SODIC-FERRI-FERROPEDRIZITE AND FERRI-CLINOFERROHOLMQUISTITE: MINERAL DATA AND DEGREE OF ORDER OF THE *A*-SITE CATIONS IN Li-RICH AMPHIBOLES

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ABSTRACT

A systematic examination of metamorphic episyenites in the Pedriza Massif, Sierra de Guadarrama, Spain, allowed detection of two more distinct Li-rich $C2/m$ amphibole species. They can be related to previously described species *via* the homovalent exchanges $^{M1}(Fe^{2+}Mg_{-1})$ and $^{M2}(Fe^{3+}Al_{-1})$, and represent the compositions richest in Fe in this compositional space. The ideal formula of ferri-clinoferroholmquistite is $^A\square\ ^BLi_2\ ^C(Fe^{3+}_2Fe^{2+}_3)\ ^TSi_8\ O_{22}\ ^X(OH)_2$, and that of sodic-ferri-ferropedrizite is $^ANa\ ^BLi_2\ ^C(Fe^{3+}_2Fe^{2+}_2Li)\ ^TSi_8\ O_{22}\ ^X(OH)_2$, with $Z = 2$. Holotype ferri-clinoferroholmquistite (IMA–CNMMN 2001–066), $^A(Na_{0.28}K_{0.00})_{\Sigma0.28}$ $^B(Li_{1.90}Na_{0.08}Ca_{0.02})_{\Sigma2.00}\ ^C(Fe^{3+}_{1.68}Fe^{2+}_{1.55}Mg_{1.06}Li_{0.28}Al_{0.26}Ti_{0.01}Mn^{2+}_{0.14}Zn_{0.02})_{\Sigma5.00}\ ^TSi_{8.00}\ O_{22}\ ^{O3}(OH_{1.79}F_{0.24})_{\Sigma2.03}$, has a 9.462(6), b 17.898(9), c 5.302(3) Å, β 101.88(4)°, V 878.6(2) Å³. Holotype sodic-ferri-ferropedrizite (IMA–CNMMN 2001–068), $^A(Na_{0.53}K_{0.03})_{\Sigma0.56}\ ^B(Li_{1.82}Na_{0.15}Ca_{0.03})_{\Sigma2.00}\ ^C(Fe^{3+}_{1.55}Fe^{2+}_{1.49}Mg_{0.95}Li_{0.58}Al_{0.21}Ti_{0.13}\ Mn^{2+}_{0.07}Zn_{0.01})_{\Sigma4.99}\ ^TSi_{8.00}\ O_{22}$ $^X(OH_{1.45}F_{0.52})_{\Sigma1.97}$, has a 9.496(4), b 17.883(8), c 5.297(2) Å, β 102.06(3)°, V 879.6(2) Å³. Sodic-ferri-ferropedrizite and ferri-clinoferroholmquistite are both black, with a vitreous luster. They have a gray streak and do not show fluorescence under long- and short-wave ultraviolet light; they are brittle with an uneven fracture, and have the characteristic {110} cleavage of monoclinic amphiboles. The calculated values of density are 3.23 and 3.24 g/cm³, and the calculated mean indices of refraction are 1.708 and 1.710, respectively. The shape of the electron density at the A sites changes as a function of the ^BLi and ^CLi contents, suggesting that cation ordering is strongly affected by local bond-valence requirements. This feature is confirmed by systematic bond-valence – bond-strength calculations, which support the sequence $(^{M4'}Li–^{O3}F–^{Am}Na) > (^{M4'}Li–^{O3}OH–^{Am}Na)$ of preferred local configurations.

Keywords: amphibole, lithium, structure refinement, ion-microprobe data, Pedriza Massif, Spain.

SOMMAIRE

Une étude systématique de la suite d'épisyénites métamorphiques du massif de Pedriza, Sierra de Guadarrama, en Espagne, nous a permis de découvrir deux nouvelles espèces d'amphiboles $C2/m$ riches en Li. On peut les relier à d'autres espèces décrites récemment par échange homovalente $^{M1}(Fe^{2+}Mg_{-1})$ et $^{M2}(Fe^{3+}Al_{-1})$; elles représentent les compositions les plus riches en Fe dans cet intervalle de composition. La formule idéale de la ferri-clinoferroholmquistite serait $^A\square\ ^BLi_2\ ^C(Fe^{3+}_2Fe^{2+}_3)\ ^TSi_8\ O_{22}\ ^X(OH)_2$, et celle de la sodic-ferri-ferropedrizite, $^ANa\ ^BLi_2\ ^C(Fe^{3+}_2Fe^{2+}_2Li)\ ^TSi_8\ O_{22}\ ^X(OH)_2$, avec $Z = 2$. L'échantillon holotype de ferri-clinoferroholmquistite (IMA–CNMMN 2001–066), $^A(Na_{0.28}K_{0.00})_{\Sigma0.28}\ ^B(Li_{1.90}Na_{0.08}Ca_{0.02})_{\Sigma2.00}\ ^C(Fe^{3+}_{1.68}Fe^{2+}_{1.55}Mg_{1.06}Li_{0.28}Al_{0.26}Ti_{0.01}Mn^{2+}_{0.14}Zn_{0.02})_{\Sigma5.00}\ ^TSi_{8.00}\ O_{22}\ ^{O3}(OH_{1.79}F_{0.24})_{\Sigma2.03}$, possède les paramètres suivants: a 9.462(6), b 17.898(9), c 5.302(3) Å, β 101.88(4)°, V 878.6(2) Å³. L'échantillon holotype de sodic-ferri-ferropedrizite (IMA–CNMMN 2001–068), $^A(Na_{0.53}K_{0.03})_{\Sigma0.56}\ ^B(Li_{1.82}Na_{0.15}Ca_{0.03})_{\Sigma2.00}\ ^C(Fe^{3+}_{1.55}Fe^{2+}_{1.49}Mg_{0.95}Li_{0.58}Al_{0.21}Ti_{0.13}Mn^{2+}_{0.07}Zn_{0.01})_{\Sigma4.99}\ ^TSi_{8.00}\ O_{22}\ ^X(OH_{1.45}F_{0.52})_{\Sigma1.97}$, fournit les paramètres a 9.496(4), b 17.883(8), c 5.297(2) Å, β 102.06(3)°, V 879.6(2) Å³. La sodic-ferri-ferropedrizite et la ferri-clinoferroholmquistite forment des cristaux noirs, avec un éclat vitreux. Ces amphiboles ont une rayure grise et ne montrent

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aucun signe de fluorescence en lumière ultra-violette (ondes courtes ou longues). Les cristaux sont cassants, la fracture est irrégulière, et ils montrent les clivages {110} caractéristiques des amphiboles monocliniques. Les valeurs calculées de la densité sont 3.23 et 3.24 g/cm^3, et les indices de réfraction moyens, calculés, sont 1.708 et 1.710, respectivement. La forme de la distribution des électrons autour du site A varie en fonction des teneurs en ^{B}Li et ^{C}Li, nous faisant penser que la mise en ordre des cations est fortement affectée par les exigeances locales en valences de liaisons. Un calcul systématique des valences de liaisons en fonction de la force des liaisons confirme notre hypothèse, et la séquence ($^{M4'}$Li–^{O3}F–^{Am}Na) > ($^{M4'}$Li–^{O3}OH–^{Am}Na) des agencements locaux préférés.

(Traduit par la Rédaction)

Mots-clés: amphibole, lithium, affinement de la structure, données de microsonde ionique, complexe de Pedriza, Espagne.

INTRODUCTION

In the new report on the nomenclature of the amphibole group, Leake *et al*. (2003) have recognized the relevance of the complete solid-solution between Na and Li at the *B*-group site, as observed in metamorphic episyenites from the Pedriza Massif, Sierra de Guadarrama, Spain (*cf.* Oberti *et al*. 2003 for a review). As a consequence, a new group of amphiboles (Group 5) defined as $0.50 < {}^B$(Mg,Fe,Mn,Li) < 1.50 atoms per formula unit (*apfu*) *and* $0.50 \leq {}^B$(Ca,Na) ≤ 1.50 *apfu*, has been added for classification purposes, and the compositional field of Group-1 amphiboles has been reduced to $1.50 < {}^B$(Mg,Fe,Mn,Li) < 2.0 *apfu*. In this paper, we report mineral data and crystal-chemical features of the amphibole end-members richest in Fe and ^{B}Li found at the Pedriza Massif, namely ferri-clinoferroholmquistite (IMA–CNMMN 2001–066) and sodic-ferri-ferropedrizite (IMA–CNMMN 2001–068). Many changes were done in the nomenclature of the Li-rich amphiboles in an attempt to rationalize the various problems that arose as a result of the latest findings. Therefore, we provide in Table 1 a summary of the situation after the Leake *et al*. (2003) report, to be used as a reference throughout this paper. A detailed discussion on the incorporation of Li at the *B*- and *C*-group sites of the amphibole structure has been provided by Oberti *et al.* (2003), together with a simple procedure for the evaluation of the Li content on the basis of electron-microprobe (EMP) data and crystal-chemical constraints. Experimental studies also have been undertaken to characterize the stability of ferri-clinoferroholmquistite (Iezzi *et al*. 2003a) and short-range order along the ferri-clinoferroholmquistite–riebeckite join (Iezzi *et al*. 2003b). On the basis of the available crystal-chemical knowledge, we address in this paper a still unexplored issue, namely the ordering and coordination of the *A*-cations in Li-rich amphiboles.

OCCURRENCE

Both the new amphiboles occur in the episyenitic bodies, located in the eastern sector of the Pedriza Massif, Sierra de Guadarrama, Spanish Central System, together with the other previously described Li-rich amphiboles (sodic-ferri-clinoferroholmquistite, sodic-ferripedrizite, ferriwhittakerite and ferri-ottoliniite; Caballero *et al.* 1998, 2002, Oberti *et al*. 2004; names modified after Leake *et al*. 2003). As with the other Li-rich amphiboles from the Pedriza Massif, these minerals formed during episyenite formation (desilication 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 oxygen isotope systematics determined on mineral concentrates) and fluid pressures ranging from 60 to 160 MPa. In general, amphiboles with higher Mg/Fe values suggest relatively higher temperature of formation with respect to the Fe-rich compositions. Experimental studies on nominal ferri-clinoferroholmquistite showed that this composition is stable in a narrow *T* range (around 500°C) and *P* varying from 1 to 7 kbar, but is replaced by Li-bearing clinopyroxene at $T \geq 600$°C (Iezzi *et al*. 2003a). There are strong inter- and intracrystalline compositional variations, and the Li content of these amphiboles seems to be controlled mainly by the composition of the fluid.

Associated minerals are: (1) a magmatic association: quartz, calcic plagioclase cores and K-feldspar (microcline), partially albitized, feldspar-armored annite and zircon, (2) an episyenitic association: albite, Li-rich augite–aegirine, 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, ferro-actinolite, chlorite, and (c) muscovite, hematite, clay minerals, and clinozoisite.

Type material was collected for both amphiboles in the Arroyo de la Yedra valley, with U.T.M. coordinates 4 28 590 longitude and 45 14 875 latitude [Spanish Military Map number 509 (19–201), scale 1:50,000, 4th edition (1986)]. The sample code is C2A for sodic-ferri-ferropedrizite and C2B for ferri-clinoferroholmquistite. The analyzed crystals and crystal concentrates from the same rock samples have been deposited at the Museo di Mineralogia, Dipartimento di Scienze della Terra, Università degli Studi di Pavia, under the codes 2001–02 (sodic-ferri-ferropedrizite) and 2001–03 (ferri-clinoferroholmquistite).

TABLE 1. A BRIEF DESCRIPTION OF THE END MEMBERS AND OF THE HOLOTYPE SPECIMENS OF THE Li-BEARING $C2/m$ AMPHIBOLES FOUND AT THE PEDRIZA MASSIF, SPAIN

End-member names and ideal compositions (after Leake et al. 2003)

Ferri-ottoliniite	Ferriwhittakerite	Sodic-ferri-ferropedrizite	Sodic-ferripedrizite	Sodic-ferri-clinoferroholmquistite	Ferri-clinoferroholmquistite
$^{A}\square$ $^{B}(NaLi)_2$ $^{C}(Mg^{2+}_3AlFe^{3+})$ $^{T}Si_8 O_{22} {}^{X}(OH)_2$ Group 5	^{A}Na $^{B}(NaLi)_2$ $^{C}(Mg^{2+}_2Fe^{3+}Li)$ $^{T}Si_8 O_{22} {}^{X}(OH)_2$ Group 5	^{A}Na $^{B}Li_2$ $^{C}(Fe^{2+}_2Fe^{3+}_2Li)$ $^{T}Si_8 O_{22} {}^{X}(OH)_2$ Group 1*	^{A}Na $^{B}Li_2$ $^{C}(Mg_2Fe^{3+}_2Li)$ $^{T}Si_8 O_{22} {}^{X}(OH_2)$ Group 1*	$^{A}\square$ $^{B}Li_2$ $^{C}(Fe^{2+}_3Fe^{3+}_2)$ $^{T}Si_8 O_{22} {}^{X}(OH)_2$ Group 1*	$^{A}\square$ $^{B}Li_2$ $^{C}(Fe^{2+}_3Fe^{3+}_2)$ $^{T}Si_8 O_{22} {}^{X}(OH_2)$ Group 1

Crystallographic data

	Ferri-ottoliniite	Ferriwhittakerite	Sodic-ferri-ferropedrizite	Sodic-ferripedrizite	Sodic-ferri-clinoferroholmquistite	Ferri-clinoferroholmquistite
a	9.535 Å	9.712 Å	9.496 Å	9.534 Å	9.480 Å	9.462 Å
b	17.876 Å	17.851 Å	17.883 Å	17.785 Å	17.845 Å	17.898 Å
c	5.294 Å	5.297 Å	5.297 Å	5.278 Å	5.283 Å	5.302 Å
β	102.59°	103.63°	102.06°	102.52°	102.03°	101.88°
V	881 Å³	892 Å³	880 Å³	874 Å³	874 Å³	879 Å³

Strongest lines in the powder-diffraction pattern (d / I_{rel} / hkl)

Ferri-ottoliniite	Ferriwhittakerite	Sodic-ferri-ferropedrizite	Sodic-ferripedrizite	Sodic-ferri-clinoferroholmquistite	Ferri-clinoferroholmquistite
8.256 100 110	8.344 91 110	8.241 100 $\bar{1}10$	8.246 24 110	8.222 61 110	8.224 100 110
4.474 21 021	4.463 41 040	4.482 21 021	4.446 22 040	4.458 19 040	4.474 31 040
4.470 33 040	3.392 69 131	4.471 33 040	3.397 28 131	3.217 12 240	3.554 19 $\bar{2}21$
3.579 19 $\bar{2}21$	3.098 67 310	3.563 23 $\bar{2}21$	3.056 100 310	3.044 100 310	3.420 30 131
3.407 45 131	2.781 27 330	3.416 41 131	2.749 54 330	2.741 53 330	3.042 54 310
3.057 56 310	2.701 100 151	3.050 60 310	2.699 60 $1\bar{5}1$	2.712 14 151	2.717 70 151
2.709 81 151	2.576 33 $0\bar{6}1$	2.714 72 151	2.494 18 $\bar{2}02$	2.341 14 112	2.586 21 $0\bar{6}1$
2.581 26 $0\bar{6}1$	2.693 28 $\bar{3}31$	2.583 22 $0\bar{6}1$	2.153 18 261	1.643 12 $\bar{3}71$	2.492 32 $\bar{2}02$
2.501 43 $\bar{2}02$	2.524 62 $\bar{2}02$	2.494 36 $\bar{2}02$	1.920 20 421	1.433 46 $\underline{2}43$	2.268 17 $\bar{3}51$
2.160 25 261	2.157 32 261	2.164 24 261	1.639 44 $\bar{4}61$	1.392 14 $\bar{6}42$	2.165 22 261
			1.396 23 $\bar{6}61$		

Selected geometrical parameters

	Ferri-ottoliniite	Ferriwhittakerite	Sodic-ferri-ferropedrizite	Sodic-ferripedrizite	Sodic-ferri-clinoferroholmquistite	Ferri-clinoferroholmquistite
<M1-O>	2.094	2.074	2.101	2.076	2.096	2.104
<M2-O>	2.014	2.021	2.009	2.007	2.007	2.010
<M3-O>	2.105	2.120	2.113	2.114	2.106	2.109
<M4-O>	2.490	2.522	2.525	2.488	2.476	2.511
<M4'-O>	2.331		2.482	2.327		
<Am-O>	2.776	2.802	2.770	2.757	2.765	2.774

Chemical formulae of the holotypes, with references:

Ferri-ottoliniite: $(Na_{0.38}K_{0.07})$ $(Li_{1.24}Na_{0.70}Ca_{0.06})$ $(Mg_{1.35}Fe^{2+}_{0.92}Mn_{0.13} Zn_{0.31}Fe^{3+}_{1.71}Al_{0.10}Ti_{0.06}Li_{0.42})$ $Si_{8.00} O_{22} (OH_{1.51}F_{0.47})$ (Oberti et al. 2004).

Ferriwhittakerite: $(Na_{0.64}K_{0.13})$ $(Li_{0.62}Na_{1.27}Ca_{0.11})$ $(Mg_{1.47}Fe^{2+}_{0.58}Mn_{0.12} Zn_{0.40}Fe^{3+}_{1.48}Al_{0.10}Ti_{0.12}Li_{0.73})$ $Si_{8.00} O_{22} (OH_{1.30}F_{0.72})$ (Oberti et al. 2004).

Sodic-ferri-ferropedrizite: $(Na_{0.53}K_{0.03})$ $(Li_{1.82}Na_{0.15}Ca_{0.03})$ $(Mg_{0.95}Fe^{2+}_{1.49}Mn_{0.07} Zn_{0.01}Fe^{3+}_{1.55}Al_{0.21}Ti_{0.13}Li_{0.58})$ $Si_{8.00} O_{22} (OH_{1.07}F_{0.93})$ (this work).

Sodic-ferripedrizite: $(Na_{0.95}K_{0.03})$ $(Li_{1.60}Na_{0.35}Ca_{0.05})$ $(Mg_{1.77}Fe^{2+}_{0.60}Mn_{0.07} Zn_{0.01}Fe^{3+}_{1.39}Al_{0.21}Ti_{0.11}Li_{0.84})$ $Si_{8.00} O_{22} (OH_{1.07}F_{0.93})$ [Oberti et al. 2000, # P(2)].

Sodic-ferri-clinoferroholmquistite: $(Na_{0.44}K_{0.03})$ $(Li_{1.66}Na_{0.30}Ca_{0.04})$ $(Fe^{2+}_{1.35}Mg_{1.21}Mn_{0.07}Zn_{0.02}Fe^{3+}_{1.54}Al_{0.20}Ti_{0.12}Li_{0.49})$ $Si_{8.00} O_{22} (OH_{1.58}F_{0.42})$ (Caballero et al. 1998).

Ferri-clinoferroholmquistite: $(Na_{0.26}K_{0.00})$ $(Li_{1.90}Na_{0.08}Ca_{0.02})$ $(Mg_{1.06}Fe^{2+}_{1.55} Mn_{0.14}Zn_{0.02}Fe^{3+}_{1.68}Al_{0.26}Ti_{0.01}Li_{0.28})$ $Si_{8.00} O_{22} (OH_{1.79}F_{0.24})$ (this work).

Note that in amphiboles of Group 1, $1.5 < {}^{B}(Mg,Fe,Mn,Li) < 2.0$ apfu; in those of Group 5, $0.5 \leq {}^{B}(Ca,Na) \leq 1.5$ and $0.5 < {}^{B}(Mg,Fe,Mn,Li) < 1.5$ apfu.

* In Group-1 amphiboles, the prefix sodic must be used if Na_{tot} exceeds 0.5 apfu.

APPEARANCE AND PHYSICAL PROPERTIES

All the Li-rich amphiboles found at Pedriza appear as intergranular granoblastic aggregates of subhedral to euhedral habit associated with fine-grained albite and pyroxene or as micro-inclusions in albite, quartz and titanite. With the naked eye, they cannot often be distinguished from one another. EMP data on thin sections show that both the amphiboles share the same textural topology and may occur in different micro-domains.

Sodic-ferri-ferropedrizite and ferri-clinoferroholmquistite are both black with a vitreous luster. They have a gray streak and do not show fluorescence under long- and short-wave ultraviolet light; they are brittle with an uneven fracture, and have the characteristic {110} cleavage of monoclinic amphiboles. Twinning has not been observed. Because the exact composition can be recognized solely from results of electron- and ion-microprobe analysis, the density and the optical properties could not be measured, given the very small size of the relict crystal. The calculated density values are 3.23 and 3.24 g/cm³, respectively. Assuming perfect compatibility, Gladstone–Dale calculations indicate that the mean index of refraction is 1.708 for sodic-ferri-ferropedrizite and 1.710 for ferri-clinoferroholmquistite.

X-RAY ANALYSIS AND STRUCTURE REFINEMENT

Crystals were selected on the basis of optical and diffraction properties. X-ray analysis and data collection were done on a Philips PW–1100 four-circle diffractometer with graphite-monochromatized MoKα

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 $-30 < \theta < 30°$. 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 (E. Cannillo, unpubl. data). More detail on data treatment and refinement can be found in Oberti *et al.* (2003), where unit-cell parameters and chemical compositions of these two crystals are presented in order to discuss the extent of $^B(NaLi_{-1})$ solid solution in amphiboles. In Table 2, we report selected crystal and refinement data, in Table 3, atom coordinates, displacement parameters and refined site-scattering (*ss*, *epfu*) values, and in Table 4, the geometrical parameters relevant for the description of the crystal structure. Lists of observed and calculated structure-factors may be obtained from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2, Canada. In these and in the following tables, specimens have been designated with their sequence number in the CNR–IGG database: 1039: sodic-ferri-ferropedrizite, 1043: ferri-clinoferroholmquistite (Table 2).

Owing to extensive intracrystalline chemical variability at the Pedriza Massif, where different amphiboles can be found at the centimeter scale, X-ray powder-diffraction data for Cu*K*α radiation were calculated from the intensities recorded on the holotype crystal. They are reported in Table 5.

CHEMICAL DATA

The complete chemical characterization of the crystals used for the structure refinement was done by electron-microprobe (EMP) and ion-microprobe analysis on the refined crystal. EMP analysis was done with an ARL microprobe at the Università di Modena e Reggio Emilia, 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*α 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: metallic Zn (LiF), V, metallic V(LiF). Data were processed using the PROBE 5.2 program (Donovan & Rivers 1990).

Concentrations of the light and volatile elements (H, Li, B, Be, F, Cl) were established with a Cameca IMS 4f probe (CNR–IGG–PV, Italy) with an $^{16}O^-$ primary beam with diameter ~10 μm (corresponding to a beam current of ~4 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 ion-microprobe analytical results for H_2O and Li_2O is around 10–15% rel., and 10% for F. The amounts of B, Be and Cl, tested at mass numbers (*amu*) 11, 9, and 37, were found to be negligible. Detailed analytical procedures were described by Ottolini & Oberti (2000). Unit formulae were calculated on the basis of 24 (O, OH, F) *apfu*, and adjusting the $Fe^{3+}:Fe_{tot}$ ratio so as to obtain 8.0 Si *apfu* [*cf.* Oberti *et al.* (2003) for details]. The good agreement between the site-scattering values calculated from the unit formula and those resulting from structure refinement (Table 6) validates the analytical approach and the unit-formula recalculation. The refined mean bond-lengths at the octahedrally coordinated sites are in agreement with the calculated $Fe^{3+}:Fe_{tot}$ ratio. Both SIMS analysis for F and H and geometrical features confirm that (OH + F) = 2 *apfu*.

CRYSTAL CHEMISTRY

As is the case for other Li-rich amphiboles, *C*-group Li is ordered at the *M*3 site. *M*-site populations can be inferred by combining refined site-scattering values and mean bond-lengths. The best partitioning of *M*(1,2,3) cations was calculated starting from the unit-formulae reported in Table 6. Ferri-clinoferroholmquistite (1043): $^{M1}(Mg_{1.02}Fe^{2+}_{0.98})$ $^{M2}(Fe^{3+}_{1.68}Al_{0.26}Ti_{0.01}Zn_{0.02}Fe^{2+}_{0.03})$

TABLE 2. CRYSTAL DATA AND SELECTED INFORMATION CONCERNING
THE STRUCTURE REFINEMENT OF THE SAMPLES INVESTIGATED

	SEQ	*a* (Å)	*b* (Å)	*c* (Å)	β (°)	*V* (Å³)	θ$_{max}$ (°)	R_{sym} %	R_{obs} %	R_{all} %	# F_{all}	# F_{obs}
ferri-clinoferroholmquistite	1043	9.462(6)	17.898(9)	5.302(3)	101.88(4)	878.6	35	2.1	2.2	3.3	2002	1709
sodic-ferri-ferropedrizite	1039	9.496(4)	17.883(8)	5.297(2)	102.06(3)	879.6	35	1.2	1.6	2.2	2006	1892

Note: 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 ($I > 3σ_I$, R_{obs}).

TABLE 3. ATOM COORDINATES, REFINED SITE-SCATTERING VALUES (ss, EPFU), ATOMIC-DISPLACEMENT PARAMETERS (B_{EQ}, Å^2) FOR FERRI-CLINOFERROHOLMQUISTITE AND SODIC-FERRI-FERROPEDRIZITE

Atom	ss	x/a	y/b	z/c	B_{eq}	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ferri-clinoferroholmquistite (SEQ 1043)											
O1		0.1122(1)	0.0914(1)	0.2020(2)	0.60	0.0013(1)	0.0005(1)	0.0065(3)	0.0000(1)	0.0006(2)	0.0000(1)
O2		0.1219(1)	0.1742(1)	0.7314(2)	0.62	0.0014(1)	0.0005(1)	0.0064(3)	0.0000(1)	0.0007(2)	0.0001(1)
O3	8.22(1)	0.1148(2)	0	0.7022(4)	0.87	0.0022(2)	0.0007(1)	0.0092(6)	-	0.0007(2)	-
O4		0.3759(1)	0.2501(1)	0.7805(2)	0.80	0.0027(1)	0.0005(1)	0.0080(4)	-0.0004(1)	0.0007(2)	0.0002(1)
O5		0.3549(1)	0.1297(1)	0.0617(2)	0.80	0.0017(1)	0.0008(1)	0.0072(4)	0.0000(1)	0.0009(2)	0.0010(1)
O6		0.3468(1)	0.1207(1)	0.5604(2)	0.89	0.0020(1)	0.0010(1)	0.0063(4)	0.0002(1)	0.0005(2)	-0.0010(1)
O7		0.3389(2)	0	0.2796(4)	0.87	0.0024(2)	0.0002(1)	0.0144(6)	-	0.0013(3)	-
T1		0.2869(1)	0.0864(1)	0.2761(1)	0.44	0.0013(1)	0.0003(1)	0.0045(1)	0.0000(1)	0.0006(1)	0.0000(1)
T2		0.2975(1)	0.1712(1)	0.7854(1)	0.46	0.0014(1)	0.0003(1)	0.0044(1)	-0.0001(1)	0.0006(1)	0.0000(1)
M1	18.81(6)	0	0.0890(1)	½	0.57	0.0019(1)	0.0004(1)	0.0054(2)	-	0.0012(1)	-
M2	24.47(4)	0	0.1820(1)	0	0.49	0.0014(1)	0.0004(1)	0.0049(1)	-	0.0006(1)	-
M3	17.11(3)	0	0	0	0.61	0.0021(1)	0.0004(1)	0.0057(2)	-	0.0005(1)	-
M4'	3.44(6)	0	0.2571(3)	½	2.03	0.0046(5)	0.0027(2)	0.0112(16)	-	0.0036(7)	-
Am	1.98(4)	0.0783(10)	½	0.1545(17)	2.66	0.0095(10)	0.0014(2)	0.0314(36)	-	0.0099(16)	-
H	0.80(7)	0.198(6)	0	0.744(11)	2.77(1.16)						
Sodic-ferri-ferropedrizite (SEQ 1039)											
O1		0.1119(1)	0.0915(1)	0.2033(1)	0.55	0.0013(1)	0.0005(1)	0.0052(2)	0.0000(1)	0.0004(1)	0.0000(1)
O2		0.1219(1)	0.1741(1)	0.7316(1)	0.61	0.0014(1)	0.0006(1)	0.0055(2)	0.0000(1)	0.0006(1)	0.0002(1)
O3	8.32(1)	0.1152(1)	0	0.7019(2)	0.91	0.0025(1)	0.0007(1)	0.0091(4)	-	0.0008(2)	-
O4		0.3754(1)	0.2501(1)	0.7817(2)	0.79	0.0026(1)	0.0005(1)	0.0074(2)	-0.0005(1)	0.0002(1)	0.0001(1)
O5		0.3546(1)	0.1292(1)	0.0626(2)	0.78	0.0017(1)	0.0009(1)	0.0060(2)	0.0000(1)	0.0008(1)	0.0011(1)
O6		0.3466(1)	0.1206(1)	0.5615(2)	0.86	0.0019(1)	0.0010(1)	0.0055(2)	0.0002(1)	0.0004(1)	-0.0011(1)
O7		0.3388(1)	0	0.2802(2)	0.85	0.0022(1)	0.0003(1)	0.0127(4)	-	0.0008(2)	-
T1		0.2857(1)	0.0864(1)	0.2767(1)	0.40	0.0013(1)	0.0003(1)	0.0035(1)	0.0000(1)	0.0004(1)	0.0000(1)
T2		0.2969(1)	0.1712(1)	0.7860(1)	0.45	0.0013(1)	0.0003(1)	0.0034(1)	-0.0001(1)	0.0004(1)	0.0000(1)
M1	17.94(4)	0	0.0882(1)	½	0.55	0.0018(1)	0.0005(1)	0.0044(1)	-	0.0011(1)	-
M2	24.67(2)	0	0.1814(1)	0	0.47	0.0013(1)	0.0004(1)	0.0044(1)	-	0.0005(1)	-
M3	14.27(2)	0	0	0	0.60	0.0020(1)	0.0003(1)	0.0058(2)	-	0.0003(1)	-
M4	1.07(6)	0	0.2703(7)	½	2.06	0.0029(8)	0.0031(4)	0.0139(31)	-	0.0051(13)	-
M4'	2.20(4)	0	0.2542(3)	½	1.76	0.0036(4)	0.0025(2)	0.0089(13)	-	0.0016(5)	-
Am	2.91(3)	0.0750(4)	½	0.1514(8)	2.52	0.0109(5)	0.0012(1)	0.0283(15)	-	0.0131(7)	-
H	0.62(5)	0.189(4)	0	0.734(8)	1.55(90)						

TABLE 4. SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) FOR THE AMPHIBOLES INVESTIGATED IN THIS WORK

SEQ	1043	1039		1043	1039		1043	1039
T1-O1	1.621(2)	1.617(1)	M1-O1	2.077(2)	2.074(1)	M4-O2 ×2		2.282(1)
T1-O5	1.615(1)	1.616(1)	M1-O2	2.139(1)	2.148(1)	M4-O4 ×2		2.121(1)
T1-O6	1.618(2)	1.618(1)	M1-O3	2.095(1)	2.083(1)	M4-O5 ×2		3.028(1)
T1-O7	1.622(1)	1.625(1)	<M1-O>	2.104	2.101	M4-O6 ×2		2.497(1)
<T1-O>	1.619	1.619	OAV	46.19	43.35	<M4-O>		2.482
TAV	2.20	3.48	OQE	1.014	1.013	M4'-O2 ×2	2.111(4)	2.073(4)
TQE	1.001	1.001	M2-O1	2.107(2)	2.097(1)	M4'-O4 ×2	2.080(2)	2.091(1)
T2-O2	1.629(2)	1.628(1)	M2-O2	2.013(2)	2.016(1)	M4'-O5 ×2	3.174(4)	3.207(3)
T2-O4	1.597(1)	1.598(1)	M2-O4	1.910(1)	1.914(1)	M4'-O6 ×2	2.678(5)	2.728(4)
T2-O5	1.633(2)	1.635(1)	<M2-O>	2.010	2.009	[8]<M4'-O>	2.511	2.525
T2-O6	1.638(1)	1.641(1)	OAV	35.69	31.69	[6]<M4'-O>	2.290	2.297
<T2-O>	1.624	1.625	OQE	1.012	1.010	Am-O5 ×2	3.110(2)	3.087(1)
TAV	10.70	11.34	M3-O1	2.117(2)	2.119(1)	Am-O5 ×2	2.720(2)	2.719(1)
TQE	1.003	1.003	M3-O3	2.093(2)	2.100(1)	Am-O6 ×2	2.649(2)	2.654(1)
T1-T1	3.092(2)	3.091(1)	<M3-O>	2.109	2.113(1)	Am-O7	2.489(2)	2.477(1)
T1-T2	3.081(1)	3.077(1)	OAV	68.28	68.02	Am-O7	2.941(3)	2.950(2)
T1-T2	3.032(1)	3.030(1)	OQE	1.021	1.021	Am-O7	2.579(2)	2.585(2)
O6-O7-O6	111.4(1)	111.2(1)	H-O3	0.770(2)	0.685(1)	<Am-O>	2.774	2.770

Polyhedron angular variance (TAV, OAV) and quadratic elongation (TQE, OQE) are as defined by Robinson *et al.* (1971). SEQ: sequence number.

^{M3}(Li$_{0.28}$Mn^{2+}$_{0.14}$Fe^{2+}$_{0.54}$Mg$_{0.04}$); sodic-ferri-ferro-pedrizite (1039): ^{M1}(Mg$_{1.00}$Fe^{2+}$_{1.00}$) ^{M2}(Fe^{3+}$_{1.55}$Al$_{0.21}$Ti$_{0.13}$Zn$_{0.01}$Fe^{2+}$_{0.10}$) ^{M3}(Li$_{0.58}$Mn^{2+}$_{0.07}$Fe^{2+}$_{0.35}$).

The most striking crystal-chemical feature of these Li-rich samples is the variation in the shape of the electron density at the A-group sites. Local order of ^{A}Na in ^{B}(Ca,Na) amphiboles was investigated by Hawthorne *et al.* (1996), who found that Na orders at the Am site in both OH- and F-sodic amphiboles. K is also known to order at the Am site in all $C2/m$ amphiboles, independent of the nature of the B and O3 constituents (*e.g.,* Hawthorne *et al.* 1996).

Oberti *et al.* (2003) noted preferential order of the A cations at the Am site in ^{B,C}Li-rich amphiboles, and an increase in the Am–Am separation with decreasing values of the ^{A}(Na,K):^{C}Li ratio, the largest Am–Am separation occurring where the ratio is 1:1 and Na is the only A cation. Figure 1 shows the shape of the electron density at the A-group sites for leakeite [^{B}Li$_{0.00}$, ^{C}Li$_{0.74}$, ^{A}(Na$_{0.67}$K$_{0.20}$), ^{O3}F$_{0.49}$ *apfu*; sample A2 in Hawthorne *et al.* 1994], ferriwhittakerite [^{B}Li$_{0.62}$, ^{C}Li$_{0.73}$, ^{A}(Na$_{0.64}$K$_{0.13}$), ^{O3}F$_{0.72}$ *apfu*; Oberti *et al.* 2004], ferri-ottoliniite [^{B}Li$_{1.24}$, ^{C}Li$_{0.42}$, ^{A}(Na$_{0.38}$K$_{0.07}$), ^{O3}F$_{0.47}$ *apfu*; Oberti *et al.* 2004], sodic-ferri-ferropedrizite [^{B}Li$_{1.82}$, ^{C}Li$_{0.58}$, ^{A}(Na$_{0.53}$K$_{0.03}$), ^{O3}F$_{0.52}$ *apfu*; this work], and ferri-clinoferroholmquistite [^{B}Li$_{1.90}$, ^{C}Li$_{0.28}$, ^{A}(Na$_{0.28}$K$_{0.00}$), ^{O3}F$_{0.24}$ *apfu*; this work]. Two projections of relevance

to the present discussion are shown in Figure 1. The one on the right is that usually provided for $C2/m$ amphiboles [onto ($\overline{2}$ 0 1), with b vertical and the electron-density lobes on a line joining the furthest O7–O7 atoms]; that on the left is onto (0 1 0), where c is rotated by 45° to allow alignment along the abscissa, and the line connecting the two closest O7 atoms is vertical. The electron density is generally concentrated at the Am sites, and the Am–Am separation actually increases as a function of the ^{A}(Na,K):^{C}Li ratio (1:0.85 for a, 1:0.95–0.93 for b and c, 1:1 for d and e). However, ^{B}Li also plays a crucial role. Lithium is far smaller than Na (0.92 *versus* 1.18 Å in [8]-coordination; Shannon 1976), and is ordered at a position ($M4'$ in Table 3) closer to the strip of octahedra and further from the double chains of tetrahedra, where it can assume a [6 + 2]-coordination. In this position, Li should provide a weaker bond-valence contribution to the O5 and O6 basal O atoms of the tetrahedra, which in turn should affect the degree of order of the A-site cations. This deduced crystal-chemical feature was verified by bond-valence calculations for the five amphibole compositions in Figure 1, done with the parameters of Brese & O'Keeffe (1991) for the Si–O bonds and those of Brown & Altermatt (1985) for the other bonds.

Bond valences for the relevant sites (Table 7) were calculated on the basis of short-range order. For the A-

TABLE 5. CALCULATED POWDER-DIFFRACTION PATTERNS FOR
FERRI-CLINOFERROHOLMQUISTITE AND SODIC-FERRI-FERROPEDRIZITE

2θ (°)	d_{calc} (Å)	I	$h\,k\,l$	2θ (°)	d_{calc} (Å)	I	$h\,k\,l$	2θ (°)	d_{calc} (Å)	I	$h\,k\,l$
				ferri-clinoferroholmquistite (SEQ 1043)							
10.76	**8.224**	**100**	**1 1 0**	32.66	2.741	16	3 3 0	44.95	2.017	10	$\underline{3}$ 5 1
17.09	5.188	5	$\underline{0}$ 0 1	**32.96**	**2.717**	**69**	$\overline{1}$ **5 1**	54.91	1.672	7	$\overline{5}$ 1 2
18.48	4.802	10	$\overline{1}$ 1 1	34.08	2.631	7	$\overline{3}$ 3 1	55.96	1.643	16	4 6 1
19.78	4.488	17	0 2 1	**34.69**	**2.586**	**20**	$\underline{0}$ **6 1**	57.27	1.609	6	4 8 0
19.84	**4.474**	**30**	$\underline{0}$ **4 0**	36.04	2.492	32	$\overline{2}$ 0 2	57.51	1.603	7	$\overline{1}$ 11 0
23.25	3.825	9	$\overline{1}$ 3 1	39.75	2.268	17	$\overline{3}$ 5 1	58.23	1.584	16	$\underline{1}$ 5 3
25.05	3.554	19	$\overline{2}$ 2 1	40.89	2.207	13	3 1 2	61.66	1.504	8	$\overline{2}$ 6 3
26.05	**3.420**	**30**	**1 3 1**	41.41	2.180	8	1 7 1	62.25	1.492	7	0 12 0
26.70	3.339	6	1 5 0	**41.72**	**2.165**	**21**	$\overline{2}$ **6 1**	67.40	1.389	16	$\overline{6}$ 6 1
27.73	3.218	8	2 4 0	43.35	2.087	9	$\underline{2}$ 0 2	68.21	1.375	7	$\underline{5}$ 1 2
29.36	**3.042**	**54**	**3 1 0**	43.42	2.084	5	$\overline{3}$ 3 2	74.08	1.280	9	$\overline{2}$ 12 2
				sodic-ferri-ferropedrizite (SEQ 1039)							
10.73	**8.241**	**100**	**1 1 0**	33.00	2.714	72	$\overline{1}$ 5 1	50.91	1.794	6	$\underline{1}$ 9 1
17.12	5.180	7	0 0 1	33.99	2.638	11	$\overline{3}$ 3 1	54.71	1.678	7	$\overline{5}$ 1 2
17.68	5.016	5	$\underline{1}$ 3 0	34.72	2.583	22	$\underline{0}$ 6 1	55.17	1.665	6	$\overline{2}$ 8 2
18.46	4.805	10	$\overline{1}$ 1 1	**36.00**	**2.494**	**36**	$\overline{2}$ **0 2**	55.94	1.644	18	4 6 1
19.81	4.482	21	0 2 1	39.67	2.272	17	$\overline{3}$ 5 1	57.21	1.610	7	4 8 0
19.86	**4.471**	**33**	$\underline{0}$ **4 0**	40.80	2.212	15	3 1 2	57.55	1.601	7	$\overline{1}$ 11 0
23.25	3.826	8	$\overline{1}$ 3 1	41.45	2.178	8	1 7 1	58.29	1.583	18	$\underline{1}$ 5 3
24.99	**3.563**	**23**	$\overline{2}$ **2 1**	**41.74**	**2.164**	**23**	$\overline{2}$ **6 1**	61.68	1.504	9	$\overline{2}$ 6 3
26.08	**3.416**	**39**	**1 3 1**	43.34	2.088	7	$\overline{3}$ 3 2	62.30	1.490	8	0 12 0
26.71	3.338	7	1 5 0	43.41	2.084	11	2 0 2	67.19	1.393	19	$\overline{6}$ 6 1
27.70	3.221	9	2 4 0	44.95	2.017	11	$\underline{3}$ 5 1	68.20	1.375	9	$\underline{5}$ 1 2
29.28	**3.050**	**60**	**3 1 0**	46.78	1.942	6	4 0 2	74.11	1.279	10	$\overline{2}$ 12 2
32.60	2.747	21	3 3 0	47.23	1.924	6	4 2 1	82.43	1.170	6	$\overline{5}$ 11 2

Cu$K\alpha$ radiation (1.5418 Å). Reflections with $I\,/\,I_0 \geq 5$; the strongest eight reflections are in bold.
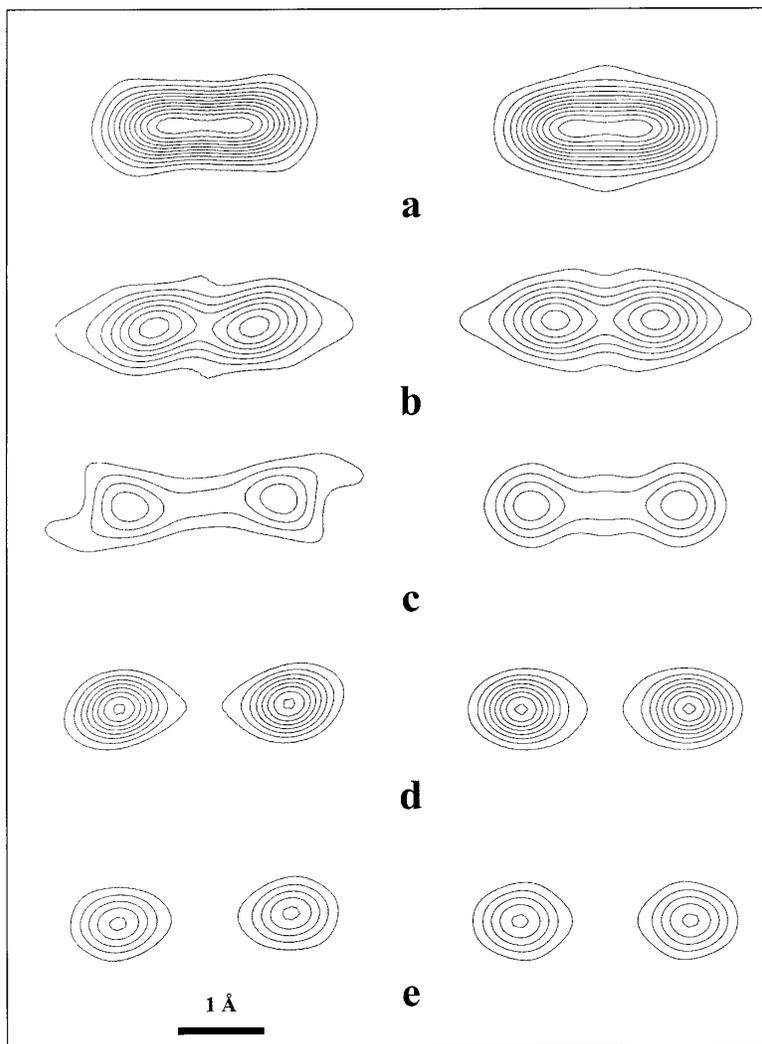
FIG. 1.   Difference-Fourier maps calculated for the *A*-group sites in leakeite (a; sample A2 in Hawthorne *et al*. 1994), ferriwhittakerite and ferri-ottoliniite (b and c; Oberti *et al*. 2004), sodic-ferri-ferropedrizite and ferri-clinoferroholmquistite (d and e; this work). Right: the "standard" projection onto $(\bar{2}\,0\,1)$, *b* vertical; left: a $(0\,1\,0)$ projection, *c* at 45° with the abscissa. Contours steps of $1\ e^-\,\text{Å}^{-3}$; first line at $2\ e^-\,\text{Å}^{-3}$.

group sites, the Na cation was considered to occur either at the *Am* or the *A2/m* sites; for the basal oxygen atoms, Na was placed at the *M4* site and Li at the *M4'* sites, and the refined atom coordinates were used for calculations. The results clearly show that $^{M4'}$Li allows an incident bond-valence sum at the O5 and O6 sites closer to the ideal value. Also, the occurrence of ^{Am}Na allows an incident bond-valence sum at the O5, O6 and O7 anions closer to the ideal value. It is also worth noting here that the presence of Li at the *M3* site, which is

coordinated to four O1 and two O3 oxygen atoms, implies shortening of the *T1*–O1 (apical) distance and lengthening of the *T1*–O5,O6,O7 distances; therefore, it further decreases the bond-valence contribution to the basal oxygen atoms of the tetrahedra.

Of the twelve anions surrounding the *A* cavity, ten are within the coordination sphere of Na and K. Thus the total ideal bond-valence required by these ten anions is $4 \times \text{O5} + 4 \times \text{O6} + 2 \times \text{O7} = 20\ vu$ (valence units). Given the calculations reported in Table 7, we

TABLE 6. RESULTS OF CHEMICAL ANALYSES (EMPA + SIMS) AND UNIT FORMULAE, AND A COMPARISON BETWEEN REFINED (REF) AND CALCULATED (CALC) GROUP-SITE SCATTERING VALUES (SS) FOR FERRI-CLINOFERROHOLMQUISTITE AND SODIC-FERRI-FERROPEDRIZITE

	1043	1039	FCFH	SFFP		1043	1039	FCFH	SFFP
SiO_2 wt%	56.11	56.25	53.18	54.75	Si *apfu*	8.00	8.00	8.00	8.00
TiO_2	0.07	1.19							
Al_2O_3	1.51	1.24			Al	0.26	0.21		
Fe_2O_3	15.63	13.92	17.67	18.19	Mg	1.06	0.95		
FeO	12.98	13.04	23.85	16.37	Ti	0.01	0.13		
MnO	1.14	0.60			Fe^{2+}	1.55	1.49	3.00	2.00
MgO	5.04	4.48			Fe^{3+}	1.68	1.55	2.00	2.00
ZnO	0.21	0.15			Mn^{2+}	0.14	0.07		
Li_2O_{SIMS}	3.80	4.20	3.31	5.11	Zn^{2+}	0.02	0.01		
CaO	0.13	0.20			Li	0.28	0.58		1.00
Na_2O	1.29	2.47		3.53	Sum C	5.00	4.99	5.00	5.00
K_2O	0.01	0.17							
F_{SIMS}	0.54	1.15			Li	1.90	1.82	2.00	2.00
H_2O_{SIMS}	1.88	1.53	1.99	2.05	Ca	0.02	0.03		
O=F	0.23	0.48			Na	0.08	0.15		
					Sum B	2.00	2.00	2.00	2.00
Total	100.11	100.11	100.00	100.00					
					Na	0.28	0.53		1.00
ss C_{calc}	105.36	99.38	130.00	107.00	K	0.00	0.03		
ss B_{calc}	6.98	7.71	6.00	6.00	Sum A	0.28	0.56		1.00
ss A_{calc}	3.08	6.40		11.00					
ss tot$_{calc}$	115.42	113.49	136.00	124.00	F	0.24	0.52		
					OH	1.79	1.45	2.00	2.00
ss C_{ref}	103.65	99.49			Sum				
ss B_{ref}	6.89	6.55			O3	2.03	1.97	2.00	2.00
ss A_{ref}	3.96	5.82							
ss tot$_{ref}$	114.50	111.86			O.S.	0.52	0.51	0.40	0.50

The formulae are calculated on the basis of 24 (O + F) and 8 Si *apfu*. Ideal values calculated for the end-members are also provided (SFFP: sodic-ferri-ferropedrizite, FCFH: ferri-clinoferroholmquistite. O.S.: Fe^{3+} / (Fe^{3+} + Fe^{2+}).

can obtain the residual bond-strength and bond-valence contributions that should be provided by the *A* cations (Δ_{bs} and Δ_{bv}), ideally 1.0 *vu*. The calculated Δ_{bv} values are very low or even negative for the amphiboles reported in this work (they approach zero for the local configuration with ^{M4}Li), which implies a low basicity for the *A* cavity. Therefore, the *A* cations should tend to minimize their Lewis acidity by maximizing their coordination number. The *Am* site is generally [9]-coordinated in amphiboles, whereas the *A*2 site is [6]-coordinated; however, the *Am*–O3 distances in the Li-rich amphiboles reported in this work (2.882 and 2.846 Å, respectively, in sodic-ferri-ferropedrizite and ferri-clinoferroholmquistite), provide an effective [10]-coordination. The presence of F is another factor allowing for stronger off-centering of the *A* cations, because it both reduces the steric hindrance (F does not protrude into the *A* cavity, whereas H does) and allows for higher bond-strength.

We can thus conclude that the sequence of preferred local configurations for ^{B}Li amphiboles is (^{M4}Li–^{O3}F–^{Am}Na) > (^{M4}Li–^{O3}OH–^{Am}Na), because the former provides the most stable configuration for the basal oxygen atoms of the tetrahedra as well as the highest coordination for the *A* cation. Generally speaking, local configurations involving ^{M4}Li should be preferred to those involving ^{M4}Na. The preference for the local configuration (^{M4}Li–^{O3}F–^{Am}Na) derived from bond-valence cal-

culations corroborates the previous observation that the amount of F in the formula unit is directly related to the *A*-site occupancy and thus indirectly related to the ^{M3}Li occupancy in all the amphiboles found so far in the Pedriza Massif (Oberti *et al.* 2003). Preferential order of ^{A}Na at the *Am* site had been noted by Hawthorne *et al.* (1996) for $^{[4]}$Al-free ^{B}Na amphiboles, and this feature further confirms the close similarity between ^{B}Li and ^{B}Na amphiboles.

NOMENCLATURE

Notwithstanding the many strong similarities between their crystal-chemical behavior (*e.g.*, the charge arrangement, the possibility of incorporating ^{C}Li, the *A*-site cation order), ^{B}Na and ^{B}Li amphiboles are presently divided into three different groups for classification

TABLE 7. SHORT RANGE BOND-STRENGTH AND BOND VALENCE INCIDENT AT THE BASAL O ATOMS AND AT THE *A* SITES IN LEAKEITE (A), FERRIWHITTAKERITE (B), FERRI-OTTOLINIITE (C), SODIC-FERRI-FERROPEDRIZITE (D) AND FERRI-CLINOFERROHOLMQUISTITE (E)

end-member*	Bond-strength	A	B	C	D	E
O5-T1	1.00	0.995	0.997	1.011	1.022	1.025
O5-T2	1.00	0.920	0.945	0.973	0.971	0.976
O5-M4(Na)	0.13	0.055	0.053	0.044	0.036	0.038
O5-M4(Li)	0.13	0.014	0.013	0.008	0.009	0.010
Σ ^{MM}Na	2.13	1.970	1.995	2.028	2.029	2.039
Σ ^{MM}Li	2.13	1.929	1.955	1.992	2.002	2.011
O6-T1	1.00	0.995	1.003	1.025	1.016	1.016
O6-T2	1.00	0.893	0.915	0.963	0.955	0.963
O6-M4(Na)	0.13	0.144	0.156	0.168	0.153	0.168
O6-M4(Li)	0.13	0.032	0.035	0.024	0.033	0.038
Σ ^{MM}Na	2.13	2.032	2.074	2.156	2.124	2.147
Σ ^{MM}Li	2.13	1.920	1.953	2.012	2.004	2.017
O7-T1 x2	2.00	1.952	2.000	2.049	1.995	2.011
Δ_{bs} **	-1.04					
Δ_{bv} (^{MM}Na) **		0.088	-0.276	-0.834	-0.602	-0.766
Δ_{bv} (^{MM}Li)		0.700	0.368	-0.114	-0.014	-0.134
Am-O5 x2		0.040	0.038	0.035	0.031	0.029
Am-O5 x2		0.071	0.076	0.083	0.084	0.084
Am-O6 x2		0.079	0.080	0.091	0.100	0.102
Am-O7		0.137	0.143	0.163	0.162	0.157
Am-O7		0.030	0.033	0.039	0.045	0.046
Am-O7		0.105	0.114	0.123	0.121	0.123
Σ		0.652	0.675	0.741	0.759	0.755
<bv>***		0.072	0.075	0.082	0.084	0.084
A-O5 x4		0.064	0.067	0.075	0.078	0.077
A-O6 x4		0.025	0.022	0.020	0.019	0.018
A-O7 x2		0.148	0.165	0.212	0.232	0.237
Σ		0.650	0.689	0.803	0.849	0.857
<bv>		0.065	0.069	0.080	0.085	0.086

* Atom coordinates from crystal A2 (Hawthorne *et al.* 1994), ferriwhittakerite and ferri-ottoliniite (Oberti *et al.* 2004), and sodic-ferri-ferropedrizite and ferri-clinoferroholmquistite (this study).
** Δ_{bs} and Δ_{bs}: total bond-strength and bond-valence required by 4 × O5 + 4 × O6 + 2 × O7 anions to agree exactly with the valence-sum rule (averaged over the anions).
*** <bv>: average bond-valence over the coordination number of cation at the *Am* and A(2/m) sites, expressed in valence units (*vu*).

purposes. Along the solid-solution series, compositions with $2.0 \geq {}^B\text{Na} > 1.5$ *apfu* and $0 \leq {}^B\text{Li} < 0.5$ belong to Group 4, those with $2.0 \geq {}^B\text{Li} > 1.5$ *apfu* and $0 \leq {}^B\text{Na} < 0.5$ to Group 1, whereas the intermediate compositions fall into the new Group 5 (Leake *et al.* 2003).

The new report provided by Leake *et al.* (2003) also brings the use of the prefix *sodic* for Group-1 amphiboles back to the original definition given in Leake *et al.* (1997), *i.e.,* $\text{Na}_{tot} > 0.5$ *apfu*. In 2001, the IMA Commission on New Minerals and Mineral Names, while discussing the case of what was then called "ferripedrizite" (Caballero *et al.* 2002), and now becomes sodic-ferripedrizite, had taken into account the authors' arguments based on the distinct crystal-chemical roles, and decided that the prefix *sodic* should have been used solely for ${}^B\text{Na} > 0.50$ *apfu*.

In our opinion, the present use of the prefix *sodic* in Group-1 amphiboles is rather unfortunate. Very few compositions (solely in the clinoholmquistite compositional field) will be able to avoid that prefix, so that it will no longer be very informative. Moreover, it also implies the possible presence of a very unfortunate name, "potassic-sodic-pedrizite", which should be assigned to a composition with ${}^A\text{K} > 0.50$ *apfu* and $\text{Na}_{tot} > 0.50$ *apfu*.

We stress once again that the crystal-chemical role of Na at the *A*- and *B*-group sites is rather different, because these sites are involved in different coupled heterovalent substitutions controlling major-element incorporation. If the two site-preferences were kept separate also for nomenclature purposes, ${}^B\text{Na} > 0.5$ *apfu* would now induce a change from Group 1 to Group 5, whereas ${}^A\text{Na} > 0.5$ *apfu* would imply the use of a distinct root-name within Group 1, which corresponds to a distinct charge-arrangement. Thus the prefix *sodic* in Group-1 amphiboles should be abolished for the sake of the effectiveness of the nomenclature.

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