TABLE 4. THE SODIC-CALCIC AMPHIBOLES: END-MEMBER NAMES AND END-MEMBER FORMULAE

End member	Formula
Richterite	$\mathrm{NaCaNaMg_5Si_8O_{22}(OH)_2}$
Ferro-richterite	$\mathrm{NaCaNaFe^{2}_{5}Si_8O_{22}(OH)_2}$
Ferri-winchite	$\mathrm{CaNaMg_4Fe^{3}Si_8O_{22}(OH)_2}$
Alumino-winchite	$\mathrm{CaNaMg_4AlSi_8O_{22}(OH)_2}$
Ferro-alumino-winchite	$\mathrm{CaNaFe^{2}_{4}AlSi_8O_{22}(OH)_2}$
Ferro-ferri-winchite	$\mathrm{CaNaFe^{2}_{4}Fe^{3}Si_8O_{22}(OH)_2}$
Alumino-barroisite	$\mathrm{CaNaMg_3Al_2Si_7AlO_{22}(OH)_2}$
Ferro-alumino-barroisite	$\mathrm{CaNaFe^{2}_{3}Al_2Si_7AlO_{22}(OH)_4}$
Ferri-barroisite	$\mathrm{CaNaMg_3Fe^{3}_{2}Si_7AlO_{22}(OH)_2}$
Ferro-ferri-barroisite	$\mathrm{CaNaFe^{2}_{3}Fe^{3}_{2}Si_7AlO_{22}(OH)_2}$
Magnesio-ferri-katophorite	$\mathrm{NaCaNaMg_4Fe^{3}Si_7AlO_{22}(OH)_2}$
Magnesio-alumino-katophorite	$\mathrm{NaCaNaMg_4AlSi_7AlO_{22}(OH)_2}$
Ferri-katophorite	$\mathrm{NaCaNaFe^{2}_{4}Fe^{3}Si_7AlO_{22}(OH)_2}$
Alumino-katophorite	$\mathrm{NaCaNaFe^{2}_{4}AlSi_7AlO_{22}(OH)_2}$
Ferri-taramite	$\mathrm{NaCaNaFe^{2}_{3}Fe^{3}_{2}Si_6Al_2O_{22}(OH)_2}$
Magnesio-ferri-taramite	$\mathrm{NaCaNaMg_3Fe^{3}_{2}Si_6Al_2O_{22}(OH)_2}$
Alumino-taramite	$\mathrm{NaCaNaFe^{2}_{3}Al_2Si_6Al_2O_{22}(OH)_2}$
Magnesio-alumino-taramite	$\mathrm{NaCaNaMg_3Al_2Si_6Al_2O_{22}(OH)_2}$
Prefixes specific to sodic-calcic amphiboles	
Alumino-	$^{vi}\mathrm{Al} \geq 1.00$

TABLE 5. THE ALKALI AMPHIBOLES: END-MEMBER NAMES AND END-MEMBER FORMULAE

End member	Formula
Glaucophane	$\mathrm{Na_2Mg_3Al_2Si_8O_{22}(OH)_2}$
Ferro-glaucophane	$\mathrm{Na_2Fe^{2}_{3}Al_2Si_8O_{22}(OH)_2}$
Magnesio-riebeckite	$\mathrm{Na_2Mg_3Fe^{3}_{2}Si_8O_{22}(OH)_2}$
Riebeckite	$\mathrm{Na_2Fe^{2}_{3}Fe^{3}_{2}Si_8O_{22}(OH)_2}$
Eckermannite	$\mathrm{NaNa_2Mg_4AlSi_8O_{22}(OH)_2}$
Ferro-eckermannite	$\mathrm{NaNa_2Fe^{2}_{4}AlSi_8O_{22}(OH)_2}$
Magnesio-arfvedsonite	$\mathrm{NaNa_2Mg_4Fe^{3}Si_8O_{22}(OH)_2}$
Arfvedsonite	$\mathrm{NaNa_2Fe^{2}_{4}Fe^{3}Si_8O_{22}(OH)_2}$
Nyboite	$\mathrm{NaNa_2Mg_3Al_2Si_7AlO_{22}(OH)_2}$
Kozulite	$\mathrm{NaNa_2Mn_4(Fe^{3},Al)Si_8O_{22}(OH)_2}$
Prefixes specific to alkali amphiboles	
Calcian	Ca ≥ 0.50 (∿3% CaO)
Lithian	Li ≥ 0.50 (∿1% $\mathrm{Li_2O}$)

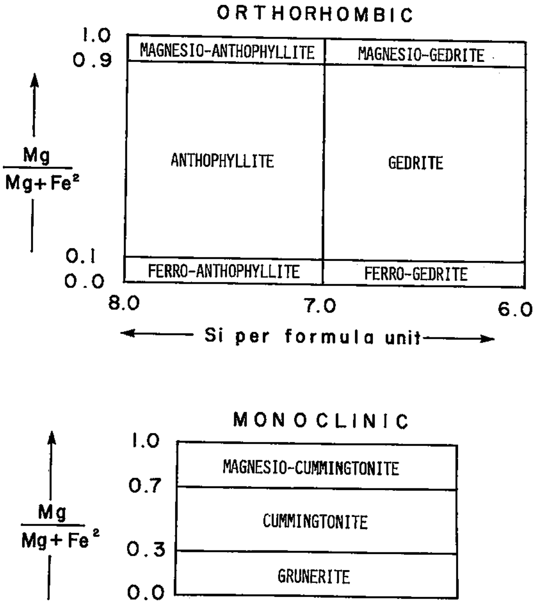

FIG. 1. The nomenclature of the iron–magnesium–manganese amphiboles for which Li < 1.0 atoms p.f.u. [after Leake (1978)].

optical properties (or both) and not confidently identifiable as near to an end-member.

For the various asbestiform amphiboles, mineralogical usage should involve the precise mineral name followed by -asbestos, thus: anthophyllite-asbestos, actinolite-asbestos. Where the nature of the mineral is not known, asbestos alone may be appropriate. Where the approximate nature of the mineral is known but not its precise composition, the assigned amphibole name should be made into an adjective followed by the word asbestos; thus anthophyllitic asbestos. For this purpose, crocidolite is used to cover alkali amphibole asbestos in general, whereas the above recommendations are to be followed if the precise composition is known.

A large number of amphibole names have been formally abandoned (Leake 1978) and should not be used; this includes barkevikite, basaltic hornblende, ferrohastingsite and carinthine. This nomenclature is fairly simple considering the complexity of the amphibole group and should result in rapid and unambiguous naming of amphiboles.

FORMULA-UNIT CALCULATION

The results of a chemical analysis of an amphibole are normally presented as the weight

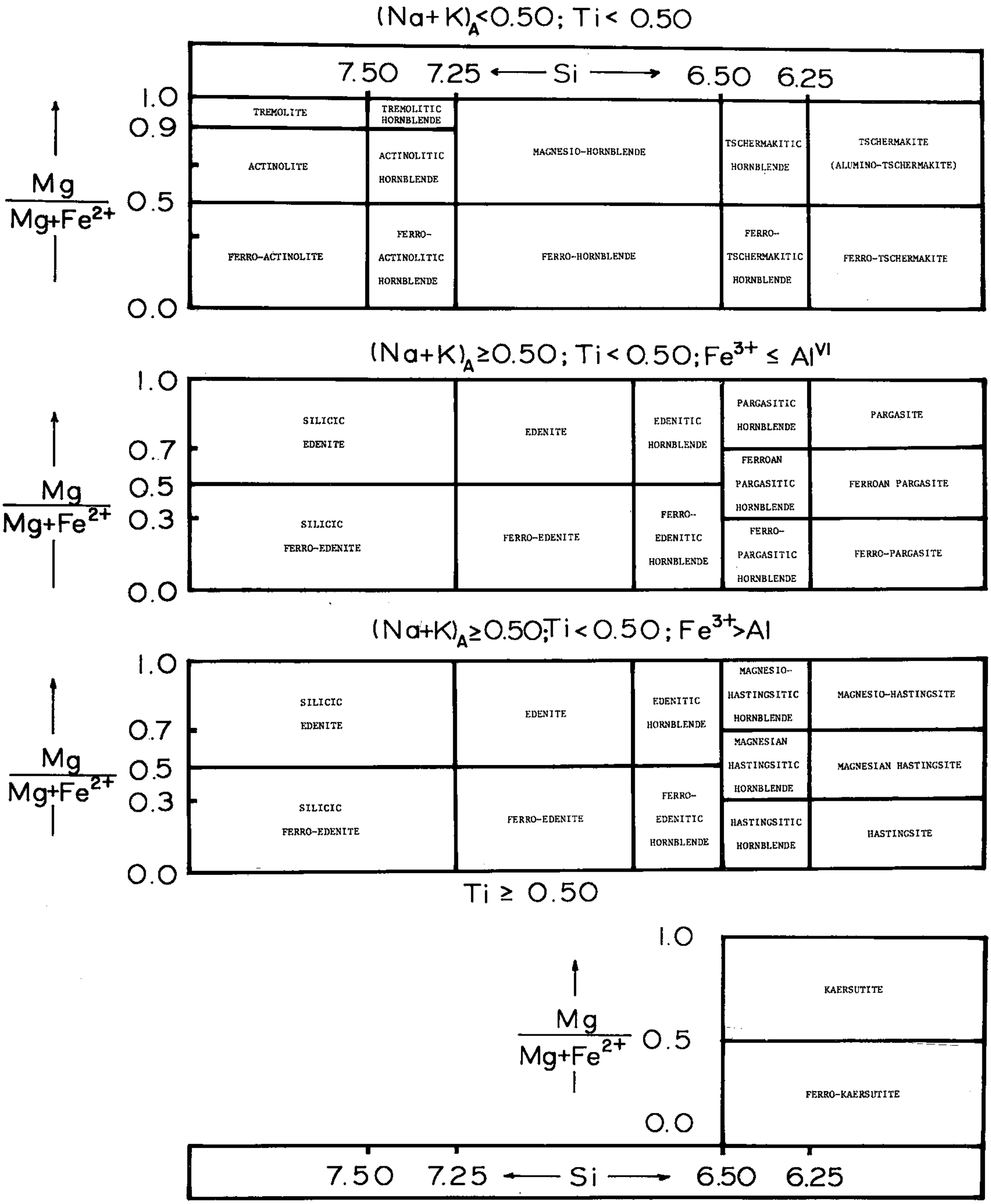

FIG. 2. The nomenclature of the calcic amphiboles [modified from Leake 1978)].

percentages of the oxides or elements present. To calculate the contents of the unit cell from this information is not a straightforward matter; a useful discussion of the inherent problems was given by Hey (1939). A chemical analysis provides the ratios of the chemical constituents in the structure, and calculation of the unit-cell contents requires normalization to some

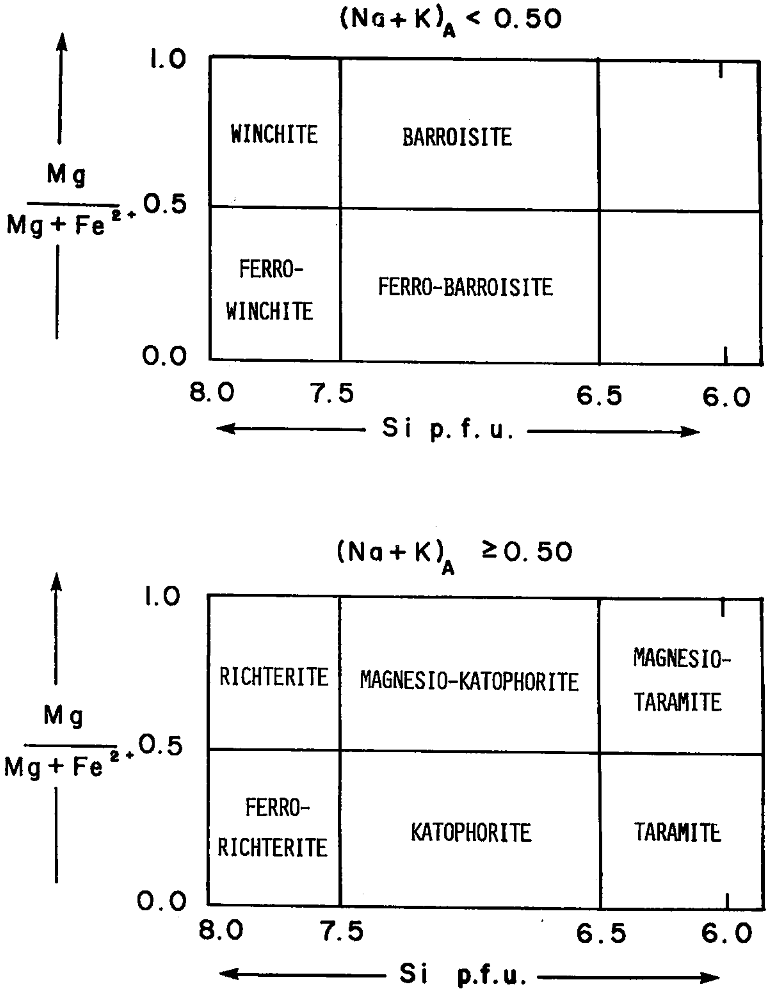

FIG. 3. The nomenclature of the sodic-calcic amphiboles [after Leake (1978)].

standard basis that is characteristic of the structure. This may be done in two ways. If the density and unit-cell volume are known, the analytical ratios may be scaled by these values to give the *empirical unit-cell contents* (Hey 1939) that are based entirely on experimental measurements. The difficulties associated with obtaining a good value for the density (purity of sample, presence of fluid inclusions, occluded space and adsorbed species) usually preclude this method. The alternative method is to scale the ratios to some basis that relates to the crystal structure; this is called the *unit-cell contents* (Hey 1939). This second method is by far the most common method of amphibole recalculation.

The chemical complexity of the amphiboles has given rise to numerous different normalization schemes. We will first examine those schemes that do not involve any adjustment of the Fe^{3+}/Fe^{2+} ratio.

24 (O,OH,F)

This method, which assumes that the total anion content of the formula unit is twenty-four, was introduced by Warren (1929, 1930) following the solution of the amphibole crystal-structure. There is no direct evidence to suggest anion vacancies in amphiboles themselves. Polysomatic intergrowths may give rise to anion vacancies, particularly at their terminations,

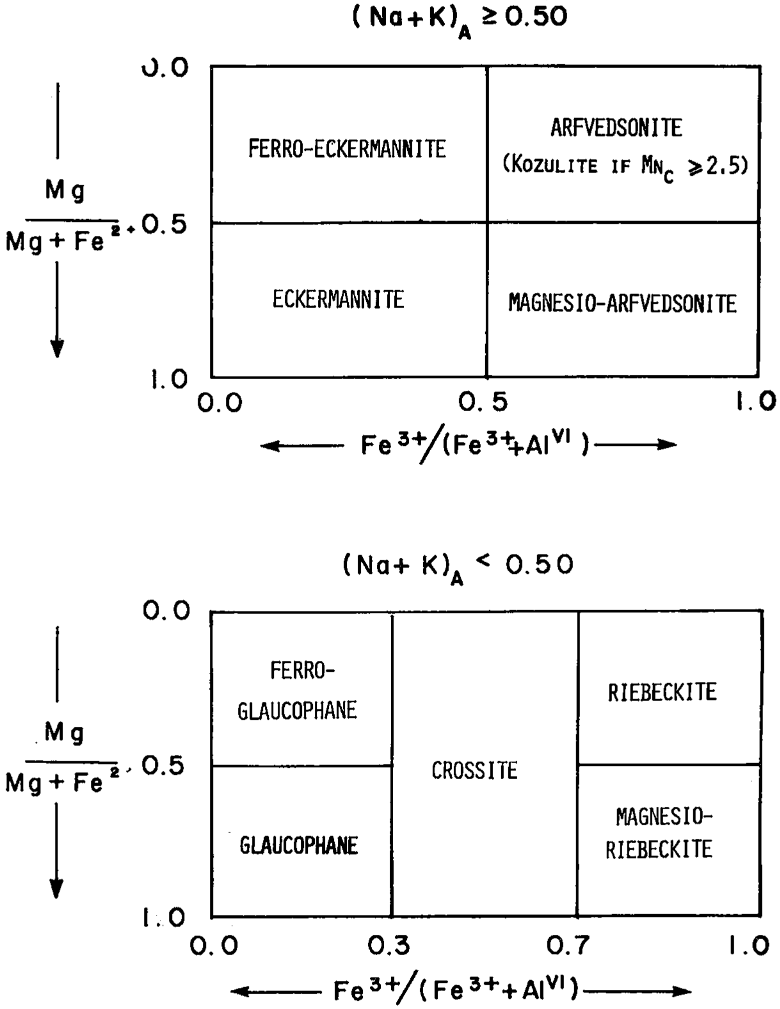

FIG. 4. The nomenclature of the alkali amphiboles [modified from Leake (1978)].

and also affect cation stoichiometry, but this has not yet been shown to be of widespread significance. Thus in principle, this is the best method of amphibole recalculation.

23(O)

This method was introduced by Miyashiro (1957) and others in order to compensate for poorly determined $H_2O(+)$ and lack of F and Cl analyses. Because most amphiboles are now analyzed by electron microprobe, this is the method most commonly used to calculate unit-cell contents. This calculation *assumes* that there are two (OH,F) per formula unit and, as indicated by Phillips (1963), is unsatisfactory for oxy-amphiboles. This point is illustrated in Table 6, which shows the cell contents calculated by both the 24(O,OH,F) and 23(O) methods for potassian oxy-kaersutite(55). In the 23(O) calculation, the sum of the C-type cations (ΣC) is significantly less than the ideal value, which is equal to or greater than 5.0. The reason for this is quite simple. In a normal amphibole, each hydrogen is associated with an oxygen; in an oxy-amphibole, the hydrogen is not present and the oxygen is now associated with a (probably trivalent or tetravalent) cation. Thus, the assumption in an oxy-amphibole that there is $(OH)_2$ in the formula unit introduces an excess of oxygen into the normalization

TABLE 6. UNIT-CELL CONTENTS FOR POTASSIAN OXY-KAERSUTITE(55), CALCULATED ON THE BASES OF 24(O,OH,F) AND 23(O), RESPECTIVELY

Analysis			24(O,OH,F)	23(O)
SiO_2	39.90	Si	5.878	5.697
TiO_2	4.65	Al	2.122	2.303
Al_2O_3	14.35	ΣT	8.000	8.000
Fe_2O_3	9.60	Al	0.370	0.113
FeO	0.04	Fe^{3+}	1.060	1.032
MnO	0.08	Fe^{2+}	0.004	0.004
MgO	14.52	Mg	3.188	3.090
CaO	12.14	Mn	0.009	0.010
Na_2O	1.90	Ti	0.515	0.499
K_2O	2.31	ΣC	5.146	4.748
H_2O^+	0.48	ΣC-5	0.146	-
H_2O^-	0.02	Ca	1.916	1.857
F	0.12	Na	-	0.143
	100.11	ΣB	2.000	2.000
-O≡F	0.06	Na	0.543	0.383
	100.05	K	0.434	0.421
		ΣA	0.977	0.804

procedure, giving rise to lower cation-totals; the method of assigning cations to their groups then leads to totals that are normally considered unacceptable.

Borg (1967a) discussed in some detail the pros and cons of 23(O) and 24(O,OH,F) calculations, and concluded that "for chemical analyses with inaccurately reported $H_2O(+)$ or F, calculation of an amphibole formula on the basis of 23(O) after discarding the reported $H_2O(+)$ is, *in most cases, as unsatisfactory* as a standard calculation including $H_2O(+)$ based on 24(O,OH,F). The sum of the cations in *X*, *Y* and *Z* groups most closely approaches theoretical values in a 23(O) calculation, but only by virtue of compensating and compounded errors of opposite sign". The arguments developed by Borg (1967a) are based on two explicity stated premises: (i) there are 24(O,OH,F) in half the unit cell and (ii) errors in $H_2O(+)$ and F are compensated by errors in wt. % of reported metal oxides. The second premise is based on the observation that "neither low nor high Σ(OH,F) is reflected in correspondingly low or high total reported oxides". This is illustrated in Figure 5, which shows the relationship between total oxide wt. % and (OH,F,Cl) content for 1059 amphiboles. Various conclusions may be drawn from Figure 5: (a) the scatter about 100% may be random error in all components; variations in (OH, F, Cl) may be real (strongly adsorbed H_2O, presence of fluid inclusions, excess structural OH, oxidation during sample preparation, deficient structural OH); (b) errors in $H_2O(+)$ and F are compensated by errors in wt. % of reported metal oxides. The skewed distribution of (OH,F,Cl) suggests *either* that at least some of the (OH,F,Cl) variation is real *or* that there is a systematic bias to low values associated with the experimental method for H_2O determination. Although conclusions (a) and (b) are equally likely just from a consideration of Figure 5, I incline toward (a) as the more reasonable. The errors of conclusion (b) are not random; they would have to be associated with the specific analytical methods used *and would be the same for all analyses;* thus, a compositional dependence of (OH,F,Cl) would be apparent. In iron-rich amphiboles, low-temperature dehydroxylation by oxidation during H_2O analysis can give rise to low $H_2O(+)$ determinations (unless evolved H_2 is measured also); however, Fe_2O_3 is not determined on the same aliquot of sample, and thus the compensating error is not measured. Premise (ii) of Borg (1967a) is thus of questionable general validity; as the ". . . compensating and compounded errors of opposite sign" are the result of these compensating errors in metallic oxides, the conclusions are not of general applicability, unless it can be shown that premise (ii) is correct.

The crucial assumption in the 23(O) calculation is that (OH, F, Cl) equals 2 in the formula unit. Whether or not this assumption is usually valid is still not known. This point is discussed in more detail in the section on the O(3) site. The cynic might ask: if numerous determinations of H_2O have not clarified the role of (OH) in this regard, why go to the trouble of analyzing for it? Hopefully, more precise analytical techniques may eventually resolve this question.

8(Si)

This method has generally been used when

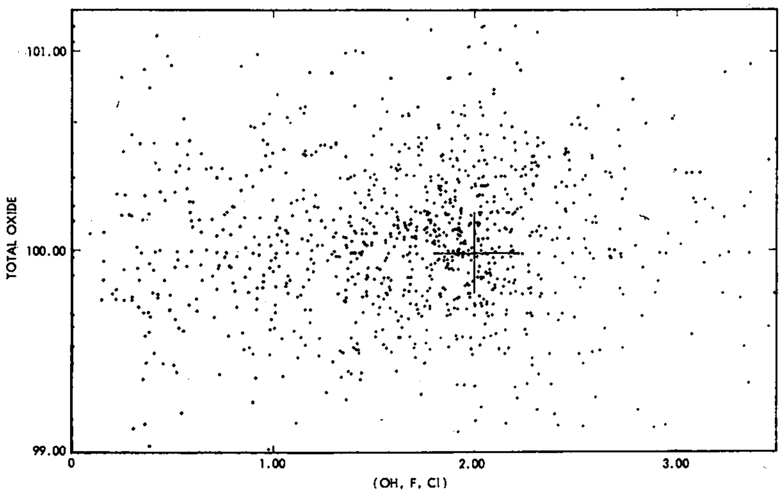

FIG. 5. Total oxide wt. % *versus* (OH, F, Cl) p.f.u. for the superior and moderate analyses of Leake (1968) [from Borg (1967a)].

the calculated Si content exceeds 8 atoms p.f.u.; there seems to be no justification at all for this method.

8(Si + Al)

This method has been used when the calculated (Si + Al) content is significantly less than 8 atoms p.f.u.; there seems to be no justification for this method. Some high-quality analyses do show (Si + Al) less than 8.0 (unpublished work by the author and others), but the structural details of this are not at all clear, and renormalizing to 8(Si + Al) simply ignores this problem. Similar problems have been noted in biotite by De Pieri (1980).

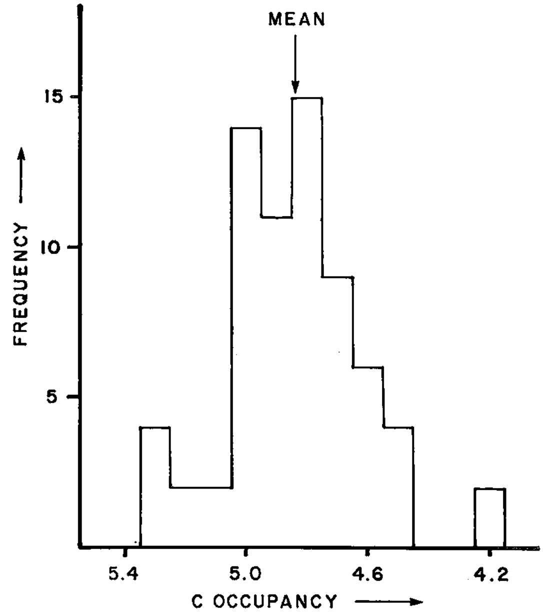

FIG. 6. Frequency diagram for the sum of C-type cations in amphiboles of the eckermannite – arfvedsonite and magnesio-katophorite – katophorite series [from Hawthorne (1976)].

13 cations

This method is based on the assumption that the sum ($Si+Al+Ti+Fe^{2+}+Fe^{3+}+Mn+Mg$) is equal to thirteen; thus these cations (types C and T) do not occupy the M(4) site(s), and B-type cations or vacanacies do not occur at the T(1,2) and M(1,2,3) sites. Experimental studies have shown that these assumptions are not necessarily true. X-ray structure refinements (Ungaretti 1980, Ungaretti *et al.* 1981, Hawthorne *et al.* 1980) have shown the presence of smaller divalent cations at the M(4) site in calcic and sodic-calcic amphiboles. Goldman & Rossman (1977a) gave extensive spectroscopic evidence for the presence of Fe^{2+} at M(4) in some calcic amphiboles. Similarly, the phase studies of Cameron (1975) on a cummingtonite – actinolite join indicate significant solid-solution of the cummingtonite component in the actinolite phase, requiring Fe^{2+} occupancy of M(4) in actinolite. Thus, the sum ($Si+Al+Ti+Fe^{2+}+Fe^{3+}+Mn+Mg$) can commonly exceed 13.0. Can this sum be less than 13.0? Here the situation is far from clear. It has generally been assumed that (T+C) cannot be less than thirteen; however, this may not be the case. In a brief study of the eckermannite - arfvedsonite amphiboles, Hawthorne (1976) showed that the sum of the C-type cations in this series is frequently less than 5.0 (Fig. 6), with a mean sum of 4.88 atoms p.f.u. It was suggested that the presence of vacancies was unlikely and that Ca might enter the M(1,2,3) sites; in fact, using the arguments of Hawthorne (1978c), one can show that vacancies at the M(3) site apparently do not cause great structural instability. Leake *et al.* (1981) have discovered amphiboles with sums of C-type cations going down to ~4.2 atoms p.f.u.; it is of interest to examine the structures of these amphiboles to see if the vacancies occur at the M(3) site as predicted by bond-valence arguments. Thus, calculation of amphibole formulae on this basis would not seem to be justified. Neumann (1976) has proposed a slight modification to this calculation to allow for some M(4) occupancy by Mn^{2+}. On the basis of Onuma diagrams (Onuma *et al.* 1968), she proposed that in amphiboles from mafic and ultramafic rocks, half the Mn be assigned to the M(4) site, whereas in amphiboles from alkaline and silicic rocks, all the Mn be assigned to the M(1,2,3) sites. The objections outlined above still stand.

15 cations

The assumptions in this model concern the behavior of Na (and K). Calculations are performed normalizing the sum of the (B+C+T) cations to 15.0, either including or excluding Na. As Na may occupy both the M(4) and A sites in most varieties of amphibole, neither assumption is particularly appropriate. Such methods may be adequate for Fe–Mn–Mg amphiboles where Na contents are very low; however, the demonstrated A-site occupancy of Na in gedrite and M(4)-site occupancy of Na in synthetic sodian magnesio-cummingtonite $NaMgNaMg_5Si_8O_{22}(OH)_2$ does cast doubt upon this method even in these circumstances.

16 cations

This is the maximum number of cations the amphibole structure can accommodate; the presence of vacancies at the A site is common in all amphibole groups, indicating that this is not a suitable basis for recalculation.

General comments

Normalization of amphibole formulae on the basis of fixed cation numbers is usually not valid; these methods often obscure certain substitutions or make results of poor analyses look acceptable. Formulae should be calculated on the basis of 24(O,OH,F), or 23(O) in the absence of H_2O analyses; note that the latter tacitly assumes the presence of two (OH,F,Cl) in the unit formula.

Calculation of Fe^{3+}/Fe^{2+} ratios

Most amphiboles are now analyzed by electron microprobe, which cannot practically distinguish between valence states of an element. This is of particular importance with regard to Fe, as the role of this element in the amphibole structure is strongly a function of its valence state, and the oxidation ratio strongly affects the recalculation procedure of the unit-cell content. The possible range of cell contents can be derived by performing the calculation twice, with the iron as FeO and Fe_2O_3, respectively. It is generally desirable to obtain more accurate estimates than these extremum values. For some amphibole types, an estimation based on experience can be quite accurate; for example, Fe^{3+}/Fe^{2+} is approximately equal to 0 for monoclinic Fe–Mn–Mg amphiboles. However, most amphiboles are not this amenable, and other methods have been developed to try and obtain this ratio.

When the unit-cell contents of an amphibole are calculated, either the calculation is based on a fixed number of anions in the formula unit [24(O,OH,F) or 23(O)] with the number of cations necessary for electroneutrality, or it is based on a fixed number of cations per formula unit with the necessary number of anions required for electroneutrality. If we wish to calculate the Fe^{3+}/Fe^{2+} ratio, it is necessary to normalize the anions to a fixed number *and* normalize the cations to a fixed number, and then adjust the Fe^{3+}/Fe^{2+} ratio to obtain electroneutrality. All of the schemes used in the literature are based on these constraints; it is irrelevant to note which conditions are assumed and which are adjusted, as the end product is the same. Because of the limitations concerning renormalization based on fixed cation-contents, these calculations only provide limiting bounds; in fact, if vacancies occur at the M(1,2,3) sites, even this is not the case.

This method was first used by Stout (1972), who calculated the maximum Fe^{3+}/Fe^{2+} ratio based on 13 cations (see above) and the minimum Fe^{3+}/Fe^{2+} ratio based on 15 cations (excluding Na) for a 23(O) anion basis. The method was also used by Papike *et al.* (1974), who calculated an Fe^{3+} content from the charge-

TABLE 7. UNIT-CELL CONTENTS FOR AN AMPHIBOLE OF BINNS (1965), CALCULATED USING THE METHOD OF ESTIMATING THE MINIMUM AND MAXIMUM BOUNDS OF THE Fe^{2+} AND Fe^{3+} CONTENTS

Analysis			Min.	Max.	23(O)	24(O,OH,F)
SiO_2	40.85	Si	6.28	6.18	6.20	6.25
Al_2O_3	14.45	Al	1.72	1.82	1.80	1.75
TiO_2	0.65	ΣT	8.00	8.00	8.00	8.00
Fe_2O_3	5.59					
FeO	18.53	Al	0.89	0.75	0.79	0.86
MnO	0.35	Ti	0.08	0.07	0.07	0.08
MgO	5.11	Fe^{3+}	0.12	0.86	0.64	0.64
CaO	10.86	Fe^{2+}	2.91	2.12	2.35	2.37
Na_2O	1.48	Mn	0.05	0.05	0.05	0.05
K_2O	0.61	Mg	1.17	1.15	1.16	1.17
H_2O	1.62	ΣC	5.21	5.00	5.06	5.16
F	0.00					
		ΣC-5	0.21	-	0.06	0.16
		Ca	1.79	1.76	1.77	1.78
		Na	-	0.24	0.17	0.06
		ΣB	2.00	2.00	2.00	2.00
		Na	0.44	0.19	0.26	0.38
		K	0.12	0.12	0.12	0.12
		ΣA	0.56	0.31	0.38	0.50

balance equation, $Fe^{3+} = {}^{iv}Al + Na^{M(4)} - (Na,K)^{A} - {}^{vi}Al - 2Ti^{4+}$, repeated the normalization procedure and calculated a new Fe^{3+} content, iterating this procedure until there was no change in the derived Fe^{+3}/Fe^{2+} ratio. An example is given in Table 7. It has been suggested that the halfway point between minimum and maximum Fe^{3+} contents be taken as an estimate of the actual Fe^{3+} content. This premise was tested for calcic and subcalcic amphiboles on the superior analyses from the compilation of Leake (1968); the results are shown in Figure 7, where it can be seen that there is (unfortunately) no significant correlation between the observed and calculated values. This is really not surprising if we consider the constraints used in the calculations; the actual values of the bounds will be functions of such factors as the amount of Fe–Mn–Mg amphibole substitution in calcic amphibole and the amount of alkali amphibole substitution in calcic amphibole, factors that are a function of bulk-rock chemistry and environment. Perhaps a detailed correlation between these calculations and the specific paragenesis of each amphibole could lead to a better estimate. It is implicit in these methods that the formula unit contains 2(OH,F,Cl); deviation from this condition will further affect the Fe^{3+}/Fe^{2+} ratios and calculations of the unit-cell content.

THE AMPHIBOLE CRYSTAL STRUCTURES

The basic amphibole structure was first characterized by Warren (1929) when he solved the crystal structure of tremolite. Evidence of structural unity throughout the minerals of the amphibole group was provided by Warren (1930) in a general survey of the structure and chemistry of the monoclinic amphiboles, and by Warren & Modell (1930b) in their solution to the crystal structure of anthophyllite. Tschermak (1872) had recognized that there was a strong relationship between the chemistry, physical properties and paragenesis of the pyroxenes and the amphiboles. Warren (1929) and Warren & Modell (1930b) showed that this relationship also extended to the unit-cell dimensions (Fig. 8) and diffraction patterns, and used this relationship to solve the structures of tremolite and anthophyllite by analogy with the known structures of diopside (Warren & Bragg 1928) and enstatite (Warren & Modell 1930a). Warren (1930) noted the striking similarity of the *h0l* reflections in tremolite and diopside, and, coupled with the similarity of the unit-cell dimensions in this projection, concluded that on the (010) projection, the tremolite and diopside structures were practically identical. Thus, the tremolite structure was constructed by incorporation within the tremolite unit-cell of "blocks of the diopside structure" and "reflexion planes". Warren found that there were only two possible relative positions of the "diopside blocks" and the mirror planes that generated a reasonable structural arrangement; as only one of these arrangements was commensurate with the measured *b* parameter of the tremolite unit-cell, the essential features of the tremolite structure were determined. The remaining atoms (2 Mg) were located by symmetry and bond-valence arguments, as were the presence and position of the hydroxyl group in the structure. Structure-factor calculations confirmed the derived atomic arrangement.

The essential feature of the amphibole structure (Fig. 11) is a double chain of corner-linked tetrahedra that extends infinitely in one direction and has the general stoichiometry $(T_4O_{11})_\infty$. The direction of infinite polymerization of the double-chain unit defines the *Z* axis of the amphibole cell in the normal orientation. The actual value of the repeat distance in the *Z*