

## The mechanism of $^{6}\text{Li}$ incorporation in amphiboles

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### ABSTRACT

The crystal structures of five monoclinic alkali amphiboles from Kajlidongri, Madhya Pradesh, India, have been refined to  $R$  indices of <2% using ~1100 observed ( $5\sigma$ ) reflections measured with  $\text{MoK}\alpha$  X-radiation; the crystals used in the collection of the X-ray data were subsequently analyzed by electron microprobe techniques. Both site-scattering refinement and an ion microprobe analysis show major Li in these crystals (up to ~1.3 wt%  $\text{Li}_2\text{O}$ ), which fall in the series ferri-eckermannite-leakeite  $[\text{NaNa}_2(\text{Mg}_4\text{Fe}^{3+})\text{Si}_8\text{O}_{22}(\text{OH})_2-\text{NaNa}_2(\text{Mg}_3\text{Fe}^{3+}\text{Li})\text{Si}_8\text{O}_{22}(\text{OH})_2]$ . HRTEM examination showed a well-behaved amphibole structure, relatively free of defects. These amphiboles contain significant Mn (up to 0.5 apfu), and all Fe and Mn are in the trivalent state. These amphiboles are indicative of strongly oxidizing conditions. In agreement with this, one crystal shows an oxy-substitution that is characterized by the occurrence of  $\text{Ti}^{4+}$  at the M1 site. Li is completely ordered at the M3 site, and the compensating trivalent cations are ordered primarily at M2. This means that  $^{6}\text{Li}$ -bearing alkali amphiboles can easily be identified in the absence of AA or ion microprobe analysis by the anomalously low X-ray scattering at the M3 site. Significant C-group Li has only been found in alkali amphiboles, where it seems to be locally associated with Na at the A site and Si at all neighboring T sites. Local charge-balance considerations suggest that  $^{6}\text{Li}$  does not occur in sodic-calcic and calcic amphiboles, in agreement with the coexistence of holmquistite and hornblende or pargasite.

### INTRODUCTION

The distribution and behavior of Li in rock-forming minerals is still not very well characterized, primarily because of difficulties in analyzing for Li at the micrometer scale. This situation is now changing with the application of microanalytical techniques and detailed crystal structure refinement to rock-forming minerals, particularly by the examination of suites of minerals from petrologically well-characterized environments.

Until recently, the only well-characterized role of Li in amphibole chemistry was as a B-group cation (occupying the M4 site) in the ferromagnesian amphiboles holmquistite and clinoholmquistite. Ungaretti et al. (1978), Hawthorne (1978a), and Ghose et al. (1986) reported the occurrence of small amounts of C-group Li in alkali amphiboles, suggesting that C-group Li could be an important constituent of alkali amphiboles in Li-bearing environments. Systematic investigation of this possibility has shown C-group Li as a major constituent in alkali amphiboles. Leakeite is a Li-bearing monoclinic alkali amphiboles, ideally  $\text{NaNa}_2(\text{Mg}_2\text{Fe}^{3+}\text{Li})\text{Si}_8\text{O}_{22}(\text{OH},\text{F})_2$ , that

was recently described by Hawthorne et al. (1992). The original material is associated with epigenetic veining in the manganeseiferous metasediments of the Kajlidongri area, Madhya Pradesh, India (Lahiri, 1971; Leake et al., 1981). A similar environment at the Hoskins mine, New South Wales, Australia (Hawthorne et al., in preparation; Ashley, 1986), also shows extensive occurrences of Li-bearing alkali amphiboles. Li-bearing alkali amphiboles also occur in the peralkaline granitic rocks of the Questa caldera, New Mexico (Hawthorne et al., 1993), and may be common constituents of such granitic rocks. Indeed, Hawthorne et al. (1993) showed that interpretation of  $f_{\text{O}_2}$  relations in such granitic rocks may be seriously in error if the  $^{6}\text{Li}$  contents of the amphiboles are ignored. Recently, the new amphibole species kornite, ideally  $\text{KNa}_2(\text{Mg}_2\text{Mn}^{3+}\text{Li})\text{Si}_8\text{O}_{22}(\text{OH})_2$ , was reported by Armbruster et al. (1993). Although no structural details are yet available, this new amphibole seems to be the K-Mn $^{3+}$  equivalent of leakeite.

Here we examine the crystal chemistry of  $^{6}\text{Li}$  incorporation in alkali amphiboles, together with the structural constraints that control ordering behavior and possible chemical variations. Figure 1 shows a view of the  $C2/m$  amphibole structure; it may be used in conjunction with the stereochemical discussions given later.

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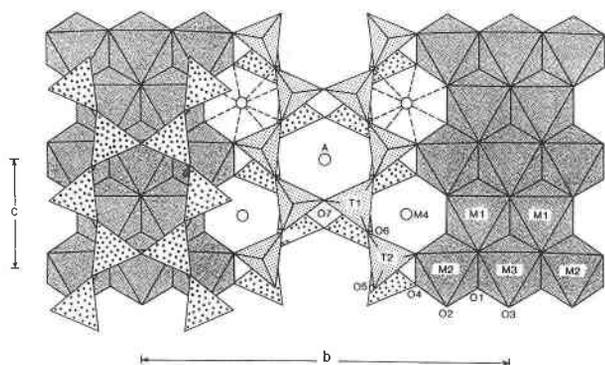


Fig. 1. A polyhedral view of the  $C2/m$  amphibole structure projected down  $a$ .

### EXPERIMENTAL METHODS

The amphiboles examined here (Table 1) are from Kajlidongri, Madhya Pradesh, India, and were obtained from B. E. Leake.

#### X-ray data collection

Crystals were selected for crystallographic analysis and intensity data collection on the basis of optical clarity and freedom from inclusions. All crystals were mounted on a Philips PW 1100 automated four-circle diffractometer and examined with graphite-monochromated  $MoK\alpha$  X-radiation; crystal quality was assessed by means of the profiles and widths of Bragg diffraction peaks. Unit-cell dimensions were calculated from least-squares refinement of the positions of 48 rows of reflections in the range  $-35^\circ < \theta < 35^\circ$ ; values for the crystals used in the collection of the intensity data are given in Table 2.

Intensity data were collected for the equivalent pairs  $hkl$  and  $\bar{h}\bar{k}l$  in the Laue group  $2/m$  in the range  $2 < \theta < 30^\circ$ , using the step-scan profile technique of Lehman and Larsen (1974). Full details of the data collection procedure are given in Ungaretti (1980) and Ungaretti et al. (1981). The intensity data were corrected for absorption by the method of North et al. (1968), corrected for Lorentz and polarization effects, averaged, and reduced to structure factors. A reflection is considered as observed if its intensity exceeds that of 5 sd, based on counting statistics.

#### Structure refinement

Fully ionized scattering factors were used for nontetrahedral cations, and both neutral and ionized scattering

TABLE 1. Sample numbering and codes

No.	Name	Sample code	SEQ*
A1	leakeite	Leake 6-11	448
A2	leakeite	Leake 7-4	441
A3	leakeite	Leake 7-1	438
A4	ferri-eckermannite	Leake 6-7	447
A5	ferri-eckermannite	Leake 6-1	446

\* Sequence number in amphibole refinement data bank at Pavia.

TABLE 2. Miscellaneous data collection and structure refinement information for Li-bearing alkali amphiboles

	A1	A2	A3	A4	A5
$a$ (Å)	9.748	9.790	9.822	9.771	9.779
$b$ (Å)	17.842	17.848	17.836	17.887	17.888
$c$ (Å)	5.287	5.287	5.286	5.289	5.287
$\beta$ (°)	104.12	104.10	104.37	103.82	103.85
$V$ (Å <sup>3</sup> )	891.84	895.87	897.14	897.61	897.95
$F_o$	1359	1358	1359	1366	1367
$F_o > 5\sigma$	1081	1025	1072	1064	1157
$R_{sym}$	1.1	2.3	1.8	1.1	1.1
$R_{cos}$	1.4	1.4	1.5	1.3	1.2
$R_{tot}$	2.4	3.1	2.8	2.2	1.7

factors were used for tetrahedral cations and O atoms (Ungaretti et al., 1983).  $R$  indices are of the standard form and are given as percentages.

All refinements were done in the space group  $C2/m$ ; the starting occupancies represented the average composition reported for these amphiboles by Hawthorne et al. (1992). For all crystals, the equivalent isotropic displacement parameters for O3, obtained using the scattering curves for O, were higher than those at other anion sites, indicating  $F \rightarrow OH$  substitution; this was later confirmed by electron microprobe analysis. Consequently, the scattering factors for  $O^-$  and  $F^-$  were used in the last cycles of refinement, with the occupancy of O3 considered as a variable parameter. The refinements converged to  $R$  indices of  $< 2\%$  for full matrix refinement of all atomic positions, those site occupancies considered as variable, and anisotropic displacement factors; in these final refinements, the scattering curves for Li and Fe were used at the M3 site. Final atomic coordinates and equivalent isotropic displacement parameters are given in Table 3, selected interatomic distances are given in Table 4, refined site-scattering powers are listed in Table 5, and observed and calculated structure factors are given in Table 6.<sup>1</sup>

#### Electron microprobe analysis

The crystals used in the collection of the intensity data were subsequently mounted, polished, and analyzed by electron microprobe techniques. The crystals were mounted in piccolite in small holes in 1-in. Cu disks; each disk also contained several crystals of tremolite and fluorriebeckite (samples 56 and 68 of Hawthorne, 1983) as a check on accuracy.

Electron-microprobe analysis was done on a fully automated Cameca SX-50 operating in the wavelength-dispersive mode with the following conditions: excitation voltage: 15 kV; specimen current: 20 nA; peak count time: 20 s; background count time: 10 s. The following standards and crystals were used for  $K$  X-ray lines: Al: hornblende, TAP; Fe: arfvedsonite, LiF; Si: diopside, PET;

<sup>1</sup> A copy of Table 6 may be ordered as Document AM-94-553 from the Business Office, Mineralogical Society of America, 1130 Seventeenth Street NW, Suite 330, Washington, DC 20036, U.S.A. Please remit \$5.00 in advance for the microfiche.

TABLE 3. Final atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement factors ( $\text{\AA}^2$ )

No.	O1				O2				O3			
	x	y	z	$B_{eq}$	x	y	z	$B_{eq}$	x	y	z	$B_{eq}$
A1	1115	886	2159	0.63	1178	1668	7270	0.60	1104	0	6965	0.76
A2	1102	905	2146	0.65	1186	1694	7315	0.66	1115	0	7002	0.96
A3	1100	905	2154	0.71	1184	1685	7284	0.76	1110	0	6975	0.91
A4	1112	881	2137	0.54	1182	1695	7326	0.57	1089	0	7083	0.76
A5	1111	882	2142	0.55	1182	1693	7318	0.60	1091	0	7075	0.77
O4				O5				O6				
x	y	z	$B_{eq}$	x	y	z	$B_{eq}$	x	y	z	$B_{eq}$	
A1	3605	2508	8018	0.80	3500	1280	816	0.74	3456	1198	5823	0.73
A2	3632	2504	8018	0.81	3497	1285	851	0.77	3435	1192	5845	0.73
A3	3623	2504	8027	0.89	3486	1281	850	0.74	3436	1193	5854	0.74
A4	3629	2504	7997	0.74	3493	1295	848	0.75	3425	1195	5833	0.71
A5	3627	2503	7996	0.77	3492	1294	849	0.74	3426	1193	5836	0.72
O7				T1				T2				
x	y	z	$B_{eq}$	x	y	z	$B_{eq}$	x	y	z	$B_{eq}$	
A1	3394	0	2979	0.84	2811	857	2929	0.41	2889	1710	7998	0.42
A2	3348	0	2963	0.93	2785	862	2934	0.43	2889	1712	8023	0.43
A3	3338	0	2983	0.94	2780	862	2944	0.46	2883	1712	8018	0.45
A4	3370	0	2957	0.83	2805	857	2930	0.39	2885	1714	8017	0.40
A5	3369	0	2956	0.85	2802	857	2932	0.40	2884	1713	8016	0.42
M1				M2				M3				
x	y	z	$B_{eq}$	x	y	z	$B_{eq}$	x	y	z	$B_{eq}$	
A1	0	823	1/2	0.72	0	1796	0	0.48	0	0	0	0.69
A2	0	865	1/2	0.54	0	1796	0	0.48	0	0	0	0.79
A3	0	848	1/2	0.70	0	1796	0	0.50	0	0	0	0.69
A4	0	882	1/2	0.52	0	1809	0	0.47	0	0	0	0.54
A5	0	877	1/2	0.56	0	1807	0	0.47	0	0	0	0.55
M4				A				Am				
x	y	z	$B_{eq}$	x	y	z	$B_{eq}$	x	y	z	$B_{eq}$	
A1	0	2751	1/2	1.17	0	1/2	0	6.50	508	1/2	1091	2.87
A2	0	2764	1/2	1.14	0	1/2	0	3.01	480	1/2	1028	2.28
A3	0	2763	1/2	1.21	0	1/2	0	4.51	399	1/2	930	2.81
A4	0	2765	1/2	1.09	0	1/2	0	5.08	478	1/2	1035	2.93
A5	0	2764	1/2	1.07	0	1/2	0	4.36	479	1/2	1014	2.81
A2				H								
x	y	z	$B_{eq}$	x	y	z	$B_{eq}$					
A1	0	4680	0	4.68	1867	0	7577	2.65				
A2	0	4744	0	4.87	1826	0	7335	2.55				
A3	0	4766	0	4.14	1845	0	7705	3.11				
A4	0	4678	0	4.52	1891	0	7547	4.13				
A5	0	4654	0	3.85	1739	0	7437	1.58				

Mg: olivine, TAP; F: fluor-riebeckite, TAP; Mn: tephroite, LiF; Ti: titanite, LiF; Ca: diopside, PET; Na: albite, TAP; K: orthoclase, PET. Each grain was analyzed at a minimum of 12 points (often twice this number, depending on the size of the exposed surface) to check for compositional zoning and to get a representative composition for the whole crystal used in the diffraction experiment. Crystals were also checked for Co and V, but they were not found in significant amounts ( $<0.02$  wt%). Data reduction was done with the  $\phi(\rho Z)$  method (Pouchou and Pichoir, 1984, 1985); the mean analysis for each grain is given in Table 7.

#### Ion microprobe analysis

Ion microprobe analysis of crystal A5 was done on a Cameca IMS 4f with an  $O^-$  primary beam  $\sim 20$   $\mu\text{m}$  in

diameter, giving a beam current of  $\sim 10$  nA. The energy-filtering technique was used to eliminate any possible molecular interference and to reduce matrix effects. Secondary positive ion currents were measured at masses 7 (Li) and 30 (Si, used as the reference element) and corrected for isotopic abundances. The results were put on a quantitative basis using empirical calibration curves based on standard silicate samples. Further details can be found in Ottolini et al. (1993).

#### Calculation of the formula unit

Oberti et al. (1992) examined the behavior of Ti in richterite and showed that  $^{16}\text{Ti}$  enters the richterite structure via the oxy-type substitution  $^{M1}\text{Ti} + 2^{O3}\text{O}^{2-} = ^{M1}(\text{Mg,Fe}) + 2^{O3}(\text{OH})^-$ . When this substitution occurs, the assumption of two monovalent anions occupying the

**TABLE 4.** Selected interatomic distances (Å) in Li-bearing alkali amphiboles\*

	A1	A2	A3	A4	A5
T1-O1	1.604	1.599	1.600	1.608	1.606
-O5	1.623	1.626	1.627	1.623	1.624
-O6	1.624	1.626	1.624	1.626	1.625
-O7	1.630	1.633	1.631	1.629	1.630
(T1-O)	1.620	1.621	1.621	1.621	1.621
T2-O2	1.620	1.618	1.618	1.617	1.616
-O4	1.585	1.589	1.588	1.590	1.589
-O5	1.652	1.655	1.656	1.652	1.653
-O6	1.665	1.666	1.664	1.662	1.664
(T2-O)	1.630	1.632	1.631	1.630	1.631
M1-O1 × 2	2.061	2.059	2.061	2.064	2.062
-O2 × 2	2.088	2.084	2.084	2.070	2.072
-O3 × 2	1.962	2.032	2.000	2.067	2.060
(M1-O)	2.037	2.059	2.049	2.067	2.064
M2-O1 × 2	2.125	2.094	2.093	2.150	2.148
-O2 × 2	2.064	2.049	2.069	2.039	2.043
-O4 × 2	1.948	1.942	1.943	1.936	1.941
(M2-O)	2.046	2.028	2.035	2.042	2.044
M3-O1 × 4	2.092	2.113	2.111	2.087	2.089
-O3 × 2	2.139	2.132	2.147	2.073	2.079
(M3-O)	2.108	2.119	2.123	2.082	2.085
M4-O2 × 2	2.412	2.409	2.409	2.415	2.415
-O4 × 2	2.380	2.369	2.385	2.357	2.358
-O5 × 2	2.906	2.878	2.883	2.876	2.877
-O6 × 2	2.508	2.520	2.525	2.519	2.542
(M4-O) × 2	2.551	2.544	2.551	2.542	2.543
(A-O)	2.887	2.899	2.903	2.908	2.906
(Am-O)**	2.794	2.812	2.823	2.819	2.819
(A2-O)	2.575	2.633	2.656	2.592	2.577

\* Standard deviations are ≤0.002.

\*\* Nine bonds are included in this average.

**TABLE 7.** Chemical analyses\* and unit formulae

	A1	A2	A5
SiO <sub>2</sub>	55.94	55.80	56.68
Al <sub>2</sub> O <sub>3</sub>	0.74	1.27	0.73
TiO <sub>2</sub>	3.80	0.03	0.46
Fe <sub>2</sub> O <sub>3</sub>	8.35	12.21	10.67
MgO	11.23	10.96	16.10
Mn <sub>2</sub> O <sub>3</sub>	4.78	3.86	1.08
CaO	0.81	0.50	1.24
Na <sub>2</sub> O	9.67	9.69	8.80
K <sub>2</sub> O	0.83	1.12	0.99
Li <sub>2</sub> O	[1.16]	[1.28]	0.45
F	0.47	1.08	0.95
H <sub>2</sub> O	(1.02)	(1.35)	(1.74)
O=F	-0.20	-0.45	-0.40
Total	98.60	98.70	99.49
Si	8.002	7.978	7.955
Al	—	0.022	0.045
Total	8.002	8.000	8.000
Al	0.125	0.192	0.076
Ti	0.409	0.003	0.049
Fe <sup>3+</sup>	0.899	1.314	1.127
Mg	2.395	2.337	3.369
Mn <sup>3+</sup>	0.520	0.420	0.115
Li	0.667	0.736	0.250
Total	5.015	5.002	4.986
Diff.	0.015	—	—
Ca	0.124	0.077	0.166
Na	1.861	1.923	1.834
Total	2.000	2.000	2.000
Na	0.821	0.764	0.581
K	0.151	0.204	0.177
Total	0.972	0.968	0.758
F	0.21	0.49	0.42
(OH)	0.97	1.29	1.58
O <sup>2-</sup>	0.82	0.22	—

\* Values in parentheses are calculated as discussed in the text.

O3 site is not valid, and they showed that renormalization of the formula unit on the basis of 23 O atoms gives incorrect (low) C-group sums. In this case, the unit formula must be renormalized on (23 + <sup>16</sup>Ti) O atoms (allowing for analyzed F content).

The (M1,M2,M3-O) bond lengths are very short for these amphiboles, indicating that most, if not all, of the Fe and Mn are in the trivalent state, and this was assumed in the initial calculation of the unit formulae. However, final oxidation states were decided on the basis of mean bond lengths and site-scattering constraints; Table 7 gives the final results.

### Transmission electron microscopy

Three samples of leakeite were prepared by Ar ion milling of selected areas of a petrographic thin section. The transmission electron microscopy was done at the

**TABLE 5.** Site-scattering values (epfu) obtained from structure refinements\*

	A1	A2	A3	A4	A5
M1	33.63	27.51	31.76	24.33	24.87
M2	39.16	46.11	44.15	42.65	41.86
M3	5.98	5.38	4.49	10.29	9.83
ΣM1, M2, M3	78.77	79.01	80.45	77.27	76.56
M4	22.80	22.50	22.31	22.91	22.89
A	11.57	12.02	13.81	9.16	9.63
O3	16.08	16.66	16.20	16.64	16.56

\* Standard deviations are in the range 0.04–0.10.

Mobil Central Research Laboratory in Princeton, New Jersey, on a JEOL JEM-2010 microscope ( $C_s = 0.5$ ,  $C_c = 1.0$  mm) equipped with a Gatan model 679 slow-scan CCD camera. Additional microscopy was done on a Philips EM400 in the Department of Geological and Geophysical Sciences and the Princeton Materials Institute at Princeton University.

### TEM CHARACTERIZATION

No microstructural evidence for exsolution of a second amphibole was observed in any of the samples. Many of the samples comprised several subgrains in nearly identical orientations. In terms of defect microstructures, (001) sections revealed very few examples of chain-width disorder, and (100) twinning was not observed. Dislocations and associated stacking faults were common, but not abundant, and were normally localized in the vicinity of subgrain boundaries. In short, the amphibole is very well behaved and relatively free of defects. A high-resolution TEM (HRTEM) image of the [110] zone orientation is shown in Figure 2. This image shows a typical view of a defect-free area in leakeite.

The amphibole does contain many inclusions of a manganese-oxide mineral, the identity of which has not yet been determined. Selected-area electron diffraction (SAED) and TEM images of the oxide-amphibole interfaces do not show any regular or systematic orientation

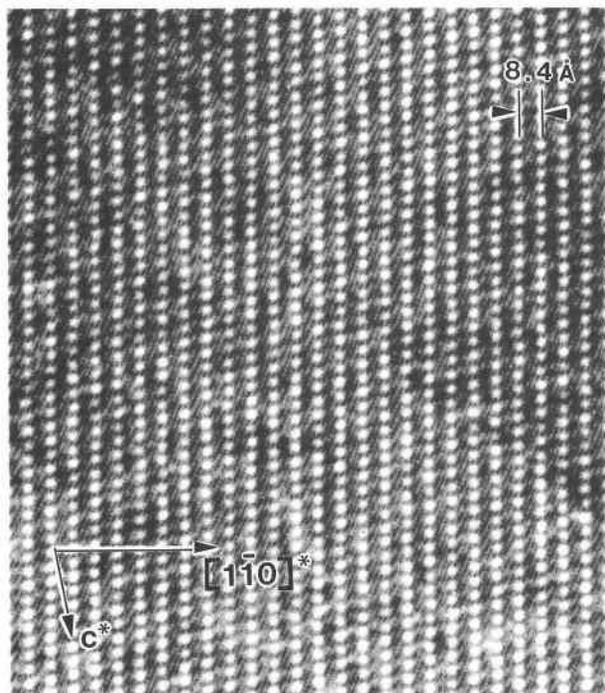


Fig. 2. HRTEM image of leakeite taken down  $[110]$ , showing a region of perfect crystal-structure in the amphibole. The  $\{110\}$  lattice fringes (8.4 Å) and  $(001)$  lattice fringes (5.12 Å) are easily visible in the image, especially by viewing at a low angle to the page. Defective areas are few in these samples.

relationship between the two minerals, and the interfaces themselves are incoherent. This observation suggests that manganese oxide was included during rapid amphibole growth, rather than exsolving out of an Mn-rich host amphibole during cooling. Additional work is planned to characterize further the manganese oxides and their relationship to the amphibole.

### Li AT THE M3 SITE

The unusual nature of these red amphiboles was first recognized through the low C-group cation sums of the original microprobe analyses (Leake et al., 1981). It is worth noting that many people discounted these analyses as being of poor quality; they were wrong, perhaps indicating that we should pay more attention to chemical analyses that deviate from our expectations, particularly as recent careful work (Dutrow et al., 1986; Hawthorne et al., 1993) has shown that light lithophile elements can be significant substituents in rock-forming silicate minerals. Crystal structure refinement indicated a very low scattering from the M3 site, a feature that supported the initial electron microprobe results and prompted the ion microprobe study.

Figure 3 shows the scattering at the M1 and M3 sites in  $\sim 600$  refined amphibole structures. Most of the data lie within a lunette bounded at the bottom by a line joining complete Mg and Fe occupancy of M1 and M3; com-

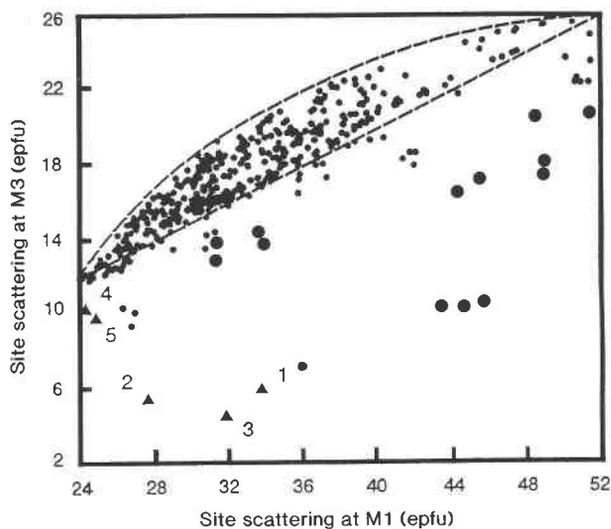


Fig. 3. Refined total scattering at M1 and M3 sites in the Li-bearing alkali amphiboles of this study compared with the distribution of values observed for  $\sim 600$  refined monoclinic amphiboles.

pared with the chemical data, this indicates that the scattering at M1 and M3 is dominated by Mg and Fe, with Fe having a distinct preference for the M3 site. There are two sets of exceptions to this generalization, the leakeites of the present study (triangles), and the igneous alkali amphiboles (solid circles) of Hawthorne et al. (1993), both of which lie significantly below the line joining Mg and Fe. In particular, the leakeites lie well below an M3 site scattering of 12e, indicating that there must be a scattering species at M3 with an atomic number  $\ll 12$ . As the M3 site is octahedrally coordinated by O and OH or F anions, the only possibilities for this additional component are Li and  $\square$  (vacancy). Ion microprobe results (Table 7) show that there is significant Li present in leakeite, sufficient to account for the very low scattering at M3 if the Li is completely ordered at that site. The final site populations are in accord with the electron and ion microprobe analyses and show that Li is always completely ordered at M3, without any significant indication of vacancies at the M1, M2, and M3 sites. Similar results have been obtained for Li-bearing alkali amphiboles from silica-oversaturated peralkaline granites (Hawthorne et al., 1993).

### SITE POPULATIONS

The crystal chemical arguments in the following sections are valid for all the samples reported here, but complete site populations are reported (Table 8) only for those crystals for which we have chemical analyses.

#### T1 and T2 sites

The observed  $\langle T1-O \rangle$  and  $\langle T2-O \rangle$  bond lengths (Table 4) indicate no  $^{4}\text{Al}$ , and the electron microprobe results (Table 7) are in accord with this.

**TABLE 8.** Complete chemical formulae and octahedral site populations from SREF + EMP results

	A		M4		M1 + M2 + M3						T1 + T2		W			
	Na	K	Na	Ca	Li	Mg	Al	Ti	Mn <sup>3+</sup>	Fe <sup>3+</sup>	Si	Al	O <sup>2-</sup>	OH	F	
A1	0.80	0.15	1.90	0.10	0.67	2.30	0.14	0.41	0.52	0.96	8.00	—	22.82	0.97	0.21	
A2	0.74	0.20	1.95	0.05	0.74	2.23	0.19	—	0.42	1.42	7.96	0.04	22.24	1.27	0.49	
A5	0.56	0.18	1.90	0.10	0.24	3.34	0.08	0.04	0.12	1.18	7.94	0.06	22.00	1.58	0.42	
	M1						M2						M3			
	Mg	Al	Ti	Fe <sup>3+</sup>	<i>d</i> <sub>obs</sub>	<i>d</i> <sub>calc</sub>	Mg	Al	Ti	Fe <sup>3+</sup>	<i>d</i> <sub>obs</sub>	<i>d</i> <sub>calc</sub>	Li	Mg	<i>d</i> <sub>obs</sub>	<i>d</i> <sub>calc</sub>
A1	1.14	0.05	0.41	0.40	2.037	2.037	0.83	0.09	—	1.08	2.046	2.044	0.67	0.33	2.108	2.104
A2	1.66	0.08	—	0.26	2.059	2.059	0.31	0.11	—	1.58	2.028	2.028	0.74	0.26	2.119	2.105
A3	1.86	0.08	—	0.06	2.064	2.065	0.72	—	0.04	1.24	2.044	2.043	0.24	0.76	2.085	2.084

\* Fe' = Fe<sup>3+</sup> + Mn<sup>3+</sup>.

### M1 and M2 sites

As outlined above, Li is ordered at M3, and hence the possible species at M1 and M2 are Mg, Al, Ti, Fe<sup>2+</sup>, and Mn<sup>3+</sup>. From the X-ray scattering viewpoint, this may be simplified to Mg' (= Mg + Al), Ti and Fe' (= Fe<sup>2+</sup> + Fe<sup>3+</sup> + Mn). For crystals A1 and A3, Ti was assigned to M1 on the basis of the M1-O3 bond lengths; the Mg' and Fe' site populations were then calculated directly from the site-scattering results (Table 8). With the assumption that Al is ordered at M2 and that the M1 site is occupied by Mg and Fe<sup>3+</sup> + Mn<sup>3+</sup> such that the observed site-scattering values are correct, the ⟨M1-O⟩ and ⟨M3-O⟩ distances calculated as described by Oberti et al. (1993) are longer and shorter, respectively, than the corresponding observed distances. This suggests the incorporation of some Al at M1. The octahedral site populations that give the best agreement with the observed site scattering and observed mean bond lengths are given in Table 8; it should be noted that this disorder of trivalent cations between M1 and M2 is characteristic of Kajlidongri amphiboles (cf. Ghose et al., 1986) and is not observed in amphiboles from the Questa caldera (Hawthorne et al., 1993).

### The M3 site

As discussed above, Li orders at the M3 site. For all samples, all the transition metals have already been assigned to M1 and M2, leaving just Mg as the other cation at M3. Thus the populations of Li and Mg may be derived directly from the site-scattering refinement (Table 8). In the leakeite crystals, the ⟨M3-O⟩ bond lengths are slightly longer (~0.007 Å) than expected for the assigned populations.

## CATION ORDERING

### Li ordering

The end-member formula for leakeite is NaNa<sub>2</sub>-(Mg<sub>2</sub>Fe<sub>2</sub><sup>3+</sup>Li)Si<sub>8</sub>O<sub>22</sub>(OH)<sub>2</sub> (Hawthorne et al., 1992). It is the only amphibole with essential monovalent cations in the octahedral strip, which obviously must entail a novel cation-ordering pattern. Hawthorne (1978b) has rationalized the polyvalent-cation ordering patterns in amphiboles in terms of bond valences; the same approach is taken here. The leakeite composition may be derived from the ferri-eckermannite composition by means of the substitution Fe<sup>3+</sup> + Li = Mg + Mg. Table 9 shows bond-

**TABLE 9.** Bond-valence tables for ferri-eckermannite (A5) and leakeite (A2) calculated with the curves of Brown (1981)

	M1	M2	M3	M4	A	T1	T2	Total
<b>Ferri-eckermannite A5</b>								
O1	0.360 <sup>x2</sup> ↓	0.328 <sup>x2</sup> ↓	0.301 <sup>x4</sup> ↓			1.043		2.032
O2	0.352 <sup>x2</sup> ↓	0.427 <sup>x2</sup> ↓		0.173 <sup>x2</sup> ↓			1.016	1.968
O3	0.361 <sup>x2</sup> ↓ →		0.307 <sup>x2</sup> ↓					1.029
O4		0.559 <sup>x2</sup> ↓		0.206 <sup>x2</sup> ↓			1.092	1.856
O5				0.087 <sup>x2</sup> ↓	0.075 <sup>x4</sup> ↓	0.995	0.922	2.079
O6				0.153 <sup>x2</sup> ↓	0.039 <sup>x4</sup> ↓	0.992	0.896	2.080
O7					0.169 <sup>x2</sup> ↓	0.979 <sup>x2</sup> →		2.127
Total	2.146	2.628	1.818	1.238	0.794	4.009	3.926	
Ideal	2.070	2.660	1.760	1.050	0.740	3.993	4.000	
<b>Leakeite A2</b>								
O1	0.369 <sup>x2</sup> ↓	0.383 <sup>x2</sup> ↓	0.215 <sup>x4</sup> ↓			1.063		2.030
O2	0.350 <sup>x2</sup> ↓	0.431 <sup>x2</sup> ↓		0.187 <sup>x2</sup> ↓			1.011	1.979
O3	0.392 <sup>x2</sup> ↓ →		0.207 <sup>x2</sup> ↓					0.991
O4		0.578 <sup>x2</sup> ↓		0.201 <sup>x2</sup> ↓			1.092	1.871
O5				0.086 <sup>x2</sup> ↓	0.099 <sup>x4</sup> ↓	0.989	0.917	2.091
O6				0.154 <sup>x2</sup> ↓	0.052 <sup>x4</sup> ↓	0.989	0.892	2.087
O7					0.198 <sup>x2</sup> ↓	0.971 <sup>x2</sup> →		2.140
Total	2.222	2.784	1.274	1.256	1.000	4.012	3.912	
Ideal	2.170	2.846	1.260	1.050	0.940	3.990	4.000	

**TABLE 10.** Selected end-member compositions for alkali amphiboles

A	B	C	T	W	Name	Exchange vector
Na	Na <sub>2</sub>	Mg <sub>3</sub> Fe <sup>3+</sup>	Si <sub>8</sub>	O <sub>22</sub> (OH) <sub>2</sub>	ferri-eckermannite	additive component
Na	Na <sub>2</sub>	Mg <sub>2</sub> LiFe <sup>3+</sup>	Si <sub>8</sub>	O <sub>22</sub> (OH) <sub>2</sub>	leakeite	<sup>M3</sup> LiFe <sup>3+</sup> ( <sup>M3</sup> MgMg) <sub>-1</sub>
□	Na <sub>2</sub>	Mg <sub>3</sub> Fe <sup>3+</sup>	Si <sub>8</sub>	O <sub>22</sub> (OH) <sub>2</sub>	magnesio-riebeckite	<sup>A</sup> □Fe <sup>3+</sup> ( <sup>A</sup> NaMg) <sub>-1</sub>
Na	Na <sub>2</sub>	Mg <sub>3</sub> Fe <sup>3+</sup>	Si <sub>7</sub> Al	O <sub>22</sub> (OH) <sub>2</sub>	ferri-nyboite	Fe <sup>3+</sup> Al(MgSi) <sub>-1</sub>
Na	Na <sub>2</sub>	Mg <sub>3</sub> TiFe <sup>3+</sup>	Si <sub>8</sub>	O <sub>22</sub> O <sub>2</sub>	—	<sup>M1</sup> Ti <sup>4+</sup> □ <sub>2</sub> ( <sup>M1</sup> Mg <sup>H</sup> H <sub>2</sub> ) <sub>-1</sub>

valence tables for leakeite (crystal A2) and ferri-eckermannite (crystal A5), respectively.

In end-member ferri-eckermannite, the M1, M2, and M3 sites are occupied by Mg, ~(<sup>M3</sup>Mg<sub>0.5</sub>Fe<sub>0.5</sub><sup>3+</sup>), and Mg, respectively (close to the occupancies in A5, except for the small amount of leakeite substitution), and the bond-valence sums around the O1–O4 anions are close to ideal (except for O4, which always shows low bond-valence sums in amphiboles). As discussed above, Li is completely ordered at the M3 site; systematically permuting the possible cations at M1, M2, and M3 for the leakeite composition gives the minimum deviation from ideality for a Pauling bond-strength model with Li ordered at M3, as is observed. The incorporation of Li at M3 decreases the bond-valence incident to O1 and O3, and this must be compensated by Fe<sup>3+</sup> at M1 or M2. The occurrence of Fe<sup>3+</sup> at M1 would seem the most direct way of compensating O1 and O3 for Li at M3. However, the incorporation of trivalent cations into the octahedral strip of unoxidized amphiboles is dominated by the need of O4 to maximize its incident bond valence, and thus the compensating Fe<sup>3+</sup> goes primarily into the M2 site (although some trivalent cations do occur at M1). The compensation of the decreased M3 bond-valence incident to O3 occurs by a change in the bond-valence distribution at the M1 site, the M1-O3 bond increasing significantly in strength relative to the M1-O1 and M1-O2 bonds.

### The incorporation of Ti in Li-bearing amphiboles

In amphiboles, Ti<sup>4+</sup> enters the M1 or M2 sites; when at M1, it is associated with dehydroxylation at O3 by means of the substitution  $\text{Ti} + 2\text{O}^{2-} = \text{Mg} + 2\text{OH}^-$ , as shown for richterite by Oberti et al. (1992). Bond-valence arguments suggest that there is strong short-range order associated with this substitution; Ti at M1 is bonded to O<sup>2-</sup> anions at the adjacent O3 sites, causing a strong contraction of the M1-O3 bond relative to that observed in richterite low in <sup>16</sup>Ti. This behavior also occurs in Li-bearing amphiboles from the Questa caldera, New Mexico (Hawthorne et al., 1993). Small amounts of Ti (and Fe<sup>3+</sup>) order at M1 when partial dehydroxylation occurs; otherwise, Ti orders at M2. Similar behavior is shown by the crystals examined here. The cell contents of crystals A1 and A2 (Table 7) are very similar, except for the fact that A1 is enriched in Ti and depleted in Fe<sup>3+</sup> relative to A2. Comparison of the refined site-scattering values for A1 and A2 (Table 5) shows that the principal differences are at the M1 and M2 sites. The M1 site in A1 shows greater scattering than the M1 site in A2, and the reverse

holds for the M2 site. This suggests that in A1, Ti occurs at M1 rather than at M2.

The observed individual and mean M1-O and M2-O bond lengths also show this mechanism to be the case. In A1, higher Ti<sup>4+</sup> and lower Mg at M1 causes ⟨M1-O⟩ to be smaller than in A2 (Table 4). In particular, M1-O3 is extremely shortened in A1 (1.962 Å vs. 2.032 Å in A2), supporting the idea of local ordering between Ti<sup>4+</sup> at M1 and O<sup>2-</sup> at O3.

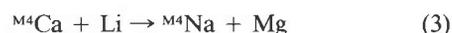
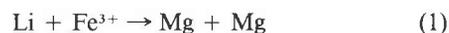
### CHEMICAL RELATIONSHIPS

End-member amphibole formulae and exchange vectors for some alkali amphiboles are given in Table 10. The choice of the additive component is somewhat arbitrary; we have chosen ferri-eckermannite because there seems to be extensive solid solution along the ferri-eckermannite-leakeite join (Hawthorne et al., 1993; this study). The exchange vector <sup>M3</sup>LiFe<sup>3+</sup>(<sup>M3</sup>MgMg)<sub>-1</sub> thus corresponds to the substitution <sup>M3</sup>Li + Fe<sup>3+</sup> → <sup>M3</sup>Mg + Mg that involves the principal compositional variations in the two occurrences in which leakeite has so far been found. The oxy-substitution <sup>M1</sup>Ti + 2O<sup>2-</sup> → <sup>M1</sup>Mg + 2OH<sup>-</sup> has also been included, as crystal A1 shows that it can be a significant component in leakeite compositions.

The ⟨T-O⟩ bonds of Table 4 show that there is no <sup>14</sup>Al at all in these leakeites and Li-bearing ferri-eckermannites. That is to be expected; among the alkali amphiboles (Table 10), only ferri-nyboite contains <sup>14</sup>Al. The incorporation of Li into the octahedral strip reduces the charge in the octahedral strip. This must be compensated by a concomitant increase in charge in other structural sites, militating against the occurrence of any <sup>14</sup>Al in such Li-bearing compositions.

### POSSIBILITIES FOR OTHER <sup>16</sup>Li AMPHIBOLES

Li could be incorporated into the octahedral strip of the amphibole structure by means of the following substitutions:



Application of these substitutions to the distinct (Mg-Al) polyvalent amphibole end-members gives nine calcic, five sodic-calcic, and three alkali Li-bearing end-members; are any of these likely candidates for minerals? First, let us

**TABLE 11.** Possible <sup>6</sup>Li-free Li-bearing end-member amphibole compositions

	A	B	C	T
1	□	Ca <sub>2</sub>	Mg <sub>3</sub> AlLi	Si <sub>8</sub> O <sub>22</sub> (OH) <sub>2</sub>
2	Na	Ca <sub>2</sub>	Mg <sub>3</sub> Li	Si <sub>8</sub> O <sub>22</sub> (OH) <sub>2</sub>
3	□	CaNa	Mg <sub>2</sub> Al <sub>2</sub> Li	Si <sub>8</sub> O <sub>22</sub> (OH) <sub>2</sub>
4	Na	CaNa	Mg <sub>3</sub> AlLi	Si <sub>8</sub> O <sub>22</sub> (OH) <sub>2</sub>
5	□	Na <sub>2</sub>	MgAl <sub>3</sub> Li	Si <sub>8</sub> O <sub>22</sub> (OH) <sub>2</sub>
6	Na	Na <sub>2</sub>	Mg <sub>2</sub> Al <sub>2</sub> Li	Si <sub>8</sub> O <sub>22</sub> (OH) <sub>2</sub>

consider where Li occurs in the octahedral strip. The M2 site is coordinated to O4, a formally (very) underbonded anion; as a result of this, the higher valent cations always occupy M2 in nonoxidized amphiboles. Thus a monovalent cation does not order at M2. If Li occurs at M1 or M3, it reduces the bond-valence incident to O1, O2, and O3. The O1 and O2 anions also bond to T1 and T2, which may contain either all Si or (Si,Al). If the O1 and O2 anions have decreased incident bond valence from T1 and T2 because of the occurrence of <sup>6</sup>Li, it is unlikely that the structure will further exacerbate the local charge-balance problem by incorporating Li at M1 or M3. Hence <sup>6</sup>Li is unlikely in amphiboles containing major amounts of <sup>4</sup>Al.

The remaining possible <sup>6</sup>Li-bearing compositions are listed in Table 11; only one of them has been observed (leakeite is the Fe<sup>3+</sup> equivalent and kornite is the K-Fe<sup>3+</sup> equivalent of 6). The problem with incorporating Li in the octahedral strip is the fact that doing so leaves the anions of the strip (O1, O2, and O3) with an insufficient associated cation charge to satisfy their bond-valence requirements. This bond valence (charge) must be transferred to these anions by strengthening the bonds from nonoctahedral cations (T1, T2, and M4) to the O1 and O2 anions; the octahedral strip must then adjust so as to strengthen the M-O3 bonds as well. The O4 anion is formally strongly underbonded and forms very short bonds to T2, M2, and M4. That prevents either T2 or M4 from increasing the strengths of their bonds to the O2 anion by incorporation of <sup>6</sup>Li into the structure, forcing the main transference of bond valence to occur through the T1-O1 bond. The strengths of this bond in <sup>4</sup>Al-free amphiboles (Hawthorne, 1983) fall into the following ranges: A site vacant: 0.99–1.02 vu; A site full: 1.04–1.11 vu. It is apparent that in the amphiboles with the A site empty, the T1-O1 bond cannot contract sufficiently to transfer enough bond valence to the octahedral strip for the latter to satisfy its anion bond-valence requirements. Thus A-site-vacant compositions 1, 3, and 5 are unlikely. In this regard, it should be noted that the Li-bearing fluorriebeckite of Hawthorne (1978a) has 0.34 Li at M3 and 0.33 (Na + K) at the A site, in accord with the above arrangement.

The same argument can be applied to the amphiboles with the A site full. In this case, the T1-O1 bond is significantly stronger (1.04–1.11 vu), but still cannot transfer sufficient bond valence to the octahedral strip to sat-

isfy the anion bond-valence requirements when the cation charge at the octahedral strip is 9 or 10<sup>+</sup> pfu. In addition, for composition 4 with the mixed MgAl occupancy of M2, there are severe local (short-range) bond-valence problems when M2 = Mg.

These arrangements leave us with composition 6, of leakeite and kornite stoichiometry, as the only <sup>6</sup>Li-rich amphibole composition, bond-valence constraints making the incorporation of <sup>6</sup>Li into any other compositions more difficult.

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#### REFERENCES CITED

- Armbruster, T., Oberhänsli, R., Bermanec, V., and Dixon, R. (1993) Hennomartinite and kornite, two new Mn<sup>3+</sup> rich silicates from the Wessels mine, Kalahari, South Africa. *Schweizerische mineralogisch-petrographische Mitteilungen*, 73, 349–355.
- Ashley, P.M. (1986) An unusual manganese silicate occurrence at the Hoskins mine, Grenfell district, New South Wales. *Australian Journal of Earth Sciences*, 33, 443–456.
- Brown, I.D. (1981) The bond-valence method: An empirical approach to chemical structure and bonding. In M. O'Keefe and A. Navrotsky, Eds., *Structure and bonding in crystals*, vol. 2, p. 1–30. Academic, New York.
- Dutrow, B.L., Holdaway, M.J., and Hinton, R.W. (1986) Lithium in staurolite: Its petrologic significance. *Contributions to Mineralogy and Petrology*, 94, 496–506.
- Ghose, S., Kersten, M., Langer, K., Rossi, G., and Ungaretti, L. (1986) Crystal field spectra and Jahn-Teller effect of Mn<sup>3+</sup> in clinopyroxenes and clin amphiboles from India. *Physics and Chemistry of Minerals*, 13, 291–305.
- Hawthorne, F.C. (1978a) The crystal chemistry of the amphiboles. VIII. The crystal structure and site-chemistry of fluorriebeckite. *Canadian Mineralogist*, 16, 187–194.
- (1978b) The crystal chemistry of the amphiboles. IX. Polyvalentcation ordering clin amphiboles. *Canadian Mineralogist*, 16, 521–525.
- (1983) The crystal chemistry of the amphiboles. *Canadian Mineralogist*, 21, 173–480.
- Hawthorne, F.C., Oberti, R., Ungaretti, L., and Grice, J.D. (1992) Leakeite, NaNa<sub>2</sub>Mg<sub>2</sub>(Fe<sup>3+</sup>Li)Si<sub>8</sub>O<sub>22</sub>(OH)<sub>2</sub>, a new amphibole from the Kajlidongri manganese mine, Jhabua district, Madhya Pradesh, India. *American Mineralogist*, 77, 1112–1115.
- Hawthorne, F.C., Ungaretti, L., Oberti, R., Bottazzi, P., and Czamanske, G.K. (1993) Li: An important component in igneous alkali amphiboles. *American Mineralogist*, 78, 733–745.
- Lahiri, D. (1971) Mineralogy and genesis of the manganese oxide and silicate rocks in Kajlidongri and surrounding areas, Jhabua district, Madhya Pradesh, India. *Economic Geology*, 66, 1176–1185.
- Leake, B.E., Farrow, C.M., and Nayak, V.K. (1981) Further studies on winchite from the type locality. *American Mineralogist*, 66, 625–631.
- Lehman, M.S., and Larsen, F.K. (1974) A method for location of the peaks in step-scan measured Bragg reflections. *Acta Crystallographica*, A30, 580–586.
- North, A.C.T., Phillips, D.C., and Mathews, F.S. (1968) A semi-empirical method of absorption correction. *Acta Crystallographica*, A24, 351–359.
- Oberti, R., Ungaretti, L., Cannillo, E., and Hawthorne, F.C. (1992) The behaviour of Ti in amphiboles. I. Four- and six-coordinated Ti in rich-terite. *European Journal of Mineralogy*, 4, 425–439.

- Oberti, R., Hawthorne, F.C., Ungaretti, L., and Cannillo, E. (1993) The behaviour of Mn in amphiboles: Mn in richterite. *European Journal of Mineralogy*, 5, 43–51.
- Ottolini, L., Bottazzi, P., and Vannucci, R. (1993) Quantification of Li, Be and B in silicates by secondary ion mass spectrometry using conventional energy filtering. *Analytical Chemistry*, 65, 1960–1968.
- Pouchou, J.L., and Pichoir, F. (1984) A new model for quantitative analysis. I. Application to the analysis of homogeneous samples. *La Recherche Aérospatiale*, 5, 4765.
- (1985) 'PAP'  $\phi(\rho Z)$  procedure for improved quantitative microanalysis. *Microbeam analysis*, p. 104–106. San Francisco Press, San Francisco, California.
- Ungaretti, L. (1980) Recent developments in X-ray single crystal diffraction applied to the crystal-chemical study of amphiboles. *Godisnjak Jugoslavenskog centra za Kristalografiju*, 15, 29–65.
- Ungaretti, L., Mazzi, F., Rossi, G., and Dal Negro, A. (1978) Crystal-chemical characterization of blue amphiboles. *Proceedings of the XI General Meeting of the International Mineralogical Association, Rock-Forming Minerals*, 82–110.
- Ungaretti, L., Smith, D.C., and Rossi, G. (1981) Crystal-chemistry by X-ray structure refinement and electron microprobe analysis of a series of sodic-calcic to alkali amphiboles from the Nybø eclogite pod, Norway. *Bulletin de Minéralogie*, 104, 400–412.
- Ungaretti, L., Lombardo, B., Domeneghetti, C., and Rossi, G. (1983) Crystal-chemical evolution of amphiboles from eclogitic rocks of the Sesia-Lanzo zone, Western Alps. *Bulletin de Minéralogie*, 106, 645–672.

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