

Ferri-ottoliniite and ferriwhittakerite, two new end-members of the new Group 5 for monoclinic amphiboles

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ABSTRACT

Mineralogical and crystal-chemical descriptions are provided for two end-members of the new Group 5 introduced by Leake et al. (2004) in the nomenclature of amphiboles. This new classification scheme recognizes the occurrence of compositions with B-site populations intermediate between (Ca,Na) amphiboles and (Mg,Fe,Mn,Li) amphiboles. Its implications for the classification and nomenclature of Li-rich amphiboles are also discussed in this paper. Holotype ferri-ottoliniite [ideally $A^{\square}B^{\square}(NaLi)^C(Mg_3Fe_2^{3+})Si_8O_{22}(OH)_2$] has $a = 9.535(3)$, $b = 17.876(6)$, $c = 5.294(2)$ Å, $\beta = 102.54^\circ(1)$, $V = 880.9$ Å³, and unit formula $A^{(K_{0.07}Na_{0.38})}B^{(Na_{0.70}Li_{1.24}Ca_{0.06})}C^{(Mg_{1.35}Fe_{0.92}Mn_{0.13}Zn_{0.31}Fe_{1.71}Al_{0.10}Ti_{0.06}Li_{0.42})}Si_8O_{22}(OH_{1.51}F_{0.47})$. Holotype ferriwhittakerite [ideally $A^{\square}Na^B(NaLi)^C(Mg_2Fe_2^{3+}Li)Si_8O_{22}(OH)_2$] has $a = 9.712(9)$, $b = 17.851(23)$, $c = 5.297(2)$ Å, $\beta = 103.63^\circ(5)$, $V = 892.5$ Å³, and unit formula $A^{(K_{0.13}Na_{0.64})}B^{(Na_{1.27}Li_{0.62}Ca_{0.11})}C^{(Mg_{1.47}Fe_{0.58}Mn_{0.12}Zn_{0.40}Fe_{1.48}Al_{0.10}Ti_{0.12}Li_{0.73})}Si_8O_{22}(OH_{1.30}F_{0.72})$. The root names have been chosen to acknowledge the contribution given to crystal-chemical studies of minerals, and particularly of amphiboles, by L. Ottolini (Pavia, Italy) and E.J.W. Whittaker (Oxford, U.K.).

INTRODUCTION AND DEDICATION

Recent work on hydrothermal epsyenites from the Pedriza Massif (Sierra de Guadarrama, Spain) led to the discovery of very unusual Li-rich amphibole compositions, and to the recognition that no miscibility gap is present in the solid solution between Na and Li at the B-group sites (Oberti et al. 2003a). During this work, a number of new monoclinic amphibole end-members were characterized (Caballero et al. 1998, 2002; Oberti et al. 2000, 2003a,b); their names were subsequently proposed and approved by the IMA-CNMMN based on the nomenclature scheme in force (Leake et al. 1997). That scheme is implicitly based on the assumption of limited solid solution between the large (Ca,Na) and small (Mg,Fe,Mn,Li) cations occurring at the B sites. Therefore, the latest findings brought to light some inadequacies in this scheme with respect to intermediate compositions, and provoked a debate within the IMA-CNMMN and the subcommittee on amphiboles about the criteria to be followed in these cases. The conclusions are provided in the new report on amphibole nomenclature (Leake et al. 2004), and mainly consist in the definition of a new group (Group 5) which includes compositions with $0.50 < B^{(Mg,Fe,Mn,Li)} < 1.50$ atoms per formula unit (apfu) and $0.50 \leq B^{(Ca,Na)} \leq 1.50$ apfu. Focusing on the topic of this paper, i.e., on the solid-solution between Na and Li at the B sites, two amphibole compositions found in the Pedriza Massif fall close to the stoichiometric intermediate $B^{(NaLi)}$ compositions predictable for this solid solution, and thus deserved new root-names. The composition with an empty A site, ideally $A^{\square}B^{\square}(NaLi)^C(Mg_3Fe_2^{3+})Si_8O_{22}(OH)_2$, is called ferri-otto-

liniite (IMA-CNMMN 2001-67A), and that with complete A-site occupancy, ideally $A^{\square}Na^B(NaLi)^C(Mg_2Fe_2^{3+}Li)Si_8O_{22}(OH)_2$, is called ferriwhittakerite (IMA-CNMMN 2001-69). Luisa Ottolini (CNR-IGG Pavia, born in 1954) gave a fundamental contribution to the advancement of ion-probe analysis of minerals, with particular reference to light elements. Eric J.W. Whittaker (Oxford, born in 1921) did pioneering work in amphibole crystal-chemistry, and greatly contributed to the settling of basic interpretative criteria and nomenclature. The authors of the present paper, as well as many other mineralogists, wish to thank both of them for their important work.

Occurrence

Both of the new amphibole end-members occur in the episyenitic bodies located in the East sector of the Pedriza Massif, Sierra de Guadarrama, Spanish Central System, together with other Li-rich amphibole end-members such as sodic-ferripedrizite, sodic-ferri-ferropedrizite, ferri-clinoferroholmquistite, and sodic-ferri-clinoferroholmquistite (Caballero et al. 1998, 2002; Oberti et al. 2003a,b).

Associated minerals are (1) a magmatic association: quartz, anorthite cores, partially albitized microcline, feldspar-armored annite and zircon; (2) a paragenetic association (episyenitic assemblage): albite, aegirine-augite, sodic-ferripedrizite, sodic-ferri-ferropedrizite, ferriwhittakerite, ferri-ottoliniite, ferri-clinoferroholmquistite, and sodic-ferri-clinoferroholmquistite, titanite, andradite, magnetite and apatite; (3) late retrograde associations: (a) taeniolite and microcline; (b) quartz, ferroactinolite, chlorite; (c) muscovite, hematite, clay minerals, clinozoisite.

Ferri-ottoliniite, ferriwhittakerite, and the other Li-rich amphiboles from the Pedriza Massif, formed during the episy-

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enitic alteration (dequartzification and albitization) of a cordierite-bearing porphyritic granite, by the action of aqueous non-magmatic fluids of low salinity, at temperatures close to 520 °C (mean *T* from O isotope in mineral concentrates) and fluid pressures ranging from 60 to 160 MPa. Higher Mg/Fe ratio suggest relatively higher temperature of crystallization with respect to the Fe²⁺-end-members. There is a strong inter- and intra-crystalline compositional variation, and the lithium content of these amphiboles seems to be controlled by the composition of the fluid.

Type material was collected from a weakly retrograded episyenitic body that occurs at Fuente Grande, 485 m NE from the place where the other Li-rich amphibole end-members (Caballero et al. 1998, 2002; Oberti et al. 2000) were collected. U.T.M. coordinates are 4 28 870 longitude and 45 15 275 latitude [Spanish Military Map number 509 (19-201), scale 1:50000, 4th edition (1986)]. The specimen code is C5-A for ferri-ottoliniite and C5-C for ferriwhittakerite. The analyzed crystals and crystal concentrates from the same rock specimens have been deposited at the Museo di Mineralogia, Dipartimento di Scienze della Terra, Università degli Studi di Pavia, under the codes 2001-01 (ferriwhittakerite) and 2001-04 (ferri-ottoliniite).

Appearance and physical properties

All the Li-rich amphiboles found at Pedriza appear as intergranular granoblastic aggregates associated with fine-grained albite and pyroxene, with sub-euhedral habits or as micro-inclusions in albite, quartz and titanite.

Ferri-ottoliniite occurs in both the outer and middle crystal zones, as well as in fractures through Na-richer amphiboles. Growth-replacement and fracture-replacement textures are widely observed. Ferri-ottoliniite is black with translucent luster. It has a gray streak and shows no fluorescence under long- and short-wave ultraviolet light. Ferri-ottoliniite is brittle with uneven fracture; it has the characteristic {110} cleavage of monoclinic amphiboles. Because the exact composition can be recognized solely after electron- and ion- microprobe analysis, the density could not be measured, but was calculated based on the available analytical data: density (calc.) = 3.27 g/cm³.

Ferriwhittakerite is present as relic cores in complex Li-rich amphiboles. Growth replacement and fracture replacement textures are widely observed, where the inner Na-rich and Fe-poor compositions are subsequently replaced by Na-poor and Fe-rich amphiboles.

Ferriwhittakerite is bluish black, with vitreous luster. It has a gray streak and shows no fluorescence under long- and short-wave ultraviolet light. It is brittle, with uneven fracture and perfect {110} cleavage. Density (calc.) = 3.22 g/cm³.

X-ray analysis and structure refinement

Crystals were selected on the basis of optical and diffraction properties. X-ray analysis and data collection was done with graphite-monochromatized MoK α X-radiation. For ferri-whittakerite, a Philips PW-1100 four-circle diffractometer was used. 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 $-30 < \theta < 30^\circ$. Due to its small size, the holotype crystal of ferri-ottoliniite was examined with a Bruker-AXS SMART APEX diffractometer. A crystal-to-detector distance of 4 cm was used to record three batches of 180 images (5 s each, ω angular increment of 1°) at ϕ rotations of 120°. The SMART software version 5.55 was used for data collection, and the SAINT+ software version 6.02 (Bruker AXS) was used to integrate the diffracted intensities. Unit-cell dimensions were calculated from least-squares refinement of the position of all the collected reflections. A full-matrix unweighted least-squares refinement on *F* was done using a program specifically written at CNR-IGG-PV to deal with complex solid solution terms (Cannillo, personal communication). More detail on data treatment and refinement can be found in Oberti et al. (2003a), where unit-cell parameters and chemical analyses of the two crystals were anticipated in order to discuss the complete ⁹(Li₁Na₁) exchange in amphiboles. Table 1 reports selected crystal and refinement data, Table 2 atom coordinates, displacement parameters, and refined site-scattering (*ss*, epfu) values, and Table 3 the geometric parameters relevant for the description of the crystal structure. Table 4¹ list observed and calculated structure factors.

Due to extensive intra-crystalline chemical variability registered at the Pedriza Massif, where different end-members can be found at the centimeter scale, X-ray powder data for CuK α radiation had to be calculated from the refined structure model. They are reported in Table 5.

Chemical data

The complete chemical characterization was carried out by combining electron-microprobe and ion-microprobe analysis with the results of the crystal-structure refinements. EMP analysis was done with an ARL microprobe at the Università di Modena,

¹ For a copy of Table 4, Document AM-04-060, 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 data refinement information for the specimens of this work

	SEQ	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	β (°)	<i>V</i> (Å ³)	space group	<i>Z</i>	θ_{max} (°)	<i>R</i> _{sym} %	<i>R</i> _{obs} %	<i>R</i> _{all} %	no. <i>F</i> _{all}	no. <i>F</i> _{obs}
ferriwhittakerite	975	9.712(9)	17.851(23)	5.297(2)	103.63(5)	892.5	<i>C2/m</i>	2	30	10.8	4.0	8.4	1353	756
ferri-ottoliniite	1041	9.535(3)	17.876(6)	5.294(2)	102.54(1)	880.9	<i>C2/m</i>	2	33	4.6	5.1	8.3	1646	1118

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*_{sym}), and for the observed and calculated structure factors (*F*) of all the reflections (*R*_{all}) and of those used for the refinement ($l > 3\sigma_l R_{obs}$).

TABLE 2. Atom coordinates, refined site-scattering values (ss, epfu), atomic-displacement parameters (B_{eq} , \AA^2 ; $\beta_{ii} \times 10^4$)

Atom	ss	x/a	y/b	z/c	B_{eq}	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
ferri-ottoliniite (SEQ 1041)											
O1		0.1126(4)	0.0907(2)	0.2063(7)	0.86	32(4)	4(1)	88(12)	-1(2)	12(5)	2(2)
O2		0.1213(4)	0.1726(2)	0.7326(7)	0.92	35(4)	7(1)	66(10)	1(2)	14(5)	-4(3)
O3	16.6	0.1141(6)	0	0.7013(9)	1.23	45(6)	6(1)	121(19)	-	15(8)	-
O4		0.3727(4)	0.2502(2)	0.7868(7)	1.11	49(4)	4(1)	97(12)	-6(2)	5(6)	2(3)
O5		0.3544(4)	0.1294(2)	0.0676(6)	0.96	38(4)	8(1)	51(11)	-3(2)	16(5)	8(2)
O6		0.3454(4)	0.1204(2)	0.5658(6)	1.00	36(4)	9(1)	59(11)	3(2)	9(5)	-12(3)
O7		0.3380(6)	0	0.2839(9)	1.07	42(6)	4(1)	132(18)	-	34(8)	-
T1		0.2856(2)	0.0860(1)	0.2806(3)	0.76	30(1)	4(1)	69(4)	0(1)	7(2)	-1(1)
T2		0.2957(1)	0.1707(1)	0.7895(3)	0.72	32(1)	3(1)	59(4)	-1(1)	6(2)	0(1)
M1	35.9	0	0.0882(1)	1/2	0.84	38(2)	4(1)	64(6)	-	14(2)	-
M2	49.7	0	0.1813(1)	0	0.68	29(2)	4(1)	56(4)	-	12(1)	-
M3	14.9	0	0	0	0.92	36(3)	6(1)	73(9)	-	11(4)	-
M4	9.0	0	0.2743(6)	1/2	2.62	111(16)	16(3)	209(39)	-	62(18)	-
Am	4.6	0.067(2)	1/2	0.136(4)	2.74	99(31)	17(6)	312(97)	-	119(42)	-
H	1.4	0.204(9)	0	0.771(9)	0.51						
M4'	3.1	0	0.2477(9)	1/2	1.92						
A	0.5	0	1/2	0	0.16						
ferriwhittakerite (SEQ 975)											
O1		0.1110(6)	0.0907(3)	0.2121(11)	0.69	24(6)	5(2)	58(18)	3(2)	18(8)	0(4)
O2		0.1195(6)	0.1711(3)	0.7325(10)	0.77	19(5)	5(2)	82(19)	0(2)	-9(8)	-3(4)
O3	17.3	0.1131(8)	0	0.7005(15)	1.27	49(10)	6(2)	97(29)	-	-8(12)	-
O4		0.3660(6)	0.2507(3)	0.7969(11)	0.97	35(6)	5(2)	91(19)	-3(2)	14(9)	-1(4)
O5		0.3513(7)	0.1290(3)	0.0802(11)	1.01	28(5)	10(1)	70(18)	-4(3)	5(7)	-3(5)
O6		0.3440(6)	0.1202(3)	0.5769(11)	0.93	28(5)	7(1)	74(18)	2(2)	0(8)	-9(4)
O7		0.3362(8)	0	0.2960(14)	0.84	15(7)	5(2)	116(27)	-	-3(11)	-
T1		0.2809(2)	0.0859(1)	0.2890(4)	0.55	20(2)	3(1)	50(7)	0(1)	4(3)	-1(1)
T2		0.2916(2)	0.1709(1)	0.7991(4)	0.63	22(2)	4(1)	52(7)	-1(1)	-1(3)	-2(1)
M1	33.3	0	0.0867(1)	1/2	0.77	23(4)	6(1)	70(11)	-	10(4)	-
M2	50.2	0	0.1798(1)	0	0.61	19(2)	4(1)	58(7)	-	4(3)	-
M3	8.9	0	0	0	0.98	30(2)	4(1)	109(33)	-	-12(12)	-
M4	17.6	0	0.2758(3)	1/2	1.24	44(8)	11(2)	105(24)	-	57(10)	-
A	1.8	0	1/2	0	2.23	66(51)	15(12)	264(164)	-	76(73)	-
Am	6.5	0.0548(18)	1/2	0.1126(31)	2.21	80(21)	15(5)	287(65)	-	151(30)	-
H	0.8	0.218(38)	0	0.786(66)	1.79						

TABLE 3. Selected refinement results [mean bond lengths (\AA) and interatomic angles ($^\circ$)] for the Li-rich amphiboles of this work

	1041	975		1041	975		1041	975
T1-O1	1.613(4)	1.606(6)	M1-O1	2.073(4)	2.065(6)	M4-O2 x2	2.355(8)	2.384(7)
T1-O5	1.620(4)	1.625(6)	M1-O2	2.125(4)	2.112(5)	M4-O4 x2	2.185(4)	2.314(6)
T1-O6	1.615(4)	1.623(6)	M1-O3	2.074(4)	2.044(6)	M4-O5 x2	2.958(7)	2.899(7)
T1-O7	1.615(4)	1.624(4)	<M1-O>	2.090	2.074	M4-O6 x2	2.462(9)	2.491(8)
<T1-O>	1.616	1.619	OAV	40.92	35.92	<M4-O>	2.490	2.522
TAV	2.59	7.11	OQE	1.012	1.011	M4'-O2 x2	2.010(4)	
TQE	1.001	1.002	M2-O1	2.112(4)	2.094(6)	M4'-O4 x2	2.140(4)	
T2-O2	1.624(4)	1.625(6)	M2-O2	2.019(4)	2.038(6)	M4'-O5 x2	3.257(4)	
T2-O4	1.601(4)	1.599(6)	M2-O4	1.911(4)	1.931(6)	M4'-O6 x2	2.842(4)	
T2-O5	1.634(4)	1.645(6)	<M2-O>	2.014	2.021	⁽⁸⁾ <M4'-O>	2.562	
T2-O6	1.638(4)	1.657(6)	OAV	31.15	30.26	⁽⁶⁾ <M4'-O>	2.331	
<T2-O>	1.624	1.631	OQE	1.011	1.010	A-O5	2.761(4)	2.802(6)
TAV	10.99	13.73	M3-O1	2.113(3)	2.115(6)	A-O6	3.258(4)	3.210(6)
TQE	1.003	1.003	M3-O3	2.105(5)	2.132(9)	A-O7	2.377(5)	2.483(8)
			<M3-O>	2.105	2.120	<A-O>	2.883	2.903
T1-T1	3.073(3)	3.069(6)	OAV	62.22	63.42	Am-O5 x2	3.046(15)	3.014(6)
T1-T2	3.074(2)	3.082(4)	OQE	1.019	1.020	Am-O5 x2	2.726(11)	2.758(6)
T1-T2	3.029(2)	3.027(4)				Am-O6 x2	2.691(15)	2.739(6)
						Am-O7	2.475(21)	2.534(8)
H-O3	0.855(5)	1.013(8)				Am-O7	3.005(23)	3.070(8)
O6-O7-O6	111.0	111.1				Am-O7	2.577(20)	2.624(8)
						<Am-O>	2.776	2.805

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

Italy. Analytical conditions were 15 kV accelerating voltage, 20 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, Ca, and Mg: clinopyroxene (ADP, PET, and RAP, respectively); Ti and Fe: ilmenite (PET, LiF); Al: sillimanite, TAP; Fe and Mn: ilmenite (LiF, PET); Al and Mn: spessartine (RAP, LiF); Na: albite (RAP); K: microcline (PET); F: fluorite (RAP); Zn: Zn100% (LiF); V, V100% (LiF). Data were processed using the

PROBE 5.2 program (Donovan and Rivers 1990).

Light and volatile elements (H, Li, B, Be, F, Cl) were analyzed with a Cameca IMS 4f probe (CNR-IGG-PV, Italy) with an $^{16}\text{O}^-$ primary beam with diameter $\sim 10 \mu\text{m}$ (corresponding to a beam current of $\sim 4 \text{nA}$). Secondary positive-ion currents were measured at masses 1 (H), 7 (Li), 19 (F), and 30 (Si, used as the reference element), and corrected for isotopic abundance. The accuracy of the SIMS analysis for H_2O and Li_2O was shown to

TABLE 5. Calculated CuK α (1.5418 Å) powder diffraction patterns for ferri-ottoliniite and ferriwhittakerite (reflections with $I/I_0 \geq 5$; the eight strongest reflections are in bold)

2 θ (°)	d_{calc} (Å)	<i>l</i>	<i>h</i>	<i>k</i>	<i>l</i>	2 θ (°)	d_{calc} (Å)	<i>l</i>	<i>h</i>	<i>k</i>	<i>l</i>	2 θ (°)	d_{calc} (Å)	<i>l</i>	<i>h</i>	<i>k</i>	<i>l</i>
ferri-ottoliniite (SEQ 1041)																	
9.90	8.938	6	0	2	0	32.54	2.752	19	3	3	0	54.37	1.687	6	5	1	2
10.72	8.256	100	1	1	0	33.06	2.709	81	1	5	1	55.11	1.666	6	2	8	2
17.16	5.168	5	0	0	1	33.83	2.650	13	3	3	1	56.00	1.642	18	4	6	1
18.42	4.817	12	1	1	1	34.76	2.581	26	0	6	1	57.15	1.612	6	4	8	0
19.84	4.474	21	0	2	1	35.90	2.501	43	2	0	2	57.57	1.601	8	1	11	0
19.87	4.469	33	0	4	0	39.54	2.279	19	3	5	1	58.34	1.582	19	1	5	3
23.22	3.831	7	1	3	1	40.61	2.222	16	3	1	2	61.64	1.505	11	2	6	3
24.88	3.579	19	2	2	1	41.51	2.175	8	1	7	1	62.33	1.490	8	0	12	0
26.16	3.407	45	1	3	1	41.82	2.160	25	2	6	1	66.92	1.398	17	6	6	1
26.71	3.338	6	1	5	0	43.16	2.096	7	3	3	2	68.41	1.371	8	5	1	2
27.67	3.224	10	2	4	0	43.60	2.076	11	2	0	2	74.07	1.280	10	2	12	2
29.21	3.057	56	3	1	0	45.02	2.014	11	3	5	1	82.17	1.173	6	5	11	2
ferriwhittakerite (SEQ 975)																	
9.91	8.926	18	0	2	0	39.07	2.306	23	3	5	1	56.78	1.621	11	4	8	0
10.60	8.344	98	1	1	0	39.59	2.276	11	1	7	1	57.63	1.599	11	1	11	0
17.62	5.034	10	1	3	0	40.01	2.254	24	3	1	2	58.38	1.581	21	1	5	3
18.27	4.857	12	1	1	1	41.62	2.170	8	1	7	1	61.40	1.510	10	6	0	2
19.89	4.463	44	0	4	0	41.89	2.157	35	2	6	1	61.45	1.509	17	2	6	3
19.91	4.459	28	0	2	1	42.60	2.122	13	3	3	2	62.43	1.488	12	0	12	0
22.10	4.023	7	1	1	1	43.85	2.064	15	2	0	2	65.81	1.419	25	6	6	1
24.51	3.633	18	2	2	1	44.99	2.015	14	3	5	1	68.41	1.371	12	5	1	2
26.27	3.392	74	1	3	1	45.62	1.988	10	4	0	2	70.56	1.335	7	1	11	2
27.51	3.243	16	2	4	0	46.80	1.941	5	1	9	0	71.86	1.314	6	1	1	4
28.81	3.098	72	3	1	0	47.11	1.929	7	4	2	1	73.21	1.293	6	7	5	1
30.25	2.954	10	2	2	1	48.59	1.874	6	2	4	2	73.96	1.282	14	2	12	2
32.18	2.781	29	3	3	0	51.09	1.788	7	1	9	1	75.32	1.262	5	4	0	4
33.17	2.701	100	1	5	1	53.23	1.721	7	5	1	2	81.31	1.183	7	5	11	2
33.27	2.693	30	3	3	1	54.27	1.690	8	1	3	3	94.57	1.049	6	5	11	2
34.83	2.576	36	0	6	1	54.93	1.672	8	2	8	2	96.03	1.037	6	7	11	0
35.58	2.524	67	2	0	2	55.86	1.646	26	4	6	1	98.49	1.018	5	1	17	1

be around 10–15% rel, and 10% for F, B, Be, and Cl ion signals, tested at 11, 9, and 37 mass numbers (amu), were negligible. Detailed analytical procedures are described by Ottolini and Oberti (2000). Unit formulae were calculated on the basis of 24 (O, OH, F) apfu, and adjusting the Fe³⁺/Fe_{tot} ratio so as to obtain 8.0 Si apfu (cf. Oberti et al. 2003a for detail). Holotype ferri-ottoliniite is: ^A(K_{0.07}Na_{0.38})^B(Na_{0.70}Li_{1.24}Ca_{0.06})^C(Mg_{1.35}Fe_{0.92}Mn_{0.13}Zn_{0.31}Fe_{1.71}Al_{1.0}Ti_{0.06}Li_{0.42})Si₈O₂₂(OH_{1.51}F_{0.47}). Holotype ferriwhittakerite is ^A(K_{0.13}Na_{0.64})^B(Na_{1.27}Li_{0.62}Ca_{0.11})^C(Mg_{1.47}Fe_{0.58}Mn_{0.12}Zn_{0.40}Fe_{1.48}Al_{1.0}Ti_{0.12}Li_{0.73})Si₈O₂₂(OH_{1.30}F_{0.72}). 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. The refined octahedral mean bond lengths are in agreement with the calculated Fe³⁺/Fe_{tot} ratio. Both SIMS analysis for F and H and geometrical features confirm that (OH + F) = 2 apfu, thus eliminating the possibility of partial dehydrogenation.

DISCUSSION AND NOMENCLATURE CHANGES FOR LI-RICH AMPHIBOLES

Leake et al. (2004) reported on the changes in amphibole nomenclature which originated by the discovery of a complete solid-solution between Na and Li at the B-group sites in amphiboles occurring in metamorphic epysyenites in the Pedriza Massif (Spain). Here we discuss the consequences of those decisions on the nomenclature of Li-rich (Li > 0.50 apfu) amphiboles.

The compositional space of ^B(Ca,Na) amphiboles (Groups 2, 3, 4) is limited by 1.5 ≤ ^B(Ca,Na) ≤ 2.0 apfu, similar to that of ^B(Mg,Fe²⁺,Mn²⁺,Li) amphiboles (Group 1), which is now 1.5 ≤

^B(Mg,Fe²⁺,Mn²⁺,Li) ≤ 2.0 apfu. When 0.5 < ^B(Mg,Fe²⁺,Mn²⁺,Li) < 1.5 and 0.5 ≤ ^B(Ca,Na) ≤ 1.5, amphiboles belong to the new Group 5. The new compositional diagram for the ^B(LiNa₁) solid-solution is shown in Figure 1, where all the analyses of Li-rich amphiboles (cf. Oberti et al. 2003a for a review) are also reported. When ^BLi is > 0.5 apfu, two new root names must be used as a reference in this compositional space. Root-name “ottoliniite” corresponds to the ideal composition ^A□^B(NaLi)^C(Mg₃AlFe³⁺)Si₈O₂₂(OH)₂, whereas root-name “whittakerite” corresponds to ^ANa^B(NaLi)^C(Mg₂AlFe³⁺Li)Si₈O₂₂(OH)₂ (Fig. 1). The proper prefixes (Leake et al. 2004) must be added to these root names to derive the correct end-member names. The use of the prefix “sodic” for Group 1 amphiboles (which had been modified by IMA-CNMMN in 2001 when dealing with the former ferripedrizite; Caballero et al. 2002) has now been brought back to the definition of Leake et al. (1997), i.e., Na_{tot} > 0.5 apfu. As a consequence, many of the formerly approved end-member names must be modified. The specimen reported by Caballero et al. (1998) is now sodic-ferri-clinoferroholmquistite; of the two specimens reported by Oberti et al. (2000), one (d1 in Fig. 1) is now ferriwhittakerite, and the second (d2) is sodic-ferripedrizite; the specimen reported by Caballero et al. (2002) is no longer an end member, because it must also be referred as sodic-ferripedrizite; specimen 975 is ferriwhittakerite, and specimen 1041 is ferri-ottoliniite. Specimens 1039 and 1043, for which analyses had been provided by Oberti et al. (2003a), are the new end-members sodic-ferri-ferripedrizite and ferri-clinoferroholmquistite. Their mineral data are reported elsewhere (Oberti et al. 2003b).

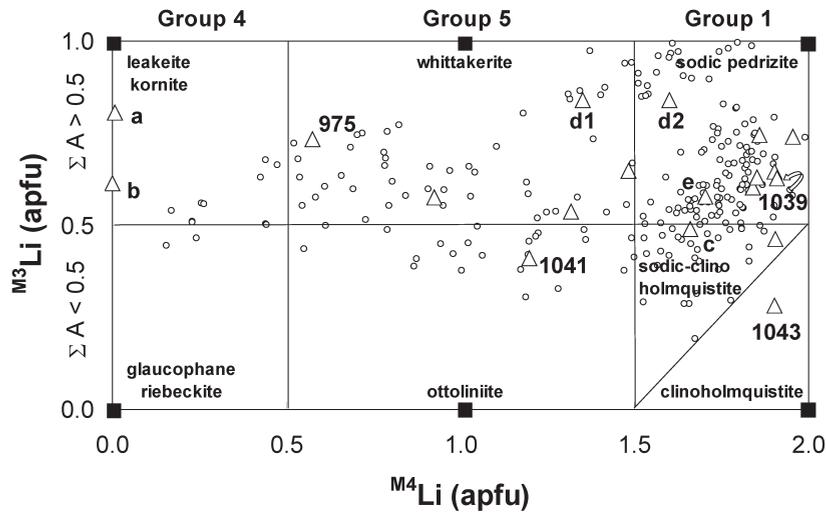


FIGURE 1. Compositional diagram relevant to the ${}^B(\text{Li}_1\text{Na}_1)$ solid solution in amphiboles. Because ${}^C\text{Li}$ is always $\leq {}^A(\text{Na},\text{K})$ the ordinate implicitly corresponds to the A-site occupancy. The root names to be used after Leake et al. (2004) are shown, which should be combined with the proper prefix to obtain the correct end-member name. a = Hawthorne et al. (1992), leakeite; b = Hawthorne et al. (1998), fluoro-ferrileakeite; c = Caballero et al. (1998), now sodic-ferri-clinoferroholmquistite; d = Oberti et al. (2000), d1 is now ferriwhittakerite and d2 is sodic-ferripedrizite; e = Caballero et al. (2002), now sodic-ferripedrizite. Open triangles are the refined crystals and open circles are the analyses reported by Oberti et al. (2003a); 975 and 1041 are ferriwhittakerite and ferri-ottoliniite (this work), 1039 and 1043 are the new end-members sodic-ferri-ferropedrizite and ferri-clinoferroholmquistite (Oberti et al. 2004b).

TABLE 6. Chemical analyses (EMPA + SIMS) and unit formulae [on the basis of 24 (O + F) and 8 Si apfu], and a comparison between refined (ref) and calculated (calc) group-site scattering values (ss)

	1041	975
SiO ₂	55.25	54.26
TiO ₂	0.52	1.07
Al ₂ O ₃	0.60	0.57
Fe ₂ O ₃	15.7	13.36
FeO	7.61	4.68
MnO	1.08	0.97
MgO	6.28	6.69
ZnO	2.90	3.66
Li ₂ O _{SIMS}	2.84	2.28
CaO	0.41	0.67
Na ₂ O	3.84	6.71
K ₂ O	0.40	0.72
F _{SIMS}	1.03	1.55
H ₂ O _{SIMS}	1.57	1.32
O=F	0.43	0.65
Total	99.60	97.86
Si	8.00	8.00
Al	0.10	0.10
Mg	1.35	1.47
Ti	0.06	0.12
Fe ²⁺	0.92	0.58
Fe ³⁺	1.71	1.48
Mn ²⁺	0.13	0.12
Zn ²⁺	0.31	0.40
Li	0.42	0.73
Sum C	5.00	5.00
Li	1.24	0.62
Ca	0.06	0.11
Na	0.70	1.27
Sum B	2.00	2.00
Na	0.38	0.64
K	0.07	0.13
Sum A	0.45	0.77
F	0.47	0.72
OH	1.51	1.30
Sum O3	1.98	2.02
OS	0.65	0.72
ss C _{cal}	101.0	92.3
ss B _{cal}	12.6	18.0
ss A _{cal}	5.5	9.5
ss tot _{cal}	119.1	119.9
ss C _{ref}	100.5	92.4
ss B _{ref}	12.1	17.6
ss A _{ref}	5.1	8.3
ss tot _{ref}	117.7	118.3

Crystal-chemical features

Inspection of the refined mean bond distances and scattering values for the various structural sites allows site populations to be derived for the two end-members of this work. The $\langle\text{T1-O}\rangle$ and $\langle\text{T2-O}\rangle$ distances confirm that only Si occurs at the tetrahedral sites. Given the good agreement between calculated and refined site-scattering values, the site populations at the A- and B-group sites are those of Table 6. A-site cations are strongly ordered at the position (Oberti et al. 2003b). More detail can be provided for the octahedral C-group sites. Based on the refined site-scattering and bond-length values, Zn is distributed between the M1 and M2 sites, similarly to what is found in other Zn-rich amphiboles from Pedriza (Oberti et al. 2003a) and from peralkaline granites at Strange Lake (Quebec; Hawthorne et al. 2001). The trivalent cations are all ordered at the M2 site, whereas Li is ordered, together with Mn²⁺, at the M3 site. The proposed site populations are: M1 = Mg_{1.21} Fe_{0.55} Zn_{0.24} (ss_{cal} = 36.0, ss_{ref} = 35.9 apfu) and Mg_{1.38} Fe_{0.45} Zn_{0.17} (ss_{cal} = 33.3, ss_{ref} = 33.3 apfu); M2 = Fe_{1.71} Al_{0.10} Ti_{0.06} Zn_{0.07} Mg_{0.06} (ss_{cal} = 49.9, ss_{ref} = 49.7 apfu) and Fe_{1.48} Al_{0.10} Ti_{0.12} Zn_{0.23} Mg_{0.07} (ss_{cal} = 50.2, ss_{ref} = 50.2 apfu); M3 = Li_{0.42} Mn_{0.13} Fe_{0.37} Mg_{0.08} (ss_{cal} = 15.1, ss_{ref} = 14.9 apfu) and Li_{0.73} Mn_{0.12} Fe_{0.13} Mg_{0.02} (ss_{cal} = 8.8, ss_{ref} = 8.9 apfu) for ferri-ottoliniite and ferriwhittakerite, respectively.

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