Mattheddleite, a new mineral of the apatite group from Leadhills, Strathclyde Region

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Synopsis

Mattheddleite, a new lead member of the apatite group with sulphur and silicon totally replacing phosphorus, occurs as tiny crystals (<0·1 mm) forming drusy cavities in specimens from Leadhills. Optically, the mineral is colourless in transmitted light and is uniaxial with ω2·017 and ϵ1·999. X-ray powder diffraction data are similar to the synthetic compound lead hydroxyapatite and may be indexed on a hexagonal cell with a 9·963 and c 7·464 Å (the cell volume is 642 Å^3). The calculated density is 6·96 g/cm^3. The strongest lines in the powder pattern are [d, (I) (hkl)]: 2·988 (100) (112, 211), 4·32 (40) (200), 4·13 (40) (111), 2·877 (40) (300), 3·26 (30) (210). Single crystal Weissenberg photographs are close to those of pyromorphite, space group $P6_3/m$. Chemically, mattheddleite does not contain S and Si in the expected 1:1 ratio, and the ideal formula may be expressed as $Pb_{20}(SiO_4)_7(SO_4)_4Cl_4$. The infrared spectrum is very similar to that of hydroxyellestadite. Associated minerals are lanarkite, cerussite, hydrocerussite, caledonite, leadhillite, susannite, and macphersonite.

The mineral is named after Matthew Forster Heddle (1828–1897), a famous Scottish mineralogist.

Introduction

In the course of examining minerals associated with macphersonite from Leadhills Dod, Strathclyde region, (Livingstone & Sarp 1984) at the Royal Museum of Scotland, a creamy white lining to a small cavity in quartz was found to consist primarily of tiny glassy crystals, the X-ray powder pattern of which could not be identified. There was a remarkable degree of similarity with the powder pattern of the synthetic compound $Pb_5(PO_4)_3OH$, lead hydroxyapatite (Powder Diffraction File 8–259). Subsequent investigations revealed that the material did not, in fact, contain phosphorus but silicon and sulphur.

On preparing a submission for the new mineral macphersonite to the International Mineralogical Association, it was learned that workers at the British Museum (Natural History) had discovered a similar apatite group mineral in specimen MM 344 of the Catty Collection, Maidstone Museum. It seemed appropriate to characterize this new phase jointly.

The label with specimen MM 344 gave the locality as Caldbeck Fells,

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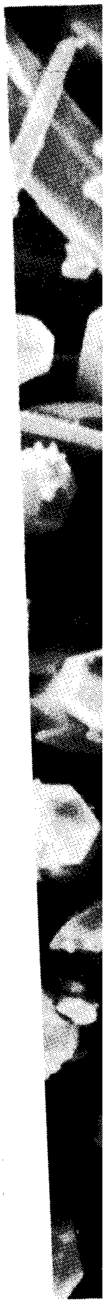
Cumberland; however, the specimen contains large, well developed crystals of lanarkite, a rare mineral which, as far as the authors are aware, is not known to occur in the Caldbeck Fells. It seems highly probable that this specimen originated from Leadhills and that the erroneous locality is due to mislabelling. Other specimens labelled Leadhills, also in the Maidstone Museum, do contain mattheddleite.

The specimen in the Royal Museum of Scotland (RMS GY 721.34) is from the Heddle Collection, consequently, it was decided to name this new mineral mattheddleite in honour of Matthew Forster Heddle (1828–1897) the famous Scottish mineralogist. The new species and the name were approved by the International Mineralogical Association Commission on New Minerals and Mineral Names prior to publication. Additional mattheddleite-bearing specimens from Leadhills have been brought to our attention by Drs. Braithwaite (1984 pers. comm.) and Faithfull (1985 pers. comm.).



DESCRIPTION

Physical and optical properties

In hand specimen RMS GY 721·34 is composed mainly of quartz with a characteristic assemblage of Leadhills secondary minerals including, caledonite, cerussite, pyromorphite, leadhillite, susannite, and the recently described mineral macphersonite. MM 344 is of similar appearance containing lanarkite, cerussite, hydrocerussite, leadhillite and caledonite.

Microscopic examination of the creamy white linings to cavities in quartz, showed them to consist of tiny crystals (up to 100 μm by 10–20 μm) forming radiating rosettiform aggregates some 0·2 mm in diameter. Scanning electron microscopy of mattheddleite in RMS GY 721·34 revealed 'solution-hollowed' hexagonal prisms. Figure 1 shows the rather more typical hexagonal prisms, some of which display a basal cleavage or fracture. Minor amounts of cerussite, a contaminant in the X-ray mounts, are also present in the cavities or in the cavity walls.

Mattheddleite has an adamantine lustre and, as it forms a white powder when crushed, hence has a white streak.

In transmitted light mattheddleite is colourless and transparent, many of the crystals showing internal 'herring-bone' growth patterns. When observed in sodium light ($\lambda = 589$ nm), the crystals are length fast, uniaxial negative with refractive indices ω 2·017(5) and ϵ 1·999(5); measurements were made quickly on freshly crushed grains under a cover slip before they became affected by the corrosive Cargille refractive index liquids (A. G. Couper pers. comm. 1982). Mattheddleite emits a dull yellow fluorescence when observed under short-wave ultraviolet light.

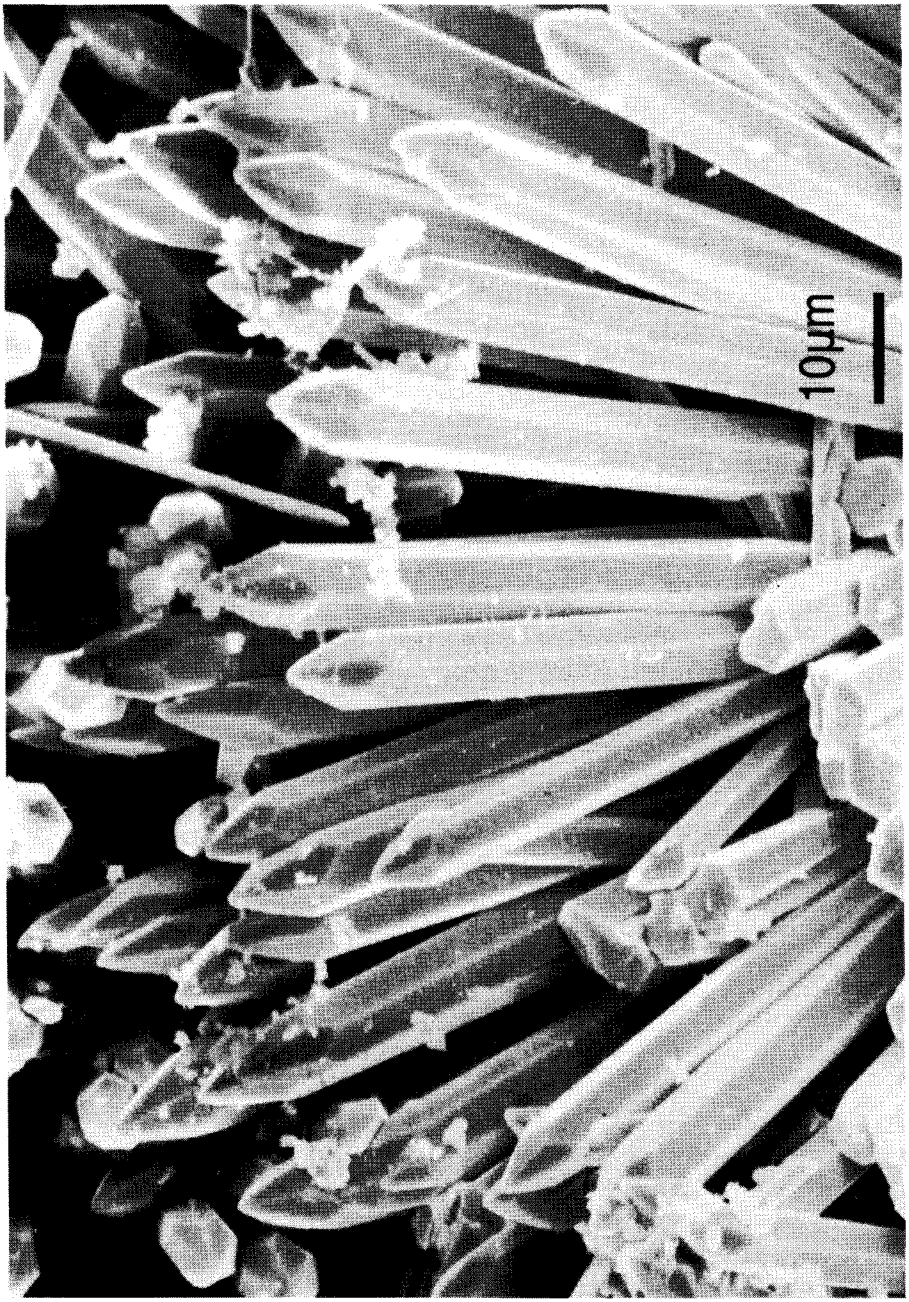


FIG. 1. Scanning electron microscope photograph of mattheddleite, from Leadhills, showing terminated hexagonal prisms (note unusual habit for apatite group minerals) and basal cleavage or fracture. (Photograph from specimen RSWB84–125, which is part of one belonging to Dr. J. Jung).

TABLE 1

X-ray diffraction data for mattheddleite

		A		B		C	
$I_{\text{est.}}$	*hkl*	$d_{\text{meas.}}$	$d_{\text{calc.}}$	$d_{\text{meas.}}$	$d_{\text{calc.}}$	$d_{\text{meas.}}$	$d_{\text{calc.}}$
10	110	4·99	4·97	4·96	4·98	5·01	5·00
40	200	4·31	4·31	4·32	4·31	4·33	4·33
40	111	4·16	4·15	4·13	4·14	4·15	4·16
5	002 201	3·71	3·75 3·73	3·71	3·74 3·73	3·71	3·74 3·75
3	—	*3·57*	—	*3·56*	—	*3·56*	—
20	102	3·44	3·44	3·41	3·43	3·42	3·43
30	210	3·26	3·25	3·26	3·26	3·28	3·28
100	112 211	3·004	2·996 2·988	2·988	2·989 2·989	2·990	2·995 3·002
40	300	2·880	2·872	2·877	2·876	2·890	2·890
3	—	—	—	—	—	*2·526*	—
2	220	—	—	2·492	2·491	2·492	2·503
2	221	—	—	2·366	2·363	2·384	2·373
5	302	2·285	2·281	2·275	2·279	2·282	2·287
5	113	2·236	2·235	2·221	2·228	2·225	2·231
5	400	2·154	2·154	2·162	2·157	2·170	2·168
20	222	2·076	2·073	2·072	2·073	2·078	2·080
15	312	2·019	2·015	2·015	2·015	2·021	2·022
15	320 213	1·977	1·976 1·985	1·977	1·979 1·979	1·979	1·989 1·984
15	321	1·916	1·911	1·918	1·914	1·925	1·922
15	410	—	—	1·885	1·883	1·894	1·892
20	004 402	1·876	1·879 1·869	1·871	1·868 1·868	1·875	1·869 1·875
2	322 114	1·741	1·749 —	1·747	1·749 1·749	1·747	1·756 1·751
5	501 412	1·682	1·679 1·681	1·682	1·681 1·681	1·691	1·689 1·688
10 br★	420	1·627	1·628	★1·627	1·631	★1·627	1·638
15	304	1·570	1·571	1·564	1·567	★1·562	1·569
15	323 510	1·549	1·551 1·547	1·558	1·550 1·550	—	—
15	332 511	1·517	1·516 1·515	1·519	1·517 1·517	1·527	1·524 1·525
2		—		1·495		1·489	
3		—		1·386		1·390	
5		—		1·365		1·367	
5		1·359		1·359		1·351	
10		1·329		1·326		1·329	
10		1·296		1·299		1·305	
5		—		1·251		1·258	
		—		+11 lines to 0·98		+10 lines to 0·98	

lines due to cerussite impurity in italics
CuKα Ni filter, 114·6 mm diameter camera

A Specimen RMS GY 721·34, Heddle Collection, Royal Museum of Scotland indexed with *a* 9·948 Å and *c* 7·504 Å

B Specimen MM 346, Maidstone Museum indexed with *a* 9·963 Å and *c* 7·464 Å

C Specimen MM 344 Maidstone Museum, also BM 1985, 178, indexed with *a* 10·01 Å and *c* 7·476 Å

Owing to the very limited quantity of material available, and the very small grain size, neither the hardness nor the density could be determined. The calculated density is 6·96 g/cm^3 using the empirical formula based on 24 (O + Cl) atoms, and Z = 1.

X-ray data

Several tiny polycrystalline fragments of the cavity lining produced powder diffraction patterns which were identical except for slightly varying amounts of cerussite impurity. The patterns are very similar to that of synthetic lead hydroxyapatite (PDF 8–259), the only significant differences being in some of the *d* spacings below 3·0 Å. Powder data are given in Table 1 and are indexed on a hexagonal cell. With some difficulty, a minute crystal was detached from the Catty Collection specimen MM 346, and unit cell dimensions of *a* 9·963(5) and *c* 7·464(5) Å (volume 642 Å^3, *c*/*a* 0·749(1)) were obtained from rotation, and zero and first layer Weissenberg photographs around *a* and *b* and refined from the powder data (Table 1, B). The *00l* absences are compatible with the space group $P6_3/m$ of pyromorphite; unfortunately it was not possible to obtain precession photographs.

Chemistry

A Cambridge Instruments Microscan IX wavelength dispersive microprobe was used with pyromorphite, troilite and quartz standards to obtain the data in Table 2. Energy dispersive analysis at the British Museum (Natural History) and wavelength dispersive analysis at the Geology Department, University of Edinburgh (with galena, wollastonite, and halite standards) on fourteen grains of

TABLE 2

Electron microprobe analysis wt.% of mattheddleite

	1	2	3
PbO	83·5	83·7	83·60
SiO_2	7·3	8·0	7·65
SO_3	6·1	5·9	6·00
Cl	2·5	2·3	2·40
	99·4	99·9	99·65
$-O \equiv Cl$	0·6	0·5	0·54
	98·8	99·4	99·11

1–2 Separate grains, single spot analysis with troilite, pyromorphite and quartz standards.

3 Average of 1 and 2.

Accelerating voltage: 20 kV; Radiations: PbMα, SiKα, SKα, ClKα.

Specimen: Maidstone Museum MM 346.

mattheddleite gave concentrations, wt%, ranging from PbO 82·5–86·9; SiO_2 7·6–8·8; SO_3 4·4–7·3 and Cl 0·6–2·1. Low totals in some of the analyses correspond generally to low Cl and thus were assumed to be due to OH substitution; this could not be checked, however, for even by combining tiny fragments from the various specimens, insufficient material was available for a 'water' determination by Perkin–Elmer elemental analyser.

Variations, particularly in the lead contents, between the analyses obtained by the various microprobes are ascribed to a combination of the different standards used and/or the correction factors applied. It is worth recording that, for some of the analyses, the iterative procedure of the ZAF computer correction program failed to converge, and the two analyses given in full (Table 2) are those believed to be the most accurate.

The average analysis in Table 2 yields the following empirical formula based on 13(O + Cl) atoms for the apatite group:– $Pb_{10\cdot14}(Si_{3\cdot45}, S_{2\cdot03})O_{22\cdot17}Cl_{1\cdot83}$ and which may be simplified to $Pb_5(SiO_4, SO_4)_3Cl$, although there is an excess of lead in the former which is necessary to retain the charge balance as the S : Si ratio is not 1·5 : 1·5. Within the apatite group the ratio of S : Si should be 1·5 : 1·5 and Rouse and Dunn (1982) demonstrated this for seventeen ellestadite analyses where the deviation of S : Si stoichiometry from 1·5 : 1·5 was only 4% (and never exceeded 9%). Mattheddleite does not contain phosphorus hence $S^{VI} + Si^{IV} \nLeftrightarrow 2\,P^{V}$ but, unlike ellestadite, the S : Si ratio does not approach unity, the average S : Si ratio being 1 : 1·675. If the formula for mattheddleite is calculated to 24 (oxygen + chlorine) atoms the empirical formula is $Pb_{10\cdot25}(SiO_4)_{3\cdot46}(SO_4)_{2\cdot04}Cl_{1\cdot85}$. This has an S : Si ratio of approximately 1 : 1·7 and leads to the ideal formula of $Pb_{20}(SiO_4)_7(SO_4)_4Cl_4$. The theoretical composition of the ideal formula requires PbO 84·6; SiO_2 7·9; SO_3 6·0 and Cl 2·7 wt% (total 100·6 less O ≡ Cl 0·6 = 100·0 wt%). This theoretical composition is close to the results given in Table 2. Apatite group minerals with fewer than 24 oxygen atoms are known (e.g. nasonite).

Nasonite contains the Si_2O_7 anion (Giuseppetti *et al.* 1971) but there is no evidence from the infrared and trimethylsilylation experiments (see below) for its presence in mattheddleite.

Infrared spectrometry

The infrared absorption spectrum of mattheddleite (Fig. 2) is simple, showing absorption bands at 1090 and 1050 cm^{-1} (S—O stretching); 960 (weak), 910 and 864 cm^{-1} (Si—O stretching); 617 and 604 cm^{-1} (O—S—O bending) and ~260 cm^{-1} (unassigned). The spectrum closely resembles that of hydroxyellestadite (Harada *et al.* 1971) with the following differences: (a) the absorption bands are shifted to lower frequencies by the presence of the heavier lead cation; (b) the main SiO_4 absorption band in mattheddleite is somewhat more intense than the main SO_4 band, whereas in hydroxyellestadite the reverse is the case, in

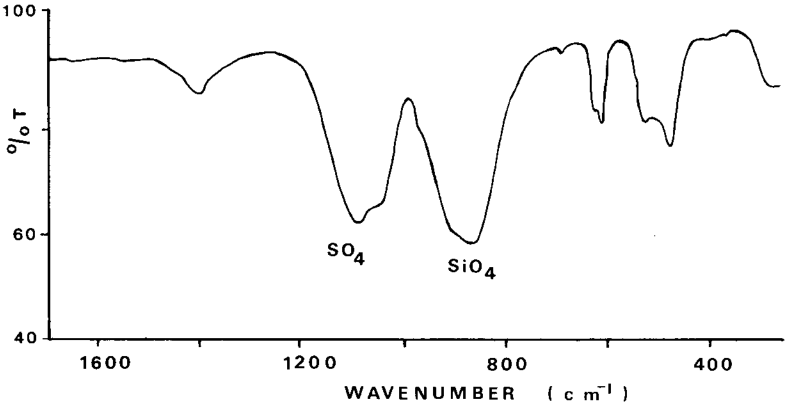


FIG. 2. Infrared absorption spectrum of mattheddleite, CsI pressed disc (specimen RMS GY 721·34).

agreement with the respective stoichiometries; (c) the CO_3^{2-} absorption bands at 1400 and 680 cm^{-1} are due to cerussite or hydrocerussite impurity.

A difference spectrum between mattheddleite in a Nujol mull and Nujol alone revealed very weak absorption at 3200–3400 cm^{-1} (O—H stretching), most probably due to a small amount of OH^- substituting for Cl^- in the structure.

Trimethylsilylation

In order to confirm the lack of $Si_2O_7^{6-}$ anions in mattheddleite, the technique of trimethylsilylation was used, which involves the formation and gas chromatographic analysis of the volatile products $SiO_4[Si(CH_3)_3]_4$ and $Si_2O_7[Si(CH_3)_3]_6$ from anions SiO_4^{4-} and $Si_2O_7^{6-}$, respectively (Currell and Parsonage 1981). By adapting the method of Kalmychkov (1982) to a micro-scale, trimethylsilylation of a few crystal fragments of mattheddleite was achieved using trimethylchlorosilane, pyridine and dimethylformamide.

The results for mattheddleite were compared with those for ellestadite, and the sorosilicates barysilite and hemimorphite and confirmed that mattheddleite contains only monomeric silicate anions.

DISCUSSION

Mattheddleite may well be the same phase as the unnamed lead hydroxyapatite reported by Temple (1955) from Whyte's Cleuch, Wanlockhead–Leadhills area. Previously, this had only been reported as an artificial phase (Hey, 1933). Ganomalite is the OH analogue of nasonite and the correspondence of low Cl values with low totals in some of the analyses suggests that OH↔Cl in mattheddleite and hence a 'hydroxymattheddleite' remains a possibility.

Type material is preserved in the Royal Museum of Scotland (RMS GY 721.34), in the British Museum (Natural History) (BM 1985, 178) and in the Maidstone Museum (MM 344).

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