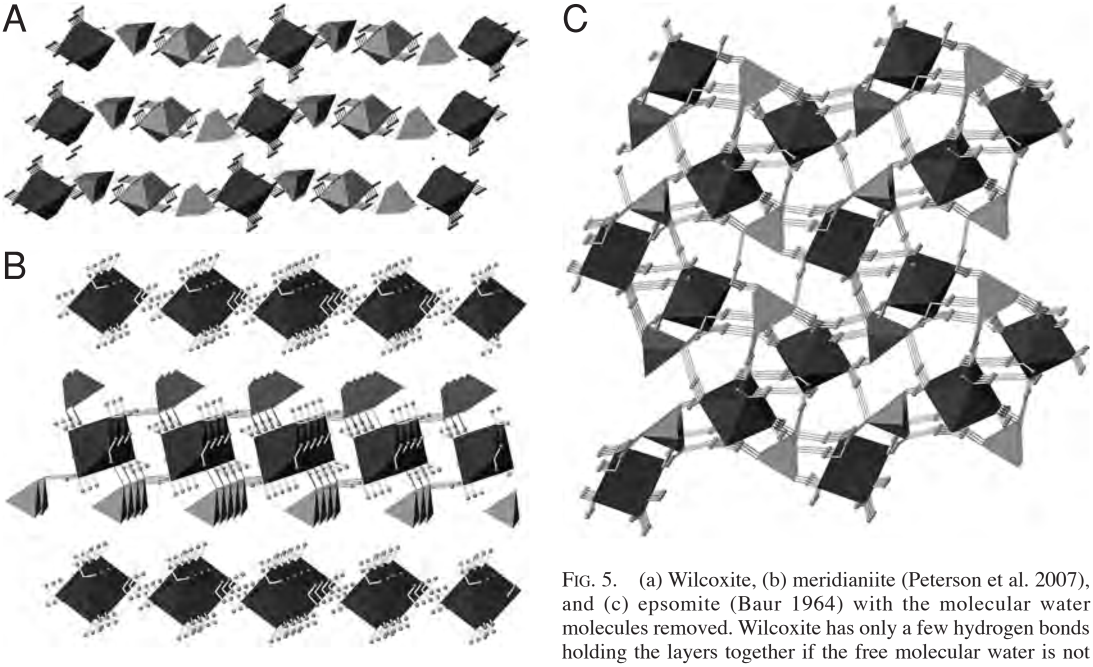

FIG. 5. (a) Wilcoxite, (b) meridianiite (Peterson et al. 2007), and (c) epsomite (Baur 1964) with the molecular water molecules removed. Wilcoxite has only a few hydrogen bonds holding the layers together if the free molecular water is not considered. Meridianiite has no linkage between the layers other than hydrogen bonds involving molecular water. Loss of water in wilcoxite and meridianiite results in abrupt and catastrophic structural disruption, whereas in epsomite there are a significant number of hydrogen bonds between the magnesium octahedra and sulfate tetrahedra. Epsomite dehydrates, whereas and wilcoxite and meridianiite melt on increasing temperature.

at 40% RH at 298 K (Chou & Seal 2003). The fact that wilcoxite, with such a high water content, is stable when the magnesium sulfate with which it coexists has become starkeyite indicates that these water molecules are more tightly bonded within the wilcoxite structure. If epsomite crystals are warmed slightly they slowly become translucent and then become an opaque white powder. Wilcoxite, however, behaves quite differently. Williams & Cesbron (1983) describe this breakdown: "If a hot or bright light source is employed, crystals

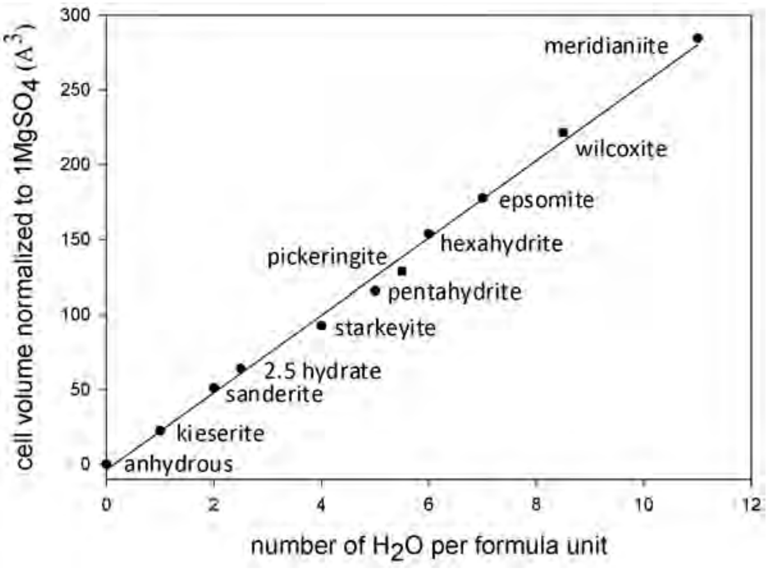

FIG. 6. Unit-cell volume *versus* the number of water molecules for magnesium-aluminum sulfates. The cell volume is normalized to the volume of anhydrous magnesium sulfate (Peterson 2011). The line indicates an effective volume of 25.3 Å^3 for the water molecule in these structures. This volume for a water molecule corresponds to an effective sphere with a radius of 1.82 Å.

dissolve in their own waters of crystallization. They become shapeless tubes with a tough outer skin filled with liquid and seem to *writhe in agony* on a smooth glass surface. If pierced with a needle they leak briefly and then seal themselves quickly." This behavior is consistent with the melting of wilcoxite followed by the diffusion of water away from the melted material to form an amorphous solid rind that reduces further loss of water from the solution. Meridianiite incongruently melts to a mixture of solution and epsomite (Peterson *et al.* 2007) at 2 °C. Perhaps if wilcoxite were melted under high relative humidity, the resulting solution might crystallize a lower-hydrate phase.

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