

## SEWARDITE, $\text{CaFe}^{3+}_2(\text{AsO}_4)_2(\text{OH})_2$ , THE Ca-ANALOGUE OF CARMINITE, FROM TSUMEB, NAMIBIA: DESCRIPTION AND CRYSTAL STRUCTURE

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### ABSTRACT

Sewardite, ideally  $\text{CaFe}^{3+}_2(\text{AsO}_4)_2(\text{OH})_2$ , is orthorhombic, *Cccm*, with unit-cell parameters derived from a crystal-structure refinement:  $a$  16.461(2),  $b$  7.434(1),  $c$  12.131(2) Å,  $V$  1484.5(6) Å<sup>3</sup>,  $a:b:c$  2.2143:1:1.6318,  $Z$  = 8. The strongest nine lines of the X-ray powder-diffraction pattern [ $d$  in Å (1)( $hkl$ )] are: 4.874(90)(202), 3.473(50)(113), 3.389(60)(220), 3.167(100)(022), 3.015(50)(510), 2.988(50)(313), 2.919(70)(511), 2.503(90)(422,314) and 1.775(50)(533,026). The mineral occurs within a vug 3 cm across on a single specimen of gangue collected from the 31<sup>st</sup> level of the Tsumeb mine, Tsumeb, Namibia, as platy to compact anhedral to subhedral masses. These masses, up to 0.3 mm in maximum size, are intimately intergrown with very dark green to black botryoidal masses of an intergrowth of two tsumcorite-group minerals. Individual fragments are between 50 and 100 µm in size, with no obvious forms, and {100} and {011} as imperfect cleavages. Sewardite has physical properties that are very similar to those of carminite; it is dark red in masses to a much lighter red to orange on thin edges of small fragments. The streak is reddish brown, and the luster, vitreous. It is translucent (masses) to transparent (on thin edges), and nonfluorescent. The hardness (Mohs) is 3½. It is brittle, and has a splintery (in the [011] direction) to uneven fracture. The calculated density is 4.156 g/cm<sup>3</sup> (for the empirical formula). In polished section, it is light bluish grey in plane-polarized reflected light in air, with ubiquitous very bright pink to red internal reflections; the mineral is very weakly birefractant, non-anisotropic, without pleochroism. Averaged results of eight electron-microprobe analyses yield CaO 11.77, ZnO 1.68, CuO 0.28, Fe<sub>2</sub>O<sub>3</sub> 31.65, As<sub>2</sub>O<sub>5</sub> 48.81, H<sub>2</sub>O [4.04], total [98.23] wt.%. The empirical formula is  $\text{Ca}_{0.99}(\text{Fe}^{3+}_{1.87}\text{Zn}_{0.10}\text{Cu}_{0.02})\Sigma_{1.99}\text{As}^{5+}_{2.01}\text{O}_{8.00}[(\text{OH})_{1.88}(\text{H}_2\text{O})_{0.12}]\Sigma_{2.00}$ , on the basis of 10 anions. The infrared-absorption spectra show bands for structural (OH), (H<sub>2</sub>O), and arsenate. The mineral's name honors Terry M. Seward, Professor of Geochemistry, ETH, Zürich, Switzerland, who collected the mineral specimen in 1982. The crystal structure has been refined to an  $R$  index of 6.1% for 451 observed reflections measured with MoK $\alpha$  X-radiation. Chains of edge- and corner-sharing  $\text{Fe}^{3+}\Phi_6$  octahedra ( $\Phi$ : O, OH) extend along the  $b$  axis and are linked by (AsO<sub>4</sub>) tetrahedra to form [ $\text{Fe}^{3+}_2(\text{AsO}_4)_2(\text{OH})_2$ ] sheets parallel to {001}; these sheets link *via* [8]-coordinated Ca atoms. Sewardite is the Ca-dominant analogue of carminite, ideally  $\text{Pb}^{2+}\text{Fe}^{3+}(\text{AsO}_4)_2(\text{OH})_2$ .

**Keywords:** sewardite, new mineral species, calcium iron hydroxide-arsenate, carminite, X-ray data, electron-microprobe data, reflectance data, infrared spectroscopy, crystal structure, Tsumeb mine, Tsumeb, Namibia.

### SOMMAIRE

La sewardite, dont la composition idéale serait  $\text{CaFe}^{3+}_2(\text{AsO}_4)_2(\text{OH})_2$ , est orthorhombique, *Cccm*, avec les paramètres réticulaires suivants, dérivés d'une ébauche de la structure cristalline:  $a$  16.461(2),  $b$  7.434(1),  $c$  12.131(2) Å,  $V$  1484.5(6) Å<sup>3</sup>,  $a:b:c$  2.2143:1:1.6318,  $Z$  = 8. Les huit raies les plus intenses du spectre de diffraction X, méthode des poudres [ $d$  en Å (1)( $hkl$ )], sont: 4.874(90)(202), 3.473(50)(113), 3.389(60)(220), 3.167(100)(022), 3.015(50)(510), 2.988(50)(313), 2.919(70)(511),

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2.503(90)(422,314) et 1.775(50)(533,026). Ce minéral se présente dans une seule cavité de 3 cm dans un échantillon de gangue prélevé au niveau 31 de la mine Tsumeb, à Tsumeb, en Namibie, en plaquettes ou masses compactes, xénomorphes à sub-idiomorphes. Ces masses, atteignant 0.3 mm, sont disposées en intercroissance intime avec des masses botryoidales vert foncé à noires qui contiennent deux minéraux du groupe de la tsumcorite. Les fragments individuels varient de 50 à 100 µm en taille, sans formes apparentes, avec {100} et {011} comme clivages imparfaits. La sewardite possède des propriétés physiques très semblables à celles de la carminite; elle va du rouge foncé où elle est massive à rouge beaucoup plus pâle ou orange en bordure mince des grains. Sa rayure est brun rougeâtre, et son éclat, vitreux. Elle est translucide (massive) à transparente (bordure mince), et non fluorescente. La dureté de Mohs est 3½. Elle est cassante, et possède une fracture en échape le long de [011] ou inégale. La densité calculée est égale à 4.156 g/cm<sup>3</sup> (d'après la formule empirique). En sections polies, la sewardite est gris bleuâtre pâle en lumière réfléchiée dans l'air (polarisation en plan), avec des reflets internes rose très brillant à rouge. Elle est très faiblement biréfléchante, non anisotrope, et sans pléochroïsme. En moyenne, les résultats de huit analyses à la microsonde électronique ont donné: CaO 11.77, ZnO 1.68, CuO 0.28, Fe<sub>2</sub>O<sub>3</sub> 31.65, As<sub>2</sub>O<sub>5</sub> 48.81, H<sub>2</sub>O [4.04], total [98.23] % en poids. La formule empirique qui en découle, sur une base de dix anions, est: Ca<sub>0.99</sub>(Fe<sup>3+</sup><sub>1.87</sub>Zn<sub>0.10</sub>Cu<sub>0.02</sub>)Σ<sub>1.99</sub>As<sup>5+</sup><sub>2.01</sub>O<sub>8.00</sub>[(OH)<sub>1.88</sub>(H<sub>2</sub>O)<sub>0.12</sub>]Σ<sub>2.00</sub>. Les spectres d'absorption dans l'infra-rouge montrent des bandes attribuées à (OH), (H<sub>2</sub>O), et des groupes arsenate dans la structure. Le nom du minéral honore Terry M. Seward, professeur de géochimie à l'institut ETH, Zürich, en Suisse, qui l'a trouvé en 1982. La structure cristalline a été affinée jusqu'à un résidu *R* de 6.1% pour 451 réflexions observées, mesurées avec rayonnement MoKα. Des chaînes d'octaèdres Fe<sup>3+</sup>Φ<sub>6</sub> à arêtes et à coins partagés (Φ: O, OH) sont orientées selon l'axe *b* et sont rattachées par des tétraèdres (AsO<sub>4</sub>) pour former des feuillets [Fe<sup>3+</sup><sub>2</sub>(AsO<sub>4</sub>)<sub>2</sub>(OH)<sub>2</sub>] parallèles à {001}; ces feuillets sont liés grâce aux atomes Ca, à coordination [8]. La sewardite est l'analogue à dominance de Ca de la carminite, dont la formule idéale est Pb<sup>2+</sup>Fe<sup>3+</sup>(AsO<sub>4</sub>)<sub>2</sub>(OH)<sub>2</sub>.

(Traduit par la Rédaction)

**Mots-clés:** sewardite, nouvelle espèce minérale, arsenate hydroxylé de calcium et de fer, carminite, données de diffraction X, données de microsonde électronique, données de réflectance, spectroscopie infra-rouge, structure cristalline, mine Tsumeb, Tsumeb, Namibie.

## INTRODUCTION

The Tsumeb mine, Tsumeb, Namibia (lat. 19°S, long. 18°E) has long been a prolific source of new mineral species; over fifty-five species have been formally characterized from this locality since the first mineral (otavite) was described in 1906 (Gebhard 1999). Here, we describe yet another new phase, sewardite, from this classic locality. The specimen in which the new phase is found was originally collected in 1982 by Dr. Terry Seward, but it has taken seventeen years, and a chance meeting between Professor Seward and the senior author at the IMA meeting in Toronto in 1998, before formal characterization of the mineral commenced. Preliminary studies by Dr. Seward in the 1980s (megascopic appearance, qualitative energy-dispersion electron-microprobe analysis and a Gandolfi camera X-ray powder-diffraction pattern) suggested a potential new mineral; further studies in Ottawa, Winnipeg and London have confirmed that this phase is, indeed, new to science.

The mineral is named *sewardite* in honor of Terry Maxwell Seward (b. 1940) who collected the mineral specimen and recognized its potential as a new species. Dr. Seward is Professor of Geochemistry at the Eidgenössische Technische Hochschule (ETH), Zürich, Switzerland, and holds dual citizenship in Canada and New Zealand. The mineral and mineral name have been approved by the Commission on New Minerals and Mineral Names, IMA (2001–54). Holotype material, consisting of a few small aggregates in two gelatin cap-

sules, is housed in the Systematic Reference Series of the National Mineral Collection at the Geological Survey of Canada, Ottawa, Ontario, under catalogue number 68095. The polished section used for the quantitative electron-microprobe and reflectance studies is preserved in the mineral collections at The Natural History Museum, London, Great Britain, as BM 2001.36.

## OCCURRENCE AND ASSOCIATED MINERALS

Sewardite was identified in a single specimen of gangue that has since been split for scientific study; the new mineral is rare, and we estimate that only 1–2 mg of pure sewardite is currently available for further study. The mineral occurs within a small 3 cm-sized vug which was collected on the 31<sup>st</sup> level of the Tsumeb mine. It is intimately intergrown with a very dark green to black botryoidal mass, identified as a member of the tsumcorite group (Krause *et al.* 1998) by routine X-ray powder-diffraction film methods. Compositionally, this botryoidal mass is composed of an intimate intergrowth of two distinct phases: one conforms to the composition of ferrilotharmeyerite; the other may be a cuprian, zincian variety of ferrilotharmeyerite or it may be the Zn-dominant analogue of lukrahnite (Krause *et al.* 2001). We hope to pursue further studies of this matrix material at a later date.

Recently, it has come to our attention that sewardite has also been identified, by both quantitative electron-microprobe analyses and Gandolfi X-ray powder camera, from Mina Ojuela, Mapimi, Durango, Mexico (U.

Kolitsch, pers. commun., 2002). There, it occurs as dark reddish spherules and rosettes of very small thin platy crystals.

#### PHYSICAL PROPERTIES

Sewardite occurs as platy to compact anhedral to subhedral masses that do not exceed 0.3 mm in maximum size and are randomly scattered throughout the dark green to black matrix. A photomicrograph of both an isolated fragment and one in matrix is shown in Figure 1. Individual fragments are 50–100  $\mu\text{m}$  in size and have {100} imperfect and {011} imperfect cleavages (orientations confirmed by a precession single-crystal study). There are no obvious crystal forms, and twinning was not observed megascopically or in X-ray single-crystal studies. Most physical properties are very similar to those of carminite; megascopic discrimination between the two minerals is virtually impossible. The color of sewardite varies from dark red in masses to a much lighter red to orange on thin edges of crystal fragments. The streak is reddish brown, and the luster is vitreous. Masses are translucent, whereas thin edges of fragments are transparent. The mineral is brittle, with a splintery (in the [011] direction) to uneven fracture, and is nonfluorescent under both long- and short-wave ultraviolet radiation. The Mohs hardness is estimated to be 3½. The density could not be measured because of the small size of available fragments and the dearth of material. The density, calculated on the basis of the empirical formula and unit-cell parameters derived from an investigation of the crystal structure, is 4.156  $\text{g}/\text{cm}^3$ .

#### OPTICAL PROPERTIES

In plane-polarized reflected light, sewardite is light bluish grey with weak, but measurable, bireflectance, no anisotropy and no pleochroism. However, under crossed polars, the mineral shows ubiquitous very bright pink to red internal reflections. Reflectance measurements in air were made relative to a Zeiss silicon carbide standard, SiC no. 472, and results are presented in Table 1. Reflectance measurements were made in oil [index of refraction ( $N_D$ ) 1.515]; the values are so low that they are considered unreliable and are not given here. This indicates, as do the low values in air, that the mineral is sensibly transparent. The indices of refraction, as calculated from the reflectances in air at 589 nm, are  $n_1 = 1.87$  and  $n_2 = 1.92$  ( $\bar{n} = 1.895$ ). The Vickers micro-hardness was not measured because there was only a single grain-mount of material available for

TABLE 1. REFLECTANCE DATA (IN AIR) FOR SEWARDITE

$\lambda$ (nm)	$R_1$ (%)	$R_2$ (%)	$\lambda$ (nm)	$R_1$ (%)	$R_2$ (%)
400	10.50	11.12	560	9.40	10.02
420	10.43	11.05	580	9.30	9.98
440	10.32	10.92	589	9.27	9.95
460	10.12	10.71	600	9.24	9.92
470	10.04	10.60	620	9.15	9.80
480	9.96	10.49	640	8.99	9.66
500	9.78	10.37	650	8.80	9.49
520	9.69	10.18	660	8.60	9.37
540	9.53	10.07	680	7.89	8.87
546	9.49	10.06	700	7.25	8.30

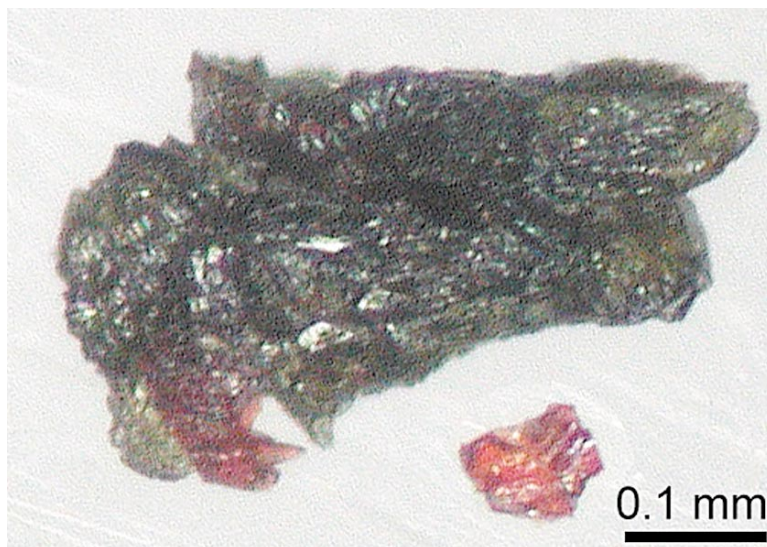


FIG. 1. Photomicrograph of an isolated fragment of sewardite as well as a fragment in green to black botryoidal matrix. Scale bar: 0.1 mm.

study, and the VHN values obtained would not have been reliable.

#### X-RAY CRYSTALLOGRAPHY

A small fragment of seawardite,  $0.009 \times 0.021 \times 0.023$  mm in size, was investigated with a Bruker P4 four-circle X-ray diffractometer equipped with a CCD detector. Systematic absences are consistent with the space group *Cccm*. The measured unit-cell parameters are:  $a$  16.461(2),  $b$  7.434(1),  $c$  12.131(2) Å,  $V$  1484.5(6) Å<sup>3</sup>,  $a:b:c$  2.2143:1:1.6318.

The unit-cell parameters,  $a$  16.436(8),  $b$  7.425(3),  $c$  12.116(5) Å,  $V$  1479(1) Å<sup>3</sup>,  $a:b:c$  2.2136:1:1.6318,  $Z$  = 8, were refined from 28 powder reflections representing  $d$  values between 3.473 and 1.347 Å for which unambiguous indexing was possible on the basis of the calculated intensities derived from the crystal structure. A fully indexed powder pattern is presented in Table 2. Powder data for seawardite and carminite are similar, though readily distinguishable, even on 57.3 mm

Debye-Scherrer powder films. Differences are in fact significant enough that it was not initially obvious that the two minerals are structurally related.

#### CHEMICAL COMPOSITION

Polished fragments of seawardite were analyzed with a Cameca SX-50 electron microprobe at an operating voltage of 15 kV, a beam current of 20 nA, a count time of 20 s on peak and 10 s on background, and a beam 10 µm in diameter. An energy-dispersion scan indicated the absence of any other elements with atomic number greater than 9 except those reported here. There is a possibility of very minor Na; however, a significant interference with a Zn *L*-line does not allow quantitative measurement of the Na peak. Therefore, Na<sub>2</sub>O is estimated to be below 0.2 wt.%. Al, V, Mn, Co, Ni and Pb were sought, but are below detection limits. The following standards were used: diopside (Ca), gahnite (Zn), azurite (Cu), fayalite (Fe) and cobaltite (As). Data were corrected using the PAP procedure of Pouchou &

TABLE 2. X-RAY POWDER-DIFFRACTION DATA FOR SEWARDITE

$I_{est.}$	$d\text{Å}_{(meas.)}$	$d\text{Å}_{(calc.)}$	$hkl$	$I_{est.}$	$d\text{Å}_{(meas.)}$	$d\text{Å}_{(calc.)}$	$hkl$
20	6.745	6.767	110	3	1.834	1.836	316
90	4.874	4.876	202	* 5	1.811	1.809	334
10	4.523	4.513	112	50	1.775	1.776	533
3	3.562	3.564	312			1.774	026
* 50	3.473	3.468	113	3	1.754	1.755	911
* 60	3.389	3.383	220	* 10	1.734	1.735	242
* 40	3.264	3.259	221	3	1.720	1.723	822
* 100	3.167	3.165	022	* 10	1.700	1.700	804
* 50	3.015	3.006	510	* 30	1.693	1.692	440
* 50	2.988	2.978	313	3	1.676	1.676	516
* 70	2.919	2.917	511	* 40	1.656	1.656	534
* 20	2.765	2.765	114			1.629	426
* 40	2.696	2.693	512	15	1.626	1.624	913
* 15	2.594	2.594	223	* 30	1.583	1.583	044
		2.508	422	* 5	1.566	1.569	733
90	2.503	2.497	314	3	1.543	1.541	227
* 10	2.442	2.438	404			1.532	535
* 5	2.411	2.411	513	20	1.531	1.530	914
* 5	2.283	2.281	115	* 15	1.516	1.515	008
3	2.258	2.256	330			1.503	1020
10	2.205	2.204	620	10	1.503	1.500	517
		2.202	711	* 5	1.484	1.485	734
* 20	2.168	2.169	621			1.470	930
		2.134	514	5	1.469	1.468	151
15	2.129	2.124	315			1.459	931
3	2.095	2.100	712	3	1.459	1.454	1111
* 5	2.056	2.055	800			1.431	915
3	2.021	2.019	006	10b	1.428	1.428	932
3	1.971	1.970	225			1.423	351
3	1.950	1.951	531	* 5	1.413	1.413	536
		1.935	116	3	1.395	1.394	735
5	1.936	1.935	623	* 15	1.381	1.382	228
3	1.908	1.904	134			1.370	1200
15	1.883	1.887	515	10b	1.370	1.369	717
* 5	1.858	1.800	532	* 25	1.347	1.346	1024
		1.856	040				

114.6 mm Debye-Scherrer powder camera, Cu radiation and Ni filter ( $\lambda$  CuK $\alpha$  = 1.54178 Å); intensities estimated visually, b = broad line; not corrected for shrinkage and no internal standard; \* = lines used for unit-cell refinement; indexed with  $a$  16.436(8),  $b$  7.425(3),  $c$  12.116(5) Å.

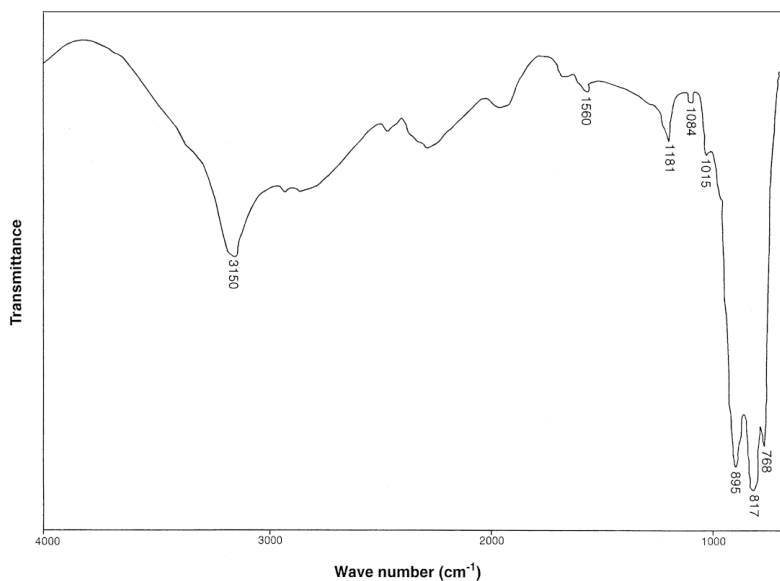


FIG. 2. Infrared-absorption spectrum for sewardite.

Pichoir (1984, 1985). The valence states for both Fe and As, as well as the number of O atoms, were determined by crystal-structure analysis prior to final interpretation of the electron-microprobe results. The paucity of pure material prevented quantitative determination of H<sub>2</sub>O. However, the presence of H as (OH) and as very minor (H<sub>2</sub>O) was confirmed both by crystal-structure analysis and by powder infrared-absorption study; the amount of H<sub>2</sub>O was therefore calculated by stoichiometry. The average of eight determinations (and standard deviations) gave CaO 11.77 (0.05), ZnO 1.68 (0.20), CuO 0.28 (0.14), Fe<sub>2</sub>O<sub>3</sub> 31.65 (0.37), As<sub>2</sub>O<sub>5</sub> 48.81 (0.37), H<sub>2</sub>O [4.04], total [98.23] wt.%. With a total of 10 anions, the empirical formula for the Ca-analogue of carminite is Ca<sub>0.99</sub>(Fe<sup>3+</sup><sub>1.87</sub>Zn<sub>0.10</sub>Cu<sub>0.02</sub>)Σ<sub>1.99</sub>As<sup>5+</sup><sub>2.01</sub>O<sub>8.00</sub>[(OH)<sub>1.88</sub>(H<sub>2</sub>O)<sub>0.12</sub>]Σ<sub>2.00</sub>. The end-member formula, CaFe<sup>3+</sup><sub>2</sub>(AsO<sub>4</sub>)<sub>2</sub>(OH)<sub>2</sub>, requires CaO 12.10, Fe<sub>2</sub>O<sub>3</sub> 34.44, As<sub>2</sub>O<sub>5</sub> 49.57, H<sub>2</sub>O 3.89, total 100.00 wt.%. Because a precise index of refraction could not be determined, a meaningful index of compatibility could not be calculated.

#### INFRARED SPECTROSCOPY

The procedures for acquiring the infrared-absorption spectrum of sewardite are identical to those reported by Roberts *et al.* (1994). The sample was analyzed using a Bomem Michelson MB-100 FTIR spectrometer equipped with a wide-band mercury-cadmium telluride detector. The transmittance spectrum (Fig. 2) shows a strong absorption band, centered at 3150 cm<sup>-1</sup>, attribut-

TABLE 3. MISCELLANEOUS INFORMATION FOR SEWARDITE

<i>a</i> (Å)	16.461(2)	crystal size (μm)	9 × 21 × 23
<i>b</i>	7.434(1)	radiation/monochromator	MoKα/Gr
<i>c</i>	12.131(2)	No. of reflections	8155
<i>V</i> (Å <sup>3</sup> )	1484.4(6)	No. in Ewald sphere	4639
Sp. Gr.	<i>Cc</i> cm	No. unique reflections	694
<i>Z</i>	8	No. <i>F</i> <sub>o</sub> > 10σ <i>F</i> <sub>o</sub>	451
<i>μ</i> (mm <sup>-1</sup> )	13.64	<i>R</i> <sub>merge</sub> %	3.4
<i>D</i> <sub>calc</sub> (g/cm <sup>3</sup> ) <sup>1</sup>	4.160	<i>R</i> <sub>obs</sub> %	6.1
		<i>wR</i> <sub>obs</sub> %	6.3
$R = \Sigma( F_o  -  F_c ) / \Sigma F_o $			
$wR = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_c^2)^2]^{1/2}$ , $w = (1 / \sigma^2(I) + 0.0005 I^2)$			

<sup>1</sup>for end-member formula

TABLE 4. POSITIONAL PARAMETERS FOR SEWARDITE

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>11</sub>
Ca(1)	0	0	1/4	0.0185(18)
Ca(2)	1/4	3/4	0	0.0101(16)
Fe	0.37896(17)	0.1321(3)	0.13404(17)	0.0056(6)
As(1)	0.04504(14)	0.7447(3)	0	0.0054(6)
As(2)	0.21374(15)	0	1/4	0.0048(6)
O(1)	0.0144(7)	0.2246(13)	0.1119(8)	0.005(3)
O(2)	0.0885(10)	0.529(2)	0	0.006(4)
O(3)	0.1219(11)	-0.114(2)	0	0.012(4)
O(4)	0.1511(8)	0.1777(14)	0.2389(9)	0.011(3)
O(5)	0.2720(7)	-0.0150(14)	0.1378(8)	0.005(3)
O(6)*	0.1711(9)	0.233(2)	0	0.005(4)
O(7)*	0.4243(11)	0	1/4	0.017(4)

\* = OH

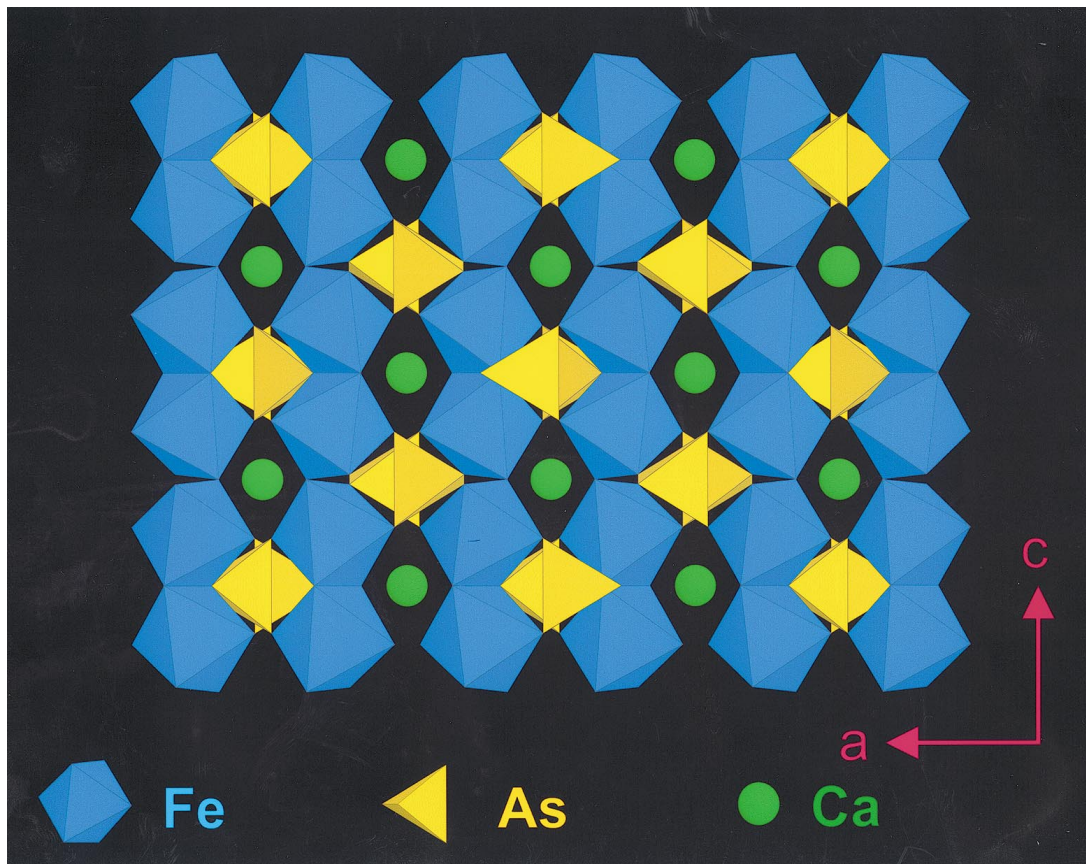


Fig. 3. Sewardite structure projected onto (010). The  $(\text{Fe}^{3+}\Phi_6)$  octahedra ( $\Phi$ : O, OH) are blue,  $(\text{AsO}_4)$  tetrahedra are yellow, and Ca atoms (in framework interstices) are green.

able to O–H stretching in the hydroxyl groups and a very weak absorption band, centered at  $1560\text{ cm}^{-1}$ , which is most likely due to H–O–H bending in the absorbed ( $\text{H}_2\text{O}$ ). Characteristic bands for arsenate are very strong and are centered at 895, 817 and  $768\text{ cm}^{-1}$ .

#### CRYSTAL STRUCTURE

The (very small) crystal selected for collection of X-ray intensity data was mounted on a Siemens P4 automated four-circle diffractometer equipped with a 1K CCD detector and  $\text{MoK}\alpha$  X-radiation. Subsequent to the collection of the intensity data, all frames were examined carefully for visually observed reflections. Because of the small size of the crystal (Table 3), no data were observed above  $2\theta = 50^\circ$ , and hence the refinement is based on data with  $2\theta \leq 50^\circ$ . A total of 8155 intensities was collected to  $50^\circ 2\theta$  using a frame width of  $0.2^\circ$ , a frame exposure time of three minutes, and a crystal-to-

detector distance of 4 cm. The cell dimensions (Table 3) were determined from 1673 reflections with  $I > 10\sigma I$ .

All calculations were done with the SHELXTL PC(PLUS) system of programs;  $R$  indices are of the form given in Table 3. Using the atom parameters of carminite [Kharisun *et al.* (1996); see also Olmi & Sabelli (1995)] the structure of sewardite was refined to convergence at an  $R$ -index of 6.1%. Because of the paucity of data due to the small size of the crystal, only isotropic-displacement parameters were used in the refinement. Final positions and displacement parameters are listed in Table 4, selected interatomic distances are given in Table 5, and a bond-valence table is given as Table 6. Structure factors may be obtained from The Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, Canada. Subsequent to the collection of the X-ray intensity data, the crystal was embedded in epoxy and quantitatively analyzed with a Cameca SX-50 electron microprobe as described above.



TABLE 5. SELECTED INTERATOMIC DISTANCES IN SEWARDITE ( $X = \text{Ca}$ ) AND CARMINITE\* ( $X = \text{Pb}$ )

		Sewardite	Carminite
$X(1)-O(1)$	x4	2.38(1)	2.547(5)
$X(1)-O(4)$	x4	<u>2.82(1)</u>	<u>2.842(5)</u>
$\langle X(1)-O \rangle$		2.60	2.695
$X(2)-O(3)$	x2	2.34(2)	2.540(7)
$X(2)-O(5)$	x4	2.44(1)	2.558(5)
$X(2)-O(2)$	x2	<u>3.13(2)</u>	<u>3.063(7)</u>
$\langle X(2)-O \rangle$		2.59	2.680
$Fe-O(7) [= OH]$		1.87(1)	1.874(3)
$Fe-O(1)$		2.07(1)	2.001(5)
$Fe-O(5)$		2.07(1)	2.018(5)
$Fe-O(4)$		1.97(1)	2.025(6)
$Fe-O(6) [= OH]$		2.08(1)	2.084(4)
$Fe-O(2)$		<u>2.09(1)</u>	<u>2.161(4)</u>
$\langle Fe-O \rangle$		2.03	2.027
$As(1)-O(3)$		1.64(2)	1.657(7)
$As(1)-O(1)$	x2	1.69(1)	1.697(6)
$As(1)-O(2)$		<u>1.76(2)</u>	<u>1.713(7)</u>
$\langle As(1)-O \rangle$		1.70	1.691
$As(2)-O(4)$	x2	1.68(1)	1.673(5)
$As(2)-O(5)$	x2	<u>1.67(1)</u>	<u>1.693(5)</u>
$\langle As(2)-O \rangle$		1.68	1.683

\* Kharisun *et al.* (1996)

Sewardite is the Ca analogue of carminite, and Tables 5 and 6 also list the data for carminite for comparison. A prominent feature of the structure is a chain of  $(Fe^{3+}O_6)$  octahedra ( $\Phi$ : O, OH) in which the octahedra link by alternately sharing edges and corners; the edge-sharing dimers in this arrangement have one pair of corners bridged by an  $(AsO_4)$  tetrahedron, and the second tetrahedron is linked to an octahedron corner *trans* to the other tetrahedron–octahedron linkage. The “free” tetrahedron vertices in this chain then link to octahedron corners in adjacent chains to form a framework. Ca occupies [8]-coordinated sites within interstices in this framework. The environments of Ca in sewardite and  $Pb^{2+}$  in carminite (Tables 5, 6) are very similar, and thus  $Pb^{2+}$  in carminite does not show stereoactive-lone-pair behavior. Such similarities in coordination of Ca and  $Pb^{2+}$  occur in several mineral pairs (*e.g.*, conicalcite–duftite, calcivolborthite–mottamite), and raise the possibility of solid solution in such minerals. This Ca–Pb substitution is not generally observed in minerals, but this may be a geochemical constraint rather than a crystal-chemical constraint. It would be interesting to examine this issue *via* attempted synthesis of solid solutions of the relevant compositions.

TABLE 6a. BOND-VALENCE TABLE FOR SEWARDITE

	Ca(1)	Ca(2)	Fe	As(1)	As(2)	$\Sigma$
O(1)	0.33 <sup>34</sup> ↓		0.43	1.23 <sup>32</sup> ↓		1.99
O(2)		0.04 <sup>32</sup> ↓	0.41 <sup>32</sup> →	1.02		1.88
O(3)		0.36 <sup>32</sup> ↓		1.41		1.77
O(4)	0.10 <sup>34</sup> ↓		0.57		1.27 <sup>32</sup> ↓	1.94
O(5)		0.28 <sup>34</sup> ↓	0.43		1.30 <sup>32</sup> ↓	2.01
O(6)			0.42 <sup>32</sup> →			0.84
O(7)			0.74 <sup>32</sup> →			1.48
$\Sigma$	1.72	1.92	3.00	4.89	5.14	

TABLE 6b. BOND-VALENCE TABLE FOR CARMINITE

	Pb(1)	Pb(2)	Fe	As(1)	As(2)	$\Sigma$
O(1)	0.31 <sup>34</sup> ↓		0.52	1.21 <sup>32</sup> ↓		2.04
O(2)		0.08 <sup>32</sup> ↓	0.34 <sup>32</sup> →	1.16		1.92
O(3)		0.31 <sup>32</sup> ↓		1.35		1.66
O(4)	0.14 <sup>34</sup> ↓		0.49		1.29 <sup>32</sup> ↓	1.92
O(5)		0.30 <sup>34</sup> ↓	0.50		1.22 <sup>32</sup> ↓	2.02
O(6)			0.42 <sup>32</sup> →			0.84
O(7)			0.73 <sup>32</sup> →			1.46
$\Sigma$	1.80	1.98	3.00	4.93	5.02	

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