

New IR and XRD data for leadhillite of ideal composition

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ABSTRACT. The infra-red spectrum and X-ray powder pattern of a chemically analysed specimen of leadhillite, a lead carbonate sulphate hydroxide mineral from Leadhills, Scotland, are shown to be different from those in the literature. The IR spectra of several specimens suggest that mutual replacement of SO_4 , CO_3 , and OH may occur in this mineral, and it is thought that this might be responsible for the observed variation in X-ray spacings.

In a recent study of leadhillite† ($\text{Pb}_4\text{SO}_4(\text{CO}_3)_2(\text{OH})_2$) from Leadhills, Scotland (Milodowski, in prep.), its infra-red absorption spectrum was observed to differ considerably from those in the literature (Moenke, 1962; Omori and Kerr, 1963), which in turn differed from each other. Mrose and Christian (1969) used IR in their investigation of leadhillite and its polymorph susannite, but no data have been published. It was also noted that, while the X-ray powder pattern of leadhillite showed the same relative intensities as those reported in the JCPDS index and in the literature, the d -spacings were significantly larger. This investigation seeks reasons for these inconsistencies by more fully characterizing the mineral using IR spectroscopy and X-ray diffraction on a chemically analysed specimen that was unambiguously identified by optical microscopy as biaxial leadhillite rather than uniaxial susannite (Palache *et al.*, 1951, p. 298).

IR spectra. The most obvious discrepancy between the IR spectrum of the leadhillite of this study

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† The principal specimen of leadhillite studied here (L1) was kindly supplied by Mr E. A. Jobbins, Mineral Curator, Geological Museum, IGS, London.

(L1) and those from the literature is in the relative intensities of the ν_3 carbonate and sulphate absorption bands near 1400 and 1100 cm^{-1} respectively; leadhillite L1 shows stronger carbonate than sulphate absorption (fig. 1a), while the leadhillite studied by Moenke shows strong sulphate and relatively weak carbonate absorption (fig. 1b). Although it is not possible, from band intensities, to make firm predictions about the relative abundances of carbonate and sulphate ions in leadhillite, the pattern shown in fig. 1a suggests that the mineral contains more carbonate than sulphate. This was confirmed by analysis, S being determined by combustion and titration of SO_2 (Rundle, 1974), C and H by CHN analyser (Hewlett Packard) or by evolved gas analysis (EGA), and Pb by atomic absorption. The excellent agreement between the observed and theoretical compositions (Table I) unambiguously establishes that the mineral reported on here is leadhillite of ideal composition. The IR absorption spectrum shown in fig. 1a is therefore authentic for pure leadhillite.

IR patterns very similar to that shown in fig. 1a

TABLE I. *Chemical composition (%) of leadhillite from Leadhills, Scotland*

	PbO	SO_3	CO_2	H_2O	Total
1.	82.05	7.47	8.17	1.60	99.29
2.	82.75	7.42	8.16	1.67	100.00

1. Specimen L1 (Milodowski, in prep.)
2. Theoretical values for $\text{Pb}_4\text{SO}_4(\text{CO}_3)_2(\text{OH})_2$.

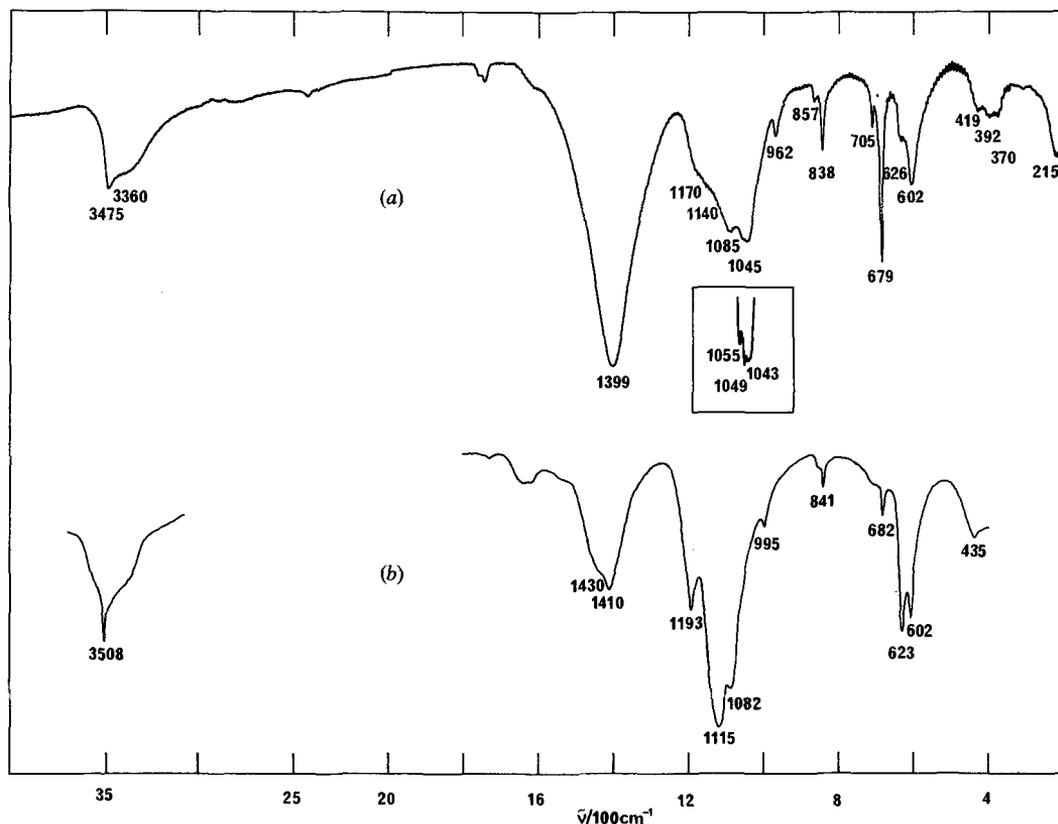


FIG. 1. Infra-red spectra of: (a) leadhillite (Milodowski, in prep.), 0.8 mg in 13 mm diameter CsI pressed disc recorded on Perkin Elmer 580B, inset run under higher resolution and ordinate expansion; (b) leadhillite, reproduced from Moenke (1962). Absorption band positions are given in cm^{-1} .

were obtained for a further three specimens of leadhillite (L2, L3, and L4)† all from the Leadhills location, giving additional support for the validity of this type of absorption spectrum. A close inspection of these spectra, however, revealed that there was some variation in the relative intensities of sulphate, carbonate, and hydroxyl absorption bands at 1045, 1399, and 3475 cm^{-1} respectively. Care was taken to minimize the effect of the contribution made by adsorbed water to the OH absorption band at 3475 cm^{-1} by heating the KBr or CsI discs to 100°C for 1 to 2 days before recording the spectra. Ratios of the areas of the OH⁻, SO₄²⁻, and CO₃²⁻ bands (Table II) suggest that specimens L2, L3, and L4 contain relatively more OH and less CO₃²⁻ and SO₄²⁻ than does L1.

† Kindly supplied by Dr W. W. Aitken (specimen L2) and Dr F. B. Atkins (specimens L3, L4), Curators of Minerals at Geology Department, University of Aberdeen, and University Museum, Parks Road, Oxford, respectively.

The SO₄²⁻:CO₃²⁻ ratio of about 0.5 was relatively constant in L1, L2, and L3 but the value of 0.4 in L4 suggests CO₃²⁻ for SO₄²⁻ substitution in addition to the OH⁻-for-CO₃²⁻ substitution in L2, L3, and L4. Unfortunately, these substitutions could not be confirmed by chemical analysis

TABLE II. Ratios of areas of infra-red absorption bands of SO₄²⁻ (1045 cm^{-1}), CO₃²⁻ (1399 cm^{-1}), and OH⁻ (3475 cm^{-1}) for four specimens of leadhillite

	SO ₄	CO ₃	OH
L1	2.9	: 6.3	: 1
L2	2.5	: 4.9	: 1
L3	2.6	: 5.4	: 1
L4	2.5	: 6.0	: 1

L1-L4, see text.

because of insufficiency of specimens L2, L3, and L4.

The complex suite of minerals commonly encountered in association with leadhillite in the oxidized zone of lead deposits includes anglesite, cerussite, lanarkite, caledonite, and linarite, but from their IR spectra, none of these minerals can account significantly for the spectrum reported by Moenke (fig. 1*b*). This spectrum is consistent with a basic sulphate-rich mineral and is reasonably close to that of basic lead sulphate (spectrum 833; Vandeberg, 1980). Omori and Kerr's specimen of leadhillite is contaminated by quartz (Erd *et al.*, 1965) and the spectrum is of poor quality. The IR data from Moenke's spectrum, tabulated by Ross (1974), are therefore not applicable to leadhillite and should be superseded by those shown in Table III. Although the assignments are analogous to those of Ross, as will now be discussed, the ν_2 sulphate assignment may be in error.

TABLE III. Assignment of sulphate vibrations (cm^{-1}) in leadhillite (after Ross, 1974)

ν_1	ν_2^*	ν_3	ν_4
962 m	419 m	1170 sh	626 sh
	392 m	1140 sh	602 s
	370 m	1085 s	
		1045 s	

s, strong; m, medium; w, weak; sh, shoulder.

* See text.

A striking feature of the leadhillite spectrum (fig. 1*a*) is the dominance of the pattern of carbonate bands at 1751, 1737 (combination), 1399 (ν_3), 1055 and 1049 (ν_1), 857 and 838 (ν_2), and 705 and 679 (ν_4). The pattern is very similar to that of cerussite, PbCO_3 , reported by White (1974) and Miller *et al.* (1960) and hydrocerussite, $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$, reported by Vandeberg (1980; spectrum 381). Similarly, the pattern of sulphate bands in fig. 1*a* resembles that of anglesite, PbSO_4 (Van der Marel and Beutelspacher, 1976), suggesting either that the Pb ions are having a dominant nearest neighbour effect on the SO_4 , CO_3 (and OH) anions or that the anions are segregated. While the nearest neighbour effect is what would be expected in such structures, results from thermal analysis of the leadhillite (L1) tend to support segregation, the mineral decomposing as if it were a mixture of lead carbonate, lead hydroxide, and lead sulphate (Milodowski, in prep.).

Following Ross (1974), the group of three bands centered on 400 cm^{-1} could be assigned to ν_2 of

sulphate (Table III) but the known weakness or absence of this vibration in sulphate spectra (Hezel and Ross, 1966), and the virtual identity of absorption in the 400 cm^{-1} region in leadhillite (fig. 1*a*), cerussite, and hydrocerussite indicate that the sulphate ions in leadhillite do not make a significant contribution in this region. The bands at 419, 392, and 370 cm^{-1} are, therefore, thought to originate either in the carbonate ions, possibly arising from summation and/or difference modes (Angino, 1967), or in the Pb-OH grouping.

X-ray diffraction. The X-ray powder pattern of the leadhillite described here (L1), while showing the same relative intensities of reflections as that in the JCPDS index (18-705), differs markedly from it in the values of the d -spacings (Table IV). For brevity, only seven of the strongest reflections are shown in Table IV, but it can be clearly seen that

TABLE IV. Seven of the strongest d -spacings (\AA) for several leadhillite specimens from Leadhills, Scotland, Co-K α

L1*			L3	L4	L2	5
d	I	hkl	d	d	d	d
11.58	mw		11.62	11.58	11.57	
4.535	m	200	4.540	4.526	4.524	4.47†
3.568	vs		3.568	3.565	3.560	3.53
2.940	ms		2.942	2.936	2.934	2.917
2.619	s		2.614	2.622	2.612	2.605
2.314	mw	005	2.315	2.313	2.309	2.303
2.111	w		2.106	2.105	2.106	2.099

L1-L4, as described in text; 5, data from JCPDS card 18-705.

* A more complete list of d spacings for L1 is given in Table V.

† 11 \AA cut-off, radiation Cu-K α .

s, strong; m, medium; w, weak; v, very.

Complete lists of spacings from powder patterns of L2, L3, and L4 can be obtained from the senior author on request.

the spacings are significantly smaller than those of L1. Spacings of L3 are probably not significantly different from those of L1, but those of L4 and L2 are intermediate between those of L1 and the JCPDS specimen, suggesting a continuous series of lattice substitutions. Microprobe analyses of L1-L4 indicated the absence of metals other than lead and a trace of cadmium (estimated by atomic absorption to be less than 0.01%), and so exclude the possibility that the variation in d -spacings is due to cation substitution in these specimens; this type of substitution can occur in leadhillite however, Yosimura (1939) having described a cuprian variety.

A more likely explanation is that the variation in d -spacings is due to different anion populations as discussed above for the variation in IR spectra.

TABLE V. X-ray powder diffraction pattern of leadhillite L1, Cu-K α

$d\text{\AA}$ (obs.)	I	hkl	$d\text{\AA}$ (calc.)	$d\text{\AA}$ (obs.)	I
11.57	m	001	11.562	1.790	vw
6.78	w	111	6.761	1.777	vw
5.80	w	002	5.781	1.739	w
4.75	vw	112	4.750	1.733	w
4.53	m	200, 140	4.549, 4.512	1.699	tr
4.24	w	201, 141	4.233, 4.203	1.643	w
3.84	vw	003	3.854	1.618	vw
3.57	vs	202	3.575	1.554	m
3.37 b	vw	033	3.368	1.520	tr
3.21 b	vw	160, 232	3.237, 3.177	1.468	tr
3.08	vw	043, 250	3.096, 3.069	1.432	tr
2.997	vw	310	3.001	1.377	w
2.939	ms	203, 143	2.941, 2.931	1.337	mw
2.892	m	004	2.891	1.307	tr
2.830	vw	223, +	2.829	1.288	m
2.729	tr	114	2.731	1.265	w
2.621	m	340, 080	2.619, 2.598	1.238	w
2.552 b	vw	341, 081	2.554, 2.535	1.197	w
2.438	w	204, 144	2.440, 2.434	1.189	mw
2.314	ms	005	2.312	1.159	mw
2.278 b	tr			1.155	mw
2.216	tr			1.123 b	w
2.112	m			1.106	vw
2.064	m			1.060	w
1.944	w			1.027	w
1.889	tr			0.977 b	vw
1.891	tr			0.945	mw

Plus eight more lines to 0.790

b, broad; w, weak; m, medium; s, strong; v, very; tr, trace; +, plus additional indices.

Replacement of the SO_4^{2-} ions by the smaller CO_3^{2-} and possibly also OH^- ions must give rise to a decrease in lattice dimensions. The a and c axial dimensions calculated from the (200) and (005) spacings near 4.53 and 2.31 \AA respectively (Table IV) place the cell sizes in the order $L3 > L1 > L4 > L2 > 5$ (JCPDS). Because it relates to specimens from two different sources, and contains no chemical analyses, the data on JCPDS card no. 18-705 is of limited value, especially since erroneous b and c parameters are used in indexing the X-ray pattern. The faulty data were transcribed from Palache *et al.*, 1951, p. 296, in which a typographical error had resulted in transposition of b and c . To replace these data, new crystallographic parameters were sought for the L1 specimen which has been shown to have the ideal composition. However, because of complex twinning, no reliable single crystal data could be obtained. For the same reason, the X-ray powder diffraction pattern (Table V) proved difficult to index completely, and no

assignments are reported below about 2.3 \AA . The pattern has been tentatively indexed to the orthorhombic system, giving calculated axial dimensions of $a = 9.094 \pm 0.003$, $b = 20.789 \pm 0.009$, and $c = 11.559 \pm 0.004$ \AA , and shows reasonable agreement between observed and calculated d -spacings. Alternative indexing to the monoclinic system gave similar axial dimensions to those above; $a = 9.099 \pm 0.009$, $b = 20.780 \pm 0.086$, $c = 11.564 \pm 0.007$, $\gamma = 90.255 \pm 0.235^\circ$. Preliminary results from electron diffraction generally supported indexing to the orthorhombic system and indicated a pronounced pseudo-hexagonal symmetry for the rows of strong reflections. Mrose and Christian (1969) have reported that leadhillite is monoclinic, with unit cell dimensions similar to those listed above.

Although the effect of the anion composition on d -spacings has not been reported previously for leadhillite, Temple (1957) concluded that the relatively large spacings of a chromian leadhillite (0.5% Cr) were probably due to partial substitution

of sulphate by the larger chromate ion. This may not be the only explanation, however, because the leadhillite reference mineral used by Temple, with *d*-spacings considerably lower than those of our ideal mineral, probably contains significant replacement of sulphate by carbonate and/or hydroxide. The chromian leadhillite may, therefore, also contain more sulphate than the reference mineral with which it was compared.

Conclusions. The new IR and X-ray data presented here provide a more complete characterization of leadhillite than existed previously. They also indicate the probable existence of an unsuspected range of anion compositions within the leadhillite structure. It may be possible that, with knowledge of its anion content, a leadhillite specimen might be placed in the galena–anglesite–cerussite sequence, and thereby help to establish more fully the inter-relationship between these minerals during weathering.

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REFERENCES

- Angino, E. E. (1967) *Am. Mineral.* **52**, 137–48.
 Erd, R. C., Lyon, R. J. P., and Madsen, B. M. (1965) *Geol. Soc. Am. Bull.* **76**, 271–82.
 Hezel, A., and Ross, S. D. (1966) *Spectrochim. Acta*, **22**, 1949–61.
 Miller, F. A., Carlson, G. L., Bentley, F. F., and Jones, W. H. (1960) *Ibid.* **16**, 135–235.
 Milodowski, A. E. *Thermal decomposition reactions of selected carbonate minerals and their detection, identification and quantitative determination by evolved gas analysis*. Unpubl. Ph.D. thesis, University of London (in prep.).
 Moenke, H. (1962) *Mineralspektren*, **1**, Akademie-Verlag, Berlin.
 Mrose, M. E., and Christian, R. P. (1969) *Can. Mineral.* **10**, 141 (Abstract only).
 Omori, K., and Kerr, P. F. (1963) *Geol. Soc. Am. Bull.* **74**, 709–34.
 Palache, C., Berman, H., and Frondel, C. (1951) *Dana's system of mineralogy*, 7th edn., **2**, John Wiley & Sons, New York.
 Ross, S. D. (1974) In *The Infrared Spectra of Minerals* (V. C. Farmer, ed.), Mineralogical Society, London, 427.
 Rundle, L. M. (1974) *Analyst*, **99**, 163–5.
 Temple, B. K. (1957) *Royal Soc. Edin. Trans.* **63**, (part 1, 1955–6), 85–113.
 Vandenberg, J. T. (1980) *An Infrared Spectroscopy Atlas for the Coatings Industry*. Federation of Societies for Coatings Technology, Philadelphia, USA, 896.
 Van der Marel, H. W., and Beutelspacher, H. (1976) *Atlas of Infrared Spectroscopy Of Clay Minerals and their Admixtures*. Elsevier Scientific Publishing Company, New York, 332.
 White, W. B. (1974) In *The Infrared Spectra of Minerals* (V. C. Farmer, ed.) Mineralogical Society, London, 227.
 Yosimura, T. (1939) *J. Fac. Sc. Hokkaido Univ.* **4**, 453–63.

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