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Ferripedrizite, a new monoclinic ^{B}Li amphibole end-member from the Eastern Pedriza Massif, Sierra de Guadarrama, Spain, and a restatement of the nomenclature of Mg-Fe-Mn-Li amphiboles

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ABSTRACT

Ferripedrizite, ideally ${}^{A}Na{}^{B}Li_2{}^{C}(Fe^{3+}_2Mg_2Li){}^{T}Si_8O_{22}{}^{X}(OH)_2$, is a new amphibole end-member found in episyenites formed after cordierite-bearing porphyritic granites in the Eastern Pedriza Massif (Central System, Spain). It contains the maximum amount of Li that can be incorporated in the amphibole structure. The name was approved by the IMA-CNMMN together with restriction of the use of the prefix sodic in the pedrizite series to compositions with ${}^{B}Na > 0.5$ apfu; its use for compositions with $Na_{tot} > 0.5$ apfu has been maintained in the rest of the Mg-Fe-Mn-Li group. Complete solid solution between ferripedrizite and leakeite [ideally, ${}^{A}Na{}^{B}Na_2{}^{C}(Fe^{3+}_2Mg_2Li){}^{T}Si_8O_{22}{}^{X}(OH)_2$] has been found in the Pedriza Massif. According to the present nomenclature rules, this join bridges three different amphibole groups. Samples with ${}^{B}(Mg + Fe + Mn + Li) \geq 1.0$ apfu and $0.\ 0 \leq {}^{B}Na \leq 0.50$ apfu belong to the Mg-Fe-Mn-Li group and are termed ferripedrizite; samples with ${}^{B}(Mg + Fe + Mn + Li) \geq 1.0$ apfu and $0.50 < {}^{B}Na \leq 0.99$ apfu belong to the Mg-Fe-Mn-Li group and are called sodic-ferripedrizite; samples with ${}^{B}(Mg + Fe + Mn + Li) < 1.0$ apfu and ${}^{B}Na \geq 1.50$ apfu belong to the sodic group and are named leakeite; samples with ${}^{B}(Mg + Fe + Mn + Li) < 1.0$ apfu and $1.0 \leq {}^{B}Na < 1.50$ apfu belong to the sodic-calcic group (albeit Ca is negligible) and deserve a new root name.

The ferripedrizite sample from Pedriza is black, vitreous, translucent, non-fluorescent, and brittle, and has gray streak, H = 6, uneven fracture, perfect {110} cleavage, $D_{meas} = 3.15$, $D_{calc} = 3.19$ g/cm^3. It is strongly pleochroic, X = yellow green, Y = green blue, Z = bluish green ($Y = Z >> X$), $Z = b$, $Y \wedge c = 15(6)°$, $X \wedge a = 3°$. It is biaxial positive: $\alpha = 1.695(1)$, $\beta = 1.700(2)$, and $\gamma = 1.702(1)$; $2V_Z = 125(17)°$, dispersion $r > v$. It is monoclinic, space group $C2/m$, $a = 9.501(1)$, $b = 17.866(2)$, $c = 5.292(1)$ Å, $\beta = 102.17(2)°$, $V = 878.1(2)$ Å^3. The ten strongest lines in the X-ray powder-diffraction pattern [d in Å,(I),(hkl)] are: 8.251(3)(110), 4.466(2)(040), 3.411(2)(131), 3.050(10)(310), 2.747(3)(330), 2.711(4)(151), 2.495(2)($\bar{2}02$), 2.161(2)(261), 1.642(4)(461), 1.394(3)($\bar{6}61$). Structure refinement and electron- and ion-microprobe analysis of a crystal with composition ${}^{A}(K_{0.04}Na_{0.52}){}^{B}(Na_{0.25}Ca_{0.05}Li_{1.70}){}^{C}(Li_{0.64}Fe^{3+}_{1.64}Mg_{1.49}Fe^{2+}_{0.85}Al_{0.21}Ti_{0.09}Mn_{0.07}Zn_{0.01})\ {}^{T}Si_8O_{22}\ {}^{X}(OH_{1.31}F_{0.69})$ are provided, together with some discussion on cation ordering.

INTRODUCTION

The occurrence of lithium in amphiboles has been known for some time. However, it was initially restricted to the B sites, and thus to the monoclinic and orthorhombic holmquistite end-members, ideally ${}^{A}\square{}^{B}Li_2{}^{C}[(Mg,Fe^{2+})_3(Al,Fe^{3+})_2]{}^{T}Si_8O_{22}{}^{X}(OH,F,Cl)_2$, which belong to the Mg-Fe-Mn-Li group. The advent of instruments capable of detecting and quantifying in situ elements with $Z < 5$ (e.g., the ion microprobe) allowed more careful investigation of Li incorporation and partitioning in amphiboles. At present, Li should also be considered a frequent substituent in sodic amphiboles with the group-charge (Ch) arrangement of arfvedsonite and eckermannite (i.e., ${}^{A}Ch = 1$, ${}^{B}Ch = 2$, ${}^{C}Ch = 11$, ${}^{T}Ch = 32$, ${}^{X}Ch = 2$), where it is preferentially or completely incorporated into the octahedral M3 site according to the coupled heterovalent exchange vectors ${}^{M2}Fe^{3+M3}Li\ {}^{M2}Fe^{2+M3}_{-1}Mg_{-1}$ (Hawthorne et al. 1994). Lithium incorporation into the other octahedral sites has been discarded on the basis of bond-valence requirements, so that the maximum octahedral Li content is 1 atom per formula unit (apfu; Hawthorne et al. 1994). Samples belonging to the leakeite series, ${}^{A}Na{}^{B}Na_2{}^{C}[(Mg,Mn^{2+},Fe^{2+})_2(Al,Mn^{3+}Fe^{3+})_2Li]{}^{T}Si_8O_{22}{}^{X}(OH,F)_2$, as well as lithian arfvedsonites and lithian eckermannites have been repeatedly found in manganese metasediments and in peralkaline granites (Hawthorne et al. 1992, 1993, 1996a, 1996b, 2001; Armbruster et al. 1993).

Li-rich amphiboles in episyenites from the Eastern Pedriza Massif, Madrid, Spain, show a widespread solid-solution which may be described by combining the homovalent ${}^{B}(Li_2Na_{-2})$ and coupled heterovalent ${}^{C}({}^{M2}Fe^{3+M3}Li{}^{M2}Fe^{2+M3}_{-1}Mg_{-1})$ exchange vectors (Caballero et al. 1998; Oberti et al. 2000). In particular, Oberti et al. (2000) described a sample with composition

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${}^{A}(Na_{0.70}K_{0.073})^{B}(Li_{1.34}Na_{0.58}Ca_{0.08})$ ${}^{C}(Mg_{1.75}Fe^{2+}_{0.32}Mn^{2+}_{0.07}Zn_{0.01}Al_{0.21}Ti_{0.11}Fe^{3+}_{1.65}Li_{0.88}{}^{T}Si_8O_{22}{}^{X}(OH_{1.35}F_{0.65})$ that was named sodic-ferripedrizite (IMA-CNMMN vote 98-061). Further work allowed identification of samples with ${}^{B}Li$ contents closer to 2 apfu, and very low ${}^{B}Na$ contents.

These new compositions, which actually define a complete solid-solution between the Mg-Fe-Mn-Li and the sodic groups, led to problems with the existing nomenclature. In fact, the revision of amphibole nomenclature reported in Leake et al. (1997) requires the use of the prefix sodic for all compositions in the Mg-Fe-Mn-Li group [defined by ${}^{B}(Mg\text{-}Fe\text{-}Mn\text{-}Li) \geq 1$ apfu] in which $Na_{tot} > 0.50$ apfu. It also requires the use of a unique root name for homovalent solid-solution, and the distinction between end-members on the basis of a hyphenated prefix. Thus there would be no way to distinguish between ${}^{A}Na^{B}Li_2{}^{C}(Fe^{3+}_2Mg_2Li)^{T}Si_8O_{22}{}^{X}(OH)_2$ and ${}^{A}Na^{B}(Li\,Na)^{C}(Fe^{3+}_2Mg_2Li)^{T}Si_8O_{22}{}^{X}(OH)_2$, the former being the amphibole with the highest Li content and the latter being the boundary between two amphibole groups and thus deserving some consideration. Moreover, the presence of a complete homovalent solid-solution between amphiboles with ${}^{B}Li$ and ${}^{B}Na$, as well as their analogous charge arrangements and crystal chemical properties, might suggest the incorporation of ${}^{B}Li$ amphiboles into the sodic group. These topics were debated at great length among the authors, the IMA-CNMMN, and its Subcommittee on Amphiboles. Finally, ${}^{B}Li$ amphiboles were kept in the Mg-Fe-Mn-Li group, the use of the prefix sodic was revised for the pedrizite series, and the new end-member, ideally ${}^{A}Na^{B}Li_2{}^{C}(Fe^{3+}_2Mg_2Li)^{T}Si_8O_{22}{}^{X}(OH)_2$, was named ferripedrizite (IMA-CNMMN vote 01-032).

This paper describes the first occurrence of ferripedrizite, and discusses crystal-chemical and nomenclature problems in the solid solution between Na and Li at the B-group sites in amphiboles. For the sake of simplicity, chemical formulae of the amphibole end-members in which Li has been reported are listed in Table 1. The holotype material has been deposited in the Museo Nacional de Ciencias Naturales, Madrid (Spain), code number MNCN-26405.

OCCURRENCE

Episyenites in the Eastern Pedriza Massif (Sierra de Guadarrama, Central System, Spain) replace cordierite-bearing monzogranites. The ferripedrizite type material has been extracted from the same rock-sample as sodic-ferriclinoferroholmquistite (Caballero et al. 1998). This rock sample was collected from the same episyenitic body located in the Arroyo de la Yedra Valley [Spanish Military Map number 509 (19-20), scale 1:50000, 4th edition (1986)] where sodic-ferripedrizite (Oberti et al. 2000) was found. The cogenetic mineral association is: albite, augite-aegirine, sodic ferri-clinoferroholmquistite, titanite, andradite, magnetite, and apatite, with some relic magmatic minerals (K-feldspar and zircon). This mineral paragenesis is sometimes partially replaced by late hydrothermal minerals such as taeniolitic micas-microcline, ferroactinolite-quartz, and sericite-hematites-argilitic minerals-clinozoisite. A detailed textural description is given in Caballero et al. (1998).

Episyenites from the Sierra de Guadarrama are non-magmatic hydrothermal rocks. The estimated age for the area is 277 ma. Stable isotope thermometry gives an average temperature of 520 °C for ${}^{B}Li$ amphibole-bearing episyenites, while fluid inclusion data suggest fluid pressures around 160 MPa for amphibole crystallization (Caballero 1993). Amphiboles are often strongly zoned, with high Na contents and low Fe^{2+}/Mg ratios in the core and low Na contents and high Fe^{2+}/Mg ratios in the rim, suggesting local paths of decreasing T, whereas strong compositional changes at small scale suggest fluid inhomogeneities. Thus ferripedrizite is likely an higher temperature precursor of (more or less sodic) ferriclinoferroholmquistite.

PHYSICAL AND OPTICAL PROPERTIES

Ferripedrizite cannot be distinguished from sodic-ferriclinoferroholmquistite with the naked eye. Electron microprobe (EMP) data from thin sections show that both amphiboles have the same textural typology and may occur in different microdomains. Similarly to sodic-ferriclinoferroholmquistite, ferripedrizite appears as intergranular granoblastic aggregates associated with fine-grained albite, both with subeuhedral habits [0.184(110) × 0.100(62) mm] and as microinclusions in albite, quartz, and titanite [0.062(43) × 0.012(13) mm].

Individual crystals are prismatic and elongated on [001] to ≈0.07 mm. They are bound by {110} cleavage faces, and the prism direction is usually terminated by irregular fractures. The {010} pinacoid is common whereas the {001} form is rarely observed.

Ferripedrizite is black, semitranslucent, and vitreous; it is non-fluorescent under long- or short-wave ultraviolet light, and has a gray streak. It is brittle and shows uneven fracture and has a Mohs' hardness of ~6. Cleavage is perfect on {110}, intersecting at ~55°; parting on (001) is poor. Measured (pycnometry) and calculated densities are 3.15(10) g/cm³ and 3.19 g/cm³ respectively.

TABLE 1. Ideal compositions of the known monoclinic amphibole end-members containing ${}^{B}Li$ and/or ${}^{C}Li$

End-member name	Group	A	B	C	T	X
clinoholmquistite	Mg-Fe-Mn-Li	☐	Li_2	Mg_3Al_2	Si_8	$(OH)_2$
ferri-clinoferroholmquistite*	Mg-Fe-Mn-Li	☐	Li_2	$Fe^{2+}_3Fe^{3+}_2$	Si_8	$(OH)_2$
ferripedrizite	Mg-Fe-Mn-Li	Na	Li_2	$Mg_2Fe^{3+}_2Li$	Si_8	$(OH)_2$
sodic-ferripedrizite	Mg-Fe-Mn-Li	Na	LiNa	$Mg_2Fe^{3+}_2Li$	Si_8	$(OH)_2$
leakeite	sodic	Na	Na_2	$Mg_2Fe^{3+}_2Li$	Si_8	$(OH)_2$
fluoro-ferroleakite	sodic	Na	Na_2	$Fe^{2+}_2Fe^{3+}_2Li$	Si_8	F_2
fluoro-arfvedsonite	sodic	Na	Na_2	$Fe^{2+}_4Fe^{3+}$	Si_8	F_2
magnesio-arfvedsonite	sodic	Na	Na_2	Mg_4Fe^{3+}	Si_8	$(OH)_2$

Note: Trivalent cations occur at the M2 site, whereas ${}^{C}Li$ occurs at the M3 site.
* Only sodic ferri-clinoferroholmquistite (with Na > 0.5 apfu) has been described so far [Caballero et al. 1998, redefined in American Mineralogist, 83, 668 (1998)].

Optic axial angles and refractive indices were measured with a spindle stage, whereas orientation was measured with an universal stage. In transmitted white light, the strongly pleochroic pattern is similar to that of the other ${}^{B}Li$ amphiboles, with X = yellow green, Y = green blue and Z = bluish green, and absorption $Y = Z >> X$; $Z = b$, $Y \wedge c$ = 15(6)°, and $X \wedge a$ ~3°.

Ferripedrizite is biaxial negative, with indices of refraction α = 1.695(1), β = 1.700(2), and γ = 1.702(1); $2V_Z$ = 125(17)° and $2V_{Z,\text{calc}}$ = 116(17)°, under monochromatic yellow light (λ = 589 nm). Dispersion is strong, $r > v$ ($2V_Z$ = 86° at 486 nm). Gladstone-Dale parameters yield a compatibility index ($1 - K_P/K_C$) of 0.0002, which is considered to be superior (Mandarino 1981).

MINERAL COMPOSITION

Wavelength-dispersive analyses of grain-mount thin sections were obtained with a JEOL-8900M electron microprobe at the Universidad Complutense of Madrid, following the procedures described in Oberti et al. (2000). A mineral concentrate was also analyzed for Li by flame photometry and for FeO by redox titration. The purity of this concentrate was estimated to be 99.3(2)% from modal analysis; the major impurity was ferro-actinolite which intimately replaces ferripedrizite.

The formula unit was calculated assuming that the tetrahedral sites are occupied by Si, as suggested by the structure refinement. The H_2O content was calculated on the basis of 24 (O, OH, F), OH + F = 2 apfu (atoms per formula unit). The calculated FeO content is 8.94(2.31) wt%, which is in close agreement with the value obtained by redox titration (7.8 ± 1.1 wt%), which supports these assumptions. The average analysis of 33 grains (51 point analyses) is given in Table 2. The estimated standard deviations are a measure of the intergranular variability in the sample, which is always wider than the observed intragranular variability due to chemical zoning.

The crystals used for structure refinement analysis (SREF) were subsequently analyzed by electron- and ion-microprobe techniques (EMP and SIMS, respectively). The results for the sample of this work are given in Table 2. SIMS analyses for light elements (H, Li, B, Be, Cl) were done at CSCC on a Cameca IMS 4f probe with an $^{16}O^-$ primary beam ~10 μm in diameter, 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. 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) and by Ottolini et al. (2000). Electron microprobe data were obtained at the University of Manitoba (Canada) with a Cameca SX50 electron-microprobe, according to the procedures described by Hawthorne et al. (1996c).

X-RAY ANALYSIS AND STRUCTURE REFINEMENT

The X-ray powder-diffraction pattern was recorded from the mineral separate with a Philips X-PERT diffractometer using graphite-monochromatized Cu*K*α X-radiation; NBS Si was used as a standard. The positions of the peaks were determined with the Philips PC-APD software, and unit-cell parameters were refined starting from the corrected *d* values with the program UNITCELL (Holland and Redfern 1997). The indexed powder-pattern and refined unit-cell parameters are given in Table 3.

Selected ferripedrizite crystals were mounted on a Philips PW-1100 four-circle diffractometer and examined with graphite-monochromatized Mo*K*α X-radiation; crystal quality

TABLE 2. Average chemical analysis and formula unit of ferripedrizite samples from the thin sections (n = 51, 33 crystals) and of the refined crystal (no. 953); unit formula calculated on the basis of 24 (O, OH, F) pfu

	Thin section	σ	953		Thin section	σ	953
SiO_2	56.74	(60)	57.77	Si	8.000		8.000
TiO_2	1.26	(33)	0.85	Ti	0.130	(36)	0.089
Al_2O_3	1.32	(33)	1.30	Al	0.220	(58)	0.212
Fe_2O_3*	14.04	(2.23)	15.73	Fe^{3+}	1.490	(231)	1.640
FeO*	8.94	(2.31)	7.31	Fe^{2+}	1.054	(289)	0.846
MnO	0.60	(11)	0.61	Mn^{2+}	0.070	(14)	0.072
MgO	6.80	(87)	7.21	Mg	1.429	(179)	1.488
ZnO	0.16	(7)	0.10	Zn	0.020	(7)	0.010
CaO	0.33	(14)	0.34	Li	0.590	(97)	0.643
Li_2O	3.98	(2)	†4.21	Sum C	5.000		5.000
Na_2O	2.92	(41)	2.88	Ca	0.050	(21)	0.050
K_2O	0.21	(4)	0.22	Li	1.670	(126)	1.70
H_2O	*1.58	(10)	†1.42	Na	0.280	(115)	0.249
F	1.15	(23)	†1.58	Sum B	2.000		2.000
F≡O	–0.48		–0.67	Na	0.520	(127)	0.524
Sum	99.54		100.87	K	0.040	(7)	0.039
				Sum A	0.560		0.563
				O	22.000		22.000
				OH	1.490	(100)	1.308
				F	0.510	(100)	0.692

* Calculated assuming OH + F = 2 apfu and T sites fully occupied by Si.
† From SIMS analysis.

TABLE 3. X-ray powder-diffraction of ferripedrizite

h k l	I_{obs}	d_{obs} (Å)	d_{calc} (Å)	*h k l*	I_{obs}	d_{obs} (Å)	d_{calc} (Å)
1 1 0	29	8.251	8.240	$\underline{0}$ 10 0	4	1.787	1.787
$\underline{1}$ 3 0	3	5.013	5.013	$\underline{4}$ 4 2	2	1.782	1.782
1 1 1	1	4.806	4.805	$\underline{1}$ 3 3	4	1.690	1.691
0 2 1	10	4.475	4.477	$\underline{5}$ 1 2	6	1.679	1.679
0 4 0	22	4.466	4.466	$\underline{2}$ 8 2	5	1.664	1.664
2 2 0	1	4.120	4.120	3 9 1	3	1.646	1.646
$\underline{1}$ 1 1	2	4.054	4.053	4 6 1	39	1.642	1.642
$\underline{2}$ 0 1	1	3.887	3.887	4 8 0	16	1.609	1.610
$\underline{1}$ 3 1	2	3.825	3.824	$\underline{1}$ 11 0	5	1.599	1.600
2 2 1	8	3.564	3.564	1 5 3	6	1.581	1.581
1 3 1	17	3.411	3.411	$\underline{4}$ 0 2	3	1.571	1.571
1 5 0	5	3.335	3.335	6 2 1	2	1.554	1.553
2 4 0	12	3.216	3.219	$\underline{6}$ 0 0	12	1.548	1.548
3 1 0	100	3.050	3.050	4 2 3	1	1.527	1.527
$\underline{2}$ 2 1	2	2.964	2.964	$\underline{1}$ 9 2	2	1.522	1.521
1 5 1	5	2.905	2.905	2 6 3	3	1.502	1.503
3 3 0	31	2.747	2.747	5 5 1	1	1.491	1.492
$\underline{1}$ 5 1	37	2.711	2.711	$\underline{0}$ 12 0	11	1.489	1.489
3 3 1	8	2.639	2.639	$\underline{6}$ 0 2	5	1.472	1.472
0 0 2	2	2.588	2.587	2 10 2	3	1.453	1.452
$\underline{0}$ 6 1	14	2.580	2.581	$\underline{3}$ 11 0	4	1.438	1.438
2 0 2	16	2.495	2.494	$\underline{4}$ 10 1	2	1.413	1.413
$\underline{1}$ 7 0	5	2.461	2.461	$\underline{6}$ 4 2	4	1.398	1.398
$\underline{3}$ 5 1	13	2.272	2.272	6 6 1	32	1.394	1.394
$\underline{4}$ 2 1	3	2.234	2.234	5 1 2	14	1.373	1.373
3 1 2	4	2.212	2.213	2 6 3	3	1.351	1.351
1 7 1	6	2.176	2.176	5 3 2	3	1.342	1.342
$\underline{2}$ 6 1	18	2.161	2.161	1 11 2	5	1.339	1.399
3 3 2	3	2.088	2.088	$\underline{7}$ 1 0	7	1.323	1.323
2 0 2	7	2.081	2.081	$\underline{5}$ 5 3	3	1.321	1.321
0 8 1	1	2.051	2.051	1 1 4	3	1.316	1.316
3 5 1	12	2.015	2.015	1 13 1	2	1.305	1.305
$\underline{1}$ 5 2	2	1.973	1.973	$\underline{7}$ 3 0	7	1.295	1.295
$\underline{4}$ 0 2	3	1.944	1.944	$\underline{6}$ 8 1	5	1.288	1.288
3 7 1	3	1.928	1.928	$\underline{5}$ 9 2	4	1.285	1.285
4 2 1	8	1.923	1.923	$\underline{2}$ 12 2	8	1.278	1.278
2 4 2	2	1.886	1.886	7 5 1	7	1.268	1.268
$\underline{5}$ 1 0	6	1.848	1.848	$\underline{4}$ 12 0	2	1.253	1.253
$\underline{1}$ 9 1	2	1.844	1.844	3 13 1	2	1.245	1.245
4 6 1	1	1.825	1.824	6 0 2	2	1.220	1.220
1 9 1	5	1.792	1.792	2 12 2	2	1.211	1.211

Calculated unit-cell parameters: a = 9.501(1), b = 17.866(2), c = 5.292(1) Å; β = 102.17(2)°, V = 878.1 Å^3.

was assessed via profile analysis of Bragg diffraction peaks. 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 $-30 < \theta < 30°$. Intensity data were collected for the monoclinic-equivalent pairs (*hkl* and $h\bar{k}l$) in the range $2 < \theta < 30°$; they were corrected for absorption, Lorentz, and polarization effects, averaged and reduced to structure factors ($R_{int} = 1.3\%$).

Structure-refinement procedures were as described in Oberti et al. (1992) and Hawthorne et al. (1995). Reflections with $I > 3\sigma_I$ were considered as observed during unweighted full-matrix least-squares refinement on *F*. Scattering curves for fully ionized chemical species were used at sites where chemical substitutions occur; neutral vs. ionized scattering curves were used at the T and anion sites (except O3). For the crystal closest to the end-member composition, refinement information and final *R* values in the space group *C*2/*m* are given in Table 4, atom positions, refined site-scattering values and atom displacement parameters are given in Table 5, and selected interatomic distances and angles are given in Table 6. Table 7[1] lists the observed and calculated structure factors.

STRUCTURAL CHANGES AND CATION ORDERING IN FERRIPEDRIZITE

The root name pedrizite refers to the ideal composition with the highest possible Li content in amphiboles (i.e., 2 ^{B}Li apfu + 1 ^{C}Li apfu = 3 apfu). It is thus expected to have structural and crystal-chemical peculiarities.

Pedrizite is related to leakeite (1 ^{C}Li apfu) by the homovalent exchange vector $^{B}(Li_2Na_{-2})$ and to clinoholmquistite (2 ^{B}Li apfu) by the coupled heterovalent exchange vectors $^{M2}Fe^{3+}\,^{M3}Li\,^{M2}Fe^{2+}_{-1}\,^{M3}Mg_{-1}$. The refined crystal shows some deviations from the ideal ferripedrizite stoichiometry. The EMP + SIMS analysis reported in Table 2 indicates that its composition is $^{A}(K_{0.04}Na_{0.52})^{B}(Na_{0.25}Ca_{0.05}Li_{1.70})^{C}(Li_{0.64}Fe^{3+}_{1.64}Mg_{1.49}Fe^{2+}_{0.85}Al_{0.21}Ti_{0.09}Mn_{0.07}Zn_{0.01})^{T}Si_8O_{22}{}^{X}(OH_{1.31}F_{0.69})$, albeit comparison of the site-scattering values calculated from the unit formula and measured by SREF analysis (the note in Table 5) suggests that ^{B}Li might be slightly underestimated, and ^{C}Li slightly overestimated. However, comparative analysis of this sample and of sodic-ferripedrizite (Oberti et al. 2000) allows extrapolation of the structural details of stoichiometric ferripedrizite.

TABLE 4. Unit-cell dimensions and crystal-structure refinement information

a (Å)	9.499(5)
b (Å)	17.864(7)
c (Å)	5.296(3)
β (°)	102.15(4)
V (Å³)	878.6
Space group	*C*2/*m*
$R_{int} \times 100$	1.3
No. all	1340
No. obs ($I > 3\sigma_I$)	1132
R all × 100	2.3
R obs ($I > 3\sigma_I$) × 100	1.6
SEQ*	953

* Sequence number in the CNR-CSCC amphibole database.

TABLE 6. Selected interatomic distances (Å) and angles (°) for ferripedrizite

T1-O1		1.614(1)	M4-O2	×2	2.196(4)
-O5		1.618(1)	-O4	×2	2.114(2)
-O6		1.617(1)	-O5	×2	3.091(4)
-O7		1.625(1)	-O6	×2	2.593(4)
<T1-O>		1.618	<M4-O>		2.498
T2-O2		1.627(1)	M4'-O2	×2	1.971(1)
-O4		1.597(1)	-O4	×2	2.101(1)
-O5		1.636(1)	-O5	×2	3.301(2)
-O6		1.641(1)	-O6	×2	2.858(1)
<T2-O>		1.625	<$^{[6]}$M4'-O>		2.310
M1-O1	×2	2.071(1)	A*m*-O5	×2	2.718(3)
-O2	×2	2.141(1)	-O5	×2	3.071(4)
-O3	×2	2.071(1)	-O6	×2	2.668(3)
<M1-O>		2.094	-O7		2.460(5)
M2-O1	×2	2.098(1)	-O7		2.566(5)
-O2	×2	2.019(1)	-O7		2.981(6)
-O4	×2	1.916(1)	<A*m*-O>		2.769
<M2-O>		2.011	O3-H		0.708(1)
M3-O1	×2	2.114(1)	T1-T1		3.085
-O3	×4	2.101(2)	O5-O6-O5		172.44
<M3-O>		2.110	A*m*-O3		2.917(6)
			A*m*-A*m*		1.832(11)

TABLE 5. Atom coordinates, refined site-scattering values (ss, epfu), atom displacement parameters (B_{eq}, Å³; $\beta_{ii} \times 10^4$) for ferripedrizite

Atom	ss*	*x*	*y*	*z*	B_{eq}	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
O1		0.1121(1)	0.0911(1)	0.2045(3)	0.61(2)	14(1)	5(1)	64(3)	–1(1)	6(1)	0(1)
O2		0.1217(1)	0.1736(1)	0.7311(2)	0.68(2)	16(1)	7(1)	59(3)	1(1)	7(1)	1(1)
O3	16.8	0.1145(1)	0	0.7011(3)	0.94(3)	24(2)	7(1)	96(5)	–	2(2)	–
O4		0.3747(1)	0.2503(1)	0.7826(2)	0.84(2)	28(1)	5(1)	77(3)	–4(1)	4(2)	1(1)
O5		0.3545(1)	0.1295(1)	0.0639(2)	0.82(2)	17(1)	10(1)	64(3)	0(1)	8(1)	9(1)
O6		0.3467(1)	0.1205(1)	0.5626(2)	0.90(2)	20(1)	11(1)	57(3)	1(1)	3(1)	–10(1)
O7		0.3395(2)	0	0.2803(3)	0.90(3)	24(2)	4(1)	125(5)	–	8(2)	–
T1		0.2856(1)	0.0864(1)	0.2779(1)	0.44(1)	13(1)	3(1)	40(1)	0(1)	3(1)	–1(1)
T2		0.2967(1)	0.1713(1)	0.7867(1)	0.46(1)	14(1)	4(1)	40(1)	–1(1)	3(1)	0(1)
M1	33.1	0	0.0878(1)	1/2	0.62(1)	20(1)	5(1)	51(1)	–	11(1)	–
M2	49.2	0	0.1810(1)	0	0.53(1)	14(1)	4(1)	48(1)	–	4(1)	–
M3	12.7	0	0	0	0.69(2)	23(1)	4(1)	63(3)	–	3(1)	–
M4	5.6	0	0.2636(3)	1/2	1.93(12)	33(5)	31(2)	72(14)	–	26(4)	–
M4'	1.6	0	0.2454(7)	1/2	1.05(1)						
A*m*	6.1	0.0720(5)	1/2	0.1453(9)	2.68(11)	114(6)	12(1)	325(18)	–	149(9)	–
H	1.3	0.1877(9)	0	0.7657(15)	0.91(7)						

* The e.s.d. on site-occupancy ranges from 0.002 to 0.004; when multiplied by the proper number of electrons, they give e.s.d. for the tabulated ss values ranging from 0.04 to 0.07 epfu. Only one decimal digit was given in order to take into account also small inconsistencies in the refined model due to the use of only two ionic species per site. Refined vs. calculated ss (epfu) for the group sites: A: 6.1 vs. 6.5; B: 7.2 vs. 8.8; C: 95 vs. 91.2; O3: 16.8 vs. 16.5.

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[1] For a copy of Table 7, Document AM-02-009, 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.

Similarly to all other amphiboles in which both small (Li^+, Mg^{2+}, Mn^{2+}, and Fe^{2+}) and large (Na^+ and Ca^{2+}) cations occupy the B-group sites, the best structure refinement was obtained by using a split-site model (M4 for Na + M4' for Li), which takes into account the fact that the two kinds of cations occur at different values of the *y* coordinate. As shown in Table 6, their coordinations are significantly different. However, the electron density distribution at the A-group sites could be modeled by using the A*m* split site alone, showing that there is no positional disorder along the *b* axis; both the A*m* and the A sites had been used in sodic-ferripedrizite. Moreover, the shift of the A*m* site from the center of the cavity in ferripedrizite (0.92 Å) is greater than in sodic-ferripedrizite (0.85 Å) and far greater than in sodic amphiboles (0.54–0.56 Å). This confirms previous suggestions that the O5 and O6 basal atoms of the tetrahedra require further bond-strength contribution when a small monovalent cation such as Li occurs at the B-group sites, and orders in a position closer to the strip of octahedra and far from the double chain of tetrahedra (M4′-O5 = 3.30, M4′-O6 = 2.86 Å). The arrangement of the relevant atoms in pedrizite is schematically represented in Figure 1.

Like other cases in which a small cation substitutes for a large cation at the B positions (e.g., the cummingtonite component in sodic and calcic amphiboles and the enstatite component in clinopyroxenes), the presence of Li at the B-group sites strongly affects unit-cell parameters, in particular the *a* edge and the β angle. They are both smaller in the ferripedrizite sample of this study (9.499 Å and 102.15°) than in sodic-ferripedrizite (9.534 Å and 102.52°). Supposing a linear behavior and neglecting the very small difference in the Ca content (0.05 vs. 0.08 apfu), it could be inferred that for stoichiometric ferripedrizite *a* ~9.426 Å and β ~101.4°. For comparison, clinoholmquistite with 0.21 ^{B}Ca apfu and 0.49 $^{A}(Na + K)$ apfu has *a* = 9.334 Å and β = 101.4° (Litvin et al. 1975), whereas the values for grunerite [ideally, $^{B}Fe^{2+}_{2}\,^{C}Fe^{2+}_{5}\,^{T}Si_{8}O_{22}\,^{X}(OH)_{2}$] with 0.14 ^{B}Ca apfu are *a* = 9.560 Å and β = 101.8° (Boffa Ballaran et al. 2001). The ionic radii in sixfold coordination are 0.76 Å for Li and 0.78 Å for Fe^{2+}, respectively.

The M4-O4 distance is particularly short in the ferripedrizite sample (2.114 Å), compared to sodic-ferripedrizite (2.170 Å) and to clinoholmquistite (2.25 Å). Because the O5 and the O6 basal atoms of the tetrahedra are, respectively, out of and at the verge of the coordination sphere of the M4 site (3.091 and 2.593 Å), the tetrahedral distances involving O5 and O6 (and O7) become shorter, whereas those involving O1, O2, and O4 lengthen (T1-O5 = 1.627, 1.622, 1.618 Å; T1-O6 = 1.624, 1.617, 1.617 Å; T1-O7 = 1.631, 1.630, 1.625 Å; T2-O5 = 1.656, 1.639, 1.636 Å; T2-O6 = 1.664, 1.644, 1.641 Å; T1-O1 = 1.600, 1.602, 1.614 Å; T2-O2 = 1.618, 1.623, 1.627 Å; T2-O4 = 1.588, 1.592, 1.597 Å in leakeite, sodic-ferripedrizite, and ferripedrizite, respectively). As a consequence, distortion parameters for both tetrahedra decrease along the join (^{T1}TQE = 1.0029, 1.0021, 1.0009; ^{T2}TQE = 1.0052, 1.0034, 1.0028; ^{T1}TAV = 12.33, 8.70, 3.76°; ^{T2}TAV = 22.46, 14.51, 11.78°; Robinson et al. 1971). A significant rearrangement of the double chain of tetrahedra is thus observed; both the T1-T1 distance and the internal angles of the ring of tetrahedra increase along the join (T1-T1 = 3.074, 3.073, and 3.089 Å; T1-O7-T1 = 141.0, 141.1, and 143.4°; T1-O6-T2 = 137.1, 139.7, 141.4°, and T1-O5-T2 = 135.3, 136.4, 137.5°).

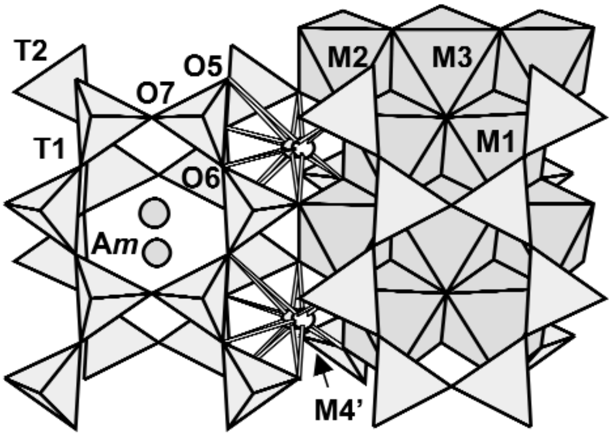

FIGURE 1. (100) projection of the ferripedrizite structure showing the peculiarities relevant to the present discussion.

The observed octahedral mean bond lengths indicate that small and highly charged cations order at the M2 site, as shown in previous studies (Hawthorne et al. 1993; Oberti et al. 1995). As is the case for leakeite, dimensional and geochemical constraints suggest that Al^{3+} is an inconvenient major octahedral constituent, and that pedrizite is unlikely to occur (actually, leakeite had been defined as an Fe^{3+} composition by default). Combination of refined mean bond-lengths and site-scattering values, and correction for the F content at O3, indicate that the M1 site is occupied by Mg and Fe^{2+}, and the M3 site by Li, Fe^{2+}, and Mn^{2+}. Thus the most likely site distribution for the unit formula reported in Table 2 is: $^{Am}(Na_{0.52}\,K_{0.04})\,^{M4,M4'}(Li_{1.70}\,Na_{0.25}Ca_{0.05})^{M1}(Mg_{1.49}Fe^{2+}_{0.51})^{M2}(Fe^{3+}_{1.64}Al_{0.21}Ti_{0.09}Fe^{2+}_{0.05}Zn_{0.01})\,^{M3}(Li_{0.64}Fe^{2+}_{0.29}\,Mn_{0.07})^{T1,T2}Si_{8}O_{22}\,^{O3}(OH_{1.31}F_{0.69})$.

SOLID SOLUTIONS AND NOMENCLATURE OF LI-BEARING AMPHIBOLES

The available EMP analyses of Li-bearing amphiboles from the Pedriza Massif are reported in Figure 2, which shows Li partitioning between the B and C sites. In the absence of a direct determination (SIMS analyses were done on ~40 of the ~200 EMP points), the Li contents at the B- and C-group sites were estimated by calculating the unit formula using the constraints obtained, when available, from combined EMP + SIMS + SREF analysis. They are: 24 (O, OH, F) apfu; OH + F = 2 apfu; Si = 8 apfu; and (Fe^{3+} + Ti + Al + Zn) ≤ 2. Low concentrations of ^{T}Al (< 0.2 apfu) might be present in the samples richest in Na, which would result in a slight overestimation of ^{B}Na.

Figure 2 shows that there is complete (homovalent) solid solution between the ferripedrizite and the leakeite series, which have the same charge arrangement. This is further confirmed by the absence of exsolution textures under SEM and TEM analysis, as well as by SAD patterns. The solid solution is basically ruled by the coupled exchange vectors $^{M2}Fe^{3+}\,^{M3}Li\,^{M2}Fe^{2+}_{-1}\,^{M3}Mg_{-1}$, which are active in both the series, and by the exchange vector $^{B}Na^{B}Li_{-1}$, which relates the two series (cf. also Oberti et al. 2000).

Miscibility gaps have been frequently proposed between

Mg-Fe-Mn-Li amphiboles and either sodic or calcic amphiboles. For instance, exsolution textures have been reported between manganocummingtonite and magnesio-arfvedsonite (Robinson et al. 1982; Shau et al. 1993), between grunerite and riebeckite (Robinson et al. 1982), and also between cummingtonite and glaucophane (Smelik and Veblen 1991). These features were ascribed to the different size and conformation of the M4 site in the presence of small and large cations, which can be avoided by exsolution of the minor component. Higher temperatures of crystallization and rapid cooling rates may extend the stability of the solid solution [e.g., to $^{B}(Mg + Mn) = 0.74$ apfu in sodic amphiboles; Oberti and Ghose 1993]. It should, however, be noted that when the charge of the exchanging cation at M4 is different, as is the case for cummingtonite and arfvedsonite, a coupled substitution at the M2 site is required to provide local charge balance. Thus the substitution of a larger monovalent cation such as Na is coupled with that of a smaller trivalent cation such as Fe^{3+}, and structural strain is extended to the octahedral strip.

In conclusion, the ferripedrizite series is very peculiar in the otherwise rather homogeneous Mg-Fe-Mn-Li group. It is the only series with Na > 0.5 apfu at the A-group sites, monovalent cations (Li and Na) at the B-group sites, and monovalent Li at the C-group sites (ordered at M3). The sodic group also shows these features, and has a strictly analogous crystal-chemical behavior. These analogies could even suggest coupling of monoclinic lithium amphiboles to sodic amphiboles. In our opinion, the only argument against this is the difference in location and coordination of Na and Li at the B-group sites. However, this suggestion was rejected by the Subcommittee on Amphiboles of the IMA-CNMMN.

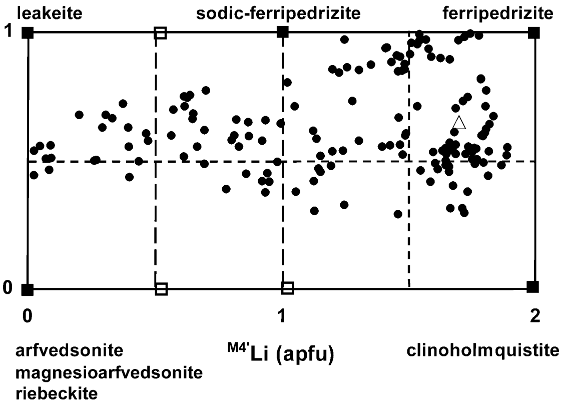

FIGURE 2. The partitioning of lithium in amphiboles from episyenites of the East Pedriza Massif. The gray triangle indicates the position of the refined sample of this work. The relevant end-member names and compositions are indicated, ignoring the Fe^{2+}/Mg ratio. Black squares indicate approved species, open squares indicate still unapproved species; this projection does not take into account the A-site occupancy, and thus the presence of a point does not necessarily implies the presence of a new species. The boundaries of the compositional fields are shown as dashed lines (long dashes indicate boudaries between different amphibole groups).

The laws in force (Leake et al. 1997) state that homovalent exchanges do not deserve different root names, but solely the use of a prefix to identify one of the two end-members of the solid solution. Unfortunately, the definition of the prefix sodic ($Na_{tot} > 0.5$ apfu for the Mg-Fe-Mn-Li group) would not allow distinction between $^{A}Na^{B}Li_2{}^{C}(Fe^{3+}_2Mg_2Li)^{T}Si_8O_{22}{}^{X}(OH)_2$ and $^{A}Na^{B}(NaLi)^{C}(Fe^{3+}_2Mg_2Li)^{T}Si_8O_{22}{}^{X}(OH)_2$, which should thus be both called sodic-ferripedrizite. Thus the use of the prefix sodic was restricted to $^{B}Na > 0.5$ apfu for the pedrizite series, and composition $^{A}Na^{B}Li_2{}^{C}(Fe^{3+}_2Mg_2Li)^{T}Si_8O_{22}{}^{X}(OH)_2$ is now named ferripedrizite.

The Mg-Fe-Mn-Li group is defined by $^{B}(Mg + Fe + Mn + Li) \geq 1.0$ apfu; the sodic group is defined by $^{B}(Mg + Fe + Mn + Li) < 1.0$ apfu and $^{B}Na \geq 1.5$ apfu; and the sodic-calcic group is defined by $^{B}(Mg + Fe + Mn + Li) < 1.0$ apfu, $^{B}(Ca + Na) \geq 1.0$ apfu, and $0.5 \leq {}^{B}Na \leq 1.49$ apfu. Thus the solid solution between ferripedrizite and leakeite actually crosses three different amphibole groups and has four possible end-members of reference, one of which hasn't yet been recognized: (1) samples with $^{B}(Mg + Fe + Mn + Li) \geq 1.0$ apfu and $0.0 \leq {}^{B}Na \leq 0.50$ apfu belong to the Mg-Fe-Mn-Li group and are named ferripedrizite; (2) samples with $^{B}(Mg + Fe + Mn + Li) \geq 1.0$ apfu and $0.50 < {}^{B}Na \leq 0.99$ apfu also belong to the Mg-Fe-Mn-Li group but are named sodic-ferripedrizite; (3) samples with $^{B}(Mg + Fe + Mn + Li) < 1.0$ apfu and $^{B}Na \geq 1.50$ apfu belong to the sodic group and are named leakeite; (4) samples with $^{B}(Mg + Fe + Mn + Li) < 1.0$ apfu and $1.0 \leq {}^{B}Na \leq 1.49$ apfu belong to the sodic-calcic group (albeit Ca might be negligible), and will deserve a new root name. The boundaries between these compositions are also shown in Figure 2.

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