The structural formula of a hydrous amphibole.

By G. D. NICHOLLS, B.A., Ph.D., F.G.S. and J. ZUSSMAN, M.A., Ph.D.
Department of Geology, University of Manchester.

[Read January 27, 1955.]

THE majority of amphiboles conform to the general structural formula $X_{2\text{-}3}Y_5Z_8O_{22}(OH,F,Cl)_2$, where X = Na, K, Ca, Y = Mg, Fe$''$, Mn, Al, Fe$'''$, Ti, and Z = Si, Al or Ti. Two X ions occupy the positions filled by Ca in the ideal tremolite structure; the additional X ions are assumed to occur in the 'A' sites which are vacant in tremolite.

For the amphiboles, therefore, the method most commonly adopted for deriving a formula from a chemical analysis is to assume that a total of 24 anions is present in the formula unit. In many published analyses, however, the amount of H_2O+ is seen to be greater than that required to make (OH,F,Cl) = 2, and it has been suggested (Hutton, 1940, and others) that extra hydrogen occurs as part of a water molecule or (OH) ion occupying some of the 'A' sites. This would imply an anion total greater than 24 and clearly cannot be demonstrated by a method of calculation which assumes 24 anions per formula unit. Moreover, if in fact the anion total does differ from 24 the calculation will yield incorrect results for the numbers of different cations. Thus, if the formula unit actually carries less than 24 anions, high values for the cation numbers will be obtained, from which it may be erroneously inferred that some Y ions are entering X positions, and the resulting high value for the total $(X+Y)$ may in some circumstances be taken as indicating occupation of the 'A' sites. This effect is exaggerated by the normal procedure of arbitrarily putting only enough Al and Ti into the Z positions to make the total number of ions there 8, the remainder of the Al and Ti being introduced into the Y group and possibly some Y ions being transferred to X positions. Again, in a case where some extra anions or water molecules are in the 'A' sites, calculation on the '24' basis not only fails to reveal the fact but gives erroneously low values for cation numbers.

Procedures for calculating structural formulae have been discussed critically and in detail by Hey (1939, 1954). It is clear that from an analysis only the relative proportions of ions are given, and in the absence of further data a formula unit may be derived from these only when an assumption is made about the numbers of one type of ion.

Hey pointed out that the numbers of the different ions in the unit cell can be determined without this assumption provided that the cell volume and the density are known with sufficient accuracy.

If the percentage of an oxide R_mO_n of molecular weight M is P, cell volume V Å.^{3}, and density D(*g./c.c.*), then the number of R atoms in the cell is given by $(Pm/100M)\times(VD/1{\cdot}6603)$. We have applied this calculation to the data published by Buddington and Leonard (1953) for an amphibole from the Tupper Lake quadrangle district of the NW. Adirondacks, New York, a sample of which was kindly sent to us by Professor Buddington. We have determined the following additional data for this amphibole, $a \sin\beta$ 9·55, b 18·14, c 5·33 Å. giving a volume for the unit cell of $923{\cdot}4\times10^{-24}$ c.c. ±0·7 %. The published density is 3·211 in which a probable error of 0·15 % is assumed.

Table I shows the chemical analysis and the numbers of ions derived from it by this 'direct' method. When these are halved the numbers of ions for comparison with the ideal formula are as follows:

TABLE I. Calculation of chemical analysis of amphibole from Tupper Lake, New York.

Analyst, Eileen K. Oslund (Buddington & Leonard, 1953, p. 894, table I, no. 1).

	(1). Analysis.	(2). No. of cations per unit cell.	(3). No. of anions per unit cell.
SiO_2	39·78	11·86	$23{\cdot}72_0$
Al_2O_3	11·39	4·00	$6{\cdot}00_0$
TiO_2	1·47	0·33	$0{\cdot}65_6$
Fe_2O_3	5·93	1·33	$1{\cdot}99_2$
FeO	14·21	3·54	$3{\cdot}54_2$
MgO	9·62	4·27	$4{\cdot}27_2$
MnO	0·68	0·17	$0{\cdot}17_2$
CaO	9·68	3·09	$3{\cdot}09_2$
Na_2O	1·57	0·91	$0{\cdot}45_4$
K_2O	1·60	0·61	$0{\cdot}30_4$
H_2O+	2·59	5·15	$2{\cdot}57_4$
H_2O-	0·25	—	—
F	1·29	—	$1{\cdot}21_6$
Cl	0·58	—	$0{\cdot}29_2$
Total	100·64	35·26	$48{\cdot}28_6$
Less O for F and Cl	0·67	—	$0{\cdot}75_4$
	99·97	Anion total	$47{\cdot}53_2$

Ca	1·546	Fe''	1·771	Si	5·930	F	0·608	H	2·574
Na	0·454	Mg	2·136	Al	2·000	Cl	0·146		
K	0·304	Mn	0·086		7·930	O	23·011		
	2·304	Fe'''	0·664				23·765		
		Ti	0·164						
			4·826						

Since the sample analysed contained 0·25 % H_2O-, 99·75 was used instead of 100 in the denominator of the expression quoted. Column 3 in table I is obtained by substituting *n* for *m*.

In his paper Hey (1954) points out the need for using in the formula derivation a density value corrected for the presence of H_2O-. When this is done in the case of the Tupper Lake amphibole the anion total comes even closer to the value assumed by Buddington and Leonard (23·89 compared with 24). It is clear that if the sample used for density determination does contain adsorbed water then the correction must be made, and ideally a separate water determination should be made on grains in the condition of those whose density is determined. If this has not been done a decision as to whether a correction should or should not be applied may depend on the texture of the specimen concerned. For example, if the grains used for density measurement are compact crystals of moderate size no correction should be made, since any H_2O- found is probably adsorbed only on the ground powder prior to analysis. Where the mineral is fibrous it is reasonable to assume that some of the H_2O- is present for both analysis and density determination, and a correction should be made. As Hey emphasized, the correction may be important, since 1 % H_2O- affects the density by approximately 2 %. Generally when H_2O- is high it is most likely that it is present initially and is not merely picked up on grinding. In the case under discussion here the nature of the crystals used for density measurement suggests that little if any adsorbed water was present. The measured density may be a little low through crystal imperfections and the true value may lie between that measured and the figure obtained by making the correction for H_2O-. Using such a value would give an anion content closer to 24 than the 23·77 quoted here and would raise slightly the values for the cation numbers. Allied to this question of H_2O- is the consideration suggested by Dr. Hey that if 1·44 out of the 2·59 % of H_2O+ is in fact H_2O-, then a calculation will show that the number of H ions is such as to make (OH,F,Cl) = 2. When only 1·15 % H_2O is assumed to be structural water and an appropriate density correction is made, the following numbers of ions are obtained:

$$\mathrm{Ca_{1\cdot63}Na_{0\cdot48}K_{0\cdot32}Fe''_{1\cdot87}Mg_{2\cdot26}Mn_{0\cdot09}Fe'''_{0\cdot70}Ti_{0\cdot18}Si_{6\cdot26}Al_{2\cdot11}H_{1\cdot21}F_{0\cdot64}Cl_{0\cdot15}O_{23\cdot54}}$$

which may be rewritten as:

$$\mathrm{(Ca,Na,K,Mn,Mg)_{2\cdot90}(Fe''Mg,Fe''',Ti,Al)_{5\cdot00}(Si,Al)_{8\cdot00}O_{22\cdot33}(OH,F,Cl)_{2\cdot00}}.$$

The anion total (24·33) is seen to differ more significantly from 24 and the new figures involve a much greater occupation of the 'A' sites by cations. Since the state of the mineral does not suggest a large amount of adsorbed water we feel that the formula originally derived is more likely. That the extra H ions present are not attended by an appropriate excess of O ions is shown by the anion total, 23·77[1] which is hardly significantly different from that assumed by Buddington in deriving his formula. It may therefore be concluded that the high value of (OH+F+Cl) cannot be attributed in this case to the presence of (OH) ions or water molecules in the 'A' sites of the structure. It is more probable that the extra H ions are linked to oxygens as (OH) replacing O. This replacement may be compensated by a deficiency of cations in the *Z* sites as suggested for the hydrogrossular structure (Hutton, 1943) and for certain 'sheet' structures (McConnell, 1950, 1951). It is conceivable that it could occur in 'chains' of the amphibole type but such an interpretation can only be made with confidence if the deficiency of cations is substantial and is closely balanced by the excess of hydrogen. Alternatively the (OH)–O replacement may be balanced by the substitution of any cation by one of lower valency. The balancing of extra H ions which occurs in the Tupper Lake amphibole cannot yet be specified since the formula may be written either as

$$(\mathrm{Ca,Na,K})_{2\cdot30}(\mathrm{Mn,Fe''',Mg,Fe''',Ti})_{4\cdot76}(\mathrm{Si,Al,Ti})_{8\cdot00}\mathrm{O}_{20\cdot44}(\mathrm{OH,F,Cl})_{3\cdot33}$$

or as

$$(\mathrm{Ca,Na,K,Mn})_{2\cdot39}(\mathrm{Mn,Fe'',Mg,Fe''',Ti,Al})_{5\cdot00}$$
$$(\mathrm{Si,(H_4),Al})_{8\cdot00}\mathrm{O}_{21\cdot77}(\mathrm{OH,F,Cl})_{2\cdot00}.$$

A further case of an amphibole with high water content (from Otago, New Zealand) has been investigated, and a direct calculation again shows extra H ions with no extra oxygen. Confirmation that the 'A' sites are indeed empty in this amphibole has been obtained in the course of an X-ray structure analysis. Full details are to be published elsewhere.

Hey has advocated that the proportion of an oxide in a mineral should be expressed for the purpose of the calculation as *P*/*S*, where *S* = analysis total minus impurities, rather than *P*/(100−impurities) as suggested here. The former procedure has the effect of spreading any errors in *P* values more or less evenly over the whole analysis as far as the cation numbers are concerned and will also give an anion total

---

[1] Using the method described by Hey (1954), the probable error in this figure is estimated to be ±0·19.

nearer the true value. If one's interest is mainly in obtaining an anion total as near as possible to the true value, clearly this is the best course to adopt. Such a case would be one where a comparison is to be made between the actual anion total and that corresponding to a structural concept. We wish to point out, however, that in many circumstances it may be preferable to use 100 instead of the analysis total, since this is the only way to obtain correct cation numbers in all cases where the corresponding *P* value is correct. In other words, an error in any one oxide determination will not influence the numbers obtained for all other cations. (An exception to this occurs where the error is such that some of an oxide should be regarded as impurity (e.g. if some H_2O- has been included in the figure for H_2O+). Use of 100 is advisable for instance if it is of prime importance to determine accurately the number of Si ions in order to see whether all the tetrahedral positions are filled by them. Furthermore, in cases where there is little uncertainty as to the number of anions structurally possible, calculation using 100 will give an anion total which is erroneous but instructively so. Suppose that F and Cl had not been determined in the Tupper Lake amphibole: table II shows the result of (1) calculating a formula on the basis of 24 anions; (2) applying the direct calculation using 100 and not 'analysis total'. It is seen that the first method cannot indicate omission of F and Cl and gives erroneous cation numbers. The second gives correct cation numbers and the low anion total suggests that some anions have been missed in analysis. It may be argued that this is already suggested by the low analysis total, but in that case there is no indication whether the deficiency is of F, Cl, or an oxide. By the direct calculation, if an

TABLE II. Calculation of formula with omission of F and Cl.

	(1).	(2).		(1).	(2).
Si	6·09	5·93	K	0·31	0·30
Al	2·05	2·00	H	2·64	2·57
Ti	0·17	0·17	F	—	—
Fe'''	0·68	0·66	Cl	—	—
Mg	2·19	2·14	O	24·00	23·39
Fe''	1·82	1·77	*X*	2·36	2·30
Mn	0·09	0·09	*Y*	5·09	4·76
Ca	1·59	1·55	*Z*	8·00	8·00
Na	0·46	0·45	Total anions	24·00	23·39

(1) Calculated on basis of 24 anions. (Note: appreciable Al in *Y* groups, no Ti in *Z*, compared with (2) where all Al and approximately half Ti is in *Z* group.)

(2) Calculated using weight of cell contents. (Note: suspiciously low anion content.)

oxide had been omitted or if an erroneously low value had been reported, this would show as a deficiency in both anion and cation total, and in some circumstances could be recognized as such. Using 'analysis total' tends to give an anion total nearer the true value in spite of a faulty analysis by 'spreading the error'. No hard ruling can be laid down as to which factor is best used, and in fact there is no reason why both calculations should not be done. One gives correct cation values for all correct *P* values, and an anion total (strictly in accord with the analysis) which is affected by experimental errors, and by omissions; the other gives a nearer approximation to the true anion and cation total 'compensating' in part for chemical errors and omissions.

Finally, we wish to point out an important aspect of the direct calculations which may be of considerable value. It is that the number of cations of a particular type can be determined by this method when *P* for its oxide alone is known (the same applies to any one anion if its *P* value is known). Thus a partial analysis can be carried out and information obtained about a chosen few ions of particular interest.

Our warmest thanks are due to Dr. M. H. Hey who allowed access to much of his work prior to its publication and has been so kindly and helpfully critical of ours.

References.

BUDDINGTON (A. F.) and LEONARD (B. F.), 1953. Amer. Min., vol. 38, p. 891. [M.A. **12**-374.]
HEY (M. H.), 1939. Min. Mag., vol. 25, p. 402.
—— 1954. Min. Mag., vol. 30, p. 481.
HUTTON (C. O.), 1940. Mem. Geol. Surv. New Zealand, no. 5, p. 15.
—— 1943. Trans. Roy. Soc. New Zealand, vol. 73, p. 174. [M.A. **9**-61.]
MCCONNELL (D.), 1950. Amer. Min., vol. 35, p. 166. [M.A. **11**-220.]
—— 1951. Clay Min. Bull., vol. 1, p. 179.
WARREN (B. E.), 1930. Zeits. Krist., vol. 72, p. 493. [M.A. **4**-278.]