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The Role of Crystal Structure in Controlling the Partitioning of Mg and Fe^{2+} Between Coexisting Garnet and Biotite

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Abstract

The distribution of Mg and Fe^{2+} between coexisting garnet and biotite is complicated by structural adjustments caused by substitution of other cations for Mg and Fe^{2+}. Ti, Al and Fe^{3+} commonly proxy for Mg and Fe^{2+} in biotite and thereby increase the positive charge on the octahedral layer. This excess in positive charge is partially compensated by increased tetrahedral substitution of Al for Si, resulting in expansion of the tetrahedral layer. Complete charge balance is achieved by having unoccupied octahedral positions. These vacancies, together with the smaller size of the substituting cations, reduce the dimensions of the octahedral layer. The resultant structural mismatch between the layers may be offset if the larger Fe^{2+} is preferentially accommodated over Mg in the octahedral positions.

Ca and Mn often substitute for Mg and Fe^{2+} in garnet and, because of their larger size, are likely to produce localized structural expansions. In order to maximize overall cell size and thereby reduce intracrystalline strains imposed by these larger cations, Fe^{2+} should be selectively accommodated in the garnet octahedral sites.

This mutual competition for Fe^{2+} is suggested as an explanation of the complication in the Fe^{2+}–Mg partitioning in this mineral pair.

Introduction

In order to establish a viable method of geothermometry, many attempts have been made to correlate temperature and the partitioning of Mg and Fe^{2+} between coexisting garnet and biotite. Although a relationship has been observed in many instances, the disturbing effects of other substituting cations have prevented an exact correlation. This report presents a crystal-structure interpretation of the influence of these other cations in governing the Mg–Fe^{2+} distribution.

The Distribution Coefficient

The theoretical basis for petrologic application of distribution coefficients has been reviewed by Ramberg and DeVore (1951) and Kretz (1959, 1961, 1963). The potential of distribution coefficients as indicators of geologic temperature is based on the relationship

$$\ln K_D = \frac{-\Delta G^\circ}{RT}$$

which is valid only if both mineral phases are ideal solid solutions between end-members. Although early workers considered that Mg and Fe^{2+} substitution in both garnet and biotite was ideal (Kretz, 1959, 1961; Mueller, 1961), recent investigations have shown that octahedral substitution of Mn and Ca in garnet are complicating factors (Frost, 1962; Albee, 1965; Sen and Chakraborty, 1968; Lyons and Morse, 1970). In addition, Kretz (1959), Albee (1965), and Saxena (1969) have pointed out that $K_D^{Bi\text{–}Gar}$ is affected by the substitution of Ti, Al, and Fe^{3+} in biotite. Although most of these workers have attempted to estimate quantitatively the influence of these substitutions on $K_D^{Bi\text{–}Gar}$, no attempt has been made to present an explanation for these effects.

Biotite

Accommodation of Excess Positive Charges

Octahedral proxying of Ti, Al, and Fe^{3+} for Mg and Fe^{2+} increases the positive charge on the biotite octahedral layer. Foster (1960) showed that biotite can accommodate the excess positive charge in two ways:

1. Through increased tetrahedral substitution of Al for Si, to provide less positive charge on the tetrahedral layer.
2. By having unoccupied octahedral positions, producing negative charges in the octahedral layer.

The majority of biotite analyses compiled by Foster (1960) show both excess Al in the tetrahedral site and vacant octahedral positions. This suggests that both mechanisms of charge compensation are used by most biotites.

Effects of Biotite Substitutions on K_D^{Bi-Gar}

Substitution of Al (effective ionic radius = 0.47 Å; all radii from Whittaker and Muntus, 1970) for Si (effective ionic radius = 0.34 Å) enlarges the tetrahedral layer. On the other hand, substitution of Ti, Al, and Fe^{3+} (effective ionic radii = 0.69 Å, 0.61 Å, and 0.73 Å respectively) for Fe^{2+} and Mg (effective ionic radii = 0.86 Å and 0.80 Å) in octahedral sites, together with an increase in the number of vacant octahedral positions, serves to reduce the dimensions of the octahedral layer. To reduce this structural mismatch, it is likely that the slightly larger Fe^{2+} would be preferred over Mg in the biotite octahedral layer. This would mean (under similar thermal conditions) that increasing octahedral Ti, Al, and Fe^{3+} substitution would increase K_D^{Bi-Gar}. Because Ti carries two additional positive charges whereas Al and Fe^{3+} carry only one, this octahedral preference for Fe^{2+} should be most clearly defined for increases in Ti substitution.

Empirical observations of Saxena (1969), Reitan (1972), and Dallmeyer (1973) have shown a positive correlation of K_D^{Bi-Gar} with increased octahedral substitution of Ti, Al, and Fe^{3+}, with Ti exerting the most profound control. These are exactly the relations predicted by the model presented here. The positive correlation of tetrahedral Al and K_D^{Bi-Gar} noted by Saxena (1969) is easily explained in terms of this model, as increased tetrahedral substitution of Al for Si is one of the mechanisms by which biotite can balance the additional charges carried by octahedral Ti, Al, and Fe^{3+}.

Garnet

Unlike biotite, where required articulation of tetrahedral and octahedral layers restricts an overall change in cell volume, the more flexible garnet framework can change size to accommodate variously sized cations. This is evidenced by the increase in cell volume through the end-members pyrope-almandine-spessartine-grossularite. Thus, substitution of the larger Ca and Mn cations (effective ionic radii = 1.08 Å and 0.91 Å) for Mg and Fe^{2+} in garnet octahedral positions should produce localized structural expansions. As a result, it seems likely that the larger Fe^{2+} would be preferentially incorporated in the garnet structure to increase overall cell size and thereby minimize local intracrystalline strains. This would require that K_D^{Bi-Gar} decrease with increasing substitution of Ca and Mn. This is, in fact, the correlation which has been observed (Frost, 1962; Albee, 1965).

Conclusions and Suggestions for Further Study

On the basis of empirical observations and the arguments presented above, the distribution of Mg and Fe^{2+} between coexisting garnet and biotite cannot be treated as a simple binary solution. The octahedral substitution of Ca and Mn in garnet and Ti, Al, and Fe^{3+} in biotite produce changes in crystal structure which may result in the preferential accommodation of Fe^{2+} with respect to Mg. Thus, structural control exerted by these substituting cations may result in the observed complicated partitioning for the mineral pair.

No detailed structure refinements of natural Ti-bearing and aluminous biotites or of garnets with low-to-intermediate Ca and Mn concentrations are available. Such data could confirm the model proposed here and, perhaps, enable more quantitative evaluation of the mechanisms controlling both inter- and intracrystalline element partitioning.

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Activity Coefficients of Coexisting Pyroxenes

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Abstract

The ferrous iron-magnesium distribution between coexisting pyroxenes in granulites from Quairading, Australia, has been shown to be markedly dependent on chemical composition (Davidson, 1968). By assuming a simple-mixture solution model (Guggenheim, 1967) for both of these pyroxenes, activity coefficients and the equilibrium constant of the exchange reaction are derived. The activity coefficients at infinite dilution of orthopyroxene and clinopyroxene are 1.56 and 1.87, respectively.

Introduction

In a study of coexisting pyroxenes in granulites from Quairading, Australia, Davidson (1968) demonstrated that the ferrous iron-magnesium distribution is composition-dependent. He made a special effort to collect rocks with a wide range of composition from a small area of uniform metamorphic grade. Because the rocks equilibrated at approximately the same temperature, the variation of the ferrous iron-magnesium distribution reflects non-ideal behavior in either one or both pyroxenes. The calcium content of the pyroxenes is approximately constant, and the pyroxenes are essentially binary solutions. Saxena (1972) pointed out that activity coefficients may be derived from the compositions of coexisting binary solutions on the basis of various assumed solution models. This method has been applied to the pyroxenes from Quairading, using the simplest non-ideal solution model for both pyroxenes.

Theory

The exchange of ferrous iron and magnesium between orthopyroxene and clinopyroxene is represented by the following equilibrium

$$MgSiO_3 + CaFeSi_2O_6 \rightleftharpoons FeSiO_3 + CaMgSi_2O_6 \quad (1)$$

The equilibrium constant in terms of mole fractions (X) and activity coefficients (γ) is given by

$$K = \left(\frac{X^{opx}_{FeSiO_3} X^{cpx}_{CaMgSi_2O_6}}{X^{opx}_{MgSiO_3} X^{cpx}_{CaFeSi_2O_6}}\right)\left(\frac{\gamma^{opx}_{FeSiO_3}\gamma^{cpx}_{CaMgSi_2O_6}}{\gamma^{opx}_{MgSiO_3}\gamma^{cpx}_{CaFeSi_2O_6}}\right) \quad (2)$$

Because the term composed of mole fractions is the distribution coefficient K_D, the preceding equation may be rewritten as

$$\ln K = \ln K_D + \ln \gamma^{opx}_{FeSiO_3} - \ln \gamma^{opx}_{MgSiO_3} + \ln \gamma^{cpx}_{CaMgSi_2O_6} - \ln \gamma^{cpx}_{CaFeSi_2O_6} \quad (3)$$

In many binary solutions, small deviations from ideality may be adequately expressed by the simple-mixture solution model (Guggenheim, 1967). Using this model for both pyroxenes, the activity coefficients are given by

$$\ln \gamma^{opx}_{FeSiO_3} = \alpha^{opx}(1 - X^{opx}_{FeSiO_3})^2 \quad (4)$$

$$\ln \gamma^{opx}_{MgSiO_3} = \alpha^{opx}(X^{opx}_{FeSiO_3})^2 \quad (5)$$

$$\ln \gamma^{cpx}_{CaMgSi_2O_6} = \alpha^{cpx}(X^{cpx}_{CaFeSi_2O_6})^2 \quad (6)$$

$$\ln \gamma_{CaFeSi_2O_6} = \alpha^{cpx}(1 - X^{cpx}_{CaFeSi_2O_6})^2 \quad (7)$$

In these expressions, the α's are the natural logarithms of the activity coefficients at infinite dilution; they are the same for the two components of a binary solution. Substituting equations (4) to (7) into equation (3), the following relationship, previously derived by Mueller (1964), is obtained

$$\ln K = \ln K_D + \alpha^{opx}(1 - 2X^{opx}_{FeSiO_3}) - \alpha^{cpx}(1 - 2X^{cpx}_{CaFeSi_2O_6}) \quad (8)$$

Measurements of compositions of coexisting pyroxenes give values for $\ln K_D$, $X^{opx}_{FeSiO_3}$, and $X^{cpx}_{CaFeSi_2O_6}$, leaving the unknowns $\ln K$, α^{opx}, and α^{cpx}.

Pyroxenes from Quairading, Australia

Davidson (1968) reports the analyses of 12 pairs of coexisting pyroxenes in basic granulites from Quairading, Australia. A least-squares method may be used to determine the three unknowns in equation (8). One sample (no. 9) was neglected because it shows signs of textural disequilibrium and,