

## SHORT-RANGE ORDER IN AMPHIBOLES FROM THE BEAR LAKE DIGGINGS, ONTARIO

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### ABSTRACT

The crystal structures of four amphiboles from the Bear Lake diggings, in the Bancroft area of Ontario, fluorotremolite, fluorrichterite and two samples of potassian fluor-magnesiokatophorite, have been refined to *R* indices in the range 1.5–2.2% using ~1380 unique reflections measured with MoK $\alpha$  X-radiation. The crystals used in the collection of the X-ray intensity data were subsequently analyzed by electron and ion microprobes, and formulae were calculated using the Fe<sup>3+</sup> and Fe<sup>2+</sup> contents established by crystal-structure refinement. Site populations were assigned from the results of site-scattering refinement and stereochemical analysis, taking into account the unit formula determined for each crystal. Difference-Fourier maps through the *A*(2/*m*) site show that the *A*(*m*) site is occupied and the *A*(2) site is vacant in all crystals. Occupancy of the *A*(*m*) site, and not the *A*(2) site, by Na imposes strong constraints on the possible patterns of short-range order in these amphiboles. The site populations of the *A*(*m*), *M*(4) and O(3) sites are in accord with the local arrangement  $A^{(m)}(Na + K)_{-O(3)}F_{-M(4)}Na$ , with lesser amounts of  $A^{(m)}(Na + K)_{-O(3)}OH_{-M(4)}Na$  and major to minor amounts of  $A_{-O(3)}OH_{-M(4)}Ca$ . The coupling of elements to specific short-range-ordered arrangements in these crystals suggests that the overall chemical variability of amphiboles is strongly constrained by local bond-valence restraints in addition to overall electroneutrality.

**Keywords:** amphibole, crystal-structure refinement, site populations, electron-microprobe analysis, SIMS analysis, short-range order, Bear Lake diggings, Ontario.

### SOMMAIRE

Nous avons affiné la structure cristalline de quatre échantillons d'amphibole provenant de l'indice de Bear Lake, près de Bancroft, en Ontario, fluorotremolite, fluorrichterite et deux cristaux de fluor-magnésiokatophorite potassique, jusqu'aux résidus *R* dans l'intervalle 1.5–2.2% en utilisant environ 1380 réflexions uniques, mesurées avec rayonnement MoK $\alpha$ . Les cristaux utilisés ont par la suite été analysés avec une microsonde électronique et une microsonde ionique, et les formules ont été calculées avec les proportions de Fe<sup>3+</sup> et de Fe<sup>2+</sup> établies par l'affinement structural. L'occupation des sites a été assignée à partir des affinements de la dispersion associée à chaque site et par analyse stéréochimique, en tenant compte des formules élémentaires de chaque cristal. La distribution des électrons obtenue par différence-Fourier au site *A*(2/*m*) montre que le site *A*(*m*) est rempli, mais le site *A*(2) est vide dans les quatre cas. Le taux d'occupation par Na au site *A*(*m*), et non au site *A*(2), impose de fortes contraintes sur les schémas possibles de mise en ordre à courte échelle dans ces amphiboles. La population des sites *A*(*m*), *M*(4) et O(3) concorde avec l'arrangement local  $A^{(m)}(Na + K)_{-O(3)}F_{-M(4)}Na$ , avec une proportion moindre de  $A^{(m)}(Na + K)_{-O(3)}OH_{-M(4)}Na$ , et des proportions majeures ou mineures de  $A_{-O(3)}OH_{-M(4)}Ca$ . Le couplage des éléments dans ces agencements locaux bien spécifiques fait penser que la variabilité en composition des amphiboles est fortement régie par les contraintes imposées par les valences de liaisons locales, en plus des exigences d'électronneutralité.

(Traduit par la Rédaction)

**Mots-clés:** amphibole, affinement de la structure cristalline, populations des sites, analyse par microsonde électronique, analyse par microsonde ionique, mise en ordre à courte échelle, indice de Bear Lake, Ontario.

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## INTRODUCTION

Hawthorne *et al.* (1996b) showed that short-range order (SRO) occurs in amphibole of tremolitic composition with significant contents of  $A^{(m)}(\text{Na} + \text{K})$ ,  $M^{(4)}\text{Na}$  and  $O^{(3)}\text{F}$ . Subsequent work on synthetic amphiboles involving both homovalent (Della Ventura *et al.* 1998, Robert *et al.* 2000) and heterovalent (Della Ventura *et al.* 1999, 2003, Hawthorne *et al.* 2000) substitutions has shown that SRO is a common feature of amphiboles. Hawthorne (1997) extended bond-valence theory (Brown 1981, 2002) to local arrangements in crystals and showed that local bond-valence requirements in amphiboles are optimized if specific arrangements of atoms occur at the local level (*i.e.*, they will occur with much greater frequency than a random occurrence of local arrangements would suggest), while other arrangements are not stable (they will not occur or will occur at a much lower frequency than a random occurrence of local arrangements would suggest). Here, we examine a series of amphiboles from the Bear Lake mineral-collecting locality, Ontario, with regard to the occurrence of SRO.

## GEOLOGICAL SETTING AND SAMPLE DESCRIPTION

The Bear Lake diggings, well-known to the mineral-collecting community, is located 8.4 km west of Tory Hill, Monmouth Township, in the Bancroft District of southeastern Ontario. Narrow “vein-dikes” of “carbonatite” are emplaced in rocks of the Glamorgan complex, consisting mostly of quartzofeldspathic gneiss, amphibolite and marble (Armstrong & Gittins 1968). The complex equilibrated in the amphibolite grade during the first pulse of the Grenvillian Orogeny, dated between 1190 and 1170 Ma (Easton 2000). The supracrustal rocks were buried to 25 km or so, where they attained a temperature close to 650°C (Anovitz & Essene 1990, Strepey *et al.* 1997). Then, upon decompression and thermal contraction, undeformed dikes of calcite of controversial origin were emplaced in the waning stages of the Grenville event.

The calcite dikes likely were emplaced between 1070 and 1040 Ma ago, at a stage of regional distension after important thrusting. The dikes are steep and subparallel, and run approximately east–west. They typically are 1 to 2 meters across, locally swell to over 3 m, and pinch out at irregular intervals in an *en échelon* fashion. Such tension gashes were possibly filled with a crust-derived silicate-bearing carbonatitic melt (*via* marble syntexis; *cf.* Lentz 1998). This low-viscosity magma crystallized the coarse euhedral crystals of amphibole (BL8, BL10 and BL11, Table 1), biotite, sanidine solid-solution (now coarsely exsolved to orthoclase perthite), titanite, augite, zircon, and fluorapatite so highly prized by collectors. These crystals, up to 5 cm across and compositionally homogeneous, generally protrude from the walls into the body of coarsely crystalline calcite, but they also

are found away from the walls, completely enclosed by calcite. The temperature of crystallization of the assemblage was above the crest of the alkali feldspar solvus (above ~625°C), resulting in the “single crystals” of perthite. Small masses of calc-silicates and carbonate also are found locally in the country rock along the contact with the dikes, possibly part of a skarn assemblage. The fluorotremolite BL TREM (Table 1) is from such an assemblage of calc-silicates. From the spatial and paragenetic relations of the four amphiboles, it is apparent that they all crystallized or equilibrated at the same temperature. The four amphiboles examined here are representative of the suite at this locality, and their characterization is part of (1) the work of RFM on the minerals from this locality, and (2) the work of FCH on SRO in amphiboles (Hawthorne 1997, Hawthorne *et al.* 1996a, b, 2000).

## EXPERIMENTAL AND RESULTS

The sample codes and amphibole names used in this work are given in Table 1, sorted in order of decreasing Si content in *apfu* (atoms per formula unit).

*X-ray data collection and structure refinement*

Experimental details are as described by Oberti *et al.* (1992). Cell dimensions, *R* indices and other data relevant to crystallographic data collection and structure refinement are given in Table 2. Final atom coordinates and anisotropic-displacement factors are listed in Table 3, selected interatomic distances and angles are given in Table 4, and refined site-scattering values (in

TABLE 1. SAMPLE NUMBERS AND NAMES OF AMPHIBOLES FROM THE BEAR LAKE DIGGINGS, ONTARIO

Sample Number	SEQ	Name
BL TREM	757	Fluorotremolite
BL 8	761	Fluororichterite
BL 10	721	Potassian fluoro-magnesiokatophorite
BL 11	762	Potassian fluoro-magnesiokatophorite

TABLE 2. CRYSTAL DATA AND MISCELLANEOUS STRUCTURE-REFINEMENT INFORMATION FOR THE BEAR LAKE AMPHIBOLES

	757	761	721	762
<i>a</i> (Å)	9.868(3)	9.866(2)	9.888(3)	9.887(3)
<i>b</i>	18.033(7)	18.019(4)	18.022(6)	18.023(9)
<i>c</i>	5.273(3)	5.274(1)	5.290(2)	5.292(2)
$\beta$ (°)	104.66(2)	104.58(2)	104.72(3)	104.66(3)
<i>V</i> (Å <sup>3</sup> )	907.7	907.4	911.7	912.2
Space group	C2/m	C2/m	C2/m	C2/m
<i>Z</i>	2	2	2	2
No. of   <i>F</i>	1375	1377	1380	1384
<i>F</i> <sub>o</sub>   > 5 $\sigma$	902	1171	1086	974
<i>R</i> (obs) %	1.6	1.5	2.2	1.6

*epfu*: electrons per formula unit) are given in Table 5. Structure factors may be obtained from The Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2.

#### Electron- and ion-microprobe analysis

Subsequent to the experimental crystallographic work, the crystals used in the collection of the X-ray intensity data were mounted, polished, and characterized by electron- and ion-microprobe analysis following the procedures described by Oberti *et al.* (1992) and Ottolini *et al.* (1993). The Fe<sup>3+</sup> and Fe<sup>2+</sup> contents of the unit formulae were calculated from the structural results and were subsequently put back into the formula-normalization process. The structural results indicate no significant dehydroxylation, and unit formulae were normalized on the basis of 24(O,OH,F) with OH + F = 2.0 *apfu*. The chemical compositions and unit formulae are given in Table 6.

#### DISCUSSION

The site populations were assigned on the basis of the refined site-scattering values (Table 5), the unit formulae calculated from the results of microprobe analysis (Table 6), mean bond-length arguments and the electroneutrality requirement. There is very close agreement between the site scattering at the C-, B- and A-group sites and the equivalent scattering calculated from the unit formula (Table 5), the mean deviations being 0.4, 0.0, 0.0 and 1.4 *epfu*, respectively.

#### The T(1) and T(2) sites

Long-range order of Si and Al over the T(1) and T(2) sites in amphibole has been considered by Oberti *et al.* (1995a), who proposed equations relating mean bond-length to Al content at these sites. Application of these equations to the <T-O> bond-lengths of Table 4 indicate that <sup>14</sup>Al is completely ordered at the T(1) site in all

TABLE 3. ATOM COORDINATES AND DISPLACEMENT PARAMETERS (Å<sup>2</sup>) FOR THE BEAR LAKE AMPHIBOLES

	x	y	z	β <sub>11</sub>	β <sub>22</sub>	β <sub>33</sub>	β <sub>12</sub>	β <sub>13</sub>	β <sub>23</sub>
<i>Crystal 757</i>									
O(1)	0.11174	0.08580	0.21765	0.0012	0.0004	0.0044	0	0.0005	-0.0001
O(2)	0.11886	0.17044	0.72518	0.0016	0.0005	0.0043	-0.0001	0.0010	-0.0001
O(3)	0.10801	0	0.71486	0.0023	0.0005	0.0066	0	0.0007	0
O(4)	0.36382	0.24797	0.79421	0.0026	0.0004	0.0054	-0.0004	0.0013	-0.0002
O(4)	0.34598	0.13269	0.09692	0.0016	0.0006	0.0048	-0.0001	0.0006	0.0006
O(6)	0.34304	0.11829	0.58939	0.0018	0.0005	0.0051	0.0001	0.0006	-0.0006
O(7)	0.33680	0	0.29379	0.0023	0.0003	0.0099	0	0.0011	0
T(1)	0.27939	0.08429	0.29682	0.0012	0.0003	0.0030	0	0.0004	-0.0001
T(2)	0.28757	0.17119	0.80386	0.0013	0.0003	0.0030	-0.0001	0.0006	0.0000
M(1)	0	0.08819	½	0.0016	0.0003	0.0034	0	0.0009	0
M(2)	0	0.17786	0	0.0013	0.0003	0.0037	0	0.0006	0
M(3)	0	0	0	0.0017	0.0004	0.0035	0	0.0004	0
M(4)	0	0.27767	½	0.0025	0.0004	0.0078	0	0.0029	0
A	0	½	0	0.0009	0.0006	0.0075	0	0.0026	0
A(m)	0.0361	½	0.0828	0.0087	0.0020	0.0236	0	0.0081	0
A(2)	0	0.4594	0	2.9					
H	0.195	0	0.775	0.4					
<i>Crystal 761</i>									
O(1)	0.11141	0.08574	0.21758	0.0013	0.0004	0.0041	-0.0001	0.0008	-0.0001
O(2)	0.11874	0.17024	0.72576	0.0012	0.0006	0.0046	-0.0001	0.0009	-0.0002
O(3)	0.10729	0	0.71471	0.0021	0.0006	0.0063	0	0.0011	0
O(4)	0.36368	0.24830	0.79410	0.0024	0.0005	0.0063	-0.0004	0.0015	-0.0002
O(4)	0.34668	0.13244	0.09605	0.0022	0.0009	0.0065	-0.0001	0.0011	0.0008
O(6)	0.34321	0.11793	0.58993	0.0018	0.0007	0.0050	0	0.0008	-0.0007
O(7)	0.33787	0	0.29323	0.0019	0.0004	0.0104	0	0.0009	0
T(1)	0.27948	0.08442	0.29672	0.0012	0.0003	0.0032	0	0.0005	0
T(2)	0.28752	0.17133	0.80369	0.0011	0.0004	0.0031	-0.0001	0.0007	-0.0001
M(1)	0	0.08845	½	0.0016	0.0004	0.0037	0	0.0010	0
M(2)	0	0.17821	0	0.0015	0.0005	0.0051	0	0.0010	0
M(3)	0	0	0	0.0016	0.0003	0.0034	0	0.0007	0
M(4)	0	0.27741	½	0.0029	0.0006	0.0096	0	0.0034	0
A	0	½	0	0.0039	0.0006	0.0258	0	0.0092	0
A(m)	0.0415	½	0.0909	0.0035	0.0022	0.0205	0	0.0061	0
A(2)	0	0.4712	0	0.0075	0.0001	0.0431	0	0.0037	0
H	0.190	0	0.794	1.8					

TABLE 3 (continued). ATOM COORDINATES AND DISPLACEMENT PARAMETERS ( $\text{\AA}^2$ ) FOR THE BEAR LAKE AMPHIBOLES

	x	y	z	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
<i>Crystal 721</i>									
O(1)	0.11024	0.08651	0.21762	0.0021	0.0006	0.0066	-0.0002	0.0011	-0.0001
O(2)	0.11935	0.17063	0.72816	0.0018	0.0007	0.0074	0	0.0010	-0.0001
O(3)	0.10643	0	0.71326	0.0029	0.0006	0.0102	0	0.0015	0
O(4)	0.36385	0.24892	0.79370	0.0033	0.0006	0.0099	-0.0004	0.0021	-0.0002
O(4)	0.34756	0.13323	0.09709	0.0024	0.0011	0.0088	0.0001	0.0011	0.0012
O(6)	0.34333	0.11807	0.59368	0.0024	0.0008	0.0103	0.0001	0.0010	-0.0008
O(7)	0.33854	0	0.29273	0.0029	0.0006	0.0159	0	0.0011	0.0000
T(1)	0.27994	0.08484	0.29855	0.0017	0.0004	0.0054	0	0.0007	0.0000
T(2)	0.28855	0.17151	0.80566	0.0017	0.0004	0.0055	-0.0001	0.0009	0.0000
M(1)	0	0.08908	½	0.0021	0.0005	0.0060	0	0.0012	0
M(2)	0	0.17910	0	0.0019	0.0005	0.0072	0	0.0012	0
M(3)	0	0	0	0.0021	0.0004	0.0057	0	0.0007	0
M(4)	0	0.27800	½	0.0034	0.0006	0.0120	0	0.0037	0
A	0	½	0	0.0045	0.0019	0.0184	0	0.0078	0
A(m)	0.0429	½	0.0948	0.0053	0.0021	0.0208	0	0.0051	0
A(2)	0	0.4721	0	3.2					
<i>Crystal 762</i>									
O(1)	0.11006	0.08655	0.21687	0.0017	0.0006	0.0050	-0.0002	0.0009	-0.0001
O(2)	0.11943	0.17052	0.72834	0.0015	0.0007	0.0060	-0.0001	0.0006	-0.0002
O(3)	0.10592	0	0.71251	0.0027	0.0007	0.0079	0	0.0012	0
O(4)	0.36348	0.24902	0.79434	0.0029	0.0006	0.0088	-0.0004	0.0020	-0.0003
O(4)	0.34769	0.13328	0.09714	0.0018	0.0011	0.0077	0.0002	0.0010	0.0013
O(6)	0.34359	0.11807	0.59439	0.0019	0.0008	0.0080	0	0.0012	-0.0008
O(7)	0.33846	0	0.29238	0.0024	0.0005	0.0139	0	0.0008	0
T(1)	0.27989	0.08495	0.29842	0.0012	0.0004	0.0042	-0.0001	0.0004	-0.0001
T(2)	0.28872	0.17153	0.80567	0.0012	0.0004	0.0043	-0.0001	0.0007	0.0000
M(1)	0	0.08890	½	0.0019	0.0005	0.0044	0	0.0010	0
M(2)	0	0.17925	0	0.0014	0.0005	0.0056	0	0.0011	0
M(3)	0	0	0	0.0017	0.0003	0.0043	0	0.0005	0
M(4)	0	0.27789	½	0.0032	0.0007	0.0113	0	0.0038	0
A	0	½	0	0.0031	0.0021	0.0144	0	0.0056	0
A(m)	0.0422	½	0.0936	0.0054	0.0022	0.0203	0	0.0047	0
A(2)	0	0.4719	0	4.2					

of the Bear Lake amphiboles. Moreover, the  $\langle T(1)-O \rangle$  values of Table 4 and the  $^{141}\text{Al}$  contents of Table 6 are in almost exact agreement with the predictive equation of Oberti *et al.* (1995a), and the site populations (Table 7) were assigned accordingly.

#### The M(1), M(2) and M(3) sites

The unit formulae derived from renormalization of the microprobe data indicate that there are seven scattering species (Al,  $\text{Ti}^{4+}$ , Fe, Mn, Zn, Li and Mg) distributed over these three sites. Where there are more than two scattering species distributed over more than one site, the site-scattering values cannot provide a unique solution for the site populations (Hawthorne 1983b). However, combination of the refined site-scattering values with the results of microprobe analysis and the detailed stereochemical changes that accompany changes in site chemistry can give reliable site-populations (Ungaretti *et al.* 1983, Hawthorne *et al.* 1993,

1996a, Oberti *et al.* 1992, 1993, 1995a, b) in complex natural amphiboles.

Of the seven scattering species noted above, Fe and Mn can each occur in more than one valence state in amphiboles, further complicating the problem of site-population assignment. We will assume that Fe can occur as both  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ , and that Mn occurs as  $\text{Mn}^{2+}$  (as expected by comparison with amphiboles in other environments). As both Zn and Mn are present in very small amounts ( $\leq 0.05$  apfu), we incorporate them with Fe as a scattering species:  $\text{Fe}^* = \text{Fe}^{2+} + \text{Fe}^{3+} + \text{Mn} + \text{Zn}$ , as these all have similar X-ray scattering factors. Similarly, Mg and Al can be combined in the same fashion:  $\text{Mg}^* = \text{Mg} + \text{Al}$ . This reduces the number of effective scattering species to four:  $\text{Mg}^*$ ,  $\text{Fe}^*$ , Ti and Li. Combination of the refined scattering values with stereochemical arguments and the microprobe data now allows assignment of site populations.

Characterization of Li-rich sodic amphiboles (Hawthorne *et al.* 1992, 1993, 1994, 1996b) has shown

that Li is completely ordered at the  $M(3)$  site. There is no strong evidence for the assignment of Ti to the individual  $M$ -sites in these amphiboles. The only direct evidence for the behavior of Ti in amphiboles is the neutron-scattering results for kaersutite (Kitamura *et al.* 1975) and the X-ray results of Oberti *et al.* (1992) on Fe-poor Ti-rich richterite, both of which show  $^{61}\text{Ti}$  ordered at the  $M(1)$  site and associated with dehydroxylation at the locally associated O(3) sites. However, small amounts of Ti have usually been assigned to the  $M(2)$  site (see Hawthorne 1983a), although there is no direct evidence of this type of behavior; here, we follow this model, but recognize that it may not be correct.

The site populations for  $M(1)$  and  $M(3)$  can be calculated directly as  $\text{Mg}^*$  and  $\text{Fe}^*$  from the refined

site-scattering values of Table 5. The  $\text{Mg}^*$  and  $\text{Fe}^*$  contents of  $M(2)$  can be calculated from the refined site-scattering value for the  $M(2)$  site after subtracting the scattering due to the amount of Ti present. The mean bond-lengths at  $M(1)$  and  $M(3)$  indicate that the  $\text{Fe}^*$  at these sites is completely in the divalent state. Except for crystal 757, the mean bond-length at  $M(2)$  indicates that there must be small ( $<0.72 \text{ \AA}$ ; radii from Shannon 1976) trivalent cations at  $M(2)$ , and all  $^{61}\text{Al}$  and  $\text{Fe}^{3+}$  were assigned to this site. The  $\text{Fe}^{3+}$  content of  $M(2)$  was calculated from the mean bond-length at that site, and the site populations were assigned as  $\text{Mg} + \text{Al} + \text{Ti} + x\text{Fe}^{2+} + y\text{Fe}^{3+}$ , with  $x + y$  constrained by the  $\text{Fe}^*$  site-population assigned to  $M(2)$ . For crystal 757, the  $\langle M(3)\text{-O} \rangle$  bond-length is shorter than expected for the assigned site-population expressed as  $\text{Mg} + \text{Fe}^{2+}$ , and so the small amount of  $^{61}\text{Al}$  present in this crystal (Table 6) was assigned to  $M(3)$  (*cf.* Oberti *et al.* 1995b).

The  $M(4)$ , A and O(3) site-populations were assigned from the unit formulae of Table 6, and are almost exactly in agreement with the refined site-scattering values. Final site-populations are given in Table 7.

#### SRO AND ITS CONSTRAINTS ON CHEMICAL VARIABILITY

Of particular interest in monoclinic amphiboles is the variation in order of the cations occupying the A cavity. This issue has been addressed by Hawthorne & Grundy (1972, 1978), Papike *et al.* (1969), Heritsch (1955), Boschmann *et al.* (1994), Docka *et al.* (1980), Prewitt (1963), Gibbs & Prewitt (1968) and Cameron *et al.* (1983). The details of the mechanism controlling this ordering were finally identified by Hawthorne *et al.* (1996a), who showed that the observed electron-density distributions within the A cavity, and their variation as a function of site populations in the amphibole structure, can be interpreted in terms of a series of short-range configurations involving the  $M(4)$ , O(3) and A sites. The relative frequency of occurrence of these patterns of SRO (Short-Range Order) was identified, and

TABLE 4. SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) IN THE BEAR LAKE AMPHIBOLES

	757	761	721	762
T(1)-O(1)	1.601	1.605	1.623	1.625
T(1)-O(5)	1.630	1.631	1.645	1.644
T(1)-O(6)	1.631	1.631	1.641	1.645
T(1)-O(7)	1.624	1.628	1.638	1.640
$\langle T(1)\text{-O} \rangle$	1.621	1.624	1.637	1.639
T(2)-O(2)	1.611	1.612	1.618	1.619
T(2)-O(4)	1.583	1.584	1.590	1.588
T(2)-O(5)	1.659	1.660	1.654	1.655
T(2)-O(6)	1.674	1.676	1.669	1.667
$\langle T(2)\text{-O} \rangle$	1.631	1.633	1.633	1.632
T(1)-O(5)-T(2)	136.500	136.200	136.000	136.000
T(1)-O(6)-T(2)	137.700	137.400	137.700	137.500
T(1)-O(7)-T(1)	138.800	138.200	137.900	138.000
M(1)-O(1) x2	2.065	2.062	2.061	2.063
M(1)-O(2) x2	2.069	2.064	2.070	2.073
M(1)-O(3) x2	2.083	2.083	2.087	2.081
$\langle M(1)\text{-O} \rangle$	2.072	2.070	2.073	2.072
M(2)-O(1) x2	2.156	2.160	2.159	2.159
M(2)-O(2) x2	2.087	2.083	2.085	2.085
M(2)-O(4) x2	2.008	2.002	1.985	1.983
$\langle M(2)\text{-O} \rangle$	2.084	2.082	2.076	2.076
M(3)-O(1) x4	2.070	2.068	2.075	2.074
M(3)-O(3) x2	2.051	2.046	2.054	2.054
$\langle M(3)\text{-O} \rangle$	2.064	2.061	2.068	2.067
M(4)-O(2) x2	2.412	2.412	2.423	2.424
M(4)-O(4) x2	2.341	2.341	2.350	2.355
M(4)-O(5) x2	2.794	2.801	2.782	2.784
M(4)-O(6) x2	2.552	2.558	2.558	2.559
$\langle M(4)\text{-O} \rangle$	2.525	2.528	2.528	2.531
A-O(5) x4	2.948	2.937	2.949	2.948
A-O(6) x4	3.153	3.147	3.139	3.138
A-O(7) x2	2.501	2.489	2.490	2.489
$\langle A\text{-O} \rangle$	2.940	2.931	2.933	2.932
A(m)-O(5) x2	3.053	3.069	3.083	3.080
A(m)-O(5) x2	2.922	2.904	2.920	2.921
A(m)-O(6) x2	2.814	2.771	2.751	2.754
A(m)-O(7)	2.493	2.501	2.500	2.497
A(m)-O(7)	3.208	3.166	3.153	3.164
A(m)-O(7)	2.603	2.595	2.607	2.605
$\langle A(m)\text{-O} \rangle$	2.876	2.861	2.863	2.864
A(2)-O(5) x2	2.392	2.534	2.555	2.553
A(2)-O(6) x2	2.712	2.823	2.822	2.819
A(2)-O(7) x2	2.605	2.543	2.541	2.540
$\langle A(2)\text{-O} \rangle$	2.570	2.633	2.639	2.637
O(3)-H	0.84	0.82		

Standard deviations are  $\leq 1$  in the final digit (except for A-O distances).

TABLE 5. REFINED\* SITE-SCATTERING VALUES ( $epfu$ ) AND EQUIVALENT ELECTRONS CALCULATED FROM THE UNIT FORMULA (DENOTED AS EMP) FOR BEAR LAKE AMPHIBOLES

	757	761	721	762
M(1)	24.8	24.9	28.7	29.1
M(2)	25.8	26.9	37.7	38.5
M(3)	12.5	12.3	14.2	14.5
$\Sigma M(1,2,3)$	63.2	64.0	80.6	82.1
$\Sigma M(1,2,3)^{\text{EMP}}$	63.1	63.9	80.5	82.0
M(4)	36.2	35.6	33.1	33.2
$M(4)^{\text{EMP}}$	36.5	35.5	33.1	32.6
A	5.5	6.7	11.1	12.3
$A^{\text{EMP}}$	5.3	7.1	11.2	11.6
O(3)	16.8	17.9	17.5	17.5
$O(3)^{\text{EMP}}$	16.6	16.7	17.2	17.3

\* standard deviations are  $\leq 2$  in the final digit.

TABLE 6. CHEMICAL COMPOSITIONS (wt.%) AND UNIT FORMULAE (*apfu*) OF THE BEAR LAKE AMPHIBOLES

	757	761	721	762
SiO <sub>2</sub>	58.34	57.27	50.71	50.46
Al <sub>2</sub> O <sub>3</sub>	0.10	0.68	3.83	4.02
TiO <sub>2</sub>	0.02	0.04	0.58	0.74
Fe <sub>2</sub> O <sub>3</sub>	0.00	0.59	4.37	4.43
FeO	2.16	1.86	7.47	8.25
MnO	0.19	0.11	0.42	0.40
ZnO	0.04	0.06	0.06	0.03
MgO	22.62	22.83	15.81	15.06
CaO	10.91	9.91	7.91	7.53
Na <sub>2</sub> O	2.12	3.20	4.52	4.70
K <sub>2</sub> O	1.01	0.99	1.60	1.69
Li <sub>2</sub> O	0.00	0.00	0.04	0.04
F	1.34	1.65	2.63	2.66
(H <sub>2</sub> O)	1.54	1.39	0.81	0.79
O=F	-0.56	-0.69	-1.11	-1.12
Total	99.83	99.89	99.65	99.68
Si	8.035	7.909	7.374	7.362
Al	0.000	0.091	0.626	0.638
ΣT	8.035	8.000	8.000	8.000
Al	0.016	0.020	0.030	0.053
Ti	0.002	0.004	0.063	0.081
Fe <sup>3+</sup>	0.000	0.061	0.478	0.486
Fe <sup>2+</sup>	0.249	0.215	0.908	1.007
Mn	0.022	0.013	0.052	0.049
Mg	4.644	4.700	3.427	3.276
Zn	0.004	0.006	0.006	0.003
Li	0.000	0.000	0.023	0.023
ΣC	4.937	5.019	4.987	4.978
□	0.000	0.019	0.000	0.000
Ca	1.610	1.466	1.232	1.177
Na	0.390	0.515	0.768	0.823
ΣB	2.000	2.000	2.000	2.000
Na	0.176	0.342	0.506	0.507
K	0.177	0.174	0.297	0.315
ΣA	0.353	0.516	0.803	0.822
F	0.584	0.721	1.210	1.277
OH*	1.416	1.279	0.790	0.723

\* OH calculated as (2 - F) *apfu*.

explained on the basis of *local* bond-valence requirements (Hawthorne 1997).

Let us examine the detailed variation in chemical composition of these amphiboles in terms of SRO. Figure 1 shows the distribution of electron density within the A cavity for the four Bear Lake amphiboles. The first significant observation is that only the A(*m*) site is occupied in each of these amphiboles; the A(2) site is vacant. Inspection of Table 6 shows that all Bear Lake amphiboles have significant K and Na at the A site. Hawthorne (1983a) reviewed previous work and concluded that K always occupies the A(*m*) site. Hawthorne *et al.* (1996a) identified the patterns of SRO shown in Table 8, listed in terms of their relative stabilities or frequencies. The A(2) site is not occupied in any of the Bear Lake amphiboles (Fig. 1), and hence local arrangements (2) and (5) (Table 8) do not occur in these amphiboles. Thus for patterns of SRO involving A(*m*)Na, arrangement (1) will be preferred, with arrangements (3) and (4) occurring only if there are residual chemical components after assignment to arrangement (1).

TABLE 7. FINAL ASSIGNED SITE-POPULATIONS (*apfu*) FOR THE BEAR LAKE AMPHIBOLES

		757	761	721	762
T(1)	Si	4.00	3.90	3.38	3.37
	Al	—	0.10	0.62	0.63
T(2)	Si	4.00	4.00	4.00	4.00
M(1)	Mg	1.93	1.94	1.67	1.62
	Fe <sup>2+</sup>	0.07	0.06	0.33	0.38
M(2)	Al	—	0.01	0.04	0.07
	Ti <sup>4+</sup>	—	—	0.06	0.08
	Fe <sup>3+</sup>	—	0.12	0.44	0.42
	Fe <sup>2+</sup>	0.15	0.06	0.46	0.51
	Mn <sup>2+</sup>	0.02	0.01	0.05	0.05
	Mg	1.83	1.80	0.95	0.87
M(3)	Mg	0.94	0.97	0.81	0.79
	Fe <sup>2+</sup>	0.03	0.03	0.17	0.19
	Al	0.03	—	—	—
	Li	—	—	0.02	0.02
M(4)	Ca	1.61	1.46	1.23	1.18
	Na	0.39	0.54	0.77	0.82
A	Na	0.81	0.32	0.51	0.51
	K	—	0.18	0.30	0.32
O(3)	F	0.58	0.71	1.21	1.36
	OH	1.42	1.29	0.79	0.64

TABLE 8. PATTERNS OF SRO INVOLVING CATION SITES ADJACENT TO THE A CAVITY, IN ORDER OF PREFERENCE\*

(1)	<sup>M(4)</sup> Na — <sup>O(3)</sup> F — <sup>A(m)</sup> Na	(4)	<sup>M(4)</sup> Ca — <sup>O(3)</sup> F — <sup>A(m)</sup> Na
(2)	<sup>M(4)</sup> Ca — <sup>O(3)</sup> OH — <sup>A(2)</sup> Na	(5)	<sup>M(4)</sup> Ca — <sup>O(3)</sup> F — <sup>A(2)</sup> Na
(3)	<sup>M(4)</sup> Na — <sup>O(3)</sup> OH — <sup>A(m)</sup> Na		

\* summarized from Hawthorne *et al.* (1996a).

Arrangements (1) and (3) involve (Na + K) at the A(*m*) site and Na at the M(4) site, and hence require that the amounts of these components be equal in these amphiboles; inspection of Figure 2 shows that this is the case. Inspection of Table 8 shows that arrangement (1) involves F at O(3), whereas arrangement (3) involves (OH) at O(3). The variation of F as a function of A(Na + K) is shown in Figure 3. There is a well-developed linear variation. However, if all SRO involved arrangement (1), the slope of the line in Figure 3 would be 2 (broken line in Fig. 3). This is not the case; the slope is less than 2 and hence some A(Na + K) and M(4)Na must also be locally involved with O(3)OH, *i.e.*, arrangement (3).

As these arrangements involve all (Na + K) at the A(*m*) site and Na at the M(4) site, the remaining arrangement(s) must involve <sup>M(4)</sup>Ca — <sup>O(3)</sup>(OH,F) — A□. Hawthorne (1997) examined the issue of SRO in amphiboles from a bond-valence perspective and emphasized the importance of defining a FBB (fundamental building block) for patterns of SRO. This FBB involves all symmetrically distinct sites in the structure, and thus the arrangements <sup>M(4)</sup>Na — <sup>O(3)</sup>(F,OH) — A(Na + K) and <sup>M(4)</sup>Ca —

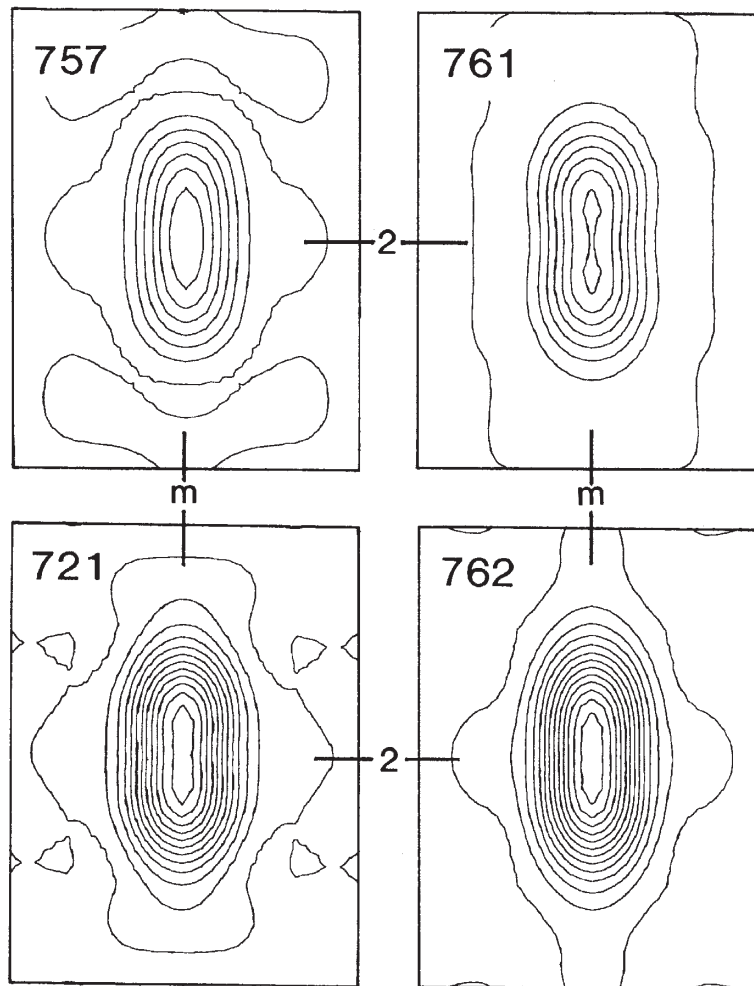


FIG. 1. Difference-Fourier maps through the  $A(2/m)$  site, parallel to  $(\bar{2}01)$  for the amphiboles of this work; the width of each map is  $2.8 \text{ \AA}$ , all maps were calculated with the  $Y$  axis horizontal (and the mirror plane vertical), with a contour interval of  $1 e/\text{\AA}^3$ , and with the  $A$  cations removed from the structural model.

$\text{O}^{(3)}(\text{OH},\text{F})-^A\Box$  dictate the composition of the rest of the crystal. The arrangements  $^{\text{M}(4)}\text{Na}-\text{O}^{(3)}(\text{F},\text{OH})-^A(\text{Na} + \text{K})$  can involve SRO patterns resembling richterite and katophorite, and the arrangement  $^{\text{M}(4)}\text{Ca}-\text{O}^{(3)}(\text{OH},\text{F})-^A\Box$  can involve SRO patterns resembling tremolite, hornblende and tschermakite. We can identify which patterns are present from the other components in the crystal. Crystal 757 consists of  $0.37 \text{ }^{\text{M}(4)}\text{Na}-\text{O}^{(3)}(\text{F},\text{OH})-^A(\text{Na} + \text{K})$  and  $0.63 \text{ }^{\text{M}(4)}\text{Ca}-\text{O}^{(3)}(\text{OH},\text{F})-^A\Box$ . There is no  $^{\text{TAl}}$  in this crystal, and hence the local arrangements must be of the tremolite type and the richterite type (*i.e.*, arrangements not involving  $^{\text{TAl}}$ ). The other  $^{\text{M}(4)}\text{Na}-\text{O}^{(3)}(\text{F},\text{OH})-^A(\text{Na} + \text{K})$  arrangement thus involves  $^{\text{MAl}}$

and  $^{\text{TAl}}$  (*i.e.*, it is the katophorite type). The amounts of these arrangements in each crystal are given in Table 9. Note that without the information as to the ordering of the  $A$ -site cations, these patterns of SRO could not have been identified, as many other arrangements would have been possible with occupancy of the  $A(2)$  site [in addition to the  $A(m)$  site].

The occurrence of SRO arrangements in amphiboles suggests that the variation in amphibole compositions in petrological processes is much more affected by crystal-chemical constraints than has hitherto been apparent. The striking variability in the SRO arrangements and bulk composition among the three amphibole crystals

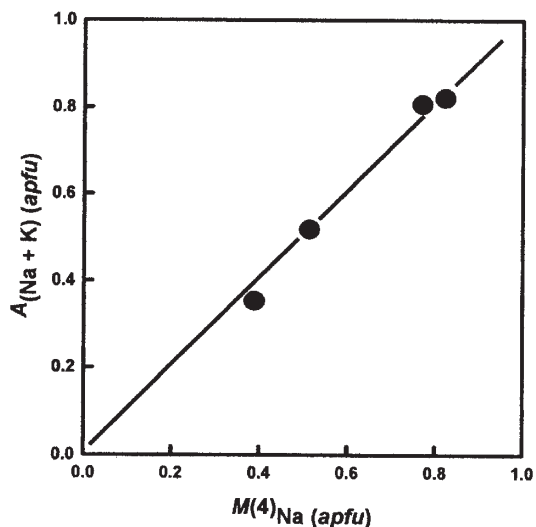


FIG. 2. The variation in  $A(\text{Na} + \text{K})$  as a function of  $M(4)\text{Na}$  in the Bear Lake amphibole crystals; the line indicates a 1:1 relation.

taken from the carbonate dikes (*i.e.*, BL8, BL10 and BL11), each homogeneous and sampled within a few meters of the other, provides important constraints on the origin of these crystals. These ramifications will be explored in a separate article on this poorly documented locality.

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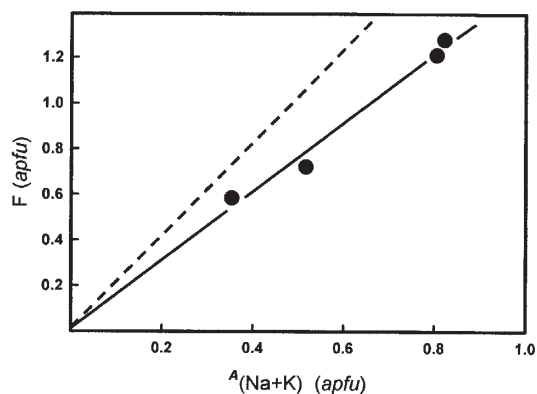


FIG. 3. The variation in F as a function of  $A(\text{Na} + \text{K})$  in the Bear Lake amphibole crystals; the black line is drawn as an aid to the eye, and the broken line indicates a 2:1 relation.

TABLE 9. PROPORTION OF SRO ARRANGEMENTS IN THE BEAR LAKE AMPHIBOLES

	757	761	721	762
Richterite	0.37	0.43	0.16	0.18
Tremolite	0.63	0.48	0.21	0.18
Katophorite	0.00	0.09	0.63	0.64

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