A new mineral, scotlandite (PbSO₃) from Leadhills, Scotland; the first naturally occurring sulphite

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ABSTRACT. Electron microprobe analysis of the new mineral scotlandite yielded Pb 72.27, S 9.95, corresponding to PbO 77.85, SO₂ 19.88, sum 97.73 wt. %. Secondary ion mass spectrometry showed the absence of Li, Be, B, C, N, and F, but the presence of very small amounts of Br. Infrared spectroscopy showed that the mineral is a sulphite with neither OH nor any other polyatomic anions. The empirical formula, calculated on the basis of Pb+S = 2 is Pb_{1.06}S_{0.94}O_{2.94} or ideally PbSO₃.

The mineral has the following vibrations of the sulphite ion in the infrared spectrum: v_3 920, 865; v_1 970 (?); v_2 620, 600; v_4 488, 470 cm⁻¹.

Scotlandite is monoclinic, with possible space groups $P2_1$ or $P2_1/m$. The unit cell dimensions are: *a* 4.542(2), *b* 5.333(2), *c* 6.413(2) Å, β 106.22(4)°, Z = 2. The strongest lines in the powder diffraction pattern are: 3.99(10) (011), 3.38(7) (110), 3.25(8) (111), 3.07(4) (002), 2.66(7) (020, 012), 2.56(4) (112), 2.24(5) (121, 102), 2.01(5) (210, 022), 1.707(4) (031), 1.538(4) (032, 004).

Scotlandite occurs as chisel-shaped or bladed crystals elongated along the *c*-axis, with a tendency to form radiating clusters. The following forms have been determined: $\{100\}, \{010\}, \{011\}, \{021\}, \{031\}, and \{032\}$. The new mineral has a pronounced cleavage along $\{100\}$, and a less good one along $\{010\}$. The crystals are pale yellow to greyish-white and colourless, sometimes transparent. Their lustre is adamantine, pearly on cleavage planes.

The mineral is optically biaxial positive, $2V_{\text{meas.}}$ 35° 24' (Na). The refractive indices are: $\alpha \sim 2.035$, $\beta \sim 2.040$, and $\gamma \sim 2.085$ (Na). Dispersion is strong, $v \gg r$. The extinction is $\beta//b$, and α : $[001] = 20^{\circ}$ (γ : $[100] = 4^{\circ}$) in the obtuse angle β . *H* (Mohs) ≤ 2 . D = 6.37 and calculated $D_x = 6.40$ g cm⁻³.

Scotlandite occurs in cavities in massive baryte and anglesite, and is closely associated with lanarkite and susannite; it represents the latest phase in the crystallization sequence of the associated lead secondary minerals. The label locality of the specimen is the Susanna vein, Leadhills, Scotland.

IN 1978 one of the authors (W.H.P.) acquired a specimen labelled 'Lanarkite, Anglesite, Leadhillite/ Susannite; Susanna Vein, Leadhills, Lanarkshire, Scotland' from Dr D. H. Garske, at that time a resident of Elmhurst, Illinois, USA. It carries the number S 0339 C. A short note on the label states that the specimen was from the collection of Howard Belsky, of Brooklyn, New York, who obtained it from the late Richard Barstow in 1974. The specimen is probably from an old collection, and is unlikely to have been collected in recent years.

Careful examination of the specimen revealed, in addition to the labelled species, the presence of tiny crystals and crystal aggregates whose optical properties and X-ray powder diffraction pattern did not match those of any known mineral species. Subsequent electron microprobe analyses yielded only lead and sulphur as detectable elements. The chemical composition of the unknown phase was resolved by infrared spectroscopy, which indicated a sulphite mineral. This was confirmed by secondary ion mass spectrometry. Thus scotlandite represents the first naturally occurring sulphite.

The mineral is named for Scotland. Both the mineral and the name have been approved by the Commission on New Minerals and Mineral Names, IMA, prior to publication.

A preliminary examination of the Leadhills collections in both the British Museum (Natural History) and the Royal Scottish Museum has not yet brought to light another scotlandite specimen (J. P. Fuller and H. G. McPherson, resp., priv. comm., 1982). A thorough study of the Leadhills suite at the Museum of Natural History, Vienna, maintained by W.H.P. has not led to the discovery of more scotlandite either. Type material has been preserved at the Institut für Geowissenschaften (Mineralogie), Universität Salzburg, Akademiestrasse 26, A-5020 Salzburg, Austria; the Institut für Mineralogie und Kristallchemie, Universität Stuttgart, Pfaffenwaldring 55, D-7000 Stuttgart 80, Federal Republic of Germany; the British Museum (Natural History), Cromwell Road, London, England; the Royal Scottish Museum, Edinburgh, Scotland; and the Royal Ontario Museum, Toronto, Canada.

H. Sarp (priv. comm., 1983) has informed the authors of a second occurrence of scotlandite at Argentolle mine, near Saint-Prix, Saône-et-Loire, France.

It is notable that roeblingite was originally formulated as a lead containing sulphite (Penfield and Foote, 1897), but was later shown by chemical methods to be a sulphate free from sulphite (Blix, 1931). Further revisions to the formula were proposed by Foit (1966) and recently, from a number of well-duplicated analyses, by Dunn et al. (1982) to $(Ca,Sr)_{12}(Mn,Ca)_{2}Pb_{4}(SO_{4})_{4}Si_{12}O_{28}(OH)_{20}$. In response to a suggestion by Dr M. H. Hey, two specimens of roeblingite from Franklin, New Jersey (one off BM 83806, and one from the W. H. Paar collection) were studied by infrared spectroscopy, details of which are intended to be published separately. The spectra show strong sulphate v_3 absorptions, but no strong absorptions distinctly attributable to sulphite.

Descriptive mineralogy. The specimen $(5 \times 5 \times 3 \text{ cm})$ consists of massive baryte with some 'limonitic' coating on one side. A large cavity is developed through the specimen and displays a variety of lead secondary minerals, including anglesite, lanarkite, leadhillite, susannite, and the new mineral scotlandite. Lanarkite is present as elongated and mostly cleaved prismatic crystals up to 1.5 cm long. Leadhillite crystals (< 1 mm) are thin tabular {001} with a hexagonal outline, and are perched on the



FIG. 1. Scotlandite crystals (approx. 1 mm), displaying the forms $\{021\}$, $\{031\}$, $\{100\}$, and $\{010\}$. In addition, the $\{100\}$ cleavage is evident on the largest crystal, to the left.

lanarkite. The susannite forms acute rhombohedral crystals (2-3 mm) either isolated or as crystal clusters at various spots in the cavity.

Scotlandite is found in the vuggy anglesite as yellowish single crystals up to 1 mm in length (fig. 1), which are sometimes arranged in fan-shaped aggregates. The colour results from minute inclusions of pyromorphite. A very thin coating of anglesite can usually be recognized on some of the scotlandite and almost certainly protects the sulphite from further oxidation. A second variety occurs in discontinuously distributed cavities between the anglesite mass containing the first variety and the baryte matrix. This variety is characterized by tiny, whitish to water-clear crystals and crystal clusters less than one millimetre in size (fig. 2a, b), which encrust large portions of the interior of the cavities.

The morphology of the scotlandite is characterized by chisel-shaped crystals elongated along the *c*-axis. The majority display the following forms: prisms {021} and/or {031}; pinacoids {100} and {010}. Very rarely additional forms, such as the prisms {011} and {032} can be determined (fig. 3). Equal development of all the reported prisms around [100] results in a somewhat rounded appearance of the contours of {100}. Parallel intergrowths of scotlandite crystals after {100} and star-like and compact radiating arrangements of such penetrating intergrowths can usually be observed (figs. 1, 2).



FIG. 2. SEM photographs. (a, left) Parallel intergrowths of scotlandite crystals, the cluster measuring ~ 1 mm across. (b, right) A portion of the cluster shown in fig. 2a enlarged, displaying the typical spear-shaped habit of scotlandite crystals.

Physical and optical properties. Scotlandite has a perfect cleavage along {100} and a good cleavage along {010}. The lustre is adamantine, and pearly on cleavage planes. Hardness (Mohs) is around 2. The density, as determined with a Berman microbalance on three fragments, weighing 5.4, 6.2, and 6.8 mg respectively, is 6.37 ± 0.02 g cm⁻³, in excellent agreement with the density, $D_x = 6.40$ g cm⁻³, calculated from its ideal formula. Compared with chemically related compounds, it is very close to the value of anglesite (6.38 g cm⁻³), but distinctly different from that of lanarkite (6.92 g cm⁻³); orthorhombic lead sulphite is of higher density ($D_{meas} = 6.54$, calculated $D_x = 6.56$ g cm⁻³) (Odin and Popovkin, 1967).

Scotlandite is optically biaxial positive, with 2V, 35° 24' (Na) (measured) and 37° 40' (calculated); the dispersion of the axial angle is strong, with $v \gg r$. The refractive indices have been determined using Cargille immersion liquids and are: $\alpha \sim 2.035$, $\beta \sim 2.040, \gamma \sim 2.085$ (Na). Applying the equation of Gladstone and Dale and using the constants of Mandarino (1976), a mean refractive index of $\bar{n} = 2.0349$ can be calculated from the theoretical chemical composition and the X-ray density. The measured mean refractive index is 2.052, thus not very far from the calculated value. The position of the indicatrix is shown in fig. 3. The good $\{010\}$ cleavage allows determination of the extinction angles, which are α : $[001] = 20^{\circ}$ and γ : $[100] = 4^{\circ}$ in the obtuse angle; β is parallel to b.

X-ray crystallography. A small crystal of scotlandite, showing some cleavage faces, was examined using Weissenberg and precession techniques. Scotlandite is monoclinic. The only systematic extinctions observed from the single crystal patterns were 0k0 where k was odd. Thus the possible space group is either $P2_1$ or $P2_1/m$. The unit cell parameters obtained from the single crystal study were used to index the X-ray powder pattern and were then refined with the indexed powder data. The results are: a 4.542(2), b 5.333(2), c 6.413(2) Å, $\beta 106.22(4)^\circ$, Z = 2. If the present a and c axes are interchanged the unit cell of scotlandite is very similar to that of molybdomenite, PbSeO₃ (Mandarino, 1965). It appears that scotlandite is the sulphur analogue of the latter. The powder diffraction data of Table I were obtained using a 114.6 mm diameter Debye-Scherrer camera and Fe-K α radiation, filtered with Mn, without standards. Intensities were estimated visually.

Electron microprobe analysis. Several handpicked fragments of scotlandite were mounted in epoxy medium then polished. These were found to be compositionally homogeneous, based on their backscattered electron images; furthermore, only Pb and S were detected by energy-dispersive X-ray analysis. Wavelength-dispersive analyses for Pb and S were performed using an acceleration voltage of 20 kV, the S-K α , Pb-M α , and Pb-L α emission lines, and a synthetic PbSO₄ standard. Cl, Br, Na, Mg, Al, Si, and P were sought but not detected. The data were processed using a version of the EMPADR VII computer program of Rucklidge and Gasparrini (1969). No shift in wavelength positions was observed for Pb and S between the scotlandite and the standard, and the surfaces of scotlandite grains showed no effects of decomposition under the stationary electron beam. A natural anglesite sample was also analysed for comparison. The results for the anglesite and scotlandite were close to those of the synthetic PbSO₄ standard, but PbO and SO₃ for scotlandite consistently totalled 101 to 103 wt. %, although the samples were



TABLE I. Indexed X-ray powder pattern for scotlandite, β -PbSO₃

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	d _{meas}	I/I ₀	d _{calc}	hkl
	4.36	2	4.361	100
	3.99	10	4.031	011
	3.38	7	3.376	110
	3.25	8	3.274	111
	3.12	1	3.166	101
	3.07	4	3.079	002
	2.91	2	2.930	102
	2.70	1/2	2.723	111
	2.66	7	2.666, 2.666	020, 012
	2.56	5	2.568	112
	2.24	5	2.243, 2.238	121, 102
	2.04	3	2.040	121
	2.01	5	2.018, 2.016	210, 002
	1.979	2	1.972	122
	1.948	1/2	1.951	113
	1.918	2	1.916	013
	1.881	1	1.896	201
	1.760	1/2	1.760	203
	1.707	4	1.708	031
	1.672	1	1.671	213
	1.634	3	1.634	13 <u>1</u>
	1.591	2	1.599, 1.583	104, 202
	1.538	4	1.539, 1.539	032, 004
	1.512	2	1.512	301
	1.465	2	1.465	204
	1.443	2	1.454, 1.430	300, 312
	1.418	3	1.424, 1.413	123, 214
	1.394	1	1.392	132
	1.370	2	1.371	124
	1.350	2	1.350	232
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Fe-K α radiation, camera diameter 114.6 mm. Intensities estimated visually.

FIG. 3. Idealized drawing of a scotlandite crystal, much resembling those in fig. 1. Also shown is the orientation of the optical indicatrix.

repolished and reanalysed several times. The average of 107 analyses is: Pb, 72.0; S, 9.9 wt. %; the remainder was assumed to be oxygen (Table II). Calculation as PbSO₃ gives a total of 97.4 wt. %, whereas calculation as PbSO₄ gives 102.3 wt. %. In comparison the anglesite gave an analytical total of 100.0 wt. %. The empirical formula, calculated on the basis of Pb+S = 2 is Pb_{1.06}S_{0.94}O, or ideally, PbSO₃. It is considered that the chemical formula of scotlandite is PbSO₃, and due to surface oxidation some portion of the mineral had formed PbSO₄, thus producing spurious totals for the analyses. Consequently, further studies by infrared spectroscopy and secondary ion mass spectrometry

were carried out in order to ascertain the chemical composition of scotlandite.

Infrared spectroscopy. The infrared spectra of two specimens of scotlandite and of numerous precipitated lead sulphite and dioxysulphite samples were measured over the 400-4000 cm⁻¹ range, in Nujol mulls between KBr plates, using a Perkin-Elmer 397 grating infrared spectrophotometer, each spectrum being calibrated against polystyrene. The spectra are all simple, related and characteristic, and are reproduced in fig. 4.

The strong broad absorption band near 900 cm⁻¹ (scotlandite 920, 865; α -PbSO₃ 965, 890; PbSO₃ · 2PbO 910 cm⁻¹) represents the ν_3 asymmetrical stretching vibration of the SO₃⁻¹ ion. The ν_1 symmetrical stretching mode, which occurs in the same region, is not resolved and is probably buried under the ν_3 absorption, though the trace of a shoulder near 970 cm⁻¹ in the spectrum of scotlandite may be due to this vibra-

	Scotlandite		Anglesite	PbSO ₃ (theoretical)
Pb	72.0		68.3	72.13
S	9.9		10.6	11.16
Total	81.9		78.9	83.29
РЬО	77.6	77.6	73.6	77.70
SO ₂	19.8			22.30
SO ₃		24.7	26.4	
Total	97.4	102.3	100.0	100.0
		Ato	mic ratios	
S/Pb	0.888		1.0	1.0

TABLE II. Electron microprobe analyses of scotlandite in wt. %

tion. The sharp absorptions near 600 cm⁻¹ (scotlandite 620 > 600; α -PbSO₃ 640 < 625; PbSO₃ · 2PbO 606 cm⁻¹) are due to the v_2 symmetrical bending mode of the SO₃⁻¹ ion; for α -PbSO₃ at least this band is very weak in the Raman spectrum (Lutz and El Suradi, 1976). The sharp absorptions near 500 cm⁻¹ (scotlandite 488, 470; α -PbSO₃ 481, 471; PbSO₃ · 2PbO 495 cm⁻¹) are due to the v_4 asymmetrical bending vibrations of the SO₃²⁻¹ ion. The spectrum of the dioxysulphite displays extra absorption bands in this region (518, 450, 400 cm⁻¹), assigned to Pb-O stretching vibrations.

The v_2 symmetrical bend, near 600 cm⁻¹ is non-degenerate, but is split into two absorptions in the spectra of both polymorphs. This could indicate that the sulphite groups in both structures occupy two sites. An X-ray structure analysis is required to resolve this problem. Both v_3 and v_4 are doubly degenerate, and their splitting in the cases of scotlandite and of precipitated α -PbSO₃ could be due to this anion site multiplicity, but is more likely to be due to lowering of the anion site symmetry. The sulphite ion in the lead dioxysulphite lattice is of normal C_{3v} symmetry, no splitting of degeneracy being observed.

The infrared spectrum of scotlandite shows conclusively that it is an anhydrous sulphite, with no OH groups or other polyatomic anions being present. Other sulphur oxyanions, e.g. SO_4^{2-} , FSO_2^{-} , FSO_3^{-} , S_2O_x (x = 3 to 8), S_yO_6 (y = 3 to 6), also HSO_3^{-} and HSO_4^{-} all give strong absorptions above 1000 cm⁻¹, where scotlandite does not absorb. Oxyanions of elements below neon in the periodic table, which would not be detected in the electron microprobe analysis, e.g. various borates, nitrites, carbonates, etc., also BF_4^{-} also all have strong absorptions above 1000 cm⁻¹.



FIG. 4. Infrared spectra of lead sulphites. (X) Absorptions due to Nujol. (1) Scotlandite, Leadhills, Lanarkshire, Scotland. (2) Precipitated orthorhombic PbSO₃. (3) Precipitated PbSO₃ · 2PbO.

Secondary Ion Mass Spectrometry

Small samples of freshly powdered scotlandite and of synthetic α -PbSO₃ were submitted to secondary ion mass spectrometry (SIMS) by Dr J. A. Van den Berg of the SIMS Consultancy Service, Chemistry Department, UMIST. The specimens were bombarded in vacuo by a 2 keV argon atom beam and the surface ion fragmentation pattern analysed by a high performance quadrupole mass spectrometer. Good results were obtained only after approximately 100 Å depth of sample surface was removed by sputter etching. Ions of Li, Be, B, C, N, and F, which would not have been detected by the electron microprobe analysis, were absent or present in very small amount, whereas O ions were abundant. Other important positively or negatively ionized fragments from scotlandite were (mass number, fragment): 80, SO₃, abundant, bracketed by a little Br (not detected in electron microprobe analysis); 96, SO₄, product of surface oxidation; 288, PbSO₃,

abundant, bracketed by a little PbBr; 304, PbSO₄, product of surface oxidation. Further ionized fragments detected include 32, O₂ and/or S; 48, O₃ and/or SO; 64, SO₂, S₂ and/or O₄; 208, Pb; 224, PbO; 240, PbO₂ and/or PbS; 416, Pb₂; 448, Pb₂S and/or Pb₂O₂; 624, Pb₃; 656, Pb₃O₂ and/or Pb₃S.

These results confirm the conclusions reached from electron microprobe analysis and infrared spectroscopy that scotlandite must be a polymorph of lead sulphite (β -PbSO₃).

Attempted synthesis. Numerous attempts were made to synthesize scotlandite by mixing aqueous solutions of lead acetate with sulphur dioxide or with sodium sulphite with or without various additives, over a wide range of reaction conditions, in particular wide variations in pH and concentrations and including seeding with traces of scotlandite.

At pH values between 3.5 and 12 the well-known orthorhombic Pnam or Pna2₁ (Odin and Popovkin, 1967) polymorph precipitated, as indicated by its characteristic infrared spectrum (fig. 4), which is identical with published spectra of precipitated lead sulphites (Rocchiccioli, 1957; Wilfong and Maust, 1974; Lutz and El Suradi, 1976). Quantitative analysis of this material by Dr R. Perry in the Chemistry Department, UMIST gave: Pb 69.9, S 10.6 wt. %. Compared with the calculated values for PbSO₃ of Pb 72.1 and S 11.2 wt. %, the somewhat low values obtained in these analyses and others quoted below are doubtless due, at least in part, to surface oxidation to sulphate. Colourless dendritic clusters of crystals up to 3 mm long were grown by slow diffusion methods, this being the first reported growth of macro-crystals of lead sulphite.

The precipitate obtained at pH values between 12 and 13.5 were of a product with a different but related infrared spectrum, shown by analysis to be a lead dioxysulphite (Found; Pb 83.1, S 4.1 wt. %. Calculated for PbSO₃ · 2PbO; Pb 84.7, S 4.3 wt. %). The infrared spectrum of this compound (fig. 4) is typically that of a sulphite and a lead oxide, with no OH absorptions present. A precipitate obtained at pH 12 gave an infrared spectrum similar to that of a mixture of the normal sulphite and the dioxysulphite, no mono-oxysulphite being detected. Various lead 'oxysulphites' have been reported, mostly in the patent literature, but although their compositions have been determined by chemical analyses, no evidence has been adduced as to what or how many phases are present, some at least being almost certainly mixtures.

Scotlandite could not be synthesized by precipitation methods. Mandarino (1965) notes that precipitation methods also failed to produce its selenite analogue molybdomenite, another polymorph being obtained. This polymorph could be converted into molybdomenite by a fusion method, under which conditions the sulphite would decompose. High-temperature conditions are unlikely to be involved in the natural formation of scotlandite and molybdomenite, which are probably the thermodynamically stable polymorphs, the alternative structures being produced under precipitation conditions because of favourable kinetics.

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