Crystal structure of macphersonite (Pb4SO4(CO3)2(OH)2): comparison with leadhillite

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ABSTRACT

The crystal structure of macphersonite ($Pb_4SO_4(CO_3)_2(OH)_2$, *Pcab*, $a = 9.242(2)$, $b = 23.050(5)$, $c = 10.383(2)$ Å) from Leadhills, Scotland has been determined to an $R = 0.053$. The structure has many features in common with its polymorph leadhillite including three distinct types of layers. Layer A includes sulphate tetrahedra, Layer B is composed of Pb and OH, while Layer C is composed of Pb and CO_3 with topology identical to that in cerussite. In both macphersonite and leadhillite these layers are stacked along [010] as ...BABCCBABCC... The double CC layer is almost identical in the two structures and forms a structural backbone and occurs in other structures including hydrocerussite and plumbonacrite. The sulphate layer shows the greatest difference between the two structures and can be described by a pattern of up or down pointing tetrahedra. For macphersonite the sequence along [001] is ...UDUDUD... while in leadhillite the sequence along [010] is ...UDDUUDDU... This latter sequence effectively doubles *b* relative to the equivalent direction in macphersonite. Susannite, a third polymorph, may have yet another sequence of sulphates to give trigonal symmetry; by heating leadhillite, displacive movements of sulphate groups may occur with a conversion to susannite.

KEYWORDS: macphersonite, leadhillite, susannite, cerussite, hydrocerussite, carbonate, sulphate.

Introduction

MACPHERSONITE (Livingstone and Sarp, 1984) is trimorphous with leadhillite and susannite with the composition $Pb_4SO_4(CO_3)_2(OH)_2$. All are found in the classic Leadhills region of southwest Scotland and represent a small fraction of the some 60 minerals identified from this region (Temple, 1956). From primary galena, oxidation products include anglesite and cerussite or hydrocerussite. These oxidized products lead to a wealth of minerals which include sulphates, carbonates, hydroxides, or mixtures thereof which include the trimorphous group above; other phases are given in Temple (1956).

Macphersonite is the rarest of the three polymorphs, only two composite crystals being known on separate specimens from the Leadhills-Wanlockhead orefield. Parallel oxidation of other primary sulphides of Cu and Zn lead to mixed metal species of carbonates, sulphates and hydroxides.

Previous studies of the these trimorphs have established their compositional identity and close relationships among their unit cell geometries (Livingstone and Sarp, 1984). They can be distinguished by differences in their X-ray patterns, albeit subtle differences in the case of susannite and leadhillite (Livingstone and Russell, 1985), or by their infrared absorption spectra (Russell *et al.*, 1984). The polymorphs can also be distinguished by their thermal behaviour (A.L., unpublished data). The structure of leadhillite was described by Giuseppetti *et al.* (1990) in which a double lead carbonate layer, nearly identical to

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layers in cerussite, anchors a structure which includes $PbSO_4$ and $Pb(OH)_2$ layers. The dimensional similarities between leadhillite and macphersonite indicate that the latter has a similar structure and our main objectives are to determine the macphersonite structure and then to compare with leadhillite and possibly suggest variations for the susannite structure.

While these objectives are primarily crystallographic, it should be pointed out that the lead carbonates, sulphates and hydroxides play a significant role in the lead acid battery chemistry. Structural derivatives where sulphate or hydroxide groups replace Pb in either the tetragonal (litharge) or orthorhombic (massicot) PbO structures comprise intermediate lead sulphates in the production of lead acid batteries (Steele *et al.*, 1997; Steele and Pluth, 1998). Detrimental to lead acid batteries is the formation of lead carbonate-hydroxides including hydrocerussite and plumbonacrite. The mechanism of formation of these phases is not well known, but their presence in battery plates reduces acid permeability within the PbO_2 network and increases the resistivity of the electrolyte (Vinal, 1955). While these two phases commonly occur, one may expect other phases including lead carbonate-sulphate-hydroxides, possibly macphersonite and/or leadhillite, may also form within lead acid batteries. Natural occurrences of lead silicate-carbonate-sulphate-hydroxides have been documented, e.g. kegelite (Dunn *et al.*, 1990), mattheddleite (Livingstone *et al.*, 1987), and an unnamed phase (Cipriani *et al.*, 1995), and given that silica within a lead acid battery is extremely detrimental, one can speculate that these or similar compounds form and effectively prevent normal electrochemical reactions.

From both an academic and industrial point of view, the description of the lead compounds of carbonate, sulphate and hydroxide may prove useful for interpreting both natural and synthetic chemical systems. The natural occurrences of minerals, such as described here, offer advantages because products are available of sufficient size for accurate documentation in contrast to industrial occurrences which are notoriously fine-grained.

Experimental details and structure solution

The occurrence of macphersonite, its relationships to other coexisting lead phases, and its properties have been described by Livingstone and Sarp

(1984). Sufficient material (NMS G 1991-31-21) was available to select a sample for single crystal studies but the common twinning made it difficult to obtain a single crystal. Multiple crystals could usually be recognized optically, but only after confirmation with routine precession photographs was a sample, free of twinning, obtained.

The sample selected for single crystal data collection was a cleavage plate with dimensions given in Table 1. Precession photographs confirmed the space group as *Pcab* with a cell of $a = 9.24$, $b = 23.0$, $c = 10.4$ Å, consistent with data reported by Livingstone and Sarp (1984). Diffractions were sharp with no indication of multiple crystals or twinning. The crystal (complete details in Table 1) was mounted on an automated Picker-Krisel 4-circle diffractometer with b offset $1°$ from the ϕ axis. Refinement using 23 diffractions ($17 < 2\theta < 34°$: $\lambda = 0.71073$ Å), each the average of automatic centring of 8 equivalent settings gave the final cell parameters (Table 1) consistent with

TABLE 1. Experimental details and crystallographic data for macphersonite

(A) Crystal-cell data

a (Å)	9.242(2)
b (Å)	23.050(5)
c (Å)	10.383(2)
V (Å^3)	2211.9(8)
Space group	*Pcab*
Z	8
Formula	$Pb_4SO_4(CO_3)_2(OH)_2$
D_{calc} (g cm^{-3})	6.480
μ (mm^{-1})	60.96

(B) Intensity measurements

Crystal size	$80 \times 55 \times 25$ μm
Diffractometer	Picker, Krisel control
Monochromator	Graphite
Radiation	MoK
Scan type	ω
2θ range	$3.5-55.0$
Diffractions measured	10,206
Unique diffractions	2,556

(C) Refinement of the structure

R 0.053	$R = \Sigma(\|F_o\|-\|F_c\|)/\Sigma\|F_o\|$
R_w 0.121	$R_w = [\Sigma w(\|F_o^2\|-\|F_c^2\|)^2/\Sigma w\|F_o^2\|^2]^{1/2}$
Variable parameters	173
'Goodness of fit' (GOF)	1.1

the precession study. A total of 10,206 intensities were collected with ω step scans, 0.02° steps, 1 sec/step, and a scan width 1.0° for a 2θ range of 3.5–55°. Merging yielded 2,556 intensities (R_{int} = 0.063), all of which were used in refinements: data collection range $h \pm 12$, $k = 0$ to 30, $l \pm 13$; mean intensity variation of 3 standard diffractions = 6%. An analytical absorption correction was applied to the data using the μ value and crystal dimensions in Table 1. Systematic absences indicated space group *Pcab* consistent with the precession study. The initial model was derived from the direct methods programme in SHELXTL[TM] (Trademark of Siemens Energy and Automation, Inc., Analytical Instrumentation, Madison, WI, USA). All Pb atoms were included in a least squares refinement using anisotropic temperature factors, and the S, O, and C positions were located in subsequent difference-Fourier maps and included in the refinement.

In the final model, 173 variables were refined: scale factor, extinction parameter, positions for 19 atoms, and anisotropic displacement factors. Neutral scattering factors found internal to SHELXTL were used. The final least-squares refinement minimized all F^2s with σ_F^2 computed from σI, the square root of [total counts + (2% of total counts)^2], w = $(\sigma_F^2)^{-2}$, R(F) = 0.053, $R_w(F^2)$ = 0.121, S =1.09; largest shift/e.s.d. ~0.002 for all parameters; maximum and minimum heights on final difference-Fourier map are +6.4 and −5.1 e$Å^{-3}$; computer programs: local data reduction, SHELXTL[TM]. Final atomic coordinates and isotropic displacement parameters are given in Table 2, anisotropic displacement parameters in Table 3, and interatomic distances in Table 4.

Discussion of structure

The macphersonite structure can be best represented as a sequence of three types of layers stacked along [010]. Layer A is composed of sulphate tetrahedra, Layer B of lead and OH, and Layer C of lead and carbonate. The stacking sequence is illustrated with a projection parallel to [100] in Fig. 1 and can be described as ...BABCCBABCC... stacking. These same layers will be shown later to occur in the leadhillite structure in which the same stacking sequence occurs. Each layer is illustrated in plan view in Fig. 2a, b and c.

Layer A, composed of sulphate groups is shown in Fig. 2a and it is apparent that the sulphates are arranged on a hexagonal net with an

TABLE 2. Positional and isotropic displacement parameters for macphersonite

Atom	x	y	z	*U_{eq}
Pb (1)	0.06550(5)	0.44671(2)	0.87282(5)	0.0166(2)
Pb (2)	0.39976(6)	0.54944(2)	0.88805(5)	0.0164(2)
Pb (3)	0.13688(6)	0.83923(2)	0.91390(5)	0.0199(2)
Pb (4)	0.53367(6)	0.66070(2)	0.65959(6)	0.0238(2)
S	0.2642(4)	0.7562(1)	0.6177(3)	0.0175(9)
O (1)	0.100(1)	0.3529(4)	0.916(1)	0.024(3)
O (2)	0.388(1)	0.5654(4)	0.6361(9)	0.016(3)
O (3)	0.112(1)	0.4219(4)	0.6375(8)	0.019(3)
O (4)	0.176(1)	0.9255(4)	0.739(1)	0.023(3)
O (5)	0.438(1)	0.6453(4)	0.870(1)	0.023(3)
O (6)	0.180(1)	0.5656(4)	0.741(1)	0.018(3)
O (7)	−0.187(1)	0.4233(4)	0.977(1)	0.022(3)
O (8)	0.734(1)	0.6948(4)	0.851(1)	0.030(3)
O (9)	0.416(1)	0.7648(5)	0.649(1)	0.037(4)
O (10)	0.682(1)	0.5632(4)	0.974(1)	0.017(3)
O (11)	0.238(1)	0.7650(4)	0.478(1)	0.028(3)
O (12)	0.172(2)	0.7949(6)	0.691(1)	0.045(4)
C (1)	0.248(1)	0.5648(5)	0.634(1)	0.011(3)
C (2)	0.251(1)	0.9237(6)	0.633(1)	0.014(3)

*U_{eq} is defined as $1/3 \sum_{i=1}^{3} \sum_{j=1}^{3} U_{ij} a_i^* a_j^* (\mathbf{a}_i \cdot \mathbf{a}_j)$

TABLE 3. Anisotropic displacement parameters for macphersonite

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pb (1)	0.0111(3)	0.0179(3)	0.0208(3)	−0.0002(2)	−0.0002(2)	0.0006(2)
Pb (2)	0.0122(3)	0.0182(3)	0.0187(3)	0.0009(2)	−0.0005(2)	0.0003(2)
Pb (3)	0.0174(3)	0.0180(3)	0.0242(3)	−0.0011(2)	−0.0034(2)	−0.0027(2)
Pb (4)	0.0188(3)	0.0222(3)	0.0303(3)	0.0027(2)	0.0024(2)	−0.0030(2)
S	0.011(2)	0.017(2)	0.025(2)	−0.001(1)	−0.002(1)	−0.001(1)
O (1)	0.014(5)	0.014(4)	0.044(7)	−0.001(4)	−0.006(5)	0.007(4)
O (2)	0.003(4)	0.026(5)	0.020(5)	−0.002(4)	0.001(3)	0.001(4)
O (3)	0.012(4)	0.037(5)	0.006(4)	0.000(4)	0.001(3)	−0.003(4)
O (4)	0.009(5)	0.040(5)	0.020(5)	−0.004(4)	0.002(4)	0.003(4)
O (5)	0.020(5)	0.015(5)	0.033(6)	0.001(4)	0.004(5)	0.002(4)
O (6)	0.011(4)	0.021(4)	0.022(5)	0.009(4)	0.004(4)	0.003(4)
O (7)	0.010(4)	0.031(5)	0.024(5)	−0.001(4)	−0.005(4)	0.003(4)
O (8)	0.033(6)	0.023(5)	0.036(6)	−0.009(5)	0.002(5)	−0.010(5)
O (9)	0.019(6)	0.033(6)	0.059(8)	0.011(6)	−0.010(6)	−0.014(5)
O (10)	0.014(5)	0.017(4)	0.020(5)	−0.002(4)	0.008(4)	0.001(4)
O (11)	0.035(6)	0.020(5)	0.028(6)	0.001(4)	−0.001(5)	0.001(4)
O (12)	0.059(9)	0.052(7)	0.023(6)	−0.012(5)	−0.006(6)	0.026(7)
C (1)	0.011(5)	0.001(4)	0.021(6)	0.000(4)	0.002(5)	0.000(4)
C (2)	0.008(5)	0.014(6)	0.019(6)	0.006(5)	0.003(5)	−0.003(4)

alternation of up or down pointing tetrahedra along [001]. Layer A is sandwiched between two B, or Pb-OH layers, one of which is shown in Fig. 2*b*. In any B layer, the Pb atoms form an approximate hexagonal array with each Pb atom approximately equidistant from three sulphate groups of layer A. The other half of the possible positions in layer B, which are again approximately equidistant from 3 layer A sulphate groups, are occupied by OH groups also in an

TABLE 4. Bond lengths (Å) for macphersonite (Pb$_4$SO$_4$(CO$_3$)$_2$(OH)$_2$)

| Pb (1) − O (1)	2.232(9)	Pb (2) − O (5)	2.245(10)	Pb (3) − O (1)	2.452(10)
− O (3)	2.545(9)	− O (7)	2.495(10)	− O (12)	2.549(11)
− O (4)	2.563(10)	− O (6)	2.570(10)	− O (10)	2.566(9)
− O (7)	2.628(10)	− O (2)	2.644(9)	− O (11)	2.661(10)
− O (2)	2.781(9)	− O (3)	2.675(9)	− O (4)	2.715(10)
− O (4)	2.807(10)	− O (10)	2.779(10)	− O (8)	2.721(12)
− O (10)	2.829(10)	− O (6)	2.937(10)	− O (9)	2.747(11)
		− O (10)	3.060(9)	− O (5)	2.922(10)
				− O (3)	3.033(10)
Pb (4) − O (5)	2.385(10)	C (1) − O (10)	1.27(2)	S − O (12)	1.449(12)
− O (2)	2.587(9)	− O (6)	1.28(2)	− O (9)	1.450(11)
− O (9)	2.637(12)	− O (2)	1.30(2)	− O (8)	1.480(10)
− O (6)	2.772(9)			− O (11)	1.488(11)
− O (8)	2.826(12)				
− O (1)	2.831(12)	C (2) − O (3)	1.27(2)		
− O (8)	2.879(11)	− O (7)	1.29(2)		
− O (11)	2.922(11)	− O (4)	1.30(2)		
− O (7)	3.059(10)				
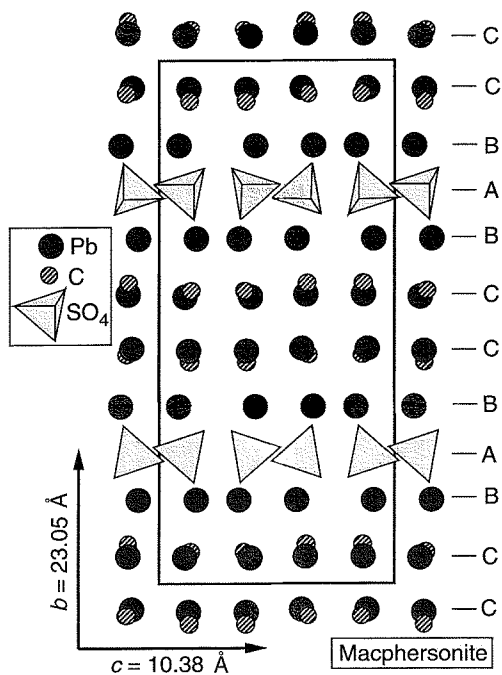
FIG. 1. Projection of Pb, C and SO_4 parallel to [100]. Clearly shown are three types of layers: A – SO_4 groups; B – Pb and OH; and C – Pb and C. The sequence of layer stacking is ....CCBABCCBA....
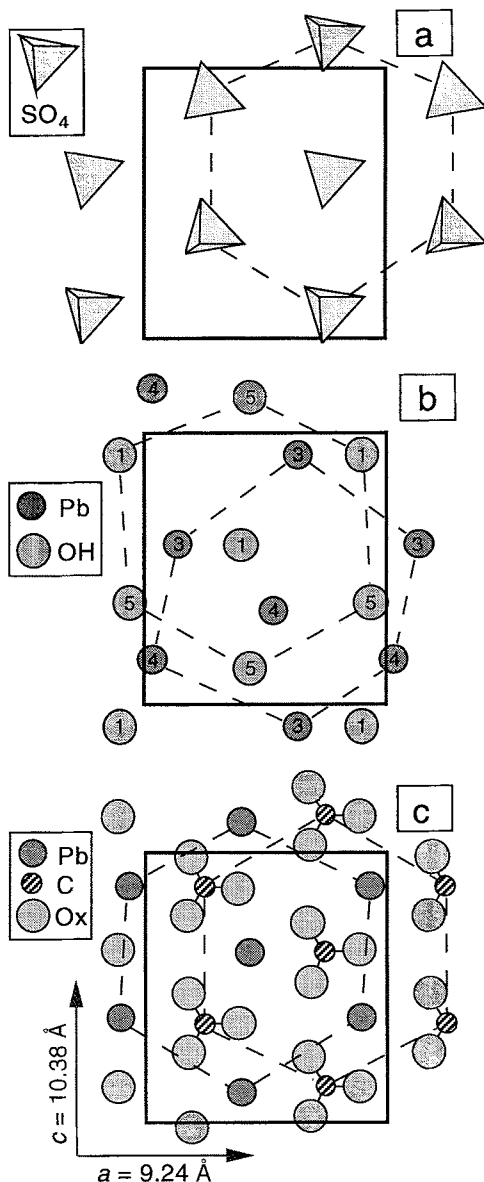

FIG. 2. (a) Layer A, (b) Layer B, and (c) Layer C in plan view by projection parallel to [010]. In (a) the SO_4 groups are in an hexagonal net as outlined by the dashed lines. Likewise in (b) the Pb atoms, Pb3 and Pb4, like the SO_4 groups in (a), lie in a distorted hexagonal net shown by the dashed lines with each Pb centred among three SO_4 groups in the adjacent A layer. Nearly coplanar with the Pb are OH groups, O1 and O5, also centred among three SO_4 units. In (c) the hexagonal net repeats for both Pb and CO_3 as indicated by dashed lines.
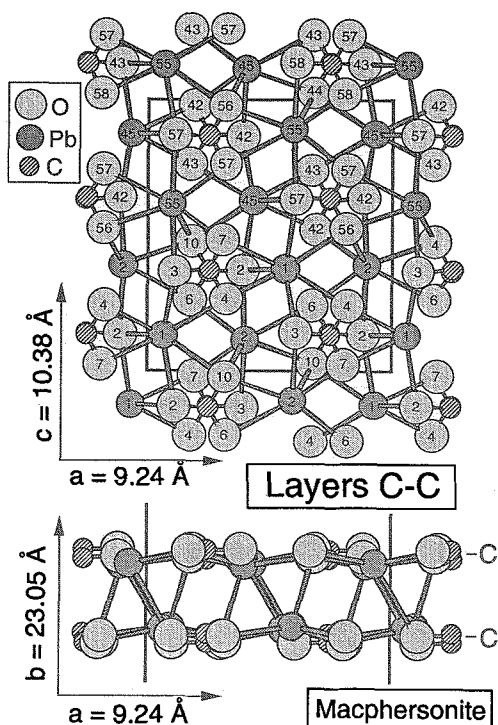
hexagonal array. In the B layer on the opposite side of layer A, Pb and OH have the same configuration but with Pb and OH interchanged.

Layer C is shown in Fig. 2c and can be considered as interpenetrating hexagonal nets of Pb and CO_3 groups. This geometry is virtually identical to that found in cerussite, $PbCO_3$ (Sahl, 1974). The two C Layers together are shown in Fig. 3 and basically reproduce a slab of the cerussite structure and might be considered as an 'anchor unit' because this unit is also found in both the hydrocerussite (Steele et al., 1998) and plumbonacrite structures (Cowley, 1955; Olby, 1966).

To better understand the crystal chemistry and physical properties of macphersonite it is helpful to consider the charges of the A, B and C layers. The A layer contains SO_4 groups with a charge of -2. Two B layers containing $Pb(OH)^+$ sandwich the A layer and together produce a neutral slab. Two C layers of $PbCO_3$, also neutral, bridge two B-A-B slabs. The weak connection between these slabs leads to the perfect {010} cleavage.

Comparison with leadhillite and cerussite

The leadhillite cell dimensions (a = 9.11, b = 20.82, c = 11.59 Å, β = 90.46°) show a close similarity to those of macphersonite with $a_{lead} \approx$ ½b_{mac}, $b_{lead} \approx 2c_{mac}$, $c_{lead} \approx a_{mac}$, and $\beta_{lead} \approx$ 90° (Giuseppetti *et al.*, 1990). The leadhillite structure is schematically shown in Fig. 4 and can be compared directly with Fig. 1. Other than the reorientation and changes in cell dimensions, the same layer sequence ...BABCCBABCC... is apparent. The double Pb-CO₃ units (Layers CC) are topologically equivalent to those of macphersonite and cerussite (Sahl, 1974).

Figure 5 (bottom) shows a comparison of the coordination within the carbonate layer (Layer C) for macphersonite and leadhillite looking perpendicular to this layer. All Pb atoms (Pb1

and Pb2 in macphersonite and Pb1 through Pb4 in leadhillite), are surrounded by six oxygens from CO₃ groups in the plane of Layer C. In these views, each Pb has an OH directly below and three oxygens above but only those with Pb-O less than 3.20 Å are shown. Thus each Pb in Layer C has nearly identical coordination geometry. Leadhillite shows marginally longer C-O bonds within the C Layer (average = 1.314 Å, range = 1.27 to 1.36 Å) than in macphersonite (average = 1.284 Å, range = 1.27 to 1.30 Å) or cerussite (average = 1.27 Å). Likewise, the Pb-O bonds in the plane of Layer C in leadhillite are on average (24 Pb-O distances average 2.672 Å) almost identical to those in macphersonite (12 Pb-O distances average 2.688 Å) and cerussite (6 Pb-O distances average 2.713 Å). All Pb-O bond lengths for Pb-OH which range from 2.20 to 2.27 Å in leadhillite are similar to those in macphersonite (2.23 to 2.25 Å).

Details of Layer B in both macphersonite and leadhillite are illustrated in Fig. 5 (top). For macphersonite the environment for both Pb3 and Pb4 is similar with 9-fold coordination: three oxygens of three CO₃ groups, four oxygens from sulphate groups, and two OH groups. For leadhillite the situation is more complex with Pb7 and Pb8 having the same number and type of coordinating oxygens as in macphersonite; however, Pb6 is nine coordinated with three oxygens from three CO₃ groups, five from sulphate groups and one OH while Pb5 is eight coordinated with three oxygens from three CO₃ groups, two from sulphate groups, and three OH. These coordinations are based on Pb-O distances less than 3.20 Å; greater coordination is present if longer bond lengths are considered.

A comparison of Layer A is illustrated in Fig. 6 and possibly shows the most significant differences between macphersonite and leadhillite. For each phase the sulphate groups can be considered to either point up (U) or down (D). For leadhillite a row of sulphate tetrahedra parallel to [010] shows the sequence ...UDDUUDDU... whereas in macphersonite the sequence along [001] is ...UDUDUDUD... This doubling of the sulphate repeat appears to be the major factor causing a doubling of the cell length in leadhillite with the additional effect of creating different coordination geometries about the Pb atoms of Layer B (see previous paragraph) in contrast to macphersonite where the coordination geometries for all Pb in Layer B is similar.
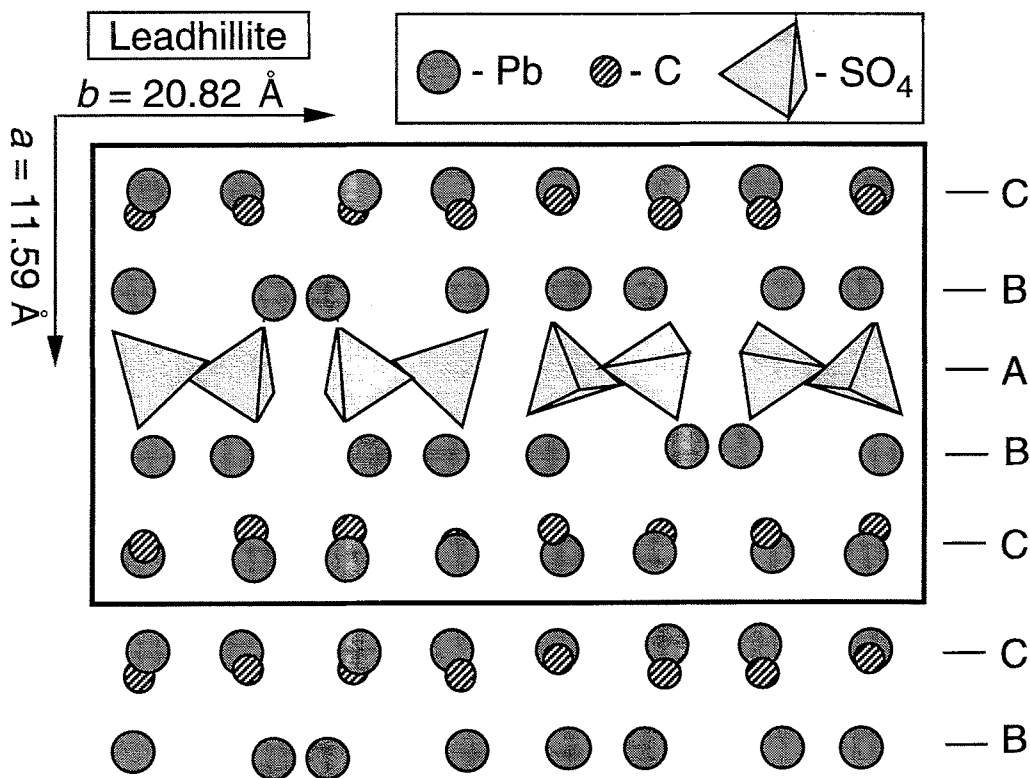
FIG. 4. The layer structure of leadhillite which can be compared with macphersonite of Fig. 1. This view clearly shows the ....CCBABCCBA.... layer sequence, identical to macphersonite.

Discussion

The above comparison of these two polymorphs has shown that they are composed of three similar units. The double carbonate sheet is nearly identical in the two structures and forms the backbone. This similarity was also recognized in the infrared spectra. The sulphate layer clearly differs between the two and is the reason for cell doubling. The differences between leadhillite and heated leadhillite have also been attributed to the relative relations of the sulphate tetrahedra while the carbonate backbone unit maintains with near-constant geometry. While the structure of susannite, the trimorph of leadhillite and macphersonite has not been determined, the reported hexagonal cell with a = 9.072 and c = 11.539 Å (Livingstone and Russell, 1985) suggests very strong relationships both dimensionally and geometrically to both leadhillite and macphersonite. We have noted the

strong hexagonal relationships in all layers of both these phases and this was also recognized by Giuseppetti et al. (1990). A major violation of the trigonal geometry is the orientation of the sulphate groups, not their position. To attain trigonal symmetry for either macphersonite or leadhillite a reorientation of sulphate tetrahedra must be made. Heating leadhillite to about 80°C as demonstrated by several studies (Mrose and Christian, 1969; Giuseppetti et al., 1990; Milodowski and Morgan, 1984) gives subtle changes in the diffraction pattern and a trigonal phase thought to be susannite. This heating may result in a minor displacement of the sulphates to give the higher symmetry also recognized in the infrared absorption. Macphersonite, on the other hand, would be more difficult to transform to susannite due to its doubled b and the two different sulphate layers in this larger cell. We propose to next investigate the susannite structure.
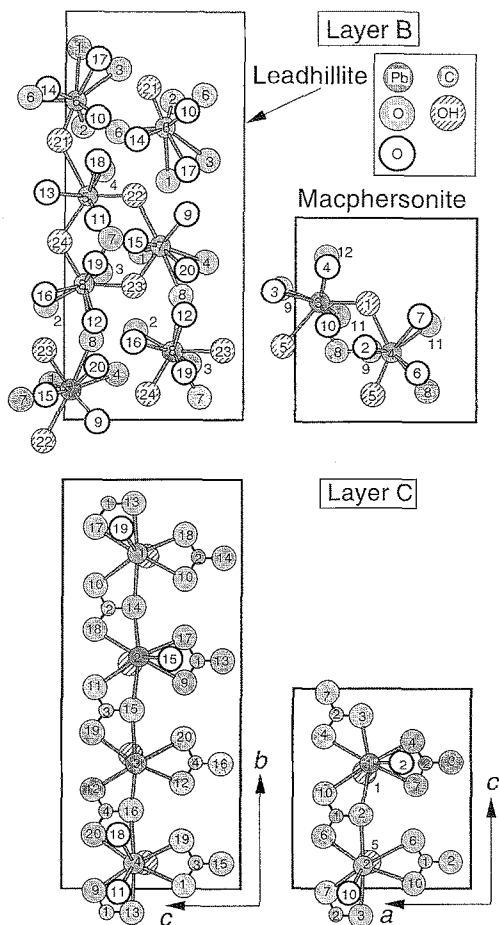
FIG. 5. Coordination details within layers B and C of leadhillite and macphersonite. Within layer B of macphersonite, Pb3 and Pb4 have similar coordination with three oxygens (unfilled symbols) shared with CO₃ groups, four oxygens shared with SO₄ groups, and two OH. For leadhillite, Pb7 and Pb8 have coordination as in macphersonite. Pb6 and Pb7 coordinate to three oxygens of CO₃ groups, but Pb6 includes five oxygens from sulphates and one OH while Pb5 includes 2 oxygens from sulphates and 3 OH. Only Pb-O bonds of 3.20 Å or less are considered. For layer C of macphersonite, each Pb is surrounded by three nearly coplanar carbonate groups, in addition to an OH directly below and oxygens (unfilled symbols) above only shown if Pb-O less than 3.20 Å. The numbers on the atoms represent sequential assignment for each atom type for leadhillite (Giuseppetti *et al.*, 1990), or from the present Table 2 for macphersonite. Views are shown perpendicular to the layers.
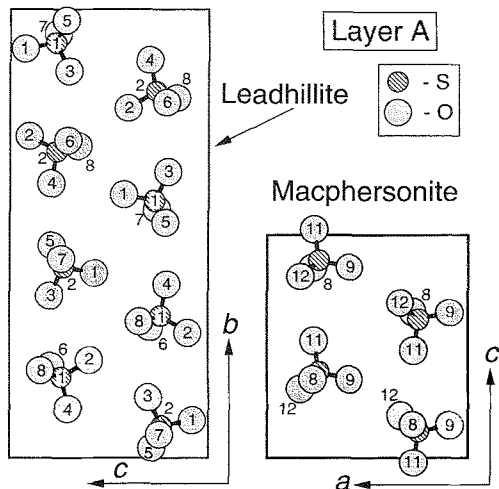
FIG. 6. Comparison of layer A for macphersonite and leadhillite. An important difference is the sequence of orientations of these tetrahedra. In macphersonite the up-down sequence along [001] is ..UDUD.. while in leadhillite the sequence is ..UDDUUDD.. which effectively doubles *b*.

Acknowledgements

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