

The recalculation of amphibole analyses

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Summary. A good chemical analysis of an amphibole will give cation numbers that can be correlated in detail with the available lattice positions. The substitutions that must be recognized are described. A more rigorous check of the analytical results becomes possible and the sources of error may be indicated.

THE crystal structure of the amphibole group minerals is now well established and the variations in chemical composition are usually related to a general formula of the type $AX_2Y_5Z_8O_{22}(O, OH, F, Cl)_2$.

In seeking to determine how closely a given chemical analysis of an amphibole corresponds with this formula, a recalculation making use of accurate values of the density and cell dimensions of the mineral is desirable, since it requires no assumption as to the total number of anions in the formula (Hey 1939, 1954). Unfortunately, this physical data is as yet available for only a small minority of the amphiboles that have been chemically analysed, and as Borneman-Starynkevich (1960) points out, the density in particular is difficult to determine with the required accuracy.

It is therefore customary to recalculate the analysis by the normal method involving an assumption of the total number of anions in the formula unit, 24 in this case. Any error in the analytical figure for water content has an unduly large effect on the atomic formula calculated in this way, and such errors are believed to be common (Riley, 1958). For this reason, many analyses have been recalculated on a basis of 23 oxygen atoms in the formula unit, omitting water from the main part of the calculation. However, it is reasonably certain that in the so-called oxyhornblendes there may be an appreciable deficiency of hydrogen atoms in the OH positions, but the charge deficiency is compensated by the oxidation of an equal number of ferrous ions to ferric. The use of 23 oxygen atoms as a basis for calculation is not valid in this case unless one-third of the oxygen atoms corresponding with these ferric ions is deducted from the oxygen total. Since there may be more ferric ions present than are required to balance the hydrogen deficiency and the proportions of ferric ions fulfilling these different functions are unknown, this correction cannot easily be made.

Borneman-Starynkevich (1960) suggests that certain cation sums may be taken as a basis of calculation—either $Y+Z = 13$, $X+Y+Z = 15$, $Si+Al = 8$ or $Si = 6$, selecting for a given analysis the sum that gives the best approach to the standard amphibole formula. There are obvious objections to the last two sums, and if the suggestion later in the present paper that defects may occur in the Y group is correct, the remaining assumptions are of only limited validity. The recalculation of amphibole analyses is therefore best made assuming 24 anions in the formula unit. Even so, authors differ widely in what they regard as a satisfactory agreement between a recalculated analysis and the theoretical formula. The analyst has no agreed standard against which his results may be tested and appreciable errors in the analysis may go undetected and unsuspected, as recently shown by Leake (1962).

Examination of a large number of amphibole analyses (Layton, 1959; Layton and Phillips, 1960) has suggested certain conclusions regarding the types of atomic substitution that may occur in the amphiboles and the limits within which a recalculated formula should be regarded as equivalent to the theoretical formula.

The conclusions, and examples of their application, are set out here in the hope that some at least of them are valid. In any event, a critical examination of the validity of these postulates by analysts and others may serve to direct attention to an aspect of amphibole mineralogy that must otherwise be a barrier to further progress in our understanding of the group. One reservation must be made—it has been shown by Gibbs *et al.* (1960) that synthetic fluor amphiboles may be prepared whose structure is appreciably different from the normal amphibole structure. The following comments apply to naturally occurring minerals, not to synthetic materials that seem to have no stable existence in nature.

The 24 anion positions in an amphibole are always fully occupied. The normal method of calculation of atomic formulae based on this assumption must show an overall balance of charge between anions and cations, even if the chemical analysis is in error. It does not, however, follow that the number of cations found will correspond with the number of available lattice positions in the amphibole structure—16 in all. If the calculated cation number is greater than this (after taking account of the role of hydrogen as discussed below) the analytical results are suspect. After allowing for various substitutions, the occupancy of each type of lattice position can be accounted for to 1% or better of the theoretical number of such sites by a reasonably good analysis.

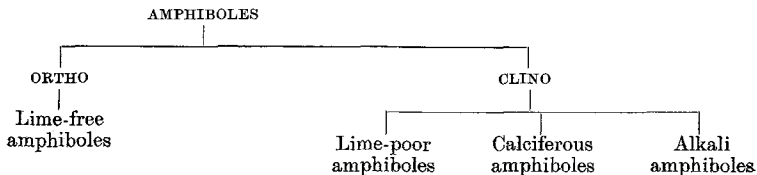
Hydrogen in excess of two hydroxyl ions per formula unit may be located

in *A* sites in the lattice. Evidence discussed later suggests that each *A* site can accommodate two hydrogen ions and these are to be counted as one in calculating the cation number as mentioned in 1. Examples of this substitution are limited and a high value for water should always be regarded as a more likely explanation.

If the amount of hydrogen is insufficient to make $\text{OH} + \text{F} + \text{Cl}$ exactly 2, the deficit is due to O^{2-} taking the place of OH, or more commonly the analytical figure for water is too low. The substitution of O^{2-} for OH can probably occur in any amphibole, not only in the so-called oxyhornblendes, but in all cases an equal number of ferric ions must be available to balance the substitution, and it is suggested that no other ion can act in this way. Experimental evidence having some bearing on this postulate has been provided by Addison *et al.* (1962).

Silicon and aluminium are the only occupants of *Z* positions, in four coordination with oxygen. Titanium is often regarded as a possible occupant of these sites, but the evidence for this is unconvincing. Particularly in the presence of ferric ions, titanium is likely to be in the quadrivalent state and its ionic radius is then appropriate to sixfold coordination. If titanium in the formula needs to be allocated to some position other than *Y*, the analysis is suspect. One Ti^{4+} in *Y* will compensate the substitution of two aluminium ions for silicon in *Z*, but it seems that another possibility is that $2\text{Mg}^{2+} = \text{Ti}^{4+} + \square$, where the square indicates a vacant *Y* position. The substitution of aluminium in *Z* must be balanced by the sum of valencies of *A* position atoms, excluding those balancing substitution in the *X* position (see below), plus the sum of valencies in excess of two per atom in the *Y* group, excluding atoms balancing $\text{OH}^- \rightarrow \text{O}^{2-}$ substitution or sodium in *X*-positions (see below) and titanium substituting for magnesium in the manner described above. Consideration of a large number of amphibole analyses also suggests that a maximum of one quarter of *Z* positions may be occupied by aluminium.

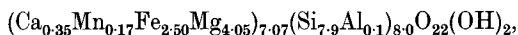
The *X* positions of the general amphibole formula are those that, together with the *A* positions, are capable of accepting ions of greater ionic radius than those normally occupying *Y* positions. The major divisions of the amphibole series according to Layton and Phillips (1960) are:



It is suggested that these major divisions are related to occupancy of the *X* positions by ions of greater ionic radius than those normally present in *Y*.

For the orthorhombic, lime-free amphiboles, the general formula is best written $AY_7Z_8O_{22}(OH)_2$. As pointed out by Whittaker (1960) the small amounts of calcium and sodium found in anthophyllites must occupy the *A* position—the larger ions cannot enter the *X* position in this structure. After eliminating from the list of anthophyllite analyses given by Rabbitt (1948) those examples that are suspect on grounds here suggested, it seems that the *A* positions can be occupied up to a limit of 50 %, but the limit of occupancy by calcium appears to be about 10 %. Whittaker (1960) would, however, allow a greater amount of calcium than this.

Layton and Phillips (1960) suggest that *the monoclinic structure of the lime-poor amphiboles*—the cummingtonite series—is formed in preference to the orthorhombic structure due to partial occupancy of *X* positions by the larger ions of calcium or manganese. This has been questioned by Mueller (1962) on theoretical thermodynamic grounds. However, exsolution relationships similar to those predicted by Layton and Phillips have been described by Asklund *et al.* (1962) and Vernon (1962), and Gibbs *et al.* (1960) have shown experimentally that calcium causes the formation of monoclinic amphiboles in melts that otherwise give an orthorhombic structure. Ghose (1961) has given details of a refined structure for cummingtonite of formula

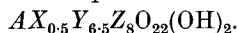


which lies within the range proposed by Layton and Phillips—



with $x < 1$. However, the calcium content was ignored in the structure analysis, as it was considered by Mueller to be due to admixed actinolite. If, in fact, calcium is an occupant of the *X* positions, it might be expected that the remainder of these sites would be preferentially occupied by Fe^{2+} , as was found by Ghose. The tendency of authors to ignore small amounts of calcium may be encouraged by analytical error—as will be suggested later, in the presence of much magnesium calcium figures tend to be inaccurate.

Limits for x in the Layton and Phillips formula would seem to be between 0.1 and 0.5 atoms per formula unit—that is, a reasonable general



The remaining monoclinic amphiboles are those having full occupancy of the X sites in accordance with the general formula. In the calciferous amphiboles, calcium is the major tenant of these sites, but, as will be shown in a later paper, there is no clear compositional break between these and the alkali amphiboles.

Sodium, but probably not potassium, may replace calcium in X positions. The charge deficit is balanced by an equal number of sodium or potassium ions entering the A position, or an equivalent number of ions of higher valency than two entering the Y positions.

It has been suggested that Mg^{2+} and Fe^{2+} , normally occupants of Y positions, can also enter the X positions in calciferous and alkali amphiboles. Whittaker (1960) states that it is usual for the largest ion present to occupy M_4 (i.e. X) in the monoclinic structure, but Zussman (1955) for actinolite and Whittaker (1949) for crocidolite found that Mg^{2+} enters M_4 in preference to Fe^{2+} ; Ghose (1961) found the reverse situation in cummingtonite. Gibbs *et al.* (1962) concluded that A and M_4 sites were filled randomly by Na^+ and Mg^{2+} in a synthetic fluor-magnesio-richterite. Mueller (1962) states that small undetermined amounts of calcium enter all positions in both cummingtonite and actinolite. It might have been expected, because of the similarity of structure throughout the monoclinic amphiboles, that the preference for X sites would in all cases be in the same sense as between one element and another. It is certainly contrary to the normal expectations of crystal chemistry to find that in a stable compound Mg^{2+} can occupy sites that are also capable of accommodating K^+ .

A factor that does not seem to have received attention in this connexion is the very real possibility of compensating errors in the magnesium and calcium figures in an otherwise good analysis. These determinations are interdependent in both the classical and rapid methods of silicate analysis, and the determination of calcium in the presence of large amounts of magnesium needs especial care (Hillebrand and Lundell, 1950). It seems prudent to suggest that a careful check is required of any analysis of a calciferous or alkali amphibole that on recalculation needs Mg^{2+} or Fe^{2+} to be placed in X positions. Similar care is also required for the reliable determination of calcium in cummingtonites.

The ionic radius of lithium is such that it should always be regarded as an occupant of Y positions, effectively replacing Mg^{2+} , not as an occupant of X positions. A substitution such as $LiAl = 2Mg$ is required to compensate the charge difference.

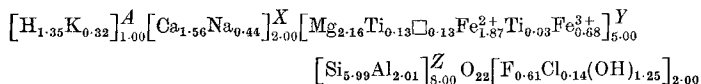
Some published analyses of alkali amphiboles require more than three

atoms per formula unit to be placed in the *A* and *X* positions. An explanation for this may be that an unduly high value for alkalis is also a possible form of analytical error.

Some examples relating to the above suggestions are now given. Recording the presence of very small amounts of various elements in the formula of an amphibole usually adds little to our understanding of these minerals, so where there is not more than 0.10 atom of an element in a certain lattice position, its equivalent in atoms of the major element of similar ionic radius and charge is substituted. Titanium may be excepted from this rule where it is required to show its function clearly. An analysis by E. K. Oslund of an amphibole from Tupper Lake, New York, is quoted by Nicholls and Zussman (1955). Recalculated on the basis of 24 anions in the formula unit the analysis gives

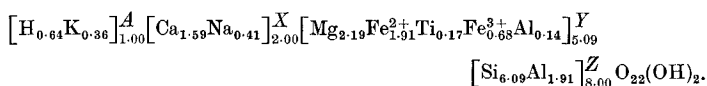
K 0.31	Mg 2.16	Ti ⁴⁺ 0.16	Si 5.99	F 0.61
Na 0.45	Fe ²⁺ 1.78	Fe ³⁺ 0.67	H 2.60	Cl 0.14
Ca 1.56	Mn ²⁺ 0.09	Al 2.02		O 23.25

A check calculation shows that the excess hydrogen is not likely to be due to an incorrect water determination, since a lower figure gives a formula departing from the theoretical. As the cations are allocated in turn to the various available lattice positions, it becomes obvious that the number of excess hydrogens is exactly twice the number of vacant *A* positions. A dynamic equilibrium in which two hydrogens occupy an *A* site, moving round to form OH groups with each in turn of the oxygen atoms coordinating the site, seems to be possible. At any given instant, the hydrogen ions would be diametrically opposed. This suggestion is compatible with the conclusions of Nicholls and Zussman that 'it is more probable that the extra H ions are linked to oxygens as (OH) replacing O'. Zussman's (1955) statement that the *A* sites are empty in another amphibole with excess hydrogen does not, of course, invalidate the above remarks, since the presence of hydrogen would not be detected by the X-ray structure analysis. On this basis and in accordance with previous suggestions the formula can be written:



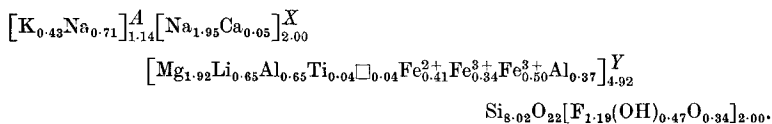
This agrees exactly with the amphibole formula, when it is recognized that most of the titanium is effectively replacing magnesium as postulated above, with associated vacancies in the *Y* positions. (Minor amounts have been consolidated in writing the formula, as previously

suggested—thus, $K_{0.32}$ includes $Na_{0.01}$, $Fe_{1.87}^{2+}$ includes $Mn_{0.09}$ and $Fe_{0.68}^{3+}$ includes $Al_{0.01}$.) Nicholls and Zussman use the cell-size and density data with the analysis to derive two possible formulae both of which have an anion total less than 24. It seems equally reasonable to assume an anion total of 24 and explain the discrepancy in their result as being due to the effect of H_2O^- on the density value, a possibility that they recognize. They also suggest that if fluorine and chlorine had not been determined, the method of calculation to 24 anions could not indicate this and would give erroneous cation numbers. The formula they derive for this case using 24 anions as the basis of calculation is



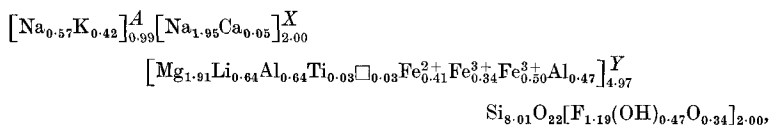
The analysis total, originally 99.97 %, would now be 98.77 %, which would in itself suggest that something had been missed. The total of Y group positions is greater than theoretical and outside the limit of 1 % suggested above. Thus, although small, this difference should nevertheless be regarded as significant and indicative of analytical error. A high Y group total commonly results from too low a value for water, but this cannot be the case here because of the excess of hydrogen. The non-determination of fluorine is the most likely of the various possibilities. The fact that although the A sites seem to be fully occupied, there is only one hydrogen to each position, might also be taken as indicating an error affecting the amount of hydrogen in A.

An analysis of eckermannite from Sweden is given by Sundius (1946, p. 10). The analysis total is good (100.15) and the formula calculated by Sundius can be written:



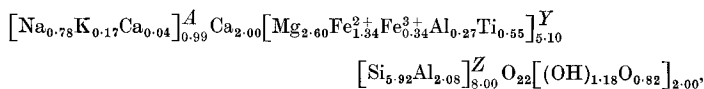
The $Fe_{0.41}^{2+}$ includes $Mn_{0.04}$ and $Zn_{0.06}$, and lithium and titanium are regarded as replacing magnesium, with corresponding amounts of aluminium for the former and vacancies for the latter. Even so, the Y group total is low. The need for O^{2-} to bring the OH positions to 2 might indicate a low value for water, but this would tend to make all the cation numbers too high, especially the Y group total. It is therefore assumed that this represents the 'oxy-amphibole' type of substitution, and the ferric ions to balance this are written separately. The major discrepancy

occurs in the *A* sites which are 14 % over occupied, suggesting a positive error in the analysis. The excess is equivalent to about 0.5 % by weight of Na₂O. Let us assume, in view of the low *Y* group total, that there has possibly been a compensating error, say in aluminium. Recalculating on this basis the formula becomes:

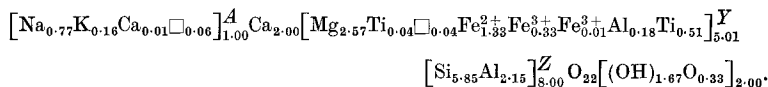


and the occupancy of the various sites is within 1 % of theoretical. There is a strong case for checking the analysis, and some indication of the probable location of the error is given.

Analysis of a hornblende by Vincent (1953, p. 34) gives a formula that can be written:

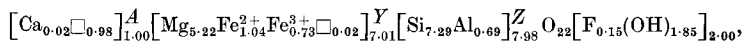


which is in good agreement with the theoretical formula and the analysis total of 99.87 is very good. It is necessary, however, to introduce O²⁻ to complete the OH positions, yet there is insufficient Fe³⁺ to compensate as postulated above. Taking this together with a *Y* group total 2 % higher than theoretical suggests that the water figure may be low. Vincent comments that the analytical figure for water is rather low and suggests that it may be due to experimental error. If we take a notional figure of 0.5 % water, the analysis total is still well within the limits for a first class analysis. Recalculation using the increased water figure gives:

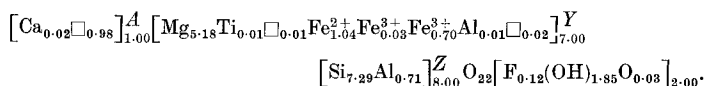


The *Y* group total is now satisfactory and ferric iron is almost exactly equal to the oxygen in the OH positions. The silicon in both these formulae is slightly less than six although, as stated above, Si₆Al₂ is believed to represent the maximum replacement of silicon by aluminium. Fairbairn (1953) reported a reciprocal systematic error in SiO₂ and Al₂O₃ (of about 0.5 %), in the co-operative investigation of the rocks G1 and W1, which would account for the above difference, so there seems to be no reason to alter this conclusion.

From Rabbitt's (1948) list of selected modern analyses of anthophyllites, analysis 21 by Raoult quoted by Lacroix (1922) is a good example. Using the cation numbers given by Rabbitt the formula is:

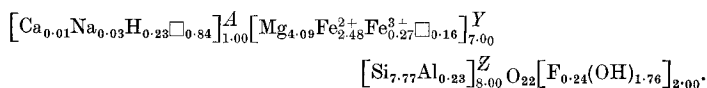


in very good agreement with the theoretical formula. However, as titanium is not included in these cation numbers, the calculation was repeated and gave:



Here a small amount of oxygen in place of OH is balanced by ferric iron, vacancies occur in *Y* due partly to titanium substituting for magnesium and partly to the calcium in *A* sites, and Al in *Z* is balanced almost entirely by ferric iron in *Y*.

Analysis 22 from the same list, by Bygden, quoted by Sundius, 1933, gives the following formula using Rabbitt's cation numbers:



where $\text{Fe}_{2.48}^{2+}$ includes $\text{Mn}_{0.02}$ and $\text{Fe}_{0.27}^{3+}$ includes $\text{Al}_{0.08}$. Vacant spaces in the *A* position are calculated assuming two hydrogens in each position as previously suggested for monoclinic amphiboles. The double charge equivalent of the *A* position ions is 0.14 so there are apparently 0.02 excess vacancies in *Y*. However, the trivalent ion total in *Y* is 0.04 greater than is required to balance Al in *Z*. This then is an example of the substitution $3R^{2+} = 2R^{3+} + \square$ in the *Y* positions, although this substitution does not seem to be at all common in the analyses so far examined. The analysis also seems to be an example of hydrogen entering *A* sites in an orthorhombic amphibole in the same way as has been suggested for the monoclinic amphibole of Nicholls and Zussman.

The analyses used here as examples are good analyses. In many published analyses much greater discrepancies occur, if the suggestions in this paper have any validity. Similarly, if the conclusions are correct, they should serve to increase the reliability of amphibole analyses by providing the analyst with a more detailed check than has hitherto been available. A better correlation of physical properties with composition in the amphibole group may also be possible if unreliable analyses can be detected in this way.

The systematic procedure for the examination of an amphibole formula calculated on the assumption of 24 anions in the formula unit can be summarized as follows:

Hydroxyl positions are first made up to 2.00 with oxygen if necessary; ferric ions equal to this number of oxygens are required in *Y* to balance the substitution; if these are not available and the cation numbers are high, a negative error in the water content is indicated. Excess hydrogen is placed in *A* sites, two per site, but excess hydrogen with low cation numbers indicates a positive analytical error in water; the possible effects of non-determination of fluorine and chlorine should not be forgotten. Next, the *Z* positions are made up to 8.00 with Al; insufficient Al, or Si less than 6.00, indicates error.

Where *X* positions can be made up to 2.00 with calcium and sodium, the amphibole is a calciferous or alkali amphibole. Calcium in excess of 2.00 may indicate error, but the extent to which it may enter *A* positions in these amphiboles is not known. Any excess sodium is put into *A* with potassium and hydrogen if available. If the amount of sodium plus potassium plus one half hydrogen in *A* is greater than 1.00, there is an error. The sum of valencies in *A* should balance the substitution of sodium for calcium in *X*, or the balance must be completed by ions of charge greater than 2 in *Y* not otherwise accounted for. In some cases manganese may be a replacement for calcium in *X* but the details of this substitution need to be checked. Analyses of anthophyllites will normally have 0.10 atom of calcium or less. Analyses of cummingtonites will have 0.10 to 0.50 atom of calcium, but manganese may also be involved. The exact possibilities require further investigation.

Finally, in the calciferous and alkali amphiboles the remaining ions should account for 5.00 *Y* positions. A good analysis will give between 4.95 and 5.05, but up to 5.10 may be reasonable for many purposes. In this and previous cases, unless there is more than 0.10 atom of any element, it is to be included as if it were the major element of similar charge and ionic radius, but titanium is excepted from this rule. After ferric ions have been allocated to balance oxygen in OH positions, the Al in *Z* is balanced by Al, Fe³⁺, Ti⁴⁺ in *Y* plus unused ions in *A* if necessary. Substitutions such as $2\text{Mg} = \text{LiAl}$, $2\text{Mg} = \text{Ti}^{4+} + \square$ and $3R^{2+} = 2R^{3+} + \square$ may be recognized in accounting for these positions, but the last mentioned seems not to be common. In anthophyllites, vacancies in *Y* may also occur due to the presence of ions in *A*. For these and the cummingtonites the analysis should account for *Y* positions to 1% or better.

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