

TWO REFINEMENTS FOR THE CALCULATION OF STRUCTURAL FORMULAE FOR PYROXENES AND AMPHIBOLES

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In minerals analyzed by electron microprobe, the ferric to ferrous iron ratio is not known. The advantages of calculating the structural formulae for these minerals on the basis of their number of cations rather than oxygens is discussed. A simple method for estimating the ferric to ferrous iron ratio for minerals with a fixed ratio of cations to oxygens is outlined.

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Today, most minerals are analyzed by the electron microprobe. As the electron microprobe does not provide a means of determining the ferric to ferrous iron ratio, calculation methods are most valuable.

With the large amounts of experimental data available that relate compositional variations to conditions of formation, it has also become increasingly important to be able to calculate structural formulae (and end-members) for the different minerals in ways that give the closest possible approximation to the true distribution of the cations between the various structural sites. Traditional methods of calculating structural formulae, however, depend upon known $\text{Fe}^{3+}/(\text{Fe}^{2+} + \text{Fe}^{3+})$ ratios.

Calculation methods

Pyroxenes

Structural formulae calculations are generally based on the assumption that the mineral contains a fixed number of anions per formula unit. This presents no problem if each element in the mineral is present in one valency state only. If an element, like iron, occurs in two valency states in the mineral, the relative proportions of the two will influence the total number of oxygens. If all the iron is considered to be divalent when in fact considerable trivalent Fe is present, then the total oxygen figure is too low ($\frac{1}{2}\text{O}$ is neglected per Fe^{3+}). Calculating the structural formula for the mineral on the basis of too few oxygens will strongly influence the distribution of cations between the structural positions.

In order to avoid this problem Hamm & Vieten (1971) have suggested that the formulae of pyroxenes should be calculated on the basis of the total number of cations instead of the total number of oxygens.

This is a very important suggestion. A falsely calculated distribution of

cations between tetrahedral and octahedral positions in pyroxenes will disturb the relative relations between the calculated amounts of aluminous and sodic end-members, Ca-Ts ($\text{CaAl}_2\text{SiO}_6$), Ti-Ts ($\text{CaTiAl}_2\text{O}_6$), jadeite ($\text{NaAlSi}_2\text{O}_6$), and acmite ($\text{NaFe}^{3+}\text{Si}_2\text{O}_6$). Since the concentrations of Ca-Ts and jadeite are very important clues to temperatures and pressures of formation (Kushiro 1969), this can be a serious error.

The traditional method for calculating ferric iron in pyroxenes is the following:

The structural formula is calculated on the basis of 6.0 oxygens.

$$\text{Fe}^{3+} = \text{Na} - (\text{Al}^{\text{IV}} - (\text{Al}^{\text{VI}} + 2\text{Ti})).$$

The calculation is reiterated until no further change in Fe_2O_3 is possible on the 0.1 percent level (Essene & Fyfe 1967, Mysen & Griffin 1973).

If the structural formulae for pyroxenes are calculated on the basis of the number of cations instead of number of oxygens, ferric iron may be calculated as the difference between actual positive charge (calculated from the amounts and valencies of the cations, assuming all iron to be ferrous), and the ideal charge (expected number of oxygens multiplied by two).

$$\text{Fe}^{3+} = |\text{ideal charge}| - \text{calculated charge}$$

$$\text{Fe}^{2+} = \text{Fe}_{\text{total}} - \text{Fe}^{3+}$$

The charge difference method suggested above has been tested against the Essene & Fyfe, Mysen & Griffin method on a wide variety of pyroxenes. The results from the two calculation methods are identical, and the *calculated* $\text{Fe}^{3+}/(\text{Fe}^{2+} + \text{Fe}^{3+})$ ratios are within 20 percent of the *analytical* values (Mysen & Griffin 1973). (Both methods assume stoichiometry.)

The advantages of the charge difference method are:

The method is extremely simple.

The method may be applied to any mineral with a fixed number of cations and a fixed number of oxygens.

The method may be used for minerals with more than one element in two valency states (for example Fe and Mn); the calculation will then give the sum of trivalent cations and the sum of divalent cations.

Amphiboles

The general formula of amphiboles can be expressed as $\text{W}_{0-1}\text{X}_2\text{Y}_5\text{Z}_8\text{O}_{22}(\text{OH},\text{O},\text{F})_2$, where W represents cations occupying the A-site; X and Y are octahedrally coordinated cations occupying the M4 and M1–M3 positions respectively. Z represents tetrahedrally coordinated small cations (Ernst 1962).

The influence of the valency state of iron on the structural formula is as important in amphiboles as in pyroxenes. The traditional method of calculating the structural formulae on the basis of 23 oxygens (neglecting the (OH,O,F)-group) will not only distort the distribution of Al between tetrahedral and octahedral sites (as in pyroxenes), but also influence the calculated A-site occupancy. Al^{IV} , Al^{VI} , and A-site filling are closely related to temperature, pressure, and F_2 , respectively (Ernst 1962, Holloway &

Burnham 1972, Helz 1973). In the complex amphiboles of intermediate compositions, important changes in Al^{IV}/Al^{VI} ratio or A-site filling may easily be masked by changes in the $Fe^{3+}/(Fe^{2+} + Fe^{3+})$ ratio. It is therefore important to find a method of calculating structural formulae for these minerals that is not dependent upon the valency state of iron. Because of possible vacancies in the A-sites, the method outlined for pyroxenes may not be used directly for amphiboles.

Mössbauer studies of amphiboles indicate the major elements have strong structural site preferences. In the calcic and sodic series, the M4 structural position is occupied by Ca and Na, whereas the M1–M3 positions are primarily occupied by Fe^{2+} , Mg, Fe^{3+} , Ti, and Al (Ernst 1970). The site preference of Mn^{2+} has not been investigated.

By plotting partition coefficients against ionic radii for hornblendes, Jensen (1973 and by pers. comm. (1975)) has shown that the optimal size of the M1–M3 structural sites is 0.78 Å, and that of the M4 site is 1.00 Å. (That of the A-site is about 1.45 Å.) Whereas Na is very differently distributed between the M4 and A-sites in different amphiboles, the ionic radius of about 0.90 Å seems to represent a divide (Fig. 1) between the 13.0 cations of smaller ionic radii falling in the tetrahedral or M1–M3 positions, and the 2–3 cations of larger radii falling in the M4 and A-sites.

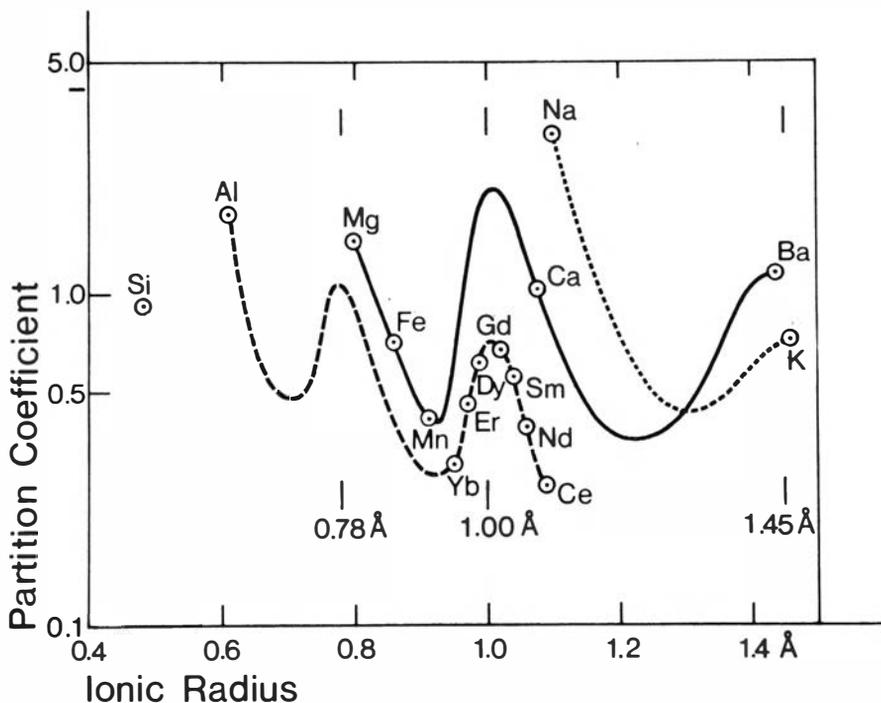


Fig. 1. Amphibole phenocrysts/matrix. Limburgite, Kakanui, N. Z. Plotted by B. B. Jensen on the basis of data from Schnetzler & Philpotts (1968). Ionic radii of Whittaker & Muntus (1970).

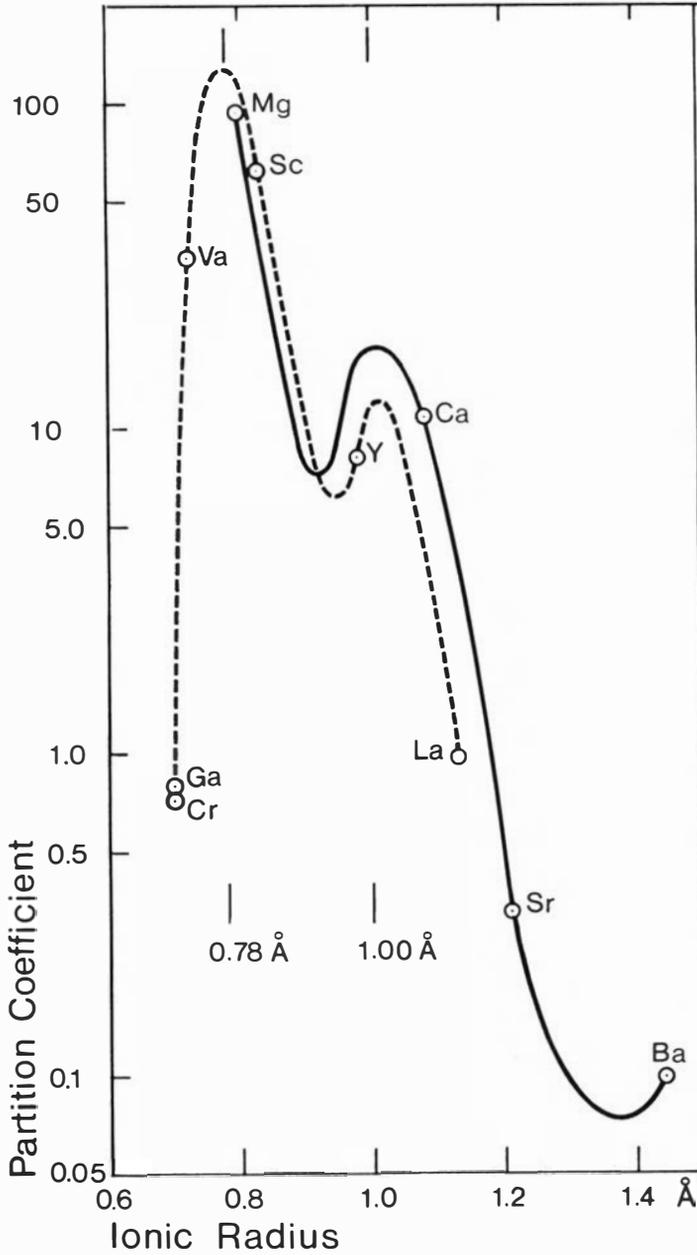


Fig. 2. Amphibole phenocrysts/matrix. Rhyolite lava, Taupo Volcanic Zone, N. Z. Data from Ewart & Taylor (1969). Ionic radii of Whittaker & Muntus (1970).

In hornblendes in mafic rocks such as basalts and dacites the differences between the peak heights for the M1–M3 and the M4 positions for each valency curve are small (Fig. 1) (Jensen 1973). In such amphiboles, Mn^{2+} , with an ionic radius of 0.91 Å (Whittaker & Muntus 1970), plots near the

centre of the trough between the M1–M3 and M4 peaks, and is thus about equally distributed between these positions. As manganese is a minor element in amphiboles from such rocks, a small deviation from the $\frac{1}{2}$ – $\frac{1}{2}$ distribution should only introduce minor errors.

In amphiboles in alkaline and silicic rocks, however, the M1–M3 peak is considerably higher than the M4 peak (Fig. 2). The great difference in peak height between the curves causes a shift of the divide between the peaks to a somewhat larger ionic radius. In such rocks it seems likely that all or most of the Mn^{2+} will fall in the smaller M1–M3 positions.

The observed difference between relative peak heights for amphiboles from mafic and silicic/alkaline rocks is due to the compositional differences between the rock types. Jensen (1973) has observed that increasing availability of an element that goes into a certain structural position in a mineral will cause a decrease in the partition coefficient mineral/matrix for that element. Mafic rocks are rich in calcium (M4), and magnesium and iron (M1–M3). Alkaline and silicic rocks are strongly enriched in alkalis (and calcium) compared to magnesium and iron. This causes strong competition for the M4 positions, and low partition coefficients element/matrix for the elements entering these positions, whereas the number of atoms competing for the M1–M3 positions is much less and the partition coefficients for the elements entering these positions are consequently high.

On the basis of the above discussion it is suggested that the structural formulae for calcic and sodic amphiboles should be calculated in the following ways:

For amphiboles from mafic and ultramafic rocks the structural formulae are calculated on the assumption that $(\text{Si} + \text{Al} + \text{Ti} + \text{Mg} + \text{Fe} + \frac{1}{2}\text{Mn}) = 13.0$ cations.

For amphiboles from alkaline and silicic rocks the structural formulae are calculated on the assumption that $(\text{Si} + \text{Al} + \text{Ti} + \text{Mg} + \text{Fe} + \text{Mn}) = 13.0$ cations.

The method has been tested on amphiboles from 23 alkaline and peralkaline plutonic rocks from the Oslo Region. The analyzed amphiboles include some Ti-poor kaersutites and magnesian arfvedsonites that appear to have full A-sites. Calculation of the structural formulae for these amphiboles assuming $\frac{1}{2}$ – $\frac{1}{2}$ distribution of Mn between the M1–M3 and the M4 structural sites gave a marked excess of cations over 1.0 in the A-site. Calculations based on the assumption that all Mn goes into the M1–M3 structural positions reduced the A-site filling to about 1.0 cation.

The structural formulae of orthoamphiboles, cummingtonites, and grunerites cannot be calculated in this way since smaller cations (Fe^{2+} , Mn^{2+} , etc.) are important constituents of the M4 position (Ernst 1962) in these amphiboles. They are probably best calculated on the basis of 15.0 cations.

The $\text{Fe}^{3+}/(\text{Fe}^{2+} + \text{Fe}^{3+})$ ratio may generally not be calculated by charge difference, as the total amount of $(\text{O} + \text{OH} + \text{F})$ varies considerably between different amphiboles (Deer et al. 1963).

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