COMPOSITION OF THE ALKALI AMPHIBOLES

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Within the last few years the amphibole group has been the subject of a number of studies. Chief among these, perhaps, was that of Kunitz.[1] This was an exhaustive chemical and optical investigation of carefully selected material, containing sixty new analyses. Many of these analyses have been used by the present writers in their study presented here in this preliminary report.

Another paper on the subject, of equal importance, was published about a year ago by Warren.[2] This investigation was concerned primarily with the crystal structure of tremolite as deduced from *x*-ray data. In addition, Warren showed that the other amphiboles were identical in structure with tremolite, and from this structural identity deduced a general expression for the composition of the amphiboles. It is significant that these two papers, based on widely diverse evidence and published within a short time of each other, reached such similar conclusions. There are, however, some important differences which will be mentioned later.

Our study is mainly concerned with the alkali amphiboles, of which we have examined upward of a hundred analyses, from various sources, both new and old. At this time we are prepared to give only the preliminary results of the chemical study. We hope that an optical study will be completed later.

Warren in his paper gives a general expression for the amphiboles which is as follows:

$$\overset{A}{(Ca, Na, K, Li)_{2-3}} \quad \overset{B}{(Mg, Fe^{II}, Fe^{III}, Al, Ti)_5} \quad \overset{C}{(Fe^{III}, Al, Si)_8}$$

$$\overset{D}{(O, OH, F)_{24}}.$$

This formula is based on the structural requirements of the amphiboles, which are:

1. The number of oxygens (D), or equivalent atoms, must be constant in all the amphiboles, *i.e.*, twenty-four in the half unit cell, which this formula represents.

2. There are five magnesium atoms, or their equivalents, which may be those listed under (B).

[1] Kunitz, W., *Neues Jahrb.*, Abt. A., Vol. **60**, pp. 171–250, 1930.
[2] Warren, B. E., *Zeit. f. Krist.*, Vol. **72**, pp. 42–57, and pp. 493–517, 1930.

3. The silicon atoms (C) do not exceed eight.

4. The (Ca, Na) group (A) may vary from two to three, which are the minimum and maximum, respectively.

In addition to these structural requirements there is the additional factor of valence, which must, of course, be satisfied.

With so many variables, and the further complication of certain atoms, such as aluminum, falling at one time into group B, and at another into group C, or as in hastingsite, being distributed in both groups, it is no wonder that the compositions of the amphiboles are so diverse.

We have found, however, that the range of replacement is for the most part comparatively limited, and that most analyses fall fairly well into a few definite types. This limited isomorphism as deduced from the examination of many analyses is essentially as follows:

(1) Ca and Na are not completely isomorphous but usually are present in a definite ratio. Thus in the hastingsite group the Ca:Na ratio is invariably 2:1. Further, calcium never exceeds two atoms in any analysis. Sodium may vary from 0 to 3.

(2) Magnesium and equivalent atoms (B) in the normal amphiboles, contribute five atoms to the formula. In the so-called deficient silica type additional aluminum is always present to the extent of making up the deficiency in silicon. The ratio, in hastingsite, Mg:Al:Si is 4:3:6, two aluminum atoms go to the silicon group (C), and one to the B group. Magnesium, in this group, never exceeds five atoms and does not drop below one atom; that is, no amphiboles are completely lacking in either magnesium or ferrous iron.

(3) Aluminum does not exceed four atoms in any amphibole analysis, and may be entirely absent, as in tremolite. Trivalent iron plays the same rôle as aluminum, with the possible exception that it does not freely replace silicon, as does aluminum.

(4) Silicon varies from a minimum of six atoms to a maximum of eight. When six atoms are present two aluminum atoms make up the deficiency.

(5) The number of oxygen atoms (and equivalents) is constant. The (OH+F) group does not exceed two, and we believe, may be absent, as in the anhydrous amphiboles.

(6) Titanium and manganese occur in relatively small amounts, we are therefore not certain as to their position in the formula. It

is not at all obvious from our analyses that titanium replaces silicon, the usual assumption.

Using the conclusions based on analyses as to the isomorphous replacements, we may modify Warren's formula so as to be more explicit concerning the replacements found in the amphiboles. The modified formula is as follows:

$$(Ca, Na)_2Na_{0-1}Mg_1(Mg, Al)_4(Al, Si)_2Si_6O_{22}(O, OH, F)_2.$$

Those elements within brackets are completely replaceable. The others can be considered as being fixed (with the exception that Fe^{II} and Fe^{III} may replace Mg and Al, respectively). This formula merely represents the limits of isomorphism as indicated above.

It might be here urged that the general formula, of which this is an example, is perhaps more nearly correct than the usual "end members," in indicating the composition variation in such a complex series as the amphiboles, or many other silicates.

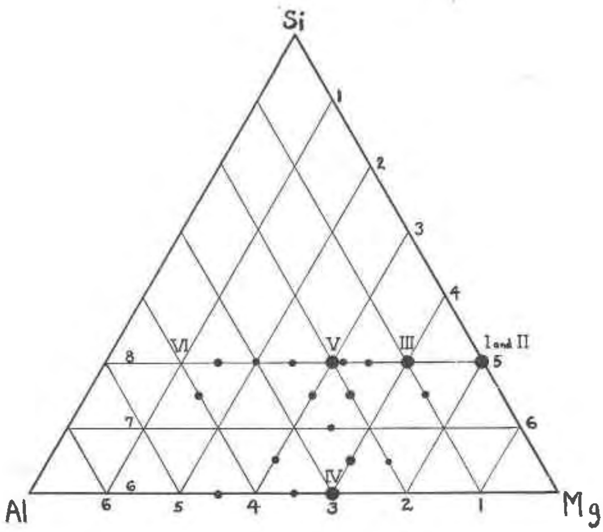

FIG. 1. Composition of the Amphiboles, Mg-Al-Si Ratios.

Fig. 1 gives the ratio of Mg:Al:Si on the assumption that in all amphiboles the sum of these three is constant. We have found that this relationship is true for the analyses we have examined. The deviation of the sum from thirteen is, we believe, within the limits of analytical error. The size of the circles representing the analyses is roughly proportional to the number of analyses falling at those positions. About half the analyses fall at four positions. Almost three-fourths of the analyses fall on the two horizontal lines indicating six and eight silicon atoms, respectively. From this diagram we can determine the most common amphibole types, which are relatively few in number. These are given in the table below.

The roman numerals in the diagram (Fig. 1) refer to the positions of the typical formulae with the corresponding numerals, given below. We have not indicated in the table the ferrous and ferric equivalents of the magnesium-aluminum formulae, since they are completely interchangeable. This accounts for the omission of well defined amphiboles such as hornblende, riebeckite and actinolite, which are simply iron equivalents of those given.

TABLE 1. TYPICAL AMPHIBOLE FORMULAE

I.	Tremolite	Ca_2		Mg_5		Si_8	O_{22}	$(OH)_2$
II.	Soda-Tremolite	Ca_1	Na_2	Mg_5		Si_8	O_{22}	$(OH)_2$
III.	Arfvedsonite		Na_3	Mg_4	Al_1	Si_8	O_{22}	$(OH)_2$
IV.	Hastingsite	Ca_2	Na_1	Mg_4	Al_1	$(Al_2\ Si_6)$	O_{22}	$(OH)_2$
V.	Glaucophane types		Na_2	Mg_3	Al_2	Si_8	O_{22}	$(OH)_2$
			Na_3	Mg_3	Al_2	Si_8	O_{23}	$(OH)_1$
		Ca_1	Na_2	Mg_3	Al_2	Si_8	O_{24}	
VI.	Glaucophane (?)		Na_2	Mg_1	Al_4	Si_8	O_{24}	

Mg and Fe^{II} are interchangeable
Al and Fe^{III} are interchangeable

Tremolite is one of the commonest of the amphiboles. An amphibole which is essentially a soda-tremolite has been analyzed in our laboratory. The analyses are, however, not entirely free from aluminum so that they fall between this soda-tremolite and arfvedsonite for which the third formula is proposed. This falls on one of the heavy dots of the preceding diagram. Hastingsite is the so-called deficient silica member. All our analyses agree very well with this formula of which a significant feature is the constant ratio of Ca:Na.

The glaucophane-riebeckite series has been found to vary considerably in the water and sodium contents. This variation is given in the three bracketed formulae. Most riebeckites correspond to the first, while many of the anhydrous amphiboles yield the third bracketed formula. The last formula represents a further variation of the anhydrous amphiboles, frequently called glaucophane.

This is conspicuous in having less magnesium than any of the other types.

While these formulae are not proposed as end members of the amphibole group, we believe that they truly represent the limiting cases in the variation of the compositions of the alkali amphiboles.

We conclude, then, that between types there is a rather limited miscibility, whereas, within the type complete isomorphism between magnesium and ferrous iron on the one hand, and aluminum and ferric iron on the other, may freely take place.

Our formulae differ from those of Kunitz mainly in that we believe that his fromulae have violated the structural requirements, as found by Warren. In our more complete study which is to follow, a fuller statement of the relationships between our formulae and those proposed by others, will be made.