

## Clinoholmquistite discredited: The new amphibole end-member fluoro-sodic-pedrizite

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### ABSTRACT

Re-examination of holotype “clinoholmquistite”, ideally  $A^{\square}B^{\square}Li_2^c(Mg_3Al_2)^tSi_8O_{22}^x(OH)_2$  (Ginzburg 1965) from the Tastyg spodumene deposit, Tuva, Siberia, Russia by EMP and SIMS analysis and structure refinement shows that the sample consists of a mixture of two distinct amphibole compositions, tremolite and a new amphibole end-member, fluoro-sodic-pedrizite, ideally  $A^{\square}Na^B Li_2^c(Mg_2Al_2Li)^t Si_8 O_{22}^x F_2$  (IMA-CNMMN 2004-002). Fluoro-sodic-pedrizite from Tastyg has the following crystal-chemical formula and unit-cell parameters:  $A(Na_{0.45}K_{0.05})^B(Li_{1.79}Ca_{0.21})^C(Al_{2.21}Mg_{1.93}Fe_{0.68}^{2+}Li_{0.08}Mn_{0.05}Fe_{0.05}^{3+})Si_8O_{22}(O_{0.98}F_{0.74}OH_{0.18})$ , and was obtained by wet-chemical analysis and normalization to 8 Si atoms per formula unit (apfu). Notably, this formula does not properly correspond to “clinoholmquistite”, because the A-site occupancy is  $>0.5$  apfu. This feature can be ascribed to the extensive calcite contamination, which had been corrected based on  $CO_2$  quantification (Ginzburg 1965), but might have been slightly underestimated. Also, the content of trivalent octahedral cations exceeds the crystal-chemical limit of 2.0 (at the M2 site) so that significant dehydrogenation is necessary for electroneutrality, despite a measured  $H_2O$  concentration of 1.67 wt%. Optical and physical properties were measured; an X-ray study (based on rotation and Laue methods) showed the following unit-cell parameters:  $a = 9.80(2)$ ,  $b = 17.83(3)$ , and  $c = 5.30(1)$  Å, and  $\beta = 105.1^\circ$ , with probable space group  $P2/m$  (Ginzburg 1965).

### INTRODUCTION

“Clinoholmquistite” was first found by Ginzburg (1965) in the Tastyg spodumene deposit, Tuva, Siberia, Russia, where it occurs at the inner contact with lithium pegmatite around oligoclase andesite. It was described as the monoclinic variety of holmquistite.

The crystal-chemical formula reported by Ginzburg (1965) is  $A(Na_{0.45}Ca_{0.05}K_{0.04})^B(Li_{1.79}Ca_{0.21})^C(Al_{2.21}Mg_{1.93}Fe_{0.68}^{2+}Li_{0.08}Mn_{0.05}Fe_{0.05}^{3+})Si_8O_{22}(O_{0.98}F_{0.74}OH_{0.18})$ , and was obtained by wet-chemical analysis and normalization to 8 Si atoms per formula unit (apfu). Notably, this formula does not properly correspond to “clinoholmquistite”, because the A-site occupancy is  $>0.5$  apfu. This feature can be ascribed to the extensive calcite contamination, which had been corrected based on  $CO_2$  quantification (Ginzburg 1965), but might have been slightly underestimated. Also, the content of trivalent octahedral cations exceeds the crystal-chemical limit of 2.0 (at the M2 site) so that significant dehydrogenation is necessary for electroneutrality, despite a measured  $H_2O$  concentration of 1.67 wt%. Optical and physical properties were measured; an X-ray study (based on rotation and Laue methods) showed the following unit-cell parameters:  $a = 9.80(2)$ ,  $b = 17.83(3)$ , and  $c = 5.30(1)$  Å, and  $\beta = 105.1^\circ$ , with probable space group  $P2/m$  (Ginzburg 1965).

Litvin et al. (1975) re-examined the holotype material of “clinoholmquistite,” corrected the space group to  $C2/m$  [ $a = 9.334(7)$ ,  $b = 17.596(10)$ , and  $c = 5.267(3)$  Å,  $\beta = 102.67^\circ$ ,  $V = 846.0$  Å<sup>3</sup>], and provided a structure refinement yielding an  $R$ -factor of 13%. Notably, these authors used the chemical formula provided by Ginzburg (1965).

While revising the crystal-chemical data available at that time, Hawthorne (1983) commented on the poor quality of the analysis and of the refinement of “clinoholmquistite” from Tastyg. In par-

ticular, he noted that some of the isotropic atomic-displacement parameters were unfeasible (especially that reported for the M4 site:  $14.74$  Å<sup>2</sup>). Based on the present knowledge of amphibole crystal-chemistry, we also realized that some additional features such as the T2-O distances and the M4 coordinates are unlikely to be true.

Recent investigation of Li-bearing monoclinic amphibole samples from the Pedriza massif (Spain) revealed extensive solid-solution between ferri-ottoliniite, ideally  $A^{\square}B^{\square}(Na_1Li)_1^c(Mg_3Fe_3^+)Si_8O_{22}(OH)_2$ , ferriwhittakerite, ideally  $A^{\square}Na^B(Na_1Li)_1^c(Mg_2Fe_3^+Li_1)Si_8O_{22}(OH)_2$ , ferri-clinoholmquistite, ideally  $A^{\square}B^{\square}Li_2^c(Mg_3Fe_3^+)Si_8O_{22}(OH)_2$ , sodic-ferripedrizite, ideally  $A^{\square}Na^B Li_2^c(Mg_2Fe_3^+Li_1)Si_8O_{22}(OH)_2$ , and the ferro counterparts of the two latter end-members (Oberli et al. 2003a,b, 2004). The absence of compositions with  $Fe^{3+} < Al$  in these minerals and in leakeites [ideally  $A^{\square}Na^B Na_2^c(Mg_2Fe_3^+Li_1)Si_8O_{22}(OH)_2$ ] and Li-bearing arfvedsonites published so far (Hawthorne et al. 1992, 1993, 1996a, 1996b, 2001) prompted us to investigate whether or not the presence of a larger M2 cation is required for the incorporation of octahedrally coordinated Li in the amphibole structure.

The only “clinoholmquistite” analysis reported is that of Ginzburg (1965). Because both the  $Fe^{2+}/Fe^{3+}$  ratio and the  $H_2O$  content were measured, normalization on 24 (O, F, OH) pfu and 2 (OH, F) is possible, and gives  $A(Na_{0.19}K_{0.05})^B(Li_{1.47}Ca_{0.26}Na_{0.27})^C(Al_{1.98}Mg_{1.89}Fe_{0.67}^{2+}Li_{0.37}Mn_{0.05}Fe_{0.04}^{3+})^T(Si_{7.82}Al_{0.18})O_{22}^x(OH_{1.27}F_{0.73})$  when the  $H_2O$  content reported by Ginzburg (1965) is slightly reduced (from 1.67 to 1.40 wt%). This formula, according to Leake et al. (2004), corresponds to the new end-member “ottoliniite”. The holotype specimen for “clinoholmquistite” (no. 67493) was thus requested from the A. E. Fersman Mineralogical Museum (Academy of Sciences, Moscow, Russia), and a few milligrams of loose crystals were obtained. Re-examination was done using modern in situ microanalytical techniques, namely electron microprobe (EMP) and ion-probe (SIMS) analysis, and

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X-ray single-crystal structure refinement. As discussed in the following section, two different amphibole compositions were found, neither of which is “clinoholmquistite,” but one of which is the new end-member fluoro-sodic-pedrize (IMA-CNMMN code 2004-002). The crystals refined and analyzed for this work are kept in the Museum of the Dipartimento di Scienze della Terra of the Università di Pavia under the number 2003-03. The rest of the holotype specimen is kept at the A. E. Fersman Mineralogical Museum (Academy of Sciences, Moscow, Russia), number 67493.

**EXPERIMENTAL METHODS AND RESULTS**

**Crystal-structure refinement**

Crystals were selected on the basis of optical and diffraction properties. Data collection was done with a Philips PW-1100 four-circle diffractometer using graphite-monochromatized MoK $\alpha$  X-radiation. Unit-cell dimensions were calculated from least-squares refinement of the *d*-values obtained from 50 rows of the reciprocal lattice by measuring the centroid of gravity of each reflection and of the corresponding antireflection in the range  $-30 < \theta < 30^\circ$ . A full-matrix unweighted least-squares refinement on *F* was done using a program specifically written at the CNR-IGG-PV to deal with complex solid solutions (Cannillo, personal communication). A number of crystals were refined and analyzed, but here we provide only the data obtained for that closest to end-member composition, together with those obtained for tremolite. Table 1 reports the correct names and selected crystal and refinement data, Table 2 lists atom coordinates, displacement parameters, and refined site-scattering (ss, epfu) values, Table 3 lists the geometric

parameters relevant for the description of the crystal structure, and Table 4<sup>1</sup> lists observed and calculated structure factors.

Due to the few crystals available and to the differences in composition, the X-ray powder-diffraction pattern for CuK $\alpha$  requested for the description of a new mineral was calculated from the single-crystal data and is reported in Table 5.

**Chemical data and crystal-chemical formulae**

Chemical characterization was done by combining electron-microprobe and ion-microprobe data for the refined crystal. EMP analysis was done in WDS mode with a Cameca SX50 at the Istituto di Geologia Ambientale e Geoingegneria (IGAG), Università di Roma La Sapienza. Analytical conditions were 15 kV accelerating voltage, 15 nA beam current, and a peak-count time of 10 s. The following standards and crystals were used for K $\alpha$  X-ray lines: Si and Ca: wolastonite (TAP and PET, respectively); Mg: periclase (TAP); Fe: magnetite (LiF); Ti: rutile (LiF); Al: corundum (TAP); Cr: Cr metal (PET); Mn: Mn 100% (LiF); Zn: Zn 100% (LiF); Na: jadeite (TAP); K: orthoclase (PET); and F: synthetic fluorophlogopite (TAP). Analytical errors are 1% rel. for major elements and 5% rel. for trace elements. Data reduction was done with the PAP method (Pouchou and Pichoir 1985).

Li and B were analyzed with a Cameca IMS 4f probe (CNR-IGG-PV, Italy) using an <sup>16</sup>O primary beam with a diameter of <5  $\mu$ m (corresponding to a beam current of  $\sim$ 2 nA). Secondary positive-ion currents were measured at masses 7 (Li), 11 (B), and 30 (Si, used as the reference element), and corrected for isotopic

<sup>1</sup> For a copy of Table 4, Document AM-05-010, contact the Business Office of the Mineralogical Society of America (see inside cover of a recent issue for price information). Deposit items may also be available on the American Mineralogist web site at <http://www.minsocam.org>.

**TABLE 1.** Selected crystal structure refinement information

	SEQ	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	$\beta$ (°)	<i>V</i> (Å <sup>3</sup> )	Space group	<i>Z</i>	$\theta_{max}$ (°)	<i>R</i> <sub>sym</sub> %	<i>R</i> <sub>obs</sub> %	<i>R</i> <sub>all</sub> %	no. <i>F</i> <sub>all</sub>	no. <i>F</i> <sub>obs</sub>
Fluoro-sodic-pedrize	1092	9.368(8)	17.616(10)	5.271(4)	102.38(4)	849.6	C2/ <i>m</i>	2	30	2.1	2.3	3.8	1288	931
Tremolite	1100	9.848(4)	18.049(5)	5.279(3)	104.73(4)	907.5	C2/ <i>m</i>	2	30	2.4	2.4	3.7	1377	1064

Notes: SEQ is the sequence number in the CNR-IGG-PV amphibole database; R are the standard disagreement indices calculated for the corrected intensities of equivalent monoclinic reflections (*R*<sub>sym</sub>), and for the observed and calculated structure factors (*F*) for all the reflections (*R*<sub>all</sub>) and for those used in the refinement ( $l > 3\sigma_l$ , *R*<sub>obs</sub>).

**TABLE 2.** Atom coordinates, refined site-scattering values (ss, epfu), and atomic-displacement parameters (*B*<sub>eq</sub>, Å<sup>2</sup>;  $\beta_{ii} \times 10^4$ )

Atom	ss	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> <sub>eq</sub>	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
fluoro-sodic-pedrize (crystal 67493 n. 4, 1092)											
O1		0.1091(2)	0.0933(1)	0.2003(3)	0.60(3)	15	5	69	0	8	-1
O2		0.1190(2)	0.1740(1)	0.7402(3)	0.67(3)	16	6	74	0	8	0
O3	8.6	0.1161(2)	0	0.6938(4)	1.02(5)	32	7	99	0	4	0
O4		0.3759(2)	0.2539(1)	0.7915(3)	0.84(4)	28	5	87	-4	7	1
O5		0.3583(2)	0.1300(1)	0.0677(3)	0.98(4)	20	11	87	0	10	13
O6		0.3472(2)	0.1235(1)	0.5650(3)	1.05(3)	22	12	90	1	6	-13
O7		0.3391(3)	0	0.2881(5)	1.00(5)	29	3	150	0	10	0
T1		0.2855(1)	0.0879(1)	0.2803(1)	0.51(1)	17	3	53	0	8	0
T2		0.2971(1)	0.1740(1)	0.7929(1)	0.53(1)	17	4	50	-1	7	0
M1	14.3	0	0.0890(1)	1/2	0.64(2)	23	5	59	0	15	0
M2	13.5	0	0.1787(1)	0	0.59(2)	16	5	60	0	6	0
M3	9.5	0	0	0	0.51(5)	22	2	51	0	6	0
M4	3.5	0	0.2587(3)	1/2	1.6(2)	33	24	93	0	26	0
A	0.9	0	1/2	0	3.2(9)	149	9	455	0	219	0
Am	3.1	0.0673(8)	1/2	0.1369(13)	2.8(2)	117	16	298	0	129	0
tremolite (crystal 67493 n. 3, 1100)											
O1		0.1117(2)	0.0859(1)	0.2179(3)	0.55(3)	13	4	59	0	3	0
O2		0.1186(2)	0.1709(1)	0.7250(3)	0.59(3)	12	5	63	-1	4	-2
O3	8.3	0.1087(2)	0	0.7155(4)	0.76(5)	20	6	78	0	10	0
O4		0.3647(2)	0.2480(1)	0.7928(3)	0.76(3)	23	4	85	-4	12	-1
O5		0.3465(2)	0.1340(1)	0.0996(3)	0.74(3)	19	6	69	0	8	7
O6		0.3437(2)	0.1184(1)	0.5902(3)	0.68(3)	16	6	60	0	8	-5
O7		0.3374(2)	0	0.2921(5)	0.79(5)	21	4	105	0	8	0
T1		0.2802(1)	0.0842(1)	0.2974(1)	0.44(1)	11	3	52	-1	5	-1
T2		0.2881(1)	0.1712(1)	0.8047(1)	0.45(1)	11	3	50	-1	6	0
M1	12.4	0	0.0880(1)	1/2	0.56(3)	15	4	61	0	8	0
M2	12.5	0	0.1770(1)	0	0.53(3)	14	4	58	0	8	0
M3	12.3	0	0	0	0.59(4)	16	4	59	0	5	0
M4	19.5	0	0.2778(1)	1/2	0.79(1)	24	5	97	0	28	0
Am	1.1	0.040(3)	1/2	0.093(5)	0.8(6)	2	13	73	0	10	0
A2	0.7	0	0.483(2)	0	2.0(6)	88	16	280	0	119	0
H	0.6	0.190(6)	0	0.759(12)	0.2						

**TABLE 3.** Selected refinement results [mean bond lengths (Å) and interatomic angles (°)]

	1092	1100		1092	1100		1092	1100
T1-O1	1.618(2)	1.605(2)	M1-O1 ×2	2.059(2)	2.065(2)	M4-O2 ×2	2.114(5)	2.407(2)
T1-O5	1.612(2)	1.634(2)	M1-O2 ×2	2.117(2)	2.076(2)	M4-O4 ×2	2.128(2)	2.330(2)
T1-O6	1.615(2)	1.634(2)	M1-O3 ×2	2.051(2)	2.084(2)	M4-O5 ×2	3.083(5)	2.768(2)
T1-O7	1.626(1)	1.624(2)	<M1-O>	2.076	2.075	M4-O6 ×2	2.585(5)	2.545(2)
<T1-O>	1.618	1.624	OAV	60.28	35.89	<sup>[6]</sup> <M4-O>	2.276	2.427
TAV	4.15	5.23	OQE	1.018	1.011	<sup>[8]</sup> <M4-O>	2.477	2.513
TQE	1.001	1.001	M2-O1 ×2	1.990(2)	2.143(2)	A-O5 ×4	2.709(2)	
T2-O2	1.632(2)	1.614(2)	M2-O2 ×2	1.944(2)	2.085(2)	A-O6 ×4	3.261(2)	
T2-O4	1.590(2)	1.587(2)	M2-O4 ×2	1.850(2)	2.016(2)	A-O7 ×2	2.358(3)	
T2-O5	1.635(2)	1.658(2)	<M2-O>	1.928	2.081	<sup>[10]</sup> <A-O>	2.859	
T2-O6	1.642(2)	1.675(2)	OAV	24.70	24.48	Am-O5 ×2	2.984(5)	3.085(2)
<T2-O>	1.625	1.634	OQE	1.008	1.008	Am-O5 ×2	2.686(4)	2.951(2)
TAV	17.39	21.46	M3-O1 ×4	2.097(2)	2.072(2)	Am-O6 ×2	2.703(5)	2.775(2)
TQE	1.004	1.005	M3-O3 ×2	2.131(3)	2.054(2)	Am-O7	2.436(7)	2.480(3)
			<M3-O>	2.108	2.066	Am-O7	2.969(8)	3.162(3)
T1-T1	3.097(2)	3.039(2)	OAV	91.67	43.14	Am-O7	2.575(7)	2.615(3)
T1-T2	3.080(2)	3.088(2)	OQE	1.029	1.013	Am-O3	2.908(8)	3.349(3)
T1-T2	3.006(2)	3.056(2)			<sup>[9]</sup> <Am-O>	2.747	2.876	
H-O3		0.775(2)	A-Am	0.850(8)	0.546(8)	<sup>[10]</sup> <Am-O>*	2.763	2.923
O6-O7-O6	112.8	107.8			A2-O5		2.725(2)	
O5-O6-O5	173.4	167.8			A2-O6		2.950(2)	
					A2-O7		2.508(3)	
					<A2-O>		2.728	

Note: Polyhedral angular variance (TAV, OAV) and quadratic elongation (TQE, OQE) as defined by Robinson et al. (1971).

abundance. The accuracy of the SIMS analysis for light elements has been shown to be around 10% rel. Detailed analytical procedures are described by Ottolini and Oberti (2000). Unit formulae were calculated on the basis of 24 (O, OH, F) apfu. The excellent agreement between the group-site scattering values calculated from the unit formula and those resulting from structure refinement (Table 6) validates the analysis and the unit-formula recalculation.

Site populations were calculated based on refined site-scattering values. The proposed formulae are:  $^A(\text{Na}_{0.64}\text{K}_{0.01})^B(\text{Li}_{1.93}\text{Ca}_{0.04}\text{Na}_{0.03})^M(\text{Mg}_{1.69}\text{Fe}_{0.31})^M(\text{Al}_{1.98}\text{Cr}_{0.01}\text{Zn}_{0.01})^M(\text{Li}_{0.64}\text{Fe}_{0.31}\text{Mg}_{0.13}\text{Mn}_{0.02})^T(\text{Si}_{3.96}\text{Al}_{0.04})^T\text{Si}_4\text{O}_{22}(\text{F}_{1.10}\text{OH}_{0.90})$  and  $^A(\text{Na}_{0.08}\text{K}_{0.05})^B(\text{Ca}_{1.85}\text{Na}_{0.15})^M(\text{Mg}_{1.96}\text{Fe}_{0.04})^M(\text{Mg}_{1.95}\text{Fe}_{0.02}\text{Mn}_{0.01}\text{Ti}_{0.01}\text{Zn}_{0.01})^M(\text{Mg}_{0.84}\text{Al}_{0.08}\text{Fe}_{0.08})^T(\text{Si}_{7.93}\text{Al}_{0.06}\text{B}_{0.01})\text{O}_{22}(\text{OH}_{1.6}\text{F}_{0.33})$  for fluoro-sodic-pedrize and tremolite, respectively.

A comparison of the refined mean bond-lengths and those calculated based on site occupancy and F content shows: (1) a significant relaxation of the M1 and M3 octahedra in fluoro-sodic-pedrize, in agreement with what is observed in other Mg-rich amphiboles with more than one octahedrally coordinated trivalent cation pfu (Oberti et al. 2003c); (2) a significant relaxation of the M2 octahedron in tremolite, in agreement with what is observed in other Mg-rich amphiboles with no octahedral trivalent cation (e.g., tremolites, richterites). Also, the M sites are strongly distorted, as shown by the very high OAV and OQE values in Table 3.

Similarly to previous findings, <sup>6</sup>Li is ordered at the M3 site, and the <sup>6</sup>M<sup>3+</sup> cations are ordered at the M2 site. Note that the B content (0.06 wt% B<sub>2</sub>O<sub>3</sub>) in tremolite is the highest yet reported for an amphibole, at least to our knowledge. It is probable that B occurs at the T1 site, similar to the heterovalent Al<sup>3+</sup> Si<sup>4+</sup> exchange.

## DISCUSSION

### “Clinoholmquistite” vs. fluoro-sodic-pedrize

The use of modern in situ micro-chemical techniques has allowed us to clarify the reason for the misidentification of “clinoholmquistite” by Ginzburg (1965) and Litvin et al. (1975).

The name “clinoholmquistite” was based on the results of wet-chemical analysis. Ginzburg (1965) realized that the analyses were affected by contamination by calcite, and corrected the Ca content based on the measured CO<sub>2</sub> content. However, he could not recognize the presence of a mixture of amphiboles, and averaged the two different amphibole compositions. Averaging over the two compositions did not allow recognition of the high F content in the more Li-rich amphibole, which is dominant at the O3 site in the new end-member. Perhaps the F dominance could have been inferred from the results of the structure refinement, in particular from the short M1-O3 and M3-O3 bonds.

**TABLE 5.** X-ray powder-diffraction data (CuKα), calculated from the single-crystal data of crystal 67493 n. 4)

<i>l</i>	2θ	<i>d</i> <sub>calc</sub>	<i>h k l</i>	<i>l</i>	2θ	<i>d</i> <sub>calc</sub>	<i>h k l</i>
75	10.90	8.120	1 1 0	18	34.85	2.574	0 0 2
11	18.57	4.779	1 1 1	21	35.19	2.551	0 6 1
11	19.40	4.575	2 0 0	55	36.18	2.483	2 0 2
26	19.97	4.450	0 2 1	19	40.17	2.245	3 5 1
66	20.16	4.404	0 4 0	21	41.06	2.198	3 1 2
15	22.13	4.016	1 1 1	13	42.06	2.148	1 7 1
26	23.46	3.792	1 3 1	29	42.37	2.133	2 6 1
21	25.22	3.532	2 2 1	10	43.90	2.063	2 0 2
50	26.40	3.375	1 3 1	12	51.69	1.768	1 9 1
18	28.12	3.173	2 4 0	29	56.85	1.620	4 6 1
83	29.73	3.005	3 1 0	26	58.74	1.572	1 5 3
19	30.52	2.929	2 2 1	14	62.28	1.493	2 6 3
31	31.13	2.873	1 5 1	13	63.35	1.468	0 12 0
28	33.10	2.707	3 3 0	29	68.21	1.375	6 6 1
100	33.45	2.679	1 5 1	14	69.29	1.356	5 1 2
13	34.37	2.609	3 3 1	18	75.19	1.264	2 12 2

Inspection of the two sets of unit-cell parameters shows that the “clinoholmquistite” crystal refined by Litvin et al. (1975) is very similar to the fluoro-sodic-pedrize refined in this work. The present sample should be slightly closer to the ideal end-member, because it has a slightly smaller β value (suggesting more <sup>6</sup>Li), and a slightly larger *a* value (suggesting more <sup>23</sup>Na).

To our knowledge, there is no other report of “clinoholmquistite” apart from Ginzburg (1965) and Litvin et al. (1975). Because this specimen was shown to be fluoro-sodic-pedrize, the amphibole end-member “clinoholmquistite” has been discredited (IMA-CNMMN 2004-002).

### Mineral data for fluoro-sodic-pedrize

Whereas the wet-chemical analyses reported by Ginzburg (1965) were biased by the presence of calcite and of tremolite, the optical and physical properties measured were those of the dominant phase, presently recognized as fluoro-sodic-pedrize. We report here the data published by Ginzburg (1965), and show that they are coherent with our crystal-chemical characterization of fluoro-sodic-pedrize and must thus be retained. Fluoro-sodic-pedrize is biaxial negative, with α = 1.610, β = 1.627, γ = 1.633;

**TABLE 6.** Chemical analyses (EMPA + SIMS) and unit formulae [on the basis of 24 (O + F)], and a comparison between refined (obs) and calculated (cal) group-site scattering values (ss) in electrons per formula unit (epfu)

	1092	1100		1092	1100
SiO <sub>2</sub>	62.43 (31)	57.66 (20)	Si	7.96	7.93
B <sub>2</sub> O <sub>3</sub> *	0.015 (1)	0.060 (4)	Al	0.04	0.06
TiO <sub>2</sub>	0.03 (3)	0.04 (3)	B	0.00	0.01
Al <sub>2</sub> O <sub>3</sub>	13.46 (12)	0.85 (3)	Σ T	8.00	8.00
Cr <sub>2</sub> O <sub>3</sub>	0.09 (5)	0.01 (2)			
MgO	9.53 (7)	23.22 (15)	Al	1.98	0.08
CaO	0.28 (5)	12.59 (17)	Mg	1.81	4.75
MnO	0.15 (3)	0.05 (3)	Ti	0.00	0.01
FeO	5.03 (24)	1.23 (2)	Cr	0.01	0.00
ZnO	0.06 (6)	0.09 (5)	Fe <sup>2+</sup>	0.53	0.14
Na <sub>2</sub> O	2.71 (18)	0.86 (2)	Mn <sup>2+</sup>	0.02	0.01
K <sub>2</sub> O	0.04 (1)	0.30 (3)	Zn <sup>2+</sup>	0.01	0.01
F	2.73 (19)	0.75 (7)	Li	0.64	0.00
Cl	0.01 (1)	0.02 (2)	Σ C	5.00	5.00
Li <sub>2</sub> O*	5.011 (76)	0.002 (1)			
H <sub>2</sub> O†	1.05	1.82	Li	1.93	0.00
Total	102.61	99.55	Ca	0.04	1.85
O=F,Cl	1.15	0.32	Na	0.03	0.15
Total	101.46	99.23	Σ B	2.00	2.00
			Na	0.64	0.08
s.s. <sub>cal</sub> C	64.2	62.5	K	0.01	0.05
s.s. <sub>cal</sub> B	6.9	38.7	Σ A	0.65	0.13
s.s. <sub>cal</sub> A	7.2	1.8			
Σ s.s. <sub>cal</sub>	78.3	103.0	F	1.10	0.33
			OH	0.90	1.67
s.s. <sub>obs</sub> C	65.1	62.1	Cl	0.00	0.00
s.s. <sub>obs</sub> B	7.0	38.9	Σ O3	2.00	2.00
s.s. <sub>obs</sub> A	7.1	3.3	Σ <sup>c</sup> R <sup>3+</sup>	1.99	0.09
Σ s.s. <sub>obs</sub>	79.2	104.3	XFe <sup>2+</sup>	0.23	0.03

\* Analyzed by SIMS.

† Calculated by stoichiometry.

2V (meas.) = 55–61°, 2V (calc.) = 61°; it is weakly pleochroic, with Z = pale pinkish brown, Y = pale orange brown, X = colorless; Y = b, Z = c, X ^ a = 15–16° (Ginzburg 1965). Fluoro-sodic-pedrize occurs as elongated prismatic crystals with a maximum length of 0.5 mm. It is pale bluish in thick crushed grains, has a white streak, a vitreous luster, and is transparent to translucent. The measured Mohs hardness is 5–6; the measured density is 3.00 g/cm<sup>3</sup> (Ginzburg 1965), and that calculated based on the new empirical formula is 3.05 g/cm<sup>3</sup>. The compatibility index is 1 - (K<sub>p</sub>/K<sub>c</sub>) = -0.008 (superior) when using the calculated density and -0.021 (excellent) when using the density given by Ginzburg (1965). This agreement further supports the conclusion that “clinoholmquistite” is actually fluoro-sodic-pedrize.

Ideal fluoro-sodic-pedrize has the formula <sup>A</sup>Na <sup>B</sup>Li<sub>2</sub> <sup>C</sup>(Mg<sub>2</sub>Al<sub>2</sub>Li)<sub>25</sub> Si<sub>8</sub> O<sub>22</sub> F<sub>2</sub>, which would require the following wt% oxides: Li<sub>2</sub>O 5.89, Na<sub>2</sub>O 4.07, MgO 10.59, Al<sub>2</sub>O<sub>3</sub> 13.40, SiO<sub>2</sub> 63.16, F 4.99, -O=F 2.10, Total 100.00 wt%.

#### On the stability of clinoholmquistite and fluoro-sodic-pedrize

As noted above, there are no reports extant on “clinoholmquistite”. Among the possible Fe-rich varieties, sodic-ferri-clinoferroholmquistite and ferri-clinoferroholmquistite have been described by Caballero et al. (1998) and Oberti et al. (2003b), respectively, from metamorphic epysienites of the Pedriza Massif, Sierra de Guadarrama, Spain. The Pedriza Massif is also the type locality for the Fe-rich varieties of sodic-pedrize (sodic-ferripedrize, Oberti et al. 2000; sodic-ferri-ferropedrize, Oberti et al. 2003b). Comparison of both intercrystalline and intracrystalline (core-to-rim) compositional variations occurring

at Pedriza also suggests that the <sup>C</sup>Li content is directly related to the Mg number and thus to the T of crystallization, whereas the <sup>B</sup>Li content is inversely related to the Mg number.

Despite the different geological environment of crystallization, all the <sup>C</sup>Li-rich amphiboles so far reported contain either dominant Fe<sup>3+</sup> (leakeite, Kajlidongri Mn metasediments, India, Hawthorne et al. 1993; fluoro-ferroleakeite, Canada Pinabete Pluton, New Mexico, Hawthorne et al. 1996b; Li-rich arfvedsonites, peralkaline granites, Strange Lake, Quebec, Hawthorne et al. 2001; Li-bearing fluoro-arfvedsonites, granitic pegmatite, Hurrigan Mountains, New Hampshire, Hawthorne et al. 1996a) or dominant Mn<sup>3+</sup> (kornite, Kalahari manganese fields, Northern Cape Province, South Africa, Armbruster et al. 1993; dellaventuraite, Kajlidongri Mn metasediments, India, Tait et al. 2005).

The occurrence of fluoro-sodic-pedrize (with Al > Fe<sup>3+</sup> and Mg > Fe<sup>2+</sup>) in the Tastyg spodumene deposit is thus an oddity in this scenario. It might be due to a very unusual geochemical environment and to unusual P-T conditions of crystallization; the presence of large amounts of F should also be important in stabilizing the structure. It is relevant in this regard to note that the Am-O3 distance in fluoro-sodic-pedrize is shorter than the longer Am-O5 and Am-O7 bonds (Table 3); this feature is unusual, and suggests interaction of F with Na at the A site. In addition, the unit-cell volume of fluoro-sodic-pedrize is among the smallest ever observed for monoclinic amphiboles, as is to be expected based on the occurrence of the smallest substituents at the M1,3 (Mg), M2 (Al), and M4 (Li) sites. The presence of F both reduces the size of the M1 and M3 octahedra and eliminates the steric hindrance between the proton and Na at the Am site.

There is no information on the compositional and genetic relations between monoclinic and orthorhombic <sup>B</sup>Li amphiboles. However, systematic investigation of the known occurrences of holmquistite (Cámara and Oberti 2004, 2005) has not identified any Li-bearing monoclinic amphibole.

The instability of the “clinoholmquistite” structure is also supported by recent experimental studies in the system Li<sub>2</sub>O-Na<sub>2</sub>O-FeO-MgO-Al<sub>2</sub>O<sub>3</sub>-Fe<sub>2</sub>O<sub>3</sub>-Si<sub>2</sub>O-H<sub>2</sub>O, which were done at T ranging between 450 and 900 °C, P between 0.1 and 1.5 GPa, and log (f<sub>O<sub>2</sub></sub>) 0.5 below and 3 above that of the Ni-NiO buffer (Iezzi et al. 2004). In the Li<sub>2</sub>O-MgO-Al<sub>2</sub>O<sub>3</sub>-Si<sub>2</sub>O-H<sub>2</sub>O system “clinoholmquistite” was never obtained, whereas the introduction of Fe<sup>3+</sup> to the system resulted in easy crystallization of ferriclinoholmquistite. Moreover, only a limited amount of Al (around 10%) was incorporated at lower T (500–600 °C) and P (0.1 GPa), whereas Mg and Fe<sup>2+</sup> were completely exchanged in ferriclinoholmquistite, the Mg-rich compositions being more stable (up to 800 °C) than the Fe<sup>2+</sup>-rich compositions (up to 500–600 °C). In contrast, there are many reported occurrences of holmquistite, and only one known occurrence of “ferroholmquistite” (Cámara and Oberti 2005). We therefore suggest that there is a structural constraint preventing the crystallization of “clinoholmquistite”, and stabilizing that of holmquistite. This issue must be further addressed by crystal-chemical studies and structure modeling of holmquistite.

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## REFERENCES CITED

- Armbruster, T., Oberhansli, R., Bernamec, V., and Dixon, R. (1993) Hennomartinite and kornite, two new  $Mn^{3+}$  rich silicates from the Wessels Mine, Kalahari, South Africa. *Schweizerische Mineralogische und Petrographische Mitteilungen*, 73, 349–355.
- Caballero, J.M., Monge, A., La Iglesia, A., and Tornos, F. (1998) Ferri-clinoholmquistite,  $Li_2(Fe^{2+}, Mg)Fe^{3+}Si_8O_{22}(OH)_2$ , a new  $^8Li$  clin amphibole from the Pedriza Massif, Sierra de Guadarrama, Spanish Central System. *American Mineralogist*, 83, 167–171.
- Cámara, F. and Oberti, R. (2004) Li-bearing amphiboles: anomalous solid-solution properties in holmquistites [ $Li_2(Al_2Mg_2)Si_8O_{22}(OH)_2$ , *Pnma*]. 32<sup>nd</sup> International Geological Congress, Florence, Abstracts, 231–16.
- — — (2005) The crystal-chemistry of holmquistites: Ferrohalmquistite from Greenbushes (Western Australia) and hints for compositional constraints in  $^8Li$  amphiboles. *American Mineralogist*, in press.
- Ginzburg, I.V. (1965) Holmquistite and its structural variety clinoholmquistite. *Trudy Mineralogicheskogo Muzeya Akademii Nauk SSSR*, 16, 73–89.
- Hawthorne, F.C. (1983) The crystal-chemistry of the amphiboles. *Canadian Mineralogist*, 21, 173–480.
- Hawthorne, F.C., Oberti, R., Ungaretti, L., and Grice, J.D. (1992) Leakeite,  $Na_2(Mg_2Fe^{3+}Li)Si_8O_{22}(OH)_2$ , a new alkali amphibole from the Kajlidongri manganese mine, Jhabua district, Madhya Pradesh, India. *American Mineralogist*, 77, 1112–1115.
- Hawthorne, F.C., Ungaretti, L., Oberti, R., Bottazzi, P., and Czamanske, G.K. (1993) Li: an important component in igneous alkali amphiboles. *American Mineralogist*, 78, 733–745.
- Hawthorne, F.C., Oberti, R., Ottolini, L., and Foord, E.E. (1996a) Lithium-bearing fluor-arfvedsonite from Hurricane Mountain, New Hampshire: a crystal-chemical study. *Canadian Mineralogist*, 34, 1015–1019.
- Hawthorne, F.C., Oberti, R., Ungaretti, L., Ottolini, L., Grice, J.D., and Czamanske, G.K. (1996b) Fluor-ferro-leakeite,  $NaNa_3(Fe^{2+}Fe^{3+}Li)Si_8O_{22}F_2$ , a new alkali amphibole from the Canada Pinabete Pluton, Questa, New Mexico, U.S.A. *American Mineralogist*, 81, 226–228.
- Hawthorne, F.C., Oberti, R., Cannillo, E., Ottolini, L., Roelofsen, J., and Martin, R.M. (2001) Li-bearing amphiboles from the Strange Lake peralkaline granite, Quebec. *Canadian Mineralogist*, 39, 1161–1170.
- Iezzi, G., Della Ventura, G., Cámara, F., Oberti, R., and Robert, J.-L. (2004) Li-bearing amphiboles: synthesis, stability and composition of clinoholmquistites. 32<sup>nd</sup> International Geological Congress, Florence, Abstracts, 231–7.
- Leake, B.E., Woolley, A.R., Birch, W.D., Burke, E.A.J., Ferraris, G., Grice, J.D., Hawthorne, F.C., Kisch, H.J., Krivovichev, V.G., Schumacher, J.C., Stephenson, N.C.N., and Whittaker, E.J.W. (2004) Nomenclature of amphiboles: additions and revisions to the International Mineralogical Association's amphibole nomenclature. *American Mineralogist*, 89, 883–887.
- Litvin, A.L., Ginzburg, I.V., Egorova, L.N., and Petrunina, A.A. (1975) On the crystal structure of clinoholmquistite. *Konstitutsiya i Svoystva Mineralov*, 9, 3–6.
- Oberti, R., Caballero, J.M., Ottolini, L., López-Andrés, S., and Herreros, V. (2000) Sodic-ferripedrizite, a new monoclinic amphibole bridging the magnesium-iron-manganese-lithium and the sodium-calcium groups. *American Mineralogist*, 85, 578–585.
- Oberti, R., Cámara, F., Ottolini, L., and Caballero, J.M. (2003a) Lithium in amphiboles: detection, quantification and incorporation mechanisms in the compositional space bridging sodic and  $^8Li$  amphibole. *European Journal of Mineralogy*, 15, 309–319.
- Oberti, R., Cámara, F., Caballero, J.M., and Ottolini, L. (2003b) Sodic-ferripedrizite and ferri-clinoferroholmquistite, mineral data and degree of order of the A-site cations in Li-rich amphiboles. *Canadian Mineralogist*, 41, 1345–1354.
- Oberti, R., Boiocchi, M., and Smith, D.C. (2003c) Fluoronyböite from Jianchang (Su-Lu, China) and nyböite from Nybø (Nordfjord, Norway): description and comparison of two high-pressure amphibole end-members. *Mineralogical Magazine*, 67, 769–782.
- Oberti, R., Cámara, F., and Caballero, J.M. (2004) Ferri-ottoliniite and ferriwhitakerite, two new end-members of the new Group 5 for monoclinic amphiboles. *American Mineralogist*, 888–893.
- Ottolini, L. and Oberti, R. (2000) Accurate quantification of H, Li, Be, B, F, Ba, REE, Y, Th, and U in complex matrices: a combined approach based on SIMS and single-crystal structure refinement. *Analytical Chemistry*, 72, 16, 3731–3738.
- Pouchou, J.L. and Pichoir, F. (1985) 'PAP'  $\pi(\rho Z)$  procedure for improved quantitative micro-analysis. *Microbeam Analysis*, 104–160.
- Robinson, K., Gibbs, G.V., and Ribbe, P.H. (1971) Quadratic elongation: A quantitative measure of distortion in coordination polyhedra. *Science*, 172, 567–570.
- Tait, K.T., Hawthorne, F.C., Grice, J.D., Ottolini, L., and Nayak, V.K. (2005) Delaventuraite,  $NaNa_3(MgMn^{3+}Ti^{4+}Li)Si_8O_{22}O_2$ , a new anhydrous amphibole from the Kajlidongri Manganese Mine, Jhabua District, Madhya Pradesh, India. *American Mineralogist*, 90, 304–309.

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