

## DISTRIBUTION OF ELEMENTS BETWEEN COEXISTING MINERALS AND THE NATURE OF SOLID SOLUTION IN GARNET

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### ABSTRACT

Distribution of iron between coexisting biotite and hornblende supports some earlier conclusions regarding the complex nature of mixing among octahedrally coordinated ions in both the minerals. Distribution of iron and magnesium between garnet and coexisting orthopyroxene, hornblende or biotite is orderly and the distribution coefficients for such pairs of minerals are a function of  $p$  and  $T$  and of the concentration of Mn and Ca in garnet. The nature of the garnet solid solution formed by the mixing of  $\text{Fe}^{2+}$ , Mg, Mn and Ca depends on the  $p$  and  $T$  of formation: (1) In garnets of high grade rocks of the granulite facies,  $\text{Fe}^{2+}$ , Mg and Mn form a nearly ideal mixture and the role of Ca is mainly that of dilution; (2) In garnets of low grade rocks of the epidote-amphibolite facies  $\text{Fe}^{2+}$ , Mn and Ca tend to mix ideally but the role of Mg in such garnets could not be ascertained. Similarity of the size of ions is important at lower  $p$  and  $T$ , whereas, the similarity of the ionization potentials of the ions assumes importance at higher  $p$  and  $T$  in deciding the nature of the final solid solution. Because of the complex nature of solid solution, the composition of garnets alone does not indicate unambiguously the metamorphic grade of the host rocks of variable composition; but in an isochemical rock series, the ratio  $\text{Mg}/\text{Fe}^{2+}$ , along with the concentration of Ca in garnets containing little Mn, may roughly indicate the metamorphic grade.

### INTRODUCTION

The purpose of this paper is to show the nature of mixing of  $\text{Fe}^{2+}$ , Mg, Mn and Ca in garnet solid solution and to confirm an earlier result (Saxena, 1966) about the nature of mixing of the octahedrally coordinated ions in hornblende and biotite. This is done by studying the chemical data on garnets and other coexisting ferromagnesian minerals in rocks of varying metamorphic grade and chemical composition.

Chemical analysis of all coexisting minerals in Caledonian epidote-amphibolites from Rissa, Norway, has been made in selected samples by electron microprobe technique (Geoscan, Cambridge). The method is described in an Appendix. These data include analyses of eight garnets and mole fractions of total iron in the coexisting biotite and hornblende (Tables 1 to 3) with probable statistical errors. Similar data from Kretz (1959), Engel and Engel (1960), Buddington (1952), Kuroda and Ogura (1963), Banno (1964) and Ramberg (1949) are used to study the distribution of iron between garnet and biotite or hornblende (Table 4). Use of chemical data on coexisting garnet and orthopyroxene in granulite facies rocks (Howie and Subramaniam, 1957, Eskola, 1952), discussed before by Kretz (1961), is also made.

The following abbreviations are used: Gar-garnet, Bi-biotite, Horn-hornblende and Opx-orthopyroxene.

TABLE 1. CHEMICAL ANALYSES OF GARNETS FROM EPIDOTE-AMPHIBOLITE FACIES ROCKS, RISSA, NORWAY

| Ref. No.   | 1       | 2     | 3     | 4    | 5       | 6      | 7       | 10    |
|--|---------|-------|-------|------|---------|--------|---------|-------|
| Sample No.   | A/65-13 | S0    | S1    | S2   | T/65-16 | B/65-8 | H/65-11 | U65/7 |
| SiO <sub>2</sub>   | 36.4    | 37.0  | 37.35 | 37.8 | 37.2    | 37.1   | 37.2    | 36.0  |
| Al <sub>2</sub> O <sub>3</sub>                                       | 19.7    | 20.7  | 21.08 | 20.0 | 20.9    | 19.5   | 20.6    | 20.1  |
| TiO <sub>2</sub>   | 0.17    | 0.12  | 0.16  | 0.0  | 0.1     | 0.07   | 0.08    | 0.05  |
| Fe <sub>2</sub> O <sub>3</sub>                                       | —       | —     | 0.67  | —    | —       | —      | —       | —     |
| Total Fe as FeO  | 27.8    | 27.6  | 25.80 | 31.4 | 28.2    | 27.8   | 28.3    | 28.1  |
| MnO  | 2.40    | 0.30  | 1.86  | 1.80 | 0.96    | 1.60   | 0.29    | 0.89  |
| MgO  | 0.9     | 2.7   | 3.28  | 4.0  | 2.5     | 2.3    | 3.3     | 3.0   |
| CaO  | 8.5     | 9.4   | 8.79  | 1.6  | 7.7     | 8.0    | 7.8     | 8.3   |
| Total  | 95.87   | 97.82 | 98.99 | 96.6 | 97.56   | 96.37  | 97.57   | 96.54 |
| Maximum statistical error ( $\pm$ ) in the oxide values listed above |         |       |       |      |         |        |         |       |
| SiO <sub>2</sub>   | 0.05    | 0.08  | —     | 0.08 | 0.22    | 0.24   | 0.11    | 0.14  |
| Al <sub>2</sub> O <sub>3</sub>                                       | 0.23    | 0.04  | —     | 0.09 | 0.04    | 0.15   | 0.11    | 0.11  |
| Total Fe as FeO  | 0.18    | 0.04  | —     | 0.18 | 0.22    | 0.35   | 0.04    | 0.10  |
| MnO  | 0.05    | 0.007 | —     | 0.04 | 0.003   | 0.07   | 0.002   | 0.008 |
| MgO  | 0.04    | 0.03  | —     | 0.02 | 0.06    | 0.09   | 0.16    | 0.11  |
| CaO  | 0.38    | 0.016 | —     | 0.05 | 0.15    | 0.38   | 0.14    | 0.11  |

Sample 3 (S1) has been analysed by wet chemical method at the Central Analytical Laboratory of Uppsala University. Other samples have been analysed by electron micro-probe technique on Geoscan. Statistical error has been calculated from the difference in the maximum X-ray intensity value and the mean of the intensity values (3 to 10) from the sample. Geoscan operation as follows: angle of incidence of electrons 90°, energy of electrons 15 kV, angle of emergence of x rays 75°, specimen current 0.1  $\mu$  A, temperature of the laboratory  $\pm 2^\circ\text{C}$ .

### THEORETICAL ASPECTS

The relationship between the chemical potential and concentration of any species, *e.g.*, *A* in a mixture (*A*, *B*, *C*)*M* is

$$\mu_A = \mu_A^\circ + RT \ln f_A x_A$$

where *R* is the gas constant, *T* is absolute temperature, *f<sub>A</sub>* is the activity coefficient of *A*, *x<sub>A</sub>* is atomic ratio *A*/(*A*+*B*+*C*), and  $\mu_A^\circ$  is the chemical potential of *A* in a standard state. If in this mixture all the activity coefficients are unity for all values of *x*, the mixture is ideal. Though in a strict chemical sense, it is difficult to conceive of an ideal mixture in silicate minerals of complex composition, it is a very useful standard of reference. We can describe other mixtures in terms of ideality and suggest how close they are to an ideal model.

Garnet may be considered as a mixture (Mg, Fe<sup>2+</sup>, Mn, Ca)Al<sub>2/3</sub>SiO<sub>4</sub>. Similarity in ionization potential (I.P.) and ionic radius of the elements is the classic requirement for formation of a solid solution. The more similar the elements are in these characteristics, the more closely the solid solution is apt to approach ideality. Mole fraction of one of the four components, *e.g.* Fe<sup>2+</sup>, may be calculated as Fe<sup>2+</sup>/(Fe<sup>2+</sup>+Mg+Mn+Ca). As

TABLE 2. ATOMIC RATIOS OF IRON IN COEXISTING MINERALS OF RISSA ROCKS<sup>a</sup>

| Ref. No. | $X_{\text{Fe}}^{\text{Gar}}$ | $X_{\text{Fe}}^{\text{Horn}}$ | $X_{\text{Fe}}^{\text{Horn}'}$ | $X_{\text{Fe}}^{\text{Bi}}$ | $X_{\text{Fe}}^{\text{Bi}'}$ |
|----------|------------------------------|-------------------------------|--------------------------------|-----------------------------|------------------------------|
| 1        | 0.993                        | 0.641                         | 0.492                          | 0.561                       | 0.483                        |
| 2        | 0.850                        | 0.415                         | 0.384                          | —                           | —                            |
| 3        | 0.817                        | 0.527                         | 0.420                          | —                           | —                            |
| 4        | 0.813                        | —                             | —                              | 0.404                       | 0.332                        |
| 5        | 0.862                        | —                             | —                              | 0.451                       | 0.378                        |
| 6        | 0.870                        | 0.485                         | 0.386                          | 0.432                       | 0.379                        |
| 7        | 0.827                        | 0.480                         | 0.347                          | 0.421                       | 0.359                        |
| 8        | —                            | 0.584                         | 0.512                          | 0.522                       | 0.466                        |
| 9        | —                            | 0.432                         | 0.363                          | 0.385                       | 0.339                        |
| 10       | 0.839                        | —                             | —                              | 0.519                       | 0.426                        |

<sup>a</sup>  $X_{\text{Fe}}^{\text{Gar}}$  or  $X_{\text{Fe}}^{\text{Horn}}$  or  $X_{\text{Fe}}^{\text{Bi}} = \text{Fe}/(\text{Fe} + \text{Mg})$ ,  $X_{\text{Fe}}^{\text{Horn}'}$  or  $X_{\text{Fe}}^{\text{Bi}'}$  =  $\text{Fe}/(\Sigma \text{ octahedral ions})$ .  
Ref. Nos. 8 and 9 are sample numbers 12/64-1 and 17/6-2 respectively.

$\text{Fe}^{2+}$  and Mg are close to each other in their ionic characters, it may be advantageous to calculate partial mole fraction (Mueller, 1961) as  $\text{Fe}^{2+}/(\text{Fe}^{2+} + \text{Mg})$ . If one of the two remaining components, *e.g.* Ca, only has the effect of dilution, the influence of changing concentration of Mn may be noted by a large proportional departure of the distribution points from the distribution curve in Roozeboom diagrams (Kretz, 1961).

In Roozeboom diagrams, the mole fraction of a certain component in a mineral is plotted against the mole fraction of the same component in a coexisting mineral. Thus we may plot  $\text{Fe}/(\text{Fe} + \text{Mg})$  ratio in garnet against  $\text{Fe}/(\text{Fe} + \text{Mg})$  ratio in coexisting hornblende or biotite. If both

TABLE 3. PERCENT STATISTICAL ERRORS ( $\pm$ ) IN THE CHEMICAL ANALYSES

| Ref. No. | Biotite |                 | Hornblende |                 |
|----------|---------|-----------------|------------|-----------------|
|          | MgO     | Total Fe as FeO | MgO        | Total Fe as FeO |
| 1        | 2.22    | 0.20            | 2.58       | 1.30            |
| 2        | —       | —               | 1.42       | 0.80            |
| 3        | —       | —               | —          | —               |
| 4        | 3.33    | 1.43            | —          | —               |
| 5        | 0.30    | 1.26            | —          | —               |
| 6        | 2.13    | 2.12            | 0.99       | 1.21            |
| 7        | 2.97    | 5.19            | 2.33       | 2.43            |
| 8        | 1.24    | 0.47            | 0.29       | 1.07            |
| 9        | 1.60    | 0.66            | 3.43       | 0.80            |
| 10       | 3.21    | 0.26            | —          | —               |

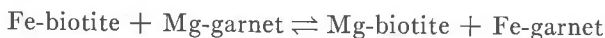
TABLE 4. ATOMIC RATIOS OF IRON IN COEXISTING MINERALS FROM ROCKS OF VARYING METAMORPHIC GRADE. DATA COLLECTED FROM LITERATURE<sup>a</sup>

| Ref. No. | $X_{\text{Fe}}^{\text{Gar}}$ | $X_{\text{Fe}}^{\text{Horn}}$ | $X_{\text{Fe}}^{\text{Horn}'}$ | $X_{\text{Fe}}^{\text{Bi}}$ | $X_{\text{Fe}}^{\text{Bi}'}$ | Remarks  |
|----------|------------------------------|-------------------------------|--------------------------------|-----------------------------|------------------------------|--|
| 1        | 0.930                        | 0.732                         | 0.672                          | 0.730                       | 0.629                        | Kretz (1959), all samples with total Fe, granulite facies. The original specimen numbers are 1 to 9, 14 to 19, 21, 22 and 25 respectively.   |
| 2        | 0.837                        | 0.578                         | 0.522                          | 0.557                       | 0.493                        |  |
| 3        | 0.834                        | 0.551                         | 0.500                          | 0.559                       | 0.498                        |  |
| 4        | 0.816                        | 0.518                         | 0.481                          | 0.474                       | 0.431                        |  |
| 5        | 0.805                        | 0.503                         | 0.466                          | 0.467                       | 0.447                        |  |
| 6        | —                            | 0.486                         | 0.445                          | 0.452                       | 0.384                        |  |
| 7        | —                            | 0.445                         | 0.428                          | 0.445                       | 0.389                        |  |
| 8        | —                            | 0.360                         | 0.345                          | 0.400                       | 0.340                        |  |
| 9        | 0.825                        | —                             | —                              | 0.593                       | 0.489                        |  |
| 10       | 0.801                        | 0.585                         | 0.549                          | 0.598                       | 0.514                        |  |
| 11       | 0.805                        | 0.538                         | 0.484                          | 0.519                       | 0.453                        |  |
| 12       | 0.827                        | 0.546                         | 0.494                          | 0.572                       | 0.468                        |  |
| 13       | —                            | 0.659                         | 0.602                          | 0.638                       | 0.551                        |  |
| 14       | —                            | 0.553                         | 0.505                          | 0.496                       | 0.457                        |  |
| 15       | —                            | 0.569                         | 0.528                          | 0.455                       | 0.412                        |  |
| 16       | 0.718                        | —                             | —                              | 0.483                       | 0.382                        |  |
| 17       | 0.783                        | —                             | —                              | 0.513                       | 0.398                        |  |
| 18       | 0.759                        | —                             | —                              | 0.500                       | 0.396                        |  |
| 19       | 0.789                        | —                             | —                              | 0.336                       | 0.244                        | Chinner (1960), upper amphibolite facies. Original specimen number 19. Engel and Engel (1960), amphibolite to granulite facies. Original specimen numbers are Qb-226, -228, -233, -100, Bgn-9, -14, -25, -18 and -21 respectively. |
| 20       | 0.753                        | —                             | —                              | 0.579                       | 0.376                        |  |
| 21       | 0.815                        | —                             | —                              | 0.556                       | 0.428                        |  |
| 22       | 0.756                        | —                             | —                              | 0.488                       | 0.352                        |  |
| 23       | 0.714                        | —                             | —                              | 0.595                       | 0.486                        |  |
| 24       | 0.766                        | —                             | —                              | 0.473                       | 0.353                        |  |
| 25       | 0.760                        | —                             | —                              | 0.551                       | 0.427                        |  |
| 26       | 0.721                        | —                             | —                              | 0.432                       | 0.351                        |  |
| 27       | 0.680                        | —                             | —                              | 0.406                       | 0.302                        |  |
| 28       | 0.675                        | —                             | —                              | 0.434                       | 0.341                        |  |
| 29       | 0.866                        | —                             | —                              | 0.529                       | 0.418                        | Green (1963), sillimanite zone. Original specimen numbers are D-2, ER-101b and ER-142 respectively.  |
| 30       | 0.867                        | —                             | —                              | 0.516                       | 0.413                        |  |
| 31       | 0.898                        | —                             | —                              | 90.53                       | 0.412                        | Buddington (1952), granulite facies. Original numbers are 7 to 10 respectively.  |
| 32       | 0.669                        | 0.406                         | 0.310                          | —                           | —                            |  |
| 33       | 0.636                        | 0.403                         | 0.304                          | —                           | —                            |  |
| 34       | 0.622                        | 0.420                         | 0.311                          | —                           | —                            | Kuroda and Ogura (1963), epidote-amphibolite facies. Original numbers are 3, 5 and 6 respectively.   |
| 35       | 0.487                        | 0.269                         | 0.212                          | —                           | —                            |  |
| 36       | 0.728                        | 0.345                         | 0.272                          | —                           | —                            |  |
| 37       | 0.773                        | 0.358                         | 0.255                          | —                           | —                            |  |
| 38       | 0.676                        | 0.347                         | 0.267                          | —                           | —                            |  |
| 39       | 0.833                        | 0.275                         | 0.236                          | —                           | —                            |  |
| 40       | 0.788                        | 0.524                         | 0.443                          | —                           | —                            | Ramberg (1949), granulite facies. Original specimen number is 37218.   |

<sup>a</sup>  $X_{\text{Fe}}^{\text{Gar}}$  or  $X_{\text{Fe}}^{\text{Horn}}$  or  $X_{\text{Fe}}^{\text{Bi}} = \text{Fe}^{2+}/(\text{Mg} + \text{Fe}^{2+})$ ,  $X_{\text{Fe}}^{\text{Horn}'}$  or  $X_{\text{Fe}}^{\text{Bi}'}$  =  $\text{Fe}^{2+}/(\Sigma \text{octahedral ions})$ .

In samples 1 to 18 only total Fe is available.

garnet and biotite are ideal binary mixtures of Fe and Mg, the distribution points describe a smooth symmetric curve with a constant distribution coefficient, provided chemical equilibrium has been closely approached at a certain defined  $p$  and  $T$ . The ion exchange equilibrium reaction is written as



and the distribution coefficient is given by

$$\frac{x_{\text{Fe}}^{\text{Gar}}}{1 - x_{\text{Fe}}^{\text{Gar}}} \cdot \frac{1 - x_{\text{Fe}}^{\text{Bi}}}{x_{\text{Fe}}^{\text{Bi}}} = K_{\text{D}(\text{Fe})}^{\text{Gar-Bi}}$$

where  $x_{\text{Fe}}$  is the mole fraction  $\text{Fe}/(\text{Fe} + \text{Mg})$ . If one of the two minerals is not an ideal binary mixture, the  $K_{\text{D}}$  value will not be constant and the distribution points will depart from the ideal curve.

In Roozeboom diagrams with  $\text{Fe}/(\text{Fe} + \text{Mg})$  in hornblende or biotite plotted against a similar ratio in garnet, there may be scattering first because of the influence of the concentration of a third element in hornblende or biotite (Kretz, 1959) and secondly because of the influence of Mn or Ca in garnet or the departure of garnet from ideality. One can minimize the scattering by using the atomic ratio  $\text{Fe}/(\sum \text{octahedrally coordinated ions})$  in hornblende or biotite (Saxena, 1966) but a suitable ion exchange equilibrium reaction cannot be written.

#### DISTRIBUTION OF IRON BETWEEN COEXISTING BIOTITE AND HORNBLLENDE

Figure 1 shows distribution points for five new coexisting pairs of biotite and hornblende from Rissa rocks and for several other samples, including those of the granulite facies (Kretz, 1959) and of the epidote-amphibolite facies (Saxena, 1966 and Ogura, 1958). Mole fraction  $x_{\text{Fe}}^{\text{Horn}}$  ( $= \text{Fe}^{2+}$  or total  $\text{Fe}/\sum \text{octahedral ions}$ ) plotted against a similarly calculated mole fraction  $x_{\text{Fe}}^{\text{Bi}}$  show that there is no difference between the loci of the distribution points for granulite facies and for epidote-amphibolite facies and the following distribution law is approximately followed:

$$\frac{x_{\text{Fe}}^{\text{Bi}}}{1 - x_{\text{Fe}}^{\text{Bi}}} \cdot \frac{1 - x_{\text{Fe}}^{\text{Horn}}}{x_{\text{Fe}}^{\text{Horn}}} = K_{\text{D}(\text{Fe})}^{\text{Bi-Horn}} = 0.9$$

The locus of the points do, however, shift as a function of the chemical concentration of Al in biotite. Ogura's samples (1-4) have a higher con-

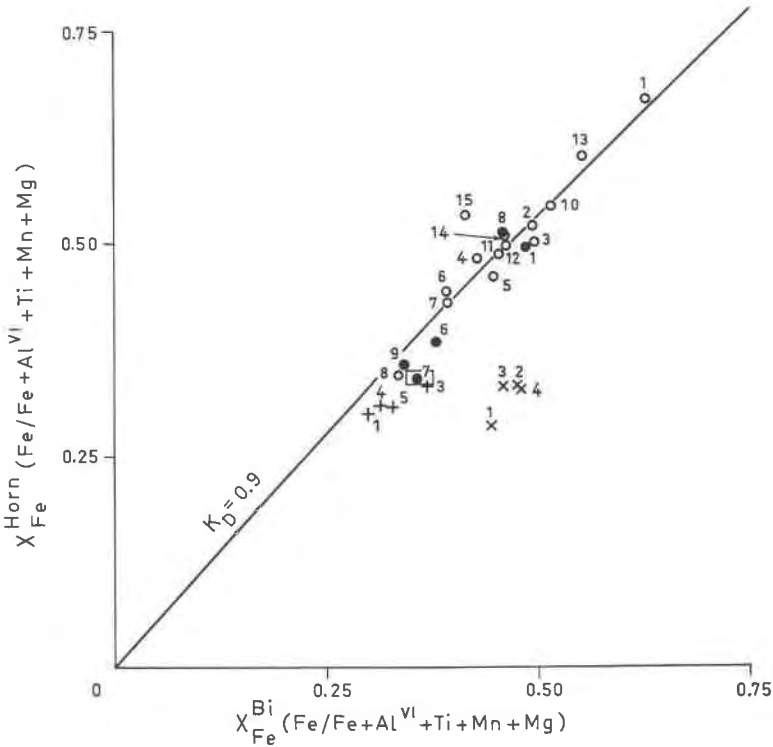


FIG. 1. Distribution of iron between coexisting biotite and hornblende in rocks of various metamorphic grades. Solid circles—samples from Rissa, Norway (Table 2), open circles—samples from various rocks listed in Table 4, plus signs—other Caledonide samples of epidote-amphibolite facies (Saxena, 1966), crosses—epidote-amphibolite facies rocks from Japan (Ogura, 1958). The mole fractions from the last two sources involve Fe<sup>2+</sup>. In all others total Fe is used. Statistical error of chemical analysis, which is mainly because of the inhomogeneity of the mineral grain, is large in sample 7 (solid circle) and is shown by a rectangle around the distribution point. The distribution curve is a solution to the equation:

$$\frac{\frac{x_{Fe}^{Bi}}{1 - x_{Fe}^{Bi}}}{1 - \frac{x_{Fe}^{Horn}}{x_{Fe}^{Horn}}} = 0.9 \text{ (average } K_D)$$

centration of tetrahedral Al in biotite, which influences the Fe<sup>2+</sup>/Mg ratio in the mineral (Ramberg, 1952) and hence the *K<sub>D</sub>* values.

DISTRIBUTION OF IRON BETWEEN GARNET AND ORTHOPYROXENE,  
HORNBLLENDE OR BIOTITE

*Garnet-orthopyroxene.* Kretz (1961) noted that besides *p* and *T*, the dis-

tribution coefficient for the distribution of iron between the two minerals is also a function of Mn in garnet. The data on six coexisting pairs of garnet and orthopyroxene from rocks of granulite facies (Table 5) show that  $K_{D(\text{Fe})}^{\text{Gar}-\text{Opx}}$  is uniform in the first three samples (9, 10 and Ch 113) which have little Mn in garnets. In other samples,  $K_D$  varies as a function of the concentration of Mn in garnet. If we calculate another mole frac-

TABLE 5. COMPOSITION OF GARNETS, MOLE FRACTIONS OF FE IN GARNET AND COEXISTING ORTHOPYROXENES IN ROCKS OF GRANULITE AND THEIR DISTRIBUTION COEFFICIENTS

| Ref.<br>No. | Ions in garnets for 12 O |       |                  |       | $X_{\text{Fe}}^{\text{Opx}}$ | $X_{\text{Fe}}^{\text{Gar}}$ | $K_{D(\text{Fe})}^{\text{Gar}-\text{Opx}}$ | $X_{\text{Fe}}^{\text{Gar}'}$ | $K_{D(\text{Fe})}^{\text{Gar}'-\text{Opx}}$ |
|-------------|--------------------------|-------|------------------|-------|------------------------------|------------------------------|--|-------------------------------|---|
|             | Ca                       | Mg    | Fe <sup>2+</sup> | Mn    |                              |                              |  |                               |   |
| 9           | 0.150                    | 1.356 | 1.577            | 0.041 | 0.36                         | 0.54                         | 2.1  | 0.54                          | 2.1   |
| 10          | 0.228                    | 1.080 | 1.668            | 0.041 | 0.40                         | 0.60                         | 2.3  | 0.60                          | 2.3   |
| Ch 113      | 0.187                    | 0.913 | 1.835            | 0.042 | 0.48                         | 0.66                         | 2.2  | 0.66                          | 2.2   |
| Ch 199      | 0.608                    | 0.443 | 1.833            | 0.071 | 0.58                         | 0.81                         | 3.1  | 0.78                          | 2.6   |
| S 347       | 0.570                    | 0.371 | 1.886            | 0.090 | 0.55                         | 0.84                         | 4.3  | 0.80                          | 3.3   |
| V 2         | 0.609                    | 0.148 | 2.059            | 0.150 | 0.73                         | 0.93                         | 5.0  | 0.87                          | 2.4   |

Chemical data: 9, 10 (Eskola, 1952), rest of the samples (Howie and Subramaniam, 1957).  $X_{\text{Fe}}^{\text{Opx}}$  or  $X_{\text{Fe}}^{\text{Gar}} = \text{Fe}^{2+}/(\text{Fe}^{2+} + \text{Mg})$ . Note that  $K_{D(\text{Fe})}^{\text{Gar}-\text{Opx}}$  varies as a function of Mn in garnet (see also Kretz, 1961).  $K_{D(\text{Fe})}^{\text{Gar}'-\text{Opx}}$  recalculated with  $X_{\text{Fe}}^{\text{Gar}'}$  as  $\text{Fe}^{2+}/(\text{Fe}^{2+} + \text{Mg} + \text{Mn})$  is rather similar in all the samples.

tion of Fe in garnet ( $x_{\text{Fe}}^{\text{Gar}'}$ ) as  $\text{Fe}^{2+}/(\text{Fe}^{2+} + \text{Mg} + \text{Mn})$  and recalculate  $K_{D(\text{Fe})}^{\text{Gar}'-\text{Opx}}$ , we find the following distribution law:

$$\frac{x_{\text{Fe}}^{\text{Gar}'}}{1 - x_{\text{Fe}}^{\text{Gar}'}} \cdot \frac{1 - x_{\text{Fe}}^{\text{Opx}}}{x_{\text{Fe}}^{\text{Opx}}} = K_{D(\text{Fe})}^{\text{Gar}'-\text{Opx}} = 2.5 \text{ (average)}$$

where  $x_{\text{Fe}}^{\text{Opx}}$  continues to be  $\text{Fe}^{2+}/(\text{Fe}^{2+} + \text{Mg})$  because the concentration of Mn in orthopyroxene is small. In five of the samples the distribution coefficient may be regarded as similar. Changing concentration of Ca does not influence the distribution coefficient. This suggests that  $\text{Fe}^{2+}$ , Mg and Mn tend to form nearly ideal mixtures in the garnet solid solution. The influence of Ca is mainly one of dilution.

*Garnet-hornblende.* In Figure 2 the mole fraction  $\text{Fe}/(\text{Fe} + \text{Mg})$  in garnet has been plotted against the mole fraction  $\text{Fe}/(\sum \text{octahedrally coordinated ions})$  in hornblende. The distribution curves for the ideal mixtures have been drawn with  $K_{D(\text{Fe})}^{\text{Gar}-\text{Horn}}$  as 9.0 for the samples of the epidote-

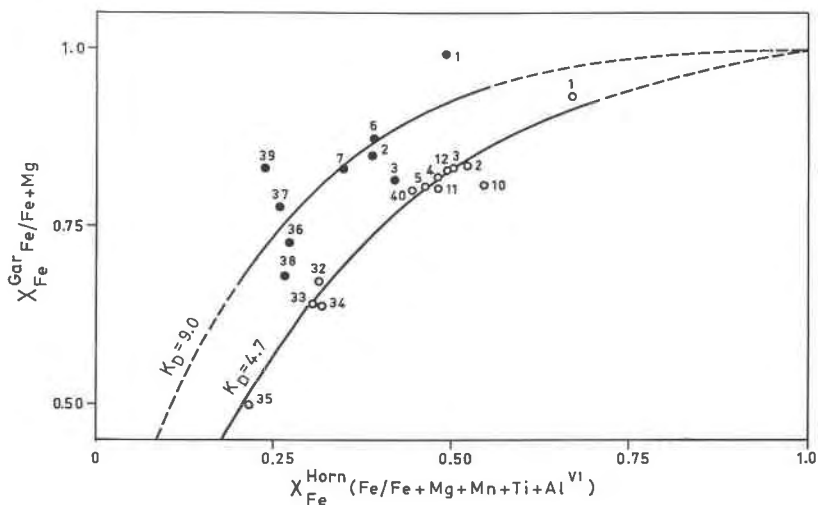


FIG. 2. Distribution of iron between coexisting garnet and hornblende in rocks of epidote-amphibolite facies and granulite facies. Samples of the granulite facies (open circles) lie on or close to a symmetric distribution curve which is drawn to follow the equation

$$\frac{\frac{\text{Gar}}{x_{\text{Fe}}} \quad 1 - \frac{\text{Horn}}{x_{\text{Fe}}}}{1 - \frac{\text{Gar}}{x_{\text{Fe}}} \quad \frac{\text{Horn}}{x_{\text{Fe}}}} = 4.7.$$

Samples of the epidote-amphibolite facies are scattered but a distribution curve may be drawn with average  $K_D$  as 9.0. Shift of the distribution coefficient from one curve to the other is a function of  $p$  and  $T$ , but the scattering in samples of the epidote-amphibolite facies is mainly a function of variable Ca and Mn in garnet and variable content of Al in hornblende. (Data in Tables 1, 2, 4 and 6).

amphibolite facies (average of samples 2, 6 and 7 Table 2) and as 4.7 for the samples of the granulite facies (average of all the samples of this facies, Table 4). The distribution points for the granulite facies lie on or close to the symmetric curve which indicates that Fe and Mg tend to mix ideally in garnet. In most of these garnets the concentration of Mn is small. Some of Kretz's samples have variable concentrations of Mn, which could have influenced the  $K_D$  values but this influence is not noted here. As these chemical analyses show only total Fe it is difficult to evaluate these samples.

The distribution points for the epidote-amphibolite facies are rather scattered. The scattering in the distribution points for two Rissa samples (1 and 3) is discussed later. A possible cause for the departure of the remaining samples from a single  $K_D$  value may be the influence of varying concentrations of Mn and Ca in garnet. The data (Table 6) show that



concentration of Mg in the garnets is more or less similar. The main variation is among the concentrations of Mn, Ca and Fe<sup>2+</sup>.  $K_{D(Fe)}^{Gar-Horn}$  increases as the concentration of Ca increases or as the concentration of Mn decreases in garnet. Thus in these low grade metamorphic rocks,  $K_{D(Fe)}^{Gar-Horn}$  appears to be influenced by the concentration of Ca in garnet and the role of Ca is not only one of dilution as in the case of high grade metamorphic rocks. Recalculated mole fraction of Fe in garnet as Fe/(Fe+Mn+Ca) and new  $K_D$  values are also listed in Table 6. The irregularity in the distribution coefficients is more likely caused by varia-

TABLE 6. COEFFICIENTS FOR DISTRIBUTION OF FE BETWEEN COEXISTING GARNET AND HORNBLLENDE AND CONCENTRATION OF IONS IN GARNETS IN ROCKS OF EPIDOTE-AMPHIBOLITE FACIES (SEE FIG. 2)<sup>a</sup>

| Ref. No. | $K_{D(Fe)}^{Gar-Horn}$ | Proportion of ions in garnet |       |                  |       | Ref. No. | $K_{D(Fe)}^{Gar'-Horn}$ | Octahedral Al in hornblende <sup>b</sup> |
|----------|------------------------|------------------------------|-------|------------------|-------|----------|-------------------------|--|
|          |                        | Mn                           | Ca    | Fe <sup>2+</sup> | Mg    |          |                         |  |
| 38       | 3.18                   | 0.435                        | 0.140 | 0.288            | 0.137 | 38       | 1.4                     | 0.38                                     |
| 36       | 5.08                   | 0.310                        | 0.206 | 0.367            | 0.137 | 36       | 1.9                     | 0.60                                     |
| 37       | 5.19                   | 0.271                        | 0.219 | 0.394            | 0.116 | 37       | 2.2                     | 0.62                                     |
| 7        | 9.0                    | 0.006                        | 0.226 | 0.634            | 0.134 | 2        | 3.7                     | 0.86                                     |
| 2        | 9.0                    | 0.006                        | 0.270 | 0.614            | 0.110 | 6        | 3.8                     | 0.98                                     |
| 6        | 10.6                   | 0.036                        | 0.235 | 0.634            | 0.095 | 39       | 4.7                     | 0.53                                     |
| 39       | 16.14                  | 0.052                        | 0.300 | 0.538            | 0.110 | 7        | 5.0                     | 1.43                                     |

<sup>a</sup> Samples 36-39 (Table 4), 2, 6 and 7 (Table 2). Samples 1 and 3 (Table 2, Fig. 2) have not been considered here since they probably represent nonequilibrium.  $K_{D(Fe)}^{Gar-Horn}$  where  $X_{Fe}^{Gar}$  is Fe/(Fe+Mg), varies as a function of Ca and Mn in garnet.

<sup>b</sup> On the right values of  $K_{D(Fe)}$  have been recalculated as  $K_{D(Fe)}^{Gar'-Horn}$ , where  $X_{Fe}^{Gar'}$  is Fe/(Fe+Ca+Mn), and, rearranged to show that concentration of octahedral Al in hornblende influences them.

tions in the intensive parameters which affect the mole fraction of Fe in hornblende. One such probability is shown in Table 6, where the distribution coefficient may be correlated approximately with the concentration of Al in the octahedral sites in hornblende. One sample is irregular. Samples 1 and 3 (Rissa rocks) are not listed in this table because work in progress shows that there may be lack of diffusion equilibrium with respect to Fe and Mg in these samples. It is possible that the mixture of Fe, Mn and Ca in garnet tends to be ideal in low grade rocks. As the concentration of Mg in these garnets does not vary significantly, it is difficult to ascertain its role in the mixture.

*Garnet-biotite.* The distribution of iron between biotite and garnet has been shown in Figure 3. It is noted that the distribution points are some-

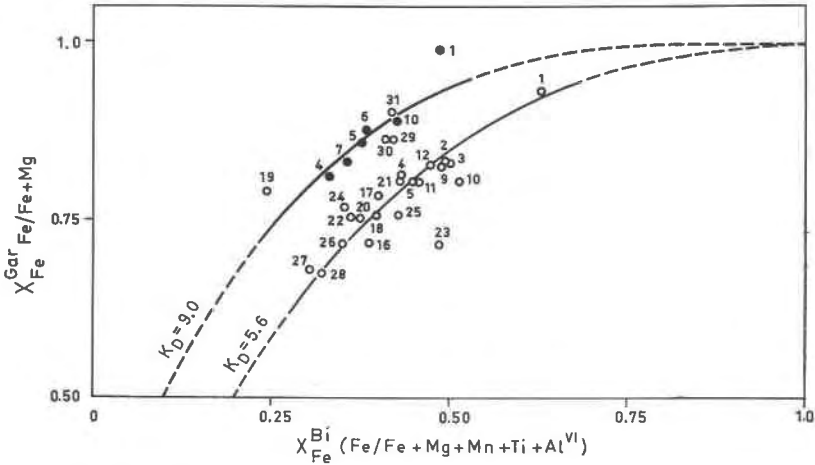


FIG. 3. Distribution of iron between coexisting garnet and biotite in rocks of epidote-amphibolite facies (Rissa, solid circles) and upper amphibolite to granulite facies (open circles). The two metamorphic environments are represented by two symmetric distribution curves, produced by changes of the distribution coefficient as a function of  $p$  and  $T$ . Scatter in samples 19, 29, 30 and 31 is a result of the variation in the concentration of Mn in garnets, but a large shift in the distribution points for samples 29–31 may also be due to a retrograde reaction. (Data in Tables 1, 2, 4 and 7.) The curves have been drawn according to the relations:

$$\frac{\frac{X_{Fe}^{Gar}}{X_{Fe+Mg}} \cdot 1 - \frac{X_{Fe}^{Bi}}{X_{Fe+Mg}}}{1 - \frac{X_{Fe}^{Gar}}{X_{Fe+Mg}} - \frac{X_{Fe}^{Bi}}{X_{Fe+Mg}}} = 9.0 \text{ or } 5.6 \text{ (average values of } K_D\text{)}.$$

what scattered but still define two distinct loci of points—two symmetric curves with different  $K_D$  values. Five of the Rissa samples lie on a curve with  $K_{D(Fe)}^{Gar-Bi}$  approximately equal to 9.0, defining the lower  $p$  and  $T$  (epidote-amphibolite facies) trend. Most of the samples of higher  $p$  and  $T$  (upper amphibolite to granulite facies) lie on a curve with  $K_{D(Fe)}^{Gar-Bi}$  approximately equal to 5.6.

The scatter of the points may be examined in relation to the variability of Mn and Ca in garnet as was done in the previous sections. The samples which depart most are 1 (Rissa, epidote-amphibolite) and 19, 29–31 and 23 (granulite facies). The data in Table 7 show the variation in  $K_D$  in samples 19, 29, 30 and 31 with the concentration of Mn in garnets. The correlation is good for the first three samples but not for the last one (Table 7). Further consideration shows that in samples 29–31 the  $K_D$  values depart too widely from the other Adirondack samples 20–28 (Table 4), which belong to granulite and upper amphibolite facies and have  $K_D$  as  $5 \pm 1$ . This departure may be due to variation in some of the

intensive variables. Green (1963) states that in these rocks (samples 29–31) retrograde metamorphism has altered some of the andalusite and staurolite and added chlorite to many assemblages. 'The mineral assemblages generally contain too many phases according to the phase rule, the excess being attributed to one or more of the following: retrograde reactions, incomplete mobility of H<sub>2</sub>O, or restricted volume of chemical equilibrium.' It is likely that the high value of  $K_D$  in sample 19 is mainly due to the concentration of Mn in garnets. There are two other samples (20–21) which contain significant concentration of Mn in garnet and yet do not show large deviation from the distribution constant. Also we cannot understand why sample 23 departs so widely. However, the overall correlation of  $K_D$  with either the metamorphic grade of the rocks or con-

TABLE 7. COEFFICIENTS FOR DISTRIBUTION OF FE BETWEEN GARNET AND BIOTITE AND CONCENTRATION OF OTHER IONS IN GARNET IN CERTAIN HIGH GRADE ROCKS FOR WHICH THE DISTRIBUTION POINTS DEPART FROM THE DISTRIBUTION CURVE IN FIG. 3

| Ref. No. | $K_{D(Fe)}^{Gar-Bi}$ | Proportion of ions in garnet |       |                  |       |
|----------|----------------------|------------------------------|-------|------------------|-------|
|          |                      | Mn                           | Ca    | Fe <sup>2+</sup> | Mg    |
| 29       | 8.99                 | 0.085                        | 0.061 | 0.739            | 0.115 |
| 30       | 9.26                 | 0.105                        | 0.059 | 0.726            | 0.110 |
| 31       | 12.56                | 0.154                        | 0.035 | 0.729            | 0.082 |
| 19       | 11.24                | 0.265                        | 0.047 | 0.543            | 0.145 |

centration of Mn in garnet is significant, particularly in view of the complex nature of mixing of Fe and Mg or other octahedrally coordinated ions in the coexisting biotites.

#### NATURE OF SOLID SOLUTION IN GARNET

We have not been able to explain the departure of some of the distribution points in both the diagrams (Figs. 2 and 3). Further in Table 1 it may be noted that sample 4 (S<sub>2</sub>) is very poor in Ca and yet the distribution point does not depart from the distribution curve in Figure 3. Most of such ambiguities are due to the fact that we have tried to treat garnet in the previous sections as a ternary mixture. We calculated partial mole fractions and explained the shift in  $K_D$  due to the influence of the concentration of either Mn or Ca. However garnet is a mixture of four components and if none of the components is in dilute concentration, the dependence of  $K_D$  on composition becomes complex. The following discussion would justify our simplifications of the previous sections.

The results of the previous sections indicate a tendency for the ions  $\text{Fe}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Mn}^{2+}$  and  $\text{Ca}^{2+}$  to mix differently in the garnet solid solution at low and high  $p$  and  $T$ . The data in Table 7 are for those samples which show a large departure from the distribution curve in Figure 3. One reason for this departure is shown to be the varying concentration of Mn in garnet. In the remaining samples (except 20–21), concentration of Mn in garnet is low. Therefore  $K_D$  is not influenced. The inference of this result together with the result in Table 5 is that in garnet of high grade rocks, the mixture of  $\text{Fe}^{2+}$ , Mg and Mn is nearly ideal and Ca has mainly a dilution effect.

Distribution coefficients  $K_{D(\text{Fe})}^{\text{Gar-Horn}}$  change as a function of the concentrations of Ca and Mn in garnets of epidote-amphibolite facies (Table 6). The data in Table 6 give indications that  $\text{Fe}^{2+}$ , Mn and Ca components in garnet tend to be more similar in their behaviour in low-grade rocks.

Statistical theory predicts that mixtures of two very similar species will be ideal (Guggenheim, 1950). It is possible to compare the character of ions with the help of ionic size and ionization potential.

|                 | $\text{Mg}^{2+}$ | $\text{Fe}^{2+}$ | $\text{Mn}^{2+}$ | $\text{Ca}^{2+}$ |
|-----------------|------------------|------------------|------------------|------------------|
| $r(\text{\AA})$ | 0.65             | 0.75             | 0.80             | 0.99             |
| $IP$ (eV)       | 14.96            | 16.16            | 15.70            | 11.82            |

It is interesting to note that  $\text{Fe}^{2+}$ , Mg and Mn are similar in IP and Ca has a much lower IP.  $\text{Fe}^{2+}$ , Mn and Ca are closer in ionic size and Mg is smaller. This suggests the relative importance of ionic size and IP of the ions in forming solid solutions under low and high  $p$  and  $T$  respectively.

The above considerations show the following probabilities. Spessertite and almandine would mix ideally at all  $p$  and  $T$ . Almandine and pyrope would approach ideal mixing closely and the deviations would not ordinarily be significant, especially at high pressure and temperature. Spessertite and grossularite might approach ideal mixing at lower  $p$  and  $T$  only. The departure from ideality at higher  $p$  and  $T$  would be large. Pyrope and grossularite would not mix ideally at lower  $p$  and  $T$ , but at higher  $p$  and  $T$ , they might show a tendency of mixing ideally. Pyrope and spessertite would mix ideally at higher  $p$  and  $T$  but their mixture would deviate to some extent from ideality at lower  $p$  and  $T$ . Mixture of almandine and grossularite would show a tendency towards ideality at lower  $p$  and  $T$  but would deviate greatly from ideality at higher  $p$  and  $T$ . All these relations have been shown diagrammatically in Figure 4. On their basis the ternary solution diagrams have been drawn in Fig. 5, which show the relationship between chemical composition and the absolute activity of the components in a chemical mixture of the type

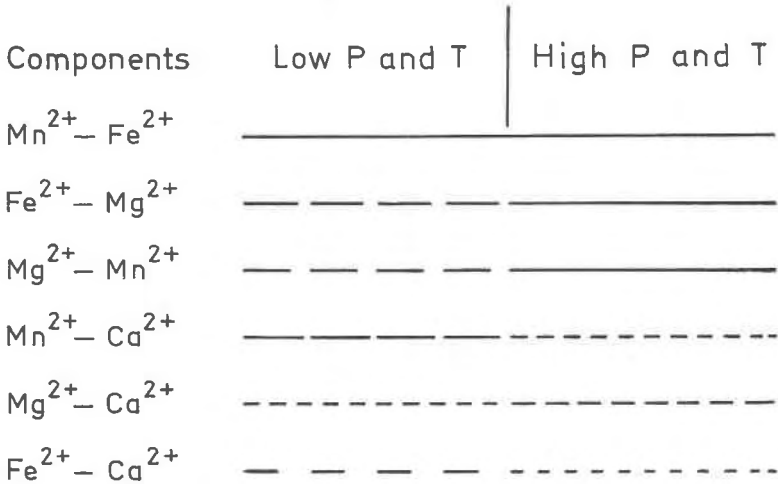


FIG. 4. A schematic diagram showing the nature of the binary mixtures in garnet. A solid line indicates that the nature of the mixture is ideal through all the  $p$  and  $T$  conditions, as in the  $(Mn-Fe^{2+})$  garnet. A broken line indicates deviations from ideality and the extent of deviation is shown by the length of the segment.  $(Fe^{2+}-Mg)$  garnet, for example, is shown as slightly non-ideal at lower  $p$  and  $T$  conditions. The shorter the length of the segment the larger is the extent of the deviation from ideality. Thus  $(Mg-Ca)$  garnet at low  $p$  and  $T$  or  $(Fe^{2+}-Ca)$  garnet at high  $p$  and  $T$  are shown as almost non-ideal mixtures.

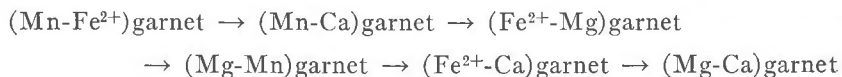
( $A, B, C$ ) $N$ . The activity surfaces for any two components are shown as planar or curved, depending upon the nature of mixing of the two components.

#### THE COMPLEXITY OF USING GARNET ALONE AS A GEOLOGIC THERMOMETER

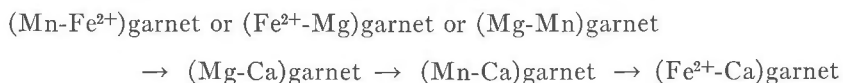
Many petrologists have in the past attempted to use the composition of garnet alone as indicative of the metamorphic grade of the host rock. These attempts have not met with any notable success. Atherton (1965) has reviewed most of such literature and he finds that a simple correlation of one or more components with grade is unlikely.

From the study of Figures 4 and 5, the difficulties inherent in using the composition of garnet alone even in an isochemical rock series become quite apparent. Mueller (1964) divides the stability relations of solid solutions into two types: *intrinsic* and *extrinsic*. Intrinsic instability is caused by the immiscibility of pure components or end members and extrinsic instability is caused by the instability of the pure components or end members of the solution relative to certain reaction products. Ideal solutions are always intrinsically stable since the excess free energy of

mixing has a fixed negative value at a given temperature and concentration. As shown in Figure 4, the ideality of solution and, therefore, the intrinsic stability of binary mixtures would decrease in the sequence



at a certain low  $p$  and  $T$ , and



at a certain high  $p$  and  $T$ . If our concept regarding the relative importance of the similarity of size or IP of the mixing ions in garnet solid solution at different  $p$  and  $T$  is valid, it would appear that  $\text{Fe}^{2+}$  and Mn would replace each other completely at all  $p$  and  $T$  and the variation in their relative concentration would largely be a matter of the bulk chemical composition. This is also reflected in the statement by Atherton (1965, p. 283) that " $\text{Mn}^{2+}/\text{Fe}^{2+}$  ratio is determined not so much by the temperature equilibrium or stability limitations of manganese garnet as by the MnO content and total composition of the system." It should be noted, however, that Mn, if available, is certainly preferred over  $\text{Fe}^{2+}$ .

The fact that certain types of chemical compositions in garnets of regionally metamorphosed rocks are rather uncommon is also in accord with the conclusions of Figures 4 and 5. For example, a garnet with high concentrations of both Mg and Ca is uncommon in metamorphic rocks. A garnet of such a composition might form at high temperatures but would probably represent a disequilibrium situation in metamorphic rocks. These considerations of binary mixtures are modified by the presence of other elements.

In cases where one of the components is in dilute concentration, we may use the ternary diagrams in Figure 5 for discussing the relation of composition with metamorphic grade. The situation shown by Figure 5A where Mg is a dilute component may be best utilized for this purpose. The mixture ( $\text{Fe}^{2+}$ , Mn, Ca) garnet tends to be ideal at lower  $p$  and  $T$ . With increasing  $p$  and  $T$ , Ca may become more and more immiscible and therefore likely driven out of the mixture. Therefore concentration of Ca in such garnets could be used as an index of metamorphic grade, provided concentrations of Mn and  $\text{Fe}^{2+}$  do not vary in the rocks. The more common situation is, however, the one shown in Figure 5B where garnet composition is least suitable for use in deciphering the metamorphic grade, since the departure from ideality is more or less similar through all  $p$  and  $T$  and variation in the concentrations is largely a function of the bulk

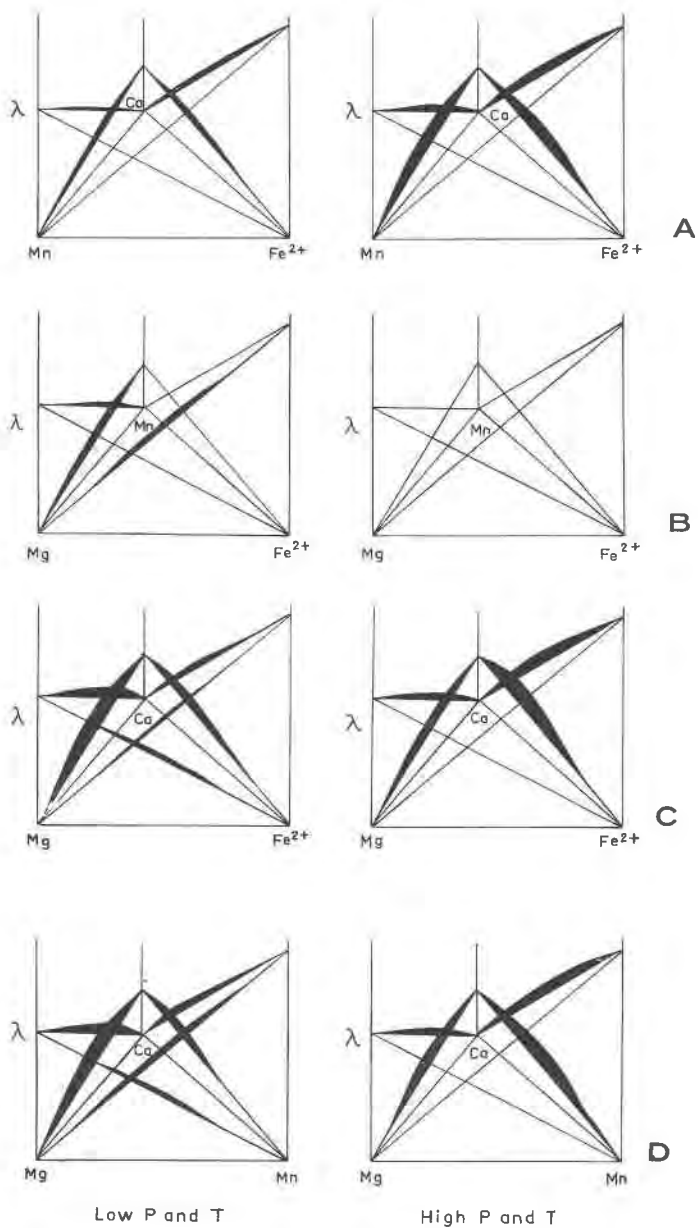
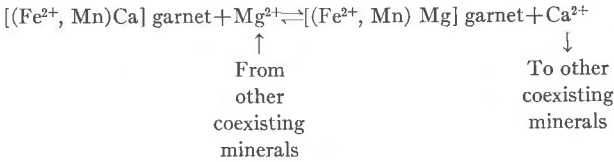


FIG. 5. Relation of composition and absolute activity in garnet presented as ternary solutions, at low and high  $p$  and  $T$ . The curvature of activity surfaces is marked by shaded areas to show the deviations from ideality. Diagram is schematic and the absolute activities of end members represented are hypothetical.

chemical composition. Figures 5C and D may be considered together since Fe<sup>2+</sup> and Mn are largely identical in their behaviour. The only helpful factor in the garnet of such composition is the probability of the following reaction in the rock:



This is based on the assumption that grossularite is more likely to be withdrawn out of a garnet solution with increasing temperature. Even if the above reaction takes place in the rocks, we are unable to use the concentration of Ca as indicating a certain *p* and *T*, for other reasons. In order to eliminate garnets, which do not have Ca because of the bulk chemical composition, it is necessary to ensure a certain minimum activity of Ca in the rock. We may, therefore, have to qualify whether the garnets coexist with calcic amphiboles or pyroxenes. It is also necessary to consider that at lower temperatures Ca would tend to mix ideally with Mn and as such may be completely replaced by it. This necessitates restriction to garnets with only a dilute concentration of Mn. We cannot still rule out the possibility that some Fe<sup>2+</sup> may be replacing Ca and vice versa in low-temperature garnets. These considerations show the complexity of using composition of garnet as indicator of metamorphic grade. In such garnets which are dilute in Mn and coexist with calcic amphiboles or pyroxenes, it is possible to use a combination of the concentration of Ca and the Mg/Fe<sup>2+</sup> ratio in garnets. The above combination would be best utilized in rocks of isochemical series. The chemical data for garnets from unchanged eclogites, variously recrystallized eclogites and certain rocks of the granulite facies have been listed in Table 8. The ratio Mg/

- A. (Fe<sup>2+</sup>, Mn, Ca) garnet is ideal with respect to all the components at low *p* and *T*, but it is non-ideal in (Mn—Ca) garnet and (Fe<sup>2+</sup>—Ca) garnet at high *p* and *T*.
- B. (Fe<sup>2+</sup>, Mg, Mn) garnet is ideal with respect to all the components at high *p* and *T*, but it is slightly non-ideal in (Mg—Mn) garnet and (Fe<sup>2+</sup>—Mg) garnet at lower *p* and *T*.
- C. In (Mg, Fe<sup>2+</sup>, Ca) garnet at low *p* and *T*, the deviations from ideality increase in the binary mixtures in the sequence (Fe<sup>2+</sup>—Mg) garnet→(Fe<sup>2+</sup>—Ca) garnet→(Mg—Ca) garnet. At high *p* and *T* the sequence is (Mg—Ca) garnet→(Fe<sup>2+</sup>—Ca) garnet. (Fe<sup>2+</sup>—Mg) garnet is ideal.
- D. In (Mg, Mn, Ca) garnet, at low *p* and *T*, the deviation from ideality is greatest in (Mg—Ca) garnet and slight in (Mn—Ca) garnet or in (Mn—Mg) garnet. At high *p* and *T* non-ideality is most marked in (Mn—Ca) garnet and slight in (Mg—Ca) garnet.



TABLE 8. ATOMIC RATIOS OF Mg AND NUMBER OF Ca IONS (ON THE BASIS OF 12 O)  
IN GARNETS FROM ROCKS OF VARIOUS METAMORPHIC GRADES

| Ref. No. | Sample No. | Mg/(Mg+Mn+Fe <sup>2+</sup> ) | Ca ions | Remarks   |
|----------|------------|------------------------------|---------|---|
| 1        | E 3        | 0.888                        | 0.373   | Ultrabasic nodule in kimberlite, Nixon <i>et al.</i> , 1963.                                      |
| 2        | G 12       | 0.806                        | 0.368   |   |
| 3        | 66118      | 0.751                        | 0.408   | Hypersthene eclogite, Yoder and Tilley, 1962.   |
| 4        | 1          | 0.722                        | 0.419   | Pyroxenic eclogite, Kokta and Nemeč, in Deer, Howie and Zussman, 1962.                            |
| 5        | E 16       | 0.661                        | 0.416   | Eclogite in kimberlite, Nixon <i>et al.</i> , 1963.   |
| 6        | E 4        | 0.548                        | 0.527   |   |
| 7        | "weiss"    | 0.621                        | 0.629   | Eclogite, Yoder and Tilley, 1962.   |
| 8        | 3          | 0.540                        | 0.420   | Garnet-pyroxene rock, Subramaniam in Deer, Howie and Zussman, 1962, granulite facies.             |
| 9        | 6          | 0.440                        | 0.538   | Eclogite gabbro, reference as above.  |
| 10       | 10         | 0.507                        | 0.498   | Granulite facies, Buddington, 1952.   |
| 11       | 8          | 0.357                        | 0.305   | Granulite facies, Buddington, 1952.   |
| 12       | 9          | 0.363                        | 0.383   | Granulite facies, Buddington, 1952.   |
| 13       | 7          | 0.316                        | 0.389   | Granulite facies, Buddington, 1952.   |
| 14       | 35083      | 0.272                        | 0.565   | Eclogite, Yoder and Tilley, 1962.   |
| 15       | 35090      | 0.294                        | 0.759   | Eclogite, Yoder and Tilley, 1962.   |
| 16       | Ch 199     | 0.188                        | 0.611   | Norite, Subramaniam, 1962, granulite facies.  |
| 17       | 13         | 0.158                        | 0.630   | Granulite facies, Buddington, 1952.   |
| 18       | 14         | 0.073                        | 0.636   | Granulite facies, Buddington, 1952.   |
| 19       | 37218      | 0.207                        | 0.617   | Granulite facies, Ramberg, 1949.  |
| 20       | 100RGC58   | 0.175                        | 0.866   | Eclogites formed or recrystallized under glaucophane schist facies, Coleman <i>et al.</i> , 1965. |
| 21       | 207RGC59   | 0.142                        | 0.946   |   |
| 22       | 62RGC58    | 0.096                        | 0.816   |   |
| 23       | 102RGC58   | 0.135                        | 0.847   | Eclogites formed or recrystallized under glaucophane schist facies, Coleman <i>et al.</i> , 1965. |
| 24       | 36NC62     | 0.137                        | 0.867   | Eclogites formed or recrystallized under glaucophane schist facies, Coleman <i>et al.</i> , 1965. |

(Mg+Mn+Fe<sup>2+</sup>) is plotted against the number of Ca ions to show the variations in their concentrations with metamorphic grade. Though the bulk chemical composition of the rocks is varying, we find an approximate relation in Figure 6 which suggests the probability of the reaction as noted above.

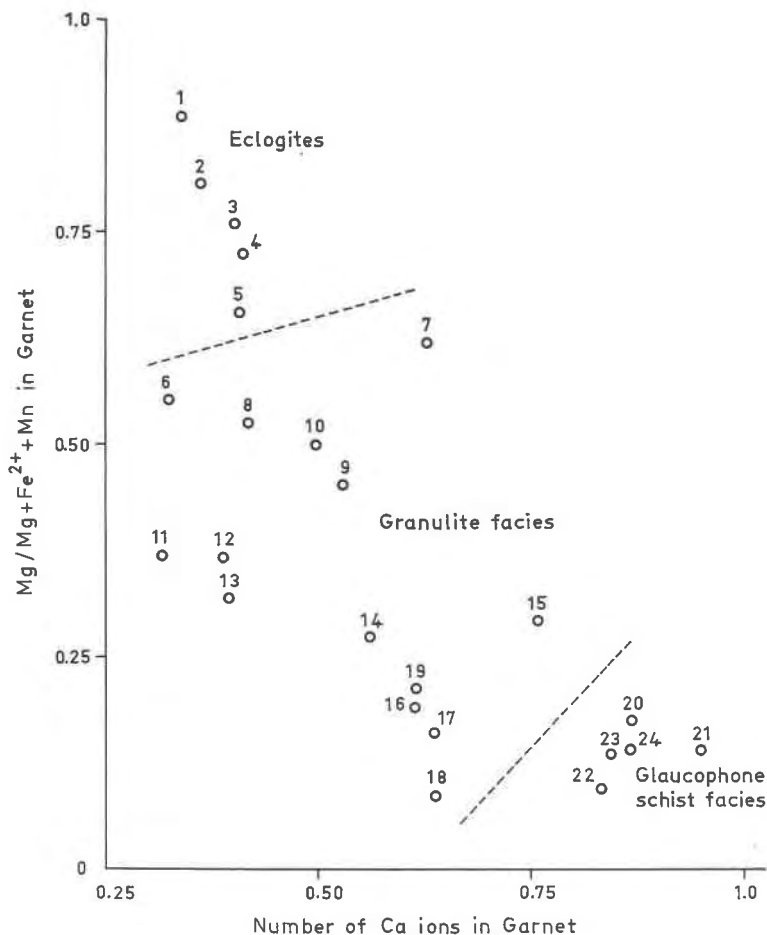


FIG. 6. Composition of garnet as related to the metamorphic grade of the host rocks. Mg/Mg+Fe<sup>2+</sup>+Mn is plotted against concentration of Ca in garnet (Table 8). Samples 1 to 6 are eclogitic rocks associated with kimberlites or other rocks which are probably of deep seated igneous origin. Sample 6 is likely to have been recrystallized. Samples 7 to 19 are either rocks of the granulite facies or eclogites formed or recrystallized under this facies (Coleman *et al.*, 1965). Samples 20 to 24 are eclogites formed or recrystallized under glaucophane schist facies.

One can only conclude that indiscriminate use of garnets alone as geological thermometer is unwarranted. With several restrictions in garnets with dilute concentration of Mn, the Mg/Fe<sup>2+</sup> ratio and the concentration of Ca may be used to judge the approximate metamorphic grade of their formation.

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#### APPENDIX

*Chemical analysis on Geoscan (Cambridge).* Selected mineral grain were analyzed in an aluminium-coated polished thin section of the rock. As *standard* a synthetic compound close in composition to the mineral sample was used. The mass absorption correction was made by M. Tong's (unpublished) formula:

$$c_A = k_A \frac{f(x) \text{ standard}}{f(x) \text{ sample}}$$

$$f(x) = \frac{1}{\left(1 + \frac{x}{\sigma}\right) 1 + h \left(1 + \frac{x}{\sigma}\right)}$$

$$x = (\mu/\rho)_{\text{sample}}^{\text{AK}\alpha} \cdot \text{cosec } \theta$$

$$(\mu/\rho)_{\text{sample}}^{\text{AK}\alpha} = \sum_i c_i (\mu/\rho)^{\text{AK}\alpha}_i$$

$$h = 3.5 \frac{A}{Z^2}$$

$$h_{\text{sample}} = \sum_i c_i h_i$$

$$\sigma = \frac{1.575 \cdot 10^6}{V_{\text{kV}}^2}$$

Where  $c_A$  is the correct concentration of an element  $A$ ,  $k_A$  is the measured concentration of the same element,  $\theta$  = angle of emergence for the X-ray

beam;  $\mu/\rho$  = mass absorption coefficient;  $c_i$  = mass concentration of element  $i$ ;  $A$  = atomic weight,  $Z$  = atomic number; and  $V_{kV}$  = accelerating voltage.

No special corrections for fluorescence and atomic number have been made. Wavelength shift has been considered negligible in the estimation of the elements concerned. Background has been determined separately on standard and sample for each element. Deadtime correction has been made by using the formula  $n = n' / (1 - pn')$  where  $n$  is the true number of counts per second  $n'$  the observed number and  $p$  the dead-time in seconds ( $3.5 \cdot 10^{-6}$  second for Geoscan). Drift has been estimated by recording the intensity readings from the standard immediately before and after the analysis. Control has been exercised for several other possible sources of errors *i.e.*, the variations in electric current, irregularity in the field of electron beam and uncertainty in the standard. Inhomogeneity of the sample has been checked by calculating the statistical errors (see Tables 1 and 3). Maximum analytical error is estimated as  $\pm 5$  percent in the values of the oxides.