

Holmquistite-bearing amphibolite from Greenbushes, Western Australia

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Abstract

Holmquistite idiomorphs occur in a hornblende–titanite–quartz–plagioclase amphibolite, in contact with a lithium (spodumene) pegmatite at Greenbushes, Western Australia. Unit cell parameters, chemical data and the results of a mineralogical investigation of holmquistite and associated minerals in the amphibolite are given.

KEYWORDS: holmquistite, amphibole, amphibolite, Greenbushes, Australia.

Introduction

THE Greenbushes pegmatites are unique in their assemblage of economic and rare minerals, including the lithium minerals spodumene, amblygonite, triphylite and holmquistite. Holmquistite is a rare lithium amphibole which has been found in the USSR (Ginzburg *et al.*, 1958), USA (Palache *et al.*, 1930), Canada (Nickel *et al.*, 1960), Zimbabwe (von Knorring and Hornung, 1961), Sweden (Palache *et al.*, 1930; Vogt *et al.*, 1958), Austria (Walter and Walitzi, 1985) and Australia. In Australia, it has been found in two places: Mt Marion (Wilkins *et al.*, 1970) and in the Greenbushes Mineral Field both in Western Australia. This study details work on the mineralogy of holmquistite and its associated minerals.

Geological background

The Greenbushes Mineral Field is located in the south west of Western Australia, approximately 220 km south of Perth and 80 km SSE of the port of Bunbury (Fig. 1). Alluvial tin was discovered in the area towards the end of last century and tin production continued from numerous small alluvial deposits until the early 1960s.

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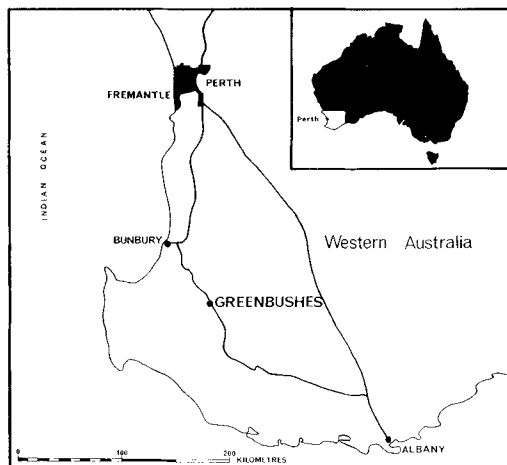


FIG. 1. Location map.

Greenbushes Tin NL was incorporated in Victoria 1974 for the development and operation of the Greenbushes Mineral Field. The discovery of niobium, tantalum and lithium deposits made Greenbushes an important mineral province not only economically, but also because of its unique assemblage of rare minerals. An account of the

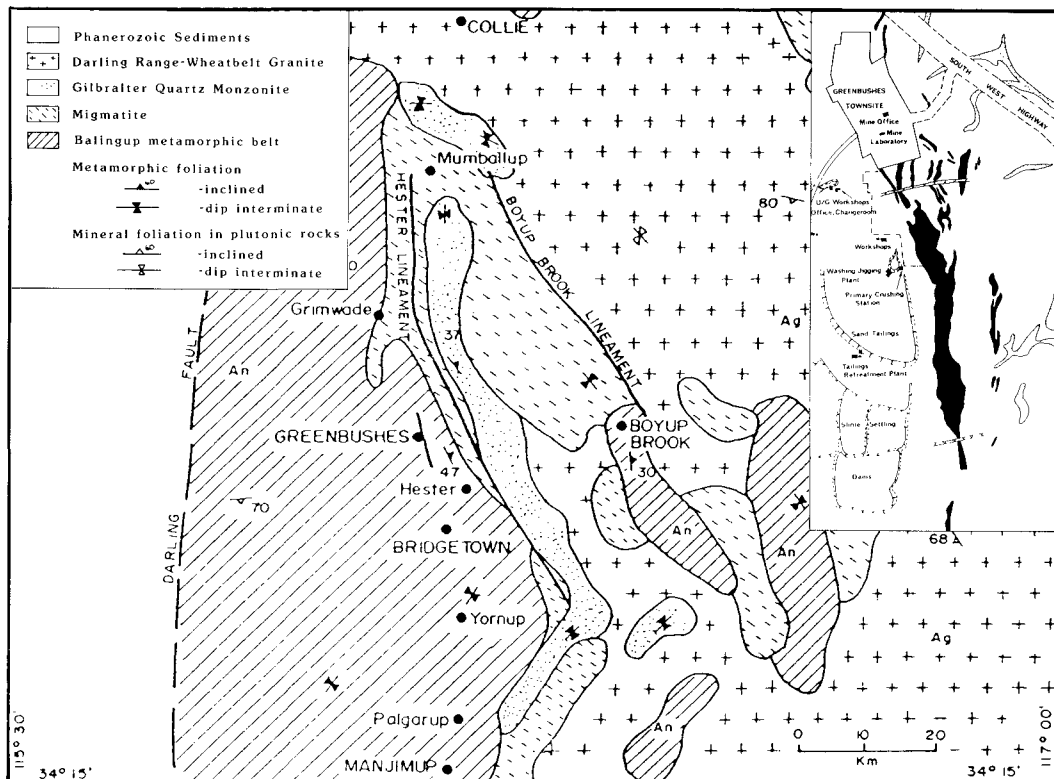


Diagram adapted from G S WA 17124
by I W Walker (1978).

Fig. 2. Geological setting of the Greenbushes Mineral Field, incorporating a map showing the pegmatite swarm (black). The two locations where holmquistite amphibolite occur are near the southern end of the Greenbushes town site.

geology of the Greenbushes Mineral Field has been published by Hatcher and Bolitho (1982). The following summary of the geology is based upon their work.

The Greenbushes pegmatite occurs in the south west of the Yilgarn Block in the Balingup Metamorphic Belt. The metasedimentary and metavolcanic rock belt strikes north-south and extends from the Darling Fault 20 km west of Greenbushes (where it is in contact with Perth Mesozoic sediments), to the Hester Lineament 7 km east of Greenbushes (where it is cut off by the Darling Range-Wheat Belt granitic batholith) (Fig. 2). Numerous dolerite dykes and sills intrude the Balingup Metamorphic Belt. Pegmatite veins of various sizes strike both north and south of the main body (Fig. 2). The Kapanga-Foxes Lodes pegmatites are developed stepwise along a major structural feature to the east of and parallel to the main body of pegmatite.

Spodumene, $\text{LiAl}(\text{Si}_2\text{O}_6)$ is the main lithium-bearing mineral found to date in discrete zones. Other lithium minerals found include amblygonite, holmquistite and triphylite. Of particular interest is the lithium amphibole holmquistite which occurs in contact zones of amphibolites and intrusive dolerite, where the Li content of the adjacent pegmatite is enriched in spodumene zones.

Mineralogy and petrography

Holmquistite has been formed by migration of lithium from the pegmatite into the amphibolite. It appears to have been formed at the expense of the hornblende. Major elements removed from the hornblende are Ca, Na and K; Fe and Al contents are also lower, but Si and Mg are higher. The two locations where holmquistite amphibolite occur, the Police Station Cut and the Lemonade Springs Cut, are not very far apart. Most

Table 1. Unit cell parameters (Å) of holmquistite from Greenbushes and other localities.

This study	Barraulte, Quebec ¹	Utoe, Sweden ²	Kola Peninsula, USSR ³	Carinthia, Austria ⁴
a 18.2827 ± 0.0014	18.30	18.36	18.27	18.260
b 17.6958 ± 0.0029	17.69	17.75	17.71	17.649
c 5.2708 ± 0.0004	5.30	5.29	5.30	5.2753

¹Nickel *et al.*, (1960).

²Vogt *et al.*, (1958).

³Ginzburg *et al.*, (1958).

⁴Walter and Walitzi, (1985).

of the samples studied come from the Lemonade Springs Cut area. Clinoholmquistite has not been identified in the samples.

Experimental

Thin sections (slip-covered and thin polished) as well as a polished mount were prepared and examined by optical, scanning electron microscopy (SEM) and electron microprobe. Holmquistite was hand-separated and crushed. The 0.5 to 0.45 mm fraction was further treated using heavy liquid separation to remove impurities. The fraction was examined under the microscope and further contaminants were removed by hand. The pure holmquistite sample was used to determine the Li, Fe(II), total Fe content and unit cell parameters.

The hornblende was separated in a similar way for the determination of its Li content by atomic absorption, after dissolution in HCl/H₂SO₄/HF. Fe(II) was determined by titration with potassium dichromate, using barium diphenylamine sulphate, after decomposition using HF/H₂SO₄, reduction of Fe(III) to Fe(II) with stannous chloride. Titration was carried out as above. All minerals were also analysed by electron microprobe methods.

The unit cell parameters of holmquistite were determined using a least-squares fitting method of the 2θ values (Table 1). Data of selected peaks were collected on a conventional powder diffractometer using Cu Kα and step-scanning (steps of 0.102θ) with counting times of 4 s per step. Quartz was the internal standard.

Optical mineralogy

Macroscopy. The hand specimens of the holmquistite-containing amphibolite are of a dark greenish-black colour. Schistosity or preferred

orientation could not be seen on the hand specimens. The large, idiomorphic, elongated, prismatic holmquistite crystals are unevenly distributed in a fine-grained, green, hornblende-rich amphibolite matrix. They are idioblastic, with some appearing in clusters, giving the impression of radial growth, as in many cases crystals grow from the same origin. When separated from the matrix, the crystals are holohedral, semi-transparent and of a pinkish–bluish–violet colour.

Various sulphides such as sphalerite, arsenopyrite, pyrrhotite and chalcopyrite are associated with the holmquistite. Hornblende and quartz are the other main minerals. The former is fine-grained and of a dark green colour.

Microscopy. The minerals identified are: hornblende, holmquistite, biotite, quartz, plagioclase, titanite (sphen), ilmenite, pyrrhotite, chalcopyrite, sphalerite, zircon, monazite, chlorite and hematite. Tetrahedrite, arsenopyrite and gudmundite were not identified under the microscope.

Green hornblende is the dominant mineral (Fig. 3). The hypidiomorphic grains are small, green-coloured, with good cleavage and with pleochroism from pale green to green. Most hornblende grains have a fresh appearance and do not show any preferred orientation. Monazite and zircon inclusions are rare and the minute crystals are usually surrounded by pleochroic haloes. Other inclusions are not common. The titanite grains vary in size and are evenly distributed throughout the sample (Fig. 3). Clusters of grains are common. Some large grains or grain clusters appears to have 'grown' around amphibole grains. The titanite is weakly pleochroic from pale brown to brown. Inclusions of pyrrhotite, sphalerite and ilmenite are widespread.

The large, elongated, idiomorphic holmquistite crystals are of a pale pinkish colour and show good cleavage (Fig. 4). They appear to be a late developed mineral. Twinned crystals have also been

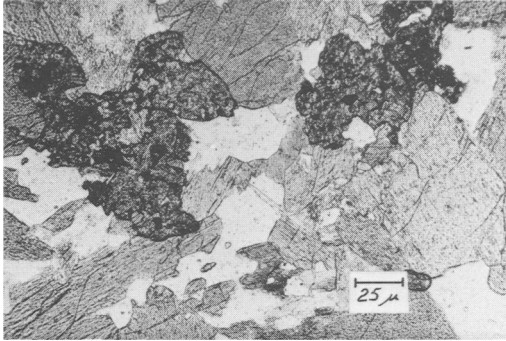


FIG. 3. Amphibolite matrix, mainly green hornblende (various shades of grey), with strong relief and good cleavage. Light areas are quartz or plagioclase. The two large clusters of titanite (dark grey, very high relief), are very distinct. Unpolarized white light.

observed. Small biotite, green hornblende and titanite grains are common inclusions.

Quartz grains are small, interstitial, with undulose extinction and filled with unidentified micro-lites and minute hornblende inclusions. Plagioclase is rare. The grains are small, probably oligoclase (biaxial negative), with numerous inclusions. The grains are difficult to distinguish

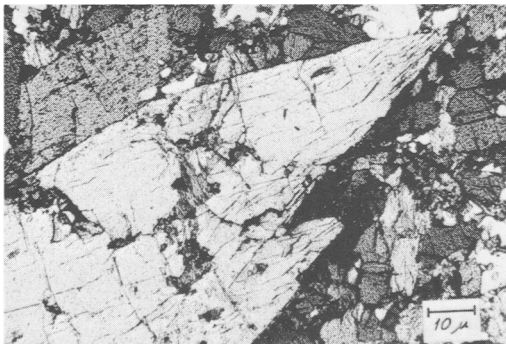


FIG. 4. Large, elongated, idioblastic holmquistite crystals with good cleavage, surrounded by the amphibolite matrix. Unpolarized white light.

from quartz because they are not twinned; the most distinct difference is the higher number and smaller size of the inclusions in the plagioclase. Biotite appears fresh with strong pleochroism from pale yellowish to orange brown. The usually small grains show the good mica cleavage. Biotite

has only been observed as inclusion in holmquistite. Numerous idiomorphic zircon crystals were observed.

Opaque minerals such as pyrrhotite, sphalerite, chalcopyrite, ilmenite and hematite, were observed either as individual grains or as inclusions in titanite. The individual grains can be large and hypidiomorphic; opaque inclusions are usually xenomorphic, subrounded and small.

Unit cell parameters

The calculated unit cell parameters of the Greenbushes holmquistite are given in Table 1. Unit cell dimensions of holmquistites from other known occurrences are also given for comparison. The unit cell dimensions of the Greenbushes holmquistite are nearest to those of the Barraute holmquistite, Quebec (Nickel *et al.*, 1980).

Chemical and microprobe analyses

The chemical composition of most of the identified minerals was determined using a Cameca electron microprobe. The calculated averages of the analyses are presented in Table 2 (sulphides) and the main minerals (green hornblende, titanite, plagioclase and holmquistite) are given in Tables 3 and 4.

The formula of the hornblende is approximately $\text{Ca}_2(\text{Mg,Fe})_4\text{Al}[(\text{Si}_{5.5}\text{Al}_{2.5})\text{O}_{22}](\text{OH,F})_2$, with Na and, to a lesser extent, K and Li replacing Ca. Small amounts of Ti and Mn replace Mg and/or Fe. With approximately 30% anorthite content the plagioclase is at the top of the oligoclase range.

The ferro-chlorite is probably chloritized biotite; it occurs as inclusions in holmquistite. The iron present has been calculated as Fe_2O_3 . The titanite and ilmenite have expected compositions and have been omitted.

Table 2 presents calculated averages of the analysed sulphides. Chalcopyrite, sphalerite, arsenopyrite and pyrrhotite are common sulphide minerals in the assemblage. Members of the tetrahedrite and gudmundite groups were less common.

Discussion

Comments made by Nickel *et al.* (1960) regarding the occurrence of holmquistite and the origin of the lithium are generally applicable to this study. In Greenbushes, as in most other places where holmquistite has been found, there is a contact between an amphibolite and a lithium-rich

Table 2. Electron microprobe analyses (wt.%) of the sulphide minerals found in the amphibolite.

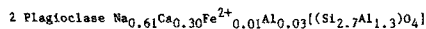
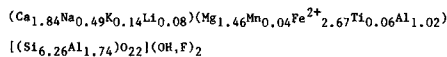
	1	2	3	4	5	6	7	8	9
Fe	58.50	9.10	5.03	6.52	8.75	6.86	28.41	33.20	32.08
Cu	0.01	1.27	0.87	38.60	37.33	38.13	0.02	1.37	0.00
Zn	0.00	54.95	59.70	0.71	0.90	1.04	0.01	0.08	0.00
Co	0.03	0.08	0.01	0.00	0.00	0.00	0.00	0.34	3.39
Ni	0.14	0.02	0.01	0.00	0.00	0.00	0.00	2.05	0.17
S	40.91	33.62	33.45	25.47	26.95	25.03	15.53	21.05	19.21
As	0.00	0.00	0.00	1.54	0.44	0.40	1.62	41.78	44.75
Sb	0.00	0.00	0.00	26.93	24.75	27.82	54.42	0.27	0.06
Bi	0.01	0.00	0.00	0.05	0.06	0.08	0.17	0.00	0.00
Ag	0.02	0.00	0.00	0.09	1.69	1.03	0.00	0.00	0.00
Au	0.01	0.00	0.00	0.03	0.09	0.00	0.00	0.00	0.03
	99.63	99.04	99.07	99.94	99.96	100.39	100.18	100.14	99.69

1 Pyrrhotite	Fe ₉ S ₁₁
2 Sphalerite (high Fe)	(Zn _{0.81} Fe _{0.16} Cu _{0.01})S _{1.01}
3 Sphalerite (low Fe)	(Zn _{0.89} Fe _{0.09} Cu _{0.01})S _{1.01}
4 Tetrahedrite	(Fe _{0.47} Cu _{2.49} Zn _{0.04})(Sb _{0.90} As _{0.07})S _{3.25}
5 Argentic tetrahedrite	(Fe _{0.60} Cu _{2.26} Zn _{0.07} Ag _{0.07})(Sb _{0.78} As _{0.04})S _{3.25}
6 Argentic tetrahedrite	(Fe _{0.49} Cu _{2.40} Zn _{0.07} Ag _{0.04})(Sb _{0.92} As _{0.04})S _{3.14}
7 Gudmundite	Fe _{1.06} (Sb _{0.94} As _{0.05})S
8 Arsenopyrite	(Fe _{0.91} Cu _{0.03} Co _{0.01} Ni _{0.06})As _{0.86} S
9 Arsenopyrite	(Fe _{0.95} Co _{0.09})AsS

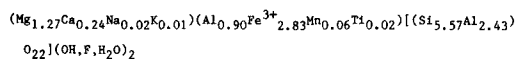
Table 3. Electron microprobe analyses (wt.%) of the silicate and oxide minerals of the amphibolite.

	1	2	3	4
SiO ₂	40.82	60.11	38.35	59.79
TiO ₂	0.53	0.00	0.12	0.01
Al ₂ O ₃	15.27	25.11	19.45	12.59
Fe ₂ O ₃	n.d.	n.d.	25.88	1.96
FeO	20.82	0.15	n.d.	12.00
MnO	0.35	0.00	0.47	0.17
MgO	6.39	0.00	5.88	8.39
CaO	11.22	6.20	1.55	0.04
ZnO	0.03	0.00	0.00	0.00
K ₂ O	0.73	0.07	0.04	0.00
Na ₂ O	1.64	6.96	0.09	0.08
Li ₂ O	0.13	n.d.	n.d.	3.10
F ⁻	0.09	0.00	0.00	0.00
H ₂ O ⁺	1.77			1.75
H ₂ O ⁻				0.14
	99.79	98.60	91.83	100.02
-OH=F	0.04	0.00	0.00	0.00
	99.75	98.60	91.83	100.02

1 Amphibole



3 Ferro-chlorite



pegmatite. It is reasonable to assume that Li has been introduced into the amphibolite from the pegmatite and therefore, holmquistite crystallized at the expense of the hornblende. Minor variations in the chemical composition of holmquistite can be expected as in any amphibole and will be controlled by the chemistry of the host rock and the conditions at the time of its formation.

Table 5 presents chemical analyses of the hornblende found associated with holmquistite in Greenbushes (this study), Mt Marion (Wilkins *et al.*, 1970) and Mtoko, Zimbabwe (von Knorring and Hornung, 1961). The hornblende has a distinctly different composition in each locality; variations in the composition of the associated holmquistite are not as marked.

Some of the published holmquistite formulae (Table 2, analyses 2, 4, 5 and 6) have been recalculated for direct comparison. The observation and comments of Wilkins *et al.* (1970) regarding the ratio of Mg:Fe²⁺ being 2:1 are not supported when comparing all results available today; there is a very wide range in the ratio, from approximately 5:1 (Utoe, Sweden) to about 8:7 (this study). The variation in the alkali atoms is from 1.5 to 2.5 (Nickel *et al.*, 1960, found 1.5 to 2.0) but there is little variation in the divalent (2.9 to 3.1) and trivalent atoms (2 to 2.3). Partial substitution of

Table 4. Chemical and modal analyses of holmquistite from other localities.

	1	2*	3	4*	5*	6*	7	8
SiO ₂	59.79	59.44	59.06	58.72	60.45	55.48	59.73	n.d.
TiO ₂	0.01	0.04	0.20	0.05	trace	0.64	0.17	n.d.
Al ₂ O ₃	12.59	12.78	12.38	13.01	7.70	14.64	11.21	n.d.
Fe ₂ O ₃	1.96	1.48	2.36	2.24	9.68	1.80	2.97	n.d.
FeO	12.00	9.20	10.84	8.94	4.38	10.36	8.92	n.d.
MnO	0.17	0.10	0.25	0.19	----	trace	0.20	n.d.
MgO	8.39	10.22	8.82	9.43	12.12	9.40	10.16	n.d.
CaO	0.04	0.71	0.21	1.00	----	1.32	0.56	n.d.
Na ₂ O	0.08	0.18	0.11	0.23	1.12	0.66	0.18	0.15
K ₂ O	0.00	0.32	0.05	0.00	0.54	0.74	0.15	0.02
Li ₂ O	3.10	3.76	3.33	2.43	2.13	2.40	3.56	3.62
F ⁻	0.00	0.12	0.18	0.14	0.43	trace	0.24	n.d.
H ₂ O ⁺	1.75	2.01	2.09	1.87	2.28	3.16	2.08	n.d.
H ₂ O ⁻	0.14	0.07	0.07	0.12	0.09	----	0.02	n.d.
CO ₂				1.54				
Total	100.02	100.43	99.95	99.91	100.92	100.06	100.15	3.79
-O=F2	0.00	0.05	0.08	0.06	0.18	0.00	0.10	
	100.02	100.38	99.87	99.85	100.74	100.00	100.05	
Formulae based on 24 (O,(OH),F) atoms								
Si	8.02	7.85	7.89	7.95	8.01	7.38	7.92	
Al(iv)	--	0.15	0.11	0.05	0.00	0.62	0.08	
Al(vi)	1.99	1.84	1.84	2.02	1.20	1.67	1.67	
Ti	0.00	0.00	0.02	0.00	0.00	0.06	0.02	
Fe ³⁺	0.20	0.15	0.24	0.23	0.96	0.18	0.30	
Fe ²⁺	1.35	1.02	1.21	1.01	0.49	1.15	0.99	
Mn	0.02	0.01	0.03	0.02	0.00	0.00	0.02	
Mg	1.68	2.01	1.76	1.90	2.39	1.86	2.01	
Ca	0.01	0.10	0.03	0.14	0.00	0.19	0.08	
Na	0.02	0.05	0.03	0.06	0.29	0.17	0.05	
K	0.00	0.05	0.01	0.00	0.09	0.13	0.03	
Li	1.67	2.00	1.79	1.32	1.14	1.28	1.90	
(OH)	1.57	1.77	1.86	1.69	2.01	2.80	1.84	
F ⁻	0.00	0.05	0.08	0.06	0.18	0.00	0.10	
O	22.43	22.18	22.06	22.25	21.81	21.20	22.06	
Z	8.02	8.00	8.00	8.00	8.01	8.00	8.00	
Y	2.19	1.98	2.10	2.25	2.16	1.91	1.99	
X	3.05	3.04	3.00	2.93	2.88	3.01	3.02	
W	1.70	2.20	1.86	1.52	2.52	1.77	2.06	
Y+X+W	6.94	7.22	6.96	6.70	7.56	6.69	7.07	

1 Greenbushes, W.A. (this paper).

2 Mt Marion, Western Australia (Wilkins *et al.*, 1970).3 Benson Mine, Mtoko, S. Rhodesia
(von Knorring and Hornung, 1961).4 Kola Peninsula, USSR (Ginzburg *et al.*, 1958).5 Utoe, Sweden (Palache *et al.*, 1930).6 North Carolina, USA (Palache *et al.*, 1930).7 Barraute, Quebec, Canada (Nickel *et al.*, 1960).

8 Koralpe, Carinthia, Austria (Walter and Wilitzi, 1985).

4 Holmquistite

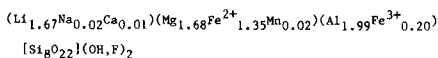


Table 5. Chemical analyses of hornblende from holmquistite amphibolite of various localities.

	1	2	3
SiO ₂	40.82	44.06	48.75
TiO ₂	0.53	0.97	0.57
Al ₂ O ₃	15.27	12.84	9.67
Fe ₂ O ₃	n.d.	3.70	1.74
FeO	20.82	14.40	11.49
MnO	0.35	0.25	0.28
MgO	6.39	8.74	12.78
CaO	11.22	11.04	11.91
ZnO	0.03	n.d.	n.d.
K ₂ O	0.73	0.31	0.17
Na ₂ O	1.64	1.72	0.77
Li ₂ O	0.13	0.15	0.18
F ⁻	0.09	0.00	0.12
H ₂ O ⁺	1.77	1.81	1.81
H ₂ O ⁻			0.16
Total	99.79	99.99	100.40

Formulae based on 24 (O,(OH),F) atoms.

Si	6.24	6.54	7.03
Al(iv)	1.76	1.46	0.97
Al(vi)	0.99	0.79	0.67
Ti	0.06	0.11	0.06
Fe ³⁺		0.41	0.19
Fe ²⁺	2.66	1.79	1.39
Mn	0.05	0.03	0.03
Mg	1.46	1.93	2.75
Ca	1.84	1.76	1.84
K	0.14	0.06	0.03
Na	0.49	0.50	0.22
Li	0.08	0.09	0.10
F ⁻	0.04	0.00	0.06
(OH)	1.80	1.79	1.74

1 This Study. 2 Mt Marion (Wilkins *et al.*, 1970).

3 Mtoko, Zimbabwe (von Knorring and Hornung, 1961).

Si by Al occurs in some holmquistites and is strong and in the North Carolina material (Palache *et al.*, 1930).

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