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DESCRIPTION OF SCHOENFLIESITE, $MgSn(OH)_6$, AND ROXBYITE, $Cu_{1.72}S$, FROM A 1375 BC SHIPWRECK, AND RIETVELD NEUTRON-DIFFRACTION REFINEMENT OF SYNTHETIC SCHOENFLIESITE, WICKMANITE, $MnSn(OH)_6$, AND BURTITE, $CaSn(OH)_6$

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ABSTRACT

Schoenfliesite, $MgSn(OH)_6$, and roxbyite, $Cu_{1.72}S$, have been identified as products of corrosion of a 1375 BC bronze harpoon head from a shipwreck in the eastern Mediterranean Sea. The atomic structures of isostructural, synthetic schoenfliesite, burtite [$CaSn(OH)_6$] and wickmanite [$MnSn(OH)_6$] have been studied by neutron powder diffraction at 4 K. The results show that the hydrogen atoms are disordered over two positions in these cubic minerals. The bond lengths in the $Sn(OH)_6$ octahedra and polyhedron volumes for the three compounds are similar, and the octahedra exhibit a systematic change in angle variance. The bond lengths in the $M(OH)_6$ octahedra and polyhedron volumes change systematically with the increase in radius of the M cation.

Keywords: schoenfliesite, roxbyite, wickmanite, burtite, crystal structure, hydrogen bonding, hydrogen disorder, shipwreck, eastern Mediterranean Sea.

SOMMAIRE

Nous avons identifié la schoenfliesite, $MgSn(OH)_6$, et la roxbyite, $Cu_{1.72}S$, comme produits de corrosion de la tête d'un harpon en bronze découvert dans l'épave d'un navire naufragé en 1375 avant Jésus-Christ dans la mer Méditerranéenne orientale. De plus, nous avons déterminé la structure cristalline des composés isostructuraux schoenfliesite, burtite [$CaSn(OH)_6$] et wickmanite [$MnSn(OH)_6$] sous leur forme synthétique par diffraction neutronique à 4 K. Les résultats montrent que les atomes d'hydrogène font preuve d'un désordre impliquant deux positions dans ces phases cubiques. Les longueurs de liaison dans les octaèdres $Sn(OH)_6$ et le volume des polyèdres sont semblables pour ces trois composés, et les octaèdres changent systématiquement dans la variance des angles. Les longueurs de liaison des octaèdres $M(OH)_6$ et le volume des polyèdres augmentent systématiquement avec le rayon ionique du cation M.

(Traduit par la Rédaction)

Mots-clés: schoenfliesite, roxbyite, wickmanite, burtite, structure cristalline, liaisons hydrogène, désordre des atomes d'hydrogène, naufrage, mer Méditerranéenne orientale.

INTRODUCTION

Schoenfliesite, $MgSn(OH)_6$, and roxbyite, $Cu_{1.72}S$, have been identified within layered products of the corrosion of the bronze on a harpoon head, retrieved from a shipwreck in the eastern Mediterranean Sea (sample KW4254). Schoenfliesite belongs to the group of hexahydroxostannates, which also include burtite, $CaSn(OH)_6$, wickmanite, $MnSn(OH)_6$, natanite, $FeSn(OH)_6$, $CoSn(OH)_6$ and $ZnSn(OH)_6$. The schoenfliesite and roxbyite are very finely intermixed, and the sample is very small, making synthesis of schoenfliesite necessary for structural characterization by Rietveld refinement. In the present study, the crystal structures of synthetic schoenfliesite, wickmanite and burtite were refined from neutron-diffraction data, and the hydrogen bonding was examined. The textural features of the schoenfliesite and roxbyite in sample KW4254 were examined, and a quantitative chemical analysis of the roxbyite was carried out.

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BACKGROUND INFORMATION

Schoenfliesite was originally described by Faust & Schaller (1971) as a product of late-stage hydrothermal alteration in a contact-metamorphic zone in the Brooks Mountain Range, Seward Peninsula, Alaska. The second occurrence, at Pitkäranta, Karelia, Russia (Nefedov *et al.* 1977), formed by late-stage hydrothermal decomposition of hulsite, $(Fe^{2+},Mg)_2(Fe^{3+},Sn)BO_5$. The third locality, in an abandoned tin mine of the Sungai Gow Tin Mine Company, Pahang Dorvel Makmu, was described by Hassan & Faud (1993). The schoenfliesite there occurs as an encrustation on cassiterite and other minerals.

Wickmanite was first described by Moore & Smith (1967) from Långban, Sweden. It occurs as octahedra up to 2 mm in size in pockets in magnetite ore and in a brecciated skarn-zone with jacobsite, richterite, and manganophyllite. Other occurrences have been described by Hubbard (1989).

Burtite was first described as a late-forming mineral in a tin-rich garnet skarn in the vicinity of the El Hamman fluorite deposit in central Morocco (Sonnet 1981). The octahedra of burtite were described as being up to 2 mm in size with an alteration rim of pale yellow varlamoffite. The crystals display apparent cubic cleavage but uniaxial (+) optics, with probable space group $R\bar{3}$. In our fine-grained synthetic $CaSn(OH)_6$, there was no evidence of peak splitting indicating departure from cubic symmetry.

Roxbyite has been described previously as small single crystals from a sample of copper flotation concentrate and drill cores from the Olympic Dam deposit at Roxby Downs, South Australia (Mumme *et al.* 1988).

OCCURRENCE

Sample KW4254 was obtained from the Ulu Burun shipwreck, excavated by the Institute of Nautical Archaeology and Texas A&M University between 1984 and 1994. The shipwreck occurred off the southwest coast of Turkey, 8.5 km southeast of Kas, along the northeastern Mediterranean coast, in the neritic, sublittoral zone. The sediment in the area is relatively impermeable fine silt- and clay-sized particles. Salinity level is estimated at 39.5 parts per thousand. The age of the shipwreck, 1375 BC (±25), is based on dendrological analysis of timber carried on the ship and the style of artifacts found as cargo (Bass 1987).

Sample KW4254 is a product of corrosion of a tin-bronze harpoon, formed as a hard, black crust. It is from the Institute of Nautical Archaeology site location p15LL2 and was excavated in 1993. We analyzed a flake, 2 mm thick and 8 mm in diameter, and a coarse powder with a volume of 5 mm^3. Sample KW4254 was mechanically removed from the harpoon using scalpels and tweezers and then air dried.

CHEMISTRY AND TEXTURAL PROPERTIES OF SAMPLE KW4254

A fragment of sample KW4254 about 1 mm in length was examined in polished section using a back-scattered electron detector and an energy-dispersion X-ray spectrometer on an ARL–SEMQ electron microprobe operating at 15 kV. The textural relations between the two phases, schoenfliesite and roxbyite, were examined by the relative level of electron back-scattering, and the phases were identified by energy-dispersion spectra.

The sample is fine grained and appears to be layered (Fig. 1). The material identified as schoenfliesite shows low electron-back-scattering, whereas the roxbyite shows a higher level of electron back-scattering. The bottom half of the fragment is very compact, with the schoenfliesite and roxbyite finely intermixed. The top half of the fragment has increasingly larger pore-spaces, with the schoenfliesite and roxbyite in separate clusters. Crystals of roxbyite attain 40 μm across.

Energy-dispersion X-ray spectra of roxbyite showed major peaks for Cu and S, and very minor peaks for Al and Si. The Al and Si peaks vary in relative size from spectrum to spectrum and are attributed to contamination by fine-grained material. Quantitative energy-dispersion analysis for Cu and S resulted in a mineral formula of $Cu_{1.72}S$. This result is consistent with the formula $Cu_{1.72-1.82}S$ reported by Mumme *et al.* (1988) for roxbyite from the type locality.

Energy-dispersion X-ray spectra of schoenfliesite showed major peaks for Sn and Mg, and minor variable-size peaks for Cu and S that are attributed to included roxbyite. Smaller peaks for Si, Al and very small peaks of variable intensity for Cl, P, Fe and Ni are attributed to contamination by admixed material. Quantitative chemical analysis of schoenfliesite was not possible, owing to the fine grain-size.

An X-ray-diffraction pattern was obtained of sample KW4254, and the results were compared to the JCPDS cards for schoenfliesite (9–27) and roxbyite (23–958).

SYNTHESIS OF RELATED COMPOUNDS

$MgSn(OH)_6$, $MnSn(OH)_6$, $CaSn(OH)_6$ and $FeSn(OH)_6$ were synthesized using the method described in Strunz & Contag (1960). An equimolar mixture of reagent-grade reactants: $K_2Sn(OH)_6$ and $M\text{Cl}\bullet X\text{H}_2\text{O}$ (M = Mg, Ca, Mn, Fe) were mixed with 10 mL of water in a 25 mL Parr Teflon pressure bomb and heated at 90°C. The product of this reaction was $M\text{Sn(OH)}_6$. The $CaSn(OH)_6$ and $MgSn(OH)_6$ were sufficiently well crystallized after 24 hours, whereas the $MnSn(OH)_6$ and $FeSn(OH)_6$ took three days. The yield ranged from four to six grams, and the products were found to be very fine grained. The $MgSn(OH)_6$ was synthesized in D_2O to reduce the incoherent neutron scattering from the hydrogen. The

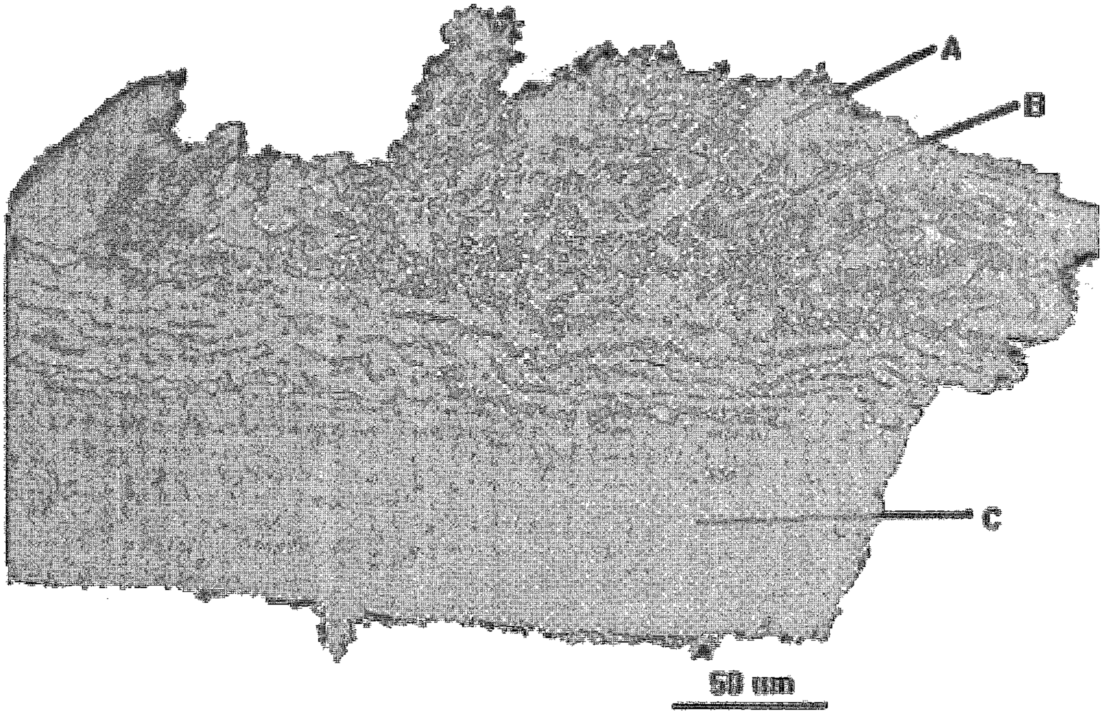

FIG. 1. Scanning electron microscope photo of KW4254, showing the layered structure of the sample: (A) roxbyite, (B) schoenfliesite, (C) fine-grained mixture of schoenfliesite and roxbyite.

water was decanted from the reaction vessel after crystallization and replaced with fresh D_2O and left for 3 days to ensure as complete as possible exchange of the hydrogen. The other samples were placed in D_2O in Parr Teflon pressure bombs at 90°C for three days after they had crystallized, with the D_2O being replaced every 24 hours. The run products were washed several times with D_2O to remove the liquid from which the products grew, and then dried at 90°C. If the products are not rinsed, KCl will precipitate on drying. $FeSn(OH)_6$ was synthesized under nitrogen in a glove box and in D_2O in which an iron wire had been boiled to prevent oxidation, but we were not successful in producing an unoxidized deuterated sample. Verification of all run products was done by X-ray diffraction.

Owing to the corrosive nature of the samples, potassium vanadium oxide ($K_{0.5}V_2O_5$), formed as a product of corrosion of the vanadium cylinders used during the collection of the neutron-diffraction data. $MgSn(OH)_6$ and $MnSn(OH)_6$ also were found to contain small quantities of sylvite, which formed during synthesis and was not completely washed from the samples. Burtite was found to contain a small quantity of calcite, which also formed during synthesis.

PREVIOUS STRUCTURAL WORK

The structure of $FeSn(OH)_6$ was first described by Strunz & Contag (1960), who found that Sn is at 0, 0, 0 and Fe is at ½, ½, ½, in space group *Pn*3*m*. The OH groups were found to be located at x,x,z with $x = 0.056$ and $z = 0.248$, octahedrally coordinating both the Sn and the Fe sites. The other hexahydroxostannates were assumed by Strunz & Contag (1960) to be isostructural in view of their similar X-ray patterns.

Cohen-Addad (1968) further refined the structures of $CaSn(OH)_6$ and $ZnSn(OH)_6$ using neutron powder-diffraction at 4 K. The $CaSn(OH)_6$ and $ZnSn(OH)_6$ were partially deuterated in their study to enhance neutron scattering. The space group was changed to *Pn*3, and the location of the oxygen was more accurately determined [$CaSn(OH)_6$: $x = -0.065$, $z = 0.269$; $ZnSn(OH)_6$: $x = -0.07$, $z = 0.263$]. The refinements were done in space group *Pn*3, with *M* located at 0, 0, 0 and Sn at ½, ½, ½, as in Cohen-Addad (1968). The hydrogen was found to be disordered over two sites. The hydrogen atoms link oxygen of different octahedra (Fig. 2). The hydrogen sites form a distorted square around an empty site at ¼, ¼, 0 (Fig. 3).

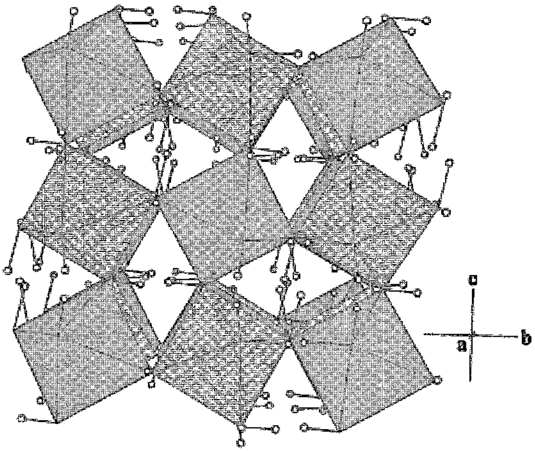

FIG. 2. Crystal structure of schoenfliesite, $MgSn(OH)_6$, as determined from neutron-diffraction data. The light-colored octahedra are $Sn(OH)_6$, the dark-colored octahedra are $Mg(OH)_6$, and the white atoms are hydrogen.

The crystal structure of $MnSn(OH)_6$ was refined using X-ray data by Christensen & Hazell (1969), with the oxygen located at 0.081, 0.930, 0.255.

The unit-cell dimensions of the various hexahydroxostannates have been reported in: Strunz & Contag (1960), Morgenstern-Badarau *et al.* (1965), Cohen-Addad (1968), Christensen & Hazell (1969), Faust & Schaller (1971), and Nefedov *et al.* (1977). Unit-cell dimensions are given in Table 1.

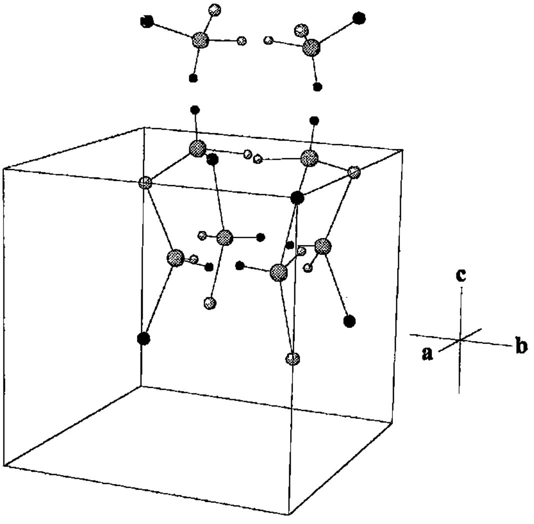

FIG. 3. Hydrogen bonding in the crystal structure of schoenfliesite showing O (large, medium shading), Sn (medium, white), Mg (medium, black), H_1 (small, white) and H_2 (small, black).

TABLE 1. UNIT-CELL PARAMETER OF HEXAHYDROXOSTANNATES

	1	2	3	4	5	6	7
$MgSn(OH)_6$	7.77	7.78			7.759	7.79	7.7449(4)
$MnSn(OH)_6$	7.88	7.892		7.885		7.85	7.8744(5)
$CaSn(OH)_6$	8.13	8.128	8.15	8.150			8.1221(3)
$CoSn(OH)_6$	7.78	7.749		7.757			
$FeSn(OH)_6$	7.79	7.757		7.630			
$ZnSn(OH)_6$		7.765	7.8	7.772			

Relevant mineral names: $MgSn(OH)_6$ schoenfliesite, $MnSn(OH)_6$ wickmanite, $CaSn(OH)_6$ burtite, $FeSn(OH)_6$ natanite. Sources: 1 Strunz & Contag (1960), 2 Morgenstern-Badarau *et al.* (1965), 3 Cohen-Addad (1968), 4 Christensen & Hazell (1969), 5 Faust & Schaller (1971), 6 Nefedov *et al.* (1977), 7 present study. Values of the unit-cell parameter are quoted in Å.

Neutron Diffraction

Neutron-diffraction data were collected on the DUALSPEC C2 high-resolution constant-wavelength powder diffractometer located at Chalk River Laboratories (Atomic Energy Canada Limited, Chalk River, Ontario, Canada). The wavelength, λ = 1.3276(1) Å, was determined by Rietveld refinement of standard powdered silicon. The neutron beam was monochromated by Si (3 3 1 plane), with a take-off angle of 73.9(9)° 2θ. The samples were packed into vanadium sample cylinders with a volume of approximately 1.5 cm^3. The data were collected using a curved bank of stationary detectors between 11.4° and 95° 2θ. The neutron-diffraction experiment was conducted with the samples cooled to 4 in a helium-filled cryostat.

Infrared Spectroscopy

The infrared spectrum for synthetic partially deuterated $MgSn(OH)_6$ was recorded using the KBr pellet technique (2 mg sample dispersed in 200 mg KBr) with a Bomem MB100 Fourier transform infrared spectrometer, which covers the range 4000 to 400 cm^{-1}. From the infrared spectra (Fig. 4), it was determined that there is a considerable amount of H_2O present in the sample after deuteration. Absorption bands at 3388 and 1635 cm^{-1} of the $MgSn(OH)_6$ pattern are due to H_2O stretching and bending vibrations, respectively. The absorption bands at 3249 and 3198 cm^{-1}, and at 2421 and 2366 cm^{-1}, are due to OH and OD (D = deuterium) stretching vibrations, respectively. The inclusion of H_2O and D_2O into the crystal structure has broadened the OH absorption band considerably. The other absorption bands are due to KO and VO vibrations from the potassium vanadium oxide corrosion product and to SnO and MgO from the schoenfliesite.

Rietveld Refinement of the Structure

$MgSn(OH)_6$, $MnSn(OH)_6$ and $CaSn(OH)_6$ were refined in space group *Pn*3. Starting atom occupancies were taken from Cohen-Addad (1968). Data were

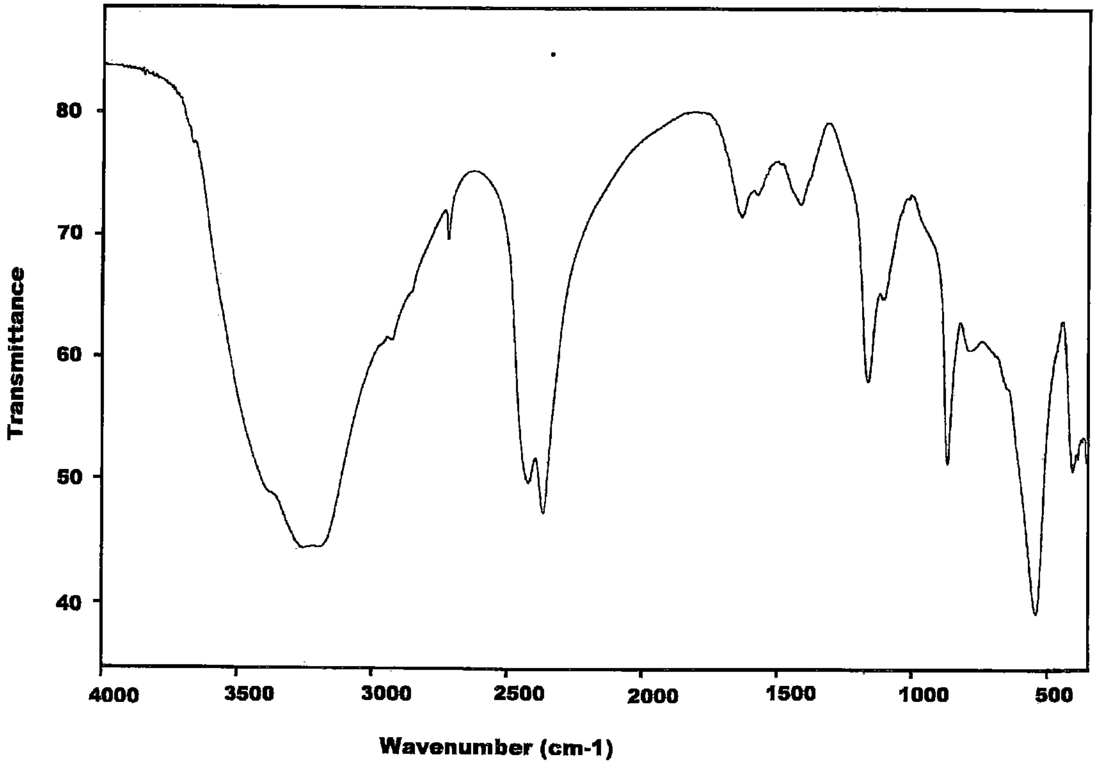

FIG. 4. Fourier-transform infrared-absorption spectrum of $MgSn(OH)_6$ from 4000 to 400 cm^{-1}.

refined using the whole-pattern least-squares refinement program GSAS (Larson & Von Dreele 1994). Peak profiles were fitted using the pseudo-Voigt profile function, with Lorentzian character of peaks modeled using a mixing parameter $\eta = \gamma_1 + \gamma_2\ (2\theta)$. Peak profiles were calculated to 1.00 peak-widths (full width at half maximum, FWHM) to either side of peak center. Peak widths were modeled using the function $H^2 = U\tan^2\theta + V\tan\theta + W$, and the background was modeled using a four-parameter polynomial function. The parameter turn-on sequence was as follows: scale factor, zero point, first background parameter, cell parameter(s), more background parameters, phase fraction parameters, and then the profile parameters together with the crystal-structure parameters. The crystal-structure parameters were refined in the order: atomic positions, isotropic temperature-factors, deuterium content and anisotropic temperature-factors. Final atomic coordinates are given in Table 2, and selected bond-distances, volumes of octahedra and angle variance are given in Table 3. The final observed and difference profile histogram is shown in Figure 5.

TABLE 2. ATOMIC PARAMETERS AND R INDICES, $MgSn(OH)_6$, $MnSn(OH)_6$, AND $CaSn(OH)_6$

		$MgSn(OH)_6$	$MnSn(OH)_6$	$CaSn(OH)_6$	$CaSn(OH)_6$*
O	*x*	–0.0619(9)	–0.0643(7)	–0.0663(8)	–0.073
	y	0.0751(9)	0.0755(9)	0.0787(7)	0.080
	z	0.254(2)	0.2586(7)	0.2694(5)	0.272
H_1	*x*	–0.044(3)	–0.0781(4)	–0.0346(66)	–0.067
	y	0.1994	0.202(5)	0.2011(63)	0.222
	z	0.2448(2)	0.234(6)	0.2869(74)	0.285
H_2	*x*	–0.222(4)	–0.201(5)	–0.1805(89)	–0.208
	y	0.074(2)	0.069(3)	0.0638(74)	0.078
	z	0.219(4)	0.270(6)	0.3026(74)	0.255
wR_p		2.59	2.54	2.38	
R_p		1.97	1.95	1.84	

* Cohen-Addad (1968). The structures of MSn(OH)$_6$ were refined in space group *Pn*3, with the M cations at 0, 0, 0 and Sn at ½, ½, ½, as in Cohen-Addad (1968).

R indices are expressed in the form $R = \Sigma(|F_o|-|F_c|) / \Sigma|F_o|$,
$wR = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma|F_o|^2]^{0.5}$, $w = 1$, as percentages.

The potassium vanadium oxide, calcite and sylvite were included in the refinements as additional phases. Starting atomic parameters for $K_{0.5}V_2O_5$ were used from Oka *et al.* (1995).

Hydrogen is disordered within the structure. Within any one square formed by four oxygen atoms (Fig. 3), hydrogen may occupy only four of eight sites. *Pn*3 symmetry will not be obeyed locally. Averaged over the

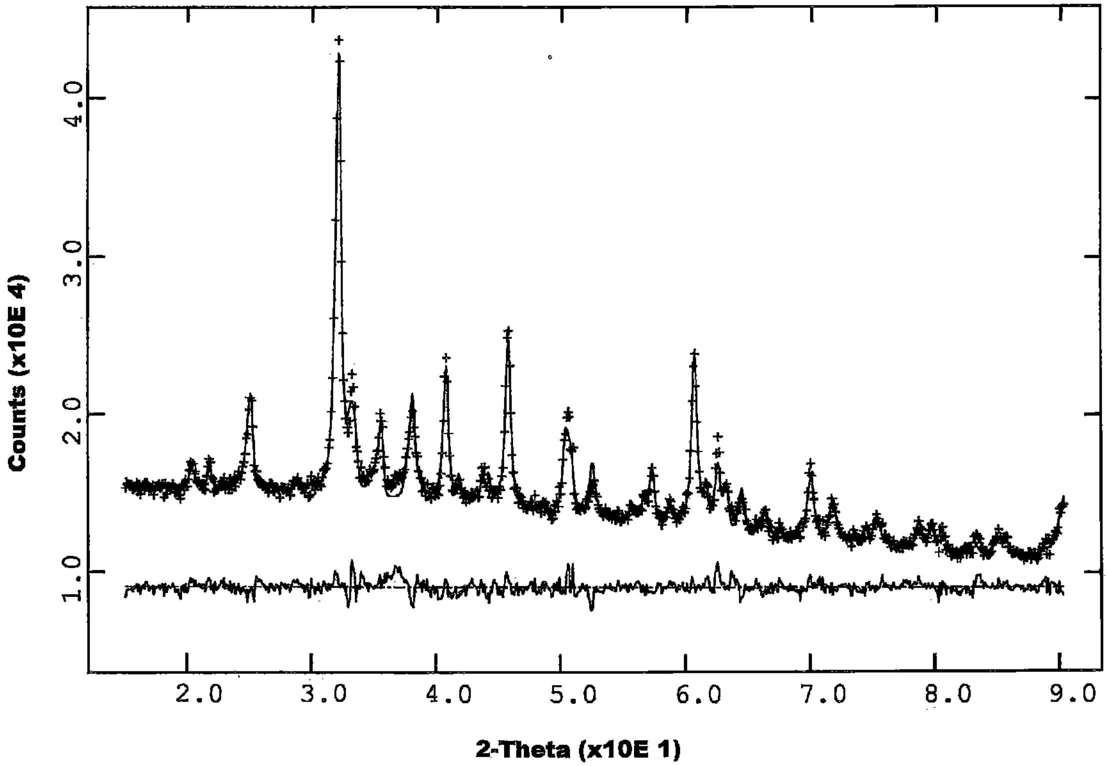

FIG. 5. The observed and difference profiles of the refined crystal-structure of schoenfliesite. Neutron-diffraction data.

TABLE 3. INTERATOMIC DISTANCES (Å), $MgSn(OH)_6$, $MnSn(OH)_6$ AND $CaSn(OH)_6$

		$MgSn(OH)_6$	$MnSn(OH)_6$	$CaSn(OH)_6$	$CaSn(OH)_6$*
%Deuterium		78.0	56.4	46.8	
$Sn(OH)_6$	Sn–O	2.044(3)	2.055(6)	2.051(4)	2.06
Octahedra	$Sn–H_1$	2.53(5)	2.70(5)	2.40(5)	2.6
	$Sn–H_2$	2.84(4)	2.46(5)	2.23(5)	2.7
	O–O	2.861(2)	2.750(2)	2.800(13)	2.81
	O–O	2.921(2)	2.860(2)	2.954(10)	3.00
Volume		11.44(7)	11.48(4)	11.54(4)	
Angle variance		1.4(2)	3.72(2)	4.8(2)	
$M(OH)_6$	M–O	2.112(2)	2.181(6)	2.342(5)	2.39
Octahedra	$M–H_1$	2.47(4)	2.51(4)	2.99(6)	3.0
	$M–H_2$	2.487(3)	2.71(4)	2.91(7)	2.8
	O–O	2.96(2)	2.952(1)	3.25(5)	3.3
	O–O	2.96(2)	2.927(2)	3.42(6)	3.45
Volume		12.43(7)	13.81(5)	17.00(5)	
Angle variance		1.1(2)	2.3(1)	0.27(4)	
O and H bonds	$O–H_1$	0.975(2)	1.02(4)	1.04(5)	1.15
	$O--H_1$	1.751(3)	1.75(4)	1.86(5)	
	O--O	2.710(2)	2.704(5)	2.668(8)	
	$O–H_2$	1.28(5)	1.08(4)	0.97(8)	1.1
	$O--H_2$	1.68(4)	1.87(4)	2.14(4)	
	O–O	2.914(2)	2.878(6)	2.846(9)	

* Cohen-Addad (1968).

entire crystal, with each hydrogen position half-occupied, the cubic symmetry is maintained.

Raw data and refinement files may be obtained from the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2.

DISCUSSION

The unique phase assemblage of sample KW4254 is due to the unusual environment of formation, namely the very high salinity of the seawater, the presence of decomposing organic material from the ship's hull, and the presence of the bronze harpoon head. The bronze corroded, allowing tin to react with magnesium, hydrogen and oxygen from the seawater to form schoenfliesite. The copper, also liberated from the corrosion of the bronze, reacted with sulfur to form roxbyite. The sulfur was likely derived from seawater, as sulfate was reduced by bacteria living in the rotting organic matter that surrounded the bronze. Samples taken nearby included calcite, aragonite and kutnohorite. Unlike KW4254, which is black, these are light blue to green.

The bond distances of the $Sn(OH)_6$ octahedra from the $MgSn(OH)_6$, $MnSn(OH)_6$ and $CaSn(OH)_6$ are all

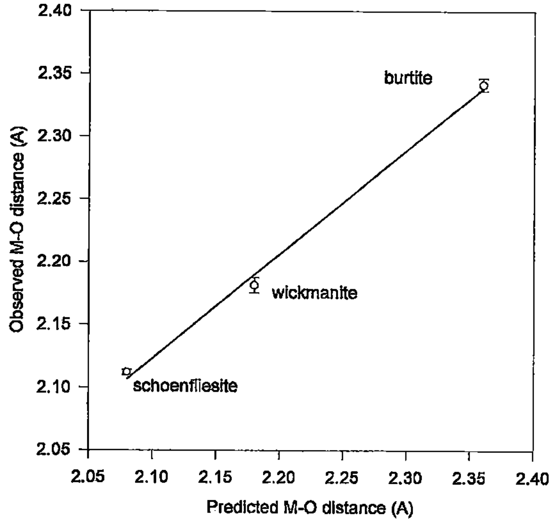

FIG. 6. Predicted *M*–O distance (Å) *versus* observed *M*–O distance (Å). Predicted ionic radii are from Shannon (1976).

very similar (Table 3). The Sn–O bond distances range from 2.044(3) to 2.055(6) Å. The systematic variance of the angles in the $Sn(OH)_6$ octahedra is due to the increased difference in the size of the $Sn(OH)_6$ and $M(OH)_6$ octahedra, caused by the increased radius of the cation. The differences in the cation radii also affect the bond distances of the $M(OH)_6$ octahedra and polyhedron volume, which increase systematically with increase of the cation radius (Fig. 6).

As discussed earlier, the H atoms are disordered over two positions in a unit cell. Within an isolated hydrogen–oxygen system, however, the hydrogen is not disordered. The four hydrogen atoms will fill every other hydrogen site within the eight-site system (Fig. 3). These isolated systems are not correlated with each other, resulting in long-range disorder. The O–H bond in an isolated hydroxyl group is approximately 1 Å. The observed bond-lengths are: 0.975 Å ($O–H_1$) and 1.28 Å ($O–H_2$) for $MgSn(OH)_6$; 1.02 Å ($O–H_1$) and 1.08 Å ($O–H_2$) for $MnSn(OH)_6$; and 1.04 Å ($O–H_1$) and 0.97 Å ($O–H_2$) for $CaSn(OH)_6$. The O–H bond lengths commonly are increased owing to the hydrogen bonding, with the presence of a second more distant oxygen. There is a relationship between the O–H and the O–O distances in nearly linear hydrogen bonds (Speakman 1975): the O–H distance increases gradually as O–O diminishes. For the $MgSn(OH)_6$ and the $MnSn(OH)_6$, the $O–H_2$ distances are longer than expected, possibly because of the incorporation of H_2O into the structure. Infrared spectroscopy of synthetic schoenfliesite confirms that there is free H_2O in the structure. Differential thermal analysis was done on natural and synthetic schoenfliesite by Faust & Schaller (1971) and was compared to results of a differential thermal analysis done on synthetic schoenfliesite by Coffen (1953). There is a small endotherm on the low-temperature side of the major endothermic trough. Morgenstern-Badarau *et al.* (1969) also noticed this feature in $MnSn(OH)_6$ and $CdSn(OH)_6$. They attributed a small decrease in the cell parameters to the loss of low-temperature H_2O from the structure. The free H_2O interacting with the bonded hydrogen atoms would cause additional lengthening of the O–H bonds. The $R\bar{3}$ symmetry observed in natural burtite by Sonnet (1981) may be the result of ordering of hydrogen into one of the two positions observed in this study.

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