

Chenite, $\text{Pb}_4\text{Cu}(\text{SO}_4)_2(\text{OH})_6$, a new mineral, from Leadhills, Scotland

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ABSTRACT. Chenite, a new lead-copper secondary mineral, has been found on specimens from the Leadhills area, Scotland. It is associated with caledonite, linarite, leadhillite, susannite, and other species, on oxidized galena with chalcopyrite. Electron microprobe analysis yielded PbO 74.5, CuO 7.8, SO_3 13.3, H_2O 4.4 (by difference), sum = 100 wt. %. The empirical formula (based on 14 oxygens) is $\text{Pb}_{3.98}\text{Cu}_{1.17}\text{S}_{1.98}\text{O}_{14}\text{H}_{5.82}$; the ideal formula is $\text{Pb}_4\text{Cu}(\text{SO}_4)_2(\text{OH})_6$, which requires PbO 75.2, CuO 6.7, SO_3 13.5, H_2O 4.6, sum = 100 wt. %.

Infra-red spectroscopy showed the presence of only SO_4^{2-} and OH^- ions, with no H_2O .

Chenite is triclinic, $P1$ or $P\bar{1}$, with $a = 5.791(1)$, $b = 7.940(1)$, $c = 7.976(1)$ Å, $\alpha = 112.02(1)$, $\beta = 97.73(1)$, $\gamma = 100.45(1)^\circ$, $V = 326.0$ Å³, $Z = 1$. The strongest lines in the X-ray powder diffraction pattern (d , $1/l$, hkl) are: 5.55, 7, 100; 4.32, 6, $1\bar{1}1$; 3.60, 10 002; 3.41, 9, 120; 3.30, 5, 022; 3.00, 5, 111; 2.80, 7, 122; 2.07, 6, 211/213/133; 1.778, 5, $3\bar{1}\bar{2}/2\bar{1}\bar{3}$.

Chenite forms minute, singly terminated, transparent to translucent sky-blue crystals from 0.1 to over 1 mm long, elongated approximately [032]. Twenty different forms (pinacoids) have been identified on the four crystals studied. A good cleavage on {100}, and traces of a second on {001}, can be observed. Optically, chenite is biaxial negative, $2V(\text{measured}) = 67 \pm 1^\circ$, $2V(\text{calc.}) = 68^\circ$ (Na). The refractive indices are $\alpha 1.871 \pm 0.005$, $\beta 1.909 \pm 0.005$, $\gamma 1.927 \pm 0.005$ (Na). Dispersion is strong, $r \gg v$. The mineral is weakly pleochroic. H (Mohs) $\sim 2\frac{1}{2}$. $D = 5.98$, and calculated $D_x = 6.044$ g cm⁻³.

KEYWORDS: chenite, new mineral, Leadhills, Scotland.

RECENTLY, two minerals have been reported from the famous lead-zinc deposits of the Leadhills-Wanlockhead district, Scotland (Wilson, 1921; Gillanders, 1981; Paar, 1983)—scotlandite, PbSO_3 (Paar *et al.*, 1984), and macphersonite, a polymorph of leadhillite and susannite (Livingstone and Sarp, 1984). This paper reports on chenite, another new mineral from Leadhills, and it seems to be very probable that this locality will provide further additions to the list of new minerals in the near future.

In 1981 a small specimen was acquired by one of us (W.H.P.) from D. Möhler (mineral dealer of Graz, Austria), displaying tiny, well-developed blue crystals which subsequently turned out to be the new mineral chenite. The specimen was labelled 'Caledonit auf Bleiglanz; Susanna Mine, Leadhills, Schottland' and was accompanied by two old labels, one relating to the well-known mineral dealer J. Böhm of Vienna, and a second one indicating that the specimen was once part of the world famous Karabaczek collection (Cassirer and Martin, 1979).

This specimen measures approximately $3 \times 3 \times 2\frac{1}{2}$ cm and consists predominantly of coarse-grained galena with minor inclusions of chalcopyrite. On one—the attractive—side, several Pb–Cu secondary minerals have formed as a result of the decomposition of the primary ores. These include caledonite, the major phase, occurring as greenish-blue to bluish-green millimetre-sized crystals rich in faces, and partly overgrown by linarite, which is present as poorly developed, intensively intergrown crystals less than 1 mm in size, and crystal aggregates. On the reverse side of the specimen very limited amounts of leadhillite are visible as irregular plates displaying a pearly lustre on the cleavage planes. Two unidentified phases occur with the chenite; their identification has not been possible yet because of the trace amounts available, but a brief mention might be warranted: a white mineral forms a single cluster of needle-like crystals about 0.2 mm long, perched on the chenite twin, and a pale blue mineral forms radiating aggregates of hair-like crystals overgrowing the altered galena. Under the scanning electron microscope the white mineral is seen to form elongated six-sided crystals capped with what appear to be hexagonal trapezohedrons. X-ray powder diffraction patterns of these phases did not match those of any published minerals.

The occurrence of chenite and the associated unidentified species is restricted to a small cavity, which is developed between weathered galena (with micro-crystals of anglesite) and densely intergrown crystals of caledonite forming the 'roof' of the cavity. Within this cavity grew twelve chenite crystals, each less than $1 \times 0.5 \times 0.2$ mm (0.1 mm^3)

in size. A twinned crystal about 1.5 mm long is located at the deepest point of the cavity. The total amount of chenite preserved on the specimen is between 8–12 mg.

The mineral has been named in honour of Dr T. T. Chen, mineralogist at CANMET, for his valuable contributions to the field of mineralogy. Both the mineral and the name had been approved by the IMA Commission on New Minerals and New Mineral Names prior to publication.

Type material has been deposited in the collections of the Smithsonian Institution, Washington, DC 20560, USA, the Royal Ontario Museum, Toronto, Canada, the Institut für Mineralogie und Kristallchemie der Universität Stuttgart, Pfaffenwaldring 55, D-7000 Stuttgart 80, Federal Republic of Germany, the Institut für Mineralogie, Kristallographie und Strukturchemie der Technischen Universität Wien, Getreidemarkt 9, A-1060 Wien, Austria, and the private collection of one of the authors (W.H.P.).

Subsequent to this investigation, a second specimen of chenite from Susanna mine, containing more and larger chenite crystals to over 1 mm in length, has been purchased by one of us (W.H.P.). In addition to chenite this specimen contains susanite, green elongated prismatic leadhillite crystals, caledonite, hydrocerussite, linarite, lanarkite and the above-mentioned white phase forming elongated six-sided crystals capped with hexagonal trapezohedrons, and is accompanied by two labels. One from Mr M. Wright, FRGS, Great Russell St., London, reads 'Suzannite, Suzannah mine, Leadhills'; the other is from the collection of Docteur Latteux.

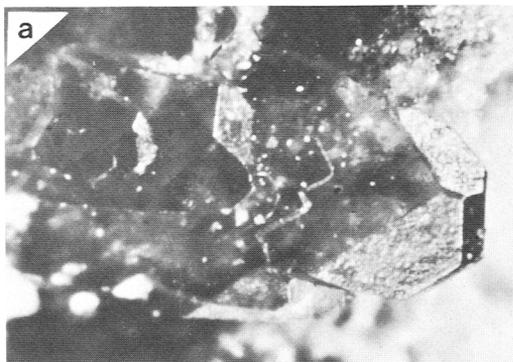


FIG. 1a. Chenite crystals in parallel intergrowth, the largest approximately 1.2 mm long. The forms visible correspond to those shown in fig. 2a, except that $\bar{2}5\bar{3}$ is very poorly developed and not recognizable in the photograph. FIG. 1b. Twinned chenite crystal about 1.5 mm long, the re-entrant angle being visible below the centre of the photograph. Associates include caledonite (background) and the white unknown mineral (clusters in foreground). The chenite twin cannot be removed without destroying it, nor can the specimen be used for mounting, to resolve the twin law of chenite.

A further specimen of chenite has been discovered among material recently collected by R.S.W.B. and J. I. Wilson from an old slag dump at the site of the ruins of Glengaber smelting mill at Meadowfoot, Wanlockhead, at the southern end of the Leadhills-Wanlockhead orefield. This chenite, identified by infra-red spectroscopy, consisted of a cluster of tiny blue elongated prismatic crystals in a cavity in slag, associated with elyite, lanarkite and various other oxidation products. This association of chenite with lanarkite, which is only thermodynamically stable in environments low in carbonic acid (Abdul-Samad *et al.*, 1982) suggests that the rarity of chenite, and presumably also of elyite, may be due to the same limitation. In the presence of carbonate the far more common caledonite is likely to be formed in preference to chenite.

Physical properties. Chenite forms minute single (rarely twinned, fig. 1b) and singly terminated, transparent to translucent sky-blue crystals of prismatic habit and roughly brick-like shape. They are elongated approximately parallel to [032] (fig. 1a). The streak is pale blue, the lustre vitreous to resinous. The hardness (Mohs) is about 2½. Fluorescence was not observed with either long or short wave ultraviolet, not surprisingly in view of the presence of copper. The crystals show a good cleavage on {100}, and traces of another on {001}. The density was determined, using a Berman microbalance, on one fragment (6.92 mg) used subsequently for infra-red and X-ray powder diffraction investigations. The density is 5.98 ± 0.02 g cm⁻³, in excellent agreement with $D_x = 6.044$, calculated from the ideal formula.

Crystallography. Four chenite crystals have been studied in detail by optical goniometry after previous determination of the lattice orientation with an X-ray four-circle diffractometer. Fig. 2 is a representation of one of these richly faceted crystals, comparable to the crystal shown in fig. 1. It is typical in habit and development of forms, eighteen different in number out of a total of twenty identified ones. Chenite is triclinic pinacoidal, ($\bar{1}$); crystal elements and angles are given in Table I. The prismatic habit of chenite results from the predominating forms {132}, {221}, and to a lesser degree, to {100}. The most prominent of these, {132}, tends to give poor reflection images due to the presence of vicinal faces, which belong to the zone [111], and which give rise to characteristic striations parallel to the given direction. Two of these vicinal forms, {253} and {154}, were found to occur also as distinct narrow faces bordering {132}. The prism-like crystals are usually terminated by a considerable number of forms which give good reflection images and tend to vary somewhat in size. Of these, {110}, which belongs to the above-

mentioned important zone [111], is usually the most prominent, followed by {010}, {001}, {101}, {111}, and {112}. In addition to the forms listed in Table I a few very small ones were noted in the vicinity of {221}; however, they could not be indexed beyond doubt.

Table I. Crystallographic elements, angle table and optical orientation for chenite *

Triclinic pinacoidal, ($\bar{1}$)

a:b:c = 0.7294 : 1 : 1.0045; α 112.02, β 97.73, γ 100.45°
 ρ_0 : q_0 : r_0 = 1.2984 : 1.0122 : 1; λ 65.81, μ 77.17, ν 75.38°
 ρ'_0 1.4364, q'_0 1.1198, r'_0 0.1357, γ'_0 0.4534

Reciprocal Cartesian matrix:

$$\begin{pmatrix} 0.1743 & 0 & 0.0170 \\ 0.0454 & 0.1404 & 0.0568 \\ 0 & 0 & 0.1254 \end{pmatrix} \quad (\text{in } \text{\AA}^{-1})$$

Forms	ϕ	ρ	A	B	C
0 0 1	16.67	25.33	77.17	65.81	-
0 1 0	0.00	90.00	75.38	-	65.81
1 0 0	75.38	90.00	-	75.38	77.17
1 1 0	43.16	90.00	32.23	43.16	67.49
-1 1 0	-61.41	90.00	136.80	61.41	84.93
-1 2 0	-36.52	90.00	111.90	36.52	75.15
0 1 1	4.93	57.65	73.58	32.68	33.13
0 -1 1	168.49	34.22	91.75	123.44	57.63
1 0 2	52.62	46.27	48.21	63.98	28.95
1 0 1	61.87	59.97	32.67	65.90	44.50
-1 0 1	-85.86	51.51	137.83	86.76	60.66
1 1 1	38.25	67.92	42.38	43.30	44.89
1 -1 1	101.27	57.27	40.82	99.46	58.49
-1 1 1	-46.01	60.16	116.86	52.96	51.68
-1 -1 2	-117.23	32.17	121.30	104.10	52.61
-2 -2 1	-133.52	74.66	147.59	151.62	96.83
1 -5 4	150.55	44.50	79.66	127.62	64.10
1 -3 2	141.52	53.17	71.11	128.80	69.74
2 -5 3	137.79	57.69	66.96	128.76	72.77
-1 -3 1	-159.01	74.06	124.05	153.86	99.32

Optical orientation **

OA1	146	21	84	107	41
OA2	89	78	18	89	72
AB	103	46	50	100	50
ON	-5	72	81	19	49
OB	-111	49	139	106	67

* All figures calculated from X-ray unit cell dimension data. For arrangement and presentation of data see Palache *et al.* (1951)

** Data for 589 nm; errors in orientation angles are estimated to be $\leq 3^\circ$.

Optics. The indices of refraction were determined by the conventional immersion methods, using both Cargille oils as well as phosphorus-diiodomethane liquids. While the Cargille oils slowly but distinctly attacked the chenite fragments, altering the indices uncontrollably, a more satisfactory investigation was carried out using the less aggressive phosphorus solutions.

A crystal ground to a sphere and orientated on a four-circle X-ray diffractometer was used to determine 2V and the optical orientation by spindle stage techniques (Bloss, 1981) and the computer

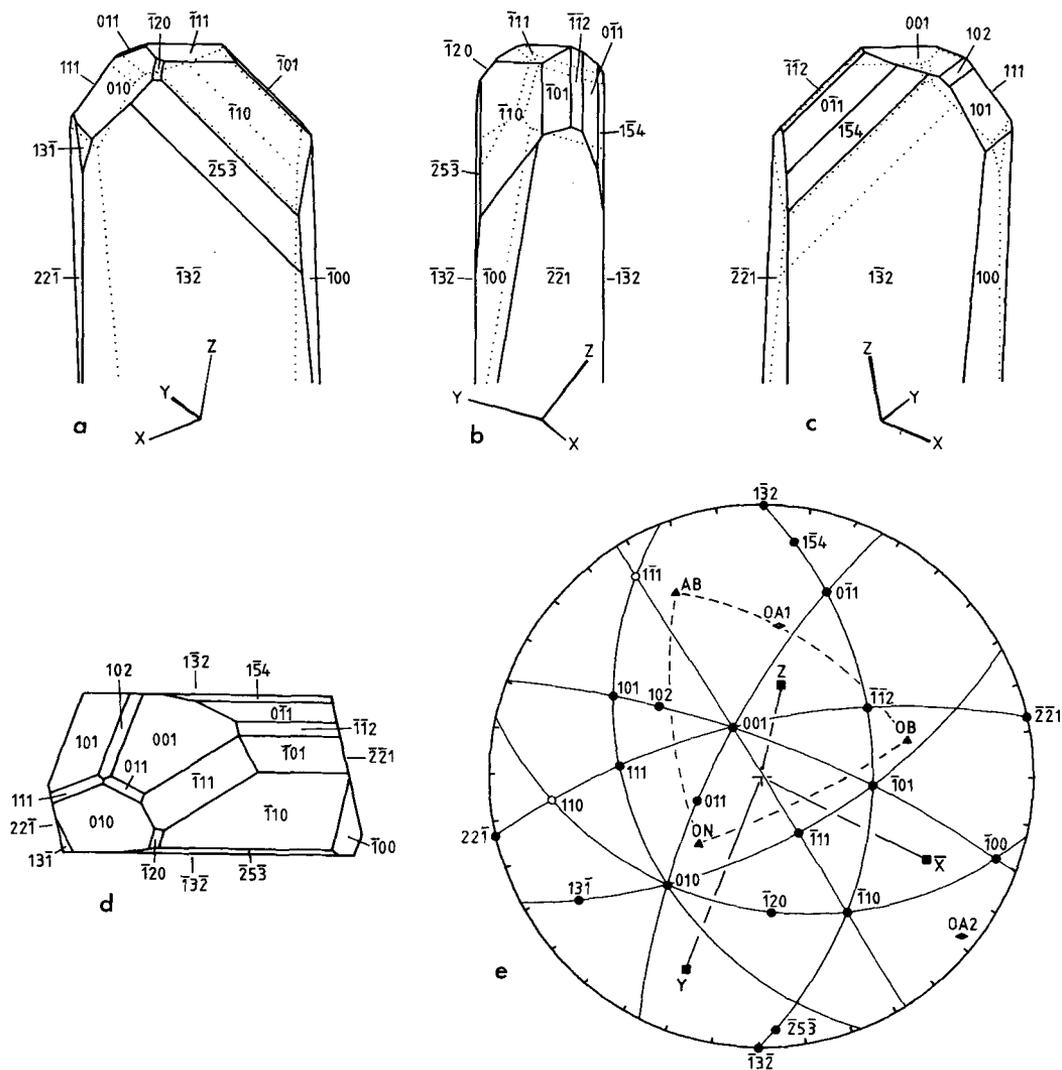


FIG. 2 (a-e). Front, side, back, and top view of a crystal of chenite (a-d). The stereographic projection (e) corresponds in orientation to (d); open circles represent faces not developed on this crystal; AB = acute bisectrix, OB = obtuse bisectrix, ON = optic normal, OA = optic axis.

program EXCALIBUR (Bloss *et al.*, 1980). The results are included in Table I and fig. 2.

Chenite is optically biaxial negative, $2V(\text{measured}) = 67 \pm 1^\circ$, $2V(\text{calculated}) = 68^\circ$ (Na). The refractive indices are $\alpha = 1.871 \pm 0.005$, $\beta = 1.909 \pm 0.005$, $\gamma = 1.927 \pm 0.005$ (Na). Dispersion is very strong $r \gg v$. The mineral is weakly pleochroic.

Applying the equation of Gladstone and Dale, and using the constants of Mandarinò (1976) a mean refractive index $\bar{n} = 1.912$ can be calculated for the theoretical chemical composition and D_x .

The measured mean refractive index is 1.900, so the compatibility is excellent.

X-ray crystallography. A small crystal of chenite, showing some faces, was examined by Weissenberg photographs, and with an automatic four-circle X-ray diffractometer (Syntex P 2₁). The cell parameters were refined from 25 strong reflections measured on the automatic four-circle diffractometer with Mo-K α radiation and a graphite monochromator. The results are: $a = 5.791(1)$, $b = 7.940(1)$, $c = 7.976(1)$ Å, $\alpha = 112.02(1)$, $\beta = 97.73(1)$,

$\gamma = 100.45(1)^\circ$, $V = 326.0 \text{ \AA}^3$, $Z = 1$. These cell parameters were used to index the X-ray powder pattern. The powder diffraction pattern data (Table II) were obtained using a 57.3 mm Debye-Scherrer camera and Fe-K α radiation, filtered with Mn, without standards. The intensities were estimated visually.

Table II. Indexed powder diffraction pattern of chenite, $\text{Pb}_4\text{Cu}(\text{SO}_4)_2(\text{OH})_6$, FeK radiation, Mn filter, camera diameter 57.3 mm. Intensity I/I_0 is estimated.

$d_{\text{obs.}} (\text{\AA})$	I/I_0	$d_{\text{calc.}} (\text{\AA})$	hkl
5.55	7	5.553	100
5.05	2	5.039	1 $\bar{1}$ 0
4.32	6	4.313	1 $\bar{1}$ 1
4.21	2	4.185	11 $\bar{1}$
3.97	3	3.992	101
3.60	10	3.605	002
3.41	9	3.415	1 $\bar{2}$ 0
3.30	5	3.298	02 $\bar{2}$
3.00	5	2.999	111
2.87	4	2.874	1 $\bar{2}$ 2
2.80	7	2.798	1 $\bar{2}$ 2
2.71	4	2.704, 2.702	120, 2 $\bar{1}$ 1
2.63	2	2.626	01 $\bar{3}$
2.60	2	2.593	03 $\bar{1}$
2.53	3	2.532, 2.530	21 $\bar{1}$, 02 $\bar{3}$
2.48	1	2.482	20 $\bar{2}$
2.41	1	2.414, 2.409	1 $\bar{5}$ 0, 10 $\bar{5}$
2.39	1	2.391, 2.391	210, 1 $\bar{3}$ 2
2.32	1	2.315	2 $\bar{2}$ 1
2.26	2	2.259, 2.256	112, 1 $\bar{2}$ 3
2.21	4	2.212	1 $\bar{2}$ 2
2.14	1	2.134	022
2.12	1	2.112	2 $\bar{3}$ 1
2.07	6	2.075, 2.069, 2.066	211, 21 $\bar{3}$, 1 $\bar{3}$ 3
2.04	1	2.038	013
1.949	4	1.949, 1.947	1 $\bar{4}$ 1, 01 $\bar{4}$
1.914	3	1.915, 1.913	124, 3 $\bar{1}$ 0
1.838	4	1.838, 1.836	10 $\bar{4}$, 1 $\bar{4}$ 0
1.803	1	1.802	004
1.778	5	1.780, 1.780	3 $\bar{1}$ 2, 2 $\bar{1}$ 3
1.750	3	1.751, 1.750	131, 2 $\bar{5}$ 3
1.704	3	1.704	301
1.678	1	1.680	3 $\bar{5}$ 0
1.658	2	1.655	30 $\bar{3}$
1.582	3	1.584, 1.583, 1.581	041, 140, 02 $\bar{5}$
1.548	2	1.546	311

Chemical composition. Chenite was chemically analysed using an ARL-SEMQ electron microprobe utilizing an operating voltage of 15 kV and a sample current of 0.025 μA , measured on brass. The standards used were cuprite (Cu), celestine (S), and PbO (Pb). A wavelength-dispersive microprobe scan indicated the absence of elements with atomic number greater than 9, other than those reported herein. The data were corrected using a modified version of the MAGIC-4 program. The resultant analysis yields PbO 74.5, CuO 7.8, SO₃ 13.3, H₂O (by difference) 4.4 wt. %. The chemical formula for chenite, taking into consideration the results of

infra-red spectroscopy (see the following section) with only SO₄²⁻ and OH⁻ anions present, and no H₂O, and calculated on the basis of 14 oxygen atoms is Pb_{3.98}Cu_{1.17}S_{1.98}O₁₄H_{5.82}; the ideal formula is Pb₄Cu(SO₄)₂(OH)₆, which requires PbO 75.2, CuO 6.7, SO₃ 13.5, H₂O 4.6, sum 100 wt. %.

Infra-red spectroscopy. Although chenite superficially resembles caledonite to some extent in appearance, it is readily distinguished from it by not effervescing in dilute hydrochloric acid, and also by infra-red spectroscopy, the spectrum of caledonite showing strong carbonate absorptions absent, of course, in that of chenite.

The infra-red spectra of the chenites from Leadhills and from the Wanlockhead slags, and of the other minerals used for comparison, were measured in 'Nujol' mulls between KBr plates, over the range 400–4000 cm⁻¹, using a Perkin-Elmer PE 397 precision grating spectrophotometer. In addition, the spectrum of caledonite was measured in hexachlorobutadiene mull over the regions of Nujol absorption (fig. 3). The spectrum of chenite was also measured by Dr A. Beran (University of Vienna) in a pressed KBr disc. This last spectrum is unfortunately complicated by absorptions due to contamination by organic glue and from considerable moisture, but shows improved resolution of the sulphate absorption bands over the mull spectra.

The infra-red spectrum of chenite is that of a hydroxide-sulphate, with traces only of water, and no evidence of other oxy-anions being present.

In the region of O–H stretching vibrations the spectrum of chenite shows three distinctive and fairly sharp absorptions at 3530, 3460, and 3300 cm⁻¹, superimposed on a weak, very broad absorption from about 3700 to 3000 cm⁻¹, centred near 3400 cm⁻¹. The three sharp absorptions are assigned to O–H stretching vibrations of hydroxide ions in three different structural environments, and the weak broad band to a hydrogen bonded O–H stretch, possibly of moisture. A very weak and broad band near 1700 cm⁻¹ is likely to be due to traces of moisture rather than structural H₂O.

The tetrahedral sulphate anion has four normal vibrational modes. The ν_1 symmetrical stretch near 1000 cm⁻¹ is forbidden in the infra-red spectrum, as is the ν_2 symmetrical bending mode near 450–500 cm⁻¹, which is doubly degenerate. The ν_3 asymmetrical stretching (near 1100 cm⁻¹) and ν_4 asymmetrical bending (near 600 cm⁻¹) modes are triply degenerate. Distortion of the anion from T_d symmetry may cause the ν_1 and ν_2 bands to appear, as weak absorptions, and the ν_2 , ν_3 and ν_4 modes to lose degeneracy, the resulting band multiplicity being dependent on the symmetry of the distortion.

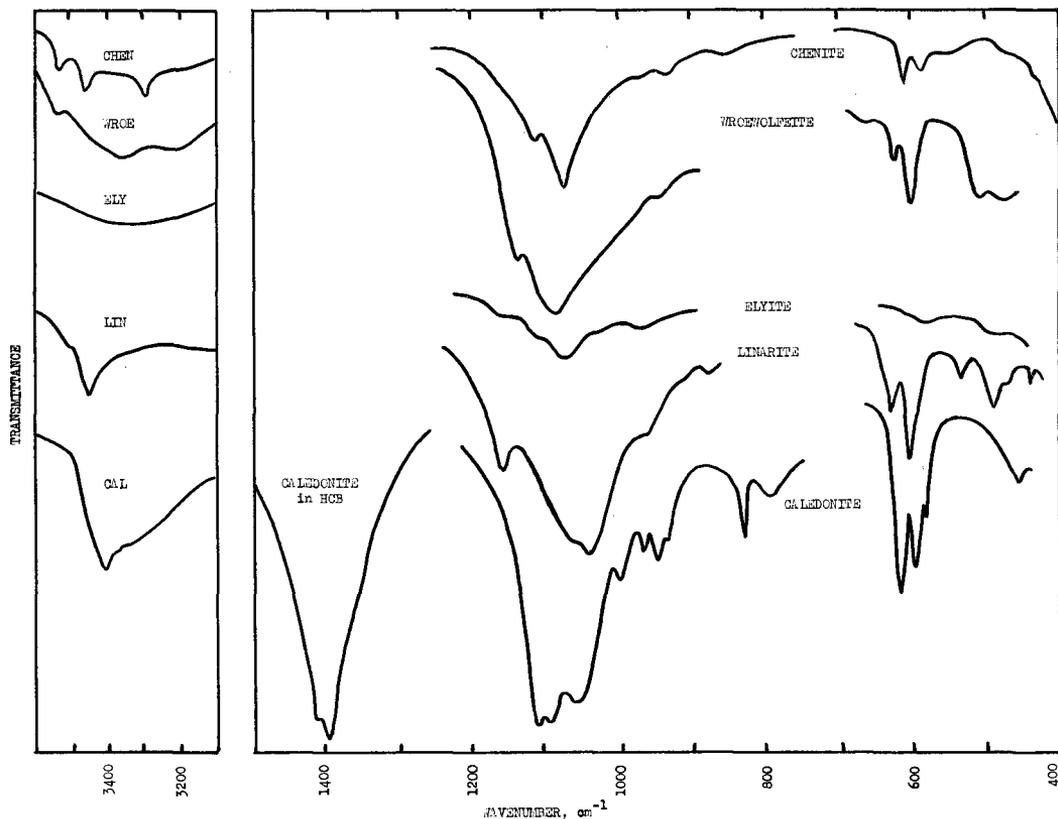


FIG. 3. Infra-red spectra of (a) chenite from Leadhills, (b) wroewolfeite from Nantycagal mine, Dyfed, Wales, (c) elyite from Wanlockhead slags (weak spectrum, from very small sample), (d) linarite from Leadhills, (e) caledonite from Leadhills (in both Nujol and hexachlorobutadiene mulls).

The spectrum of chenite shows a weak absorption near 935 cm^{-1} assigned to the forbidden ν_1 mode of the sulphate ion, and a weak band at 485 cm^{-1} (clearly visible on the pressed disc spectrum) assigned to the forbidden ν_2 mode. A strong, broad band with maxima at 1070 and 1115 cm^{-1} is the ν_3 band of sulphate, and two fairly sharp absorptions at 620 and 590 cm^{-1} are assigned to the ν_4 band. If these assignments are correct, and none of them are due to metal-OH bands, this band multiplicity is consistent with a C_{3v} symmetry for the distorted sulphate anion.

Additional very weak absorptions at 430 and 860 ($= 2 \times 430$) cm^{-1} are probably due to overtones.

Minerals closely related chemically to chenite include linarite $\text{PbCuSO}_4(\text{OH})_2$, elyite $\text{Pb}_4\text{CuSO}_4(\text{OH})_8$ and caledonite $\text{Pb}_5\text{Cu}_2\text{CO}_3(\text{SO}_4)_3(\text{OH})_6$. The infra-red spectra of the sulphate ions in these minerals are rather similar, but the O-H spectra are

rather different, and that of caledonite has extra absorptions due to the carbonate ion, particularly strongly near 1400 cm^{-1} (fig. 3). Of the lead-free basic copper sulphate minerals, the infra-red spectrum of chenite more closely resembles that of wroewolfeite in the regions of sulphate absorption than those of langite, posnjakite, ktenasite, devil-line, serpierite, spangolite, and 'woodwardite' (Braithwaite, 1982).

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