Highly aluminous hornblendes: compositions and occurrences from southwestern Massachusetts

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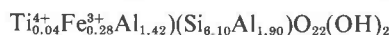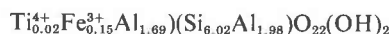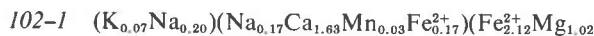*Burlington, Vermont 05401*

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Abstract

. Highly aluminous hornblendes were found in two metamorphosed rocks of the Walloomsac Formation, southwestern Massachusetts. Specimen 102–1 is a hornblende–almandine–biotite–chlorite–quartz gneiss in the upper part of the almandine zone. Specimen 289–2, near the base of the formation, is a hornblende–almandine–biotite–plagioclase–quartz schist in the staurolite zone. Microprobe analyses of the most aluminous hornblendes (assuming intermediate Fe^{3+} values; see text for details) give half-unit cell contents (23 oxygens) as:

$102-1$ $(K_{0.07}Na_{0.20})(Na_{0.17}Ca_{1.63}Mn_{0.03}Fe^{2+}_{0.17})(Fe^{2+}_{2.12}Mg_{1.02}$

$Ti^{4+}_{0.02}Fe^{3+}_{0.15}Al_{1.69})(Si_{6.02}Al_{1.98})O_{22}(OH)_2$

$289-2$ $(K_{0.11}Na_{0.15})(Na_{0.13}Ca_{1.79}Mn_{0.04}Fe^{2+}_{0.04})(Fe^{2+}_{1.87}Mg_{1.39}$

$Ti^{4+}_{0.04}Fe^{3+}_{0.28}Al_{1.42})(Si_{6.10}Al_{1.90})O_{22}(OH)_2$

A re-evaluation of Al^{IV} *vs.* Al^{VI} occupancy of calcic and subcalcic amphiboles of the literature recalculated to 23(O) suggests that several analyses from specimen 102–1 are more tschermakitic than any amphiboles previously reported regardless of the Fe_2O_3 approximation used. A standard Al^{VI} *vs.* Al^{IV} plot (such as that described by Leake in 1971) is unsatisfactory because it fails to distinguish the Al^{VI} content due to glaucophane-type [$Na(M4)$,$Al^{VI} \rightarrow$ Ca,Mg] substitutions and the Al^{IV} content due to edenite-type substitutions [$Na(A)$,$Al^{IV} \rightarrow$ □,Si].

On an $[Al^{VI} - Na(M4)]$ *vs.* $[Al^{IV} + Na(M4)]$ plot, the alkali-rich end-members of hornblende are shifted away from tschermakite. Such a plot clearly shows the unusual composition of the southwestern Massachusetts amphiboles and of natural tschermakitic amphiboles in general. The approximate substitutional limitation $Al^{VI} - Na(M4) = 0.75[Al^{IV} + Na(M4)]$ changes slightly to $0.82[Al^{IV} + Na(M4)]$ when Fe^{3+}, Ti^{4+}, and Cr^{3+} are included with Al^{VI}, suggesting a very strongly defined limitation of maximum octahedral R^{3+} occupancy in calcic amphiboles.

Introduction

Amphibole having the composition of the tschermakite or ferrotschermakite endmember, $Ca_2[(Mg,Fe)_3Al_2](Al_2Si_6)O_{22}(OH)_2$, has not been found in nature. Leake (1965, 1971), after a painstaking analysis of the problem, suggests that in natural

calcic amphiboles, and perhaps subcalcic amphiboles as well, the content of Al^{VI} seldom exceeds a well-defined limit. This limit can be given by the relation $Al^{VI} = 0.6\ Al^{IV} + 0.25$. Several analyses of highly aluminous hornblende have been reported which, though closely approaching tschermakite, still are within the limits of maximum Al^{VI} determined by Leake. One such amphibole is from a kyanite–garnet–biotite–hornblende gneiss from the Lukmanier area, Switzerland (Frey, 1969). The mineral association suggests moderate to high pressure as well as highly aluminous rock composition. Frey presented a chemical analysis of the hornblende, which was partly reanalyzed by Leake (1971, Table 1, no. 6). Its composition based on 23(O) is:

$$(Na,K)_{0.23}(Na_{0.27}Ca_{1.66}Mn_{0.01}Fe^{2+}_{0.06})$$

$$(Fe^{2+}_{1.41}Mg_{1.83}Fe^{3+}_{0.35}Ti_{0.05}Al_{1.36})$$

$$(Si_{6.23}Al_{1.77})O_{22}(OH)_2.$$
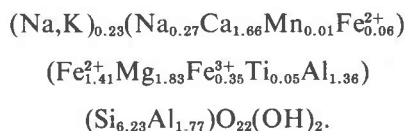
Two other analyses of Al-rich hornblende were reported by Bunch and Okrusch (1973); both are magnesium-rich, highly aluminous (20.0–22.6 weight percent Al_2O_3) amphiboles from corundum and spinel-bearing marbles. The structural formula of the more aluminous amphibole of Bunch and Okrusch, based on 24(O,OH,F), is $(Na,K)_{0.70}Ca_{1.99}(Mg_{3.35}Fe_{0.01}Ti_{0.16}Al^{VI}_{1.47})(Si_{5.74}Al_{2.26})(O,OH,F)_{24}$. On the basis of high A-site occupancy (0.69–0.83) and high Al^{IV} occupancy (2.25–2.26) calculated to 24(O,OH,F), Bunch and Okrusch termed these two amphiboles Al-pargasites.

Hawthorne and Grundy (1973) presented a structural refinement on a ferrotschermakite from the Frood Mine, Sudbury. The chemical formula is $(Na_{0.13}K_{0.14})(Na_{0.10}Ca_{1.86}Fe^{2+}_{0.04})(Mn_{0.02}Fe^{2+}_{2.06}Mg_{1.22}Ti_{0.10}Fe^{3+}_{0.30}Al_{1.30})(Si_{6.0}Al_{2.0})O_{22}(OH)_2$.

In the course of regional mapping in southwestern Massachusetts and adjacent Connecticut, Zen collected hornblende-bearing samples; two of these are reported here in detail. The hornblendes from these two rocks were analyzed by the electron microprobe, and both hornblendes are exceptionally rich in Al^{VI} when cast in terms of formula contents. In conventional projections, the hornblendes approach tschermakite more closely than even the hornblende described by Hawthorne and Grundy.

General geology and description of rocks

The two rock samples containing the high-aluminum hornblendes are from the Walloomsac Formation (Middle Ordovician) immediately underlying the

Table 1. Optical properties of amphibole from samples 102–1 and 289–2, southwestern Massachusetts

		Sample 102–1		Sample 289–2	
X*	=	1.658	light tan	1.659	light tan
Y	=	1.669	green	1.6665	brown green
Z	=	1.676	blue green	1.673	pale green
		Z = Y > X		Z = Y > X	
$2V_x$(calc.)	=	77°		86°	
Z∧C	=	7.4±1°		14.3±1°	
Z'∧C(max.)[+]	=	10.2±1°		15.6±1°	
a[△]	=	9.746 Å		9.802 Å	
b	=	18.06 Å		18.05 Å	
c	=	5.334 Å		5.323 Å	
V	=	907.7 Å³		910.2 Å³	
β	=	104°48'		104°53'	
Space group		$\underline{C}$ 2/m		$\underline{C}$ 2/m	

*X, Y, Z, Z∧C measurements determined on single grains mounted on spindle stage using sodium illumination; index measurements to ±0.001.

[+]Maximum extinction angle lies in prism zone between [100] and [010].

[△]Unit cell data provided by Malcolm Ross (U.S.G.S.) from X-ray precession single crystal photographs. Approx. error ± 0.2%; no exsolution or twinning observed.

Taconic allochthon (Zen and Hartshorn, 1966) in the Bashbish Falls quadrangle in southwestern Massachusetts (Fig. 1). The metamorphic event was probably Acadian (Zen and Hartshorn, 1966; M. A. Lanphere and Zen, unpublished data). The progressive regional metamorphism in this area will be reported elsewhere by Zen.

Sample 102–1 (Fig. 1) is a garnet–hornblende rock showing a faintly gneissic fabric. The rock is medium-grained, having grains as much as 5 mm across. The outcrop is on the Appalachian Trail; it is about 2 meters wide and several meters long, but could not be traced laterally. It is intercalated in more typical Walloomsac schist locally containing the chlorite–chloritoid–almandine–biotite–plagioclase–muscovite–ilmenite–quartz assemblage (samples 103–1 and 103–2, to be referred to again later), near the boundary of the staurolite zone. Sample 102–1 contains the assemblage almandine–hornblende–chlorite–biotite–muscovite–quartz–plagioclase–magnetite–apatite. The garnet has a prominent sieve texture with quartz inclusions but is not visibly zoned. The pleochroic hornblende (Table 1) is as much as 2 mm across, and also shows sieve texture but is not visibly zoned. Biotite occurs as 0.1 mm euhedral grains and
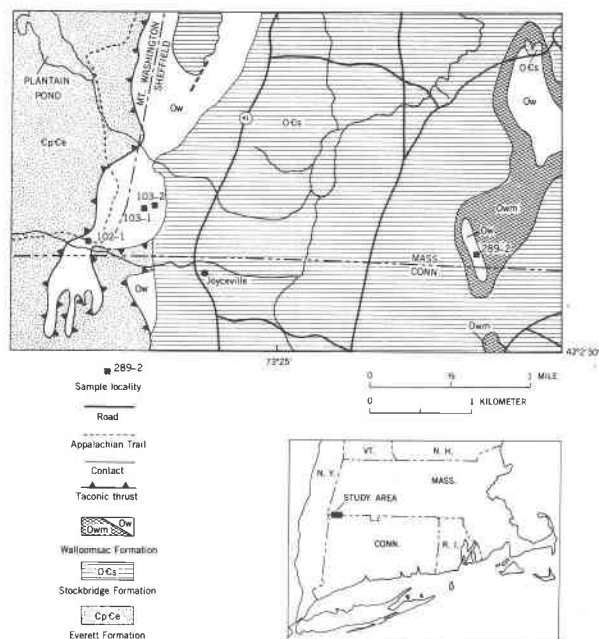
Fig. 1. Map showing generalized geology of a part of the Bashbish Falls quadrangle in southwestern Massachusetts and sample localities (after Zen and Hartshorn, 1966).

is pleochroic yellow to brown. The chlorite is very pale green and as much as 0.5 mm across, showing euhedral or ragged outlines. Plagioclase is rare and shows occasional albite twinning. Quartz has polygonal outlines, suggesting textural equilibrium. Euhedral large (as much as 0.5 mm) apatite grains are scattered through the rock. Muscovite is very rare and is in small euhedral grains.

Sample 289–2 (Fig. 1) is a grey, medium-grained calcareous schist from near the base of the Walloomsac Formation (Zen and Hartshorn, 1966). The adjacent noncalcareous schists contain the assemblage staurolite–almandine–biotite–chlorite–muscovite–quartz–plagioclase, and the distribution of assemblages and isograds show the metamorphic grade of the rock to be considerably higher than that of sample 102-1. Sample 289–2 contains, in addition to hornblende, biotite, almandine, plagioclase (An ∼ 90), magnetite, and quartz (Zen, unpublished data). Neither muscovite nor chlorite was observed. Hornblende and garnet both show strong sieve texture and rudimentary crystal faces, and are about 1 mm across. Brown biotite is found in books and in irregular plates. Plagioclase grains are 1–2 mm across, mainly showing rounded outlines, and are zoned but show little twinning; a few grains are irregular and show polysynthetic albite twins. Quartz is about 0.2 mm across and is polygonal. Rare, euhedral magnet-

ite is scattered in the rock. All the minerals except quartz and magnetite show abundant inclusions of carbonaceous dust trains defining a pre-existing foliation surface which is locally isoclinally folded on a microscopic scale. Dust also tends to accumulate along grain boundaries. The inclusion trains are not disrupted across grain contacts, suggesting that the main phase of recrystallization took place in a static condition.

Unit-cell dimensions of the hornblende from the two samples, kindly measured by Malcolm Ross, are given in Table 1.

Analytical procedures and results

Mineral analyses were obtained by means of an automated, four-spectrometer, ARL-EMX SM electron microprobe at SUNY Stony Brook. Data reduction procedures are those of Bence and Albee (1968) with a modified version of the a-matrix of Albee and Ray (1970).

Analytical points were selected on grains from different areas in the thin section to establish intergrain and intragrain compositional variations. Data were obtained for Si, Al, Ti, Fe, Mn, Mg, Ca, Na, K, and Cr. Analyses were not made for Li and the trace elements, but these data are being gathered. The amount of H_2O in hydrous phases was determined by difference (Bence and Albee, 1968). Although the H_2O analyses and the inability of the electron microprobe to measure proportions of Fe^{2+} and Fe^{3+} in the hornblendes pose serious problems, meaningful calculations of mineral compositions can still be made.

Mineral chemistry

Analyses were made of biotite, hornblende, and garnet in sample 289-2, and of chlorite as well in sample 102-1. In addition, we obtained electron microprobe data on all the Fe–Mg-bearing minerals of two samples, 103-1 and 103-2, which are pelitic rocks of the Walloomsac Formation found near specimen 102-1 (Fig. 1); these samples contain the assemblage chloritoid–chlorite–biotite–garnet and provide useful comparisons with the minerals of the hornblende-bearing assemblages (Fig. 2A).

All the garnets contain sufficient calcium (mainly in the grossular component) to plot significantly away from the AFM face of the ACFM diagrams; the Ca/(Ca+Fe+Mg+Mn) is about 0.20 to 0.25 for garnets from the hornblende-bearing rocks. On the AFM projection, garnets from the hornblende-bearing rocks show little scatter, and the observed scatter does not affect the main groupings of garnets in each
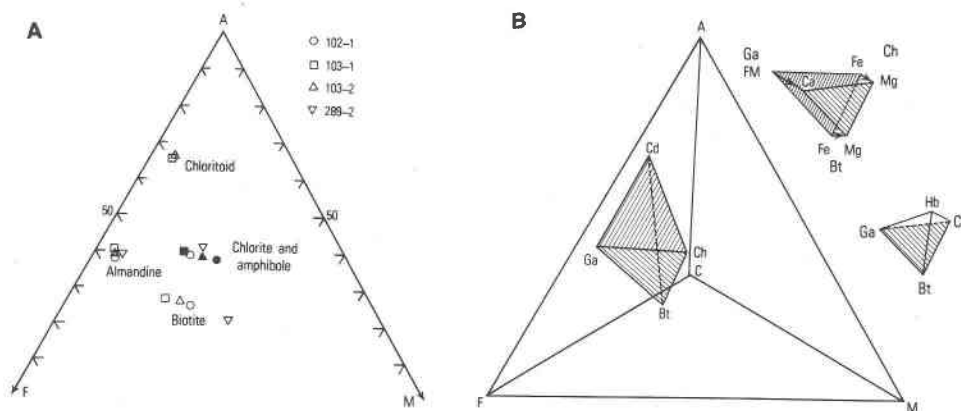
Fig. 2. (A) Summary AFM projection for mineral compositions from specimens 102–1, 103–1, 103–2, and 289–2. Solid symbols in the chlorite and amphibole region refer to chlorite; open symbols in this area refer to hornblende. $A = Al - 2Ca/3 - K - Na$; $F = Fe$ (total); $M = Mg$ (all in atomic proportions). (B) ACFM projection. Chloritoid (Cd), biotite (Bt) and chlorite (Ch) are located on the AFM base, but garnet (Ga) is part way toward the C apex. The two upper faces of the Ch–Bt–Cd–Ga tetrahedron are Ga–Cd–Ch and Ga–Bt–Ch. The latter assemblage is compatible with hornblende (Hb), but in passing from Cd-coexistence to Hb-coexistence, Bt and Ch increase in Mg/Fe ratio at the same time Ga becomes more calcic, so the Ga–Bt-Ch 3-phase assemblage is a prism in the tetrahedron (insets).

rock or the comparison of major differences between rocks.

In 103-1 and 103-2 only garnet and plagioclase contain significant amounts of Ca. Biotite, chlorite, and chloritoid all lie on the AFM base of the ACFM tetrahedron. Sample 102-1 has two phases (in addition to plagioclase) containing significant Ca: garnet and hornblende. Biotite and chlorite are common with 103-1 and 103-2. As the tetrahedron defined by the four phases of 102-1 has a bounding face whose mineralogy is common with a bounding face of the tetrahedron of 103-1 and 103-2, it must lie in the more Ca-rich direction. This, plus the fact that garnet has a higher Fe/Mg ratio than all the other phases, implies that Fe/Mg ratios of biotite and chlorite in the hornblendic assemblage are less than that in the chloritoid-bearing assemblage (Fig. 2B).

Thus, because garnet, chlorite, and biotite all change in composition systematically within the 3-phase assemblage (garnet becoming more calcic as biotite and chlorite become more magnesian), in the ACFM diagram the 3-phase assemblage garnet–chlorite–biotite occupies a triangular prism rather than a simple triangle (Fig. 2B). Indeed, the assemblage garnet–chlorite–biotite, without either hornblende or chloritoid, is quite common in the area, and the mineral chemistry provides an explanation of this fact.

The assemblage of 289-2 contains hornblende, biotite, and garnet but is without chlorite. Minerals from this rock, therefore, may be expected to be more magnesian than the corresponding minerals in 102-1. Comparison of mineral analyses of the two rocks

(Fig. 2A) shows a slight shift in the hornblende and garnet compositions in this direction, and a very large shift in the biotite composition—from a Fe/Mg atomic ratio of about 1.5 to about 0.9. Rock 289-2 is metamorphosed to slightly higher grade than 102-1, however, so the compositional shift may reflect the effect of both grade and different bulk compositions.

Chemistry of the hornblendes

Selected analyses for hornblende in samples 102-1 and 289-2 are reported in Table 2; the complete data are available in microfiche form[1]. Possible minimum and maximum values of Fe_2O_3 have been initially approximated for these hornblendes using the two stoichiometric constraints suggested by Stout (1972, see also Papike *et al.*, 1974): (1) restriction of Ca to the $M4$ site; and (2) restriction of K to the A site. Fe_2O_3/FeO variation has a large effect on the calculated cation-to-oxygen ratio in the resulting structural formula (Robinson *et al.*, 1971); a maximum-Fe_2O_3 estimation reduces either (Mg,Fe,Mn) ($M4$) occupancy to 0.0 or Na(A) occupancy to 0.0. Further increases in Fe_2O_3 would require violating one or both of the constraints of Stout (1972). Minimum Fe_2O_3 values are approximated either at $Fe_2O_3 = 0.0$ if no Ca enters the A site or at higher values of Fe_2O_3 if all Na is confined to the A site [no Na($M4$) occupancy].

Table 2. (A) Selected chemical analyses of aluminous amphiboles from southwestern Massachusetts. Total Fe is calculated as FeO (total). Anhydrous structural formulae are based on 23(O). (B) Structural formulae assuming maximum Fe_2O_3 allowed by stoichiometry. (C) Structural formulae assuming minimum allowable Fe_2O_3 (see text). (The full table is available in microfiche form.)

	102–1			289–2	
	Area 3A	Area 3B	Area 2	Area 1	
Sample	3–1	3–8	2–1	1–1	1–5
			A		
SiO_2	39.61	40.78	42.34	39.74	41.30
Al_2O_3	20.46	19.23	16.31	18.33	19.10
TiO_2	.19	.21	.26	.39	.33
FeO	19.29	18.76	18.11	17.00	17.73
MgO	4.50	4.64	7.53	7.36	6.29
MnO	.23	.24	.17	.34	.34
CaO	9.98	11.23	11.00	10.93	11.35
Na_2O	1.28	1.08	1.14	1.18	.95
K_2O	.35	.36	.31	.45	.59
TOTAL	95.89	96.53	97.17	95.72	97.98
			B		
T_{Si}	6.002	6.135	6.235	5.956	6.062
Al	1.998	1.865	1.765	2.044	1.938
$M(1-3)$					
Al	1.656	1.544	1.066	1.194	1.366
Fe^{3+}	.297	.272	.788	.723	.553
Ti	.022	.024	.029	.044	.036
Fe^{2+}	2.009	2.088	1.443	1.395	1.624
Mn	.000	.031	.021	.000	.042
Mg	1.016	1.040	1.653	1.644	1.376
$M4$					
Fe^{2+}	.129	.000	.000	.007	.000
Mn	.030	.000	.000	.043	.000
Ca	1.620	1.809	1.735	1.755	1.783
Na	.221	.191	.265	.195	.217
A_{Na}	.155	.124	.061	.148	.053
K	.068	.069	.058	.086	.110
			C		
T_{Si}	6.039	6.171	6.344	6.031	6.136
Al	1.961	1.829	1.656	1.969	1.864
$M(1-3)$					
Al	1.715	1.601	1.224	1.310	1.480
Fe^{3+}	.000	.000	.000	.137[a]	.000
Ti	.022	.024	.029	.045	.037
Fe^{2+}	2.241	2.329	2.065	1.843	2.090
Mn	.000	.000	.000	.000	.000
Mg	1.023	1.047	1.682	1.665	1.393
$M4$					
Fe^{2+}	.218	.045	.204	.178	.113
Mn	.030	.031	.022	.044	.043
Ca	1.630	1.821	1.766	1.777	1.807
Na	.122	.103	.008	.001	.036
A_{Ca}	.000	.000	.000	.000	.000
Na	.257	.214	.323	.346	.236
K	.068	.069	.059	.087	.112

[a] Fe^{3+} value based on Fe_2O_3 minimum value = 1.2%.

A third constraint is required to estimate the maximum Fe_2O_3 value for eight of the eighteen analyses presented in Table 2A. If only the two constraints discussed above are applied, analyses 3-1, 3-2, 3-3, 3-4, 3-7, 2-2, 1-1, 1-2 of Table 2B would have the sums $Al^{VI} + Fe^{3+} + 2Ti^{4+}$ ($= y^*$) greater than 2.0 for structural formulae calculated for Fe_2O_3 maximum values[2]. An evaluation of 840 calcic and subcalcic amphibole analyses from the literature, considered to be good analyses on stoichiometric grounds, resulted in only 24 having y^* values greater than 2.0, and these are largely kaersutites (Doolan, 1975). On this basis, we have decided to set a maximum value for y^* in calcic and subcalcic amphiboles at 2.0 (with the possible exception of kaersutites). In practice, this third constraint supersedes constraint (2) above for the eighteen formulae of Table 2B, because all maximum Fe_2O_3 structural formulae have some Na in the A site.

Structural formulae based on calculated Fe_2O_3 maximum values are presented in Table 2B; those based on Fe_2O_3 minimum values are presented in Table 2C. Intermediate values of Fe_2O_3, which are the means of maximum and minimum values, as well as other critical parameters of the structural formula [A site, Na($M4$), y^*, Al^{IV}, Al^{VI}, Mg, Fe^{2+}, $Fe^{3+}/(Fe^{2+} + Fe^{3+})$, $Fe^{2+}/(Fe^{2+} + Mg)$] are presented in Table 3.

The analyses are arranged in Tables 2 and 3 according to data taken from the same grain in a given thin section. The prefix numbers, 2 and 3, for rock 102-1 refer to separate grains. All analyses reported for sample 289-2 are from the same grain.

The data of Tables 2 and 3 show significant inter- and intragrain compositional variation. In particular, Al/Si, $Fe^{2+}/(Fe^{2+} + Mg)$, and the amounts of "FeO" and MgO are highly variable. Less pronounced but statistically significant variations are noted for CaO and TiO_2. Variations in the concentrations of Na_2O, K_2O, and MnO are not statistically significant. There is no obvious correlation of the chemical analysis of individual points with location of the point within the grain.

Hornblende from 289-2 is similar to that in 102-1

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[2] Octahedral Ti^{4+} substitution for R^{2+} requires twice as much compensation as octahedral R^{3+} substitutions. Robinson *et al.* (1971) defined y to represent the total "R^{3+}" compensation in octahedral sites, $y =$ octahedral $Al^{VI} + Fe^{3+} + Cr^{3+} + 2Ti^{4+}$. We refer to this quantity as y^* and reserve the term y for R^{3+} substitutions only, so that *in our notation* $y =$ octahedral $Al^{VI} + Fe^{3+} + Cr^{3+}$ (see Fig. 4) and $y^* = y + 2Ti^{4+}$. We prefer these notations because they serve to distinguish the roles of R^{3+} and R^{4+} substitutions in the general calcic and sodic amphibole formula. Detailed discussion of this and related matters will be the topic of a separate note.

Table 3. Summary of critical variables of the amphibole structural formulae for analyses of full Table 2(A), assuming intermediate values of Fe_2O_3. Formulae based on 23(O)

Sample	Anal.	A-site	Na($\underline{M4}$)	$\underline{y}*$ [b]	Al^{IV}	Al^{VI}	Fe^{2+}	Fe^{3+}	Mg	fe^{2+} [c]	fe^{3+} [d]	Fe_2O_3 [e]
	3-1	0.274	0.172	1.877	1.980	1.686	2.299	0.149	1.020	0.693	0.061	1.30
	3-2	0.294	0.127	1.812	1.978	1.527	2.132	0.235	1.198	0.640	0.099	2.10
	3-3	0.325	0.120	1.811	2.014	1.544	2.164	0.231	1.104	0.662	0.096	2.05
	3-4	0.312	0.119	1.795	1.987	1.472	2.169	0.266	1.179	0.648	0.109	2.35
102-1	3-5	0.356	0.092	1.576	1.839	1.257	2.128	0.258	1.367	0.609	0.108	2.30
	3-6	0.347	0.068	1.596	1.875	1.286	2.155	0.256	1.306	0.623	0.106	2.25(1.75)
	3-7	0.271	0.150	1.825	1.947	1.556	2.328	0.226	1.013	0.697	0.088	2.00
	3-8	0.238	0.147	1.756	1.847	1.573	2.231	0.136	1.043	0.681	0.057	1.20
	3-9	0.243	0.189	1.766	1.821	1.524	2.180	0.197	1.088	0.667	0.083	1.75
	3-10	0.195	0.236	1.772	1.731	1.453	2.113	0.273	1.189	0.640	0.114	2.45
	2-1	0.251	0.137	1.597	1.711	1.145	1.856	0.394	1.668	0.527	0.175	3.55
	2-2	0.239	0.183	1.645	1.701	1.124	1.748	0.451	1.795	0.493	0.205	4.01
	1-1	0.334	0.098	1.771	2.007	1.252	1.712	0.430	1.655	0.508	0.201	3.80(2.60)
	1-1'	0.334	0.103	1.635	1.866	1.323	1.881	0.231	1.547	0.549	0.109	2.10
289-2	1-2	0.299	0.131	1.734	1.899	1.275	1.794	0.337	1.592	0.530	0.158	3.02
	1-3	0.283	0.158	1.559	1.684	1.169	1.808	0.294	1.753	0.508	0.140	2.65
	1-4	0.271	0.142	1.730	1.858	1.372	1.914	0.278	1.418	0.574	0.127	2.50
	1-5	0.256	0.128	1.773	1.901	1.423	1.913	0.277	1.384	0.580	0.126	2.50

[a] $Structural\ formula\ designations\ based\ on\ 23(O)$.

[b] $y* = (Al^{VI} + Fe^{3+} + 2Ti^{4+})$

[c] $fe^{2+} = Fe^{2+}/(Fe^{2+} + Mg)$

[d] $fe^{3+} = Fe^{3+}/(Fe^{2+} + Fe^{3+})$

[e] Fe_2O_3 is in weight percent. Uncertainty is equal to intermediate values shown except where otherwise shown in brackets.
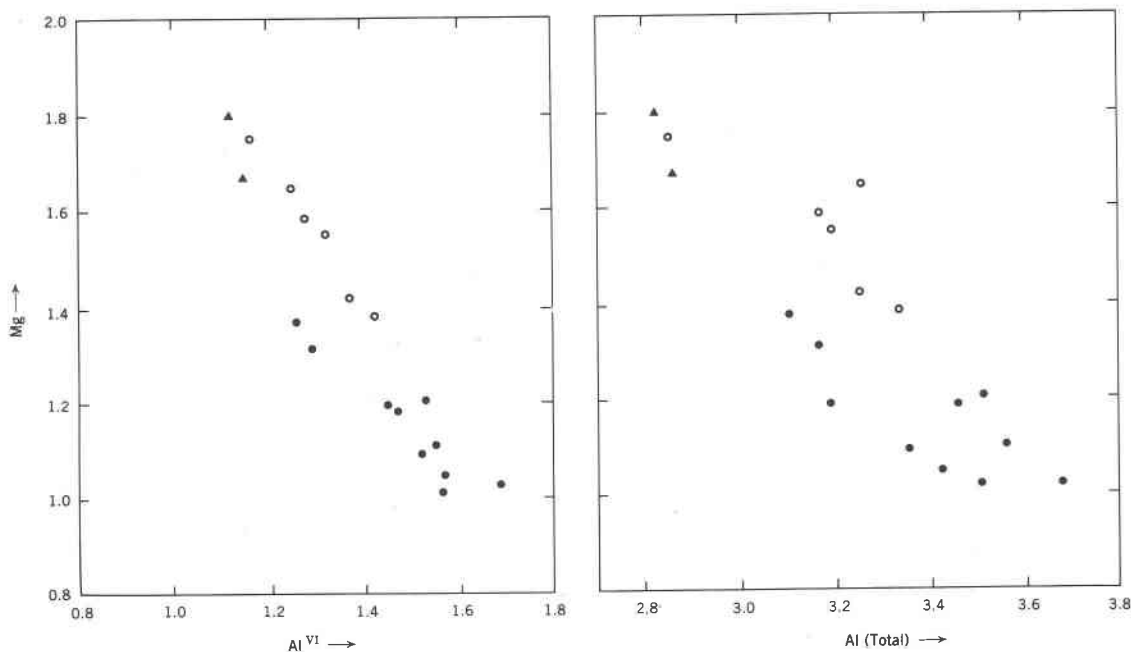
Fig. 3. Atomic Mg *vs.* Al and atomic Mg *vs.* Al^{VI} based on intermediate values of Fe_2O_3 for analyses listed in Table 2 and structural formula data listed in Table 3. Closed triangles refer to specimen 102–1, area 2; closed circles refer to specimen 102–1, area 3; and open circles refer to specimen 289–2.

		SUBST.	A	M(4)	M(1-3)	T	x	w	y	z
CALCIC AMPHIBOLES	Tremolite (Tr)	——		Ca$_2$	Mg$_5$	Si$_8$	0	0	0	0
	Edenite (Ed)	(1)	Na	Ca$_2$	Mg$_5$	Si$_7$Al	1	0	0	1
	Common Hornblende (C.H.)	(2)		Ca$_2$	Mg$_4$Al	Si$_7$Al	0	0	1	1
	Tschermakite (Ts)	(2,2)		Ca$_2$	Mg$_3$Al$_2$	Si$_6$Al$_2$	0	0	2	2
	Pargasite (Pa)	(1,2)	Na	Ca$_2$	Mg$_4$Al	Si$_6$Al$_2$	1	0	1	2
	Al-Pargasite (Al-Pa)	(1,2,2)	Na	Ca$_2$	Mg$_3$Al$_2$	Si$_5$Al$_3$	1	0	2	3
SUBCALCIC AND SODIC AMPHIBOLES	Richterite (Ri)	(4)	Na	NaCa	Mg$_5$	Si$_8$	1	1	0	0
	Ekrite (Ek)	(3)		NaCa	Mg$_4$Al	Si$_8$	0	1	1	0
	Glaucophane (Gl)	(3,3)		Na$_2$	Mg$_3$Al$_2$	Si$_8$	0	2	2	0
	Barroisite (Ba)	(2,3)		NaCa	Mg$_3$Al$_2$	Si$_7$Al	0	1	2	1
	Mboziite (Mb)	(1,2,3)	Na	CaNa	Mg$_3$Al$_2$	Si$_6$Al$_2$	1	1	2	2
	Eckermanite (Ec)	(3,4)	Na	Na$_2$	Mg$_4$Al	Si$_8$	1	2	1	0
	Kataphorite (Ka)	(1,3)	Na	CaNa	Mg$_4$Al	Si$_7$Al	1	1	1	1
	? (?)	(1,3,3)	Na	Na$_2$	Mg$_3$Al$_2$	Si$_7$Al	1	2	2	1

END-MEMBER COMPOSITIONS OF CALCIC AND SODIC AMPHIBOLES

$$(Na_x) \quad (Ca_{2-w}, Na_w) \quad (Mg_{5-y} R^{3+}_y) \quad (Si_{8-z}, Al_z) \quad O_{22}(OH)_2$$

| A | M(4) | M(I)–M(3) | T |

Fig. 4. End-member compositions of calcic and sodic amphiboles derived through appropriate substitutions of: (1) edenite [Na(A), $Al^{IV} \rightarrow \square$, Si]; (2) common hornblende ($Al^{IV}, Al^{VI} \rightarrow$ Mg, Si); (3) ekrite [(Na($M4$), $Al^{VI} \rightarrow$ Ca, Mg]; and (4) richterite [Na(A), Na($M4$) $\rightarrow \square$, Ca($M4$)] into ideal tremolite. In the generalized structural formula shown, x = total A-site occupancy, w = Na($M4$), y = Al^{VI} + Fe^{3+} + Cr^{3+}, z = Al^{IV}. Mg could be other divalent cations, and A-site Na could be potassium. To maintain charge balance, $x + y = z + w$. The effect of Ti substitution in $M(1-3)$ sites is discussed in the text; for these amphiboles the charge-balance equation becomes $x + y + 2Ti = w + z$. Nomenclature after Robinson *et al.* (1971) with the addition of Al-pargasite (Bunch and Okrusch, 1973) and mboziite (Brock *et al.*, 1964).

but appears more homogeneous; compared with 102-1, the analyzed points (Tables 2, 3) tend to have greater magnesium content for a given content of aluminum (Fig. 3). For both samples, Fe^{2+} increases as Al content increases.

Graphical representation of tschermakitic hornblende

The hypothetical tschermakite, $Ca_2(Mg_3Al_2)$ $(Al_2Si_6)O_{22}(OH)_2$, according to the idealized structural formula given in Figure 4, has the following characteristics: A site (x) = 0, Na($M4$)(w) = 0, Al^{VI} (y) = 2, $Al^{IV}(z)$ = 2. Among all end-member compositions of calcic and sodic amphiboles (Fig. 4), it is the only one that contains 2 Al^{VI} atoms with no A-site or Na($M4$) occupancy. In a graphical analysis of the tschermakitic content of hornblende, it is important to plot tschermakite in such a way as to show these characteristics.

The conventional plot for tschermakitic amphiboles is to show Al^{IV} *vs.* Al^{VI} (Fig. 5A). This figure, modified from Leake (1965, 1971), plots approximately 840 analyses selected from the literature according to the stoichiometric criteria for good analyses as outlined by Doolan (1975), and is based on the anhydrous formula for 23(O)[3]. End-member compositions, as explained in Figure 4, are also plotted. Leake's line of maximum Al^{VI} as a function of Al^{IV}, determined on the basis of approximately 1500 amphiboles calculated on the hydrous basis, is also plotted. Many of the analyses that are deficient in H_2O plot above the line when calculated on the hy-

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[3] We are aware of the implications of using the 23(O) procedure of calculation, but it seems to be the only method that is applicable for comparing all published data on natural amphiboles (see, for example, Robinson *et al.*, 1971).
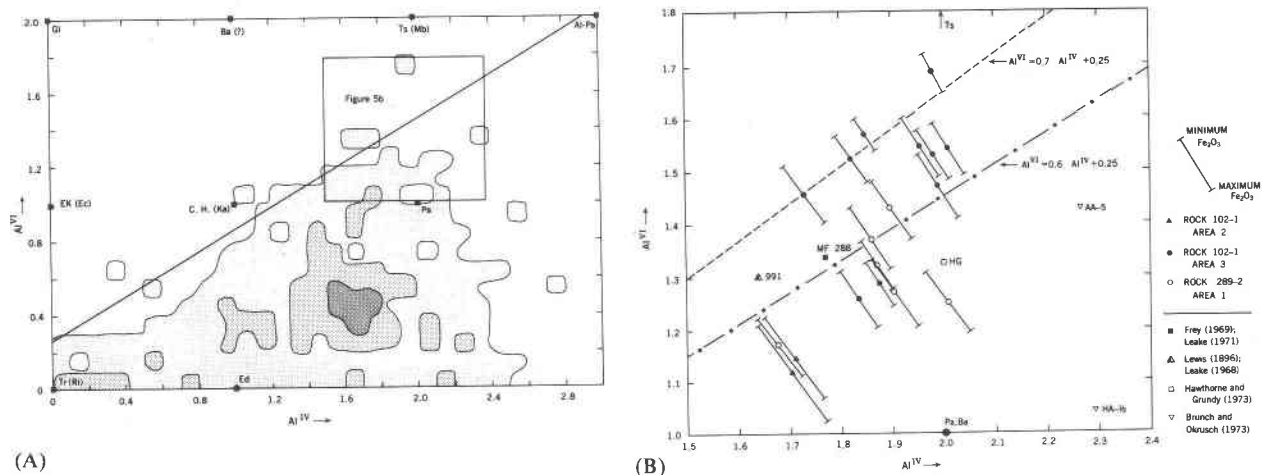
(A)

(B)

Fig. 5. (A) Al^{IV} *vs.* Al^{VI} for approximately 840 selected analyses from the literature screened through the criteria outlined by Doolan (1975). The data are calculated on the basis of 23(O) and contoured on the basis of a 0.17 percent counting square using 0.7, 4, 9 percent contour intervals. The limiting Al^{VI} *vs.* Al^{IV} line of Leake (1965, 1971) is represented by the solid line. For abbreviations, see Fig. 4. (B) Al^{IV} *vs.* Al^{VI} for tschermakitic hornblendes from southwestern Massachusetts determined on the basis of intermediate values of Fe_2O_3 (Table 3), and other highly aluminous hornblendes reported in the literature: Numbers 991 (Lewis, 1896, in Leake, 1968, 1971); MF288 (Leake, 1971); AA-5, HA-1/2 (Bunch and Okrusch, 1973); and HG (Hawthorne and Grundy, 1973). Error bars refer to uncertainty of Fe_2O_3 approximation (see text, and Stout, 1972). The dash-dot line refers to limiting line of Leake (1965, 1971; $Al^{VI} = 0.6$ $Al^{IV} + 0.25$). Dashed line is suggested limiting line ($Al^{IV} = 0.7Al^{IV} + 0.25$).

drous basis but now plot below the line (*cf.* Fig. 1 of Leake, 1965). Several analyses having (OH + F + Cl) greater than 2 which plot below the line on the hydrous basis now plot above the line. Nevertheless, in general Leake's (1965) line of maximum Al^{VI} *vs.* Al^{IV} serves as the limiting value for Al^{VI} *vs.* Al^{IV} for calcic amphiboles recalculated on the anhydrous basis.

Figure 5B is a plot of Al^{IV} *vs.* Al^{VI} (Tables 2 and 3) for the tschermakitic hornblendes for southwestern Massachusetts. Also plotted are highly aluminous calcic amphiboles reported in the literature. Note that 10 of the 18 analyses of tschermakitic hornblendes from this study, plus MF288 and 991, plot above the line of Leake (1971) even if maximum Al^{IV} and minimum Al^{VI} values are plotted.

Although Figure 5 clearly shows the limits of Al^{VI} with respect to Al^{IV}, it fails to distinguish these limits for truly tschermakitic substitutions ($Al^{VI},Al^{IV} \rightarrow$ Mg,Si). Amphiboles that undergo glaucophane-type substitutions [Na($M4$),$Al^{VI} \rightarrow$ Ca, Mg] would tend to shift points above the limiting line of Figure 5, whereas amphiboles with edenite-type substitutions [Na(A),$Al^{IV} \rightarrow \square$, Si] would shift points below the line. Because amphiboles that plot near tschermakite in the Al^{IV} *vs.* Al^{VI} plot (*e.g.,* "mboziite") could have total (Na + K) values ranging from 0 to 2.0, care must be taken in plotting natural amphiboles containing significant (Na + K).

A better way to study the relation of Al^{VI} *vs.* Al^{IV}

occupancy due to tschermakite-type ($Al^{VI},Al^{IV} \rightarrow$ Mg,Si) substitutions is to remove the effect of glaucophane-type [Na($M4$),$Al^{VI} \rightarrow$ Ca,Mg] substitutions. Figure 6A is a plot of [$Al^{VI} -$ Na($M4$) *vs.* $Al^{IV} +$ Na($M4$)] for the analyses of Figure 5A. In this plot, edenite-type and glaucophane-type substitutions shift amphibole compositions in a direction parallel to the abscissa, whereas tschermakite-type substitution shifts compositions in a diagonal direction (slope of +1). This plot, therefore, results in the graphical separation of calcic, aluminous, low-alkali-bearing amphiboles (tschermakite) from edenite and glaucophane end members. The solid line is Leake's (1965) line of maximum Al^{VI} *vs.* Al^{IV} (Fig. 5A), and the dashed line approximates the upper limit of [$Al^{VI} -$ Na($M4$) *vs.* $Al^{IV} +$ Na($M4$)]. The equation of the dashed line is $Al^{VI} -$ Na($M4$) = 0.75[$Al^{IV} +$ Na($M4$)]. The data for amphiboles from southwestern Massachusetts and other aluminous hornblendes are shown in Figure 6B. All aluminous hornblendes now plot just below the line of Leake (1965) if intermediate values of Fe_2O_3 for southwestern Massachusetts amphiboles are used. The limiting line of $Al^{VI} -$ Na($M4$) defined by Figure 6A seems to better approximate the trend of substitution of the southwestern Massachusetts hornblendes; the trend of substitution lies just below minimum $Al^{IV} +$ Na($M4$) and maximum $Al^{VI} -$ Na($M4$) values (minimum Fe_2O_3) of six of the amphibole analyses reported here.
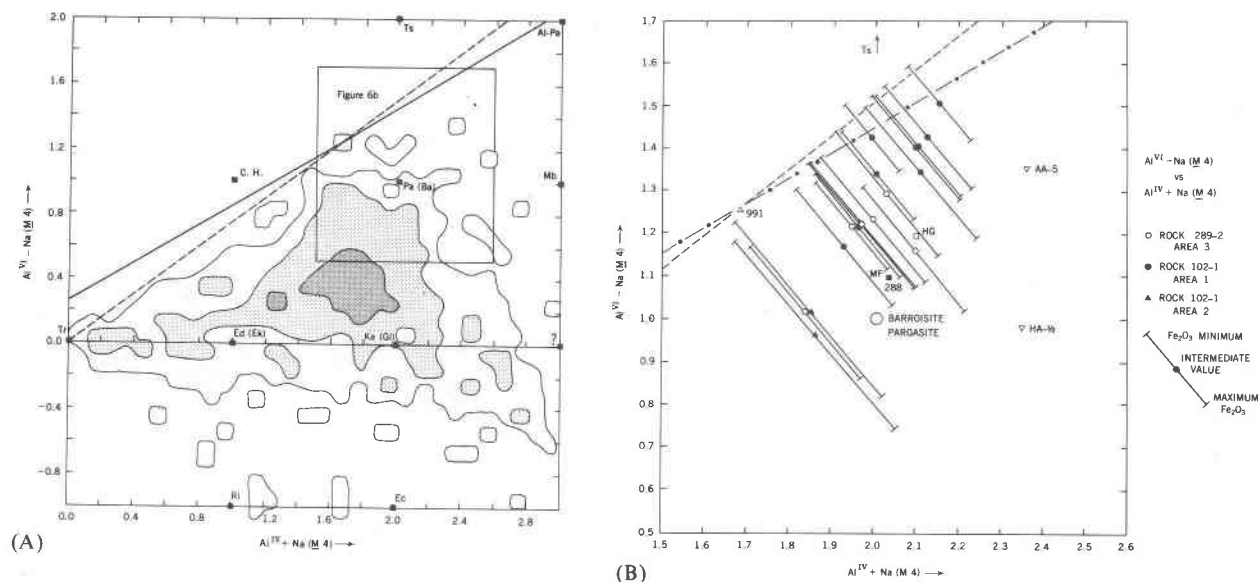
Fig. 6. (A) $Al^{IV} + Na(M4)$ vs. $Al^{VI} - Na(M4)$ for approximately 840 calcic and subcalcic amphibole analyses used in Fig. 5A. Note the shift of sodic and subcalcic end members away from tschermakitic compositions. Data are contoured on basis of 0.12 percent counting square using 1–3–8 percent contour intervals. Solid line from Leake (1965); dashed line is our preferred limit. For abbreviations, see Fig. 4. (B) $Al^{IV} + Na(M4)$ vs. $Al^{VI} - Na(M4)$ for tschermakitic hornblendes from southwestern Massachusetts. Minimum, maximum, and intermediate values of coordinates are plotted incorporating the effect of Fe_2O_3 variation on the occupancy designations of the structural formula (see text). Limiting lines of Leake (1965, 1971) and of 6(A) are represented by dash-dot and dashed lines respectively. Aluminous hornblendes from Leake (1971), MF-288; Bunch and Okrusch (1973), AA-5, HA-1/2; and Hawthorne and Grundy (1973), HG, are plotted for reference.

Defining tschermakites by charge-balance

Al^{VI} occupancy does not adequately define the octahedral substitution of $R^{3+} \rightarrow R^{2+}$ balanced by $Al^{IV} \rightarrow Si$ because Fe^{3+}, Cr^{3+}, and Ti^{4+} also can be in octahedral positions. The schemes of substitution of Ti^{4+} in amphibole are not well understood. The following coupled substitutions, analogous to those found in pyroxenes, are probably descriptive:

$$2Na(M4), Ti \rightarrow 2Ca(M4), Mg$$

$$Ti, 2Al^{IV} \rightarrow Mg, 2Si^4$$
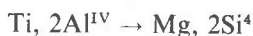
One effect of both schemes of substitution is that each Ti plays the role of two R^{3+} cations. Therefore, in the generalized forms of charge-balancing substitutions of the two schemes, namely $Na(M4),(Al^{VI},Fe^{3+},Cr^{3+}, Ti^{4+}) \rightarrow Ca,Mg$ and $(Al^{VI},Fe^{3+}, Cr^{3+},Ti^{4+}),Al^{IV} \rightarrow Mg,Si$, the total increase in charge in the $M(1-3)$ sites must be equal to $Al^{VI} + Fe^{3+} + Cr^{3+} + 2Ti^{4+}$. This is the quantity defined as y^* in this paper; it is a measure of total glaucophane-type and tschermakite-type substitutions in terms of charge balance. The quan-

tity $y^* - Na(M4)$ is a measure of tschermakite-type substitution alone.

In Figure 7A, the 840 analyses plotted in Figure 6A are replotted according to the charge-balance coordinates $y^* - Na(M4)$ vs. $Al^{IV} + Na(M4)$. The shift in points between these two plots reflects the amount of $y^* - Al^{VI}(= 2Ti^{4+} + Cr^{3+} + Fe^{3+})$ in these analyses. The contoured maximum at $1.7[Al^{IV} + Na(M4)]$, $0.3[Al^{VI} - Na(M4)]$ in Figure 6A is shifted upward by approximately 0.75 in Figure 7A. This amount corresponds to a probable average $Fe^{3+} + 2Ti^{4+}$ value for pargasitic–hastingsitic amphiboles. Amphiboles having $Al^{IV} + Na(M4)$ values greater than 2.0 show the largest change and are largely ferric and titaniferous igneous amphiboles including kaersutites. All amphibole analyses are below a well-defined limiting line defined by the equation $y^* - Na(M4) = 0.82[Al^{IV} + Na(M4)]$. The predominant trend of the 16 percent contour maximum follows a well-defined slope of approximately 0.65. Similar slopes have been reported by Robinson et al. (1971, Fig. 8) and Hietanen (1974, Fig. 5), who used slightly different coordinates and smaller numbers of analyses. Figure 7A shows that the compositional variation of truly calcic amphiboles (no glaucophane-type substitution) can

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[4] The substitution $Mg(OH)_2 \rightleftharpoons TiO_2$ is possible (D. R. Wones, written communication, 1976), but without independent H_2O analysis, the extent of this substitution is not determinable.
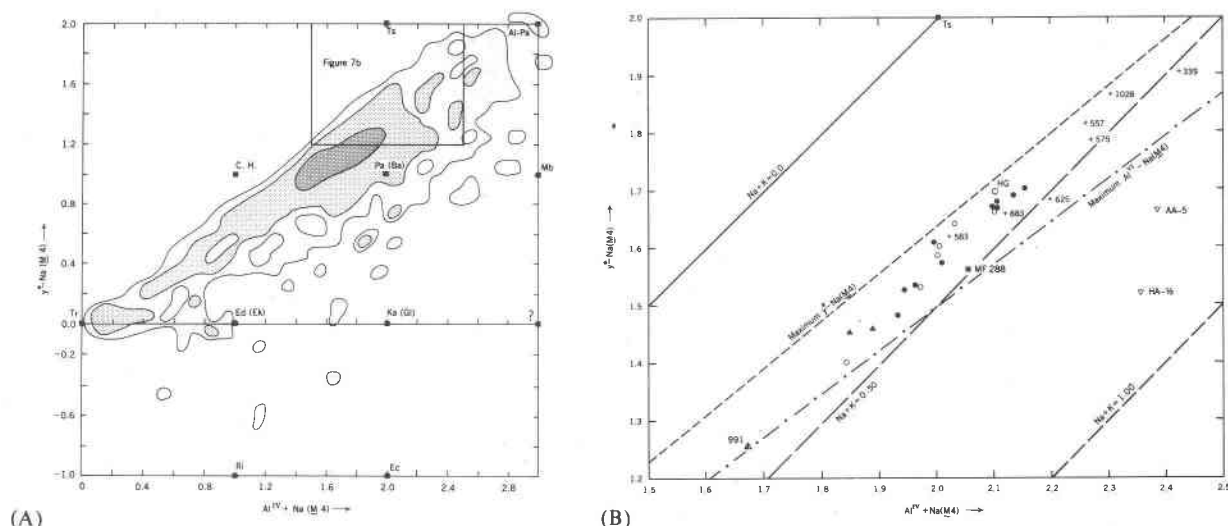
(A)   (B)

Fig. 7. (A) $y^* - Na(M4)$ vs. $Al^{IV} + Na(M4)$ plot for all amphiboles of Figs. 5A and 6A. Data are contoured using a 0.12 percent counting square and 1, 3, and 16 percent contour intervals. The strong linear trend approximates the tremolite–Al-pargasite line, the slope of which is 0.65. For abbreviations, see Fig. 4. (B) $y^* - Na(M4)$ vs. $Al^{IV} + Na(M4)$ plot for southwestern Massachusetts hornblendes determined from intermediate values of Fe_2O_3 in Table 3. Aluminous hornblendes reported in the literature are plotted for reference (symbols same as in Fig. 6). Crosses and sample numbers refer to analyses in Leake (1968), calculated on anhydrous 23(O) basis. Short dashed line is limiting relation $y^* - Na(M4) = 0.82 [Al^{IV} + Na(M4)]$. Dash-dot line refers to limiting $Al^{IV} - Na(M4) = 0.75$ $[Al^{IV} + Na(M4)]$ line from Fig. 6A. Solid line refers to (Na + K) (total) values of 0.0; long dash lines refers to (Na + K) (total) values of 0.25, 0.50, and 1.00.

be described as ultimately trending to the hypothetical end member "Al-pargasite" $NaCa_2(Mg_3Al_2)$ $(Al_3Si_5)O_{22}(OH)_2$, as defined by Bunch and Okrusch (1973).

Data for aluminous hornblendes from southwestern Massachusetts and others previously referred to are plotted in Figure 7B with $y^* - Na(M4)$ and $Al^{IV} + Na(M4)$ coordinates. Also plotted are the limiting line $y^* - Na(M4)$ vs. $Al^{IV} + Na(M4)$, and the limiting line $Al^{VI} - Na(M4)$ vs. $Al^{IV} + Na(M4)$. Note that all the aluminous amphiboles are below the limiting line $y^* - Na(M4) = 0.82[Al^{IV} + Na(M4)]$ defined for 840 analyses of calcic and subcalcic amphiboles. Of the amphiboles shown, sample HG (Hawthorne and Grundy, 1973) and the hornblendes from southwestern Massachusetts closely approximate maximum octahedral occupancy for calcic amphiboles defined by these coordinates. Changes in Fe_2O_3/FeO ratio have little effect on the position of the plotted points relative to the proposed limits; the uncertainty of the real Fe_2O_3 values for these amphiboles will not significantly alter these conclusions. Other calcic amphiboles from the literature (Leake, 1968) showing high R^{3+}, R^{4+} octahedral occupancy are also plotted in Figure 7B (plus symbols). These additional analyses contain significantly higher Ti^{4+}

and Fe^{3+} than the Sudbury or southwestern Massachusetts amphiboles.

Figure 7 is also useful in defining limits of total (Na + K) for natural tschermakitic hornblendes, as lines having slopes of $+1$ represent lines of equal (Na + K). Inspection of Figure 7B suggests that amphiboles which approach maximum $y^* - Na(M4)$ values but which have $Al^{IV} + Na(M4)$ values close to that of tschermakite are limited by (Na + K) values of no less than approximately 0.35. Indeed, only a few published analyses are tschermakitic in terms of $Al^{IV} + Na(M4)$ values and have (Na + K) values less than 0.50.

Discussion and summary

Natural, highly aluminous amphiboles commonly contain some Al^{VI} occupancy attributable to glaucophane-type substitutions [$Na(M4), Al^{VI} \rightarrow Ca, Mg$]. Limits of Al^{VI} occupancy assigned only to tschermakite-type substitutions [$Al^{VI} - Na(M4)$] are significantly lower than the limiting total Al^{VI} values. In both the Al^{IV} vs. Al^{VI} plot (Fig. 5) and the $Al^{VI} - Na(M4)$ vs. $Al^{IV} + Na(M4)$ plot (Fig. 6), several analyses from rock 102–1 are more tschermakitic than those previously described in the literature, irrespective of Fe_2O_3 approximations. These analyses

raise the limiting Al^{VI} vs. Al^{IV} line of Leake (1965, 1971) from $Al^{VI} = 0.6Al^{IV} + 0.25$ to $Al^{VI} = 0.7Al^{IV} + 0.25$. After corrections are made for glaucophane-type substitution, the limiting line which best defines the compositional variation of naturally occurring tschermakitic amphiboles is $Al^{VI} - Na(M4) = 0.75[Al^{IV} + Na(M4)]$ (Fig. 6).

Compositional limitations are even more precisely determined if tschermakitic substitution is defined by charge balance [i.e., $(Al^{VI} + Fe^{3+} + 2Ti^{4+} + Cr^{3+})$, $Al^{IV} \rightarrow Mg,Si$] after corrections for glaucophane-type substitutions on octahedral occupancy of R^{3+} (Fig. 7). However, the limiting line for octahedral occupancy of R^{3+} is raised only slightly over that determined for Al^{VI} after correction for glaucophane substitutions: from 0.75 to $0.82[Al^{IV} + Na(M4)]$ (Fig. 7B). This confirms Leake's (1971) observation that highly aluminous amphiboles approaching tschermakite in composition have low values of $Fe^{3+} + Cr^{3+} + Ti^{4+}$.

The amphibole analysis of Hawthorne and Grundy (1973) plots closer to tschermakite defined by charge-balance criteria than all other amphibole analyses known to us. Additional material of this amphibole is not available, but F. C. Hawthorne (written communication, 1974) believes that the amphibole is igneous in origin, resulting from "filter pressing" processes associated with the emplacement of the Sudbury complex.

The highly aluminous hornblendes from southwestern Massachusetts are slightly more alkalic and more aluminous than the analyses of Hawthorne and Grundy (1973) and represent the most tschermakitic hornblende of metamorphic origin yet reported in the literature.

It has commonly been assumed that high tschermakite content reflects high-pressure conditions (e.g., Leake, 1965, 1968, 1971; Hietanen, 1974; Kostyuk and Sobolev, 1969). This inference partly stems from the failure to separate glaucophanitic components of aluminous amphiboles (e.g., Hietanen, 1974, Fig. 5). Analysis MF288 of Frey (1969) modified by Leake (1971) from the Lukmanier area, Switzerland, is an example of a tschermakitic amphibole formed under relatively high-pressure conditions (amphibole coexists with garnet and kyanite). It is characterized by a significantly higher $Na(M4)$ occupancy than either the amphibole of Hawthorne and Grundy (1973) or the hornblende from southwestern Massachusetts. The coexisting mineral assemblages from southwestern Massachusetts suggest pressures which could be as high as existed in the Lukmanier area. There is,

however, no empirical evidence to suggest that true tschermakites are necessarily favored by high pressure. The suggested igneous origin of the ferrotschermakite from the Frood Mine, Sudbury, implies that at least some natural tschermakites formed at high temperatures.

The experimental results of Jasmund and Schäfer (1972) indicate that solubility of the tschermakitic component in tremolite is limited to a composition of $Tr_{45}Ts_{55}$ (i.e., slightly more tschermakite-rich than the "common hornblende" of Figs. 4–7). Indeed, Figure 6A shows a sharp reduction of the number of analyses showing tschermakitic content greater than about 50 percent. The present study also suggests that in natural amphiboles maximum content of tschermakite is accompanied by an edenitic substitution, the approximate ratio of common hornblende to edenite being 1:0.35 (Fig. 6A). For most calcic amphiboles, increasing amounts of Fe^{3+}, Ti^{4+}, and Cr^{3+} substituting for Al in octahedral coordination appears to enhance the tschermakitic content (compare Fig. 6A with 7A). Hornblendes from southwestern Massachusetts and Sudbury (Hawthorne and Grundy, 1973) are abnormally tschermakitic perhaps partly because of their large Fe/Mg values.

Acknowledgments

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