THE CRYSTAL CHEMISTRY OF ALKALI AMPHIBOLES
FROM THE KAJLIDONGRI MANGANESE MINE, INDIA

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ABSTRACT

The crystal structures of eight sodic–calcic and sodic amphiboles from the Kajlidongri manganese mine, India, have been refined to R values of 1–2% using single-crystal $MoK\alpha$ X-ray data. The crystals used in the collection of the intensity data were subsequently analyzed by electron- and ion-microprobe techniques. Site populations were assigned from the results of site-scattering refinement and stereochemical analysis, taking into account the unit formula determined for each crystal. These amphiboles range in composition from richterite to magnesioriebeckite to magnesio-arfvedsonite. All amphiboles contain Li, which ranges from 0.03 to 0.30 *apfu* and is completely ordered at the $M(3)$ site. The amount of F in each crystal is equal to twice the amount of Li, suggesting that Li, which is ordered at the $M(3)$ site, is locally associated with F at both the adjacent $O(3)$ sites. The patterns of electron density in the A cavity and the populations at the A, $O(3)$ and $M(4)$ sites are in accord with previously proposed patterns of short-range order in monoclinic amphiboles. The compositions of these amphiboles lie along the join richterite–magnesioriebeckite and show a surprising degree of coherence in their major-element compositions considering the heterogeneity of the host rocks.

Keywords: amphibole, crystal-structure refinement, electron-microprobe analysis, ion-microprobe analysis, Kajlidongri, India.

SOMMAIRE

Nous avons affiné la structure cristalline de huit amphiboles des groupes sodique–calcique et sodique provenant de la mine de manganèse Kajlidongri, en Inde, jusqu'à un résidu de l'ordre de 1–2% en utilisant des données en diffraction X sur monocristaux (rayonnement $MoK\alpha$). Les cristaux utilisés pour le prélèvement des données d'intensité ont par la suite été analysés avec des microsondes électronique et ionique. La population des sites a été établie par affinement de la dispersion propre aux sites et par analyse stéréochimique, compte tenu de la formule unitaire de chaque cristal. Ces amphiboles ont une composition dans la série richtérite à magnésioriebeckite ou magnésio-arfvedsonite. Le Li est présent dans chaque amphibole, entre 0.03 et 0.30 *apfu*, et il occupe le site $M(3)$. La quantité de F dans chaque cristal est égal à deux fois la teneur en Li, ce qui laisse supposer que le Li, situé uniquement sur le site $M(3)$, serait localement associé aux atomes de F sur les sites $O(3)$ adjacents. La distribution de la densité des électrons dans la cavité A et les populations aux sites A, $O(3)$ et $M(4)$ concordent avec l'hypothèse déjà proposée d'une mise en ordre à courte échelle parmi les amphiboles monocliniques. Ces amphiboles de la série richtérite–magnésioriebeckite montrent un degré de cohérence surprenant dans leurs compositions globales, compte tenu l'hétérogénéité des roches encaissantes.

(Traduit par la Rédaction)

Mots-clés: amphibole, affinement de la structure cristalline, données de microsonde électronique, données de microsonde ionique, Kajlidongri, Inde.

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INTRODUCTION

The behavior of Li in amphiboles was characterized in detail by Hawthorne *et al.* (1992, 1993, 1994) and Oberti *et al.* (2000, 2003a, b, 2004). Lithium can be incorporated at the $M(3)$ and $M(4)$ sites in monoclinic amphiboles, up to a limit of 3 *apfu* (atoms per formula unit). There is complete solid-solution between Li and (Mg, Fe^{2+}) at the $M(3)$ site and between Li and Na at the $M(4)$ site, although the possible dependences of these schemes on temperature are not fully understood. Monoclinic Li-rich amphiboles have been found in three distinct parageneses: (1) peralkaline granite (Hawthorne *et al.* 1993, 1996a, 2001, Oberti *et al.* 2005), (2) episyenite (Caballero *et al.* 1998, 2002, Oberti *et al.* (2000, 2003a, b, 2004) and (3) manganiferous metasediments (Hawthorne *et al.* 1992, 1994, Armbruster *et al.* 1993, Tait *et al.* 2005). The mechanisms of incorporation of Li into amphiboles in peralkaline granites (Hawthorne *et al.* 1994) and episyenites (Oberti *et al.* 2003a) are now well understood. However, the situation is not the same for amphiboles in manganiferous metasediments. The chemical compositions of the amphiboles in this paragenesis are somewhat more complicated than those of amphiboles from peralkaline granites and episyenites, involving considerable variation in Mn^{3+}

and Ti^{4+}, and concomitant variation in H. In order to further understand the incorporation of C-group Li into amphiboles, we have examined a series of amphiboles from manganiferous metasediments that do not contain significant Mn or Ti, and which have stoichiometric H contents (*i.e.*, OH + F = 2 *apfu*; atoms per formula unit).

THE KAJLIDONGRI MINE

The metasedimentary rocks of the Precambrian Aravalli Supergroup occur in western India in Madya Pradesh, Rajasthan and Gujarat (Crawford 1969), and consist predominantly of phyllites, quartzites and carbonates intruded by post-tectonic granites (Lahiri 1971). Interbedded with phyllites, quartz schists and gondites (noncalcareous Mg-rich meta-argillites and meta-arenites), the manganiferous ores of Kajlidongri occur in quartz-rich rocks that contain syngenetic bands of Mn oxide and Mn silicate minerals. A later phase of supergene activity produced concordant epigenetic veins of quartz, feldspar, calcite and Mn silicates (Nayak 1966, 1969a, b, Lahiri 1971), including a wide variety of Mn- and Li-bearing amphiboles (Hawthorne *et al.* 1992, 1994, Tait 1999).

ANALYTICAL METHODS

X-ray data collection and structure refinement

The amphiboles examined here are named in Table 1. Experimental details are as described by Oberti *et al.* (1992). Unit-cell parameters, R indices and other information pertinent to data collection and refinement are given in Table 2. Final coordinates and anisotropic-displacement parameters of atoms are given in Table 3, selected interatomic distances and angles are listed in Table 4, and the refined site-scattering powers are listed in Table 5. Tables of observed and calculated structure-fractures are available from the Depository

TABLE 1. KAJLIDONGRI AMPHIBOLES:
SAMPLE NUMBERS AND NAMES

Sample	SEQ*	Name
KAJ(2)	723	Magnesioriebeckite
KAJ(2) N.12	787	Magnesioriebeckite
KAJ(3) N.1	724	Magnesioriebeckite
KAJ(5)	725	Potassian ferrian richterite
KAJ(6) N.1	790	Richterite
KAJ(6) N.2	791	Magnesioriebeckite
KAJ(6) N3	792	Ferrian richterite
KAJ(11) N.7	793	Magnesio-arfvedsonite

* SEQ: sequence number in amphibole database at Pavia.

TABLE 2. CRYSTAL DATA AND STRUCTURE REFINEMENT INFORMATION
FOR THE KAJLIDONGRI AMPHIBOLES

	723	787	724	725	790	791	792	793
a (Å)	9.700(4)	9.703(2)	9.708(4)	9.838(3)	9.885(2)	9.773(2)	9.857(5)	9.743(3)
b (Å)	17.917(6)	17.917(3)	17.909(8)	17.929(5)	17.960(4)	17.912(3)	17.947(7)	17.874(6)
c(Å)	5.300(2)	5.300(1)	5.300(4)	5.282(2)	5.279(2)	5.292(1)	5.283(3)	5.288(2)
$\beta(°)$	103.70(3)	103.74(2)	103.78(4)	104.15(2)	104.27(2)	103.87(2)	104.14(3)	103.81(2)
$V(Å^3)$	894.8	895.1	895.0	903.3	908.3	899.4	906.2	894.4
Space group	$C2/m$	$C2/m$	$C2/m$	$C2/m$	$C2/m$	$C2/m$	$C2/m$	$C2/m$
No.⎮F⎮	1360	1363	1361	1374	1376	1367	1375	1361
No.⎮F_o⎮	944	1071	987	735	1066	1053	772	1087
R(obs) %	1.5	1.4	2.5	1.8	1.3	1.3	1.6	2.1
R(all) %	3.0	2.1	3.7	5.8	2.2	2.2	4.8	3.0

TABLE 3. POSITIONS AND ANISOTROPIC-DISPLACEMENT COEFFICIENTS OF ATOMS
IN THE KAJLIDONGRI AMPHIBOLES*

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
				723					
O(1)	0.11147	0.08838	0.21218	0.001	0	0.004	−0.0001	0	−0.0001
O(2)	0.11814	0.16977	0.7339	0.001	0	0.005	−0.0001	0	−0.0002
O(3)	0.10987	0	0.71055	0.001	0	0.005	0	0	0
O(4)	0.36396	0.25063	0.79943	0.002	0	0.006	−0.0003	0.001	−0.0001
O(5)	0.35051	0.13094	0.08602	0.002	0	0.005	−0.0001	0	0
O(6)	0.34248	0.12083	0.58063	0.002	0	0.004	0	0	−0.0007
O(7)	0.33644	0	0.29729	0.002	0	0.0107	0	0.001	0
T(1)	0.28329	0.08567	0.29284	0.001	0	0.003	0	0	0
T(2)	0.29024	0.17102	0.80243	0.001	0	0.003	−0.0001	0	0
M(1)	0	0.08851	1/2	0.002	0	0.004	0	0.001	0
M(2)	0	0.1813	0	0.001	0	0.004	0	0	0
M(3)	0	0	0	0.002	0	0.004	0	0	0
M(4)	0	0.27709	1/2	0.004	0	0.012	0	0.005	0
A	0	1/2	0	2.06					
A(m)	0.0491	1/2	0.1088	2.2					
A(2)	0	0.47547	0	1.37					
H	0.1934	0	0.7602	0.3					
				787					
O(1)	0.11131	0.08832	0.2123	0.001	0	0.004	−0.0001	0	0
O(2)	0.11818	0.16979	0.73388	0.001	0	0.005	−0.0001	0	−0.0002
O(3)	0.10962	0	0.7109	0.002	0	0.006	0	0	0
O(4)	0.36397	0.25062	0.79935	0.002	0	0.006	−0.0003	0.001	−0.0001
O(5)	0.35048	0.13101	0.08618	0.002	0	0.005	0	0	0
O(6)	0.34241	0.12068	0.58071	0.002	0	0.005	0	0	−0.0006
O(7)	0.33686	0	0.29685	0.002	0	0.0107	0	0.001	0
T(1)	0.2831	0.08565	0.29283	0.001	0	0.003	0	0	0
T(2)	0.29023	0.17104	0.80251	0.001	0	0.003	−0.0001	0	0
M(1)	0	0.0885	1/2	0.002	0	0.004	0	0	0
M(2)	0	0.18127	0	0.001	0	0.004	0	0	0
M(3)	0	0	0	0.002	0	0.004	0	0	0
M(4)	0	0.27705	1/2	0.004	0	0.0113	0	0.004	0
A	0	1/2	0	1.27					
A(m)	0.0471	1/2	0.1051	2.07					
A(2)	0	0.4685	0	1.1					
H	0.1919	0	0.7588	1.2					
				724					
O(1)	0.11138	0.08818	0.21307	0.001	0	0.005	0	0	0
O(2)	0.11826	0.16968	0.73294	0.001	0	0.006	−0.0001	0	0
O(3)	0.10952	0	0.71088	0.001	0	0.007	0	0	0
O(4)	0.36387	0.25081	0.79967	0.002	0	0.008	−0.0004	0	0
O(5)	0.35053	0.13082	0.08647	0.001	0	0.006	−0.0001	0	0
O(6)	0.34249	0.12075	0.58113	0.001	0	0.006	0	0	−0.0004
O(7)	0.33684	0	0.29579	0.002	0	0.0114	0	0	0
T(1)	0.28307	0.08567	0.29294	0.001	0	0.004	0	0	0
T(2)	0.29009	0.17115	0.80247	0	0	0.004	−0.0001	0	−0.0001
M(1)	0	0.08833	1/2	0.002	0	0.005	0	0.001	0
M(2)	0	0.18124	0	0	0	0.005	0	0	0
M(3)	0	0	0	0.001	0	0.005	0	0	0
M(4)	0	0.27691	1/2	0.003	0	0.0131	0	0.004	0
A	0	1/2	0	2.11					
A(m)	0.0469	1/2	0.0998	2.22					
A(2)	0	0.46785	0	1.86					
H	0.1919	0	0.7804	3.99					
				725					
O(1)	0.11083	0.08795	0.21527	0.002	0	0.005	0	0	−0.0001
O(2)	0.11849	0.16966	0.72929	0.001	0	0.005	0	0	−0.0002
O(3)	0.10876	0	0.70971	0.002	0	0.009	0	0.001	0
O(4)	0.36275	0.24944	0.79813	0.003	0	0.005	−0.0005	0.001	−0.0004
O(5)	0.34799	0.13017	0.08863	0.002	0	0.007	0	0.001	0.001
O(6)	0.3422	0.11814	0.58718	0.002	0	0.004	0	0	−0.0005
O(7)	0.33575	0	0.29365	0.002	0	0.0125	0	0.001	0
T(1)	0.27876	0.08542	0.29451	0.001	0	0.004	−0.0001	0	0
T(2)	0.28763	0.17141	0.8026	0.001	0	0.003	−0.0001	0	−0.0001
M(1)	0	0.08782	1/2	0.002	0	0.003	0	0	0
M(2)	0	0.18029	0	0.001	0	0.005	0	0	0
M(3)	0	0	0	0.001	0	0.004	0	0	0
M(4)	0	0.27707	1/2	0.003	0	0.0111	0	0.004	0
A	0	1/2	0	0.005	0.003	0.0337	0	0.0112	0
A(m)	0.0436	1/2	0.095	0.008	0.003	0.0243	0	0.008	0
A(2)	0	0.4644	0	0.01	0.002	0.0447	0	0.006	0
H	0.1854	0	0.7305	0.69					
M(42)	0	0.2634	1/2	1.28					

TABLE 3 (cont'd). POSITIONS AND ANISOTROPIC-DISPLACEMENT COEFFICIENTS OF ATOMS
IN THE KAJLIDONGRI AMPHIBOLES*

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
790									
O(1)	0.11114	0.08684	0.21596	0.001	0	0.004	−0.0001	0	−0.0001
O(2)	0.11843	0.17002	0.72862	0.001	0	0.005	−0.0001	0	−0.0002
O(3)	0.10766	0	0.71329	0.001	0	0.005	0	0	0
O(4)	0.3628	0.2489	0.79596	0.003	0	0.006	−0.0004	0.001	−0.0001
O(5)	0.34647	0.13072	0.09103	0.002	0	0.005	0	0	0
O(6)	0.34131	0.11757	0.58864	0.002	0	0.005	0	0	−0.0007
O(7)	0.33547	0	0.29293	0.002	0	0.0112	0	0	0
T(1)	0.27828	0.08523	0.29549	0.001	0	0.003	−0.0001	0	0
T(2)	0.28671	0.17157	0.80256	0.001	0	0.003	−0.0001	0	0
M(1)	0	0.08862	1/2	0.002	0	0.004	0	0	0
M(2)	0	0.18051	0	0.001	0	0.004	0	0	0
M(3)	0	0	0	0.002	0	0.004	0	0	0
M(4)	0	0.27708	1/2	0.003	0	0.0109	0	0.004	0
A	0	1/2	0	0.002	0.002	0.0219	0	0.005	0
A(m)	0.0271	1/2	0.0606	0.004	0.002	0.0285	0	0.007	0
A(2)	0	0.4756	0	0.004	0.003	0.0283	0	0.005	0
H	0.1883	0	0.7549	3.18					
791									
O(1)	0.11105	0.08823	0.21329	0.001	0	0.004	0	0	−0.0001
O(2)	0.11812	0.16983	0.73232	0.002	0	0.006	0	0	−0.0001
O(3)	0.10934	0	0.71051	0.002	0	0.007	0	0	0
O(4)	0.3635	0.25012	0.79902	0.003	0	0.007	−0.0004	0.001	−0.0002
O(5)	0.34912	0.13033	0.08632	0.002	0	0.006	0	0.001	0
O(6)	0.34189	0.11954	0.5833	0.002	0	0.005	0	0	−0.0007
O(7)	0.33578	0	0.29502	0.003	0	0.0114	0	0.001	0
T(1)	0.28082	0.0857	0.29355	0.001	0	0.004	0	0	−0.0001
T(2)	0.28869	0.1713	0.80229	0.001	0	0.003	−0.0001	0	0
M(1)	0	0.08847	1/2	0.002	0	0.004	0	0.001	0
M(2)	0	0.18122	0	0.001	0	0.004	0	0	0
M(3)	0	0	0	0.002	0	0.004	0	0	0
M(4)	0	0.27695	1/2	0.004	0	0.0129	0	0.005	0
A	0	1/2	0	0.005	0.002	0.0233	0	0.007	0
A(m)	0.0378	1/2	0.0894	0.007	0.002	0.0204	0	0.008	0
A(2)	0	0.471	0	0.005	0.002	0.0492	0	0.009	0
H	0.2024	0	0.755	2.7656					
792									
O(1)	0.11135	0.08738	0.21455	0.001	0	0.004	−0.0001	0	−0.0002
O(2)	0.11812	0.16992	0.72948	0.002	0	0.006	−0.0001	0	0
O(3)	0.10791	0	0.7127	0	0	0.007	0	0	0
O(4)	0.36256	0.24917	0.79719	0.003	0	0.007	−0.0004	0.001	−0.0002
O(5)	0.34726	0.13053	0.08996	0.001	0	0.006	0	0.001	0
O(6)	0.34133	0.11808	0.58724	0.002	0	0.005	0	0	−0.0007
O(7)	0.33554	0	0.2936	0.002	0	0.0124	0	0.001	0
T(1)	0.2789	0.08538	0.29474	0.001	0	0.003	−0.0001	0	−0.0001
T(2)	0.28712	0.17152	0.80254	0.001	0	0.003	−0.0001	0	−0.0001
M(1)	0	0.0886	1/2	0.002	0	0.004	0	0	0
M(2)	0	0.18091	0	0.001	0	0.005	0	0	0
M(3)	0	0	0	0.002	0	0.003	0	0	0
M(4)	0	0.27716	1/2	0.003	0	0.0113	0	0.004	0
A	0	1/2	0	0.006	0.002	0.0272	0	0.0103	0
A(m)	0.0302	1/2	0.0832	0.0103	0.003	0.0212	0	0.009	0
A(2)	0	0.4649	0	0.0106	0.002	0.0389	0	0.006	0
H	0.1842	0	0.7481	1.87					
793									
O(1)	0.11117	0.08875	0.21361	0.002	0	0.005	0	0	0
O(2)	0.11823	0.16942	0.73213	0.002	0	0.007	−0.0001	0	−0.0001
O(3)	0.11047	0	0.70579	0.003	0	0.01	0	0	0
O(4)	0.36327	0.25057	0.79957	0.003	0	0.009	−0.0004	0.001	−0.0002
O(5)	0.35032	0.12952	0.08446	0.002	0	0.006	0	0	0
O(6)	0.34301	0.11995	0.58179	0.002	0	0.006	0	0	−0.0005
O(7)	0.33677	0	0.2955	0.003	0	0.0133	0	0.001	0
T(1)	0.28083	0.0858	0.29283	0.002	0	0.005	0	0	0
T(2)	0.28921	0.17125	0.80174	0.002	0	0.005	−0.0001	0	0
M(1)	0	0.08723	1/2	0.002	0	0.006	0	0.001	0
M(2)	0	0.18031	0	0.002	0	0.006	0	0	0
M(3)	0	0	0	0.002	0	0.006	0	0	0
M(4)	0	0.27635	1/2	0.004	0	0.0144	0	0.005	0
A	0	1/2	0	0.006	0.002	0.0245	0	0.009	0
A(m)	0.0517	1/2	0.1088	0.007	0.002	0.0244	0	0.007	0
A(2)	0	0.4678	0	2					
H	0.1892	0	0.7547	0.78					

* standard deviations are <5 in the last figure.

of Unpublished Data on the MAC web site [document Magnesioriebeckite CM46_455].

Electron-microprobe analyses

The crystals used in the collection of the X-ray intensity data were subsequently mounted, polished and analyzed by electron- and ion-microprobe techniques following the procedures described by Oberti *et al.* (1992) and Ottolini *et al.* (1993). Preliminary ion-microprobe examination showed that the O(3) site is completely filled with (OH) and F, and thus (H_2O) contents were first calculated assuming (OH) + F = 2.00 *apfu*. The lithium contents were determined quan-

titatively by ion-microprobe analysis. The Fe^{3+} content was derived from the observed <$M(2)$–O> distance and the mean bond-length – aggregate-cation-radius relation of Hawthorne (1983a). In fact, all Fe is in the trivalent state, and the resulting chemical compositions and unit formulae are given in Table 6.

TABLE 5. REFINED SITE-SCATTERING VALUES (*epfu*) AND CORRESPONDING VALUES CALCULATED FROM THE UNIT FORMULAE DERIVED FROM ION- AND ELECTRON-MICROPROBE ANALYSES OF THE KAJLIDONGRI AMPHIBOLES

	723	787	724	725	790	791	792	793
$M(1)$	24.2	24.1	24.4	24.9	24.5	24.3	24.3	25.3
$M(2)$	48.4	47.9	47.0	36.7	31.4	43.3	34.5	44.5
$M(3)$	11.9	11.8	11.7	9.9	12.0	11.1	11.7	9.1
$\Sigma M(1,2,3)$	84.5	83.9	83.1	71.5	67.8	78.8	70.5	79.0
$\Sigma M(1,2,3)^{MP}$	84.1	83.9	82.3	71.8	68.0	79.3	71.3	78.6
$M(4)$	22.3	22.1	22.6	26.3	28.7	23.4	26.8	22.5
$M(4)^{MP}$	23.1	23.6	22.7	26.2	28.8	23.5	27.7	22.4
A	2.1	2.4	3.1	9.7	9.7	6.4	9.2	7.8
A^{MP}	0.8	2.2	2.2	9.1	9.7	5.8	8.6	7.4
O(3)	16.0	16.3	16.3	16.4	16.0	16.5	16.1	16.6
O(3)^{MP}	16.1	16.2	16.2	16.2	16.0	16.2	16.1	16.5

* Standard deviations are ≤1 in the final digit for XREF data.

TABLE 4. SELECTED INTERATOMIC DISTANCES (Å)* AND ANGLES (°)* FOR KAJLIDONGRI AMPHIBOLES

	723	787	724	725	790	791	792	793
$T(1)$–O(1)	1.620	1.620	1.620	1.602	1.602	1.612	1.602	1.606
$T(1)$–O(5)	1.620	1.621	1.619	1.629	1.626	1.624	1.624	1.625
$T(1)$–O(6)	1.624	1.624	1.625	1.629	1.626	1.624	1.627	1.623
$T(1)$–O(7)	1.618	1.619	1.620	1.631	1.633	1.626	1.631	1.626
<$T(1)$–O>	1.620	1.621	1.621	1.623	1.622	1.621	1.621	1.620
$T(2)$–O(2)	1.622	1.622	1.620	1.614	1.612	1.619	1.616	1.618
$T(2)$–O(4)	1.597	1.597	1.598	1.585	1.584	1.592	1.583	1.592
$T(2)$–O(5)	1.643	1.643	1.647	1.656	1.662	1.650	1.661	1.650
$T(2)$–O(6)	1.652	1.654	1.653	1.671	1.676	1.662	1.672	1.661
<$T(2)$–O>	1.629	1.629	1.630	1.632	1.634	1.631	1.633	1.630
$M(1)$–O(1) ×2	2.068	2.067	2.065	2.063	2.066	2.066	2.071	2.062
$M(1)$–O(2) ×2	2.073	2.073	2.071	2.071	2.066	2.071	2.065	2.078
$M(1)$–O(3) ×2	2.081	2.081	2.077	2.066	2.084	2.079	2.083	2.053
<$M(1)$–O>	2.074	2.074	2.071	2.067	2.072	2.072	2.073	2.064
$M(2)$–O(1) ×2	2.152	2.151	2.154	2.148	2.172	2.154	2.168	2.131
$M(2)$–O(2) ×2	2.027	2.029	2.034	2.063	2.070	2.041	2.062	2.037
$M(2)$–O(4) ×2	1.922	1.922	1.920	1.961	1.972	1.935	1.962	1.937
<$M(2)$–O>	2.034	2.034	2.036	2.057	2.071	2.043	2.064	2.035
$M(3)$–O(1) ×4	2.089	2.088	2.087	2.088	2.079	2.089	2.083	2.093
$M(3)$–O(3) ×2	2.065	2.062	2.063	2.073	2.054	2.067	2.055	2.093
<$M(3)$–O>	2.081	2.079	2.079	2.083	2.070	2.081	2.074	2.093
$M(4)$–O(2) ×2	2.424	2.423	2.420	2.415	2.414	2.418	2.417	2.411
$M(4)$–O(4) ×2	2.345	2.345	2.348	2.359	2.354	2.352	2.358	2.350
$M(4)$–O(5) ×2	2.850	2.849	2.850	2.853	2.845	2.860	2.848	2.873
$M(4)$–O(6) ×2	2.484	2.488	2.489	2.551	2.573	2.519	2.558	2.506
<$M(4)$–O>	2.526	2.526	2.527	2.545	2.547	2.537	2.545	2.535
A–O(5) ×4	2.851	2.853	2.850	2.871	2.899	2.000	2.886	2.828
A–O(6) ×4	3.218	3.215	3.213	3.162	3.155	3.000	3.166	3.196
A–O(7) ×2	2.487	2.483	2.480	2.499	2.505	2.000	2.502	2.482
<A–O>	2.925	2.924	2.921	2.913	2.923	2.000	2.921	2.906
$A(m)$–O(5) ×2	3.019	3.012	3.011	2.974	2.978	2.000	2.962	3.017
$A(m)$–O(5) ×2	2.827	2.829	2.815	2.842	2.865	2.000	2.885	2.790
$A(m)$–O(6) ×2	2.772	2.784	2.797	2.833	2.897	2.000	2.837	2.743
$A(m)$–O(7)	2.496	2.486	2.500	2.486	2.498	2.000	2.441	2.519
$A(m)$–O(7)	3.080	3.101	3.133	3.247	3.348	3.195	3.234	3.078
$A(m)$–O(7)	2.645	2.635	2.607	2.598	2.565	2.621	2.646	2.619
<$A(m)$–O>	2.829	2.830	2.832	2.848	2.877	2.839	2.854	2.813
$A(2)$–O(5) ×2	2.502	2.410	2.399	–	2.557	2.450	2.403	2.380
$A(2)$–O(6) ×2	2.940	2.866	2.858	–	2.880	2.872	2.785	2.842
$A(2)$–O(7) ×2	2.552	2.546	2.546	–	2.543	2.546	2.580	2.547
<$A(2)$–O>	2.656	2.607	2.601	–	2.660	2.623	2.589	2.590
$T(1)$–O(5)–$T(2)$	136.5	136.4	136.4	135.5	135.9	136.0	135.8	135.5
$T(1)$–O(6)–$T(2)$	141.2	141.2	141.1	137.7	137.4	139.6	138.0	139.3
$T(1)$–O(7)–$T(1)$	143.2	142.8	142.7	139.8	139.2	141.6	139.9	141.1
O(5)–O(6)–O(5)	171.5	171.4	171.6	170.4	171.1	170.0	172.0	172.0
$T(1)$–$T(2)$–$T(1)$	120.0	120.0	119.9	119.4	119.8	119.3	119.9	119.9
$T(2)$–$T(1)$–$T(1)$	89.4	89.4	89.4	90.0	89.7	90.1	90.0	89.6

* Standard deviations are ≤2 in the final digit.

TABLE 6. CHEMICAL COMPOSITIONS AND CORRESPONDING UNIT FORMULAE FOR KAJLIDONGRI AMPHIBOLES

	723	787	724	725	790	791	792	793
SiO_2 wt.%	56.99	56.70	57.37	57.21	57.83	57.28	57.31	57.56
Al_2O_3	0.67	0.70	0.78	0.48	0.31	0.63	0.40	0.61
TiO_2	0.01	0.00	0.03	0.06	0.00	0.00	0.00	0.41
Fe_2O_3	16.03	16.90	16.08	8.42	4.71	13.00	7.63	12.18
MnO	0.15	0.13	0.08	0.40	0.71	0.46	0.69	1.10
MgO	15.16	15.26	15.18	18.50	21.24	16.43	19.68	15.18
CaO	0.81	0.94	0.66	3.92	5.26	1.47	3.83	1.14
Na_2O	6.92	6.95	7.30	6.71	5.93	7.57	6.60	8.39
K_2O	0.22	0.27	0.26	1.02	1.57	0.71	1.26	0.70
Li_2O	0.00	0.23	0.20	0.42	0.05	0.25	0.08	0.62
F	0.24	0.38	0.52	0.54	0.16	0.38	0.19	1.06
H_2O	2.02	1.97	1.90	1.89	2.09	1.97	2.07	1.65
O=F	–0.10	–0.16	–0.22	–0.23	–0.07	–0.16	–0.08	–0.45
Total	99.12	100.27	100.14	99.35	99.79	99.99	99.66	100.14
Si *apfu*	8.006	7.906	7.980	7.978	7.999	7.980	7.973	8.030
Al	–	0.094	0.020	0.022	0.001	0.020	0.027	0.000
ΣT	8.006	8.000	8.000	8.000	8.000	8.000	8.000	8.030
Al	0.111	0.021	0.108	0.057	0.050	0.083	0.039	0.100
Fe^{3+}	1.695	1.773	1.683	0.884	0.490	1.363	0.799	1.279
Mn	0.018	0.015	0.009	0.047	0.083	0.054	0.081	0.130
Ti	0.001	0.000	0.003	0.006	0.000	0.000	0.000	0.043
Mg	3.175	3.172	3.148	3.846	4.380	3.412	4.081	3.155
Li	0.000	0.129	0.112	0.236	0.028	0.140	0.045	0.348
ΣC	5.000	5.110	5.063	5.076	5.031	5.052	5.045	5.055
ΣC–5	–	0.110	0.063	0.076	0.031	0.052	0.045	0.055
Ca	0.122	0.140	0.098	0.586	0.780	0.219	0.575	0.170
Na	1.878	1.750	1.839	1.337	1.189	1.729	1.384	1.774
ΣB	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000
Na	0.007	0.129	0.130	0.476	0.401	0.316	0.396	0.495
K	0.039	0.048	0.046	0.181	0.277	0.126	0.224	0.125
ΣA	0.046	0.177	0.176	0.652	0.678	0.442	0.620	0.620
OH	1.893	1.832	1.765	1.750	2.000	1.833	1.916	1.446
F	0.107	0.168	0.229	0.238	0.000	0.167	0.084	0.468
O^{2-}	–	–	0.006	0.012	–	–	–	0.086
Σ	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000

* see text for discussion of normalization procedure.

SITE POPULATIONS

The site preferences and site populations were assigned on the basis of (1) the refined site-scattering values (Table 5), (2) the unit formulae derived from the chemical compositions determined by electron- and ion-microprobe analyses (Table 6), (3) the observed bond-lengths (Table 4), (4) the constraint that all sites except A be fully occupied, (5) the electronic neutrality of the resulting formulae. First, we examine the agreement between the refined site-scattering values and the equivalent electrons from the unit formulae for the $M(1,2,3)$, $M(4)$ and A groups (Fig. 1). This agreement is good for all groups, with root-mean-square deviations of 0.4, 0.5 and 0.7 *epfu* (electrons per formula unit), respectively. Given the smaller total numbers of electrons at the A sites, the agreement for this group is not satisfactory in all cases. However, this is to be expected, as (1) the electron density in the A cavity of monoclinic amphiboles is quite difficult to model accurately, and (2) all errors in the chemical composition and normalization procedure accumulate at the A site. Nevertheless, the agreement is sufficient to assign accurate site-populations.

The T sites

These amphiboles contain only minor Al: $0.051 \leq Al \leq 0.128$ *apfu*, and the calculated formulae distribute Al between the C-group and the T-group cations. The short $<T(1)–O>$ distances (Table 4) are in accord with almost complete occupancy of $T(1)$ by Si (Oberti *et al.* 1995), and there is no relation between $^{[4]}Al$ and $<T(1)–O>$, as expected from the relations presented by Hawthorne & Oberti (2007).
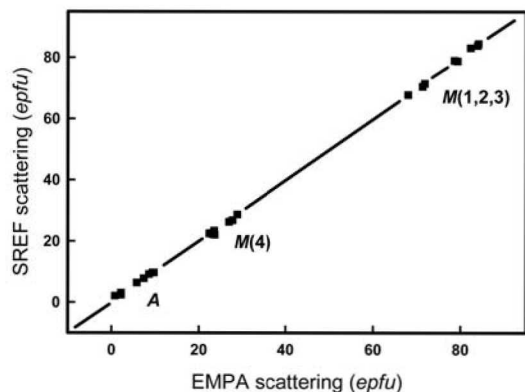
The M(2) site

The refined site-scattering values (Table 5) indicate that most, if not all, of the Fe present in each crystal occurs at this site. Inspection of the $<M(2)–O>$ distances suggests that it is all in the trivalent state (Hawthorne 1983a). Thus all C-group Al was assigned to $M(2)$, together with all Fe in each crystal and sufficient Mg to fill the site. Comparison of the observed and calculated site-scattering at $M(2)$ (Fig. 2) shows that the assigned site-populations are in accord with the refined site-scattering values.

The M(1) and M(3) sites

Inspection of Table 5 shows that the dominant constituent at $M(1)$ and $M(3)$ is Mg, in accord with the unit formulae of Table 6. As shown by Hawthorne *et al.* (1992, 1993, 1994), Oberti *et al.* (2000, 2003a, b, 2004, 2005) and Tait *et al.* (2005), C-group Li is completely ordered at the $M(3)$ site. Assigning the Li in this way and filling the balance of the site with Mg gives calculated site-scattering values that are close to the refined values (Table 5). The dominant species at $M(1)$ is Mg, but the refined site-scattering values indicate small amounts of an additional constituent with a higher atomic number than Mg. The small amounts of excess scattering (relative to Mg) at $M(1)$ correlate well with the amount of Mn (+ Ti) in the unit formulae, suggesting that Mn is the "heavy" constituent at $M(1)$. The small amount of Ti in crystal 793 was assigned to $M(1)$, together with the corresponding amount of O^{2-} at $O(3)$ (Table 6) according to the short-range arrangement $^{M(1)}Ti$ $^{O(3)}O^{2-}{}_2$. The low $^{M(1)}Ti^{4+}$ content in crystal 793 is in accord with the higher B_{equiv} value at the $M(1)$ site in this amphibole (0.65 *versus* 0.48–0.54 Å^2 for the other crystals).

FIG. 1.   Variation in refined scattering values for the A, $M(4)$ and $M(1,2,3)$ sites *versus* the numbers of electrons for the A, B [≡ $M(4)$] and C [≡ $M(1,2,3)$] -group cations in the Kajlidongri amphiboles of Table 1; the line denotes the 1:1 relation.
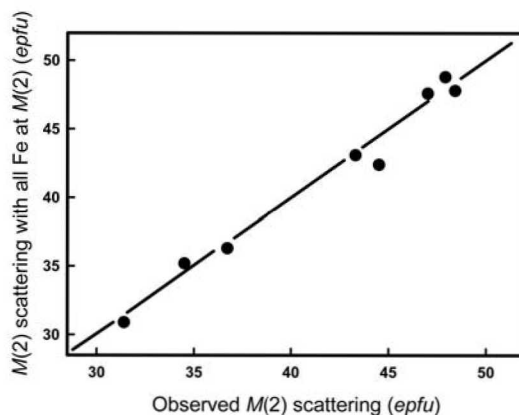
FIG. 2.   Variation in the effective scattering at the $M(2)$ site calculated with all Fe at $M(2)$ *versus* the observed (refined) site-scattering at $M(2)$.

The M(4) site

The sums of the *C*-group cations in these amphiboles are generally larger than 5 *apfu*, leaving a small excess of *C*-group cations to be assigned to the *B*-group [*i.e.*, the *M*(4) site] (Table 6). All Ca was assigned to *M*(4), together with sufficient Na to fill the site. As all Fe was assigned to the *M*(2) site as Fe^{3+}, this leaves either Mg or Li to be assigned to the *M*(4) site [actually the *M*(4)' site]. The issue of which cation, Li or Mg, is to be assigned to the *M*(4) site is examined in Figure 3. In Figures 3a and 3b, the full lines are the calculated relations between the site scattering and the compositional variable on the abscissa. In Figures 3c and 3d, the full lines are the 1:1 relation between the calculated site-scattering with Mg (Fig. 3c) and Li (Fig. 3d) assigned to the *M*(4) site and the observed site-scattering values. Figures 3a and 3b show the relation between the scattering determined by SREF at the *M*(3) site as a function

of ^{C}Li, with Mg (Fig. 3a) and Li (Fig. 3b) assigned to *M*(4) as excess *C*-group cations, respectively. Figures 3c and 3d show the relation between the scattering determined by SREF at the *M*(4) site as a function of the calculated scattering at *M*(4) using Mg (Fig. 3c) and Li (Fig. 3d), respectively, assigned to *M*(4) as excess *C*-group cations. There is not a lot to choose between Figure 3a and Figure 3b, whereas for *M*(4), there is better agreement for Li assigned to *M*(4). Of course, the differences between the two models shown in Figure 3 are not large because the amounts of Li in these amphiboles is not large. Thus although the data do indicate that some Li occurs at *M*(4) in preference to Mg, our confidence in this result is not high.

The A sites

The contents of the *A* cavity show reasonable agreement with the sums of the refined site-scattering
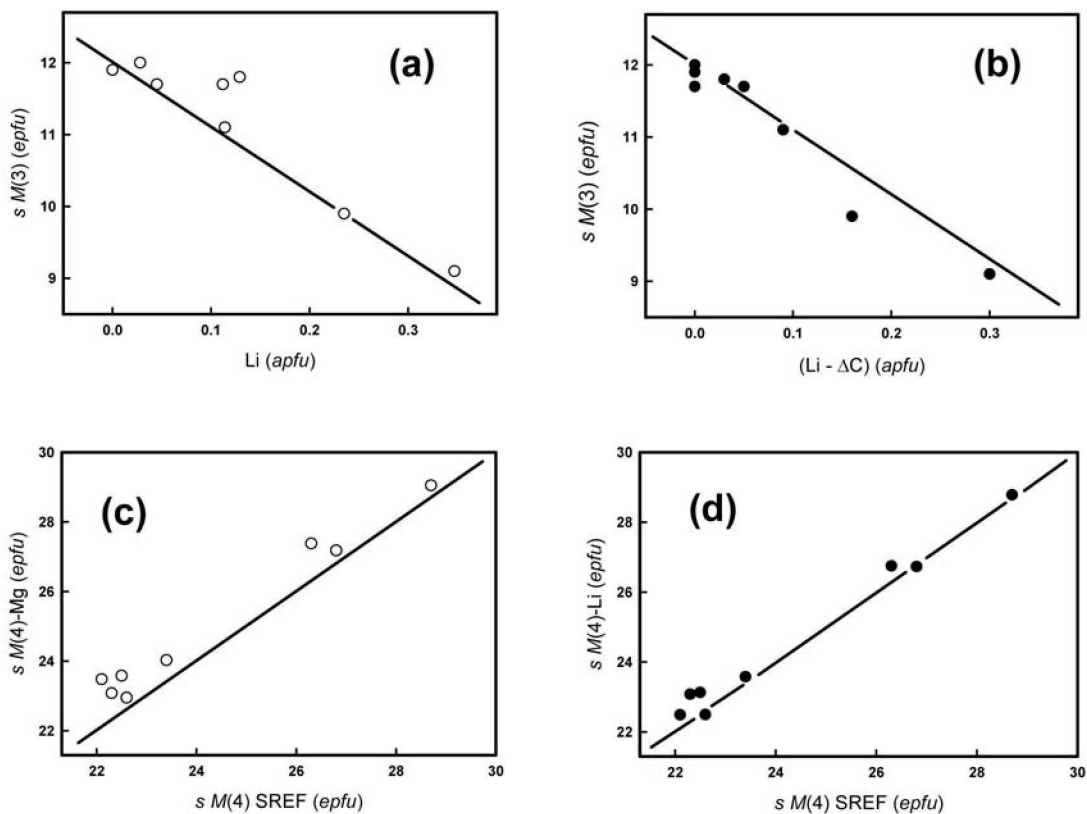
FIG. 3.   Comparison of refined scattering at the (a), (b) *M*(3) and (c), (d) *M*(4) sites with Li content and with the effective scattering at the *M*(4) site from the unit formula using two different assignments; in each figure, the straight lines show the ideal relations; (a) refined scattering at the *M*(3) site as a function of total Li (*i.e.*, excess *C* cations assigned to the *B* group are Mg); (b) refined scattering at the *M*(3) site as a function of Li assigned to the *C* group (*i.e.*, excess *C* cations assigned to the *B* group are Li); (c) the effective scattering of cations assigned to *M*(4) where Mg is at *M*(4) *versus* the refined scattering at *M*(4); (d) effective scattering of cations assigned to *M*(4) where Li is at *M*(4) *versus* the refined scattering at *M*(4).
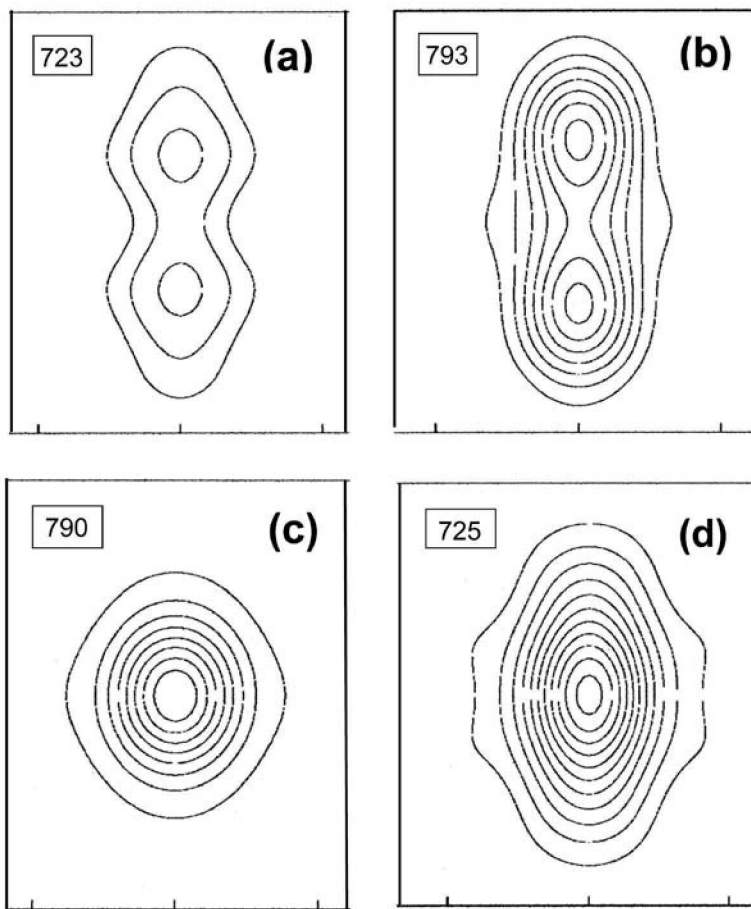
FIG. 4.   Difference-Fourier maps through the $A(2/m)$ site for crystals (a) 723, (b) 793, (c) 790 and (d) 725; all maps were calculated with the A cations removed from the structure model and are oriented parallel to $(\overline{2}01)$.

TABLE 7. SITE POPULATIONS (*apfu*) FOR KAJLIDONGRI AMPHIBOLES

		723	787	724	725	790	791	792	793
$M(1)$	Mg	1.98	1.98	1.99	1.96	1.92	1.95	1.92	1.87
	Mn	0.02	0.02	0.01	0.04	0.08	0.05	0.08	0.13
$M(2)$	Al	0.11	0.02	0.11	0.06	0.05	0.08	0.04	0.10
	Fe^{3+}	1.69	1.77	1.68	0.88	0.49	1.36	0.80	1.28
	Mg	0.20	0.21	0.21	1.05	1.46	0.56	1.16	0.58
	Ti	–	–	–	0.01	–	–	–	0.04
$M(3)$	Mg	1.00	0.97	0.95	0.84	1.00	0.91	1.00	0.70
	Li	–	0.03	0.05	0.16	–	0.09	–	0.30
$M(4)$	Li	–	0.11	0.05	0.07	0.03	0.05	0.05	0.05
	Ca	0.12	0.14	0.10	0.59	0.78	0.22	0.57	0.17
	Na	1.88	1.75	1.85	1.34	1.19	1.73	1.38	1.78
A	Na	0.07	0.13	0.13	0.47	0.40	0.32	0.40	0.48
	K	0.04	0.05	0.05	0.18	0.28	0.13	0.22	0.12
	Σ	0.11	0.18	0.18	0.65	0.68	0.45	0.62	0.60
$O(3)$	OH	1.89	1.83	1.77	1.76	2.00	1.83	1.92	1.53
	F	0.11	0.17	0.23	0.24	0.00	0.17	0.08	0.47

values at the A sites (Fig. 1). As is usual for monoclinic amphiboles with (partly or completely) filled A-sites, there is significant positional disorder of the cations occupying the A cavity (Hawthorne & Grundy 1972, Hawthorne 1981, 1983a, b). Selected difference-Fourier maps, calculated with the A cations removed from the structure models, are shown in Figure 4. There are two distinct types of electron-density distribution: (1) discrete centers of maximum density at the $A(m)$ site (Figs. 4a, b), and (2) a single center of density at the $A(2/m)$ site (Figs. 4c, d). The electron density within the A cavity is a function of the type of cation [K occupies the $A(m)$ site, and Na occupies the $A(m)$ and $A(2)$ sites]. The Na occupancy of $A(m)$ and $A(2)$ is affected by SRO (short-range order) of cations occupying the sites adjacent to the A cavity (Hawthorne et al. 1996b), and will be discussed later.

VARIATIONS IN CHEMICAL COMPOSITION

Inspection of Table 1 shows that, except for crystal 793, the amphiboles examined here are either magnesioriebeckite or (in some cases adjectively modified) richterite. The primary differences between these two compositions involve Fe^{3+}, Mg, ^BNa and $^A(Na + K)$. Figure 5 shows the variation in Fe^{3+} as a function of ^BNa. There is a linear variation in composition exactly between end-member richterite (RICH) and end-member magnesioriebeckite (RIEB). This coherence of the data gives us confidence in our derivation of the exact Fe^{3+} contents, and indicates a very restricted variation in amphibole composition. This is borne out by Figures 6 and 7, which show the variations in Fe^{3+} as a function of $^A(Na + K)$ and ^BNa as a function of $(Mg + Mn^{2+} + Li)$, respectively. The largest departure from linearity with the end-member compositions in Figure 6 is for crystal 793, which is actually magnesioarfvedsonite; the deviation from linearity for 793 is still quite modest, and the different name is a result of a slight excess of $^A(Na + K)$ for the amount of Fe^{3+} present, which just moves the crystal into the different compositional field. In Figure 7, the data depart slightly from exact linearity with the end-member compositions. A small amount of Fe^{2+} may be present, but the trends of Figures 5, 6 and 7 suggest that (if present) it must be small (<0.05 *apfu*). It is surprising, at least to us, that such a locally heterogeneous and low-temperature environment can result in such a coherent variation in amphibole composition.

THE BEHAVIOR OF ^CLI IN AMPHIBOLES

Lithium is a significant component of the *C*-group cations in amphiboles from silica-oversaturated peral-kaline granitic rocks, episyenites and manganiferous metasediments. However, comparison of the behavior of Li in amphiboles from these three types of paragenesis has been confounded by the complexity of the amphiboles in manganiferous metasediments. In addition to incorporating significant ^CLi, these amphiboles can also contain major to dominant O^{2-} at the O(3) site (Hawthorne *et al.* 1994, Tait *et al.* 2005) and also can contain significant to major amounts of Mn^{3+} (Hawthorne *et al.* 1995, Tait *et al.* 2005). However, in the present work, these complexities have been avoided by judicious selection of samples with O(3) = OH + F and only minor Mn (which is probably in the divalent state). Figure 8 shows the variation of Li as a function of Ca content in amphiboles from Kajlidongri (this work only), and compares them with the well-developed trends for the Virgin Canyon pluton, U.S.A.
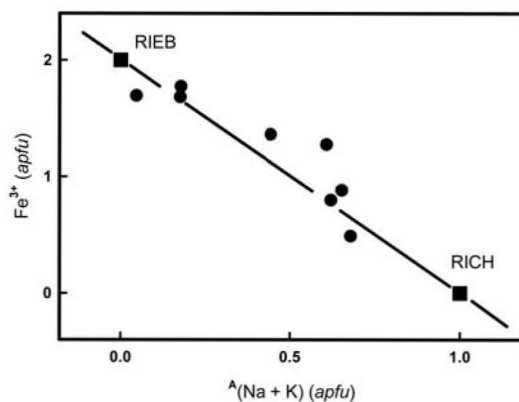
FIG. 6. Variation in Fe^{3+} as a function of $^A(Na + K)$ in Kajlidongri amphiboles; legend as in Figure 5.

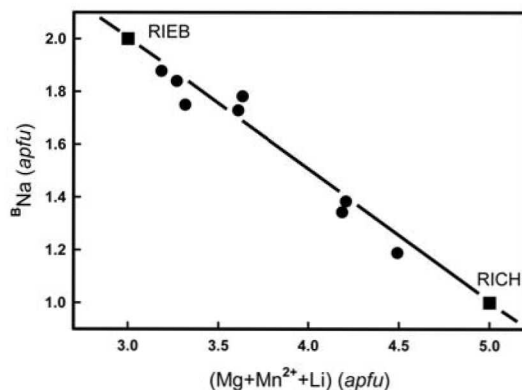FIG. 5. Variation in Fe^{3+} as a function of ^BNa in Kajlidongri amphiboles; RICH = end-member richterite. RIEB = end-member magnesioriebeckite.

FIG. 7. Variation in ^BNa as a function of $(Mg + Mn^{2+})$ in Kajlidongri amphiboles; legend as in Figure 5.

(Hawthorne *et al.* 1993) and the Strange Lake pluton, Canada (Hawthorne *et al.* 2001) shown as heavy lines. Although Li decreases with increasing Ca, the amphiboles from Kajlidongri (circles, Fig. 8) do not show the well-developed correlations shown by amphiboles from Virgin Canyon and Strange Lake. Hawthorne *et al.* (2001) ascribed the trends for the Virgin Canyon and Strange Lake amphiboles to the effect of progressive fractionation of the parent magma rather than a crystal-chemical effect of the amphibole structure itself. This being the case, one does not expect a similar trend for amphiboles from Kajlidongri, with its totally different paragenesis.

On the other hand, Li shows a strong positive correlation with the amount of F at O(3) (Fig. 9). The slope of the relation in Figure 9 is ~1:2, suggesting that Li is locally associated with F at each of the coordinating O(3) sites. Ferro-sodic-pedrizite (Oberti *et al.* 2005) shows a similar behavior. However, the Li-bearing amphiboles from Virgin Canyon, Strange Lake and the Pedriza Massif, Spain (Oberti *et al.* 2003a) show no such correlation. In the Virgin Canyon and Strange Lake suites (Hawthorne *et al.* 1993, 2001), F is invariably in excess of $2 \times$ Li *apfu*, meaning that there is sufficient F in these amphiboles to ensure that Li is locally coordinated by F at the adjacent two O(3) sites (although, of course, we cannot know from the data if Li actually does assume this local coordination in Virgin Canyon and Strange Lake amphiboles). However, in Pedriza massif amphiboles (Oberti *et al.* 2003a), ^{C}Li is generally greater than F/2 *apfu*, and can be greater than F. These observations point to a different behavior of F at the very different conditions of these paragenesis. The amphiboles at Kajlidongri formed at much lower temperature than the amphiboles at Virgin Canyon,

Strange Lake, or Pedriza, and the lack of any F in excess of twice the amount of Li suggests that F cannot enter the O(3) site in the absence of Li under the conditions at Kajlidongri, and *vice versa*, Li cannot enter the $M(3)$ site in the absence of F. This, in turn, suggests that Li *and* F may have been transported solely as $[LiF_2(H_2O)_4]^{-1}$ complexes in the associated hydrothermal fluid at Kajlidongri. This is obviously not the case at Virgin Canyon and Strange Lake, where the amphiboles are magmatic in origin.

SHORT-RANGE ORDER OF ALKALI CATIONS IN THE *A* CAVITY

As indicated in Figure 4, there are four distinct patterns of electron density in the amphiboles examined here, and we can divide them into two different types: (1) the electron density is elongate in the mirror plane (vertically in Fig. 4) with two distinct maxima and either none or only minor density visible along the 2-fold axis perpendicular to the mirror plane (Figs. 4a, b); (2) the electron density shows only one maximum and is only slightly elongate within the mirror plane (Figs. 4c, d). It has long been known that K exclusively occupies the $A(m)$ site in monoclinic amphiboles (Hawthorne 1983a, and references therein). However, the behavior of Na is more complicated. Hawthorne *et al.* (1996b) have shown that the occupancy of the different sites within the *A* cavity in monoclinic amphiboles is dictated by the patterns of short-range order of the adjacent $M(4)$ cations and O(3) anions, which in turn are constrained by the chemical composition of the amphiboles. Their findings indicate that the relative sequence of ordering patterns is as follows: $^{M(4)}Na-^{O(3)}F-^{A(m)}Na > ^{M(4)}Ca-^{O(3)}OH-^{A(2)}Na > ^{M(4)}Na-^{O(3)}OH-^{A(m)}Na >> ^{M(4)}Ca-^{O(3)}F-^{A(m)}Na, ^{M(4)}Ca-^{O(3)}F-^{A(2)}Na.$
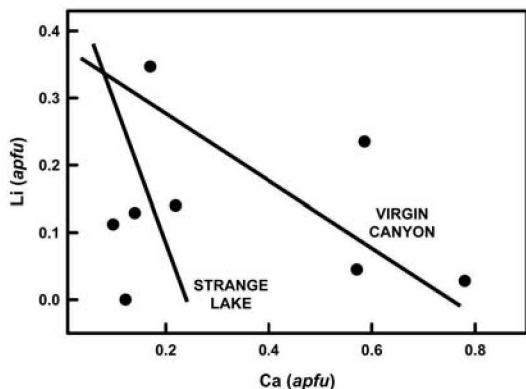
FIG. 8. Variation in Li content as a function of Ca content for the Kajlidongri amphiboles; the trends for amphiboles from peralkaline igneous rocks are shown by the straight lines labeled Strange Lake and Virgin Canyon.
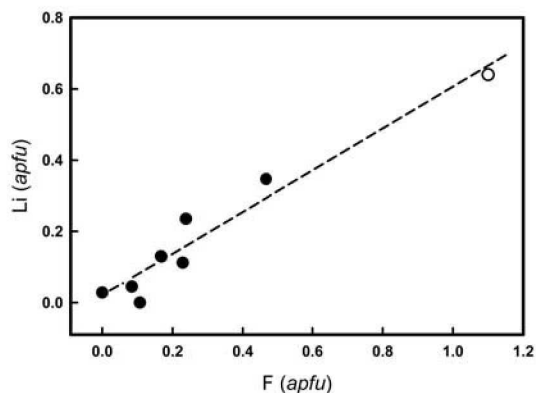
FIG. 9. Variation in Li content as a function of F content in Kajlidongri amphiboles (black circles) and fluoro-sodic-pedrizite (white circle); the straight line denotes the least-squares fit to the data.

Hawthorne *et al.* (1996b) has shown that where the O(3) site is occupied by (OH), the K atom is closer to the $A(2/m)$ site (*i.e.*, the electron density is less extended in the mirror plane) than where the O(3) site is occupied by F. This occurs as a result of a repulsive interaction between K at the $A(m)$ site and H associated with (OH) at the O(3) site. Where the O(3) site is occupied by F, such a repulsion no longer occurs, and K can relax to a more off-centered position, a tendency that is increased by the occurrence of Li at $M(3)$ and the ensuing need for bonding between the A cation and F at O(3). The type-(1) amphiboles, in which the A-site electron density is strongly elongate in the mirror plane (Figs. 4a, b), has ^AK less than $^{O(3)}F$, and hence there is sufficient F for a local association of K and F, accounting to some extent for the more elongate electron-density in these amphiboles. In the type-(2) amphiboles, in which the A-site electron density is only slightly elongate in the mirror plane (Figs. 4c, d), ^AK is greater than $^{O(3)}F$, and there is insufficient F to ensure local association of K and F. Hence most K must be locally associated with (OH) at the adjacent O(3) site, accounting for the less elongate electron-density in these amphiboles (Figs. 4c, d).

In type-(1) amphiboles (crystals 723, 724, 725, 787, 791, 793), all K at the $A(m)$ site is associated with F at the O(3) site; however, there is sufficient F remaining to allow most ^ANa to be locally associated with F at O(3). After assigning Na to the (most preferred) $^{M(4)}Na–^{O(3)}F–^{A(m)}Na$ arrangement, there is 0.00, 0.00, 0.00, 0.01, 0.04 and 0.14 Na *apfu* to assign to other arrangements. The next most preferable local arrangement is $^{M(4)}Ca–^{O(3)}OH–^{A(2)}Na$, and there is sufficient Ca (just about) for this arrangement to occur in 791 and 793. Thus in the type-(1) amphiboles, there is zero to a small amount of $^{A(2)}Na$ present, as indicated in the variation in the electron-density patterns (Figs. 4a, b).

In type-(2) amphiboles (crystals 790, 792), the amount of K invariably exceeds the amount of F, and hence K at the $A(m)$ site is associated with both F and (OH) at the O(3) site. All arrangements involving ^ANa must also involve $^{O(3)}OH$, *i.e.*, the optimum arrangement $^{M(4)}Na–^{O(3)}F–^{A(m)}Na$ cannot occur because there is no F available. The next most preferred arrangement is $^{M(4)}Ca–^{O(3)}OH–^{A(2)}Na$; there is sufficient Ca for this to occur and account for the remaining A-site Na, in turn accounting for the increased electron-density along the 2-fold axis in these amphiboles (Fig. 4c, d).

Thus we see that the patterns of electron density at the A sites are in accord with the variations in the chemical compositions of these amphiboles. So the obvious question follows: does the occupancy of the different A-sites drive the variation in the occupancies of adjacent sites, and in turn, bulk composition of the amphiboles, or does the bulk composition drive the occupancy of the different A-sites? We suggest that neither of these alternatives represent the situation correctly. We suggest

that during crystallization, the optimum pattern of short-range order condenses from the possible amphibole constituents that are immediately adjacent to that specific part of the crystal. If this is the case, short-range order plays a major role in controlling the composition of the amphibole during crystallization.

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