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Raman spectroscopy of lead sulphate-carbonate minerals – implications for hydrogen bonding

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Abstract

The Raman spectrum of the basic carbonate-sulphate minerals known as leadhillite, susannite and caledonite have been measured and the spectra compared with the Raman spectra of cerussite, hydrocerussite and anglesite. Characteristic spectral patterns are observed for each mineral. The wavenumber position of the hydroxyl stretching bands is used to estimate the hydrogen bond distances in the minerals. The hydrogen bond distances for leadhillite polymorphs vary from 2.783 to 2.916 Å. In comparison the estimated hydrogen bond distances for hydrocerussite are much longer with values of 2.961 and 3.127 Å. The width of the hydroxyl stretching vibration provides an estimate of the variation of hydrogen bond distances for the OH groups in the mineral. The variation in bond length is greater for the longer hydrogen bonds. Characteristic sulphate and carbonate vibrations are also identified.

Keywords: leadhillite, susannite, caledonite, macphersonite, cerussite, hydrocerussite, Raman spectroscopy

INTRODUCTION

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Many minerals can be formed through the acidic aqueous oxidation of lead in the presence of carbon dioxide. (GEE, C. et al., 1997; LIVINGSTONE, A. and SARP, H., 1984; PAAR, W. H. et al., 1986; REWITZER, C. and HOCHLEITNER, R., 1989; RUESENBERG, K. A. and PAULIS, P., 1996) This lead corrosion can result in the formation of mixed anionic and cationic species such as leadhillite ($\text{Pb}_4\text{SO}_4(\text{CO}_3)_2(\text{OH})_2$) and its polymorphs susannite and macphersonite and caledonite ($\text{Cu}_2\text{Pb}_5(\text{SO}_4)_3(\text{CO}_3)(\text{OH})_6$). The structure of many of these minerals has been known for some time. (PALACHE, C., 1911; PALACHE, C. and GOLDSCHMIDT, V., 1911; PALACHE, C. and LA FORGE, L., 1909; PALACHE, C. and LA FORGE, L., 1911; RICHMOND, W. E. and WOLFE, C. W., 1938) Other minerals than may form are lanarkite and hydrocerussite. The mineralogy and weathering of historical lead slags and polluted soils from five historical smelting sites in Britain were examined using SEM with energy dispersive X-ray spectroscopy (SEM/EDX). (GEE, C. et al., 1997) Indeed the mineral diversity is caused by different composition of sources, age of slags, and different storage. Some sixty two phases were found in the slags. The most abundant phases were sulfates, carbonates, and oxides, followed by arsenates, phosphates, chlorides, sulfides, and elements. (RUESENBERG, K. A. and PAULIS, P., 1996) The sulphates of lead are formed in the oxide zones of base metal sulphides. Many complex species as with those of copper may form. The mixed anionic species (sulphate/carbonate) may form according to the partial pressure of carbon dioxide. Studies of the chemistry of formation of these minerals are very rare.

		Space group	<i>a</i>	<i>b</i>	<i>c</i>	β	<i>Z</i>
Leadhillite	monoclinic	$P2_1/a$	9.08	20.76	11.56	89.88	8
Susannite	trigonal	$P\bar{3}$	9.05		11.54		3
Macphersonite	monoclinic	$Pcab$	10.38	23.10	9.53		8
Caledonite	orthorhombic	$Pmn2_1$	20.088	7.1436	6.542		2
Hydrocerussite	trigonal	Not known	5.24		23.74		3

Table 1 Unit cell summary for leadhillite, susannite, macphersonite, caledonite and hydrocerussite (GIACOVAZZO, C. et al., 1970; GIACOVAZZO, C. et al., 1973; GIUSEPPETTI, G. et al., 1990; STEELE, I. M. et al., 1998; STEELE, I. M. et al., 1999)

The crystal structure of leadhillite and its polymorphs susannite and macphersonite are monoclinic. (GIUSEPPETTI, G. et al., 1990) The space groups and structural dimensions are given in **Table 1**. Leadhillite shows a clear trigonal pseudo-symmetry in a sub-cell. Leadhillite has a (001) layer structure with pairs of centrosymmetric carbonate sheets, each of them being formed by $8(\text{PbCO}_3)$, alternating with pairs of centrosymmetric sulfate sheets, each of them being formed by $8[\text{Pb}(\text{SO}_4)0.5\text{OH}]$. The arrangements of the atoms in the carbonate sheet are practically coherent with the trigonal symmetry: and all Pb atoms are surrounded by 9 carbonate O, and, with a short bond (2.2 Å), by 1 OH of the sulfate sheet. On the other hand, the atomic arrangements in the sulfate sheet deviate from the trigonal symmetry. (GIUSEPPETTI, G. et al., 1990) Susannite is composed of SO_4 (= A), Pb (= B), and Pb- CO_3 (= C) layers. (STEELE, I. M. et al., 1999) The stacking sequence of these layers along [001] is ...ABCCBABCCB... and is the same sequence found in the other trimorphs. The two C layers are equivalent to a slab of cerussite. The clear difference among the trimorphs is the relative orientation of SO_4 tetrahedra within the layer A. The crystal structure of **macphersonite** has many features in common with its polymorph leadhillite including three distinct types of layers. Layer A includes sulfate tetrahedra, Layer B is composed of Pb and OH, whereas Layer C is composed of Pb and CO_3 with topologically identical to that in cerussite. In both macphersonite and leadhillite these layers are stacked along [010] as ...BABCCBABCC... The sulfate layer shows the greatest difference between the two structures and can be described by a pattern of up or down pointing tetrahedra. **Caledonite** is orthorhombic. The CO_3 and SO_4 groups provide the connections among the Pb polyhedra, and between these and the Cu-O chains (GIACOVAZZO, C. et al., 1973).

The vibrational spectroscopy of cerussite and anglesite has been reported. (COLEYSHAW, E. E. et al., 1994) The infrared spectrum of the three polymorphs leadhillite, susannite and macphersonite has also been reported. (RUSSELL, J. D. et al., 1984) The spectra were found to be very similar but could be used to distinguish

between the minerals. The complexity of the IR absorption spectra was found to change with the structure and symmetry of the polymorphs. The frequency of the OH stretching band was found to increase, appearing at 3462, 3474, and 3484 cm^{-1} , in the series susannite, leadhillite and macphersonite. Well-resolved carbonate and sulphate vibrations were observed. In this work, a Raman spectroscopic study of the mixed anionic minerals of lead and lead-copper is made and a comparison is made with the spectra of cerussite, hydrocerussite and anglesite.

EXPERIMENTAL

Minerals:

The minerals were obtained from the Mineralogical Research Company. Leadhillite and caledonite originated from the Hard Luck Claim, near Baker, San Bernardino County, California. Susannite originated from the Herzog Julius Shaft, Astfeld, Schlackental, Harz Mountains, Germany.

Raman microprobe spectroscopy

The crystals of the minerals were placed and orientated on a polished metal surface on the stage of an Olympus BHSM microscope, which is equipped with 10x and 50x objectives. The microscope is part of a Renishaw 1000 Raman microscope system, which also includes a monochromator, a filter system and a Charge Coupled Device (CCD). Raman spectra were excited by a Spectra-Physics model 127 He-Ne laser (633 nm) at a resolution of 2 cm^{-1} in the range between 100 and 4000 cm^{-1} . Repeated acquisition using the highest magnification were accumulated to improve the signal to noise ratio in the spectra. Spectra were calibrated using the 520.5 cm^{-1} line of a silicon wafer. Spectroscopic manipulation such as baseline adjustment, smoothing and normalisation were performed using the Spectracalc software package GRAMS (Galactic Industries Corporation, NH, USA). Band component analysis was undertaken using the Jandel 'Peakfit' software package, which enabled the type of fitting, function to be selected and allows specific parameters to be fixed or varied accordingly. Band fitting was done using a Gauss-Lorentz cross-product function with

the minimum number of component bands used for the fitting process. The Gauss-Lorentz ratio was maintained at values greater than 0.7 and fitting was undertaken until reproducible results were obtained with squared correlations of r^2 greater than 0.995.

RESULTS AND DISCUSSION

The Raman spectra of the hydroxyl stretching region of the selected multi-anionic minerals leadhillite, susannite, caledonite, hydrocerussite together with the cerussite (lead carbonate) and anglesite (lead sulphate) minerals are shown in **Figure 1**. The spectroscopic analysis of the data is reported in **Table 2**. The Raman spectrum of leadhillite in this region shows two bands at 3481 and 3386 cm^{-1} with band widths of 28.0 and 72.0 cm^{-1} respectively. Studies have shown a strong correlation between OH stretching frequencies and both the O \cdots O bond distances and with the H \cdots O hydrogen bond distances. (EMSLEY, J., 1980; LUTZ, H., 1995; MIKENDA, W., 1986; NOVAK, A., 1974) The elegant work of Libowitzky (1999) showed that a regression function could be employed relating the above correlations with regression coefficients better than 0.96. (LIBOWITZKY, E., 1999) Two types of OH units are identified in the structure and the known hydrogen bond distances used to predict the hydroxyl stretching frequencies. In this work we have used the Libowitzky function to predict hydrogen bond distances for the OH units in the crystal structure. In this way we calculate the hydrogen bond distances by the use of the Raman hydroxyl stretching bands. The data in **Table 3** fundamentally distinguishes between types of OH units according to the hydrogen bond distances, namely strongly hydrogen bonded and weakly hydrogen bonded. (LIBOWITZKY, E., 1999) To the best of our knowledge, no neutron diffraction studies of these minerals have been forthcoming and hence no hydrogen bond distances are known. Such information may also be obtained from well-performed X-ray diffraction studies. In this set of data, the hydroxyl stretching frequencies have been used to predict the hydrogen bond distances for these minerals and by using the band width of the hydroxyl stretching frequencies estimates of the variation in the hydrogen bond distances predicted.

The predicted hydrogen bond distances for the three polymorphs leadhillite, susannite and caledonite vary between 2.783 and 2.916 Å (**Table 3**). These hydrogen

bond distances are a function of the distances between the sulphate and carbonate sheets. In contrast the predicted hydrogen bond distances for hydrocerussite are 3.127 and 2.961 Å. These hydrogen bonds are long. It is suggested that the carbonate sheets for hydrocerussite are further apart in comparison with leadhillite. For each of the minerals it is apparent there are at least two hydrogen bonds. One bond is long compared with the other. **Table 3** also shows the variation in hydrogen bond distances as might be predicted from the width of the hydroxyl stretching band. For leadhillite, for the wavenumber position of 3481 cm⁻¹ the estimated hydrogen bond distance with variation of $\pm 0.02\text{Å}$. For the longer hydrogen bond the variation in hydrogen bond length is $\pm 0.052\text{ Å}$. For caledonite the variation of the 2.828 Å hydrogen bond is $\pm 0.032\text{ Å}$. The variation in bond length is greater for the longer hydrogen bonds.

Mineral		Observed Raman band positions (cm ⁻¹) $\pm 2\text{ cm}^{-1}$	Estimated hydrogen bond distance (Å)	Estimated hydrogen bond distance variation (Å)
leadhillite	OH 1	3481	2.87 ₁	2.85 ₁ to 2.89 ₅
	OH 2	3386	2.78 ₉	2.73 ₇ to 2.87 ₆
susannite	OH 1	3513	2.91 ₆	2.85 ₀ to 3.04 ₇
	OH 2	3377	2.78 ₃	2.75 ₆ to 2.81 ₈
caledonite	OH 1	3439	2.82 ₈	2.79 ₆ to 2.87
	OH 2	3417	2.81 ₁	2.80 ₃ to 2.81 ₇
	OH 3	3379	2.78 ₅	2.77 ₅ to

				2.79 ₆
hydrocerussite	OH 1	3576	3.12 ₇	3.00 ₂ to 3.34 ₈
	OH 2	3536	2.96 ₁	2.92 ₅ to 3.00 ₂

Table 3 Correlation between hydroxyl stretching frequencies and estimated hydrogen bond distances.

In comparison to the Raman spectrum of the hydroxyl stretching region of leadhillite, the spectrum of the hydroxyl stretching region of susannite shows complexity with multiple bands observed. The crystal structure of susannite is composed of layers of SO₄ (= A), Pb (= B), and Pb-CO₃ (= C) layers with the stacking sequence of these layers along [001] is ...ABCCBABCCB. The observation of complexity in this region is attributed to disordering in this stacking sequence. If the Theory of Libowitzky applies to Raman hydroxyl stretching bands (the original work applied the relationship between OH band position as measured using infrared spectroscopy and H-bond distances) then the multiple bands for susannite would suggest that multiple hydrogen bond distances are observed.

The Raman spectrum of the hydroxyl stretching region of caledonite more closely resembles that of leadhillite. Bands are observed at 3439, 3417 and 3379 cm⁻¹. Such hydroxyl stretching wavenumbers would suggest that the H-bond distances for the OH units for caledonite are 2.823, 2.810 and 2.785Å which are in agreement with expected hydrogen bond distances. For hydrocerussite two hydroxyl stretching bands are observed at 3576 and 3536 cm⁻¹. These wavenumber positions would indicate hydrogen bond distances of 3.126 and 2.961 for the hydrogen bonds formed between the OH units and the carbonate units in hydrocerussite. The infrared bands for hydrocerussite are almost in an identical position to that of the Raman bands. Thus the use of Raman OH stretching bands for the calculation of hydrogen bond distances is justified.

In the Raman spectrum of the 800 to 1500 cm^{-1} region bands are observed which are attributable to the CO and SO stretching (Figure 2 and Table 2). The SO_4 stretching band for anglesite is observed at 978 cm^{-1} which compares well with the position of the bands at 964 cm^{-1} for leadhillite and 977 cm^{-1} for caledonite. The Raman spectrum of caledonite shows an additional band at 950 cm^{-1} . The Raman spectrum of anglesite shows low intensity bands at 1060, 1068, 1135, 1141 and 1156 cm^{-1} . The position of these bands is in excellent agreement with published data. (COLEYSHAW, E. E. et al., 1994; CRANE, M. J. et al., 2001; GRIFFITH, W. P., 1970) The first two bands are assigned to the A_g modes and the last three to the B_g modes. There is some difficulty in finding the position of these bands for the mixed anionic carbonate-sulphate minerals because of the intense CO_3 stretching bands. Low intensity bands are observed for leadhillite at 1014, 1030, 1097 and 1174 cm^{-1} . These bands may be assigned to SO_4 v_3 vibrational modes. These bands are broad with bandwidths of 8.8, 20.1, 17.2, 22.1 cm^{-1} respectively. For susannite bands are observed at 1012, 1026, 1105 and 1154 cm^{-1} . For caledonite bands are observed at 1101 and 1124 cm^{-1} .

The Raman spectrum of cerussite shows an intense band at 1054 cm^{-1} assigned to the CO_3 symmetric stretching vibration. For cerussite the antisymmetric CO_3 stretching bands are observed at 1360, 1376, 1424 and 1477 cm^{-1} . The Raman spectrum of hydrocerussite shows an intense band at 1053 cm^{-1} , attributed to the CO_3 symmetric stretching vibration. A similar intense band is observed for leadhillite at 1054 cm^{-1} . Low intensity bands are observed for susannite and caledonite at 1048 and 1053 cm^{-1} . These two minerals are on a rock matrix and the reason why the intensity of the bands is low is ascribed to orientation effects. The Raman spectrum of hydrocerussite displays bands at 1365, 1375, 1378, 1420 and 1479 cm^{-1} . The bands are attributed to v_3 antisymmetric stretching vibrations. For leadhillite a single band at 1375 cm^{-1} is observed. A very low intensity band is observed in this position for susannite and for caledonite two bands are observed at 1358 and 1392 cm^{-1} . A number of bands are observed for both hydrocerussite and caledonite in the 1674 to 1736 cm^{-1} region. These bands are attributed to overtones and combination bands.

The Raman spectra of the low wavenumber region are reported in Figure 3. For anglesite two sets of bands are observed at 361, 440 and 451 cm^{-1} and at 608, 620

and 642 cm^{-1} . The bands are assigned to the ν_2 and ν_4 vibrational modes. The position of the bands is in excellent agreement with published data. (COLEYSHAW, E. E. et al., 1994; CRANE, M. J. et al., 2001; GRIFFITH, W. P., 1970) For leadhillite the out-of-plane bending modes are observed at 599 and 626 cm^{-1} . The in-plane bending modes are observed at 428 and 458 cm^{-1} . The Raman spectrum of susannite shows bands at 602 and 628 cm^{-1} and at 427 , 450 , 427 and 497 cm^{-1} for these vibrational modes. Similarly the Raman spectrum of caledonite shows bands at 426 , 456 and 475 cm^{-1} and at 605 and 628 cm^{-1} . For cerussite two sets of bands are observed at 669 , 674 , 681 and 694 cm^{-1} and at 815 , 825 and 838 cm^{-1} . These two sets of bands are attributed to the ν_4 and ν_2 vibrational modes. For hydrocerussite, bands are observed at 671 , 681 and 694 cm^{-1} and at 837 , 866 and 887 cm^{-1} . In comparison for leadhillite bands are observed at 599 and 626 cm^{-1} and also at 852 and 859 cm^{-1} . For caledonite, ν_2 bands are observed at 825 and 848 cm^{-1} .

CONCLUSIONS:

Raman spectroscopy has enabled the spectroscopic analysis of the basic lead carbonate and sulphate minerals. Each phase has its own characteristic Raman spectrum enabling identification. Raman spectroscopy allows the hydroxyl unit OH stretching vibrations of the four minerals to be obtained. The position of the OH stretching vibrations was used to estimate the hydrogen bond distances in the mineral structure. Such measurements are normally obtained from well-performed X-ray diffraction or neutron diffraction studies. The significance of this work rests with the identification of these phases on the surfaces of the corroded products of lead. Such corrosion products may be identified in old slag heaps and old water pipes.

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Table 2 Raman spectroscopic analysis of the minerals leadhillite, susannite, caledonite, hydrocerussite, cerussite and anglesite

Leadhillite Pb₄SO₄(CO₃)₂(OH)₂	Susannite Pb₄SO₄(CO₃)₂(OH)₂		Caledonite Pb₅Cu₂(SO₄)₃(CO₃)(OH)₆		Hydrocerussite Pb₃(CO₃)₂(OH)₂		Cerussite PbCO₃		Anglesite PbSO₄	
	Raman	Raman	Raman	Raman	Raman	Raman	Raman	Raman	Infrared	Raman
3481 3386	3630 3550 3513 3447 3377 3307 3241 3179	3439 3417 3379		3576 3536						
1719 1704 1674		1674		1736 1705 1679	1731					
1375		1392 1358		1479 1420 1378 1375 1365	1446		1477 1424	1484		
1097	1154 1105	1124 1109 1083			1381		1376 1360	1369		
1054 1016	1048 1026 1011	1053		1053 1031	1060		1054 1031	1053		1060 1068 1135 1141 1156
964	964	977 950								978 841

856			848	887		834	838		
703			825	866			825		
677			791	837			815		
			722	737					
626		628	628	694			694	698	
599		602	605	681				685	
				671				678	
		497							642
458		470	475	417		675	681		620
428		450	456	391			674		608
		427	427	376					
360		393		318			669		
307		363	344						
262			316						
			278						
			251						
220		239	229	221			470		451
195		203	152	177			396		440
173				152			380		361
							244		
							233		
							227		
							217		
							175		
							147		
							145		
							131		

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Figure 3 Raman spectra of the low wavenumber region of (a) leadhillite (b) susannite (c) caledonite (d) hydrocerussite (e) anglesite

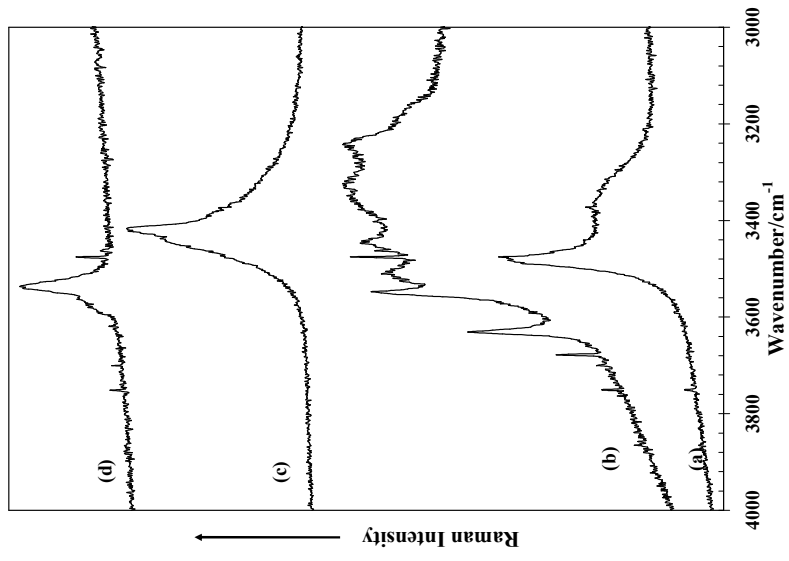


Figure 1

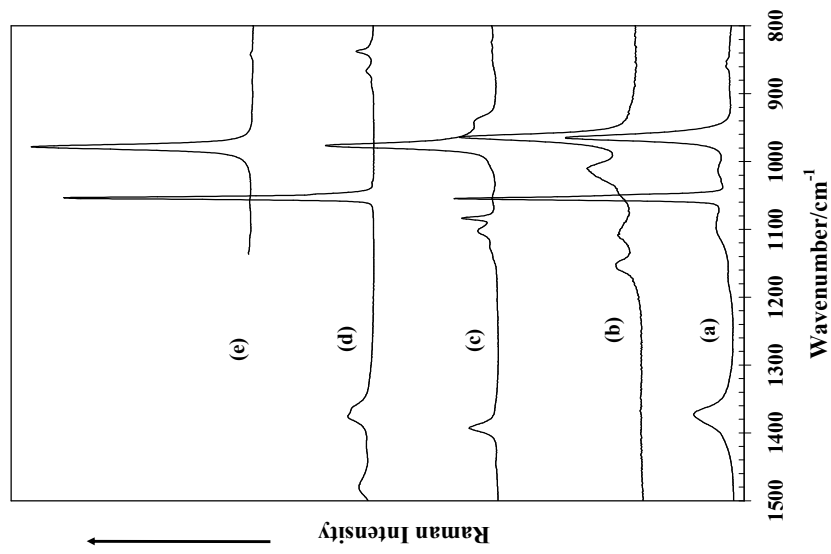


Figure 2

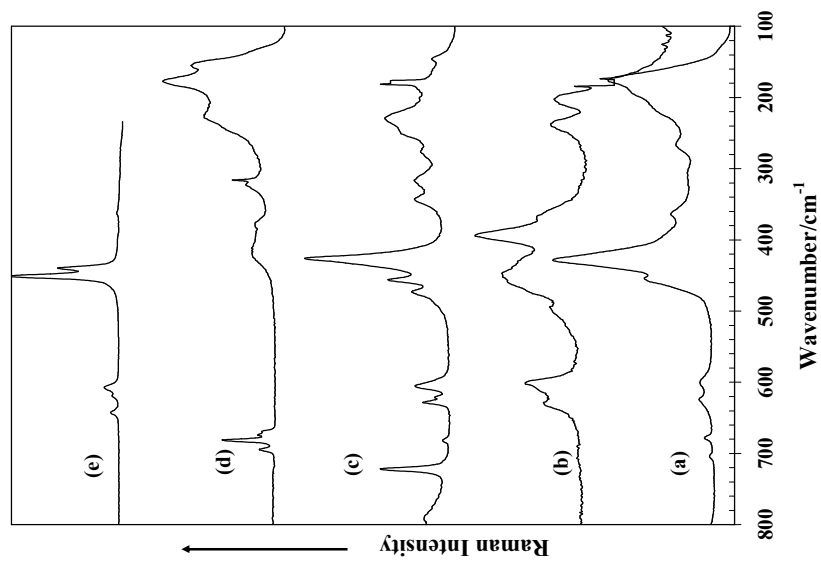


Figure 3

