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New Data on Welshite, e.g. Ca2Mg3.8Mn0.62+Fe0.12+Sb1.55+O2 [Si2.8Be1.7Fe0.653+Al0.7As0.17O18], an Aenigmatite-Group Mineral

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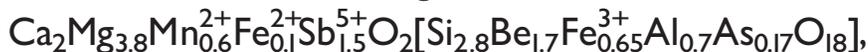
New data on welshite, e.g. $Ca_2Mg_{3.8}Mn^{2+}_{0.6}Fe^{2+}_{0.1}Sb^{5+}_{1.5}O_2[Si_{2.8}Be_{1.7}Fe^{3+}_{0.65}Al_{0.7}As_{0.17}O_{18}]$, an aenigmatite-group mineral

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ABSTRACT

Electron and ion microprobe data on two samples of welshite from the type locality of Långban, Sweden, gave analytical totals of 99.38−99.57 wt.% and BeO contents of 4.82−5.11 wt.%, corresponding to 1.692−1.773 Be/20 O. Mössbauer and optical spectra of one of these samples gave $^{[iv]}Fe^{3+}/\Sigma Fe = 0.91$, $^{[vi]}Fe^{2+}/\Sigma Fe = 0.09$, and no evidence of Mn^{3+}. The resulting formula for this sample is $Ca_2Mg_{3.8}Mn^{2+}_{0.6}Fe^{2+}_{0.1}Sb^{5+}_{1.5}O_2[Si_{2.8}Be_{1.7}Fe^{3+}_{0.65}Al_{0.7}As_{0.17}O_{18}]$, and that for the second sample, $Ca_2Mg_{3.8}Mn^{2+}_{0.1}Fe^{2+}_{0.1}Fe^{3+}_{0.8}Sb^{5+}_{1.2}O_2[Si_{2.8}Be_{1.8}Fe^{3+}_{0.65}Al_{0.5}As_{0.25}O_{18}]$, is related by the substitution involving tetrahedral and octahedral sites: $0.59^{[vi,iv]}(Fe,Al)^{3+} \approx 0.42^{[vi]}(Mg,Mn,Fe)^{2+} + 0.21(^{[vi]}Sb,^{[iv]}As)^{5+}$, i.e. $3^{[vi,iv]}M^{3+} = 2^{[vi]}M^{2+} + ^{[vi,iv]}M^{5+}$. Welshite is distinctive among aenigmatite-group minerals in the high proportion of Fe^{3+} in tetrahedral coordination and is unique in its Be content, substantially exceeding 1Be per formula unit. Given the cation distributions in other minerals related to aenigmatite, we think it is reasonable to assume that at least one tetrahedral site is >50% occupied by Be and that one octahedral site is >50% occupied by Sb, so that welshite should be retained as a distinct species with its own name in the aenigmatite group.

KEYWORDS: welshite, aenigmatite group, Långban deposit, Sweden.

Introduction

Moore (1967, 1970*b*, 1978; *cf.* Machin and Süsse, 1974) introduced welshite as an aenigmatite-group mineral with the ideal formula $Ca_2Mg_4Fe^{3+}Sb^{5+}O_2[Si_4Be_2O_{18}]$ from the Långban Fe-Mn deposit, Sweden, which is renowned for its variety of unusual Be minerals (e.g. Magnusson, 1930; Moore, 1970*b*). Crystallographic studies confirmed welshite as an aenigmatite-group mineral. However, the chemical analysis totalled only 93.7 wt.% and the empirical formula calculated therefrom,

$Ca_{2.35}Mg_{3.53}Mn_{0.13}Fe^{3+}_{1.06}Sb_{1.42}As_{0.29}Al_{0.38}$ $Si_{3.03}Be_{1.49}O_{20}$, differs substantially from the ideal formula and deviates in several important respects from that expected of aenigmatite-group minerals. For example, the formula is deficient in total cations (13.68 *vs.* 14), but contains an excess of Ca (2.35 *vs.* 2.00) compared to other Ca-dominant members of the aenigmatite group. No other aenigmatite-group mineral or mineral related to this group contains more than 1Be per formula unit. Kunzmann (1999) recommended that welshite be renamed "beryllio-antimono-dorrite" because its composition plots in the field for dorrite in terms of its (Si-Na) and Ti contents.

For these reasons, we have reinvestigated welshite in two samples from the type (and

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only) locality of Långban, Sweden with the objective of a more complete characterization of its chemical composition and to assess its relationship with other aenigmatite-group minerals and its species status. One sample is from the collections of the Swedish Museum of Natural History (Naturhistoriska Riksmuseet, NRM85006), and the other, from the private collection of Per Nysten (PN).

Mineral associations

Welshite is associated in sample NRM85006 with dolomite, phlogopite, richterite, roméite, $(Ca,Na)_2Sb_2O_6(O,OH,F)$, berzeliite, $Ca_2Na(Mg,Mn^{2+})_2(AsO_4)_3$ and adelite, $CaMg(AsO_4)(OH)$, a paragenesis similar to that of Moore (1978). The paragenesis in sample PN includes no As phases, but several additional Sb^{5+} phases: katoptrite, $(Mn^{2+},Mg)_{13}(Al,Fe^{3+})_4$ $Sb_2^{5+}Si_2O_{28}$, filipstadite, $(Mn^{2+},Mg)_4Sb^{5+}Fe^{3+}O_8$, ingersonite, $Ca_3Mn^{2+}Sb_4^{5+}O_{14}$, and tegengrenite, $(Mg,Mn)_2Sb_{0.5}^{5+}(Mn^{3+},Si,Ti)_{0.5}O_4$, a mineral newly described from the nearby Jakobsberg deposit (Holtstam and Larsson, 2000). The difference in association between the two samples is reflected in the differing chemical composition of welshite.

Cell parameters

A prismatic crystal, $\sim 0.2 \times 0.2 \times 0.3$ mm, of welshite from sample PN was mounted on a glass fibre. Single-crystal X-ray diffraction (XRD) studies (Stoe four-circle diffractometer) of the

crystal at $T = 293$ K, using Mo-$K\alpha$ radiation (0.71073 Å) indicated a triclinic symmetry. The unit-cell parameters (Table 1) were determined and refined from the θ values of 22 accurately centred reflections in the range $25.2° < 2\theta < 40°$ and corrected for Lorentz, polarization and absorption effects using the Stoe program REDU4. The cell parameters are close to those reported by Moore (1978), although the cell volume is larger and the calculated density for the measured composition (see below) substantially higher.

In addition, attempts were made to refine the crystal structure. Data were collected for several different crystals from sample PN, including the one for which cell parameters are given. For this crystal 4941 reflections were collected in the range $0° < 2\theta < 60°$ at $T = 293$ K on a Stoe image-plate diffractometer equipped with a rotating anode. The lattice parameters were determined by analysing the obtained reciprocal space with the program RECIPE provided with the STOE image-plate system. Since four-circle diffract-ometer measurements give more accurate reflec-tion positions, that unit cell was used in the subsequent analysis. Normalized E-value inten-sity statistics indicated the centrosymmetric space group $P\bar{1}$ (No. 2). The structure was solved in this space group giving an R value near 0.20. The atom positions obtained agreed well with those obtained by Bonaccorsi *et al*. (1990). However, severe reflection overlap hindered the refinement of the different distributions of the metal cations among the different sites. In addition, when the

TABLE 1. Cell parameters and density of welshite.

	PN (this study)	Moore (1967, 1978)
a (Å)	10.381 (1)	10.28 (2)
b (Å)	10.766 (2)	10.69 (2)
c (Å)	8.881 (1)	8.83 (2)
α (°)	105.92 (1)	106.1 (2)
β (°)	96.33 (1)	96.3 (2)
γ (°)	124.97 (1)	124.8 (2)
V (Å^3)	735.7(2)	720.1
D_{meas} (g/cm^3)	–	3.77
D_{calc} (g/cm^3)	3.948	3.71

Moore (1967, 1978) reported only the parameters of the pseudomonoclinic cell and their uncertainties; Machin and Süsse (1974) transformed the cell to the triclinic cell given here. We have assumed that Moore's uncertainties could be applied to the triclinic cell. Moore (1978) calculated this density for the composition $Ca_2Mg_4Fe^{3+}Sb^{5+}O_2[Si_4Be_2O_{18}]$ and the given volume

metal ions were refined with anisotropic displacement parameters, these parameters become non-positive definite. Attempts were also made to solve and refine the structure in the noncentrosymmetric space group $P1$ (No. 1). This choice of space group did not improve the outcome of the subsequent refinements.

Mössbauer spectroscopy

A room-temperature ^{57}Fe Mössbauer spectrum of sample PN was recorded with a constant acceleration system working in conjunction with a 1024 channel MCA using a nominal 50 mCi ^{57}Co/Rh source and a gas-filled proportional counter as the detector. The absorber was prepared from a mixture of 3.2 mg of mineral powder and ~60 mg transoptic polymer powder; the absorber density was ~0.1 mg Fe/cm^2. A thin foil of metallic iron (α-Fe) was used for velocity calibration and consequently, the reported Mössbauer hyperfine parameters are given relative to α-Fe at room temperature. A fit of the spectrum recorded was carried out using a computer program (Jernberg and Sundqvist, 1983) assuming Lorentzian line shapes and equal values of intensity and FWHM (full width at half maximum) of the two components of each fitted quadruple doublet. Paucity of material precluded attempts to record the Mössbauer spectrum of sample NRM85006.

The ^{57}Fe Mössbauer spectrum of the sample PN (Fig. 1) reveal three resolved absorption peaks and it is dominated by an intense quadrupole doublet characterized by a very small centroid shift (CS). The spectrum fit was performed using two quadrupole doublets, which is the minimum number required to account for the three observed absorption lines. Fitting models including a larger number of doublets did not improve the fit substantially and were consequently discarded. The Mössbauer parameters (Table 2) derived for
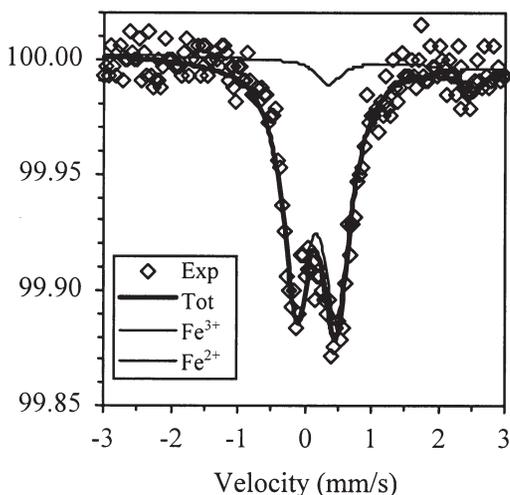

FIG. 1. Mössbauer spectrum of sample PN.

the intense resonance doublet indicate that this resonance absorption is due to ferric iron. The centroid shifts obtained for this doublet are considerably smaller than observed for octahedrally coordinated ferric Fe, but it falls within the range of CS-values recorded for tetrahedrally coordinated ferric Fe in a range of para- and diamagnetic minerals (Coey, 1984). The recorded quadrupole splitting (QS) of 0.61 mm/s for this doublet indicates that the distortion of the Fe^{3+}-site in welshite is moderate. In addition to the ferric Fe doublet, a very weak doublet amounting to ~9% of the Fe content of this sample is attributed on the basis of the high CS-value to ferrous Fe in a relatively large polyhedron, such as an octahedron.

Optical absorption spectroscopy

Polarized optical absorption spectra of two welshite crystals from sample PN were measured

TABLE 2. Mössbauer spectral data on welshite (sample PN).

	Set 1 (Fe^{3+})	Set 2 (Fe^{2+})
Intensity (%)	91	9
Centroid shift (mm/s)	0.19	1.42
Quadrupole splitting (mm/s)	0.61	2.13
FWHM (mm/s)	0.45	0.38

$\chi^2 = 2.23$

at room temperature in the range 30,000–12,500 cm^{-1} using a Zeiss MPM 800 single beam microscope spectrometer, which was equipped with a 75 W Xenon arc lamp as light source and a photomultiplier detector. Incident light was polarized with a Glan-Thompson prism and a concave holographic grating served as monochromator. UV-transparent lenses (Zeiss Ultrafluar 10×) were used as objective and condenser during the measurements and the beam spot size was kept constant at 40 µm. The spectral resolution throughout was 2.5 nm and spectral data were collected in 1 nm steps over three cycles. Air served as a reference medium in all measurements.

The crystals were oriented using interference figures and then transferred to a glass slide and embedded in a thermoplastic resin; the resulting slab was polished on two parallel surfaces. The resulting 45 µm thick, double-sided polished crystal absorbers were removed from the thermoplastic during warming at 90°C. Prior to measuring the optical spectra, the two crystals were washed thoroughly in acetone to remove thermoplastic remnants. The two crystal absorbers were oriented ⊥ to the optical directions α and γ so that E∥β and E∥γ spectra were obtained from one crystal and E∥α and E∥β spectra from the other.

The welshite crystals selected for optical absorption measurements displayed distinct extinction and undistorted optical interference figures of good quality. These observations do not rule out the presence of sub-microscopic twinning. However, twinning neither affects the position (energy) of absorption bands observed in optical spectra, nor does it cause enhancement of the maximum linear absorption coefficient for an absorption band. Furthermore, twinning does not increase absorption band anisotropy, rather it could decrease it. With these general observations in mind, the recorded optical absorption spectra of welshite can be interpreted in a fruitful way.

The optical spectra recorded are consistent with absorption $\alpha \approx \gamma < \beta$ and weak pleochroism (Fig. 2; Moore, 1978, reported "not discernibly pleochroic"), which differs from the pleochroic schemes of aenigmatite, rhönite and serendibite, $\alpha \leqslant \beta < \gamma$ (Deer *et al.*, 1978). There is a set of fairly narrow absorption bands superimposed on a strong UV absorption edge that extends far into the visible spectral region. These bands are centred at 25,050, 23,600, 22,150, 20,650, 18,350 and 15,050 cm^{-1}. Due to the strong UV

absorption, discrete bands at higher wavenumbers could not be observed. The positions of the observed absorption bands are typical of tetrahedrally coordinated ferric Fe (Burns, 1993, and references therein). None of the bands in the present welshite spectra has the characteristic energies or widths associated with electronic d–d transitions in trivalent Mn in silicate minerals (Burns, 1993). Consequently, it may be concluded that virtually all Mn is present in the divalent state in welshite sample PN.

As to the assignment of the observed bands, their intensity and anisotropy present some problems. As all electronic d–d transitions in ferric Fe are spin-forbidden, bands due to such transitions typically produce absorption bands characterized by low molar extinction coefficients, i.e. ε ranges from 0.01 to 15 l mole^{-1} cm^{-1}, with higher ε values being characteristic of absorption bands due to d–d transitions in tetrahedrally coordinated ferric Fe. The same also holds for bands due to divalent Mn. In the present spectra all observed absorptions are strongly pleochroic showing very high intensities in E∥β, but the bands are very weak in E∥α spectra and virtually missing in E∥γ spectra. Based on the EMP-determined Fe-concentrations for welshite PN, and using the Fe valence distribution determined by Mössbauer spectroscopy, ε-values of 10–40 l mole^{-1} cm^{-1} are calculated for the various bands in our E∥β spectra. These values are unexpectedly high for single-ion spin-forbidden d–d transition bands and consequently, additional mechanisms providing anisotropic band intensity enhancements seem to be operative in welshite. One explanation for the intensified [iv]Fe^{3+}-
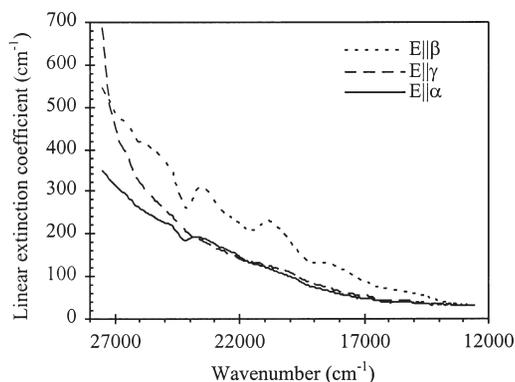

FIG. 2. Polarized optical absorption spectra of sample PN.

derived absorption bands is that they are due to electronic transitions in clusters of 3d cations. Absorption spectra of phlogopite (Smith *et al.*, 1983), hematite (Rossman, 1996) and spinel (Andreozzi *et al.*, 2001) illustrate that optically active Fe^{3+}-Mn^{2+} and Fe^{3+}-Fe^{3+} clusters may produce absorption bands of unusual intensity at energies typical for the d−d transitions of the co-operating single 3d cations. In welshite, optically active 3d-cation clusters involving $^{[iv]}Fe^{3+}$-$^{[iv]}Fe^{3+}$ and $^{[iv]}Fe^{3+}$-$^{[vi]}Mn^{2+}$ interaction are also possible, but the orientation of the absorption suggests the latter is more likely. Assuming that the optical orientation of welshite is similar to that in serendibite, aenigmatite and rhönite (Walenta, 1969; Deer *et al.*, 1978), the optical axial plane would be roughly parallel to (010) and β would be oriented at a relatively high angle to the 'walls' of octahedra extending parallel to the *a* axis and oriented parallel to the (011) plane (Merlino, 1972, illustrated here in Fig. 3). By analogy with aenigmatite (Cannillo *et al.*, 1971) and the synthetic compound SFCA (Hamilton *et al.*, 1989), Fe^{3+} is likely to be concentrated in *T3*, but could also occupy *T2*, *T5* and *T6*, so that enhanced absorption due to $^{[iv]}Fe^{3+}$-$^{[iv]}Fe^{3+}$ clusters would most likely be in the (011) plane and contribute relatively little absorption to the β direction. Alternatively, enhanced absorption due to $^{[iv]}Fe^{3+}$-$^{[vi]}Mn^{2+}$ clusters could have more effect on β. The *T3* site shares a corner with M6 (Fig. 3), a relatively large octahedron (Cannillo *et al.*, 1971; Bonaccorsi *et al.*, 1990) that is a likely site for Mn^{2+}, and such a $^{[iv]}Fe^{3+}$-$^{[vi]}Mn^{2+}$ cluster would be oriented at a high angle to the (011) plane.

Chemical composition

Concentrations of heavier elements (Z>9) were determined using a Cameca SX50 electron microprobe (EMP) operated at 20 kV accelerating potential and 12 nA sample current (Table 3). The following standards were used for calibration: Al_2O_3 (Al), $CaSiO_3$ (Ca and Si), GaAs (As), MgO (Mg), $MnTiO_3$ (Mn, Ti), Fe_2O_3 (Fe), Sb_2O_3 (Sb) and ZnS (Zn), and the PAP-routine (Pouchou and Pichoir, 1984) was used for data corrections. Wavelength dispersive scans revealed no detectable amounts of any other elements (Moore, 1978, reported no other element except for a trace of B using emission spectroscopy).

Lithium, Be and B were determined using secondary ion mass spectrometry (SIMS) with a

TABLE 3. Composition of welshite.

	NRM85006	PN
	wt.%	
SiO_2	19.47	19.42
Al_2O_3	2.96	3.92
MgO	17.43	17.41
Fe_2O_3	13.03	5.92
FeO	1.12	0.53
MnO	1.01	4.64
ZnO	0.04	0.08
CaO	12.86	12.50
Sb_2O_5	22.89	28.09
As_2O_5	3.44	2.24
BeO	5.11	4.82
B_2O_3	0.005	0.002
Li_2O	0.007	0.002
Total	99.38	99.57
Formulae per 20 oxygen atoms		
Si	2.811	2.839
Be	1.773	1.692
Fe^{3+}	0.651	0.652
Al	0.504	0.675
As	0.260	0.171
B	0.001	0.001
Total IV	6.000	6.030
Fe^{3+}	0.765	0.000
Mg	3.751	3.794
Mn	0.124	0.574
Fe^{2+}	0.135	0.064
Zn	0.004	0.009
Sb	1.227	1.525
Li	0.004	0.001
Ca	1.989	1.958
Total VI, VIII	7.999	7.925
Total cations	13.999	13.955

Formula for NRM85006 is normalized to 14 cations in order to calculate the Fe^{3+}/Fe^{2+} ratio

Cameca ims 4f ion microprobe operated at the University of New Mexico (UNM) by a UNM-Sandia National Laboratories consortium. Analyses were made using primary $^{16}O^-$ ions accelerated through a nominal potential of 10 kV. A primary beam current of 15 nA was focused on the sample over a spot diameter of 10−15 μm. Prior to each analysis, the sample surface was rastered over an area of 100 × 100 μm for 2 to 4 min. Ion imaging of the rastered area was used to confirm the nature of the analytical target.
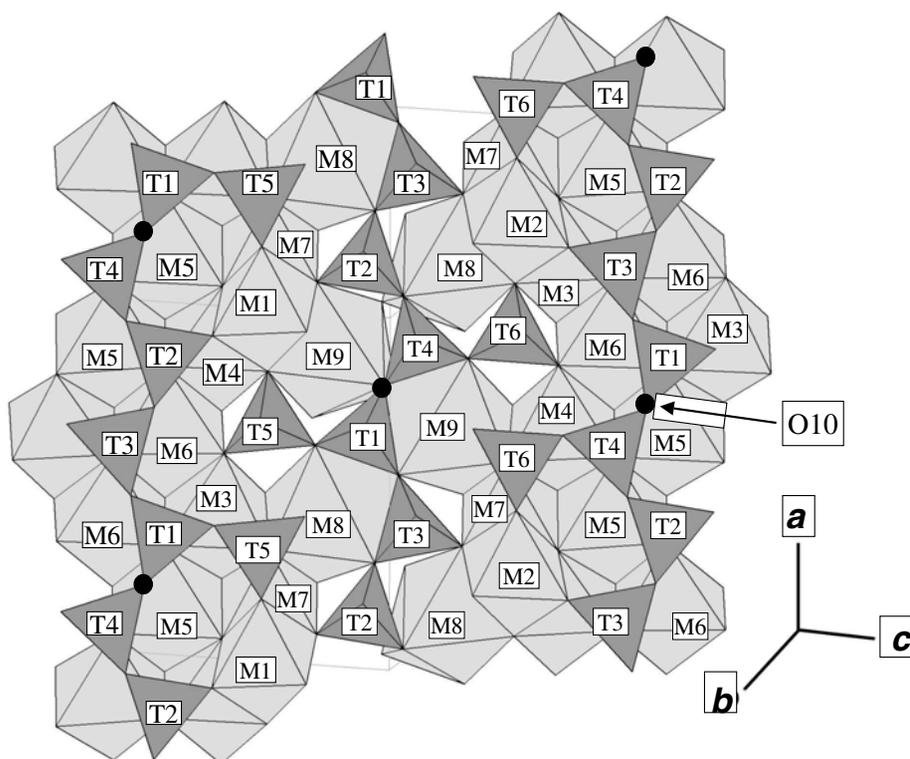
FIG. 3. Diagram of the presumed crystal structure of welshite, which is taken from the crystal structure of 'makarochkinite' refined by J. Barbier (Barbier *et al.*, 2001; Barbier, pers. comm., 2000). The view is approximately in the [122] direction. Filled circle marks O10, which is the oxygen bridging the two most highly polymerized tetrahedra *T*1 and *T*4, where Be resides in khmaralite and 'makarochkinite'.

Sputtered secondary ions were energy-filtered using a sample-offset voltage of 105 V, energy window of ± 25 V. The analyses involved repeated cycles of peak counting on ^7Li, ^9Be, ^{11}B and ^{30}Si. Each spot analysis involved 10 counting cycles. The signals for $^9Be^+$ and $^{27}Al^{3+}$ were sufficiently resolved at mass resolution of ~320 (routine conditions) to measure Be at the high concentrations found in welshite. The analytical procedure included counting on a background position to monitor detection noise. Li (ppm), BeO (wt.%) and B (ppm) were calculated from measured $^7Li^+/^{30}Si^+*SiO_2$, $^9Be^+/^{30}Si^+*SiO_2$ and $^{11}B^+/^{30}Si^+*SiO_2$ (count ratio*wt.% by EMP analyses) calibrated by the following standards (all minerals): surinamite for Be (no. 2292C, Grew *et al.*, 2000), 'makarochki-nite' for Be (possibly equivalent to høgtuvaite from the Urals, Russia, Barbier *et al.*, 2001, and Barbier, pers. comm.), prismatine for B (no.

BM1940,39), and three tourmaline-group minerals for B and Li (Dyar *et al.*, in press). The Li, Be and B contents of these standards were determined from atomic absorption (Li) and by crystal structure refinement (Be, B). Grew *et al.* (2000) estimated a reproducibility of $\pm 10\%$ for BeO contents of ~1 wt.% and for B contents ranging from ~10 to ~100 ppm, using this approach.

The major difficulty in EMP and SIMS analyses of welshite is the absence of standards close in composition to welshite, which is unusual in being an Sb-rich Mg-Be-Fe silicate (Table 3). Moore (1978) attributed the low oxide sum in his analyses to the uncertainties in the corrections due to the unusual composition of welshite and to the use of As and Sb metals as standards for a silicate. The situation for SIMS analyses is more acute because no correction scheme is available for matrix effects on the target ion (e.g. Be ion) yield

relative to Si ion yield, i.e. measured Be/Si count ratios cannot be corrected for differences in composition between unknown and standard. Grew *et al.* (1998), Ottolini and Hawthorne (1999) and Hughes *et al.* (2000) reported over-estimates of B content due to differences in composition between unknowns and standards, even in cases where they are closely related in crystal structure or isostructural. Surinamite and 'makarochkinite' are both related structurally to one another and to welshite, yet give significantly different BeO contents when used to calibrate measurements on welshite (Table 4). Of the two standards, 'makarochkinite' is closer both structurally and chemically to welshite in that both are Ca-dominant, Al-poor members of the aenigmatite group. Nonetheless, the significant differences in composition, largely in Sb + Mg in welshite *vs.* Fe in 'makarochkinite', could result in substantial matrix effects.

Another major difficulty is determining the valences of Mn, Fe, As and Sb. Mössbauer spectroscopy of PN shows that 91% of the total Fe is tetrahedrally coordinated Fe^{3+} and 9% is octahedrally coordinated Fe^{2+} (see above). In the absence of a direct determination, the Fe^{3+}/Fe^{2+} ratio was calculated assuming 14 cations/20 cations for NRM 85006, resulting in a somewhat higher Fe^{3+}/Fe^{2+} ratio for this sample compared to PN. Optical absorption spectra of sample PN

show no evidence of trivalent Mn. Antimony and arsenic are both presumed to be pentavalent as both are pentavalent in associated minerals, e.g. roméite, filipstadite. In addition, Mn^{2+}, Fe^{3+} and Sb^{5+} occur together in melanostibite, $Mn(Sb^{5+},Fe^{3+})O_3$ (Moore 1968*a,b*) and filipstadite (Dunn *et al.*, 1988; Holtstam *et al.*, 1998), and Mn^{2+}, As^{5+} and Sb^{5+}, occur in manganostibite, $(Mn^{2+},Fe^{2+})_7Sb^{5+}As^{5+}O_{12}$ (Moore, 1970*a*; Holtstam *et al.*, 1998), implying that the mix of valences presumed for welshite is possible. Assuming these valences and the BeO content obtained through calibration with 'makarochkinite', we get reasonable analytical totals as well as cation totals (PN) and Ca contents consistent with aenigmatite-group stoichiometry (Table 3).

The cations known to be tetrahedrally coordinated either by measurement or by strong presumption, namely Fe^{3+}, Si and Be, together with As^{5+} and Al^{3+}, sum to 6/20 O in PN as expected by aenigmatite-group stoichiometry. Assuming that As^{5+} and Al^{3+} are tetrahedrally coordinated is reasonable given that As^{5+} is, with rare exception, tetrahedrally coordinated in minerals and Al^{3+} is tetrahedrally coordinated in other Al-poor aenigmatite-group minerals, i.e. Al-poor rhönite (Bonaccorsi *et al.*, 1990) and dorrite (Cosca *et al.* 1988). Thus, a simplified formula, $Ca_2Mg_{3.8}Mn^{2+}_{0.6}Fe^{2+}_{0.1}Sb^{5+}_{1.5}O_2^{[iv]}[Si_{2.8}Be_{1.7}Fe^{3+}_{0.65}Al_{0.7}As_{0.15}O_{18}]$, can be given for PN. The cations that are placed in tetrahedral sites in PN sum to 6.755 per 20 O in NRM85006, which implies there is too much Fe^{3+} to be accommodated on the T sites, and thus some Fe^{3+} must occupy octahedral sites in NRM85006 (Table 3).

The main difference in composition between the two samples is in Fe^{3+}, Mn^{2+} and Sb^{5+} (Table 3), which can be summarized by the following relationship

$$0.59^{[vi,iv]}(Fe,Al)^{3+} \approx 0.42^{[vi]}(Mg,Mn,Fe)^{2+} + 0.21(^{[vi]}Sb,^{[iv]}As)^{5+}$$

calculated from the formulae in Table 3. This substitution comes close to balancing both in terms of total number of cations (~0.6) and in charge (~1.8−1.9), and can be condensed to $3^{[vi,iv]}M^{3+} = 2^{[vi]}M^{2+} + {}^{[vi,iv]}M^{5+}$. The proposed substitution is similar to one of the substitutions derived by Kunzmann (1999) to relate welshite and aenigmatite: $3^{[vi]}Fe^{3+} = 2^{[vi]}Mg^{2+} + {}^{[vi]}Sb^{5+}$. However, our substitution involves tetrahedral as well as octahedral sites. The higher Sb content of PN relative to NRM 85006 reflects the Sb-rich environment implied by the greater diversity of

TABLE 4. Results of the SIMS analyses of welshite.

	NRM85006	PN
BeO wt.%		
Session 1 (Sur)	4.37 ± 0.13	4.21 ± 0.16
Session 2 (Sur)	4.52	4.26
Session 2 (Mkr)	5.11	4.82
Li ppm		
Session 1	34 ± 1	8.7 ± 3
Session 2	33	6.5
B ppm		
Session 1	20 ± 3	7.5 ± 2
Session 2	13	7.3

Session 1 − average of four measurements for PN and of three measurements of NRM85006 ($\pm 1\sigma$); Session 2 − average of two measurements each. (Sur) − surinamite used as standard. (Mkr) − 'makarochkinite' used as standard

Sb-bearing minerals in PN, whereas its lower As content is consistent with the absence of As minerals from this sample.

Calculations from the data in Tables 1 and 3 and the Gladstone-Dale constants of Mandarino (1981) gave −0.073 ("fair") for our calculated density and −0.124 ("poor") for Moore's (1978) measured density, whereas substituting Eggleton's (1991) constants for those of Mandarino (1981) wherever possible gave −0.054 ("good") and −0.103 ("poor"), respectively. In both cases an average of Moore's (1978) values for $\alpha = 1.81(1)$ and $\gamma = 1.83(1)$ were used; the average including β, which Moore did not report, could differ as Moore observed $2E \sim 45°$. The relatively poor compatibility could be due to differences in chemical composition between PN and the sample that Moore (1978) used to measure the refractive indices, whereas inclusions in the grains used to measure density could have resulted in an underestimate. A more serious problem could be the Gladstone-Dale constant for Sb_2O_5, which Mandarino (1981) reported as having questionable reliability and which Eggleton (1991) did not consider.

Structural implications

Welshite is distinctive among aenigmatite-group minerals for its high proportion of Fe^{3+} in tetrahedral coordination, and sample PN is unique in that all the Fe^{3+} is tetrahedrally coordinated. Both samples differ from other Be minerals in the aenigmatite group (høgtuvaite, 'makarochkinite') and related minerals (surinamite, khmaralite and sapphirine) in that it contains >1 Be per formula unit. Chemical analyses and crystal structure refinements give a stoichiometric 1Be per formula unit (16 oxygen atoms) in surinamite (Moore and Araki, 1983; Barbier *et al*. 2001, submitted) and a maximum of 1Be per formula unit (20 oxygen atoms) in høgtuvaite, 'makarochkinite', khmaralite and synthetic beryllian sapphirine (Grauch *et al*., 1994; Yakubovich *et al.*, 1990; Barbier *et al.*, 1999, 2001, submitted; Christy *et al*. 2000, in press). Be in surinamite is almost entirely confined to the single tetrahedral site linked to three other tetrahedra. There are two such highly polymerized sites in høgtuvaite, 'makarochkinite', khmaralite and synthetic beryllian sapphirine (e.g. Fig. 3) and Be is present in both, but is absent from the other tetrahedral sites. The highly polymerized sites share a corner (O10) and thus Be-O-Be bridges would be inevitable if

Be occupied both T sites simultaneously; hence the upper limit of 1Be per formula unit in the four minerals. There are two alternatives in welshite. Either Be is restricted to the highly polymerized sites and Be-O-Be bridges are present, or significant Be occupies other tetrahedral sites, most likely those sharing two corners with other tetrahedra, i.e. chain tetrahedra. The charge deficiencies resulting from Be being present instead of Al or Si on these sites could be offset by the presence of As^{5+} on tetrahedral sites and Sb^{5+} on octahedral sites sharing corners with the Be-bearing tetrahedra. Thus, the presence of the highly charged cations allows the incorporation of more than 1Be per formula unit, the upper limit in aenigmatite-group and related minerals lacking significant quantities of pentavalent cations.

Status of welshite as a distinct species and name

Kunzmann (1999) recommended that welshite be renamed "beryllio-antimono-dorrite" because Moore's (1978) composition for welshite plots within the field he defined for dorrite, i.e. $2 \leqslant (Si-Na) < 3$ and $0 \leqslant Ti < 0.5$ per 20 oxygen atoms. The two compositions given in Table 3 also plot in Kunzmann's (1999) dorrite field. We see no need for the new name "beryllio-antimono-dorrite" because the name welshite has priority. Moreover, a name not derived from dorrite emphasizes the distinctiveness of welshite from dorrite. It is not merely the amount of Be and Sb present that distinguishes welshite from dorrite, as Kunzmann (1999) maintains, but the proportion of a given site occupied by these constituents; this is the basic criterion for distinguishing isostructural mineral species (Nickel and Grice, 1998). It is highly likely that the site occupancies are very different in dorrite and welshite. Given what is known about cation distribution in other aenigmatite-group minerals and minerals related to them, Be is probably concentrated in at least one of the more polymerized T sites, as is the case in 'makarochkinite', khmaralite and surinamite (see above). Thus, at least one of these sites would be >50% occupied by Be, a sufficient condition for welshite to be a species distinct from dorrite, which lacks Be. As regards the octahedral sites, Ti tends to be concentrated in the $M7$ site, e.g. aenigmatite (Cannillo *et al*., 1971), 'makarochkinite' (Yakubovich *et al*., 1990) and terrestrial rhönite (Bonaccorsi *et al*., 1990). Thus, given the

presence of at least 1.25Sb in welshite, it would be highly likely that one site, probably $M7$, would be >50% occupied by Sb, also a sufficient condition for welshite to be distinct. In summary, pending a full-scale structural refinement, there seems to be no reason not to retain welshite as a distinct species and name in the aenigmatite group.

Acknowledgements

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