Dedicated to the memory of Alan John Criddle

Tripuhyite, FeSbO$_4$, revisited

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ABSTRACT

The exact nature of tripuhyite remains controversial more than 100 years after the first description of the mineral. Different stoichiometries and crystal structures (rutile or tri-rutile types) have been suggested for this Fe-Sb-oxide. To address these uncertainties, we studied tripuhyite from Tripuhy, Minas Gerais, Brazil (type material) and Falotta, Grisons, Switzerland using single-crystal and powder X-ray diffraction (XRD), optical microscopy and electron microprobe analysis.

Electron microprobe analyses showed the Fe/Sb ratios to be close to one in tripuhyite from both localities. Single crystal XRD studies revealed that tripuhyite from the type locality and from Falotta have the rutile structure ($P4_2/mnm$, $a = 4.625(4)$ $c = 3.059(5)$ and $a = 4.6433(10)$ $c = 3.0815(9)$ Å, respectively). Despite careful examination, no evidence for a tripled c parameter, characteristic of the tri-rutile structure, was found and hence the structure was refined with the rutile model and complete Fe-Sb disorder over the cationic sites in both cases (type material: $R_1 = 3.61\%$; Falotta material: $R_1 = 3.96\%$). The specular reflectance values of type material tripuhyite and lewisite were measured and the following refractive indices calculated (after Koenigsberger): tripuhyite $n_{min} = 2.14$, $n_{max} = 2.27$; lewisite (cubic) $n = 2.04$.

These results, together with those of ^{57}Fe and ^{121}Sb Mössbauer spectroscopy on natural and synthetic tripuhyites reported in the literature, indicate that the chemical formula of tripuhyite is $Fe^{3+}Sb^{5+}O_4$ (FeSbO$_4$). Thus, tripuhyite can no longer be attributed to the tapiolite group of minerals of general type AB_2O_6. A comparison of the results presented with the mineralogical data of squawcreekite suggests that tripuhyite and squawcreekite are identical. In consequence, tripuhyite was redefined as $Fe^{3+}Sb^{5+}O_4$ with a rutile-type structure. Both the proposed new formula and unit cell (rutile-type) of tripuhyite as well as the discreditation of squawcreekite have been approved by the Commission on New Mineral and Mineral Names (CNMMN) of the International Mineralogical Association (IMA).

Introduction

TRIPUHYITE was described in 1897 as a new mineral with composition $Fe_2^{2+}Sb_2^{5+}O_7$ (Hussak and Prior, 1897) from Tripuhy, Minas Gerais, Brazil. Since its discovery more than 100 years ago, tripuhyite has been reported from a number of localities worldwide. However, no large crystals of this mineral species are known. For this reason, and because syntheses of larger crystals always failed, a conventional single-crystal XRD study and subsequent structure determination has never been performed for tripuhyite.

To date, the exact chemical formula of tripuhyite remains uncertain. Furthermore, the
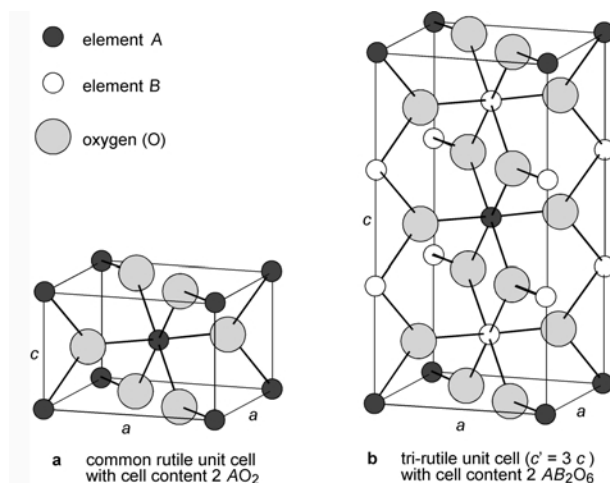
FIG. 1. The crystal structures of rutile and tri-rutile in perspective views.

unit cell of the mineral is also uncertain, with some authors giving a rutile cell, while others refer to a tri-rutile cell. The latter has a tripled c parameter compared to common rutile (Fig. 1), a fact that is reflected in small differences between the powder XRD patterns of 'rutile' and 'tri-rutile'. In order to resolve these uncertainties, we obtained type material tripuhyite from the collection of the Natural History Museum, London. We also obtained single crystals of tripuhyite found in vugs within the radiolarite-hosted Mn ores of the Falotta deposit (Grisons, Switzerland). This material was studied using single-crystal and powder XRD, ore microscopy and electron microprobe analysis.

The aim of this paper is to present the results of the structural, optical and chemical investigations of tripuhyite from both localities. We also discuss the order of Fe and Sb in natural and synthetic tripuhyite in general and in the refined crystal structures, in particular.

The CNMMN commission of the International Mineralogical Association has approved the redefinition of tripuhyite as $FeSbO_4$ with a rutile-type unit cell and the discreditation of squawcreekite ($FeSbO_4$) as a valid mineral species with 17:0:0 and 16:1:0 votes, respectively (vote #02-A).

Previous studies on tripuhyite and other Fe-antimonates

A large number of papers in the mineralogical and chemical literature deal with tripuhyite and related synthetic compounds. This section provides an overview of the previous work, which emphasizes the origin of the current uncertainty about the exact nature of tripuhyite. The relevant data from this review are condensed in Table 1.

Chemical compositions

Tripuhyite, with the empirical formula $Fe_2Sb_2O_7$, was named by Hussak and Prior in 1897. Palache et al. (1951) compiled known data of tripuhyite and proposed the formulae $Fe^{3+}SbO_4$ and $Fe_2^{2+}Sb_2O_7$. Mason and Vitaliano (1953) gave $FeSbO_4$ as the most likely formula for tripuhyite. Gakiel and Malamud (1969) used a sample of tripuhyite from Djebel Nador for a ^{57}Fe Mössbauer study and showed that Fe in this sample is in the ferric state. They followed Mason and Vitaliano (1953) in writing $FeSbO_4$ as the formula of tripuhyite. By ^{121}Sb Mössbauer spectroscopy, Baker and Stevens (1977) determined the oxidation state of Sb in tripuhyite from Djebel Nador to be pentavelent. Baptista (1981) erroneously gave the formula $Fe_2Sb_2O_6$ for tripuhyite when referring to Mason and Vitaliano (1953). Teller et al. (1985) reported the Fe/Sb ratio in synthetic $FeSbO_4$ to be 1. A new find of tripuhyite at Falotta (Oberhalbstein, Switzerland) led to Geiger and Cabalzar (1988) agreeing with the opinions of Mason and Vitaliano (1953) and of Gakiel and Malamud (1969) in writing the tripuhyite formula as $FeSbO_4$.

TABLE 1. Selected relevant data on tripuhyite retrieved from the literature.

Reference	Year	C	Formula	Origin	Fe	Sb	Fe:Sb	SG	ST	PM	SC
Hussak and Prior	1897	N	$Fe_2Sb_2O_7$	Tripuhy	Fe^{2+}						
Byström et al.	1941	S	$FeSb_2O_6$	Synthetic				$P4/mnm$*	3R	XD	
Brandt	1943	S	$FeSb_2O_6$ & $FeSbO_4$	Synthetic				$P4/mnm$*	3R R	XD	
Palache et al.	1951	N	$FeSbO_4$ or $Fe_2Sb_2O_7$	Tripuhy	Fe^{3+}** Fe^{2+}						
Mason and Vitaliano	1953	N	$FeSbO_4$	El Sonora					3R‡	XD	
Tavora	1955	N	$FeSbO_4$	Tripuhy	Fe^{3+}*		1:1†		3R	XD	
Gakiel and Malamud	1969	N	$FeSbO_4$	Djebel Nador	Fe^{3+}						
Donaldson et al.	1971	S		Synthetic				$P4_2/mnm$	R	XD	
Baker and Stevens	1977	N	$FeSbO_4$	Djebel Nador		Sb^{5+}			R		
Amador and Rasines	1981	S	$FeSbO_4$	Synthetic				$P4_2/mnm$		XD	
Baptista	1981	N	$FeSb_2O_6$¶	Tripuhy					3R	XD	
Teller et al.	1985	S	$FeSbO_4$	Synthetic			1:1	$P4_2/mnm$	R	ND	
Berry et al.	1986	S	$FeSbO_4$	Synthetic				$P4_2/mnm$	3R		
Berry et al.	1987a	S	$FeSbO_4$	Synthetic	Fe^{3+}	Sb^{5+}		$P4_2/mnm$	3R		ED
Berry et al.	1987b	S	$FeSbO_4$	Synthetic	Fe^{3+}	Sb^{5+}	1:1	$P4_2/mnm$	3R		ED
Geiger and Cabalzar	1988	N	$FeSbO_4$	Falotta							
Benvenutti et al.	1991	S	$FeSbO_4$	Synthetic							
Davanzo et al.	1996	S	$FeSbO_4$	Synthetic							
Berlepsch and Brugger	1999	N	$FeSbO_4$	cf. Table 2			1:1	$P4_2/mnm$		XD	XD
This study	2003	N	$FeSbO_4$	cf. Table 2			1:1	$P4_2/mnm$		XD	XD

C = compound; N = natural; S = synthetic
SG = space group
ST = structure type; 3R = tri-rutile; R = rutile
PM = powder methods; XD = X-ray diffraction; ND = neutron diffraction
SC = singly crystal; ED = electron diffraction
* old notation; ** interpreted or assumed oxidation state(s); † ~1:1 with Sb > Fe; ‡ based on a very weak 101 reflection; ¶ incorrect formula

Unit-cell dimensions

Byström et al. (1941) listed $FeSb_2O_6$ among the antimonates and tantalates isomorphous with $ZnSb_2O_6$, a compound itself isomorphous with the mineral tapiolite, $FeTa_2O_6$, for which the crystal structure was found to be of the tri-rutile type [Goldschmidt (1926) in: Byström et al. (1941)]. Using X-ray powder methods, Brandt (1943) found synthetic $FeSbO_4$ to have a rutile structure ($a = 4.623$, $c = 3.011$ Å). The author also reported that, depending on the heating conditions during the synthesis, $FeSbO_4$ was formed together with $FeSb_2O_6$, which has the tri-rutile structure. This result has not been reproduced (e.g. Donaldson et al., 1975).

X-ray powder photographs of byströmite, $MgSb_2O_6$, the first antimonate with the tri-rutile structure to be recognized as a mineral, and of tripuhyite, were interpreted by Mason and Vitaliano (1953) to be based on similar structures. The authors suggested a tri-rutile structure for tripuhyite, basing this structure assignment on the "very" weak 101 reflection in the X-ray powder pattern ($I_{101} = 20$ on a scale of 100). Based on X-ray powder methods, Tavora (1955) confirmed the tri-rutile cell and chemical formula of tripuhyite established by Mason and Vitaliano (1953). Amador and Rasines (1981) indexed the powder diffraction pattern of $FeSbO_4$ using the space group $P4_2/mnm$ and the unit-cell constants

a = 4.6388(2) and c = 3.0773(2) Å. By X-ray powder methods Baptista (1981) confirmed the tri-rutile cell established by Mason and Vitaliano (1953) and Tavora (1955).

Ongoing confusion

According to current classifications, the $MSbO_4$ (M = Cr, Fe, Rh, Al, Ga) compounds belong to the random rutiles whereas the MSb_2O_6 (M = Mg, Co, Ni, Cu, Zn) compounds belong to the tri-rutiles. Among the $MSbO_4$ and MSb_2O_6 compounds reported earlier, only M = Fe was claimed in both variants. However, the synthesis of $FeSb_2O_6$ failed and, as a matter of fact, $FeSbO_4$ was invariably obtained (Donaldson *et al.*, 1975).

In the 1980s, chemists became interested in compounds of the $FeSbO_4-\alpha-Sb_2O_4$ system because of their role as active and selective catalysts for the oxidation and ammoxidation of propylene (Teller *et al.*, 1985). A Rietveld analysis of neutron-diffraction data of synthetic $FeSbO_4$ showed an excellent agreement between their results (a = 4.6365(6) and c = 3.0742(6) Å) and the cell dimensions given by Amador and Rasines (1981). Specifically, there are no extra lines suggestive of a tri-rutile phase. In $FeSbO_4$ the Fe/Sb occupancy is entirely random and uniform (Teller *et al.*, 1985).

Berry *et al.* (1986) reported on the superlattice in synthetic $FeSbO_4$ obtained at 1000ºC. A detailed description of the identification of the space group and detection of cation order in $FeSbO_4$ using conventional and convergent-beam electron diffraction is given by Berry *et al.* (1987*a,b*). The authors conclude that iron antimonate crystallizes as an ordered tripled rutile-like structure and that superlattice reflections generated from this ordered cell will not be easily visible and are not observed in XRD patterns.

Sample descriptions

Tripuhyite has been reported from numerous localities from all over the world. For our studies we used type material from Tripuhy (sample E 1565, BM 86044, P 8716, obtained courtesy of P. Tandy, The Natural History Museum, London). Additional material from Falotta and Grube Clara was obtained courtesy of P. Hottinger (Ipsach, Switzerland) and from Djebel Nador (sample # 40172) and McDerwitt Mine (sample # 30874) courtesy of J. Arnoth (Natural History Museum, Basel). See Table 2 for details of the localities and experiments.

Type material of tripuhyite forms massive aggregates of grains up to ~0.1 mm in size. Embedded in this fine-grained matrix are substantially larger grains of lewisite up to ~0.35 mm (*cf.* the section on ore microscopy for more details). Tripuhyite from Falotta forms radiating aggregates of golden-yellow needles. From SEM images (*cf.* Berlepsch and Brugger, 1999) an idealized crystal form was deduced and compared to that of squawcreekite (Fig. 2). Tripuhyite from Djebel Nador forms microcrystalline yellowish crusts on nadorite ($PbSb^{3+}O_2Cl$) crystals. The material is unsuitable for single-crystal studies and EMP analyses. Note that the

TABLE 2. Samples used in the present study.

Mineral	Locality	SEM	EMP	OM	PD	UCD	SD
Tripuhyite[1]	Tripuhy, Brazil[2]		X	X	X	X	X
Lewisite[1]	Tripuhy, Brazil			X	X	X	
Tripuhyite	Falotta, Switzerland[3]	X	X		X	X	X
Tripuhyite	Djebel Nador, Algeria[4]	X			X	X	
Tripuhyite	Grube Clara, Germany[5]	X					
Tripuhyite	McDerwitt Mine, USA[6]	X					

SEM = scanning electron microscopy; EMP = electron microprobe analysis; OM = ore microscopy; PD = powder diffraction; UCD = unit cell determination; SD = structure determination.
[1] Type material; [2] Três Cruzes, Tripuí (former official spelling: Tripuhy) Ouro Preto, State of Minas Gerais, Brazil (type locality); [3] Falotta, Oberhalbstein, Grisons, Switzerland; [4] Hamman N'bail near Djebel Nador, Constantine, Algeria; [5] Grube Clara, Oberwolfach, Black Forest, Germany; [6] McDerwitt Mine, Humboldt County, Nevada, USA.

risk of handling contaminated material is obvious when such samples are used for powder diffraction. Tripuhyite from Grube Clara forms small aggregates of tiny, brown-yellow crystals too small for our purposes (maximum crystal dimensions: ~0.02 × 0.01 × 0.002 mm). The situation is similar for the tripuhyite from the McDerwitt Mine.

Experimental

Chemical analyses

Tripuhyite was analysed with a Cameca SX-50 electron microprobe (EMP) operated at 15 kV using a finely focused 25 nA beam with a diameter of 1−2 μm. For the sample from Tripuhy, the beam was scanned over a 5 × 5 μm surface in order to reduce sample damage. This procedure could not be applied to the samples from Falotta due to the small crystal sizes. The measured X-ray lines and the analytical standards were: Sb-$L\alpha$ (synthetic Sb_2O_3), Fe-$K\alpha$ (hematite), and Ti-$K\alpha$ (rutile). The line As-$L\alpha$ (adamite) was used to estimate the As contents. After correction for the interference with the Sb-$L\beta$ X-ray lines, it appears that the analysed tripuhyites contain <0.2 wt.% As. The results from the EMP analyses are summarized in Table 3. The empirical
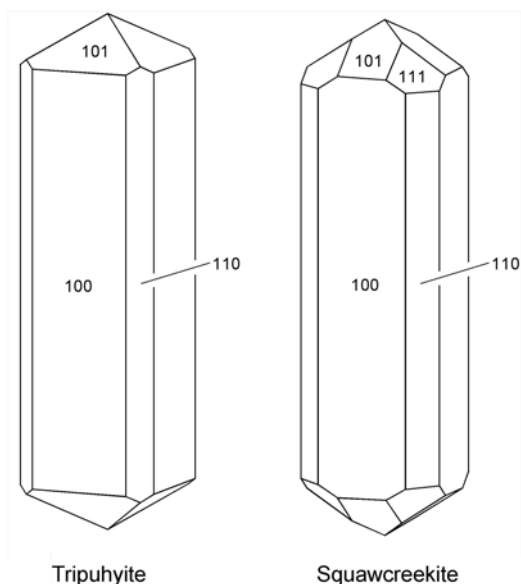
formulae derived from these data, normalized on four oxygen atoms p.f.u., are $Fe_{0.935(14)}$ $Sb_{1.065(14)}O_4$ and $Fe_{1.055(25)}Sb_{0.945(24)}O_4$ for tripuhyite from Tripuhy and Falotta, respectively. The finding of small amounts of Mn in tripuhyite from Falotta, reported by Geiger and Cabalzar (1988) and based on EDS analyses, were not confirmed in our study.

Ore microscopy
The optical properties of lewisite and tripuhyite in reflected light

A fragment of the sample containing the holotype of lewisite and tripuhyite was mounted in epoxy resin, cut with a diamond saw, then ground with carborundum and polished with diamond abrasives. This section was photographed at a colour temperature of ~3200 K with a JVC digital camera mounted on a Zeiss Axioplan reflected light microscope. The images were collected with Synoptics software and manipulated with Adobe® Photoshop® 6 software. Two photographs of the polished fragment (taken in the same orientation) in plane-polarized light and between crossed polars are combined in Fig. 3.

In plane-polarized reflected light the euhedral to subhedral crystals of lewisite, most of which are fractured, are a darker and very slightly brownish grey in comparison with the lighter, fine-grained euhedral to anhedral tripuhyite groundmass or matrix. The assemblage in which these minerals were originally found at Tripuhy was described in detail by Hussak and Prior

FIG. 2. Idealized crystal habits of tripuhyite from Falotta and squawcreekite, based upon SEM images (Berlepsch and Brugger, 1999).

TABLE 3. Electron microprobe analyses (wt.%) of tripuhyite from Tripuhy and Falotta.

Sample origin	Tripuhy, Brazil	Falotta, Switzerland
# of analyses	13	7
Sb_2O_5	69.3 (0.4)[1]	62.3 (1.4)
Fe_2O_3	30.0 (0.7)	34.3 (1.1)
Sum[2]	99.3 (0.6)	96.6 (1.1)
Sb (a.p.f.u.)	1.065 (0.014)	0.945 (0.024)
Fe (a.p.f.u.)	0.935 (0.014)	1.055 (0.025)

[1] Standard deviation σ_{n+1}
[2] TiO_2 < 0.05 wt.%; As_2O_5 < 0.2 wt.% not included
Formulae normalized on four oxygen atoms p.f.u.:
Tripuhy: $Fe_{0.935(14)}Sb_{1.065(14)}O_4$
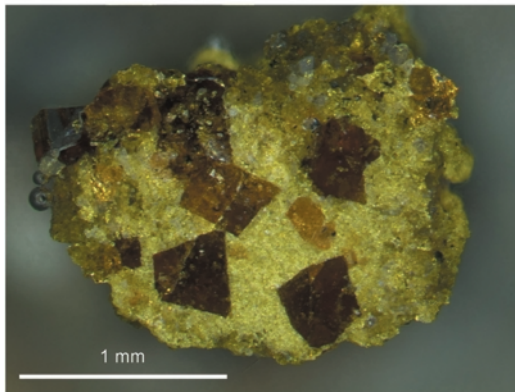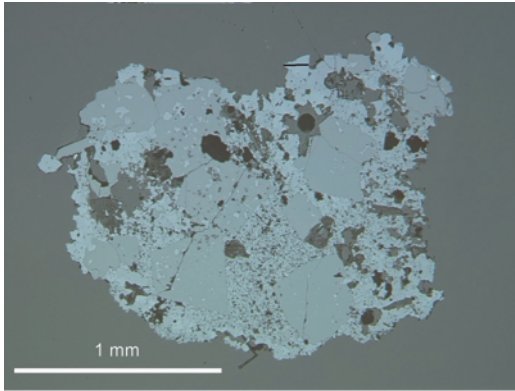Falotta: $Fe_{1.055(25)} Sb_{0.945(24)}O_4$

FIG. 3. Photomicrographs of the polished holotype fragment (taken in the same orientation) in plane-polarized light and between crossed polars.

(1895, 1897) and it was from here that they described the then new mineral derbylite (1895). Between crossed polars, lewisite varies in colour and translucency from an almost opaque very dark brown through orange-brown to pale yellow. It is supposed that the variation in colour and opacity is related to variation in the composition of the mineral. Internal reflections are abundant (Fig. 3) and mask any anisotropy though, as the mineral is cubic, this would be anomalous.

Compared with lewisite, internal reflections in the much smaller grains of tripuhyite are colourless to pale honey yellow. In order to obtain the image between crossed polars, not only were very high levels of illumination used but some software changes (in saturation, reduction in contrast and increase in brightness) were needed to produce an image which corresponded to that seen by the naked eye (AJC's eye).

Reflectance measurements

As should be apparent from these pictures, selection of areas suitably representative of the minerals for the measurement of reflectance was not easy: it was almost impossible to find grains free from internal reflections that were also free from fractures or included minerals. In the case of the fine-grained tripuhyite, the most anisotropic grain had to be found photometrically as internal reflections were ubiquitous and any extinction positions were masked by them. Visible spectrum measurements of the specular reflectance of the two minerals were made relative to an SiC reflectance standard (Zeiss no. 472) using a Zeiss MPM800 microscope-spectrophotometer. Measurements were made in two media, air and
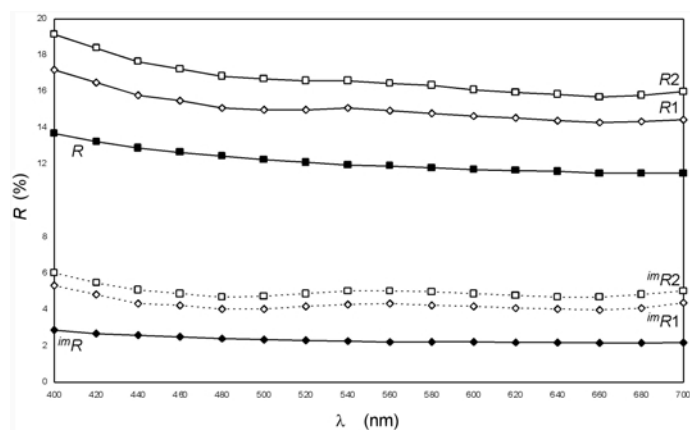

FIG. 4. The reflectance spectra of tripuhyite (empty symbols) and lewisite (filled symbols).

an immersion oil (Zeiss N_D = 1.515). Although the grains of lewisite are relatively large, it was necessary to use high-power objectives to avoid areas seriously affected by internal reflections. The bandwidth of the grating monochromator was set at 5 nm and measurements made at an interval of 10 nm from 400 to 700 nm. Once set up, the conditions of measurement were unchanged for the measurement of both minerals. R maxima and minima for tripuhyite were found photometrically; these were orthogonal and five sets of reflectance data were collected for each vibration direction of the crystal on rotation of the microscope stage at intervals of 90º. These five sets were averaged and the highest and lowest values were accepted. Although lewisite is cubic, R data were obtained in the same way, but as expected, variation in the measured values was smaller than acceptable measurement error (see later).

The reflectance data for the two minerals are tabulated together with their colour values which were calculated relative to the illuminants A and C of the International Commission on Illumination (CIE = Commission Internationale de l'Éclairage) in Table 4. The reflectance spectra are illustrated graphically in Fig. 4. The dispersion of the reflectance values of tripuhyite follow a generally downward trend from the blue end of the spectrum (400 nm) to the red, but an upward inflection of the curves from ~500 to 600 nm is characteristic of the mineral. The dispersion of the bireflectance is constant, hence, although tripuhyite is detectably bireflectant it is not pleochroic. The spectra from both media used for measurement for lewisite follow a similar (but uninflected) downward trend to those of tripuhyite, and, as is evident from the photomicrograph in plane-polarized light in Fig. 3, the air reflectance values are 4−6% lower and the oil reflectance ~2% lower than those of tripuhyite.

Specular reflectance data obtained at the NHM in London have been used routinely since the mid-1970s to calculate the other optical constants – refractive indices (n) and absorption coefficients (k) – and since Embrey and Criddle's (1978) recommendations, to test the reliability of the original measurements. These recommendations were aimed at opaque minerals, however, and as Criddle (1990a,b) showed, an understanding of the relationship between the three constants R, n and k gives the observer a much clearer understanding of the qualitative optical properties of transparent to translucent to weakly opaque but

TABLE 4. Specular reflectance data and colour values for tripuhyite and lewisite.

λ (nm)	R_1	Tripuhyite R_2	$^{im}R_1$	$^{im}R_2$	Lewisite R	^{im}R
400	17.20	19.15	5.35	6.05	13.70	2.89
420	16.50	18.40	4.85	5.50	13.25	2.70
440	15.80	17.65	4.35	5.10	12.90	2.61
460	15.50	17.25	4.25	4.90	12.65	2.52
480	15.10	16.85	4.05	4.70	12.45	2.42
500	15.00	16.70	4.05	4.75	12.25	2.36
520	15.00	16.60	4.20	4.90	12.10	2.32
540	15.10	16.60	4.30	5.05	11.95	2.28
560	14.95	16.45	4.35	5.05	11.90	2.23
580	14.80	16.35	4.25	5.00	11.80	2.24
600	14.65	16.10	4.20	4.90	11.70	2.24
620	14.55	15.95	4.10	4.80	11.65	2.21
640	14.40	15.85	4.05	4.70	11.60	2.20
660	14.30	15.70	4.00	4.70	11.50	2.19
680	14.35	15.80	4.10	4.85	11.50	2.18
700	14.45	16.00	4.40	5.05	11.50	2.20
COM:						
470	15.20	17.00	4.15	4.80	12.55	2.46
546	15.00	16.60	4.35	5.10	11.85	2.27
589	14.70	16.25	4.25	5.00	11.75	2.21
650	14.35	15.80	4.00	4.65	11.55	2.19
CIE: C = 6774 K						
X	0.305	0.304	0.308	0.309	0.303	0.302
Y	0.311	0.310	0.315	0.316	0.309	0.302
Y^0%	14.90	16.40	4.20	4.90	11.90	2.28
$λ_d$	478	477	479	485	476	460
P_e%	2.50	3.00	0.90	0.50	3.40	5.00
CIE: A = 2856 K						
X	0.443	0.442	0.445	0.445	0.442	0.444
Y	0.407	0.406	0.409	0.409	0.405	0.399
Y^0%	14.80	16.30	4.20	4.90	11.85	2.28
$λ_d$	491	490	503	509	488	c551
P_e%	1.20	1.50	0.60	0.60	1.60	2.35

highly refrigent minerals. Few examples are given in the Criddle papers from 1990, so the opportunity is taken wherever appropriate to illustrate these relationships in very weakly absorbing minerals as typified here by lewisite and tripuhyite. Lewisite, being isotropic, provides the simpler illustration. The dispersion of the reflectance values in both media are monotonic and, in oil, the measured values are low, <3% throughout the spectrum. Any errors in measurement in these low oil values might have, indeed, are likely to have, a significant effect on optical constants calculated using the Koenigsberger simultaneous equations with R and ^{im}R values.

The values in Table 5 are calculated from the values in Table 4. Superficially, the *n* values look alright and follow the same monotonous trend as the reflectance curves. However, the absorption coefficients from 400 to 560 nm, excluding the value at 540 nm, are prefixed with '*i*' for an imaginary value (Embrey and Criddle, 1978). This means that the refringences are equally suspect. Now if the two columns of refringences calculated using the Fresnel equations (which assume a value of zero for the absorption) are examined, it is apparent that the refringences at the blue end of the spectrum are lower than those calculated using Koenigsberger's equations and *vice versa* at the red end. In qualitative terms, one might interpret this to mean that lewisite is transparent – within measurement error – at the blue end of the spectrum and that its absorption slowly increases through the yellow, orange to red parts of the spectrum. To the casual observer, it may come as a surprise that reflectance data measured to three significant figures supply constants that reveal the physical relationship between the absorption and the reflectance and that these correspond to what one sees in terms of the colour and transparency/opacity of the mineral. To the microscope-spectrophotometrist they are evidence that the measured data are as reliable as it is currently possible to obtain. Optical data gathered together in Dana 7th edition (Palache *et al.*, 1951) for romeite exclude

refractive indices for the Ti-bearing lewisite, but confirm a considerable range in *n* depending on composition and weak to moderate anomalous birefringence in some varieties.

Larsen (1921 in Palache *et al.*, 1951) succeeded in measuring the refractive indices for the optically positive biaxial mineral tripuhyite from a sample from Tripuhy: $n_\omega = 2.19-2.20$, $n_\varepsilon = 2.33$. He noted that the dispersion was very strong with $r < v$. He must be congratulated in determining these values on crystals as small as those available in the Tripuhy type sample, particularly as one supposes that he used S-Se melts at a wavelength of 589 nm or longer (the wavelength is not specified). When measuring the reflectance values of biaxial minerals at unknown crystallographic and optical orientations, it must be accepted that optical values derived from them are approximate (the representation surfaces of each of the constants at every wavelength is independent). In practical terms, the two-media method of deriving the constants is unsuccessful even with crystals specially cut and polished to correspond to individual principle axes. Having said that, there is no other technique that could provide even approximate values for the small crystals of tripuhyite that were available. What spectral reflectance measurements can do is provide measured values that enable observations to be confirmed, and given the results obtained for *n* and for *k* from *R* and from *imR* using the Fresnel and Koenigsberger equations, it is possible to evaluate their reliability. The first thing one notices from the data in Table 6 is the fairly high values of the calculated absorption coefficients (except for R_2 from 400 to 500 nm). When the refractive indices paired with these are compared with those calculated independently from the air and oil reflectance values (for $k = 0$) they are seen to be consistently lower, except for R_2 from 400 to 500 nm where they are consistently higher. We know that the imaginary values for the absorption coefficients are false and that their associated refringences are also, and the chances are that the mineral is transparent for the vibration direction measured, hence the most likely values for *n* at these wavelengths is an average of the n_{air} and n_{oil} values. Of course, if this applies for these wavelengths, when from 500 nm onwards to 700 nm the position is reversed, which values are likely to be more reliable, the lower values associated with the high absorption or the higher values where the absorption is discounted? The answer is that we cannot know, but from visual inspection, the crystal measured was nearly

TABLE 5. Refractive indices and absorption coefficients calculated from *R* and *imR* for lewisite.

λ (nm)	R (Koenigsberger)		R (Fresnel)	
	n	*k*	n_{air}	n_{oil}
400	2.19	*i* 0.16	2.18	2.17
420	2.16	*i* 0.16	2.14	2.14
440	2.12	*i* 0.07	2.12	2.12
460	2.11	*i* 0.05	2.10	2.10
480	2.10	*i* 0.11	2.09	2.09
500	2.08	*i* 0.08	2.08	2.07
520	2.07	*i* 0.04	2.07	2.07
540	2.05	0.06	2.06	2.06
560	2.06	*i* 0.10	2.05	2.05
580	2.04	0.07	2.05	2.05
600	2.03	0.13	2.04	2.05
620	2.03	0.11	2.04	2.04
640	2.02	0.11	2.03	2.04
660	2.01	0.14	2.03	2.03
680	2.02	0.13	2.03	2.03
700	2.01	0.16	2.03	2.04

TABLE 6. Refractive indices and absorption coefficients calculated from R and ^{im}R for tripuhyite.

| λ (nm) | R_1 (Koenigsberger) | | R_1 (Fresnel) | | R_2 (Koenigsberger) | | R_2 (Fresnel) | |
	n	k	n_{air}	n_{oil}	n	k	n_{air}	n_{oil}
400	2.31	0.46	2.42	2.46	2.61	i 0.33	2.56	2.54
420	2.30	0.37	2.37	2.40	2.59	i 0.44	2.50	2.47
440	2.28	0.26	2.32	2.34	2.52	i 0.40	2.45	2.42
460	2.25	0.29	2.30	2.32	2.49	i 0.38	2.42	2.39
480	2.23	0.28	2.27	2.29	2.46	i 0.36	2.39	2.37
500	2.21	0.30	2.26	2.29	2.41	i 0.25	2.38	2.37
520	2.23	0.24	2.26	2.28	2.35	0.21	2.38	2.38
540	2.18	0.39	2.27	2.31	2.32	0.33	2.38	2.40
560	2.15	0.44	2.26	2.32	2.29	0.38	2.36	2.40
580	2.14	0.43	2.25	2.30	2.28	0.37	2.36	2.39
600	2.13	0.43	2.24	2.29	2.26	0.39	2.34	2.37
620	2.14	0.43	2.23	2.28	2.25	0.37	2.33	2.36
640	2.12	0.41	2.22	2.27	2.26	0.34	2.32	2.35
660	2.10	0.41	2.22	2.27	2.23	0.39	2.31	2.35
680	2.10	0.43	2.22	2.28	2.23	0.39	2.31	2.35
700	2.04	0.48	2.24	2.30	2.19	0.48	2.33	2.40

colourless and not entirely free from internal reflections. Thus, errors in reflection are almost certainly greater in oil than in air (and, indeed, the calculated refringences in oil are higher than in air) and the conclusion may be drawn that the lower overall refringence values correspond more closely to the real figures. It is probable that repeated measurement of several grains of tripuhyite would reveal the truth, but the facts are that the values obtained are a close match to the data of Larsen (1921 in Palache *et al.*, 1951) and that the characteristic dispersion of the reflectance is also present in the other constants. Errors there undoubtedly are, but simple arithmetic shows that these are of the order of R 0.1−0.2% and ^{im}R 0.1−0.2% – the kind of figures that can be the product of internal reflection, and note that, when immersed in an oil of higher refractive index than air these reflections are more easily seen and, of course, add a larger increment to the measured specular reflectance. What remains is that the reflectance values for tripuhyite are reliable and provide an excellent example of the limitations of dealing with minerals containing strong internal reflections.

X-ray powder diffraction

Calculated powder XRD patterns of $FeSbO_4$ in the rutile and for $Fe_{1.5}Sb_{1.5}O_6$ in the tri-rutile structure are given in Table 7. The former is based on the results from the structure refinement of tripuhyite from Tripuhy (*cf*. Tables 8 and 10), the latter was calculated using the only known tri-rutile structure model with a cation ratio of 1, i.e. that of ferrotapiolite $Fe_{1.5}Ta_{1.5}O_6$ (Christensen *et al.*, 1976), and replacing Ta by Sb. The measured X-ray powder diffraction diagrams of tripuhyite from Falotta and of squawcreekite (Foord *et al.*, 1991) are given in the same Table for comparison.

Single crystal X-ray diffraction studies
Type material

A small crystal fragment of type material tripuhyite was extracted from the polished section (*cf*. Fig. 3) and mounted on an Enraf Nonius CAD4. The X-ray data collection for a tri-rutile structure model was performed at 293 K with the use of graphite-monochromated Mo-$K\alpha$ X-radiation. Cell dimensions were refined from 16 reflections with high θ angles yielding tetragonal symmetry and the (common rutile) cell parameters listed in Table 8. Experimental details are given in Table 9. Diffraction data were collected up to θ = 30º. Data reduction, including background and Lorentz polarization correction, was carried out with the SDP program system (Enraf Nonius, 1983). An empirical absorption correction was applied using the ψ-scan technique (360º with a 10º step size) and showed no significant effect. For structure solution and refinement the known rutile space group $P4_2/mnm$ was used.

TABLE 7. X-ray powder diffraction data: calculated for tripuhyite (with rutile and tri-rutile cell) and measured for tripuhyite and squawcreekite.

Calculated values for Cuα₁ X-radiation						Measured values for Cuα₁ X-radiation					
$Fe_{1.5}Sb_{1.5}O_6$*			$FeSbO_4$**			$FeSbO_4$ (Falotta)[†]			$FeSbO_4$ (Sq. Creek)[‡]		
hkl	d_c (Å)	I_c/I_0	hkl	d_c (Å)	I_c/I_0	hkl	d_m (Å)	I_{est}[¶]	hkl	d_m (Å)	I_{meas}[¶]
002	4.5700	2									
101	4.1303	12									
110	3.2739	100	110	3.2739	100	110	3.275	100	110	3.3039	100
112	2.6614	2									
103	2.5451	71	101	2.5523	70	101	2.562	80	101	2.5844	49
200	2.3150	18	200	2.3150	18	200	2.315	30	200	2.3342	17
113	2.2303	7	111	2.2352	6	111	2.249	20	111	2.2583	4
210	2.0706	2	210	2.0706	2				210	2.0892	1
211	2.0194	4									
114	1.8738	3									
213	1.7125	63	211	1.7147	63	211	1.7173	70	211	1.7316	36
220	1.6370	16	220	1.6370	16	220	1.6340	20	220	1.6500	12
006	1.5233	8	002	1.5295	8	002	1.5361	30	002	1.5505	3
310	1.4641	13	310	1.4641	13				310	1.4756	8
116	1.3811	13	112	1.3857	14	112	1.3914	40			
303	1.3768	19	301	1.3779	20	301	1.3790	40	301	1.3907	10
206	1.2725	6	202	1.2761	6	202	1.2805	30	202	1.2910	2
323	1.1833	10	321	1.1840	10	321	1.1844	10	321	1.1940	2
400	1.1575	4	400	1.1575	4	222	1.1205	10			
226	1.1152	8	222	1.1176	8				222	1.1300	4
330	1.0913	4	330	1.0913	4				330	1.1005	2
316	1.0556	10	312	1.0577	10						
413	1.0536	11	411	1.0542	11						
420	1.0353	5	420	1.0353	5						
109	0.9920	4	103	0.9958	4						
406	0.9216	6	402	0.9230	5						
219	0.9118	11	213	0.9148	11						
510	0.9080	6	510	0.9080	6						
336	0.8871	7	332	0.8884	7						
503	0.8860	3	501	0.8863	3						
433	0.8860	12	431	0.8863	11						
426	0.8563	10	422	0.8574	11						
309	0.8484	8	303	0.8508	9						
523	0.8275	19	521	0.8277	19						
440	0.8185	4	440	0.8185	4						
329	0.7966	14	323	0.7985	14						
530	0.7940	7	530	0.7940	7						
516	0.7800	37	512	0.7808	36						
31*10*	0.7753	8									
600	0.7717	26	600	0.7717	27						
444	0.7705	9									

* Hypothetical compound based upon the ferrotapiolite structure (Christensen *et al.*, 1976), i.e. a tri-rutile structure with Fe:Sb = 1:1 and the unit-cell parameters a = 4.63 and c = 9.14 Å; 100 reflections with I_c < 2 were omitted.
** Based upon structure data for tripuhyite from Tripuhy (Tables 8 and 10); 17 reflections with I_c < 2 were omitted.
[†] Tripuhyite from Falotta; six additional lines could not be indexed and are interpreted as the result from impurities.
[‡] Squawcreekite from Squaw Creek (Sq. Creek) tin deposit (Foord *et al.*, 1991).
[¶] I_{est} = estimated intensities, I_{meas} = measured intensities.

TABLE 8. Unit-cell parameters of tripuhyite, squawcreekite, rutile and cassiterite.

	Tripuhyite		Squawcreekite	Rutile	Cassiterite
Locality	Tripuhy	Falotta	Squaw Creek		
Data origin	CAD4	CCD	STOE/NICOLET		
Formula	$FeSbO_4$	$FeSbO_4$	$FeSbO_4$*	TiO_2	SnO_2
Crystal system	tetragonal	tetragonal	tetragonal	tetragonal	tetragonal
Space group	$P4_2/mnm$	$P4_2/mnm$	$P4_2/mnm$	$P4_2/mnm$	$P4_2/mnm$
a (Å)	4.625(4)	4.6433(10)	4.6673(7)	4.594	4.738
c (Å)	3.059(5)	3.0815(9)	3.1006(8)	2.959	3.187
V (Å^3)	65.43	66.44	67.54	62.4	71.5
Z	1	1	1	2	2
Reference**	[1]	[1]	[2]	[3]	[3]

* simplified formula obtained from inhomogeneous grains
** [1] this study; [2] Foord *et al.* (1991); [3] Baur and Khan (1971)

The structure of type material tripuhyite was solved by direct methods with the program SHELXS-97 (Sheldrick, 1997) and refined with the program SHELXL-97 and applying neutral atom scattering factors (Sheldrick, 1997). The Fe/Sb ratio was set according to the EMP analyses (Table 3) and the sum Fe + Sb set equal to one. Anisotropic displacement parameters were refined for all atoms in the last cycles. The refinement was stopped when the maximum shift/esd for varied parameters dropped below 1%. Fractional atomic coordinates, site occupancy factors, and an-/isotropic displacement parameters are listed in Table 10, selected interatomic distances are given in Table 11.

Falotta material

A tiny needle-like crystal fragment of tripuhyite from Falotta, elongated parallel to *c*, was used for X-ray data collection at 298 K. Cell parameters (Table 8) and intensities were collected on a Siemens SMART CCD system (Bruker, 1998) with graphite-monochromatized Mo-Kα X-radiation. About a half sphere in the reciprocal lattice was measured and a total of 389 reflections in the range $0 < 2\theta < 56.7°$ was collected with an exposure time of 5 min per frame. Table 9 contains a summary of the conditions of CCD data collection and the structure refinement parameters. All diffraction intensities were corrected empirically for absorption by using a pseudo-ψ-scan correction. Because a half sphere of diffraction data was collected in reciprocal space, symmetry equivalent reflections exhibit a high redundancy. This allows a ψ-scan-like absorption correction to be applied. Data reduction, including intensity integration, background, and Lorentz-polarization corrections, was carried out with the program SAINT+ (Bruker, 1999).

To test for superlattice reflections the intensity integration was done for the tri-rutile cell, but no significant intensities were found, indicative of a tripled cell. The space group $P4_2/mnm$, proposed by the program XPREP (Bruker, 1997), is the same as reported in literature. The structure was solved with direct methods (SHELXS by Sheldrick, 1997) and the rutile model kept for subsequent refinement (SHELXL by Sheldrick, 1997). The final refinement, applying neutral scattering factors, was performed with anisotropic displacement parameters for the metal position. To test variable occupancy on the (Fe, Sb) site, individual Fe/Sb populations were allowed to vary. However, strong correlation of occupancy and scaling factors made it impossible to obtain any reasonable result. The Fe/Sb ratio was set according to the results obtained from the EMP analyses (with Fe + Sb = 1). Fractional atomic coordinates, site occupancy factors, isotropic and anisotropic displacement parameters, and selected interatomic distances are listed in Table 10.

Results and discussion

Chemical composition

The chemical analyses of tripuhyite from Tripuhy and Falotta both have an Fe:Sb ratio close to 1 (Table 3). A similar result was reported by Teller

TABLE 9. Summarized CAD4 and CCD data collection and structure refinement parameters for tripuhyite from Tripuhy and Falotta.

Tripuhyite from	Tripuhy	Falotta
Diffractometer	Enraf Nonius CAD4	Siemens SMART CCD
X-ray radiation	MoK_α	MoK_α
X-ray power	50 kV, 40 mA	50 kV, 40 mA
Temperature	293 K	293 K
Detector to sample distance		5.518 cm
Rotation width		0.3°
Frame size		512×512 pixels
Time per frame		5 min
Reflections measured	378	389
Index range	$-1 < h < 7$	$-7 < h < 3$
	$-1 < k < 7$	$-6 < k < 7$
	$-1 < l < 5$	$-5 < l < 5$
Unique reflections	65	57
Reflections $> 2\sigma(I)$	53	46
R_{INT}	6.89%	5.00%
R_σ	5.21%	2.50%
# of least squares parameters	7	8
R_1	3.57%	3.61%
R_1 (all data)	4.18%	5.74%
wR_2	8.59%	10.40%
GoF	1.069	1.251

$R_{INT} = \Sigma|F_o^2 - F_o^2(\text{mean})|/\Sigma F_o^2$
$R_\sigma = \Sigma\sigma(F_o^2)/\Sigma F_o^2$
$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$
$wR_2 = \{(\Sigma w[F_o^2 - F_c^2]^2/\Sigma w[F_o^2]^2)\}^{1/2}$
$GoF = \{(\Sigma w[F_o^2 - F_c^2]/[n - p])\}^{1/2}$
$w_{Tripuhy} = 1/(\sigma^2[F_o^2] + [0.0363\ P]^2 + 3.42\ P)$
$w_{Falotta} = 1/(\sigma^2[F_o^2] + [0.0532\ P]^2)$
$P = (\max(F_o^2,0) + 2\ F_c^2)/3$

et al. (1988) for synthetic $FeSbO_4$. Based upon the type of deposits where tripuhyite occurs, it is reasonable to assume the high oxidation states 3+ and 5+ for Fe and Sb, respectively. However, lewisite from Tripuhy contains substantial amounts of Sb^{3+}, and thus questions the plausibility of the above assumption (Rouse *et al.*, 1998; Zubkova *et al.*, 2000).

For tripuhyite from Djebel Nador, the above oxidation states have been confirmed by means of Mössbauer spectroscopy (Gakiel and Malamud, 1969; Baker and Stevens, 1977). All these results strongly suggest the correct formula of tripuhyite to be $FeSbO_4$. Contrary to the high oxidation states in tripuhyite, the cations in schafarzirkite, $Fe^{2+}Sb_2^{3+}O_4$, have low oxidation states. Presumably a compound $FeSb_2O_6$, that requires Fe^{2+} *vs.* Sb^{5+}, does not exist at all because Fe would adopt the high oxidation state.

X-ray powder diffraction

From the data given in Table 7 the differences between the calculated powder patterns of $FeSbO_4$ (rutile structure) and $Fe_{1.5}Sb_{1.5}O_6$ (tri-rutile structure) become obvious. The latter has seven more reflections than the former. The 101 reflection is the strongest among these characteristic reflections, and its presence has been used by a number of authors as evidence for a tri-rutile cell (e.g. Mason and Vitaliano, 1953; Tavora, 1955). Mason and Vitaliano (1953; PDF-7-349) attributed $d_{obs} = 4.225$ Å to the 101 reflection. This is significantly different from the expected value, $d_{calc} = 4.130$ Å (Table 7). Refinement of the powder pattern PDF-7-349, using the program UnitCell (Holland and Redfern, 1997), shows that $d_{4.225}$ Å is the only line that cannot be accounted for within the stated precision, and that all other lines are compatible with a rutile-cell. It thus

TABLE 10. Fractional atomic coordinates, site occupancy factors (sof), isotropic and anisotropic displacement parameters, and selected bond distances, with estimated standard deviations in parentheses, for tripuhyite from Tripuhy and Falotta.

Tripuhyite from Tripuhy: $Fe_{0.935(14)}Sb_{1.065(14)}O_4$

Atom	sof	x/a	y/b	z/c		U_{eq} (Å^2)
Fe1	0.47	0	0	0		0.0136(7)
Sb1	0.53	0	0	0		0.0136(7)
O1	1.0	−0.304(2)	0.304(2)	0		0.008(2)
Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
(Fe,Sb)1	0.0164(8)	0.0164(8)	0.08(1)	0	0	-0.01(1)

Tripuhyite from Falotta: $Fe_{1.055(25)}Sb_{0.945(24)}O_4$

Atom	sof	x/a	y/b	z/c		U_{eq} (Å^2)
Fe1	0.53	0	0	0		0.0070(6)
Sb1	0.47	0	0	0		0.0070(6)
O1	1.0	0.193(1)	-0.193(1)	0.5		0.006(2)
Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
(Fe,Sb)1	0.0091(7)	0.0091(7)	0.0029(7)	0	0	0.0007(4)

M−O bond distances:
Tripuhy: 1.9933(115) 2 ×   2.0095(74) 4 ×
Falotta: 2.0066(67) 2 ×   1.9841(43) 4 ×

appears likely that this reflection results from an impurity, e.g. cervantite α-Sb_2O_4, rather than pointing toward a tri-rutile structure. In the case of Tavora (1955; PDF 7-65) d_{obs} = 4.13 Å matches well with d_{calc} but the powder diagram contains seven unindexed reflections and it is possible that d_{obs} = 4.13 Å results from another phase too.

Tripuhyite from Falotta provided a fairly good film but the powder diffraction pattern contains six lines that cannot be indexed with the rutile cell. Two of these six lines could be indexed with the tri-rutile cell but the corresponding I_{calc} are 0.2 and 0.3 (on a scale of 1000) and these reflections, therefore, were attributed to impurities. Geiger and Cabalzar (1988) indexed their X-ray powder pattern of tripuhyite from Falotta with a tri-rutile cell and using ten d-values. Their tri-rutile cell is based upon d = 4.11 Å with I_{101} = medium (on a scale with seven increments from very weak to strong). It is important to point out that our studies (single crystal and powder) do not confirm these findings. The XRD powder diagram of tripuhyite from Djebel Nador did not reveal new aspects. Several lines could not be indexed

and for the d_{obs} value of 4.23 Å the same argument applies as above.

Amador and Rasines (1981) gave very accurate cell data for $FeSbO_4$, obtained from an XRD powder pattern and indexed on the basis of a rutile cell. In their neutron diffraction study Teller et al. (1988) measured a 2θ range wide enough to find possible reflections indicative of a tri-rutile cell. However, the authors wrote that all diffraction peaks are accounted for by the phases α-Sb_2O_4 (known naturally as cervantite) and $FeSbO_4$.

Squawcreekite

Squawcreekite was described by Foord et al. (1991) as a new mineral with composition $(Fe^{III}_{0.29}Sb^{V}_{0.29}Sn_{0.28}Ti_{0.13}Al_{0.01})_{\Sigma=1.00}O_2$ and $(Fe^{III}_{0.36}Sb^{V}_{0.35}Sn_{0.19}Ti_{0.08}Al_{0.01})_{\Sigma=1.00}O_2$, ideally $Fe^{3+}Sb^{5+}O_4$. The cell parameters (Table 8) indicate a common rutile structure. Foord et al. (1991) report that single-crystal X-ray precession photographs of squawcreekite failed to show any supercell reflections, indicative of a doubling or tripling along c, and from systematic extinctions and by analogy to cassiterite the space group

$P4_2/mnm$ was chosen.

The powder XRD pattern of squawcreekite (Table 7) basically corresponds to those calculated and measured, respectively, for tripuhyite and indexed with a rutile cell. Foord *et al.* (1991) measured squawcreekite with epitaxial Fe- and Sb- bearing cassiterite and their X-ray powder diffraction pattern showed no line around $4.1-4.3$ Å. Thus the authors indexed it with a common rutile cell. The X-ray powder diffraction pattern of squawcreekite has the same three strongest lines but differs slightly in the d_{obs} values compared to tripuhyite Since squawcreekite contains significant amounts of Sn (Foord *et al.*, 1991), the systematic shift towards larger interplanar spacings (Table 7) can easily be explained by the enlarged unit cell due to the incorporated Sn (Table 8).

Foord *et al.* (1991) refer in their work on squawcreekite only to Brandt (1943), Donaldson *et al.* (1975), Amador and Rasines (1981) and the PDF 34-372 (synthetic $FeSbO_4$). There is no link to previous mineralogical work on Fe-Sb-oxides, e.g. tripuhyite or schafarzikite. In the light of all uncertainties related to the true nature of tripuhyite, especially the question if tripuhyite has a rutile or tri-rutile structure, one encounters a big information gap in the work of Foord *et al.* (1991). A recent work by Sergeev *et al.* (1997) reports a 'high content of W (up to 0.36 formula units) and the presence of about one molecule of water in the formula' of squawcreekite from Olimpiada deposit in Russia.

Fe-Sb order/disorder

The difference in the number of electrons between Fe (28) and Sb (51) is so big that any significant degree of order of Fe and Sb in the crystal structure of tripuhyite can be detected by both single-crystal and powder XRD experiments. In our experiments we found no indications at all for such a phenomenon. The measured intensities of the 101 reflection (in the tri-rutile cell) are virtually zero compared to the intensities of the 303 reflections that are significant (Tripuhy: 25290(318); Falotta: 1660(50)). As shown in Table 7, the intensity ratio of 101/303 powder reflections in an ordered tri-rutile structure of $Fe_{1.5}Sb_{1.5}$ composition is calculated to be 0.63. However, our results do not contradict the possible existence of isolated, tiny domains, with a higher degree of order, in the crystal structure of tripuhyite. Berry *et al.* (1987*a,b*) used

the TEM technique and detected Fe-Sb order in $FeSbO_4$, synthesized at 1000ºC, and thus attributing a tri-rutile structure model to $FeSbO_4$. A similar result was reported by Landa-Cánovas *et al.* (1997) for non-stoichiometric $Sb_{0.9}V_{1.1}O_4$. Applying XRD the authors found only basic rutile reflections; a rutile superstructure (but not a tri-rutile one) was revealed when the sample was studied by electron diffraction (Landa-Cánovas *et al.*, 1997). The latter authors comment that the average disorder observed by XRD is nevertheless compatible with the electron microscopy results because the ordered domains extend only tens of nanometers and can therefore not be resolved by XRD. Furthermore, the rutile superstructure was only detected when the Sb:V ratio was 0.9: 1.1 but not for a ratio of 1:1 and it was suggested that superstructure formation (and correspondingly V,Sb order) is linked to cation vacancies for non-stoichiometric compositions.

Conclusions

Combined with data from the literature, the new data presented in this paper show unambiguously that tripuhyite has a rutile structure, has the ideal chemical formula $FeSbO_4$, and has no long-range Fe-Sb order. The proposed new formula $FeSbO_4$ and unit cell (rutile-type) of tripuyhite have been approved, and squawcreekite, as defined by Foord *et al.* (1991), has been discredited by the CNMMN of the IMA (proposal #02-A) in favour of tripuhyite which has priority for historical reasons. The example of tripuhyite shows how confusing and/or erroneous data can survive in literature for a long time. Since its description in 1897 there exist uncertainties about the true nature of tripuhyite. As shown in this contribution there are various sources for these errors: (1) mixing data resulting from analyses of synthetic *vs.* natural samples; (2) using data from single-technique analyses performed on insufficiently characterized material; (3) differences in the observation scales (e.g. X-ray *vs.* TEM); and (4) simple typing mistakes.

References

Amador, J. and Rasines, I. (1981) Crystal data for the double oxides $MSbO_4$ (M=Cr, Fe). *Journal of Applied Crystallography*, **14**, 348−349.

Baker, R.J. and Stevens, J.G. (1977) [121]Mössbauer Spectroscopy. Part II. Comparison of structure and bonding in Sb(III) and Sb(V) minerals. *Revue de Chimie Minérale*, **14**, 339−346.

Baptista, A. (1981) Contribuição ao estudo da lewisita e da tripuíta. *Anais da Academia Brasileira de Ciências*, **53**, 283−287 (in Portuguese).

Baur, W.H. and Khan, A.A. (1971) Rutile-type compounds. IV. SiO_2, GeO_2 and a comparison with other rutile-type structures. *Acta Crystallographica*, **B27**, 2133−2139.

Benvenutti, E.V., Gushikem, Y., Vasquez, A., Decastro, S.C. and Zaldivar, G.A. (1991) X-ray photoelectron-spectroscopy and Mössbauer-spectroscopy study of iron(III) and antimony(V) oxides grafted onto a silica-gel surface. *Journal of the Chemical Society D, Chemical Communications*, **19**, 1325−1327.

Berlepsch, P. and Brugger, J. (1999) Über Tripuhyit ($FeSbO_4$) und Squawcreekit ($FeSbO_4$). *Schweizer Strahler*, **11/9**, 425−437 (in German and French).

Berry, F.J., Holden, J.G. and Loretto, M.H. (1986) The superlattice in iron antimonate: the detection of cationic ordering by electron diffraction. *Solid State Communications*, **59/6**, 397−399.

Berry, F.J., Holden, J.G., Loretto, M.H. and Urch, D.S. (1987a) Iron antimonate. *Journal of the Chemical Society, Dalton Transactions*, **7**, 1727−1731.

Berry, F.J., Holden, J.G. and Loretto, M.H. (1987b) Identification of space group and detection of cationic ordering in iron antimonate using conventional and convergent-beam electron-microscopy. *Journal of the Chemical Society, Faraday Transactions*, **83**, 615.

Brandt, K. (1943) X-ray studies on ABO_4 compounds of rutile type and AB_2O_6 compounds of columbite type. *Arkiv for Kemi, Mineralogi och Geologi*, **17A(15)**, 1−8.

Bruker AXS (1997) *XPREP Ver. 5.1: A computer program for data preparation and reciprocal space exploration*. Bruker Analytical X-ray systems, Madison, WI 53719-1173, USA.

Bruker AXS (1998) *SMART Ver. 5.0/NT: A software package for CCD detector systems*. Bruker Analytical X-ray systems, Madison, WI 53719-1173, USA.

Bruker AXS (1999) *SAINT+ Ver. 6.01/NT: A computer program for data reduction*. Bruker Analytical X-ray systems, Madison, WI 53719−1173, USA.

Byström, A., Hök, B. and Mason, B. (1941) The crystal structure of zinc metantimonate and similar compounds. *Arkiv for Kemi, Mineralogi och Geologi*, **15B(4)**, 1−8.

Christensen, A.N., Johansson, T. and Lebech, B. (1976) Magnetic properties and structure of chromium niobium oxide and iron tantalum oxide. *Journal of Physics C*, **9**, 2601−2610.

Criddle, A.J. (1990a) The reflected-light polarizing microscope and microscope-spectrophotometer. Pp. 1−36 in: *Advanced Microscopic Studies of Ore Minerals* (J.L. Jambor, and D.J. Vaughan, editors). Short course handbook, vol. **17**, Mineralogical Association of Canada, Ottawa.

Criddle, A.J. (1990b) Microscope-photometry, reflectance measurement, and quantitative color. Pp. 135−170 in: *Advanced Microscopic Studies of Ore Minerals* (J.L. Jambor, and D.J. Vaughan, editors). Short course handbook, vol. **17**, Mineralogical Association of Canada, Ottawa.

Davanzo, C.U., Gushikem, Y., Decastro, S.C., Benvenutti, E.V. and Vasquez, A. (1996) $FeSbO_4$ phase formed at the surface of antimony(V) oxide grafted on silica-gel. *Journal of the Chemical Society, Faraday Transactions*, **92**, 1569−1572.

Donaldson, J.D., Kjekshus, A., Nicholson, D.G. and Rakke, T. (1975) Properties of Sb-compounds with rutile-like structures. *Acta Chemica Scandinavica*, **A29**, 803−809.

Embrey, P.G. and Criddle, A.J. (1978) Error problems in the two-media method of deriving the optical constants n and k from measured reflectances. *American Mineralogist*, **63**, 853−862.

Enraf Nonius (1983) *Structure determination package (SDP)*. Enraf Nonius, Delft, Holland.

Foord, E.E., Hlava, P.F., Fitzpatrick, J.J., Erd, R.C. and Hinton, R.W. (1991) Maxwellite and squawcreekite, two new minerals from the Black Range Tin District, Catron County, New Mexico, U.S.A. *Neues Jahrbuch für Mineralogie Monatshefte*, 363−384.

Gakiel, U. and Malamud, M. (1969) On the valence of iron in tripuhyite: a Mössbauer study. *American Mineralogist*, **54**, 299−301.

Geiger, T. and Cabalzar, W. (1988) Tripuhyit − ein neuer Fund von Falotta GR. *Schweizer Strahler*, **8**, 1−7.

Holland, T.J.B. and Redfern, S.A.T. (1997) Unit cell refinement from powder diffraction data: the use of regression diagnostics. *Mineralogical Magazine*, **61**, 65−77.

Hussak, E. and Prior, G.T. (1895) Derbylite and zirkelite, two new Brazilian minerals.

Mineralogical Magazine, **11**, 80−88.

Hussak, E. and Prior, G.T. (1897) On tripuhyite, a new antimonate of iron, from Tripuhy, Brazil. *Mineralogical Magazine*, **11**, 302−303.

Landa-Cánovas, A.R., Hansen, S. and Ståhl, K. (1997) Rutile superstructure of $Sb_{0.9}V_{1.1}O_4$. *Acta Crystallographica*, **B53**, 221−230.

Mason, B. and Vitaliano, C.J. (1953) The mineralogy of the antimony oxides and antimonates. *Mineralogical Magazine*, **30**, 100−112.

Palache, C., Bermann, H. and Frondel, C. (1951) *The System of Mineralogy of J.D. Dana and E.S. Dana*, 7th edition, Vol. 2. John Wiley & Sons Inc., New York, London.

Rouse, R.C., Dunn, P.J., Peacor, D.R. and Wang, L. (1998) Structural studies of the natural antimonian pyrochlores. *Journal of Solid State Chemistry*, **141**, 562−569.

Sergeev, N.B., Kuz'mina, O.V. and Zvezdinskaya, L.V. (1997) Squawcreekite, $Fe^{3+}SbO_4$, from the Olimpiada deposit in the Enisei Ridge: the first find in Russia. *Transactions of the Russian Academy of Science, Earth Sciences Sections*, **356(7)**, 1110−1112 (translation from *Doklady Akademii Nauk SSSR*, **356(4)**, 525−527).

Sheldrick G.M (1997) *SHELXS−97 and SHELXL-97. Computer programs for crystal structure determination and refinement*. University of Göttingen, Germany.

Tavora, E. (1955) X-ray diffraction powder data for some minerals from Brazilian localities. *Anais da Academia Brasileira de Ciências*, **27**, 7−27.

Teller, R.G., Brazdil, J.F., Grasselli, R.K. and Yelon, W. (1985) Phase cooperation in oxidation catalysis − structural studies of the iron antimonate-antimony oxide system. *Journal of the Chemical Society, Faraday Transactions*, **81**, 1693.

Zubkova, N.V., Pushcharovsky, D.Y., Atencio, D., Arakcheeva, A.V. and Matioli, P.A. (2000) The crystal structure of lewisite, $(Ca,Sb^{3+},Fe^{3+},Al,Na, Mn,\square)_2(Sb^{5+},Ti)_2O_6(OH)$. *Journal of Alloys and Compounds*, **296**, 75−79.