American Mineralogist, Volume 85, pages 1526–1533, 2000

Symesite, $Pb_{10}(SO_4)O_7Cl_4(H_2O)$, a new PbO-related sheet mineral: Description and crystal structure

MARK D. WELCH,[1,*] MARK A. COOPER,[2] FRANK C. HAWTHORNE,[2] AND ALAN J. CRIDDLE[1]

[1] Department of Mineralogy, The Natural History Museum, Cromwell Road, London, SW7 5BD, U.K.
[2] Department of Geological Sciences, University of Manitoba, Winnipeg, Manitoba, R3T 2N2, Canada

ABSTRACT

Symesite, $Pb_{10}(SO_4)O_7Cl_4(H_2O)$, is a Pb sheet mineral found in the oxidized zone of a Carboniferous Mn-Pb-Cu deposit at Merehead Quarry, Somerset. It occurs as pink crystal blebs up to 2 mm long and as pink crystalline aggregates up to 1 cm in diameter, and is associated with cerussite, hydrocerussite, paralaurionite, blixite, chloroxiphite, pyrolusite, coronadite, hematite, parkinsonite, and mereheadite. Crystals of symesite are blocky, translucent pink with a vitreous luster and a white streak. Mohs hardness is 4, $D_{meas} = 7.3(2)$ g/cm^3 and there is a perfect cleavage parallel to {001}; the refractive indices exceed 2. Electron-microprobe analysis gave the following composition (wt%): PbO 90.66, SO_3 3.15, Cl 5.83 (O = Cl 1.32), sum 98.32, giving the anhydrous formula $Pb_{10.31}S_{1.00}O_{11.22}Cl_{4.18}$; solution of the crystal structure gave the ideal formula $Pb_{10}(SO_4)O_7Cl_4(H_2O)$. The six strongest peaks in the X-ray powder-diffraction pattern [*d* in Å, (*I*), (*hkl*)] are: 2.911 (10)(414, $3\bar{2}3$), 3.286 (9)(004), 2.955 (9)($41\bar{2}$), 2.793 (8)($7\bar{1}1$, 131), 6.573 (4)(002), 3.768 (4)(412, $3\bar{2}1$). The structure of symesite was solved by direct methods and refined to an *R* index of 4.0%. Symesite is triclinic, space group $B\bar{1}$, $a = 19.727(2)$, $b = 8.796(1)$, $c = 13.631(2)$ Å, $\alpha = 82.21(1)$, $\beta = 78.08(1)$, $\gamma = 100.04(1)°$, $V = 2242.4(5)$ Å^3, $Z = 4$. The structural unit of symesite is a $[Pb_{10}(SO_4)O_7]^{4+}$ single sheet; adjacent sheets are linked by layers of Cl. One-eleventh of the Pb atoms are replaced by S, with the addition of an apical oxygen to form an SO_4 tetrahedron and a compensating O vacancy within the PbO sheet. The distribution of Pb and SO_4 groups is highly ordered and defines a 22 cation-site superstructure motif within the PbO sheet. Eight of eleven interlayer anion sites are occupied by Cl, two are occupied by O of H_2O groups, and one site is vacant. Incident bond-valence sums at O atoms indicate that hydrogen bonds occur between the H_2O group and the apical oxygen of the SO_4 group, providing additional linkage between adjacent PbO sheets. The structure of symesite is closely related to those of tetragonal PbO and the family of PbO-related sheet minerals that includes nadorite, thorikosite, mereheadite, parkinsonite, and kombatite. There are ten non-equivalent Pb sites with coordination numbers of five, seven, or eight; these polyhedra are variants of the $Pb[O_4Cl_4]$ square-antiprism that is characteristic of these minerals.

INTRODUCTION

The PbO-related oxychlorides have sheet structures in which litharge-like sheets and layers of Cl are intercalated. What makes them particularly interesting from a crystal-chemical point of view is the diverse range of elements that substitute into these structures: As, Sb, V, Mo, W, P, Si, and I. Charge balance is provided by Cl which forms layers between the PbO-like sheets. Almost all structural studies of these oxychlorides have used single-crystal X-ray diffraction and have defined two types of substructure, related topologically to tetragonal PbO (litharge) or orthorhombic PbO (massicot). The (sub) structures obtained in these studies imply that the distribution of Pb and the substituent group within the PbO layers is disordered. However, a study of parkinsonite by electron diffraction (Welch et al. 1996) revealed weak but sharp superstructure reflections arising from ordering of Pb and Mo, in this case as Pb_7Mo and Pb_9Mo motifs. The superstructure reflections were missed in most previous XRD studies, possibly because of the high X-ray absorption coefficients of these minerals. In contrast, the very thin crystallites observed by electron diffraction (TEM) transmit electrons sufficiently well to allow superstructure reflections to be recorded in 1–2 min exposures. The relations between the substructure and superstructure were deduced from the electron-diffraction patterns in which the substructure reflections are much more intense than the superstructure reflections. In comparison, an eight-day exposure was needed to record very faint superstructure reflections by X-ray precession photography. For symesite, the TEM observations suggest that, far from being disordered, Pb and S are highly ordered within the PbO layers. The only X-ray study to date that has recognized a superstructure is that of Cooper and Hawthorne (1994) for kombatite, $Pb_{14}(VO_4)_2O_9Cl_4$.

Symesite is a hydrated Pb-S-oxychloride, $Pb_{10}(SO_4)O_7Cl_4(H_2O)$, and a new member of the nadorite family of Pb-sheet minerals. The mineral and name have been approved by the Commission on New Minerals and Mineral Names of the International Mineralogical Association. It is named for Robert Symes (1937–) of the Department of Mineralogy, the Natural History Museum (London), in recognition of his many contri-

---

* E-mail: mdw@nhm.ac.uk

0003-004X/00/0010–1526$05.00

butions to the mineralogy of the ore deposits of South-West England, including Merehead Quarry. Type material is deposited at the Natural History Museum, London (Specimen BM1998,37).

OCCURRENCE

Symesite occurs at Merehead Quarry, Somerset (51°12'N, 2°26'W), with other secondary Pb minerals in veins of Mn- and Fe-oxide minerals cutting Carboniferous limestone. It occurs as pink blebby crystals up to 2 mm long, has a vitreous luster, and a single well-developed cleavage; it also occurs as formless pink polycrystalline aggregates up to 1 cm in diameter and intergrown with mendipite. Associated minerals include cerussite, hydrocerussite, paralaurionite, blixite, chloroxiphite, pyrolusite, coronadite, hematite, and the Pb-oxychloride sheet minerals parkinsonite and mereheadite. The Pb-oxychlorides at Merehead Quarry are thought to have formed by interaction of primary galena with low-temperature, metalliferous brines along fractures cutting the original Mn-Fe-Pb-Cu ore body (Symes and Embrey 1977). However, no replacement textures have been observed, and it is possible that these minerals precipitated directly from a cooling brine.

RESULTS

Chemical composition

Initial semi-quantitative chemical survey (EDS) of symesite made using a Hitachi S-2500 instrument indicated that the only detectable elements were Pb, S, and Cl. Microprobe analyses of symesite (WDS) were obtained using a CAMECA SX50 instrument operated at 20 kV and 20 nA with a 1 μm focused beam-spot (Table 1). Element standards were PbO (litharge), $SrSO_4$ (celestine) and NaCl. Analysis totals, corrected for chlorine, ranged from 98.5–99.6 wt%. The average empirical formula normalized to one S per formula is $Pb_{10.31}SO_{11.22}Cl_{4.18}$. This suggests an ideal anhydrous formula $Pb_{10}(SO_4)O_7Cl_4$, which is similar to that of sundiusite, $Pb_{10}(SO_4)O_8Cl_2$ (Dunn and Rouse 1980).

Optical and physical properties

In hand specimen, symesite is translucent pink "Venetian pink," individual grains are blocky and have a vitreous luster. The mineral has a white streak, a Mohs hardness of 4 and a single perfect {001} cleavage parallel to the PbO/Cl sheets. D_{meas} = 7.3(2) g/cm^3 (mean of seven measurements on a Berman balance) and D_{calc} = 7.23 g/cm^3. The refractive indices of symesite exceed 2 and so optical characterization was done in polarized reflected light. A symesite crystal was mounted in epoxy resin and diamond-polished. A Zeiss MPM 800 microscope spectrophotometer was used for qualitative examination and to measure its reflectance spectra. In plane-polarized light, symesite has low specular reflectance, is gray, and is not visually bireflectant or pleochroic. Between crossed polars, it is very weakly anisotropic. Reflectance measurements were made in air and in oil (Zeiss N_D = 1.515), and a Zeiss SiC reflectance standard, number 472, was used with the ×20 air and oil objectives. The reflectance data are given in Table 2 and are in accord with the mineral's gray appearance. Refractive indices were calculated from the reflectance data in air and oil, assuming absorption to be zero (Fresnel equations) and using the two-media method with the Königsberger equations (Criddle 1998). At 590 nm with $k = 0$, the refractive indices corresponding to R_1 and R_2 are 2.15 and 2.18, and for ${}^{im}R_1$ and ${}^{im}R_2$ are 2.18 and 2.19. The difference between these values is small, as are the differences between them and refringence values calculated by the two-media method, where n_1 is 2.12 and n_2 is 2.16. The absorption coefficients corresponding to these values are 0.25 and 0.17, respectively.

TABLE 1. Microprobe data for symesite

	Ideal	Analyzed *
PbO	91.48	90.66 (69)
SO_3	3.28	3.15 (5)
Cl	5.81	5.83 (5)
H_2O	0.74	na
	101.31	99.64
O = Cl	1.31	1.32
Total	100.00	98.32
Pb/Cl	2.5	2.47

* Average of 17 analyses; na = not analyzed; numbers in brackets are 1σ of the mean.

Transmission electron microscopy

A TEM study of symesite was made prior to the single-crystal X-ray structure determination to check for evidence of a superstructure, looking particularly for weak superstructure reflections that might be missed in short-term X-ray experiments. A fragment of the same symesite crystal for which the structure determination was made was gently crushed and the powder was deposited onto a holey-carbon copper grid for TEM

TABLE 2. Reflectance data for symesite

λ (nm)	R_1	R_2	${}^{im}R_1$	${}^{im}R_2$
400	17.20	17.95	5.07	5.65
420	16.50	17.40	4.69	5.28
440	15.90	16.90	4.40	4.99
460	15.50	16.50	4.17	4.77
470	15.20	16.30	4.07	4.67
480	15.10	16.10	3.98	4.58
500	14.90	15.80	3.83	4.43
520	14.50	15.50	3.70	4.30
540	14.30	15.30	3.61	4.19
546	14.20	15.30	3.59	4.17
560	14.10	15.20	3.53	4.11
580	14.00	15.00	3.47	4.05
589	13.90	15.00	3.44	4.02
600	13.90	14.90	3.43	3.99
620	13.80	14.80	3.39	3.96
640	13.80	14.80	3.37	3.93
650	13.70	14.70	3.37	3.91
660	13.70	14.70	3.34	3.90
680	13.60	14.65	3.32	3.88
700	13.60	14.60	3.30	3.86
Color values for CIE illuminant C				
x	0.3003	0.3011	0.2925	0.2942
y	0.3045	0.3055	0.2944	0.297
Y%	14.2	15.3	3.58	4.16
ld	474	474	473	474
Pe%	5	4.6	9	8.1

examination. Observations were made using a JEOL CX200 transmission electron microscope operated at 200 kV; these conditions minimized beam damage (melting). Long-exposure photographs (2–3 min) of symesite revealed rows of many closely spaced weak, but sharp, superstructure reflections in reciprocal-lattice planes parallel to the cleavage and PbO layers (Fig. 1). A two-dimensional superstructure motif was inferred from the geometrical relations between super- and substructure reflections; the resulting superstructure motif within the PbO layers has 22 cation sites. The empirical Pb:S ratio found by electron-microprobe analysis is very close to 10:1. Hence, the electron-diffraction patterns point strongly to the superstructure motif being due to ordering of Pb and S within the PbO layers.

X-ray structure solution and refinement

A blocky cleavage fragment of symesite was carefully ground to a thin plate parallel to (001) of dimensions 0.23 mm × 0.21 mm × 0.02 mm, and then attached to a glass fiber and mounted on a Siemens *P*4 four-circle diffractometer equipped with Mo$K\alpha$ X-radiation. Cell dimensions were determined from the setting angles of 30 automatically aligned reflections in the range $14 < 2\theta < 30\%$. No special procedure was needed to arrive at the true cell, as several moderately strong superstructure reflections were present in the reflection array. Symesite is triclinic, space group $B\bar{1}$, with $a = 19.727(2)$, $b = 8.796(1)$, $c = 13.631(2)$ Å, $\alpha = 82.21(1)$, $\beta = 78.08(1)$, $\gamma = 100.04(1)°$, $V = 2242.4(5)$ Å^3, $Z = 4$. We have used the *B*-centered space group to conform to related oxychlorides of the nadorite family, most of which have PbO and Cl sheets and cleavage parallel to {001}. The axial transformation matrix for $P \rightarrow B$ is $(0\bar{1}\bar{1}/100/01\bar{1})$. The corresponding cell parameters for the *P* cell ($Z = 2$) are $a = 8.796(1)$, $b = 10.768(2)$, $c = 13.096(2)$ Å, $\alpha = 68.87(1)$, $\beta = 86.52(1)$, $\gamma = 75.79(1)°$, $V = 1120.9(3)$ Å^3. The entire sphere of data was collected on the primitive cell from 4 to 60° 2θ ($-12 \leq h \leq 12$, $-15 \leq k \leq 15$, $-18 \leq l \leq 18$), and the cell later transformed to the $B\bar{1}$ setting. Unless explicitly stated otherwise, all descriptions that follow refer to the $B\bar{1}$ cell. Symesite absorbs X-rays strongly ($\mu = 75.4$ mm^{-1}) and an absorption correction was essential. Psi-scan data were measured for 26 reflections uniformly distributed between 4 and 60° 2θ at increments of 4° along the diffraction vector. A thin-plate correction with a glancing angle of 15° reduced *R*(azimuthal) from 26.0 to 6.8%. Intensities were corrected for Lorentz, polarization, and background effects, and then reduced to structure factors; of the 4469 remaining unique reflections, 3493 were classed as observed ($|F_o| > 5\sigma F_o$).

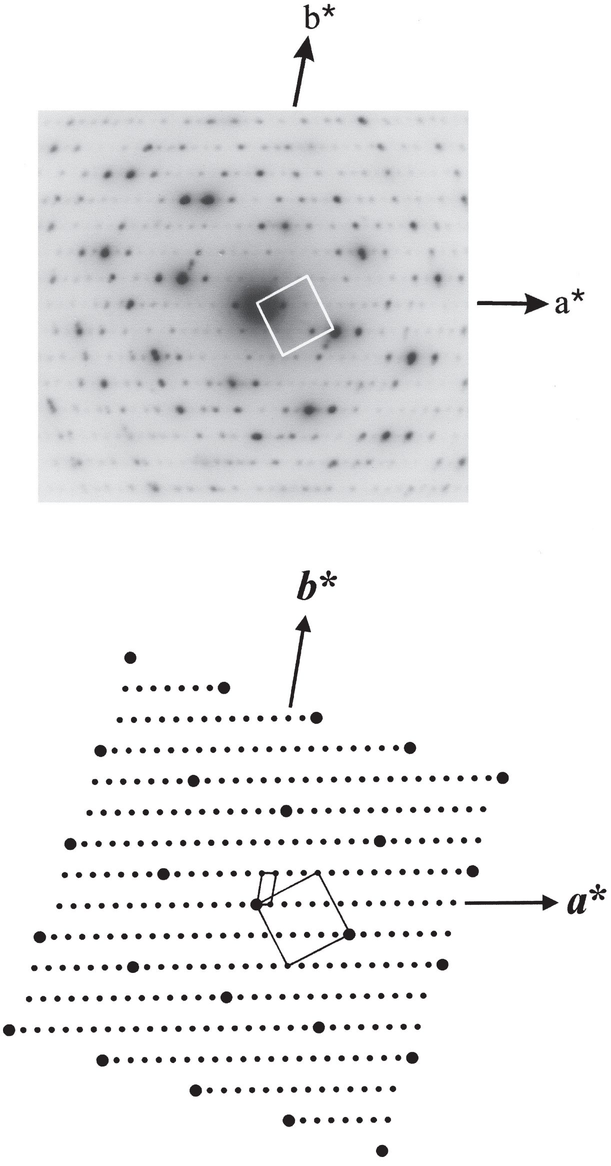

FIGURE 1. (**a**) Electron-diffraction pattern of symesite with the beam normal to the {001} cleavage and the PbO-SO_4 sheets. In addition to the relatively strong substructure reflections ($h + k = 2n$), there are rows of many weak, sharp superstructure reflections. A reciprocal 0.25/Å^1 × 0. 25/Å^1 subcell is indicated, and a* and b* directions for the $B\bar{1}$ supercell are shown. (**b**) Reciprocal subcell and $B\bar{1}$ supercells are indicated.

Structure solution and refinement were done using the SHELTXL PC (Plus) package of programs. The structure of symesite was refined to final *R* values of $R_{obs} = 4.0\%$ and $wR_{obs} = 5.0\%$ ($w = 1$). A direct-methods solution gave the Pb and Cl positions. The non-sulfate O atoms were located by successive cycles of least-squares refinement and difference-Fourier synthesis. One of the initial Cl assignments was found to have four surrounding peaks at approximate S-O distances in a tetrahedral configuration; this Cl assignment was then changed to S and the four surrounding peaks were incorporated into the refinement model as oxygen atoms. The isotropic displacement and positional parameters associated with each of the four sulfate oxygen atoms were unstable during refinement and unreasonable S-O distances resulted. Site-occupancy refinement of the S and surrounding O sites clearly showed full occupancy by the respective assigned scattering species. In the final refinement model, the S-O distances were constrained to be 1.475 Å and the isotropic-displacement parameters for the four O atoms were refined with the constraint that the values be equal. The final *R* value did not improve with this treatment of the

SO_4 group; however, the refinement was stabilized during successive cycles of least-squares and the result makes crystal-chemical sense.

Atom parameters, interatomic distances, and bond-valence data for symesite are given in Tables 3, 4, and 5, respectively. Structure-factor data (Table 6) are deposited.[1]

X-ray powder diffraction

A small fragment of symesite was crushed and deposited onto a single-crystal Si substrate and the X-ray powder-diffraction pattern was collected using an Enraf-Nonius position-sensitive detector (PSD) diffractometer operated at 45 kV and 45 mA. Monochromatic Ni-filtered Cu$K\alpha_1$ radiation (λ = 1.54056 Å) was used. The angle of incidence of the beam at the sample was set at 7° and a 0.1 mm divergence slit was used. Data were collected simultaneously at 2θ = 7–123° for 1 h. The diffraction pattern was corrected against an external α-Si_3N_4 standard run just before the symesite pattern was collected; the structure and cell parameters of this standard were refined from neutron powder-diffraction data by K.S. Knight (Rutherford-Appleton Laboratory, U.K.). Data were corrected using a cubic-spline function recommended by Enraf, and cell parameters were calculated from 17 well-resolved reflections using the LSUCREPC least-squares cell-refinement program (Garvey 1986). Use of the Si substrate and external standard was required due to the very small amount of sample available; no Si reflections were present in the diffraction pattern. X-ray powder-diffraction data for symesite are given in Table 7. The Debye-Scherrer diffraction pattern showed an additional weak symesite reflection at 9.37° 2θ due to (011), d_{calc} = 9.438 Å. Symesite cell parameters were refined for the primitive cell, starting parameters for the refinement were taken from the single-crystal structure determination, and peaks were assigned by comparing *d* values and intensities from the powder-diffraction pattern calculated from the structure with the observed powder-diffraction data. Cell parameters for the *P* cell derived from the powder pattern (Table 7) are in close agreement with the single-crystal data (above).

DISCUSSION

Structure topology

The structure of symesite is based upon alternating PbO and Cl sheets parallel to (001). One eleventh of the Pb sites are replaced by S that occurs as SO_4 tetrahedra within the PbO sheet, and the excess charge is balanced by introducing layers of Cl atoms between each PbO-SO_4 sheet. There is an oxygen vacancy next to each SO_4 tetrahedron forming a local polar SO_4-□ pair. These pairs order within the PbO sheet, leading to a 22 cation-site superstructure (Fig. 2). The vacancies that replace oxygen atoms in the PbO-SO_4 sheet are compensated by addition of an apical oxygen completing the tetrahedral coordination around S. The configuration of the Cl interlayer sheet is shown in Figure 3. This sheet compensates for the high-charge cation (S^{6+}) that replaces Pb^{2+}; eight of eleven sites are occupied by Cl, one site is vacant and two sites are occupied by O

TABLE 3. Atom parameters for symesite

	x	*y*	*z*	U_{eq} *	U_{11}*	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S	0.0078(4)	0.2544(11)	0.1866(8)	293(27)	207(31)	452(45)	215(47)	–74(38)	–18(32)	77(32)
Pb1	0.82782(5)	0.0100(1)	0.1516(1)	159(3)	148(4)	132(4)	193(6)	–47(4)	–28(4)	21(3)
Pb2	0.20839(5)	0.5489(1)	0.1468(1)	151(3)	165(4)	136(4)	178(6)	–78(4)	–57(4)	37(3)
Pb3	0.91743(5)	0.6592(1)	0.1589(1)	174(3)	146(4)	194(4)	196(6)	–88(4)	–37(4)	32(4)
Pb4	0.74960(5)	0.3610(1)	0.1582(1)	154(3)	155(4)	143(4)	177(6)	–78(4)	–41(4)	27(3)
Pb5	0.28295(5)	0.1886(1)	0.1591(1)	143(3)	146(4)	131(4)	159(6)	–53(4)	–43(4)	17(3)
Pb6	0.66701(5)	0.7222(1)	0.1285(1)	165(3)	169(4)	151(4)	205(6)	–75(4)	–83(4)	35(3)
Pb7	0.37766(5)	0.8428(1)	0.1443(1)	166(3)	131(4)	149(4)	211(6)	–74(4)	–14(4)	9(3)
Pb8	0.11177(5)	0.8864(1)	0.1523(1)	159(3)	150(4)	161(4)	179(6)	–60(4)	–58(4)	21(3)
Pb9	0.46460(5)	0.4403(1)	0.1449(1)	178(3)	145(4)	149(4)	229(6)	–26(4)	–49(4)	2(3)
Pb10	0.56724(5)	0.1162(1)	0.1439(1)	177(3)	158(4)	178(4)	221(7)	–103(4)	–63(4)	33(4)
Cl1	0.4486(4)	0.1997(8)	0.0252(7)	241(23)	204(28)	245(29)	284(48)	–68(30)	–87(30)	20(25)
Cl2	0.8124(4)	0.7275(8)	0.0260(7)	244(23)	236(30)	274(30)	263(46)	–113(32)	–79(31)	87(26)
Cl3	0.6322(4)	0.4249(8)	0.0121(7)	259(25)	261(32)	233(30)	310(51)	–118(32)	–84(33)	54(27)
Cl4	0.2739(4)	0.9080(8)	0.0195(7)	246(23)	257(30)	201(27)	296(48)	–89(30)	–82(32)	35(25)
O1	0.0321(26)	0.1060(32)	0.2046(48)	1036(76) †						
O2	0.0147(26)	0.2892(56)	0.0756(10)	1036(76) †						
O3	0.0598(20)	0.3721(44)	0.2150(47)	1036(76) †						
O4	–0.0691(7)	0.2300(55)	0.2296(42)	1036(76) †						
O5	0.6821(9)	0.5229(20)	0.2333(17)	164(34)						
O6	0.1413(9)	0.6865(22)	0.2450(18)	196(37)						
O7	0.5036(9)	0.2610(21)	0.2351(17)	173(35)						
O8	0.2157(9)	0.3468(20)	0.2640(17)	158(34)						
O9	0.7793(9)	0.1482(20)	0.2725(17)	149(33)						
O10	0.6374(9)	0.1767(20)	0.2498(17)	150(33)						
O11	0.3256(9)	0.9930(20)	0.2455(17)	145(33)						
O12	0.0947(18)	0.6320(41)	0.0098(34)	643(91)						

* U_{eq} and U_{ij} × 10^4.
† Constrained to be equal.

---

[1] For a copy of Table 6, document item AM-00-053, contact the Business Office of the Mineralogical Society of America (see inside front cover of recent issue) for price information. Deposit items may also be available on the American Mineralogist web site (http://www.minsocam.org or current web address).

TABLE 4. Selected interatomic distances (Å) in symesite

Pb1-O9^{i}	2.27(2)	Pb2-O8	2.27(2)	Pb3-O10^{h}	2.30(2)	Pb4-O5	2.31(2)
Pb1-O10^{i}	2.27(2)	Pb2-O8^{f}	2.27(2)	Pb3-O7^{h}	2.42(2)	Pb4-O5^{h}	2.41(2)
Pb1-O9	2.33(2)	Pb2-O6	2.30(2)	Pb3-O5^{h}	2.38(2)	Pb4-O10	2.48(2)
Pb1-O4^{l}	3.02(4)	Pb2-O3	2.96(4)	Pb3-O2^{b}	3.14(2)	Pb4-O9	2.50(2)
Pb1-O12^{k}	3.49(3)	Pb2-O12	3.31(5)	Pb3-Cl2	3.10(1)	Pb4-Cl2	3.36(1)
Pb1-Cl2^{d}	3.21(1)	Pb2-Cl4	3.29(1)	<Pb3-O>	2.56	Pb4-O12^{k}	3.42(4)
Pb1-Cl4^{b}	3.46(1)	Pb2-Cl3^{b}	3.38(1)	<Pb3-Cl>	3.10	Pb4-Cl3	3.42(1)
<Pb1-O>	2.68	Pb2-Cl2^{b}	3.64(1)			Pb4-Cl4^{b}	3.65(1)
<Pb-Cl>	3.34	<Pb2-O>	2.62			<Pb4-O>	2.62
		<Pb2-Cl>	3.44			<Pb4-Cl>	3.48
Pb5-O11^{d}	2.33(2)	Pb6-O9^{h}	2.20(2)	Pb7-O11	2.26(2)	Pb8-O6	2.26(2)
Pb5-O6^{f}	2.40(2)	Pb6-O5	2.21(2)	Pb7-O8^{f}	2.27(2)	Pb8-O11^{j}	2.29(2)
Pb5-O11^{f}	2.43(2)	Pb6-O4^{f}	2.57(4)	Pb7-O1^{f}	3.02(7)	Pb8-O7^{f}	2.49(2)
Pb5-O8	2.48(2)	Pb6-Cl2	2.91(1)	Pb7-O3^{f}	3.10(5)	Pb8-O1^{a}	2.77(4)
Pb5-Cl4^{d}	3.32(1)	Pb6-Cl3	3.28(1)	Pb7-Cl4	3.00(1)	Pb8-O12	3.18(4)
Pb5-Cl1	3.38(1)	Pb6-Cl4^{e}	3.46(1)	Pb7-Cl1^{a}	3.26(1)	Pb8-Cl4	3.29(1)
Pb5-Cl2^{b}	3.52(1)	Pb6-Cl1^{b}	3.49(1)	Pb7-Cl3^{b}	3.39(1)	Pb8-Cl2^{e}	3.76(1)
Pb5-Cl3^{b}	3.75(1)	<Pb6-O>	2.33	Pb7-Cl1^{b}	3.83(1)	<Pb8-O>	2.60
<Pb5-O>	2.41	<Pb6-Cl>	3.29	<Pb7-O>	2.66	<Pb8-Cl>	3.53
<Pb5-Cl>	3.49			<Pb7-Cl>	3.37		
Pb9-O7	2.21(2)	Pb10-O7	2.25(2)	O12-O2	3.07(6)		
Pb9-O6^{f}	2.30(2)	Pb10-O10	2.25(2)	O12-O2^{k}	2.80(7)		
Pb9-O3^{f}	2.71(6)	Pb10-O1^{g}	2.80(4)	O2-O12-O2^{k}	91(2)°		
Pb9-Cl1	2.86(1)	Pb10-O4^{g}	3.30(5)				
Pb9-Cl3^{b}	3.38(1)	Pb10-Cl3	2.96(1)				
Pb9-Cl3	3.46(1)	Pb10-Cl1	3.24(1)				
Pb9-Cl1^{b}	3.58(1)	Pb10-Cl4^{b}	3.51(1)				
<Pb9-O>	2.41	Pb10-Cl1^{c}	3.86(1)				
<Pb9-Cl>	3.32	<Pb10-O>	2.65				
		<Pb10-Cl>	3.39				

Equivalent positions:
a = x, 1 + y, z; b = 1 – x, 1 – y, –z; c = 1 – x, –y, –z; d = x, –1 + y, z; e = 1 – x, 2 – y, –z; f = 1/2 – x. 1 – y, 1/2 – z; g = 1/2 – x, –y, 1/2 – z; h = 3/2 – x, 1 – y, 1/2 – z; i = 3/2 – x, –y, 1/2 – z; j = 1/2 – x, 2 – y, 1/2 – z; k = –x, 1 – y, –z; l = 1 + x, y, z.

TABLE 5. Bond-valence values (v.u.) for symesite

	S	Pb1	Pb2	Pb3	Pb4	Pb5	Pb6	Pb7	Pb8	Pb9	Pb10	H1	H2	Sum
O1	1.50							0.12	0.19		0.18			1.99
O2	1.50			0.09								0.20	0.20	1.99
O3	1.50		0.13					0.10		0.21				1.94
O4	1.50	0.12					0.28				0.07			1.97
O5				0.43	0.51		0.65							1.99
					0.40									
O6			0.52			0.41			0.58	0.52				2.03
O7				0.40					0.34	0.65	0.59			1.98
O8			0.56			0.35		0.56						2.03
			0.56											
O9		0.56			0.33		0.67							2.05
		0.49												
O10		0.56		0.52	0.35						0.59			2.02
O11						0.49		0.58	0.54					2.00
						0.39								
O12		0.05	0.07		0.06				0.09			0.80	0.80	1.87
Cl1						0.10	0.07	0.14		0.41	0.15			0.99
								0.03		0.06	0.03			
Cl2		0.16	0.05	0.21	0.11	0.07	0.36		0.04					1.00
Cl3			0.10		0.09	0.04	0.13	0.10		0.10	0.31			0.95
										0.08				
Cl4		0.08	0.13		0.05	0.12	0.08	0.28	0.13		0.07			0.94
Sum	6.00	2.02	2.12	1.65	1.90	1.97	2.24	1.91	1.91	2.03	1.99			

Notes: Calculated using the parameters of Brown (1981) for Pb^{2+}-O and Brese and O'Keeffe (1991) for Pb^{2+}-Cl.

of an H_2O group. The association of PbO and Cl sheets, SO_4 and H_2O groups is shown in Figure 4.

Pb coordination

Most of the ten distinct Pb sites (Fig. 5) are simple variants of the $Pb[O_4Cl_4]$ square antiprism that is an important component of other PbO-like oxychloride sheet minerals. All show the one-sided arrangement of short bonds to oxygen that is typical of stereoactive $6s^2$ lone-pair behavior for Pb^{2+}. Five sites are eightfold-coordinated (Pb2, Pb4, Pb5, Pb7, Pb10), four sites are sevenfold-coordinated (Pb1, Pb6, Pb8, Pb9) and one site is fivefold-coordinated (Pb3). Four Pb atoms (Pb1, Pb2, Pb4, Pb8) are bonded to O12 of the H_2O group in the Cl sheet. Pb-O12 bond-valences range from 0.05–0.09 v.u., bringing the bond valence incident at O12 close to the ideal value of 2 v.u. The coordination of Pb3 is unusual, with three short Pb-O bonds,

TABLE 7. X-ray powder-diffraction data for symesite

			P-cell			*B*-cell		
I_{obs}	d_{obs} (Å)	d_{calc} (Å)	*h*	*k*	*l*	*h*	*k*	*l*
4	6.573	6.578	0	1	–1	0	0	2
3	3.805	3.807	1	–2	–2	4	1	0
3	3.787	3.793	2	2	1	3	–2	–1
4	3.768	3.771	1	–1	–3	4	1	2
		3.758	2	1	2	3	–2	1
9	3.286	3.289	0	2	–2	0	0	4
9	2.955	2.963	1	–3	–1	4	1	–2
		2.956	2	3	0	3	–2	–3
10	2.911	2.912	1	0	–4	4	1	4
		2.907	2	0	3	3	–2	3
8	2.793	2.793	3	0	–1	1	3	1
		2.791	1	3	4	7	–1	1
3	2.190	2.193	0	3	–3	0	0	6
		2.187	1	4	5	9	–1	1
1	2.153	2.154	1	5	2	7	–1	–3
2	2.128	2.129	3	–2	1	1	3	–3
		2.129	3	2	–3	1	3	5
1	2.103	2.103	1	1	6	7	–1	5
2	1.977	1.978	2	–3	–5	8	2	2
2	1.970	1.970	4	3	3	6	–4	0
1	1.756*	1.757	0	5	6	11	0	1
		1.754	4	–2	–3	5	4	1
		1.753	3	5	5	10	–3	0
		1.751	4	–1	–4	5	4	3
		1.750	5	2	0	2	–5	–2
2	1.745*	1.747	5	1	1	2	–5	0
		1.747	0	4	7	11	0	3
		1.745	1	6	1	7	–1	–5
		1.743	3	4	6	10	–3	2
2	1.725	1.725	3	–3	2	1	3	–5
		1.724	3	3	–4	1	3	7
3	1.711	1.709	1	–5	1	4	1	–6
		1.708	2	–5	–3	8	2	–2
		1.708	2	5	–2	3	–2	–7
3	1.685	1.686	1	2	–6	4	1	8
		1.685	2	–2	5	3	–2	7
		1.682	2	–1	–7	8	2	6

Notes: Powder-diffraction cell parameters for *P*-cell: a = 8.821(6)Å, b = 10.776(6)Å, c = 13.134(7)Å, α = 68.96(4)°, β = 86.52(5)°, γ = 75.65(4)°, *V* = 1128.4(7)Å^3; for *Z = 2;* for *hkl* the transformation matrix $P \rightarrow B$ in symesite is $(0\bar{1}\bar{1}/100/01\bar{1})$, with the convention that *h* is always positive.
* Not used in refinment.

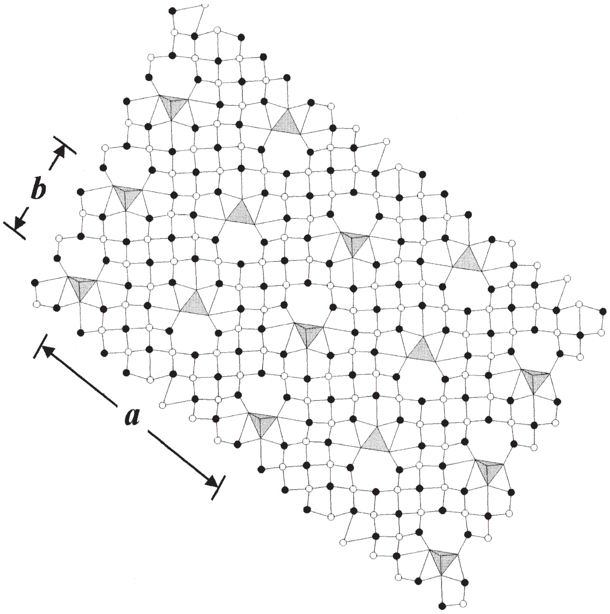

FIGURE 2. The {001} PbO-SO$_4$ sheet in symesite, showing the ordering pattern of Pb and S; Pb atoms are black circles, O atoms are white circles, sulfate groups are gray tetrahedra. The apical atoms of SO$_4$ tetrahedra in adjacent (200) rows point in opposite directions; note the juxtaposition of SO$_4$ tetrahedra and oxygen vacancies.

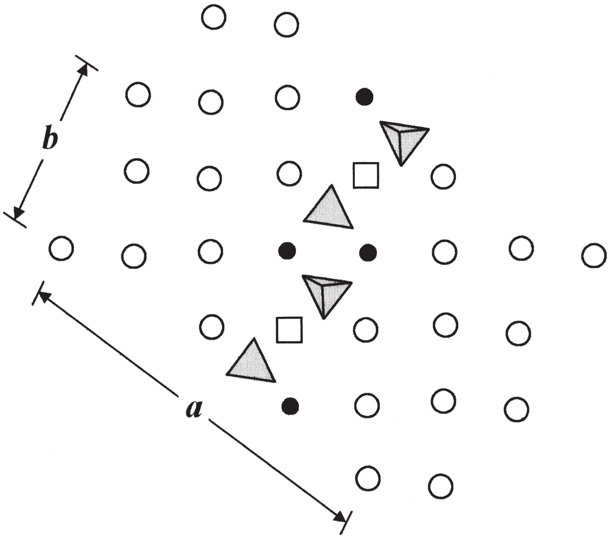

FIGURE 3. The {001} Cl-H$_2$O layer in symesite. Eight of eleven anion sites are occupied by Cl (white circles), two by O12 of H$_2$O groups (small black circles), and there is one vacant site (square). The Cl and O12 atoms are approximately coplanar. The apical O2 atoms of the SO$_4$ tetrahedra lie midway between Cl and PbO sheets. Upward-pointing tetrahedra are in the PbO sheet below the Cl layer, and downward-pointing tetrahedra are in the PbO sheet above the anion layer.

one Pb-Cl bond, and a long bond (3.14 Å) to the O2 apical oxygen of the SO$_4$ group. Pb3 is the only Pb atom that is bonded to O2.

S coordination

There is one distinct S site coordinated by four oxygen atoms in a tetrahedral arrangement. Three of the four oxygen atoms belong to the PbO sheet and the apical oxygen lies approximately midway between the PbO and Cl sheets. An oxygen vacancy is next to the SO$_4$ group in the PbO sheet. The large U_{eq} values (Table 3) for all the atoms of the SO$_4$ group suggest some dynamic positional disorder of the tetrahedron within the PbO layer.

H$_2$O and H-bonding

The O12 atom was identified as part of an H$_2$O group from its very low incident bond-valence sum (0.3 v.u.) coming from four very long Pb-O bonds (Tables 4 and 5); Pb-O12 distances

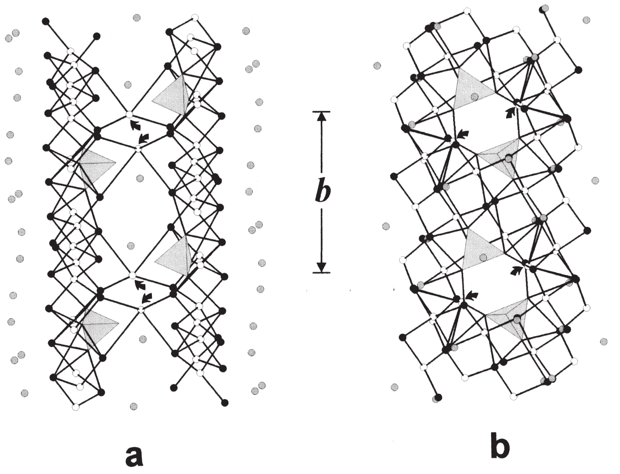

FIGURE 4. The structure of symesite viewed (**a**) parallel to, and (**b**) perpendicular to, the PbO and Cl sheets. Orientation (**b**) is obtained by rotating (**a**) 90° to the left about the b axis. Pb atoms are black circles, Cl atoms are gray circles, O atoms are white circles, SO_4 groups are gray tetrahedra; only Pb-O bonds are shown for clarity. The O12 atoms of H_2O groups in the Cl layer are indicated by arrows. O2-O12 distances are 2.80(7) and 3.07(6) Å with inter-oxygen angles of 91(2)°.

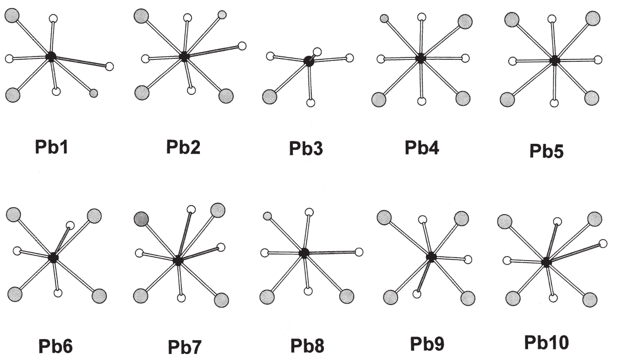

FIGURE 5. The ten different Pb sites in the symesite structure. Large gray circles are Cl, small gray circles are O12 atoms, small white circles are O, and small black circles are Pb. Coordination numbers range from five (Pb3) to eight (Pb2, Pb4, Pb5, Pb7, Pb10). The coordination polyhedra are variants of the $Pb[O_4Cl_4]$ square-antiprism, some with missing O atoms and/or Cl. Long Pb-O bonds (2.5–3.3 Å), excluding Pb-O12 bonds, are shown shaded.

range from 3.18 to 3.49 Å. The remaining 1.7 v.u. comes from the two O-H bonds of H_2O, each contributing ~0.8 v.u. to O12 (Hawthorne, 1992). The bond valence incident at O2 from S and Pb is only 1.59 v.u. The hydrogen atoms of the H_2O group each form a hydrogen bond with the apical O2 atom of a nearby SO_4 tetrahedron in the adjacent PbO sheet, thus linking PbO sheets and increasing interlayer cohesion, bringing the bond valence incident at O2 to close to the ideal value of 2 v.u.

Bond-valence characteristics

The Pb-O bond-lengths range from 2.20 to 3.49 Å and the resulting bond-valences (Table 5) range from 0.05 v.u. (Pb1-O12) to 0.67 v.u. (Pb6-O9). Pb-Cl bonds range from 2.86 (Pb9-Cl1) to 3.86 Å (Pb10-Cl1), with bond valences of 0.03–0.41 v.u. Pb-O12 bonds range from 3.18 to 3.49 Å and have bond valences of 0.05 to 0.09 v.u. These very long Pb-O12 bonds contribute a total of 0.27 v.u. to O12, holding the H_2O group within the symesite structure and promoting the hydrogen bonding necessary to satisfy the bond-valence requirements of O2 (the apical SO_4 oxygen and hydrogen bond acceptor). Similarly, although weak, the long Pb-Cl bonds are relevant because they hold the layers together. Except for Pb3, the bond-valence sums about the Pb atoms range from 1.90 to 2.24 v.u. and are within the normal range for Pb-bearing structures. Pb3 has an incident bond-valence sum of 1.65 v.u.

Relation to other structures

Symesite is a member of the Pb sheet-mineral family that includes nadorite, $PbSbO_2Cl$ (Giuseppetti and Tadini 1973), mereheadite, $Pb_2O(OH)Cl$ (Welch et al. 1998), and thorikosite, $(Pb_3Sb_{0.6}As_{0.4})O_2(OH)Cl_2$ (Rouse and Dunn 1985). These minerals are related structurally to the group of synthetic "Aurivillius" phases (Aurivillius 1982) in which halogen layers occur between PbO layers, as in symesite, or between every second or third PbO layer, as in asisite (Pb-Si), kombatite (Pb-V), sahlinite (Pb-As) and parkinsonite (Pb-Mo). The last three minerals all have superstructures arising from Pb-X ordering. Asisite, nominally $Pb_7SiO_8Cl_2$ (Rouse et al. 1988), but probably $Pb_9SiO_{10}Cl_2$, is likely to have a ten-site ordering motif similar to $Pb_9MoO_{11}Cl_2$ parkinsonite (Welch et al. 1996). Cation ordering is a major feature of this mineral group.

There are strong structural similarities between kombatite (Cooper and Hawthorne 1994) and symesite, both of which have tetrahedral oxyanions within the PbO sheet. Oxyanion arrangements in symesite and kombatite are compared in Figure 6. In symesite, a single Pb atom is replaced by S and the three adjacent O atoms are pulled in to provide the necessary coordination for S, with the addition of an extra apical oxygen atom to complete the tetrahedral coordination. The fourth oxygen that was linked to the replaced Pb atom is replaced by a vacancy. Note that this local association of tetrahedral oxyanion and □ is polar in the plane of the PbO sheet. In kombatite, a pair of VO_4 tetrahedra replaces a pair of next-nearest-neighbor Pb atoms, and the intervening oxygen is replaced by a vacancy. The pair of tetrahedral oxyanions in kombatite (VO_4 groups) occurs in the same PbO sheet, whereas in symesite, each oxyanion pair has SO_4 tetrahedra from adjacent PbO sheets. The point symmetries of the oxyanion-pair topologies in kombatite and symesite are 2 and $\bar{1}$, respectively. The nearest-neighbor SO_4-□ groups point in opposing directions (Fig. 2), suggesting the possibility of a polymorphic form in which nearest-neighbor clusters point in the same direction.

Symesite also has structural similarities with the synthetic S-substituted PbO-related sheet-phases tribasic Pb sulfate, $3PbO{\cdot}PbSO_4{\cdot}H_2O$, and tetrabasic Pb-sulfate, $4PbO{\cdot}PbSO_4$, both of which form as intermediates in the production of lead storage batteries (Steele et al. 1997; Steele and Pluth 1998). These

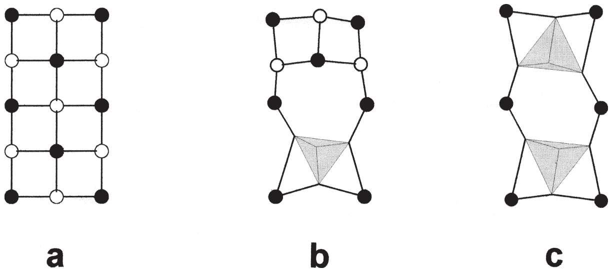

FIGURE 6. The local structure around the SO_4 tetrahedron in symesite (**b**) compared with litharge (**a**) and the VO_4 tetrahedra in kombatite (**c**).

compounds have litharge- or massicot-like structures in which some of the Pb is replaced by S that forms regular SO_4 tetrahedra within the sheets, as in symesite. However, despite the given formula, there are no H_2O groups in tribasic Pb-sulfate; instead, H atoms occur as pairs of hydroxyls replacing Pb ($Pb^{2+} = 2H^+$). Symesite is unique in the minerals of this type in having an H_2O group as an essential part of its structure.

Rouse and Dunn (1990) described a pink, litharge-related, sulfur-bearing oxychloride from Brilon, Germany, and found its substructure by single-crystal XRD; its crystal structure is unknown. This phase is monoclinic (pseudotetragonal) with cell parameters $a = 3.945$, $b = 3.933$, $c = 13.119$ Å, $\beta = 91.11°$ and with an empirical formula $Pb_4\,O_{2.8}\,[Cl_{1.6}\,(SO_4)_{0.4}]$, $Z = 1$. Rouse and Dunn (1990) commented that X-ray precession photographs had numerous weak and poorly defined (by few reflections) layer lines, which indicate large supercell translations along each axis. However, the photographs were insufficient to characterize the supercell. Only the substructure could be defined. The "Brilon mineral" was not accepted as a new mineral primarily because the nature of the supercell, although present, was not determined. The comments made by Rouse and Dunn (1990) regarding the quality of their diffraction patterns are typical of the difficulties encountered in characterizing these Pb-oxychloride minerals. If we recalculate the composition (anhydrous) of Rouse and Dunn (1990) to four Cl per formula we obtain $Pb_{10}\,(SO_4)\,O_7\,Cl_4$, which is isochemical (except for H_2O) with symesite. The crystallographic and chemical evidence suggests that the Brilon mineral and symesite are probably the same mineral. The possibly hydrous nature of the Brilon mineral could easily have been overlooked in a chemical analysis because H_2O constitutes only 0.7 wt% in symesite.

Sundiusite, $Pb_{10}\,(SO_4)\,O_8\,Cl_2$ (Dunn and Rouse 1980), is similar chemically to symesite, but has a much lower Cl content. It is monoclinic with $a = 24.67$, $b = 3.781$, $c = 11.881$ Å, $\beta = 100.07°$, $Z = 2$. It is white/colorless, has a white streak and a perfect {100} cleavage. Dunn and Rouse (1980) suggested that sundiusite is a PbO-related sheet mineral, although its structure was not determined. Symesite is easily distinguished from sundiusite by color, cell parameters, and chemical compositions (Cl content).

ACKNOWLEDGMENTS

We thank Chris Alabaster of the Department of Geology, Bristol University for donating the symesite sample used in this work. MDW thanks Barbara Cressey for providing him with access to the TEM at the Science and Engineering Electron Microscopy Centre, Southampton University. F.C.H was supported by Natural Sciences and Engineering Council of Canada Research, Major Equipment and Major Installation Grants.

REFERENCES CITED

Aurivillius, B. (1982) On the crystal structure of a number of non- stoichiometric mixed lead oxide halides composed of PbO-like blocks and single halogen layers. Chemica Scripta, 19, 97–107.

Brese, N.E. and O'Keeffe, M. (1991) Bond-valence parameters for solids. Acta Crystallographica, B47, 192–197.

Brown, I.D. (1981) The bond-valence method: An empirical approach to chemical structure and bonding. In M.O'Keeffe and A. Navrotsky, Eds., Structure and bonding in crystals, vol. 2, 1–30. Academic Press, New York.

Cooper, M. and Hawthorne, F.C. (1994) The crystal structure of kombatite, $Pb_{14}(VO_4)_2O_9Cl_4$, a complex heteropolyhedral sheet mineral. American Mineralogist, 79, 550–554.

Criddle, A.J. (1998) Ore Microscopy and Photometry (1890–1998). In Modern Approaches to Ore and Environmental Mineralogy. L. Cabri and D.J. Vaughan, Eds. Mineralogical Society of Canada Short-course Series, Volume 27, 1–75.

Dunn, P.J. and Rouse, R.C. (1980) Sundiusite, a new lead sulfate oxychloride from Långban, Sweden. American Mineralogist, 65, 506–508.

Garvey, R.G. (1986) Least-squares unit-cell refinement with indexing on personal computer. Powder Diffraction, 1, 114.

Giuseppetti, G. and Tadini, C. (1973) Riesame della struttura cristallina della nadorite, $PbSbO_2Cl$. Periodico di Mineralogia, 42 (3), 335–45.

Hawthorne, F.C. (1992) Bond topology, bond valence and structure stability. In the Stability of Minerals. G.D.Price and N.L.Ross Eds. Mineralogical Society Series, Volume 3, 25–87.

Rouse, R.C. and Dunn, P.J. (1985) The structure of thorikosite, a naturally occurring member of the bismuth oxyhalide group. Journal of Solid State Chemistry, 57, 389–395.

Rouse, R.C. and Dunn, P.J. (1990) A new lead sulfate oxychloride related to the nadorite group from Brilon, Germany. Neues Jahrbuch fuer Mineralogie, Monatschefte, H8, 337–342.

Rouse, R.C., Peacor, D.R., Dunn, P.J., Criddle, A.J., Stanley, C.J., and Innes, J. (1988) Asisite, a silicon-bearing lead oxychloride from the Kombat mine, South West Africa, Namibia. American Mineralogist, 73, 643–650.

Steele, I.M. and Pluth, J.J. (1998) Crystal structure of tetrabasic lead sulfate (4PbO . $PbSO_4$): an intermediate phase in the production of lead-acid batteries. Journal of the Electrochemical Society, 145, 528–533.

Steele, I.M., Pluth, J.J., and Richardson, J.W. (1997) Crystal structure of tribasic lead sulfate ($3PbO.PbSO_4.H_2O$) by X-rays and neutrons: an intermediate phase in the production of lead acid batteries. Journal of Solid State Chemistry, 132, 173–181.

Symes, R.F. and Embrey, P.G. (1977) Mendipite and other rare oxychloride minerals from the Mendip Hills, Somerset, England. Mineralogical Record, 8, 298–303.

Welch, M.D., Schofield, P.F., Cressey, G., and Stanley, C.J. (1996) Cation ordering in lead-molybdenum-vanadium oxychlorides. American Mineralogist, 81, 1350–1359.

Welch, M.D., Criddle, A.J., and Symes, R.F. (1998) Mereheadite, $Pb_2O(OH)Cl$: a new litharge-related oxychloride from Merehead Quarry, Cranmore, Somerset. Mineralogical Magazine, 62, 387–393.

MANUSCRIPT RECEIVED DECEMBER 8, 1999
MANUSCRIPT ACCEPTED JUNE 20, 2000
PAPER HANDLED BY ROBERTA OBERTI