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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,

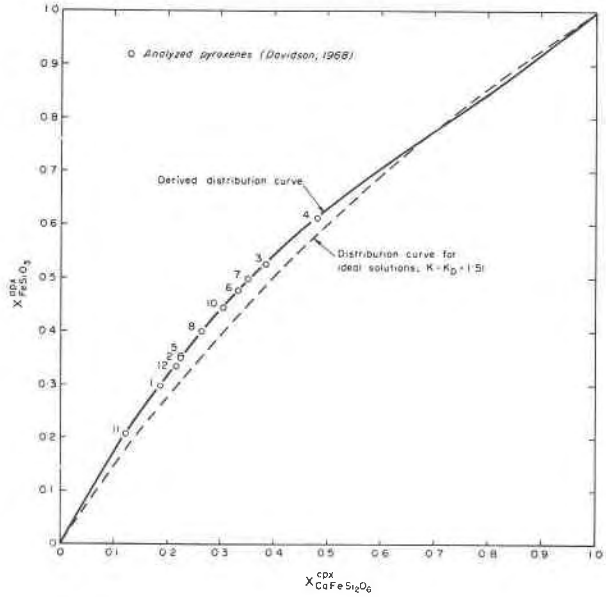

FIG. 1. The compositions of coexisting pyroxenes from Quairading, Australia.

according to Davidson (1968), gives an anomalous K_D value. The following results were obtained

$$\ln K = 0.412, \; K = 1.51$$

$$\alpha^{opx} = 0.447, \; \gamma^{opx} \text{ at infinite dilution} = 1.56$$

$$\alpha^{cpx} = 0.625, \; \gamma^{cpx} \text{ at infinite dilution} = 1.87$$

The derived distribution curve and the original data points are plotted in Figure 1. Also shown is the distribution curve expected if both pyroxenes were ideal solutions, in which case $K = K_D$.

The activity coefficients of orthopyroxene are in good agreement with those calculated from Mössbauer spectroscopy at 700°C and 800°C (Saxena and Ghose, 1971). Saxena (1971) also considered the iron-magnesium distribution between coexisting pyroxenes. From a knowledge of the partitioning of iron and magnesium between the *M*1 and *M*2 sites of orthopyroxene (Saxena and Ghose, 1971), he obtained the following results for six selected granulites: $T = 680°\text{C}$, $K = 1.64$, $\alpha^{cpx} = 0.54$. It is interesting to note that the present approach, which treats activity coefficients in both pyroxenes as unknowns, gives comparable results. This method could be generally useful if accurate analyses of coexisting binary solutions are available.

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