The missing sulphur in mattheddleite, sulphur analysis of sulphates, and paragenetic relations at Leadhills, Scotland

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ABSTRACT

Published electron microprobe analyses of mattheddleite, a lead sulpho-silicate apatite from Leadhills, Scotland, have 9–13% IV site deficiencies. However, galena was used as a standard for S, which suggested that low S resulted from a shift in the S-Kα peak. Wavelength scans with a PET crystal show that the S-Kα peak is shifted down by 0.0026 Å for sulphates relative to sulphides. Quantitative analyses show a ~30% increase of S in mattheddleite using a celestite standard, which fills the IV site, but with Si > S, on average Pb5Si2Si1.8O11.7Cl0.6(OH)0.4. Direct analysis of oxygen with the electron probe implies that the charge imbalance engendered from the inequality of Si and S is compensated with substitution of a vacancy (□), as in Pb5Si2Si1.8O11.7□0.3[Cl0.6(OH)0.4] or Pb5Si2Si1.8[O11.7□0.3][ClOH]0.7□0.3. Calculation of OH as 1–Cl suggests the presence of both OH- and Cl-dominant mattheddleite at Leadhills, but direct analysis of H is needed to confirm the dominance of OH in the channel site. Wavelength-dispersive analyses of S in apatite and other sulphates must be undertaken with sulphate standards: use of sulphide standards yields a negative error on the order of 10–20% in the resultant S concentration. Reactions of mattheddleite with other Pb minerals at Leadhills show that their stability depends on fluid composition as well as pressure and temperature. An X-ray map of Cl shows complex zoning between Cl-poor and Cl-rich mattheddleite, recording rapid changes in the fluid chemistry during late-stage hydrothermal processes at Leadhills.

KEYWORDS: mattheddleite, sulphate, apatite, wavelength shift, Cl migration, Leadhills, phase equilibria.

Introduction

Sulphatoan apatite is known to occur as a result of charge-compensated substitutions that allow $S^{6-}$ to substitute for $P^{5+}$ in the IV site. Exchange involving sulphate in the apatite group includes (1) $2P^{5+} = Si^{4+} S^{6-}$, which points towards ellestadite, Ca$_3$(SiO$_4$)$_{0.5}$(SO$_4$)$_{1.5}$(F,Cl,OH) (e.g., McConnell, 1937; Harada et al., 1971) and mattheddleite, Pb$_5$(SiO$_4$)$_{0.5}$(SO$_4$)$_{1.5}$(Cl$_2$,OH) (Steele et al., 2000); and (2) $R^2P^{5+} = Na^+ S^{6-}$, which leads to cesanite, Na$_3$Ca$_2$(SO$_4$)$_2$OH (Cavarretta et al., 1981; Piotrowski et al., 2002; Chakhmouradian and Medi, 2006) and carbonatite, Na$_3$Pb$_2$(SO$_4$)$_3$Cl (Seeliger and Berdesinski, 1956). An X-ray structure refinement by Hughes and Drexler (1991) on hydroxylellestadite revealed partial ordering of Si and S in different IV sites, which should also be evaluated for mattheddleite. Apatite with minor sulphate has been reported in oxidized granites (Peng et al., 1997; Streck and Dilles, 1998; Barth and Dorais, 2000; Core et al., 2006), carbonatites and alkaline igneous rocks (Liu and Comodí, 1993), and in hydrothermal veins (Shiga and Urashima, 1987). Apatite from most igneous and metamorphic rocks has approximately stoichiometric substitution on the VIII and IV sites, but electron microprobe analyses of mattheddleite yielded 8% (Livingstone et al., 1987) and 13% (Steele et al., 2000) deficiency on the IV site. In their refinement of the crystal structure of mattheddleite Steele et al. (2000) assumed full occupancy of the IV site with Si = S. They concluded that the absorption correction in the microprobe analysis
of S had a systematic error, and that the mattheddleite formula is Pb$_3$(SiO$_4$)$_1$(SO$_4$)$_{1.5}$ (Cl,OH). It is difficult to distinguish Si from S in an X-ray structure refinement, and that conclusion is in need of further tests.

Livingstone et al. (1987) and Steele et al. (2000) used galena as a standard for wavelength dispersive (WDS) analyses of mattheddleite with an electron microprobe. However, the peak position of the S-K$_\alpha$ line is known to shift to lower wavelengths in sulphates relative to sulphides. Measurements of the peak shift on the electron microprobe using sulphate and sulphide standards was used nearly 40 y ago to identify the valence state of sulphur in the biotite group mineral anadinite (Lovering and Widdowson, 1966a,b). The shift has also been used to determine whether sulphide or sulphate is substituted in silicate glass (Connolly and Haughton, 1972; Carroll and Rutherford, 1988; Wallace and Carmichael, 1994; Matthews et al., 1999). It seemed likely, therefore, that the deficiency in the IV site of mattheddleite might be an artifact of the standards rather than representing a real IV deficiency or one related to errors in mass absorption coefficients.

Sample description

The minerals of the Leadhills district in Scotland have been described by Brown (1919), Temple (1956), Gillanders (1981) and Livingstone (2002). The Pb minerals in the system Pb-Si-C-O-S-H that have been reported at Leadhills include anglesite (PbSO$_4$), cerussite (PbCO$_3$), galena (PbS), hydrocerussite (Pb$_3$(CO$_3$)$_2$(OH)$_2$), lanarkite (Pb$_2$O$_3$O$_4$), lead (Pb), minium (Pb$_3$O$_4$), plattnerite (PbO$_2$), scotlandite (PbSO$_4$), and the polymorphs of Pb$_4$SO$_4$(CO$_3$)$_2$(OH)$_2$ (leadhillite, macphersonite, susannite) (Temple, 1956; Abdul-Samad et al., 1982; Livingstone and Sarp, 1984; Paar et al., 1984b; Livingstone and Russell, 1985; Livingstone et al., 1987; Livingstone, 2002). Other Pb minerals in this system include alamosite, PbSiO$_3$, and plumbotsumite, Pb$_2$Si$_4$O$_8$(OH)$_{16}$, which have been found at Tsuimb (Keller and Dunn, 1982). Brown (1919) suggested that some samples of minium might be the product of smelting at Leadhills, and it is possible that the occurrences of native lead there have a similar origin. Livingstone et al. (1987) characterized the new mineral mattheddleite from a secondary vein at Leadhills associated with quartz-caledonite-cerussite-leadhillite-susannite-
macphersonite and lanarkite-cerussite-hydrocerussite-leadhillite-caledonite.

A mattheddleite sample from Leadhills, Scotland, was used to evaluate the wavelength shift in its S-K$_\alpha$ peak and compare analyses using sulphide vs. sulphate standards. It is sample NMS G 1878.49.488.2 from the National Museums of Scotland and is labelled as ‘mattheddleite with leadhillite and susannite from Leadhills, Lanarkshire’, the same sample as studied by Steele et al. (2000). The mattheddleite sample consists of small aggregates of transparent crystals. It was mounted in epoxy, polished and examined with backscattered electron (BSE) imaging on a CAMECA SX-100 electron microprobe. The BSE image shows central areas with blades with a higher average atomic number (Z) intergrown with large euhedral crystals with lower Z, all surrounded by equant to elongate crystals with intermediate contrast (Fig. 1).

Energy dispersive spectroscopy (EDS) shows that the latter area has Pb+Si, Si and Cl, which is consistent with mattheddleite. The two intergrown phases in the interior of the crystal aggregate are both rich in Pb+Si but lack Si and Cl. Anglesite,

![Image](image.png)

**Fig. 1.** BSE image of a lower Z (darker contrast) Pb sulphate (leadhillite and/or susannite) with high Z (bright contrast) blades (hydrocerussite) and rims of intermediate Z phase (mattheddleite). The dark areas were voids (now plastic). The vertical bands in the leadhillite are the result of electron beam damage. Image collected at 15 kV, 30 nA, a point beam, and a 2 μm step per pixel, 200 ms dwell time per pixel, for the 1024 × 1024 μm scan, total time 14 h.
cerussite, galena, hydrocerussite, lanarkite, scotlandite and the leadhillite polymorphs are difficult to distinguish with routine EDS observations on a carbon-coated sample as a result of severe overlap of S-Kα and Pb-Mα peaks, and the potential contribution of the carbon coat to C-Kα. The average atomic number Z (in parentheses) of each end-member mineral was calculated from the ideal formulae as follows: anglesite (59.4), scotlandite (62.3), the leadhillite polymorphs (65.0), cerussite (65.3), lanarkite (66.7), hydrocerussite (67.2), shannonite (70.5) and galena (73.2). The average Z for Cl-mattheddeite (65.3) and OH-mattheddeite (65.7) was calculated using an idealized formula with Si=S, comparable to an average Z of 65.5 calculated directly from analytical data in this paper for the real mattheddeite. It is evident that most of the Pb minerals have a larger Z than mattheddeite. The low Z phase inside the mattheddeite aggregates is probably leadhillite, although the presence of susannite or macphersonite cannot be excluded.

Slow BSE scans revealed subtle contrast in the mattheddeite (Fig. 1), and X-ray mapping of the Cl was therefore undertaken. Images that were first collected over 20 min showed Cl zoning but were noisy because of the relatively low count rates for Cl. Additional slower scans were obtained including a 14 h scan (Fig. 2). They show remarkable oscillatory zoning in the Cl content of the mattheddeite that is only poorly resolved even in the BSE image obtained at lower magnification (Fig. 1). A spectacular SEM image of a variably resorbed mattheddeite specimen from Caldbeck Fells was shown by Cooper and Stanley (1990). Several zones of high, low and

Fig. 2. False colour X-ray map of Cl distribution showing a leopard-skin pattern in zoned mattheddeite. The Cl map reveals at least seven growth zones with different Cl, best seen in the labelled elongate grain near the bottom of the image (traverse shown in Fig. 3). Scan conducted at 15 kV, 30 nA, a point beam, 1 μm step per pixel, 200 ms dwell time per pixel, for the 512 x 512 μm scan, and total time 14 h. The yellowish-white areas (stage 6) have the highest Cl (~2.5 wt.% Cl), and the golden brown areas have the lowest Cl (~1 wt.% Cl). Using the lighter areas as a guide allows one to identify the timing of growth of the mattheddeite aggregates. In hexagonal cross-sections, one can see the white-yellow near a few margins, but stage 2 growth (lighter yellow, itself delicately zoned in Cl, cf. dip in peak shown in Fig. 3) is more commonly developed in the cross-sections. The large crystals (orange-brown euhedra) overgrown by mattheddeite are a leadhillite polymorph with blades of hydrocerussite (cf. Fig. 1), and marginal, deep brown areas are cavities filled by epoxy. The leadhillite and hydrocerussite have a higher background reading for Cl than the epoxy, which produces minor apparent Cl in the scan, which is uncorrected for Cl background. Cl analyses along the line A–A’ are shown in Fig. 3.
medium Cl growth are best resolved in long cross-
sections. The large crystal with the line near the
bottom of Fig. 2 was selected for a detailed
traverse. From the core outward, zones 1 and 4 are
lowest in Cl (dark brown areas), and zone 6 is
highest (yellowish-white areas). One elongate
grain in the image was selected for a detailed
analytical traverse; the result shows that the Cl
has two peaks of growth with declining values
between the peaks (Fig. 3). The initially separate,
euhedral crystals were welded together into a
leopard-skin mass primarily during growth of
zone 4. Cathodoluminescence images were
collected on the same area as Fig. 2 but revealed
little contrast.

Analytical procedures

Analytical conditions that were employed are
summarized in Table 1. Natural alamosite,
\( \text{PbSiO}_3 \) (Boucher and Peacor, 1968) has been
demonstrated by electron microprobe analysis to
have no observable solid solutions, and it was
used for the analysis of \( \text{Pb} \), \( \text{Si} \) and \( \text{O} \). For
comparison, a galena standard was used for \( \text{Pb} 
\) and \( \text{S} \), and a Cameca routine that shifts the
wavelength position between standards and
unknowns was also employed (Table 2). Wavelength
scans over \( S-K\alpha \) were obtained on matthedite, anhydrite, celestite, pyrite, troilite
and galena. The scans were centred around the
peak on four different PET crystals on the SX-100
electron microprobe at the University of Michigan
(Fig. 4). The Cameca peaking routine yields a
shift of 0.0026 Å (30 in 10,000 Sinθ units) in the
peak positions between the sulphides and the
sulphates. A similar shift is the basis for
distinguishing sulphate vs. sulphide species in
basaltic glass (e.g. Carroll and Rutherford, 1988).
Peaking the \( S-K\alpha \) peak on a sulphide standard
with default Cameca procedures places the
spectrometer on the shoulder of the \( S-K\alpha \) peak for
sulphates, thus giving low peak S values for
sulphate unknowns. Analysing a peak on its
shoulder means that the result is sensitive to the
exact shape and location of the peak, which
depends on the diameter of the Rowland circle,
the detector slit size, the spectrometer crystal and
its size, each of which may vary from machine to
machine. Thus, one cannot anticipate a fixed
correction to the low S that is caused by the
wavelength shift in different laboratories, and it
should be calibrated in each facility.

Wavelength scans were also conducted across
the \( \text{Pb-M}\gamma \) and \( S-K\alpha \) peaks in order to select
background measurement positions for \( \text{Pb} \) and \( S \)
that avoid striking the tails of the other peaks
(Fig. 5). Careless placement of the low-wave-
length background position for \( \text{Pb} \) and the high-
wave-length background setting for \( S \) may lead to
reduced \( \text{Pb} \) or \( S \) levels in matthedite due to an
anomalously raised background for \( \text{Pb} \) or \( S \).
Wavelength scans conducted across \( \text{Pb-M}\gamma \) and
\( \text{Cl-K}\alpha \) on matthedite showed that no back-
ground interference was encountered during
quantitative analysis of its Cl.

Trace and minor elements were analysed separately at higher current and over a longer
period to improve the detection limits (Table 1).
The elements F, Ca, Mn, V, As, Sr, Y, Ba, La, Ce,
Pr, Nd, Sm, Gd and Th were analysed both in
matthedite and the alamosite standard. To

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![Graph showing Cl content vs distance](image-url)

**Fig. 3.** Traverse of wt.% Cl for the elongate grain (marked as line \( \text{A} - \text{A}' \) in Fig. 2) showing variation in Cl along the
length of the matthedite crystal. The second zone near the core of the grain is to the right and the rim is to the left.
The very narrow zone of low Cl in the core of the elongate crystal was unintentionally excluded from the scan. The
value of 1.0 wt.% Cl for stage 3 corresponds to 0.37 Cl p.f.u. and 2.5 wt.% Cl for stage 6 is ~0.93 Cl p.f.u. Every
third analysis from this traverse is in Table 3.
SULPHUR IN MATTHEDDLEITE, LEADHILLS, SCOTLAND

Table 1. Analytical conditions for analysis of mattheddaleite.\(^1\)

<table>
<thead>
<tr>
<th>Element line</th>
<th>Crystal(^4)</th>
<th>Standards</th>
<th>Background λ shift(^2)</th>
<th>DL (ppm)(^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F-Kα</td>
<td>PC1</td>
<td>Henry Mtns. fluor-topaz</td>
<td>+2000</td>
<td>330</td>
</tr>
<tr>
<td>O-Kα</td>
<td>LPC0</td>
<td>Peacock alamosite</td>
<td>+4000, −3000</td>
<td>1100</td>
</tr>
<tr>
<td>Na-Kα</td>
<td>LTAP</td>
<td>Tiburon albite</td>
<td>+500</td>
<td>260</td>
</tr>
<tr>
<td>Si-Kα</td>
<td>TAP</td>
<td>alamosite, wollastonite</td>
<td>+500</td>
<td>320</td>
</tr>
<tr>
<td>P-Kα</td>
<td>LPET</td>
<td>synthetic alfsorite</td>
<td>+500</td>
<td>580</td>
</tr>
<tr>
<td>S-Kα</td>
<td>LTAP</td>
<td>Maybe celestite</td>
<td>+540, −1870</td>
<td>360</td>
</tr>
<tr>
<td>Cl-Kα</td>
<td>PET</td>
<td>synthetic alfsorite</td>
<td>+500</td>
<td>440</td>
</tr>
<tr>
<td>Ca-Kα</td>
<td>PET</td>
<td>ANU wollastonite</td>
<td>+500</td>
<td>360</td>
</tr>
<tr>
<td>Mn-Kα</td>
<td>LLIF</td>
<td>Broken Hill rhodonite</td>
<td>+500</td>
<td>270</td>
</tr>
<tr>
<td>V-Kα</td>
<td>LLIF</td>
<td>synthetic (V_2O_5)</td>
<td>+900</td>
<td>230</td>
</tr>
<tr>
<td>As-Lα</td>
<td>LTAP</td>
<td>natural olivenite</td>
<td>±600</td>
<td>250</td>
</tr>
<tr>
<td>Sr-Lα</td>
<td>LPET</td>
<td>Maybe celestite</td>
<td>±500</td>
<td>700</td>
</tr>
<tr>
<td>Y-Lα</td>
<td>PET</td>
<td>syn. Y-Al garnet (YAG)</td>
<td>−1600, slope 0.81</td>
<td>520</td>
</tr>
<tr>
<td>Ba-Lα</td>
<td>LLIF</td>
<td>synthetic alfsorite</td>
<td>±500</td>
<td>1100</td>
</tr>
<tr>
<td>La-Lα</td>
<td>LLIF</td>
<td>synthetic LaPO(_4)</td>
<td>±500</td>
<td>980</td>
</tr>
<tr>
<td>Ce-Lα</td>
<td>LLIF</td>
<td>synthetic CePO(_4)</td>
<td>±500</td>
<td>970</td>
</tr>
<tr>
<td>Pr-Lβ</td>
<td>LLIF</td>
<td>synthetic PrPO(_4)</td>
<td>−520, slope 1</td>
<td>2260</td>
</tr>
<tr>
<td>Nd-Lα</td>
<td>LLIF</td>
<td>synthetic NdPO(_4)</td>
<td>+1800, −1930</td>
<td>960</td>
</tr>
<tr>
<td>Sm-Lβ</td>
<td>LLIF</td>
<td>synthetic SmPO(_4)</td>
<td>±500, −512</td>
<td>1340</td>
</tr>
<tr>
<td>Gd-Lβ</td>
<td>LLIF</td>
<td>synthetic GdPO(_4)</td>
<td>±500, −420</td>
<td>1420</td>
</tr>
<tr>
<td>Pb-Lα</td>
<td>PET</td>
<td>Peacock alamosite, galena</td>
<td>+1500, −900</td>
<td>1330</td>
</tr>
<tr>
<td>Th-Mα</td>
<td>PET</td>
<td>synthetic ThSiO(_4)</td>
<td>+800, −1300</td>
<td>1250</td>
</tr>
</tbody>
</table>

\(^1\) analyses at 15 kV, 10 nA, 5 µm beam, 30 s for peak, 30 s for background(s)
\(^2\) units 10,000\(\times\)Sinθ
\(^3\) DL = detection limit of individual analysis
\(^4\) L, in front of PC0, TAP, PET, LIF means large spectrometer crystal

Minimize interferences, Lβ lines were used for Pr, Sm and Gd, and Mβ was chosen for Th (Table 1). None of the above elements was found at a level exceeding its detection limit. The detection limit of the heavy elements (Ba, REE, Th) is in the range 900–1400 ppm, not optimal for their

![Graph](image)

Fig. 4. Wavelength scans across the S-Kα peaks of mattheddaleite, anhydrite, celestite, pyrite and galena using a PET crystal (2\(\sigma\) = 8.75 Å). The counts are normalized to unity for the highest point on each scan to facilitate comparisons among the different phases. The peak positions of the sulphates are at ~5.372 Å and the sulphides at 5.374 Å. The S-Kα peak for trolite (not shown) is located at the same position as that for galena and pyrite.
Table 2. Matthedleite analyses with different procedures.

<table>
<thead>
<tr>
<th>Standard</th>
<th>Celestite</th>
<th>Galena</th>
<th>Galena shifted</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt.% oxide</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SO₃</td>
<td>7.20</td>
<td>5.57</td>
<td>6.90</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>n.d.³</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>SiO₂</td>
<td>7.84</td>
<td>7.88</td>
<td>7.90</td>
</tr>
<tr>
<td>PbO</td>
<td>82.89</td>
<td>82.96</td>
<td>82.83</td>
</tr>
<tr>
<td>Cl</td>
<td>1.45</td>
<td>1.36</td>
<td>1.39</td>
</tr>
<tr>
<td>H₂O⁴</td>
<td>0.31</td>
<td>0.32</td>
<td>0.32</td>
</tr>
<tr>
<td>Cl=O</td>
<td>-0.32</td>
<td>-0.25</td>
<td>-0.26</td>
</tr>
<tr>
<td>Sum⁵</td>
<td>99.27</td>
<td>97.84</td>
<td>99.08</td>
</tr>
<tr>
<td>Atoms⁶</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>1.21</td>
<td>0.94</td>
<td>1.16</td>
</tr>
<tr>
<td>P</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Si</td>
<td>1.76</td>
<td>1.76</td>
<td>1.77</td>
</tr>
<tr>
<td>Pb</td>
<td>5.00</td>
<td>5.00</td>
<td>5.00</td>
</tr>
<tr>
<td>O</td>
<td>11.65</td>
<td>10.85</td>
<td>11.53</td>
</tr>
<tr>
<td>Cl</td>
<td>0.55</td>
<td>0.52</td>
<td>0.53</td>
</tr>
<tr>
<td>OH⁷</td>
<td>0.45</td>
<td>0.48</td>
<td>0.47</td>
</tr>
<tr>
<td>IV site</td>
<td>2.97</td>
<td>2.70</td>
<td>2.93</td>
</tr>
</tbody>
</table>

¹ average analysis of the same 9 points as in Table 2
² shift in peak position corrected with a Cameca routine
³ not detected
⁴ back-calculated
⁵ incl. −Cl=O
⁶ normalized to Pb = 5
⁷ 1−Cl

One wishes to improve the analytical results for these trace elements, another analytical technique such as inductively couple plasma-mass spectrometry should be employed.

The possibility of Cl migration during electron microbeam analysis, as was reported in chlorapatite (Stormer et al., 1993), is also in need of evaluation before undertaking quantitative analysis of apatite group minerals. To evaluate migration of Cl, time tests were undertaken with (1) a point beam at 15 kV and 25 nA (the analytical conditions of Steele et al., 2000), (2) a point beam at 15 kV and 10 nA, and (3) a 5 µm wide beam at 15 kV and 10 nA. The results of (1) and (2) show a gradual Cl increase in the apatite with time, whereas (3) shows no change in Cl within the precision of the method (Fig. 6). The effect on the Cl analyses of Steele et al. (2000) depends on the Cl counting time and whether Cl was the first element analysed on a given spectrometer (which is likely in this case). The Cl content as measured by Steele et al. (2000) would have risen by ~1.4% of the amount present (OAP) over 30 s and by 2.8% OAP over 60 s, with the average Cl increasing by half that during the total counting time, or only 0.15−0.27 wt.% at 30−60 s of analysis time, an insignificant increment. The effect of orientation described by Stormer et al. (1993) was also evaluated by time tests with a point beam on Cl-rich areas from a hexagonal cross section vs. a long section of apatite, but the results were similar until after 8 min, after which the measured Cl in the cross-section was lost more rapidly. The amount of Cl increase at a given voltage, current and beam size depends on the total electron

Fig. 5. Wavelength scan across the Pb-Mα and S-Kα peaks showing the placement of the locations of background positions for both Pb and S.
exposure time before which the Cl analysis is completed. Such tests are essential before undertaking quantitative measurements of halogens on apatite, but mattheditleite does not appear to be perturbed for analysis at reasonable times and currents, even with a point beam.

Oxygen was analysed directly on mattheditleite to evaluate the possibility of an anion deficiency resulting from the inequality of Si and S in the formula. Natural alamosite (Boucher and Peacor, 1968) was selected as a standard after preliminary calculations of ZAF factors for O between mattheditleite and alamosite showed only minor corrections. Mineral formulae in this study were calculated with cation-based normalization procedures (e.g. Afifi and Essene, 1988; Essene, 1989). The mattheditleite analyses were normalized to 5 Pb atoms because the numbers of anions were not measured directly, and the occupancy of the IV site (S+Si) is under evaluation in this contribution. The average O in the mattheditleite sample is 12.1 per formula unit (p.f.u.), and subtracting 0.4 p.f.u. OH assuming it is equal to 1–Cl leaves 11.7 (p.f.u.) for the framework O (Table 3).

Quantitative analyses of mattheditleite were obtained using both galena and celestite as standards for S. The OH was calculated as 1–Cl and the equivalent wt.% H2O was back-calculated from the molar OH (Tables 2 – 5). For analysis of the host hydrocerussite and leadhillite, the wt.% CO2 was initially calculated as the difference from 100% in order to provide an adequate matrix for the ZAF corrections. The Pb and S levels in the analyses indicate that the low-Z phase in the host is a leadhillite polymorph and the high-Z blades are hydrocerussite. The CO3 and OH were assumed to be stoichiometric in these two phases and the wt.% H2O and CO2 in the analyses was back-calculated (Table 5). The high totals in hydrocerussite are attributed to partial degassing of H2O and/or CO2 that produced an increased wt.% PbO during the analysis. Its low apparent S and Si may also reflect fluorescence of S and Si by Pb X-rays interacting with the surrounding leadhillite.

**Analytical results**

The wavelength scans in the position of the S-Kα peak showed a systematic shift of the sulphides vs. the sulphates including mattheditleite (Fig. 4). Electron microprobe analysis of mattheditleite using sulphide standards will yield low S because the peak position for the sulphides is located on the shoulder of the S peak for mattheditleite. That was confirmed by direct analysis of the mattheditleite using celestite as a standard for S (Table 4) compared to galena (Table 2). The apparent S level of mattheditleite analysed with a celestite standard is ~30% higher than that analysed with a galena standard. This observation shows why electron microprobe analyses in Livingstone et al. (1987) and Steele et al. (2000) produce deficiencies on the IV site of mattheditleite. The peak shift routine using a galena standard improved the mattheditleite analyses, although the result for S is still not the same as that using a celestite standard.
Table 3. Analyses along a traverse of matheudeite including direct measurement of oxygen\(^1\).

<table>
<thead>
<tr>
<th>Wt. %</th>
<th>2</th>
<th>5</th>
<th>8</th>
<th>11</th>
<th>14</th>
<th>17</th>
<th>20</th>
<th>23</th>
<th>26</th>
<th>29</th>
<th>32</th>
<th>35</th>
<th>38</th>
<th>ave.(^2)</th>
<th>s.d.(^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>2.81</td>
<td>2.76</td>
<td>2.83</td>
<td>2.80</td>
<td>2.82</td>
<td>2.83</td>
<td>3.07</td>
<td>2.98</td>
<td>3.01</td>
<td>2.96</td>
<td>2.98</td>
<td>3.03</td>
<td>3.03</td>
<td>2.90</td>
<td>0.12</td>
</tr>
<tr>
<td>P(^3)</td>
<td>0.03</td>
<td>0.01</td>
<td>0.00</td>
<td>0.00</td>
<td>-0.02</td>
<td>0.00</td>
<td>0.02</td>
<td>0.01</td>
<td>0.02</td>
<td>-0.03</td>
<td>-0.03</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>-</td>
</tr>
<tr>
<td>Si</td>
<td>3.80</td>
<td>3.61</td>
<td>3.76</td>
<td>3.75</td>
<td>3.83</td>
<td>3.75</td>
<td>3.54</td>
<td>3.60</td>
<td>3.62</td>
<td>3.71</td>
<td>3.61</td>
<td>3.68</td>
<td>3.53</td>
<td>3.65</td>
<td>0.10</td>
</tr>
<tr>
<td>Pb</td>
<td>76.04</td>
<td>76.15</td>
<td>77.21</td>
<td>77.60</td>
<td>76.54</td>
<td>75.97</td>
<td>77.07</td>
<td>76.65</td>
<td>76.76</td>
<td>76.59</td>
<td>76.51</td>
<td>77.07</td>
<td>76.91</td>
<td>76.67</td>
<td>0.44</td>
</tr>
<tr>
<td>Cl</td>
<td>1.67</td>
<td>2.45</td>
<td>1.60</td>
<td>0.98</td>
<td>0.94</td>
<td>1.16</td>
<td>1.80</td>
<td>1.71</td>
<td>1.67</td>
<td>1.35</td>
<td>1.49</td>
<td>1.65</td>
<td>1.86</td>
<td>1.57</td>
<td>0.10</td>
</tr>
<tr>
<td>H(^4)</td>
<td>0.01</td>
<td>0.07</td>
<td>0.12</td>
<td>0.12</td>
<td>0.10</td>
<td>0.05</td>
<td>0.06</td>
<td>0.06</td>
<td>0.09</td>
<td>0.08</td>
<td>0.07</td>
<td>0.05</td>
<td>0.07</td>
<td>0.01</td>
<td>-</td>
</tr>
<tr>
<td>Cl=O</td>
<td>-0.37</td>
<td>-0.61</td>
<td>-0.54</td>
<td>-0.35</td>
<td>-0.22</td>
<td>-0.21</td>
<td>-0.26</td>
<td>-0.40</td>
<td>-0.38</td>
<td>-0.37</td>
<td>-0.30</td>
<td>-0.33</td>
<td>-0.36</td>
<td>-0.34</td>
<td>-</td>
</tr>
<tr>
<td>Sum</td>
<td>98.71</td>
<td>99.68</td>
<td>100.08</td>
<td>99.72</td>
<td>98.76</td>
<td>98.48</td>
<td>99.69</td>
<td>99.15</td>
<td>99.25</td>
<td>99.11</td>
<td>98.88</td>
<td>99.50</td>
<td>99.46</td>
<td>99.37</td>
<td>0.45</td>
</tr>
</tbody>
</table>

Atoms\(^5\)

| S     | 1.20 | 1.17 | 1.19 | 1.17 | 1.19 | 1.20 | 1.29 | 1.26 | 1.27 | 1.25 | 1.26 | 1.27 | 1.27 | 1.22 | 0.05 |
| P\(^3\) | -0.01 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | -0.01 | -0.01 | 0.00 | 0.00 | 0.00 | -   |
| Si    | 1.84 | 1.75 | 1.80 | 1.79 | 1.85 | 1.82 | 1.70 | 1.73 | 1.74 | 1.79 | 1.74 | 1.76 | 1.69 | 1.77 | 0.05 |
| Pb    | 5.00 | 5.00 | 5.00 | 5.00 | 5.00 | 5.00 | 5.00 | 5.00 | 5.00 | 5.00 | 5.00 | 5.00 | 5.00 | 5.00 | 0.00 |
| O     | 12.54 | 12.50 | 12.26 | 12.08 | 12.30 | 12.51 | 11.89 | 11.94 | 11.93 | 12.27 | 12.10 | 11.78 | 11.87 | 12.12 | 0.24 |
| Cl\(^6\) | 0.64 | 0.94 | 0.60 | 0.37 | 0.36 | 0.45 | 0.68 | 0.65 | 0.63 | 0.51 | 0.57 | 0.63 | 0.71 | 0.59 | 0.15 |
| OH\(^7\) | 0.36 | 0.06 | 0.40 | 0.63 | 0.64 | 0.55 | 0.32 | 0.35 | 0.37 | 0.49 | 0.43 | 0.37 | 0.29 | 0.41 | 0.15 |
| IV site | 3.04 | 2.93 | 2.98 | 2.95 | 3.03 | 3.02 | 2.99 | 3.00 | 3.00 | 3.02 | 3.00 | 3.03 | 2.96 | 2.99 | 0.03 |
| O\(^7\) | 12.19 | 12.44 | 11.87 | 11.45 | 11.66 | 11.96 | 11.58 | 11.59 | 11.56 | 11.78 | 11.67 | 11.41 | 11.58 | 11.71 | 0.27 |

\(^1\) every 3rd analysis (numbered from rim to core) in the traverse on Fig. 2  
\(^2\) ave (average) and s.d. (standard deviation) from mean of 38 analyses  
\(^3\) negative values retained to yield meaningful average  
\(^4\) back-calculated  
\(^5\) normalized to Pb = 5  
\(^6\) 1—Cl  
\(^7\) framework O after subtraction of OH
SULPHUR IN MATTHEDDLEITE, LEADHILLS, SCOTLAND

Table 4. Analyses of mattheedleite grains using a celestite standard for S.

<table>
<thead>
<tr>
<th>Oxide wt.%</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>ave</th>
<th>s.d.</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO(_3)</td>
<td>6.88</td>
<td>7.05</td>
<td>7.59</td>
<td>7.55</td>
<td>7.33</td>
<td>7.45</td>
<td>7.06</td>
<td>6.71</td>
<td>7.22</td>
<td>7.20</td>
<td>0.17</td>
</tr>
<tr>
<td>Si(_2)O(_4)</td>
<td>7.95</td>
<td>8.14</td>
<td>7.29</td>
<td>7.53</td>
<td>7.73</td>
<td>7.73</td>
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<td>8.26</td>
<td>7.93</td>
<td>7.84</td>
<td>0.12</td>
</tr>
<tr>
<td>PbO</td>
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<td>83.24</td>
<td>81.52</td>
<td>83.02</td>
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<td>82.51</td>
<td>83.52</td>
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<td>82.61</td>
<td>82.89</td>
<td>0.80</td>
</tr>
<tr>
<td>Cl</td>
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<td>1.01</td>
<td>1.94</td>
<td>1.85</td>
<td>1.74</td>
<td>1.70</td>
<td>1.21</td>
<td>0.87</td>
<td>1.45</td>
<td>1.45</td>
<td>0.53</td>
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<tr>
<td>H(_2)O(_3)</td>
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<td>0.33</td>
<td>0.32</td>
<td>0.31</td>
<td>0.32</td>
<td>0.32</td>
<td>0.33</td>
<td>0.32</td>
<td>0.32</td>
<td>0.31</td>
<td>0.13</td>
</tr>
<tr>
<td>Cl=O</td>
<td>−0.28</td>
<td>−0.24</td>
<td>−0.43</td>
<td>−0.41</td>
<td>−0.38</td>
<td>−0.38</td>
<td>−0.27</td>
<td>−0.19</td>
<td>−0.32</td>
<td>−0.32</td>
<td></td>
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<tr>
<td>Sum</td>
<td>99.54</td>
<td>99.54</td>
<td>98.23</td>
<td>99.73</td>
<td>100.06</td>
<td>99.33</td>
<td>99.89</td>
<td>99.98</td>
<td>99.00</td>
<td>99.37</td>
<td>0.99</td>
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Atoms\(^4\)

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<th>1.15</th>
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<th>1.30</th>
<th>1.27</th>
<th>1.23</th>
<th>1.26</th>
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<th>1.13</th>
<th>1.22</th>
<th>1.21</th>
<th>0.07</th>
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<td>0.00</td>
<td>0.00</td>
<td>0.01</td>
<td>0.00</td>
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<td>0.01</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
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<tr>
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<td>1.66</td>
<td>1.69</td>
<td>1.72</td>
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<td>1.85</td>
<td>1.78</td>
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<td>5.00</td>
<td>5.00</td>
<td>5.00</td>
<td>5.00</td>
<td>5.00</td>
<td>5.00</td>
<td>5.00</td>
<td>5.00</td>
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<td>11.76</td>
<td>11.61</td>
<td>11.57</td>
<td>11.72</td>
<td>11.65</td>
<td>0.45</td>
</tr>
<tr>
<td>Cl</td>
<td>0.49</td>
<td>0.38</td>
<td>0.75</td>
<td>0.70</td>
<td>0.66</td>
<td>0.65</td>
<td>0.46</td>
<td>0.33</td>
<td>0.55</td>
<td>0.55</td>
<td>0.05</td>
</tr>
<tr>
<td>OH(^5)</td>
<td>0.51</td>
<td>0.62</td>
<td>0.25</td>
<td>0.30</td>
<td>0.34</td>
<td>0.35</td>
<td>0.54</td>
<td>0.67</td>
<td>0.45</td>
<td>0.45</td>
<td>0.05</td>
</tr>
</tbody>
</table>

1 s.d. (standard deviation) of a single analysis: calculated from peak and background counts for standard and unknown
2 not detected
3 back-calculated
4 normalized to Pb = 5
5 1−Cl

(Table 2). The peak shape for S-K\(_α\) may change subtly for sulphates vs. sulphides, such that the peak shift program does not fully correct the result.

Step analyses every 2 \(\mu\)m were collected along the length of the zoned crystal labelled in Fig. 2. The wt.% Cl varies between 0.9 and 2.4 (equivalent to \(X_{\text{Cl}} = 0.3−0.9\), Table 3; Fig. 4). Examination of the long section of some mattheedleite grains reveals a more complete history of Cl oscillations with three maxima (Fig. 3). These data are in general agreement with the ranges reported by Livingstone et al. (1987), who observed variation in Cl of 0.56−2.1 wt.% (\(X_{\text{Cl}} = 0.2−0.7\)), and Steele et al. (2000), who showed a zoned mattheedleite that varied from 1.0 wt.% Cl in the core up to 2.7 wt.% on the rim (\(X_{\text{Cl}} = 0.4−1.0\)).

The Pb mineral with low Z was also analysed (Table 5). It has an analytical total without CO\(_2\) or H\(_2\)O of ~90% and molar Pb/S of ~4, suggesting that it is a leadhilitic polymorph. Leadhilitic and susannite were reported in the original description of the sample under study. The elements Na, P, Cl, V, As, Sr and Ba were also sought in this phase but are below their detection limits. This

<table>
<thead>
<tr>
<th>Wt./% # analyses</th>
<th>Leadhilitic</th>
<th>Hydrocerussite</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>8</td>
<td>2</td>
</tr>
<tr>
<td>SiO(_2)</td>
<td>n.d.(^1)</td>
<td>0.15</td>
</tr>
<tr>
<td>P(_2)O(_5)</td>
<td>n.d.</td>
<td>0.03</td>
</tr>
<tr>
<td>SO(_3)</td>
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<td>0.80</td>
</tr>
<tr>
<td>PbO</td>
<td>83.66</td>
<td>87.74</td>
</tr>
<tr>
<td>CO(_2)</td>
<td>8.25</td>
<td>11.53</td>
</tr>
<tr>
<td>H(_2)O(_2)</td>
<td>1.69</td>
<td>2.36</td>
</tr>
<tr>
<td>Sum</td>
<td>100.90</td>
<td>102.61</td>
</tr>
</tbody>
</table>

Atoms\(^5\)

<table>
<thead>
<tr>
<th></th>
<th>Pb = 4</th>
<th>Pb = 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>n.d.</td>
<td>0.02</td>
</tr>
<tr>
<td>P</td>
<td>n.d.</td>
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<tr>
<td>S</td>
<td>0.98</td>
<td>0.08</td>
</tr>
<tr>
<td>Pb</td>
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<tr>
<td>O</td>
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<td>8.27</td>
</tr>
<tr>
<td>H</td>
<td>2.00(^4)</td>
<td>2.00(^4)</td>
</tr>
</tbody>
</table>

1 not detected
2 back-calculated
3 Pb/2
4 0.667*Pb

Table 5. Analyses of other Pb minerals.
phase contains blades of a phase with higher BSE contrast (Fig. 1). It is beam-damaged after only a few seconds of electron beam exposure, even using a 5 μm scanning beam at 10 nA and 15 kV. The beam damage shows up as a bright spot in BSE contrast, indicating that it is rapidly degassed, thus increasing its average Z. The analyses indicate that the low-Z mineral in the host is a leadhillite polymorph and that the high-Z blades are hydrocerrusite.

**Discussion**

**IV site occupancy of mattheddleite**

Mattheddleite was confirmed to have a fully occupied IV site, as concluded by Steele et al. (2000), based on structure-refinement studies. The cause of the apparent IV site deficiency observed in electron microprobe analyses of mattheddleite is here linked to problems of wavelength shift of the S-Kα peak position, rather than errors in the absorption correction for S (Steele et al. 2000). Using galena as a standard reduces the IV site occupancy in mattheddleite by ~10% (Table 2), compared with nearly stoichiometric analyses of the same spots obtained with a celestite standard (Tables 3, 4).

**The existence of OH-dominant mattheddleite**

The analytical data in this study provide some evidence for variation between OH-dominant mattheddleite (OH$_{6.5}$Cl$_{1.4}$) and Cl-dominant mattheddleite (up to OH$_{6}$Cl$_{1.4}$) in a zoned crystal of mattheddleite. The CI-rich mattheddleite forms distinct zones in mattheddleite (Figs 2, 3). The variation of CI observed in this study is on such a small scale that a structure refinement of a crystal from this sample would represent an average across an inhomogeneous sample. Ferraris et al. (2006) obtained HRTEM measurements on a fluorapatite with minor substitution of Na, Si, S and Cl. They found nanoscale domains ofapatite with different compositions inferred to be claselite and chlorapatite in the host fluorapatite. Such modulations may be the precursor of larger-scale exsolution, as reported by Stalder and Rozendaal (2002) between ‘OH-pyromorphite’ and fluorapatite. Mattheddleite could have similar domains, although the short time and temperature scale involved with formation of hydrothermal veins may not be conducive to even nanoscale exsolution. Additional mattheddleite samples should be studied from Leadhills to establish the physical and chemical properties of the possible new mineral, ‘OH-mattheddleite’, and to distinguish it from the CI-dominant mineral mattheddleite.

**Imbalance between Si and S in mattheddleite**

In the original description of mattheddleite, the moles of Si were not matched by S (Livingstone et al., 1987), unlike ellesstite group minerals (Rouse and Dunn, 1982). That result remains unchanged in this study. The cause of the imbalance of Si to S in average mattheddleite relative to the expected ideal formula, Pb$_5$S$_{1.6}$Si$_{1.2}$O$_{11.7}$Cl$_{0.3}$(OH)$_{0.4}$, is difficult to resolve. Minor element substitution does not appear to play a role in perturbing the formula of mattheddleite. Steele et al. (2000) analysed Be, B, Mg, Al, P, Cr, Mn, As and V, but did not find measurable levels of those elements in mattheddleite. In this work, F, Ca, Mn, V, As, Sr, Y, Ba, La, Ce, Pr, Nd, Sm, Gd, Pb and Th were included in analyses but were not detected at levels above the detection limits (Table 1). Thus, only five of the 25 elements that were analysed in the two studies were detected in the same sample of mattheddleite. The average of 75 mattheddleite analyses in this study yields Pb$_5$S$_{1.3}$Si$_{1.3}$O$_{11.7}$(Cl)$_{0.6}$(OH)$_{0.4}$] normalized to five Pb cations. Possible explanations for the deficiency of ~0.6 charges p.f.u. include substitution of: (1) REE$^{3+}$ or Th$^{4+}$ on the IX site, e.g. Pb$_{4.4}$RE$_{0.6}$Si$_{1.3}$Cl$_{0.6}$OH)$_{0.4}$ or Pb$_{4.7}$Th$_{0.3}$Si$_{1.3}$Cl$_{0.3}$OH)$_{0.4}$; (2) vacancy on the CI site, Pb$_5$S$_{1.2}$Si$_{1.4}$O$_{11.7}$(Cl)$_{0.6}$OH)$_{0.4}$; (3) Cl on one of the O sites and OH on the R site, Pb$_5$S$_{1.2}$Si$_{1.8}$[O$_{11.4}$Cl$_{0.8}$]OH; (4) Pb$^{4+}$ on the VI site Pb$_{0.7}$Pb$_{0.3}$S$_{1.2}$Si$_{1.8}$O$_{11.7}$(OH)$_{0.4}$; (5) oxygen vacancy, Pb$_5$S$_{1.2}$Si$_{1.8}$[O$_{11.7}$OH]Cl$_{0.6}$(OH)$_{0.4}$; or (6) a combination of the above explanations.

The absence of detectable Pb, Y, REE and Th indicates that model 1 is untenable. Model 2 does not include enough Cl for most of the mattheddleite analyses. By shifting some of the Cl to the O site, model 3 requires an extra 0.6 OH p.f.u. if that site is filled, such that an accurate determination of H$_2$O would reveal that contribution. The mattheddleite sample of this study, however, is so heterogeneous that even a SIMS determination of H would represent some averaged value. Substitution of Cl for O and O for Cl + OH could be tested by structure refinements. The possibility of Pb$^{4+}$ (model 4)
SULPHUR IN MATTHEDDEITE, LEADHILLS, SCOTLAND

seems unlikely in the large cation sites of apatite. Model 5 is appealing as the substitution is well established in another apatite structure, finneminite, Pb₃[AsO₄][Cl] (Effenberger and Pertlik, 1997), and the formula normalized to Pb = 5 remains correct. However, considering the lack of arsenate in mattheddeite, the structure may not tolerate an anion deficiency or a lower valence for S. Including the O from the OH, models 3 and 4 have 12.4 O p.f.u. and model 5 has 12.1 O p.f.u.

Direct analysis of oxygen in mattheddeite was undertaken in order to test among the viable models (Table 3). The 1σ uncertainty of an individual analysis of O is 0.11 wt.% or 0.9 p.f.u. (Table 1). The average O in the zoned mattheddeite crystal is 12.1±0.2 p.f.u., where the uncertainty is calculated based on deviations from the mean of 38 analyses (Table 3). This result confirms a deficiency in O, although the uncertainty in the average value is large enough to accommodate models 3 and 4 at the 1σ limit of the average O. The analysis of O suggests but does not definitively indicate the possibility of a 0.3 p.f.u. vacancy (□) substitution in the O site: Pb₃Si₂₅₁₈[O₁₁ sevenths₁₁₈][Cl₀₆₁₈(OH)₀₄], or 0.3 Cl p.f.u. for O: Pb₃Si₁₇₁₈[O₁₁ sevenths₁₁₈][Cl₀₃₁₈(OH)₀₄], Minor substitution of O for OH was noted on the OH site in synthetic Pb-Ca fluorovanadinite (Dong and White, 2004a,b), where the additional O is not related to an oxygen deficiency, but this mechanism does not address a charge imbalance in mattheddeite with Si > S. Structure refinements should be undertaken on homogeneous crystals of mattheddeite to evaluate the possible of a 2.5% vacancy in the O site, 0.3 Cl + OH substituting for that O, or a 20–30% vacancy in the Cl site.

Mattheddeite reactions

The anglesite, cerussite, galena, hydrocerussite, lanarkite, lead, mattheddeite, minium, plattnerite, scotlandite, and the polymorphs leadhellite, macphersonite and susannite at Leadhills suggest the possibility of redox equilibria relating these minerals in the system Pb-Si-S-C-O-H. The minerals Shannonite (Roberts et al., 1995) and plumboharonite (Keller and Durn, 1982) may also be considered as possible additional phases. A reaction may be calculated with OH mattheddeite in f8−fO₂ space and any one of the other Pb minerals, each of which would involve either quartz or a solution with dissolved aqueous silica. Reactions may also be balanced with stoicho-

metric mattheddeite, a Pb carbonate, a Pb sulphate and quartz or aqueous silica that involve only the fluid species H₂O and CO₂, as in the following equilibria:

\[ \text{mattheddeite} + \text{CO}_2 + \text{H}_2\text{O} = \]
\[ \text{lanarkite} + \text{hydrocerussite} + \text{silica} (\text{xl, aq}) \] (1)
\[ 6\text{Pb}_2(\text{SiO}_4)_{1.5}(\text{SO}_4)_{1.5}(\text{OH}) + \text{H}_2\text{O} + 8\text{CO}_2 = \]
\[ 9\text{Pb}_2\text{OSO}_4 + 4\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2 + 9\text{SiO}_2 \]

\[ \text{mattheddeite} + \text{hydrocerussite} + \text{CO}_2 + \text{H}_2\text{O} = \]
\[ \text{leadhellite} + \text{silica} (\text{xl, aq}) \] (2)
\[ 6\text{Pb}_2(\text{SiO}_4)_{1.5}(\text{SO}_4)_{1.5}(\text{OH}) + 2\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2 + 4\text{H}_2\text{O} + 14\text{CO}_2 = \]
\[ 9\text{Pb}_4\text{SO}_4(\text{CO}_3)_2(\text{OH})_2 + 9\text{SiO}_2 \]

\[ \text{mattheddeite} + \text{CO}_2 = \]
\[ \text{lanarkite} + \text{cerussite} + \text{silica} (\text{xl, aq}) \] (3)
\[ 2\text{Pb}_2(\text{SiO}_4)_{1.5}(\text{SO}_4)_{1.5}(\text{OH}) + 4\text{CO}_2 = \]
\[ 3\text{Pb}_2\text{OSO}_4 + 4\text{Pb}_3\text{CO}_3 + 3\text{SiO}_2 + \text{H}_2\text{O} \]

\[ \text{hydrocerussite} + \text{CO}_2 = \text{cerussite} + \text{H}_2\text{O} \] (4)
\[ \text{Pb}_3(\text{CO}_3)_2(\text{OH})_2 + \text{CO}_2 = 3\text{Pb}_2\text{CO}_3 + \text{H}_2\text{O} \]

These and related reactions will behave similarly to the many equilibria that have been formulated for marbles in T−X(H₂O)−X(CO₂) space. Equilibrium assemblages with mattheddeite or hydrocerussite will form at higher T or from an aqueous fluid with less CO₂ than lanarkite-hydrocerussite-quartz, leadhellite-quartz, and cerussite. Reactions 1 and 3 each bound the stability of mattheddeite, and their intersection yields an invariant point through which reaction 4 also passes. If reactions 1 and 2 are both stable, reaction 1 must occur at lower T than reaction 2. The formation of mattheddeite later than leadhellite-quartz at Leadhills is counterintuitive considering reaction 2, and it suggests that the fluid evolved to a more CO₂-depleted composition, or that a hotter fluid was introduced in the later stages of hydrothermal activity. The Leadhills deposit may have formed from a boiling fluid in the presence of a gaseous phase rich in CO₂ and a liquid rich in H₂O. If any of the reactions 1−4 intersect the CO₂−H₂O solvus, it becomes invariant in T−X space in the presence of two fluid species. If so, and if only very minor amounts of additional fluid species such as SO₂, NaCl, HCl, or SO₃ are present, these reactions will serve as useful thermometers at a given fluid pressure.

Abdul-Samad et al. (1982) measured the free energy of lanarkite with solution techniques at
would buffer the composition of the fluid if formed at equilibrium. Paar et al. (1984a) inferred that scotandite, lanarkite and susanite were the latest-stage minerals at Leadhills. The overgrowths of mattheddleite on leadhillite (and/or susanite) and hydrocerussite (Fig. 1) also suggest that mattheddleite is a later part of the paragenesis. Dissolution textures were observed on leadhillite crystals from Cåldbeck Fells (Cooper and Stanley, 1990). The process of dissolution on earlier-formed Pb minerals may provide a supply of lead for the later paragenetic sequence involving Pb minerals. Reactions 1–4 apply to later stages of the paragenetic sequence. The extended paragenetic sequence at Leadhills is galena ↔ anglesite ↔ cerussite ↔ leadhillite-susanite-hydrocerussite ↔ mattheddleite-lanarkite-scotandite, where lanarkite and scotandite are also late but the parageneses of which are still not well established relative to mattheddleite or each other. The role of plattnerite at Leadhills is unclear, and whether muntum or native lead occur as Leadhills minerals remains to be established. Consideration of reactions among the Pb minerals collectively indicates that their relative stability depends on fluid composition for a given P-T. In many hydrothermal environments, however, equilibrium processes are overstepped with crystallization from a supersaturated fluid as well as nucleation and growth of metastable phases at low temperatures (<200°C). The role of metastability during crystallization of the hydrothermal assemblages at Leadhills (Livingstone, 1993) is in need of further evaluation. Equilibrium assemblages and reactions would provide only an approximate guide to the understanding of disequilibrium systems.

Cl zoning in mattheddleite

The remarkable oscillatory zoning of Cl in mattheddleite must be related to salinity changes in the hydrothermal fluid. One may posit an exchange reaction between OH-Cl mattheddleite and aqueous fluid:

\[
\text{OH-dominant mattheddleite} + \text{HCl} = \text{Cl-dominant mattheddleite} + \text{H}_2\text{O}
\]

The Cl/OH content of mattheddleite thus is controlled by pH as well as pCl or chlorinity and T. The amount of OH in mattheddleite will also depend on whether the vacancy substitutes in the
structure or not. Three cycles of high Cl are evident in the analytical traverse (Fig. 3), where the Cl peaks indicate a physicochemical change in the fluid. The reports of vanadinite, mimetite and pyromorphite (lead chloride vanadate, arsenate and phosphate, respectively) in veins at Leadhills (Brown, 1919; Temple, 1956; Gillanders, 1981; Livingstone, 1994b) indicate that late-stage fluids were highly oxidized and enriched in Cl. The hydrothermal fluid at Leadhills probably varied in salinity as it migrated and evolved as a result of crystallization, dissolution and/or replacement of earlier crystallized solids. The Cl variations observed in mattheddleite may result from degassing during boiling and/or mixing with a more saline fluid.

**Recommendations**

**Analysis of sulphate-bearing minerals**

The sulphate in apatite or indeed that in any other sulphate standards with wavelength dispersive methods on an electron microprobe. Livingstone and Sarp (1984) reported analyses of Leadhills macphersonite including S with a galena standard at uncharged conditions with an electron microprobe. The S is less than expected by ~10% of the article present, which probably resulted from the use of the galena standard. Macphersonite from Saint-Prix, France, was analysed by gravimetric means, and there the S is much closer to stoichiometric levels. Sarp and Perroud (1991) used chalcopyrite in the analysis of S in cameralite. Liu and Comodi (1993) employed sphalerite as a standard for analysis of S in apatite, obtaining 0.02–1.64 wt.% SO\textsubscript{3} in 24 samples from carbonatites and alkaline igneous rocks. Livingstone (1994a) obtained 0.09–0.23 wt.% SO\textsubscript{3} in plumbum apatite with galena as a standard for S. Golebiowska et al. (2002) used a pyrite standard for S in the analysis of a sulphate-bearing mimetite. The S standards were not specified in several studies involving WDS analyses of sulphoan scapolite (Griffin et al., 1979; Okrusch et al., 1979; Austrheim and Griffin, 1985), alunite (Deyell and Dipple, 2005; Deyell et al., 2005), and scotlandite (Sarp and Burri, 1984). The scotlandite analysis of Sarp and Burri (1984) has a low analytical total and 22% deficiency of S compared to Pb, suggesting a large systematic error in the S, which implies that a sulphide standard was used in its analysis. Scotlandite is a sulphite and not a sulphate, and the possibility of a shift in the position of the S-K\textalpha peak between sulphites and sulphates remains to be evaluated. Scotlandite may show solid solution towards alamonsite via the exchange Si-S, it may contain Ba or Sr, and substitutions such as REE-Al-Pb-S should be evaluated. A systematic error of negative 10–20% OAP is anticipated whenever sulphide standards are used for sulphates with WDS analysis.

Sulphate standards were employed in WDS analyses of S in apatite group minerals (Rouse and Dunn, 1982; Shiga and Urashima, 1987), scotlandite (Paar et al., 1984a), scapolite (Coolen, 1980; Moëcher and Essene, 1990, 1991), baryte and celestite (Boundy et al., 2002), and complex hydrous sulphate minerals (Keller et al., 1979; Paar et al., 1984b; Jackson, 1990; Li et al., 1992; Peacor et al., 1999a,b; Rouse et al., 2001; Drouet and Navrotsky, 2003; Pe-Piper and Dolansky, 2005). These analyses are not anticipated to have serious errors due to systematic shifts in the position of the S peak. Selecting the proper standard for a phase with S in an unknown bonding type should necessitate wavelength scans on the known vs. selected sulphate and sulphide standards to decide upon the best standard for that phase.

**Significance of sulphate substitution in apatite-group minerals**

Studies of rock-forming apatite should include routine analysis of S with a sulphate standard. Core et al. (2006) used the sulphate substitution of apatite to evaluate the oxidation state and degassing history during crystallization of granitic rocks. They extracted the thermodynamic properties of hydroxylellestadite from experiments and showed that its substitution in apatite, buffered in the presence of anhydrite-quartz and clino-pyroxene-quartz, is favoured at more oxidizing conditions. Such applications will continue to be limited, however, until S is routinely analysed in rock-forming apatite from a wide variety of associations. Sulphur may be present in any apatite with detectable Na or Si, and therefore it should be included in the electron microprobe analytical procedure.

**Future geochemical studies at Leadhills**

Growth of zoned mattheddleite appears to be a faithful recorder of changes in the composition of the hydrothermal fluid. Fluid-inclusion studies in the lead minerals and/or cogenetic quartz may be
useful in unravelling the fluid chemistry, and whether the hydrothermal fluid(s) underwent one or more stages of boiling or degassing as it evolved. Measurement of the brine and CO₂ content in fluid inclusions would be of considerable interest in understanding the salinity and alkalinity of the ore fluid, and its changes during the later stages of hydrothermal activity that produced the lead mineral assemblages at Leadhills.

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