# THE DISTRIBUTION OF MAJOR AND MINOR ELEMENTS AMONG SOME CO-EXISTING FERROMAGNESIAN SILICATES[1]

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## ABSTRACT

Co-existing chlorite, biotite, and hornblende from a schist have been analyzed spectrographically for major and minor constituents. It is found that the relative amounts of the elements in the three minerals can be explained by a consideration of electronegativities.

The amount of aluminium in the silicon positions seems to depend upon the relative electronegativities of the oxygens surrounding this site, which is in turn governed by the degree of polymerization in the silicate structure, and other structural differences. The extent to which aluminium replaces silicon in the tetrahedra influences the concentration of elements in the octahedral sites. The elements with similar electronegativities behave in a similar fashion. Cobalt, nickel, chromium, titanium, and vanadium are iron-like; manganese, zirconium, and scandium are more similar to magnesium.

The minerals used in this study were taken from a relatively small schist body in the Michipicoten District of Ontario. In the central portion of this schist is a zone of irregular quartz-scheelite veins. The schist is bordered on two sides by granodioritic masses. Portions of the schist are conglomeratic in appearance, suggesting a clastic origin.

The silicate minerals analyzed include biotite, hornblende, and chlorite. A study has also been made of the trace element distribution in the pyrite, and is discussed in the following paper (Nickel, 1954). Other minerals in the schist include quartz, calcite, albitic plagioclase, and minor epidote. Microcline is present locally.

It is suggested that the minerals were more or less in equilibrium with each other at the time of their formation and that, therefore, the distribution of a particular element approaches an equilibrium state as determined by the particular physico-chemical conditions at that time. It is generally true that the different structures of the silicate minerals distinguish between ions that exhibit dissimilar properties. Size and charge of the ion are major factors in determining its position in the structure but as Shaw (1953) has pointed out, these factors are not sufficient to adequately explain trace element distribution. Fyfe (1951) and Ramberg (1952) have suggested that electronegativity is of importance in governing the relative distribution of ions among various minerals.

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Electronegativity, a measure of the bond character of an atom, is considered to be a combination of the ionization potential and electron affinity of the atom (Fyfe, p. 538). In the succeeding pages the writer will endeavor to show the importance of this property in determining the distribution of some major and minor elements among co-existing chlorite, hornblende, and biotite.

The elements here considered are, of course, those that could be detected by spectrographic analysis, and only those are included that occur in tetrahedral and octahedral sites in the mineral structures. This excludes, then, elements such as potassium, calcium, and sodium. These large ions are not considered here because the amount of these elements is more or less fixed in certain of the minerals. Biotite, for example, requires one atom of potassium in its formula, while chlorite and hornblende do not generally have any of this element.

The electronegativity values to be used in the discussion have been obtained from Fyfe (1951) and are listed in Table 1.

TABLE 1. ELECTRONEGATIVITIES OF SOME ELEMENTS

| | | | |
|---|---|---|---|
| $Mg^{\cdot\cdot}$ | 1.2 | $V^{\cdot\cdot\cdot\cdot}$ | 1.6 |
| $Sc^{\cdot\cdot\cdot}$ | 1.3 | $Fe^{\cdot\cdot}$ | 1.65 |
| $Zr^{\cdot\cdot\cdot\cdot}$ | 1.4 | $Ni^{\cdot\cdot}$ | 1.7 |
| $Mn^{\cdot\cdot}$ | 1.4 | $Co^{\cdot\cdot}$ | 1.7 |
| Al | 1.5 | $Si^{\cdot\cdot\cdot\cdot}$ | 1.8 |
| $Cr^{\cdot\cdot\cdot}$ | 1.6 | $Fe^{\cdot\cdot\cdot}$ | 1.8 |
| $Ti^{\cdot\cdot\cdot\cdot}$ | 1.6 | O | 3.5 |

## PROCEDURES

The minerals for analysis were separated by means of a magnetic separator and heavy liquid methods.

The analyses were carried out spectrographically on a Jarrell-Ash 21-foot grating instrument with a D.C. arc source. A complete description of the analytical methods can be found in Nickel (1953), but a brief outline will be given here.

Separate burnings were made for the determination of the major and minor constituents. For the major element analysis, the silicate samples together with the internal standards—cobalt, molybdenum, and strontium—were fused with boric acid and lithium carbonate. The bead was crushed, mixed with graphite, and arced in a graphite electrode. Spectrum evaluation was carried out as described by Honerjaeger-Sohm & Kaiser (1944). For the minor constituents, the sample was mixed with palladium internal standard and graphite. This was pre-heated to drive the water from the hydrous silicates, then arced. Because of the considerable range of wavelengths of the spectrum lines used in the evaluation, the "bridge" or external standard method described by Kaiser (1944) was used. A pure iron spectrum was used as external standard.

For the purpose of better comparing the behavior of the cations in the silicate minerals analyzed, the weight percentages, as determined spectrographically, have been recalculated to atomic fractions of their sites in the mineral structures. The average values of these atomic fractions are given in Table 2.

TABLE 2. THE ATOMIC FRACTIONS OF THE ELEMENT SITES IN BIOTITE, HORNBLENDE AND CHLORITE

*(Average values from* 13 *biotite,* 13 *hornblende, and* 8 *chlorite analyses)*

| | *Biotite* | *Hornblende* | *Chlorite* |
|---|---|---|---|
| Al in tetrahedral position | 0.390 | 0.108 | 0.298 |
| Al in octahedral position | — | — | 0.160 |
| Fe in octahedral position | 0.298 | 0.200 | 0.207 |
| Mg in octahedral position | 0.631 | 0.733 | 0.533 |
| Co in octahedral position | $1.72 \times 10^{-4}$ | $1.16 \times 10^{-4}$ | $1.28 \times 10^{-4}$ |
| Ni in octahedral position | $2.20 \times 10^{-3}$ | $1.30 \times 10^{-3}$ | $1.95 \times 10^{-3}$ |
| Cr in octahedral position | $4.20 \times 10^{-3}$ | $1.05 \times 10^{-3}$ | $2.89 \times 10^{-3}$ |
| Ti in octahedral position | $2.16 \times 10^{-2}$ | $0.902 \times 10^{-2}$ | $0.484 \times 10^{-2}$ |
| V in octahedral position | $8.33 \times 10^{-4}$ | $5.00 \times 10^{-4}$ | $2.90 \times 10^{-4}$ |
| Mn in octahedral position | $3.78 \times 10^{-3}$ | $4.80 \times 10^{-3}$ | $3.17 \times 10^{-3}$ |
| Zn in octahedral position | $1.60 \times 10^{-4}$ | $2.29 \times 10^{-4}$ | $0.836 \times 10^{-4}$ |
| Sc in octahedral position | $0.324 \times 10^{-4}$ | $1.43 \times 10^{-4}$ | $0.086 \times 10^{-4}$ |

## SILICON AND ALUMINIUM

Aluminium can occupy both four and six coordinated positions in silicate structures. Reference to the generalized formulae of biotite—$K(Mg,Fe,Al)_3(Si,Al)_4O_{10}(OH)_2$, hornblende—$Ca_2(Mg,Fe,Al)_5(Si,Al)_8O_{22}(OH)_2$, and chlorite—$(Fe,Mg,Al)_3(Si,Al)_2O_5(OH)_4$ shows that the number of atoms in the tetrahedral (Si,Al) positions are four, eight, and two, respectively. Thus, if the total aluminium and silicon in these minerals is greater than the above values, some of the aluminium can be considered to be in octahedral coordination. The atomic fractions of aluminium and silicon in the biotite samples analyzed add up to approximately four, with few exceptions, showing that all or almost all of the aluminium in biotite is in tetrahedral coordination. In hornblende the aluminium and silicon atomic fractions add up to approximately eight, indicating that the same is true of this mineral. In chlorite, however, there is a considerable excess of aluminium and silicon atomic fractions over two. This excess is probably in octahedral sites in the chlorite.

In Table 2 the values of Al/Al&Si (for aluminium in tetrahedral position) are based on total aluminium for biotite and hornblende. In the case of chlorite, only that quantity is used that, together with silicon, adds up to an atomic fraction of two.

As can be seen from Table 2, both biotite and chlorite have a higher Al/Al&Si ratio than hornblende. There is a relationship between increasing polymerization in silicate structures and increasing tendency for aluminium to replace silicon (Ramberg, 1952). This is clearly shown by the analyses, since biotite and chlorite have sheet structures, and hornblende a double chain structure.

The reason for less aluminium in the tetrahedral positions of chlorite than in biotite can be explained by structural differences in these two minerals. *X*-ray diffraction analysis of the analyzed chlorite indicates that it has the McMurchy structure (the powder patterns exhibit a fairly strong 14 kX reflection). It can thus be considered to consist of alternating mica-like and brucite-like layers (Bragg, 1937). The degree to which aluminium replaces silicon depends on the relative electronegativity of the oxygens at the four corners of the tetrahedra (Ramberg 1952, p. 344). The most striking difference in the environment of these oxygen atoms in biotite and chlorite is that in biotite the oxygens forming the base of the polymerized sheet are weakly attached to potassium, whereas in chlorite they are bound to (OH). Now the electronegativity of (OH) is more similar to that of oxygen than is potassium, therefore in chlorite the O—OH bond is probably more covalent than the O—K bond in biotite. This will tend to make the basal oxygens of the sheet more electronegative in biotite than in chlorite, which in turn will make the tetrahedral site in biotite more favorable for aluminium than that in chlorite. This is indeed shown to be the case in the samples analyzed. The distribution of tetrahedrally coordinated aluminium and silicon depends, of course, on the bonding from layer to layer, which is in turn dependant on the distribution of divalent and trivalent cations in the two types of layers; the latter may in turn well be dependant on the aluminium-silicon relationships. In circular reasoning of this type one must begin somewhere, so the writer has here, as in the case of hornblende and biotite, started with the aluminium and silicon.

## IRON AND MAGNESIUM

The octahedral sites of hornblende, biotite, and chlorite can be occupied by magnesium, iron, and aluminium, as well as by most of the trace elements analyzed—namely chromium, nickel, cobalt, titanium, vanadium, manganese, zirconium, and scandium. The major elements will be considered first, because the behavior of the minor elements is largely influenced by that of the major ones.

H. Ramberg (1952) has shown that the replacement of silicon by aluminium will decrease the electronegativity of the non-bridging oxygen, resulting in an increase of the iron-magnesium ratio (p. 345). This same factor should also influence the amount of aluminium in six-fold position.

It was shown above that the aluminium in silicon position increases from hornblende to chlorite to biotite. This, then, would tend to progressively decrease the electronegativity of the oxygen atoms surrounding the octahedral sites in these minerals. Therefore hornblende, with its non-bridging oxygens having the highest electronegativity, would favor those cations of lowest electronegativity; biotite, on the other end of the scale, would be more likely to favor cations of high electronegativity. The cations under consideration have the following electronegativities: $\mathrm{Mg}^{\cdot\cdot}1.2$; $\mathrm{Al}^{\cdot\cdot\cdot}1.5$; and $\mathrm{Fe}^{\cdot\cdot}1.65$. Thus they should preferentially occupy the sites in hornblende, chlorite, and biotite, respectively.

This is the case in the samples analyzed. Biotite has a higher atomic fraction of iron than either hornblende or chlorite (Table 2); chlorite is the only mineral that contains appreciable aluminium in the octahedral site; and hornblende has a higher magnesium content than either biotite or chlorite (Table 2).

It is not certain which of these three cations is preferred by the brucite-like layer in chlorite. Since the octahedrally-coordinated aluminium is present in significant quantities only in the chlorite, which can be expected on the basis of the above reasoning applying to the mica-like layer, it appears, that the selective effect of the brucite-like layer is not very great, or is similar to that of the mica-like layer.

It is reasonable to expect the minor elements in six-fold coordination to behave like iron, magnesium, or aluminium, depending on their respective geochemical similarities to these elements. Figure 1 illustrates the relative amounts of these cations in the octahedral sites in biotite, chlorite, and hornblende (in chlorite this includes octahedral sites in both layers). The iron and magnesium values represented are the average values from Table 2, while the aluminium is the average octahedrally-located aluminium from Table 2, which was by subtracting tetrahedral aluminium from total aluminium. If only iron and magnesium were to be considered as governing the behavior of the minor elements, the iron-like ions should be highest in biotite, and equal in chlorite and hornblende (See Fig. 1). The magnesium-like elements should increase from chlorite through biotite to hornblende. But one would expect the aluminium content of chlorite to affect this distribution. If the iron-like elements are favorably affected by the presence of aluminium, their content in chlorite would probably be greater than that in hornblende; if unfavorably, then the reverse would be the case. The magnesium-like minor elements should behave in an analogous manner.

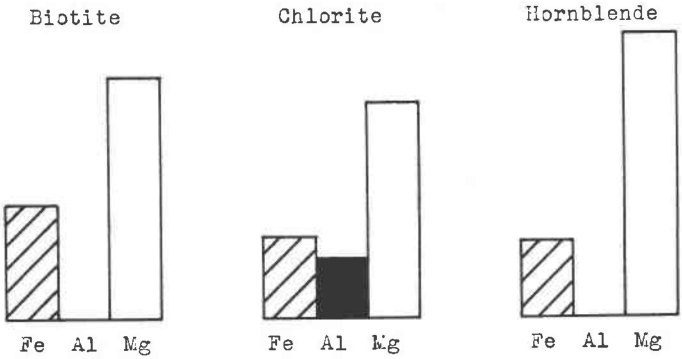

FIG. 1. Diagrammatic representation of relative amounts of iron, magnesium, and aluminium in six-fold coordination.

### COBALT, NICKEL AND CHROMIUM

Cobalt, nickel, and chromium behave similarly in that they are most abundant in biotite, least in hornblende, and intermediate in chlorite, as shown in Table 2. Their distribution, in part, parallels that of iron since they are highest in biotite. This is to be expected because of the similarity of the electronegativities of these elements: $Fe^{\cdot\cdot}$1.65; $Co^{\cdot\cdot}$1.7; $Ni^{\cdot\cdot}$1.7; and $Cr^{\cdot\cdot\cdot}$1.6. Since cobalt, nickel, and chromium are higher in chlorite than in hornblende, one must assume that the six-coordinated aluminium favors the presence of these ions more than does magnesium. The reason for this may well be that the electronegativity of aluminium (1.5) is closer to that of these minor elements than is that of magnesium (1.2).

### TITANIUM AND VANADIUM

Titanium and vanadium are probably present as tetravalent ions because these valence states are most common in rock-forming minerals (Rankama and Sahema, 1949). These elements have a relatively high concentration in biotite, and a lesser one in hornblende and in this way are similar to cobalt, nickel, chromium, and iron. The difference, however, is that chlorite contains less of these elements than does hornblende. Normally one would expect these elements to behave in a fashion analogous to that of iron, because of their similar electronegativities—1.65 for iron and 1.6 for both $Ti^{\cdot\cdot\cdot\cdot}$ and $V^{\cdot\cdot\cdot\cdot}$. It may be that these two elements, both having a high charge, may be less readily taken up by chlorite because it already contains a rather high proportion of trivalent aluminium in six-coordinated positions and it is necessary for the net charge to remain neutral. This might be accomplished by substituting more trivalent aluminium for tetravalent silicon but, as has been pointed out above, this substitution is somewhat limited in chlorite.

## MANGANESE, ZIRCONIUM AND SCANDIUM

The behavior of this group of elements is similar to that of magnesium. Manganese, zirconium, and scandium occur most abundantly in hornblende, less so in biotite, and least of all in chlorite. This is to be expected because the electronegativities of these ions is rather similar: $Mg^{\cdot\cdot}$1.2; $Mn^{\cdot\cdot}$1.4; $Zr^{\cdot\cdot\cdot\cdot}$1.4; and $Sc^{\cdot\cdot\cdot\cdot}$1.3.

Wager & Mitchell (1951) suggest that scandium and zirconium probably occupy calcium sites in minerals. This is rather difficult to evaluate in these analyses because hornblende contains the most calcium, as well as the most magnesium. It will be noted, however, that the manganese and zirconium contents are approximately a factor of two greater in hornblende than in the other two silicates. Scandium is up to ten times more abundant in hornblende than in chlorite and biotite, suggesting that scandium may replace calcium, whereas zirconium and manganese probably do not. This may be explained by the lower electronegativity of scandium, which is closer to that of calcium (1.0) than is zirconium.

## CONCLUSIONS

It has been shown that the electronegativities of the elements can be used to predict their distribution among the minerals in which they occur.

The degree to which silicon is replaced by aluminium in the silicon-oxygen tetrahedra appears to exert an important influence on the other structural sites in the minerals. Biotite has the most aluminium in the silicon position, hornblende the least, the chlorite an intermediate amount. This is explained by the effective electronegativities of the oxygens surrounding the tetrahedral sites. The hornblende structure is the least polymerized of these minerals, so that these oxygens have the smallest relative electronegativities of the three minerals. Chlorite has less aluminium than biotite because of the effect of the hydroxyl units on the electronegativity of the bridging oxygens.

The major elements capable of filling the octahedral sites (Fe, Mg, Al) are preferentially taken up by the minerals according to their electronegativities and that of the oxygen atoms surrounding the sites. Thus hornblende, whose octahedral oxygens have the greatest electronegativity, contains more electropositive magnesium than the other minerals. Biotite, whose oxygens have the smallest electronegativity value, contains the most iron, which has a high electronegativity. Chlorite contains the most aluminium, which has an intermediate electronegativity value.

The minor elements fall into groups having similar electronegativities and these behave according to the major element they most resemble. Thus cobalt, nickel, and chromium, with electronegativities similar to that of iron, are most abundant in biotite, the mineral richest in iron.

The enrichment of these elements in chlorite relative to hornblende is probably due to the effect of octahedrally coordinated aluminium in chlorite.

Titanium and vanadium are also richer in biotite than in the other two minerals, but are higher in hornblende than in chlorite. It is suggested that the high charge of these cations is responsible for this.

The behavior of manganese, zirconium, and scandium parallels that of magnesium. These elements have similar electronegativities.

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