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Crystal structure of mattheddleite: a Pb, S, Si phase with the apatite structure

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ABSTRACT

The crystal structure of mattheddleite ($Pb_5(Si_{1.5}S_{1.5})O_{12}(Cl_{0.57}OH_{0.43})$, $P6_3/m$, a = 10.0056(6), c = 7.4960(9) Å) from Leadhills, Scotland has been determined to R = 0.065. The structure is that of apatite where Pb replaces Ca, equal amounts of S and Si replace P and the X anion is OH + Cl. The composition deduced from the structural refinement differs from that of microprobe analyses by giving full occupancy of the tetrahedral site and equal Si and S to preserve charge balance. We conclude that the microprobe analysis is incorrect possibly due to large and inaccurate absorption corrections. For the crystal analysed, the X anion position is zoned from an OH-rich interior to a Cl-rich exterior. The Pb(2) atom is disordered which may be analogous to the disordering of the Ca(2) site in Cl-rich, Ca apatites.

KEYWORDS: pyromorphite, mattheddleite, ellestadite, apatite.

Introduction

MATTHEDDLEITE is a rare mineral of the apatite group with the approximate composition, $Pb_5(SiO_4,SO_3)_3Cl$. It was first recognized in the classic Pb mineral region at Leadhills, Scotland (Livingstone *et al.*, 1987), but has since been reported from Caldbeck Fells, Cumbria (Cooper *et al.*, 1988; Cooper and Stanley, 1991), and at Dyfed, Wales (Rust, 1990; Green *et al.*, 1996). Calcium apatites with Si and S are included in the ellestadite group of minerals and it has been shown that Si and S substitute in near equal atom amounts for P to maintain charge balance ($Si^{4+} + S^{6+} \rightleftharpoons 2P^{5+}$) (Rouse and Dunn, 1982). In their description of mattheddleite, Livingstone *et al.* (1987) pointed out that: (1) mattheddleite does not contain P; (2) S does not equal Si on an atomic basis; and (3) Si + S is not sufficient to fill the tetrahedral site. In fact, their sample from Leadhills, Scotland showed a S:Si ratio of 1:1.675 instead of the expected 1:1 for charge balance in the apatite structure. In all other respects including optics, X-ray diffraction (XRD) pattern, and chemistry, they concluded that mattheddleite belonged to the apatite group.

The intent of this study is to use the crystal structure determination of mattheddleite to investigate the non-equality of Si and S as well as describe the features of this unusual apatite group structure. In particular, we wish to compare the structures of pyromorphite ($Pb_5(PO_4)_3Cl$) and natural apatite ($Ca_5(PO_4)_3Cl$) with mattheddleite with respect to details of the cation and anion sites. Previously, a range of positions of Cl, OH and F (Hughes *et al.*, 1989) as well as disorder for one of the cation sites (Hughes *et al.*, 1990) among Ca apatites has been demonstrated. Structure determinations of pyromorphite (Dai and Hughes, 1989; Hashimoto and Matsumoto, 1998) show neither cation disorder nor a variation in anion position.

Composition determination

To first confirm the composition of mattheddleite, a sample from Leadhills, Scotland (NMS G

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1878.49.488.2) was obtained from the National Museums of Scotland. Several single terminated crystals were mounted in epoxy and polished to expose a surface along the crystal length approximately through the centre. Electron microprobe analyses were made both to verify the homogeneity as well as the conclusion in Livingstone *et al.* (1987) that Si was not equal to S and that their sum was not sufficient to fill the tetrahedral site.

Using line scans with ~2 μm step size, the crystal was seen to be homogeneous with respect to Si, S and Pb but not for Cl. A backscattered electron image is shown in Fig. 1 with three line profiles indicated. The concentration of Cl along these profiles is illustrated in Fig. 2*a* and *b* which clearly show enrichments of Cl at the grain edges and termination as well as for a central internal area. Lower values of Cl, however are common, and in fact represent the bulk of the volume. From the ideal formula for mattheddleite (Livingstone *et al.*, 1987) written as $Pb_{20}(SiO_4)_7(SO_4)_4Cl_4$, the wt.% Cl is equal to 2.7%. This value is approximately equal to the highest edge values on the profiles of Fig. 2*a,b* suggesting that the edges have only Cl as the X anion. Scans for F indicated no values above the detection limit of ~0.1%. It is assumed that in areas where Cl ranges to low values of 1.2 wt.%, OH is substituting for Cl in the X site. Because an entire prism similar to that shown in Fig. 1 was used for intensity data collection, an average Cl concentration of 1.4 wt.% was estimated, which would represent a Cl fraction of 0.55 with the balance equal to 0.45 OH in the X site when averaged over an entire prism.

Point analyses were made for Pb, Si, S and Cl and the results are presented in Table 1. The operating conditions were 15 kV and 25 nA with a focused beam. Because absorption is a major correction, analyses at 10 kV were also made but with results essentially identical to those at 15 kV given in Table 1. The standards were: natural PbS for Pb and S, synthetic anorthite glass for Si, and synthetic crystalline $Ca_5P_3O_{12}Cl$ for Cl. The results given in Table 1 basically agree with the results of Livingstone *et al.* (1987) that atomic Si is not equal to S but rather has an average ratio of 1 S for 2.12 Si atoms for this Leadhills sample. This differs slightly from the value given in Livingstone *et al.* (1987) (column 1, Table 1) for a sample from another location. Other elements including Mg, Al, P, Ca, Mn, As and V were sought but none was detected. From the results given in Table 1, the cation values normalized to Pb = 5.0 results in a deficiency in the tetrahedral

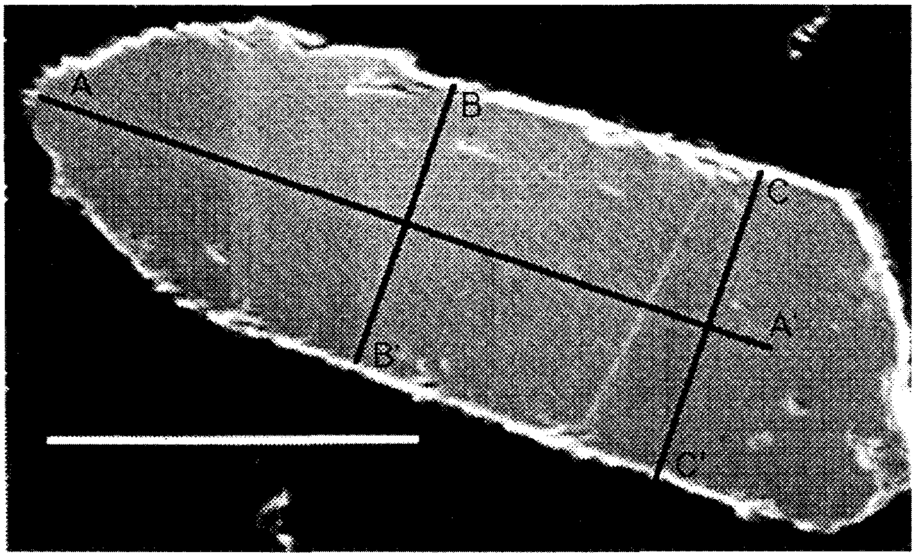

FIG. 1. Backscattered electron image of a single mattheddleite crystal. Three line profiles are indicated for which Si, S, Pb and Cl-*K*α intensities were determined. Those for Si, S and Pb were essentially flat while profiles for Cl are illustrated in Fig. 2. Scale bar = 50 μm.

site from the ideal value of 3.0. In fact, Si + S sums to an average of 2.60 to give an apparent composition including the above Cl results of $Pb_5(Si_{1.77}S_{0.83})O_{12}(Cl_{0.55}OH_{0.45})$. This formula gives a positive charge of +22 *vs.* a negative charge of −25. In the absence of any other detectable element with Z >10, the possibility remains that the tetrahedral site is partially occupied by a light element such as B, Be or C to provide both full occupancy and charge balance. A borosilicate Pb-apatite, $Pb_5(B_2Si)O_{10}$, which has a vacant halogen site has been described (Moore and Eitel, 1957) confirming that B can occur in Si-bearing apatites. Likewise, McConnell (1973) has summarized his proposal that the substitution of 4 C for 3 P occurs in the apatite structure.

Laser ablation ICP-MS showed that B and Be were below detection (<1 ppm) in the same crystals used for electron probe analysis. However, C analysis was inconclusive due to the relatively high C content of the analytical system and the epoxy mounting medium. Likewise, electron probe microanalysis for C was inconclusive. It might be noted that an infrared (IR) absorption spectrum (Livingstone *et al.*, 1987) showed the presence of CO_3^{2-} absorption bands which were assigned to cerussite or hydrocerussite impurity. We are left with several possibilities: (1) for an unknown reason the microprobe analyses are in error; (2) another element is present with the only high-charge tetrahedral species not ruled out being C; or (3) there are cation vacancies in the structure, some compensated for by anion vacancies. To resolve these possibilities we turn to single crystal structural results and conclude that inaccurate microprobe analyses are the most likely explanation.

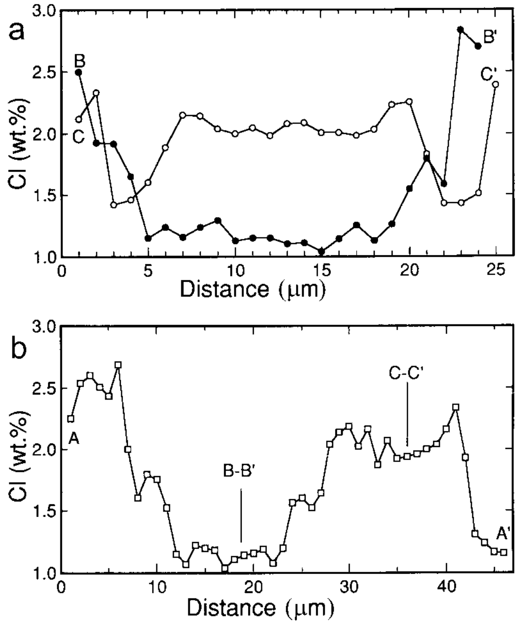

FIG. 2. (*a*) Chlorine concentration profiles for lines B−B′ and C−C′ from Fig. 1. The edges are enriched in Cl with a concentration nearly that representing full occupancy of the anion site (2.7 wt.% Cl). (*b*) Chlorine profile along traverse A−A′ of Fig. 1. The crystal termination near A is enriched in Cl but also there is enrichment toward the base of the crystal. Crossing positions of profiles B−B′ and C−C′ are indicated.

TABLE 1. Electron microprobe analyses of mattheddleite.

	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
PbO	83.6	84.8	84.5	85.5	84.7	84.1	84.7	85.6	85.6	85.0
SiO_2	7.65	7.94	7.91	8.28	8.11	8.24	8.41	8.13	7.70	8.06
SO_3	6.00	5.47	5.04	5.17	5.24	5.39	5.07	5.04	5.74	5.14
Cl	2.40	2.17	1.41	1.00	1.05	0.99	1.56	1.03	2.40	1.24
	99.65	100.38	98.86	99.95	99.10	98.72	99.74	99.80	101.44	99.44
−O=Cl	0.54	0.49	0.32	0.23	0.24	0.22	0.35	0.23	0.54	0.28
Total	99.11	99.89	98.54	99.72	98.86	98.50	99.39	99.57	100.90	99.16
S:Si 1:	1.70	1.94	2.09	2.14	2.06	2.04	2.21	2.15	1.79	2.09

(1) average from Livingstone *et al.* (1987); (2, 7, 9) end near crystal termination; (3,5,8,10) crystal centre; (4) crystal edge; (6) broken end

Structural solution

The sample selected for single crystal data collection was a singly-terminated hexagonal prism with dimensions given in Table 2. Precession photographs confirmed the space group as $P6_3/m$ with cell dimensions consistent with those of apatite. The diffractions were sharp with no indication of multiple crystals or twinning. The crystal (complete details in Table 2) was mounted on an automated Picker-Krisel 4-circle diffractometer with *c* offset by 4° from the ϕ axis. Refinement using 20 diffractions ($19 < 2\theta < 32°$: $\lambda = 0.71073$ Å), each the average of automatic centring of 8 equivalent settings gave the final cell parameters (Table 2) consistent with the precession study. A total of 5,988 intensities were collected with ω step scans, 0.02° steps, 1 s/step, and a scan width of 1.5° for a 2θ range of 3.0–55°. Merging yielded 541 intensities ($R_{\text{int}} = 0.03$), all of which were used in refinements: the data collection range was $h \pm 12$, $k = 0$ to 12, $l \pm 9$; mean intensity variation of three standard diffractions was 3%. An analytical absorption correction was applied to the data using the μ value and crystal dimensions in Table 2. Systematic absences indicated space group $P6_3/m$, consistent with the precession study.

The initial structural model was that of apatite but with Pb substituted for Ca in the Ca(1) and Ca(2) positions with full occupancy, Si and S in the ratio of 2:1 with full occupancy in the tetrahedral site, oxygen in O(1), O(2) and O(3) positions, and chlorine placed at 0,0,0 with full occupancy. This Cl position is based on results from other Pb apatites (Hashimoto and Matsumoto, 1998) where the *X* ion is at $z = 0$ in contrast to Ca apatites where the *X* ion *z* value is ~0.06. While this model does not agree with the chemical analysis with respect to the Si and S combined occupancy of 0.87 and the Cl occupancy of 0.55 based on the estimate from microprobe scans, the refinement should point to these descrepencies. In this model, 40 variables were refined: scale factor, extinction parameter, positions for 6 atoms, and anisotropic displacement factors. Neutral scattering factors from SHELXTL were used. The final least-squares

TABLE 2. Experimental details and crystallographic data for mattheddleite.

(A) Crystal-cell data	
a (Å)	10.0056(6)
b (Å)	10.0056(6)
c (Å)	7.4960(9)
V (Å^3)	649.9(1)
Space group	$P6_3/m$
Z	2
Formula	$Pb_5(Si_{1.5}S_{1.5})O_{12}(Cl_{0.57}OH_{0.43})$
D_{calc} (g cm^{-3})	6.822
μ (mm^{-1})	65.05
(B) Intensity measurements	
Crystal size	130 × 30 × 30 µm
Diffractometer	Picker, Krisel control
Monochromator	Graphite
Radiation	Mo-$K\alpha$
Scan type	ω
2θ range	4.7–55.0
Diffractions measured	5,988
Unique diffractions	541
(C) Refinement of the structure	
R 0.065	$R = \Sigma(\lvert\lvert F_0\rvert - \lvert F_c\rvert\rvert)/\Sigma\lvert F_0\rvert$
R_w 0.117	$R_w = [\Sigma w(\lvert F_0^2\rvert - \lvert F_c^2\rvert)^2/\Sigma w\lvert F_0^2\rvert^2]^{1/2}$
Variable parameters	44
'Goodness of fit' (GOF)	1.23

refinement minimized all F^2 values with σ_{F^2} computed from σI, the square root of [total counts + (2% of total counts)^2], $w = (\sigma_{F^2})^{2-}$, $R(F) = 0.065$, $R_w(F^2) = 0.117$, $S = 1.23$; largest shift/e.s.d. ~ −0.014 for all parameters; the maximum and minimum heights on final difference-Fourier map are +4.0 and −4.0 e Å^{-3}; and computer programs: local data reduction, SHELXTL. Following refinement, the major peaks on the difference Fourier map were close to Pb(2) suggesting disorder at this position. The displacement parameter for Cl was large suggesting that the electron density should be lowered consistent with the partial occupancy of Cl and assumed OH. The displacement parameter of the tetrahedral site was not abnormal relative to that of P in published structures of pyromorphites (Dai and Hughes, 1989; Hashimoto and Matsumoto, 1998). The relatively high resultant *R* value of 0.096 and the residual peaks close to Pb(2) suggested that this model could be improved.

In the next refinement stage, Pb(2) was not fixed at $z = 1/4$ giving two equal half atoms. Disorder in the equivalent Ca(2) position in some apatites has also been recognized (Sudarsanan and Young, 1978; Hughes *et al.*, 1990). In contrast to their two split Ca(2) positions both with $z = 1/4$, we allowed Pb(2) to occupy a general position but with half occupancy. The *X* site was fixed at 0,0,0 as there was no indication of significant electron density elsewhere along *c* as observed for some natural ternary Ca apatites (Hughes *et al.*, 1990). The initial occupancy of the *X* site was set at Cl+OH = 1.0 but the ratio of Cl to OH was refined. The fractions of Si and S were calculated relative to five Pb atoms to give a Si:S ratio of 0.59:0.28 and the occupancy of the tetrahedral site was fixed at 0.87 with this Si:S ratio. The results of this refinement showed a reduction of R to 0.065 mainly due to the splitting of Pb(2). The Cl:OH ratio refined to 0.57:0.43 in very good agreement with that estimated from the microprobe results.

The tetrahedral site remained a problem with an occupancy <1 and unequal Si:S which gives a deficiency of positive charge. An attempt was first made to allow the total occupancy of this site to refine from the initial 0.87 value but maintaining a Si:S ratio of 0.59:0.28. While the *R* value did not change, the occupancy of this site increased from 0.87 to 1.01(2) suggesting that additional electron density was required for this site. Another attempt filled this site with C to give a Si:S:C ratio of 0.59:0.28:0.13. Refining the amount of C resulted in a total occupancy of 1.28(9) again with no change in *R* which apparently is not sensitive to these minor changes. Both these attempts indicated that additional electron density was required in the tetrahedral site but that this could not be rationalized with the microprobe analyses. Both of these trial refinements indicated that the required average electrons/atom in the tetrahedral site was near 15 to satisfy the X-ray data. This would correspond to the average of equal occupancy for Si and S with the tetrahedral site filled. Because an end-member of the ellestadite series close to $Ca_5Si_{1.5}S_{1.5}O_{12}(OH,F,Cl)$ exists (Rouse and Dunn, 1982), we next attempted a refinement where Si = S and refined the total occupancy anticipating that this would be close to 1.0. Indeed, the occupancy was 0.99(3). From this result we conclude that there is no problem with charge balance or partial occupancy in matthed-

TABLE 3. Positional and isotropic displacement parameters for mattheddleite.

Atom	*x*	*y*	*z*	$*U_{eq}$
Pb (1)	1/3	2/3	0.0057(2)	0.0331(5)
Pb (2)	0.2507(2)	−0.0004(2)	0.2136(3)	0.0402(8)
** S,Si	0.4058(7)	0.3814(7)	1/4	0.014(2)
O (1)	0.332(2)	0.487(2)	1/4	0.028(4)
O (2)	0.589(2)	0.480(3)	1/4	0.039(5)
O (3)	0.357(2)	0.275(2)	0.082(2)	0.038(3)
** *X*	0	0	0	0.035(4)

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

** S,Si = $S_{0.5}Si_{0.5}$; $X = Cl_{0.57}OH_{0.43}$

TABLE 4. Anisotropic displacement parameters for mattheddleite.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pb (1)	0.0364(5)	0.0364(5)	0.0264(7)	0.0	0.0	0.0182(3)
Pb (2)	0.0296(7)	0.0415(8)	0.050(2)	0.0058(8)	0.0176(8)	0.0182(6)
S,Si	0.013(3)	0.010(3)	0.020(3)	0.0	0.0	0.008(2)
O (1)	0.034(10)	0.033(10)	0.025(9)	0.0	0.0	0.023(9)
O (2)	0.010(8)	0.040(12)	0.059(14)	0.0	0.0	0.007(8)
O (3)	0.055(9)	0.032(7)	0.035(8)	−0.003(7)	−0.007(7)	0.029(7)
Cl,OH	0.032(5)	0.032(5)	0.042(9)	0.0	0.0	0.016(3)

dleite based on our single crystal X-ray results, but this is inconsistent with the microprobe analysis. Final atomic coordinates and isotropic displacement parameters are given in Table 3, anisotropic displacement parameters in Table 4, and interatomic distances in Table 5 for this final structural model.

Discussion

The electron microprobe analyses of mattheddleites from two locations using three different microprobes all indicated Si > S in the tetrahedral site, that the total occupancy of this site was <1.0, and that there was thus an excess of negative charge. The present single crystal structural analysis of mattheddleite results in a model consistent with Si = S, full occupancy in the tetrahedral site, and no residual charge unbalance. The absence of any other detectable element with the possible exception of C, precludes any other substitution in the tetrahedral site to give both charge balance and full occupancy. An additional argument for Si = S might be made from the predicted and observed T–O bond lengths. Using an average S–O length of 1.49 and an average Si–O length of 1.63 Å (Baur, 1970), the resulting predicted bond length should be 1.56 Å which compares favourably with an observed average of 1.568 Å. The X-ray results are the simplest and avoid any complex structural model. At the same time it is difficult to summarily exclude the microprobe results. Possibly the only argument that might be made is that large corrections are required due to absorption of Si and S X-rays by Pb, and these coefficients may not be sufficiently accurate. While analyses of ellestadite (Rouse and Dunn, 1982) give a Si:S ratio of 1:1, the absorption coefficients of Pb are about twice those of Ca for Si and S X-rays and thus absorption corrections, in particular, are much greater for mattheddleite compositions.

The zoning in Cl clearly shown in Fig. 2 may in part be the cause of the apparent splitting of Pb(2). From studies of Ca apatites, it has been shown that there is a strong interaction between Ca(2) and the *X* anion (Cl, F, OH). In particular, the presence of Cl can be correlated with a splitting of Ca(2) (Sudarsanan and Young, 1978; Hughes *et al.*, 1990). Because a zoned crystal was used for data collection, the exterior was enriched in Cl (Fig. 2) and based on Ca apatites would tend to cause a splitting of Pb(2); the interior of the crystal has OH > Cl and would tend not to have

TABLE 5. Bond lengths (Å) for mattheddleite ($Pb_5Si_{1.5}S_{1.5}O_{12}(Cl_{0.57},OH_{0.43})$).

Pb (1) –O (1) x3	2.57(1)	Pb (2)–O (2)	2.36(2)	Si,S –O (1)	1.56(2)
–O (2) x3	2.76(2)	–O (3)	2.42(1)	–O (3)	1.56(2)
–O (3) x3	2.93(2)	–O (3)	2.60(1)	–O (3)	1.56(2)
		–O (3)	2.85(1)	–O (2)	1.59(2)
		–O (3)	2.93(2)		
		–O (1)	2.97(2)		
		–Cl,OH	2.977(2)		

this effect. Confirmation of these interactions must await unzoned crystals.

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