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THE CRYSTAL CHEMISTRY OF SIMPSONITE

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ABSTRACT

The examination of simpsonite was prompted by a discrepancy between its apparently variable chemical composition and fairly uniform optical, physical and structural properties, as published in the literature. The present study of simpsonite from seven of its nine known localities confirms the formula $Al_4Ta_3O_{13}(OH)$, with locally major substitution of Nb for Ta, and trace Fe, Ti, Sn for Al, Ta. The yellow to white color, white streak, blue-white cathodoluminescence in an electron beam and fluorescence under short-wave UV light are virtually uniform for all specimens. Optically uniaxial negative, simpsonite has a hardness of 7½, a n (ω) in the range 2.025–2.040 (± 0.005, Na light), and a density in the range 6.68–6.82 g/cm^3; a ranges from 7.385(1) to 7.387(1), and c, from 4.515(1) to 4.516(1) Å. The refinement of the crystal structure in space group $P3$ to $R = 5.3\%$, $wR = 6.9\%$ established full order of Al and Ta and the geometry of individual octahedral sites, and identified the location of (OH) groups in a position extremely unfavorable for F substitution, in accord with the absence of fluorine in all reliably analyzed samples of the mineral.

Keywords: simpsonite, tantalum, oxide mineral, crystal chemistry, mineral data, crystal structure.

SOMMAIRE

Nous avons entrepris une étude de la simpsonite à cause d'une inconsistance entre sa composition chimique, apparemment variable, et ses propriétés optiques, physiques et structurales, relativement uniformes d'après la littérature. Nous fondons notre analyse sur sept des neuf exemples connus de cette espèce. Nous en confirmons la formule, $Al_4Ta_3O_{13}(OH)$, et la substitution importante du Nb au Ta dans certains cas; des traces de Fe, Ti et Sn peuvent substituer au Al ou au Ta. Sa couleur, du jaune au blanc, sa rayure blanche, une cathodoluminescence bleu-blanc dans le faisceau d'électrons et une fluorescence en lumière ultra-violette (ondes courtes) sont effectivement des propriétés de tous les échantillons. La simpsonite est optiquement uniaxe négative, possède une dureté de 7½, $n(\omega)$ 2.025–2.040 (± 0.005, lumière émise par le Na), densité 6.68–6.82, a 7.385(1)–7.387(1), c 4.515(1)–4.516(1) Å. L'affinement de la structure dans le groupe spatial $P3$ mène à un résidu R de 5.3% (wR 6.9%). Les résultats confirment l'ordre complet des atomes Al et Ta, et la géométrie des sites octaédriques individuels. De plus, nous identifions la position des groupements OH, dans un site très peu propice à une substitution par le F, en accord avec l'absence de fluor dans tout échantillon dont la composition est connue par méthode analytique fiable.

(Traduit par la Rédaction)

Mots-clés: simpsonite, tantale, oxyde, chimie cristalline, données minéralogiques, structure cristalline.

INTRODUCTION

Simpsonite is a rare oxide mineral of aluminum and tantalum, although it is abundant enough at some localities to significantly contribute to the economic reserves of tantalum. It was discovered in a granitic pegmatite at Tabba Tabba, western Australia by Bowley (1939), who described its physical, optical and compositional properties. Taylor (1939) reported on its X-ray crystallography in a companion paper. Eight additional localities have since been discovered, and examined in eleven independent studies (Table 1).

On the basis of published data, the chemical composition of simpsonite is apparently variable, but its structural, physical and optical properties

TABLE 1. SIMPSONITE LOCALITIES

Locality	Initial Reference
1. Tabba Tabba, W. Australia	Bowley (1939)
2. Alto do Giz, Rio Grande do Norte, Brazil	Guimarães (1944)
3. Onça mine, Rio Grande do Norte, Brazil	Pough (1945)
4. Mdara mine, Bikita, Zimbabwe	Kerr & Holmes (1945)
5. Leshaia, northern Kola Peninsula, USSR	Sosedko & Denisov (1958)
6. Benson mine, Mtoko, Zimbabwe	von Knorring & Hornung (1963)
7. Mumba, Lake Kivu, Zaire	Safiannikoff & van Wambeke (1961)
8. Tanco pegmatite, Manitoba	Cerný et al. (1981)
9. Manono mine, Shaba, Zaire	Sarp & Deferne (1983)

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are uniform. Unfortunately, few of the studies listed in Table 1 involved samples from more than a single locality; thus the degree of true chemical variability could not be assessed under controlled laboratory conditions. A study of the crystal chemistry and structure of simpsonite was undertaken largely for this reason (Ercit 1986). We have examined samples from as many localities as possible by contemporary mineralogical methods, which are generally much improved over those used by earlier investigators.

PREVIOUS WORK

On the basis of published chemical data for simpsonite (Table 2), the following ideal formulae have been proposed: $CaO{\cdot}5Al_2O_3{\cdot}4Ta_2O_5{\cdot}2H_2O$ (Bowley 1939), $Al_6Ta_4O_{19}$ (Guimarães 1944, Kerr & Holmes 1945), $Al_8Ta_6O_{27}$ (Macgregor 1946), $AlTaO_4$ (Palache *et al.* 1944) and $Al_4Ta_3O_{13}(OH,F)$ (von Knorring & Hornung 1963, and subsequent studies). Two probable sources of this variability are: (1) contamination, as shown for example by the presence of SiO_2, and (2) error in the chemical analyses, as shown by comparisons of compositions of samples from the same locality but analyzed by different laboratories.

Published physical and optical properties are given in Table 3. The data are reasonably comparable, with only a few exceptions. An apparent change of optic sign reported for simpsonite from the Benson pegmatite (von Knorring & Hornung 1963) was due to a misprint, and a positive optic sign reported by Bowley (1939) for

TABLE 2. PUBLISHED COMPOSITIONS OF SIMPSONITE

	1	2	3	4	5	6	7	8	9	10	11	12
Al_2O_3 (wt%)	16.75	18.64	26.15	25.20	25.06	22.58	23.79	23.52	24.47	23.26	23.89	20.89
Fe_2O_3	0.14	0.48	——	——	——	0.11	0.00	0.88	——	0.00	0.00	——
TiO_2	——	——	——	0.02	0.05	——	0.10	0.08	——	——	0.00	——
SnO_2	2.00	1.19	——	0.10	0.47	0.42	1.45	1.31	0.00	1.17	1.00	——
Nb_2O_5	0.33	0.32	——	1.82	1.61	6.05	1.84	1.80	3.65	1.29	2.10	——
Ta_2O_5	72.31	71.48	73.65	71.54	67.92	60.01	69.46	66.20	88.32	72.74	70.48	78.10
Li_2O	——	——	——	——	——	——	——	——	——	——	0.04	——
Na_2O	1.16	0.68	——	——	——	0.39	0.35	0.46	——	0.00	0.07	——
K_2O	0.12	0.42	——	——	——	0.23	0.13	0.44	——	0.00	0.16	——
MgO	——	——	——	0.00	0.01	0.00	0.00	0.00	——	——	——	——
CaO	3.40	3.19	——	0.12	0.12	0.32	0.41	1.40	——	0.00	0.00	——
MnO	0.06	0.04	——	0.00	0.44	0.03	0.32	0.38	——	——	——	——
FeO	0.16	0.44	——	0.16	3.65	0.82	0.60	0.69	——	——	——	——
PbO	0.43	——	——	——	——	0.00	0.00	0.00	——	0.00	——	——
SiO_2	1.78	2.34	——	1.00	0.50	6.01	1.60	2.40	——	——	0.85	——
ZrO_2	——	——	——	——	——	0.05	0.00	0.00	——	——	——	——
P_2O_5	——	——	——	——	——	0.55	0.00	0.00	——	——	——	——
H_2O^+	1.35	1.39	——	——	——	0.19	0.12	0.62	——	——	1.20	0.90
H_2O^-	0.20	0.03	——	——	——	0.27	0.32	0.03	——	——	0.06	——
F	0.21	0.38	——	0.00	0.00	0.00	0.00	0.00	——	——	0.25	——
O=F	-0.09	-0.18	——	0.00	0.00	0.00	0.00	0.00	——	——	-0.10	——
	100.44	100.88	99.80	99.96	99.83	100.03	100.49	100.21	96.44	98.46	100.06	98.89

1,2. Tabba Tabba; Bowley (1939). Contaminated with microlite, quartz and muscovite. 3. Alto do Giz; Guimarães (1944). Average of 2 analyses. 4. Alto do Giz; Kerr & Holmes (1945). 5. Bikita; Kerr & Holmes (1945). 6-8. Bikita; Macgregor (1946). 9. Leshala; Sosedko & Denisov (1958). 10. Leshala; Voloshin & Pakhomovskii (1983). Average of 5 analyses. 11. Mtoko; von Knorring & Hornung (1963). Contaminated with muscovite. 12. Manono; Sarp & Deferne (1983).

"0.00": not detected, "——": not sought

TABLE 3. PUBLISHED PHYSICAL, OPTICAL AND CRYSTALLOGRAPHIC DATA FOR SIMPSONITE

Locality	$n(\omega)$	$n(\epsilon)$	Optic Sign	*D* (g/cm³)	*H*	Color	Fluorescence	Cleavage	*a* (Å)	*b* (Å)	Reference
Tabba Tabba	2.06		–?	5.92		CL		none	6.2	4.5	Bowley (1939), Taylor (1939)
Alto do Giz	2.045	2.005	–	6.77 to 6.81	7½	W to Y	B-W to Y	none			Pough (1945)
Onça				6.60 to 6.70		W to Y	B-W	none	7.377	4.514	Pough (1945), Kerr & Holmes (1945)
Bikita	2.035	1.995	–	6.68 to 6.84	7½	Y	B-W	none			Sosedko & Denisov (1958)
Leshala	2.034	1.976	–	6.61	7	W to Y	Y-B	none	7.377	4.516	Saflannikoff & van Wambeke (1961)
Mtoko	2.036	2.004	–	6.72	>7	W	B-W	none	7.38	4.51	von Knorring & Hornung (1963), Borisov & Belov (1962)
Manono	2		–			Y		none	7.39	4.50	Sarp & Deferne (1983)

CL: colorless, W: white, Y: yellow, B: blue simpsonite from Tabba Tabba was not substantiated in later studies (Macgregor 1946, von Knorring & Hornung 1963).

A summary of all published crystallographic data also is given in Table 3. These data are more uniform than the chemical data. Only Taylor's (1939) data differ from those of the other studies; however, re-interpretation of her data (Kerr & Holmes 1945) showed that the reported *a* periodicity is actually *d*(110). Subsequent recalculation of *a* gives results consistent with the other studies. A notable discrepancy also is observed between the space groups of Taylor (1939) and Borisov & Belov (1962).

The crystal structure of simpsonite was solved by Borisov & Belov (1962). Their work confirmed the stoichiometry $Al_4Ta_3O_{13}(OH)$ and $P\bar{3}$ diffraction symmetry for the mineral; also, they correctly determined the atom positions. However, their model was refined from projections using photographic data, resulting in high *R* indices ($<R>$ = 15.2%).

SAMPLES AND EXPERIMENTAL METHODS

Samples were obtained from all known localities of simpsonite except Manono and Mtoko. Except for the Leshaia sample, there was enough material for powder diffractometry and for determination of the physical properties. For most localities, only one sample was available, with the exception of Mumba and Tabba Tabba (two samples each), and Tanco and Alto do Giz (more than 20 samples). The sources of the samples are given in Table 4.

The ω index of refraction was determined in Na light using the Becke line method, with Cargille oils as immersion liquids, at the Royal Ontario Museum. The liquids were calibrated using a two-circle goniometer and the minimum-deviation method (D. Sturman, pers. comm.).

Infrared absorption spectra were collected on pellets prepared from a mixture of 0.22 g KBr and 0.0006 g simpsonite, on a Nicolet MX-1 Fourier transform IR spectrometer calibrated by laser interferometry and checked against a polystyrene internal standard.

TABLE 4. SIMPSONITE SAMPLES USED IN PRESENT STUDY

Sample No.	Locality	Source
F-8,9	Tanco	P. Černý
GSC-1	Mumba	Geological Survey of Canada (NMC 62089)
KO-1,2	Leshaia	A.V. Voloshin
L-12	Alto do Giz	Harvard University (97557A.1)
L-13	Bikita	Smithsonian Institute (NMNH 105760)
L-14	Mumba	" " (NMNH 136445)
L-15	Alto do Giz	" " (NMNH 104738)
L-16	Onça	" " (NMNH 104739)
L-17	Alto do Giz	" " (NMNH 105002)
L-18	Tabba Tabba	" " (NMNH 103440)
ROM-1	Alto do Giz	Royal Ontario Museum (M22607)
ROM-2	Tabba Tabba	" " " (M19325)
RVG series	Alto do Giz	R.V. Gaines
SMP series	Tanco	T.S. Ercit, P. Černý

Densities were measured with a Roller–Smith Berman balance, model B. Toluene was used as the immersion liquid. All samples used in the experiments weighed between 15 and 25 mg (in air). Each crystal fragment was weighed five times on each of three separate days to test the reproducibility of the results.

Electron-microprobe analyses were carried out with a MAC 5 instrument operating in the wavelength-dispersion mode. Non-standard conditions of operation were necessary to minimize high absorption: 20 kV (Ta, Ti, Fe), 15 kV (Nb,Sn), 10 kV (Al) and 40 nA (measured on brass), a 10-s collection time, and a beam diameter of 1–3 μm. Data were reduced with the program EMPADR VII (Rucklidge & Gasparrini 1969) using an improved ZAF routine. The following standards were used for the analysis of simpsonite: manganotantalite (Ta*L*α), stibiotantalite (Nb*L*α), YAG (Al*K*α), cassiterite (Sn*L*α), and titanite (Fe*K*α, Ti*K*α).

X-ray powder-diffraction data were obtained with a Philips PW 1050 diffractometer, goniometer speed 0.25° 2θ/min., using Ni-filtered Cu*K*α radiation and synthetic LiF as an internal standard [a = 4.02080(1) Å, calibrated against NBS Si, batch 640a]. Unit-cell refinement was done by a modified version of the CELREF program of Appleman & Evans (1973). Precession cameras (Charles Supper Co.) were used to determine diffraction symmetry using Zr-filtered Mo*K*α radiation and a precession angle of 25°.

Intensity data for the structure refinement were collected on a hand-shaped, equant fragment from sample L–15, using a Nicolet *R*3*m* four-circle diffractometer according to the experimental method of Ercit *et al.* (1986). Twenty-five intense reflections were used in centering the crystal; least-squares refinement of the setting angles gave the cell parameters in Table 5 and the orientation matrix used for data collection. Two asymmetric units of data were collected to a maximum sinθ/λ of 0.7035 and were merged to give the numbers of unique reflections in Table 5. The data were corrected for absorption (using ψ-scan data and an

TABLE 5. REFINEMENT OF THE SIMPSONITE STRUCTURE: MISCELLANEOUS DATA

a· (Å)	7.381(1)	Crystal size (mm)	0.12 x 0.14 x 0.10
c	4.516(1)	μ (Mo*K*α, cm^{-1})	385
V ($Å^3$)	213.1(1)	Total F_o, Obs. F_o	868, 867
Space Group	*P*3	Final *R*, *wR* (%)	5.3, 6.9

$R = \Sigma(|F_o|-|F_c|)/\Sigma|F_o|$

$wR = [\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$, $w=1$

ellipsoidal approximation to the crystal shape), $L{\cdot}p$ and background effects using the SHELXTL package of programs. A reflection was considered observed if $|F|$ is greater than $3\sigma(|F|)$, resulting in the numbers of observed reflections given in Table 5. The structure refinement was done with the program X in the SHELXTL package. Scattering curves for neutral atoms and anomalous dispersion coefficients were taken from Cromer & Mann (1968) and Cromer & Liberman (1970), respectively.

PHYSICAL AND OPTICAL PROPERTIES

The physical and optical properties of all simpsonite samples examined in this study are summarized in Table 6. All samples are yellow to white in color. None fluoresce under long-wave ultraviolet light; however, under short-wave UV light, most fluoresce blue-white, except for samples from Alto do Giz, which fluoresce yellow. All samples have a prominent but short-lived blue-white cathodoluminescence under the electron beam. Powdered simpsonite is invariably white. In thin section, simpsonite is colorless and is uniaxial negative. As a test of variability in terms of optical properties, the ω index of refraction was measured for 10 samples. This species shows little variability in ω, which ranges only from 2.025 to 2.040 (± 0.005).

TABLE 6. PHYSICAL, OPTICAL AND STRUCTURAL PROPERTIES OF SIMPSONITE

Sample	Color	$n(\omega)$	Optic Sign	D (g/cm^3)	H	a (Å)	c (Å)
L-12	yellow	2.040	-	6.73(5)	7½	7.385	4.516
L-13	yellow	2.030	-	6.59(3)	7½	7.387	4.515
L-14	yellow	2.035	-	-----	7½	7.387	4.515
L-15	yellow	2.035	-	6.82(4)	7½	7.385	4.516
L-16	yellow	2.035	-	6.76(5)	7½	7.385	4.515
L-17	yellow	2.040	-	6.79(2)	7½	7.386	4.516
L-18	white	2.025	-	6.31(1)	7½	-----	-----
ROM-2	white	2.025	-	-----	7½	7.387	4.515
SMP-2	white	2.025	-	6.68(1)	7½	7.387	4.515

All refractive index determinations are ± 0.005. For unit-cell parameters, σ=0.001 Å.

Simpsonite has no cleavage, but has a conchoidal fracture. All samples have a Mohs hardness of 7½. Their densities range from 6.31 to 6.82 g/cm^3; however, macroscopically unaltered material has a smaller range, from 6.68 to 6.82 g/cm^3.

Simpsonite crystals are subhedral to euhedral. Euhedral crystals most commonly consist of a hexagonal prism and a basal pinacoid; however, more complex forms have been found (Pough 1945). Prism faces are invariably striated parallel to Z and commonly show features of parallel growth.

CHEMISTRY

The results of the electron-microprobe analyses are given in Table 7. The samples are all similar in chemistry and stoichiometry, in contrast with the results of earlier studies. Al and Ta are the dominant cationic constituents; Nb can be a major constituent (to 8.6% Nb_2O_5), and Sn can be a minor constituent (to 1.9% SnO_2); Ti (to 0.02% TiO_2) and Fe (to 0.03% Fe_2O_3) are present in trace quantities only. Ca, Mn and Si were not detected.

On the basis of considerations of charge and size, Fe should reside at the Al site, and Nb should occur at the Ta site. The ratio of (Al+Fe):(Ta+Nb) is close to 4:3 in all samples; the apparently large variations indicated by earlier studies must have been due to problems in wet-chemical analysis and to contamination. The cation sums are tightly distributed about 7 (mean cation sum = 6.997, mean absolute deviation = 0.011 cations p.f.u.) if formulae are calculated on a basis of 27 negative charges per formula unit. This suggests that the fourteenth anion in the formula unit is exclusively monovalent. The ideal formula for simpsonite is thus $Al_4Ta_3O_{13}(OH)$. Using this formula and the measured densities (Table 6), the number of formula units per unit cell, Z, is 1.

The site preferences of Sn and Ti are unknown and are difficult to assess given the minor amounts that tend to occur in simpsonite. Either Sn and Ti are disordered over the Al and Ta sites, or they are localized at the Ta site and charge balance is achieved by substitution of minor hydroxyl at the O sites. Given the small amounts of Sn and Ti, it is not presently possible to assess the models.

A part of the infrared absorption spectrum for simpsonite L-15 covering the range 3000–3800 cm^{-1}

TABLE 7. RESULTS OF ELECTRON-MICROPROBE ANALYSIS OF SIMPSONITE

	F-8	F-9	L-12	L-13	L-14	L-15	L-16	L-17	L-18
Al_2O_3 (wt%)	23.0	22.9	23.3	23.3	24.3	22.8	23.0	22.8	22.6
Fe_2O_3	0.0	0.0	0.0	0.0	0.01	0.0	0.03	0.0	0.0
TiO_2	0.0	0.0	0.01	0.01	0.0	0.0	0.02	0.02	0.03
SnO_2	1.5	0.9	0.05	1.0	0.9	0.0	0.1	0.02	1.9
Nb_2O_5	0.9	0.8	1.1	0.0	8.6	0.0	0.2	0.7	1.0
Ta_2O_5	71.9	72.6	73.3	74.9	64.6	76.4	74.8	74.6	72.4
H_2O	1.0	1.0	1.0	1.0	1.1	1.0	1.0	1.0	1.0
	98.3	98.2	98.6	100.2	99.5	100.2	99.2	99.1	98.9
Cations per 13(O)+1(OH)									
Al	3.99	3.99	4.02	3.99	3.97	3.93	3.98	3.95	3.92
Fe	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ti	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sn	0.09	0.05	0.07	0.06	0.05	0.00	0.01	0.00	0.11
Nb	0.06	0.06	0.00	0.00	0.54	0.00	0.02	0.05	0.06
Ta	2.87	2.91	2.91	2.96	2.44	3.04	2.99	2.98	2.89
	7.01	7.00	7.01	7.01	7.00	6.97	7.00	6.98	6.99

All H_2O calculated on a basis of 1(OH) per formula unit.

Sample L-15 was analyzed against YAG (Al) and manganotantalite (Ta).
All other samples analyzed against sample L-15 (Al,Ta) assuming ideal $Al_4Ta_3O_{13}(OH)$ stoichiometry for simpsonite L-15.

See Table 4 for localities.

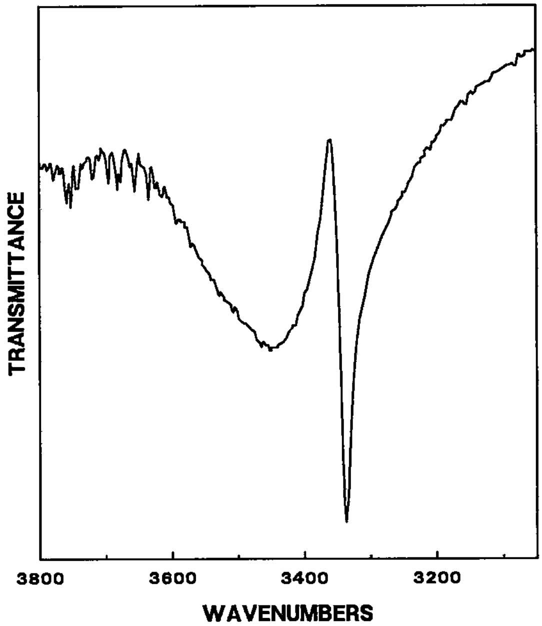

FIG. 1. Infrared absorption spectrum of simpsonite, sample L-15, in the O–H stretching region. The sharp absorption at 3300 cm^{-1} is assigned to O–H stretching in simpsonite. The broad absorption at 3450 cm^{-1} is due to adsorbed water in the KBr pellet.

TABLE 8. POWDER-DIFFRACTION DATA FOR SIMPSONITE L-17

d(obs)	*I*	*d*(calc)	*hkl*	*d*(obs)	*I*	*d*(calc)	*hkl*
6.40 Å	13	6.40	10.0	1.362	6	1.362	20.3
4.52	19	4.52	00.1	1.333	10	1.334	41.1
3.69	62	3.69	11.0	1.305	2	1.305	40.2
		3.69	10.1	1.278	7	1.278	21.3
3.196	30	3.198	20.0	1.230	10	1.230	32.2
2.859	67	2.859	11.1	1.209	3	1.209	42.0
2.609	37	2.610	20.1	1.167	9	1.168	33.1
2.417	40	2.418	21.0			1.167	41.2
2.257	6	2.258	00.2	1.168	3	1.168	42.1
2.131	59	2.132	30.0	1.148	9	1.148	31.3
		2.131	21.1	1.129	2	1.129	00.4
1.926	25	1.926	11.2	1.113	2	1.113	51.1
		1.926	30.1			1.113	50.2
1.844	10	1.844	20.2	1.096	2	1.096	40.3
1.773	16	1.774	31.0	1.079	2	1.080	11.4
1.651	100	1.651	31.1	1.066	10	1.066	60.0
1.599	3	1.599	40.0			1.066	42.2
1.550	2	1.550	30.2	1.051	11	1.051	32.3
1.507	12	1.507	40.1	1.038	7	1.038	60.1
1.468	5	1.467	32.0	1.024	10	1.024	52.0
1.395	54	1.396	41.0			1.024	43.1
		1.396	32.1			1.024	51.2

Philips PW1050 powder diffractometer; Ni-filtered Cu$K\alpha$ radiation; LiF internal standard. Intensities are integrated intensities, not peak heights.

is given in Figure 1. The spectrum is characterized by a strong absorption at the low frequency of 3300 cm^{-1}, indicative of the presence of substantial hydroxyl in the structure. The frequency of the O–H stretching indicates that the hydrogen bonding is strong, which makes the hydroxyl site in simpsonite an extremely unlikely locus of F-for-(OH) substitution. Although F has been reported in bulk analyses of simpsonite, it has only been reported in samples contaminated with microlite and micas (muscovite and lepidolite). A fair correlation (R = 0.73) exists between F and Na + K + Li + Ca contents, representative of alkali plus alkaline-earth components of the purported F-bearing contaminants. It is probable that most of the F, if not all, is contained in the typically F-rich contaminant phases, such as lepidolite or microlite.

X-RAY CRYSTALLOGRAPHY

X-ray powder-diffraction data for all samples are identical, as are the unit-cell parameters (Table 6). Consequently, the powder-diffraction data for sample L-17 (Table 8) can be taken as representative of simpsonite. The X-ray powder diffractograms consist of groups of strong reflections that regularly repeat themselves with increasing 2θ, indicative of the layer structure of simpsonite.

Precession photographs were taken for three samples: L-13, L-15 and L-17. The photographs show $P\bar{3}$ diffraction symmetry; $P\bar{3}$ or $P3$ are possible space-groups. The diffraction pattern has a strong pseudo-$P6/m$ diffraction symmetry that accounts for the earlier assignment of this space group to simpsonite (Taylor 1939; however, we have found that reconstruction of Taylor's data shows the true 3-fold character of the unique axis).

STRUCTURE REFINEMENT

Tests based on E statistics applied to the total set of intensity data indicate an acentric space-group for simpsonite, *i.e.*, $P3$: $<E^2-1> = 0.735$ for reflections with $\sin\theta/\lambda > 0.1$. A three-dimensional Patterson synthesis gave only one heavy atom at $x = 0.113$, $y = 0.394$. These parameters were used to refine the Ta position; the origin was fixed by setting z(Ta) = 0. At this stage, a difference Fourier synthesis showed the two Al positions. Refinement of the cation positions and isotropic temperature-factors resulted in an R index of 9.5%, and a subsequent difference Fourier map gave the six anionic sites. Refinement of all atom positions, anisotropic temperature-factors and an extinction correction resulted in final values of R = 5.3%, wR = 6.9% for this fully ordered model. An attempt to disorder Ta and Al resulted in divergence, which shows that the assumption of full order among cations is valid. Final positional and thermal parameters are given in Tables 9 and 10, respectively; bond lengths and angles are given in Table 11. Observed and calculated structure-factors are available from the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2.

TABLE 9. POSITIONAL PARAMETERS FOR SIMPSONITE

	This Study			Borisov & Belov (1962)		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
Ta	0.1118(1)	0.3910(1)	0	0.112	0.391	0
Al(1)	0.423(2)	0.303(2)	0.496(2)	0.423	0.297	0.500
Al(2)	0	0	0.499(4)	0	0	0.500
O1	0.246(5)	0.062(4)	0.730(7)	0.237	0.067	0.720
O2	0.392(5)	0.472(5)	0.777(8)	0.376	0.474	0.765
O3	0.192(4)	0.238(5)	0.274(7)	0.183	0.227	0.274
O4	0.482(5)	0.111(5)	0.265(7)	0.481	0.113	0.266
O5	1/3	2/3	0.194(9)	1/3	2/3	0.204
O6	2/3	1/3	0.691(10)	2/3	1/3	0.703

TABLE 10. THERMAL PARAMETERS FOR SIMPSONITE

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	U_{eq}
Ta	85(5)	88(5)	119(5)	42(4)	9(3)	3(3)	98(4)
Al(1)	120(34)	149(37)	139(34)	59(26)	14(23)	7(28)	139(30)
Al(2)	87(32)	87(32)	159(66)	0	0	0	131(30)
O1	77(100)	125(102)	148(103)	-2(81)	20(65)	7(76)	140(80)
O2	261(139)	464(213)	154(122)	295(147)	-55(88)	-70(93)	242(137)
O3	231(123)	146(101)	111(101)	102(103)	-67(85)	-24(73)	159(91)
O4	112(110)	239(125)	210(121)	-3(115)	63(102)	46(95)	227(99)
O5	95(104)	95(104)	53(148)	48(52)	0	0	81(85)
O6	354(170)	354(170)	98(171)	0	0	177(85)	269(127)

All *U* values are Å^2 x10^4.

TABLE 11. SELECTED BOND-LENGTHS AND ANGLES FOR SIMPSONITE

Ta Octahedron		Al(1) Octahedron		Al(2) Octahedron	
Ta-O1b	1.87(3) Å	Al(1)-O1a	1.91(3)	Al(2)-O1 x3	1.94(3)
-O2a	2.10(4)	-O2a	1.88(4)	-O3 x3	1.91(3)
-O2b	2.00(4)	-O3a	1.83(3)	**<Al(2)-O>**	1.93
-O3a	1.96(4)	-O4b	1.97(4)		
-O4b	1.98(3)	-O4c	1.87(3)		
-O5a	2.06(2)	-O6a	1.91(3)		
<Ta-O>	2.00	**<Al(1)-O>**	1.90		
O1b-O2a	2.95(5) Å	O1a-O2a	2.66(5)	O1-O1 x3	2.84(4)
-O2b	2.77(6)	-O3a	2.57(5)	-O3 x3	2.68(4)
-O3a	2.99(4)	-O4b	2.63(5)	-O3 x3	2.57(5)
-O4b	2.89(5)	-O6a	2.73(3)	O3-O3 x3	2.80(5)
O2a-O2b	2.94(5)	O2a-O3a	2.79(4)	**<O-O>**	2.72
-O3a	2.77(4)	-O4c	2.82(5)		
-O5a	2.53(5)	-O6a	2.72(4)		
O2b-O4b	2.73(5)	O3a-O4b	2.73(6)		
-O5a	2.53(5)	-O4c	2.83(4)		
O3a-O4b	2.85(6)	O4b-O4c	2.64(5)		
-O5a	2.82(4)	-O6a	2.45(5)		
O4b-O5a	2.91(4)	O4c-O6a	2.45(5)		
<O-O>	2.81	**<O-O>**	2.67		
O1b-Ta-O2a	96(1) °	O1a-Al(1)-O2a	89(2)	O1-Al(2)-O1 x3	94(1)
-O2b	91(1)	-O3a	87(2)	-O3 x3	88(2)
-O3a	103(1)	-O4b	85(2)	-O3 x3	84(1)
-O4b	97(1)	-O6a	91(1)	O3-Al(2)-O3 x3	94(1)
O2a-Ta-O2b	92(2)	O2a-Al(1)-O3a	98(2)	**<O-Al(2)-O>**	90.0
-O3a	86(1)	-O4c	97(2)		
-O5a	75(1)	-O6a	92(2)		
O2b-Ta-O4b	87(1)	O3a-Al(1)-O4b	92(2)		
-O5a	77(1)	-O4c	100(2)		
O3a-Ta-O4b	93(1)	O4b-Al(1)-O4c	87(2)		
-O5a	89(1)	-O6a	78(2)		
O4b-Ta-O5a	92(1)	O4c-Al(1)-O6a	81(2)		
<O-Ta-O>	89.8	**<O-Al(1)-O>**	89.8		

Equivalent positions are a: *x*, *y*, *z* b: -*y*, *x*-*y*, *z* c: *y*-*x*, -*x*, *z*

The gross structural features (Fig. 2, Table 9) are the same as those reported by Borisov & Belov (1962). Tantalum and aluminum occur in octahedral interstices in an approximately hexagonal closest-packed array of oxygen atoms. All Ta atoms occupy one layer in the packing (at $z = 0$), and all

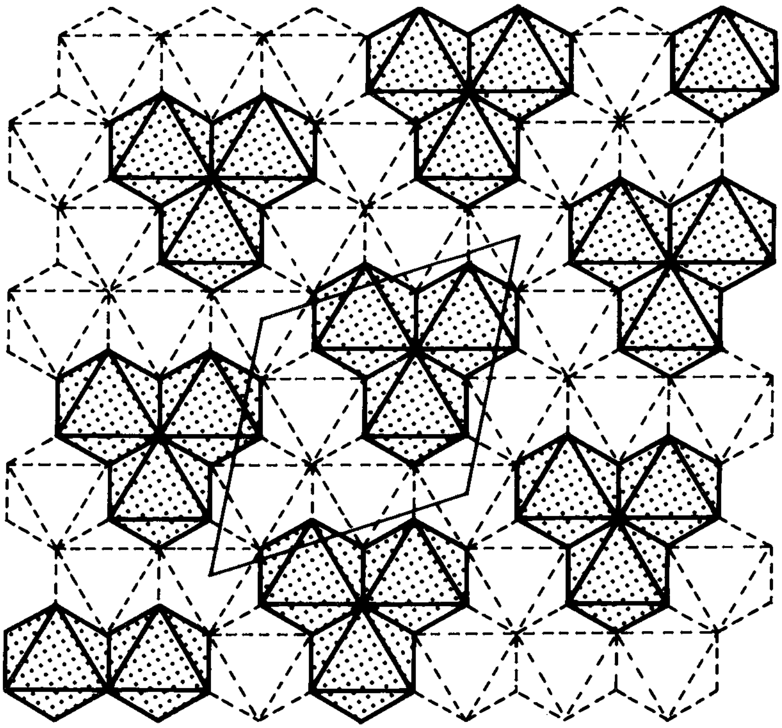

FIG. 2. The ideal structure of simpsonite, as projected along *Z*. Solid lines represent polyhedra of one level, and broken lines, those of adjacent levels. Ta-bearing polyhedra are shaded; Al-bearing polyhedra are unshaded. One unit cell is two layers of polyhedra deep; the outline of one unit cell is shown in fine rule.

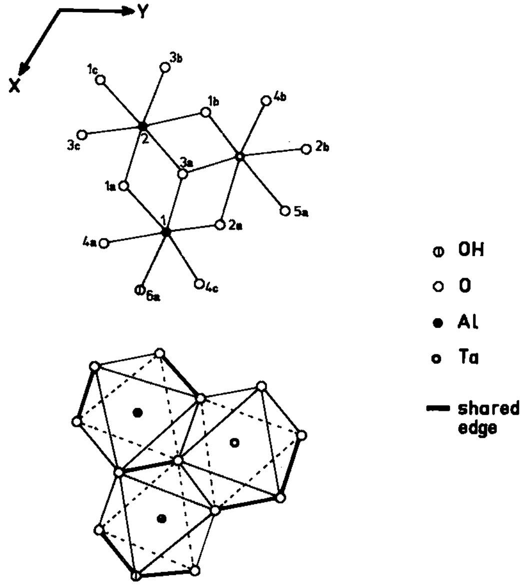

FIG. 3. Coordination polyhedra in simpsonite. See Table 9 for the coding of the oxygen atoms. Note that shared edges are between like polyhedra only (Al–Al and Ta–Ta, not Al–Ta).

Al atoms occupy the adjacent layer (at $z \simeq 0.5$). Each TaO_6 octahedron shares two edges with adjacent octahedra, forming dense $[Ta_3O_{13}]^{11-}$ trimers. Al occupies interstices which, in projection, correspond to unoccupied octahedra of the Ta layer. As such, the Al layer consists of a sheet of AlO_6 octahedra, each octahedron sharing three edges with adjacent AlO_6 octahedra. The Al and Ta layers connect *via* corner-sharing of their polyhedra.

Details of the crystal structure are shown in Figure 3. All polyhedra show features in good agreement with Pauling's rules. The shared edges of each polyhedron are shorter than the unshared ones. The Al(1) polyhedron has three shared and nine unshared edges. The shared edges are not symmetrically disposed about the polyhedron, so that cation–cation repulsion displaces the Al(1) cation toward the side of the polyhedron with the fewest shared edges. On the other hand, the Al(2) polyhedron has three shared edges symmetrically disposed about the polyhedron (three-fold symmetry), resulting in balanced repulsive forces; consequently, Al(2) sits at the center of its polyhedron. The Ta-bearing polyhedron has two adjacent shared edges; Ta–Ta repulsion across the shared edges displaces the Ta cation well toward the opposing corner of its polyhedron.

TABLE 12. EMPIRICAL BOND-VALENCE TABLE FOR SIMPSONITE

	O1	O2	O3	O4	O5	O6	SUM
Ta	1.21	0.58 0.79	0.90	0.84	0.65 x3↓		4.97
Al(1)	0.50	0.54	0.61	0.42 0.55		0.50 x3↓	3.12
Al(2)	0.46 x3→		0.50 x3→				2.88
SUM	2.17	1.91	2.01	1.81	1.95	1.50	

Bond valences (in *v.u.*) derived from the curves of Brown (1981) and Ercit (1986).

Empirical bond-valences are given in Table 12. All bond-valence sums to the cations and anions approach their ideal values closely, except for O6 and, to a lesser degree, O4. The sum at O6 (1.50 *v.u.*) implies that much, if not all, of the hydroxyl in the structure is located at this position. A bond valence of 2 - 1.50 = 0.50 *v.u.* is assigned to the O–H bond, which corresponds to a bond length of 1.19 Å. The low bond-valence sum of 1.81 *v.u.* to the nearby O4 suggests the presence of hydrogen bonding between the proposed H atom and O4, which explains why the bond-valence sum to O6 is higher than ideal for an oxygen atom of a hydroxyl group.

Because O6 marks the common corner of three edge-sharing Al(1) octahedra, the H atom bonded to it must lie above or below the plane of Al octahedra, but not within it. Furthermore, because O6 lies on a triad axis, the O–H bond must be perpendicular to this plane. Whether the H atom were to lie above or below O6, the OH bond would protrude into a tetrahedral interstice (Fig. 4). In the first case, the lower tetrahedron is bound by one unshared and three shared faces between three symmetrically equivalent O4 atoms and O6. For this location, the calculated O6–H distance of 1.19 Å gives an O4–H distance of 1.71 Å. Each O4–H bond would have 0.23 *v.u.* associated with it, resulting in a bond-valence sum of 1.20 *v.u.* for the H atom and of 2.05 *v.u.* for O4. In the second case, the upper tetrahedral interstice has no shared faces between its bounding anions (one O6 and three O4 atoms), a much more favorable location for the H atom than in the first model. Here, the O6–H distance of 1.19 Å gives an O4–H separation of 2.08 Å. Each O4–H bond would have 0.15 *v.u.* associated with it, resulting in a sum of 0.96 *v.u.* to the proposed H atom and of 1.97 *v.u.* to O4, clearly superior to the first model, and providing a better match to the experimental data.

On the basis of both steric and bond-valence considerations, we conclude that the undetected H atom lies 1.19 Å above O6. The O6–H bond has approximately 0.50 *v.u.* associated with it; hydrogen bonding to three nearby O4 atoms accounts for the remaining 0.50 *v.u.*

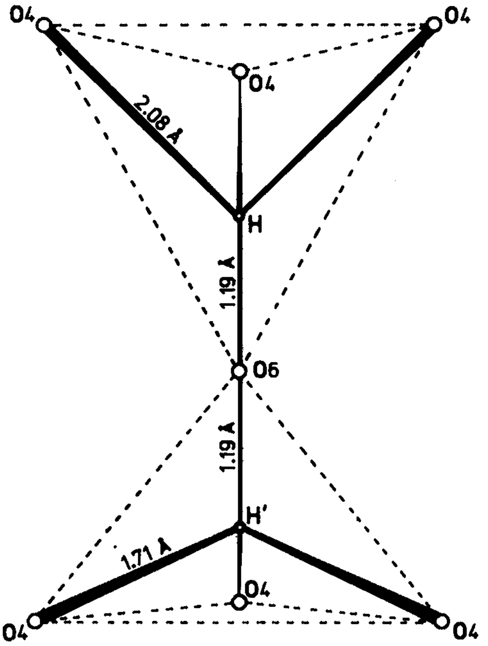

FIG. 4. Geometry about potential sites for the hydrogen atom in simpsonite. Solid lines: potential H–O bonds. Dashed lines: polyhedron edges. The H–O distance and distribution of bond valences indicate that the H site is preferred over the H′ site.

The observed bond-valence sum of 1.50 *v.u.* to O6 is 50% greater than the ideal condition for localization of F at the OH site. Quite clearly, the requirements of hydrogen bonding preclude significant F-for-(OH) substitution, in agreement with the earlier conclusion that all F reported in analyses is due to contamination.

CONCLUSIONS

In contrast to the apparent discrepancy between variable chemistry and rather uniform physical, optical and structural properties, indicated by earlier studies, the present work establishes simpsonite as a mineral with a simple chemical composition and stoichiometry. The formula $Al_4Ta_3O_{13}(OH)$ is confirmed, with locally substantial substitution of Nb for Ta; Fe, Sn and Ti occur in trace quantities. This uniform chemistry explains the virtually constant indices of refraction, density, hardness, unit-cell dimensions and, to a large extent, color, fluorescence and cathodoluminescence. However, the causes for the last two properties remain to be determined.

The refinement of the crystal structure confirms its principal features established earlier, including the space group $P3$. Steric and bond-valence considerations and the energetics of the infrared absorption spectrum indicate that hydroxyl is located at a position that is extremely unfavorable for F substitution, which explains the absence of fluorine in all reliably analyzed samples of simpsonite.

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