

The Energetics of Natural Garnet Solid Solution

II. Mixing of the Calcium Silicate End-Members

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Abstract. Approximate mixing properties of the dominant calcium silicate end-member components of natural garnets, namely grossularite, andradite and uvarovite, have been derived through theoretical thermodynamic and crystal chemical analysis, and appropriate reduction of the available experimental data. The stability of the solid solution with respect to phase separation in the ternary system has been analyzed. Finally, a general model is presented as to the approximate mixing properties of multicomponent natural garnet solid solution involving substitutions in both eight and six coordinated sites.

Introduction

Natural garnets, the general formula for which can be written as $[X_3^{2+}]^{\text{VIII}}[Y_2^{3+}]^{\text{VI}}\text{Si}_3\text{O}_{12}$, consist of multicomponent solid solution with the eight coordinated $X^{2+} = \text{Fe, Mg, Ca, Mn}$, and the six coordinated $Y^{3+} = \text{Al, Fe, and Cr}$. The thermodynamic mixing properties of the aluminosilicate end-member components, $X_3^{2+}\text{Al}_2\text{Si}_3\text{O}_{12}$, have been discussed in the first part of this work (Ganguly and Kennedy, 1974). The purpose of this paper is to explore the approximate mixing properties of the dominant calcium silicate end-member components of natural garnet, namely grossularite ($\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$), andradite ($\text{Ca}_3\text{Fe}_2^{3+}\text{Si}_3\text{O}_{12}$), and uvarovite ($\text{Ca}_3\text{Cr}_2^{3+}\text{Si}_3\text{O}_{12}$).

Theoretical Model

As in the first part, we begin by adopting the “simple mixture” formalism of Guggenheim (1967) to treat the mixing properties of calcium silicate end-members.

The excess free energy of mixing in a binary solution is then given by

$$\Delta G^{\text{ex}} = W_{12} X_1 X_2 \quad (1.1)$$

which is symmetrical to the composition, X . W_{12} is an adjustable interaction parameter, and in general is a function of P and T .

$$\left(\frac{\partial W}{\partial P} \right)_T = \frac{\Delta V^{\text{ex}}}{X_1 X_2} \quad (1.2)$$

$$\left(\frac{\partial W}{\partial T} \right)_P = - \frac{\Delta S^{\text{ex}}}{X_1 X_2} \quad (1.3)$$

ΔV^{ex} and ΔS^{ex} represent respectively excess volume and excess entropy of mixing. It has been shown by Novak and Gibbs (1971), from an analysis of 56 silicate garnets, that the unit cell edge of silicate garnets varies linearly with the mean radius of X^{2+} and Y^{3+} ions. Since the cell dimension of the calcium silicate garnets, as given later in this paper, differs from one another by very small amounts, this observation implies that the cell volume, a_0^3 , also varies linearly with the mean Y^{3+} radius or composition; thus, $\Delta V^{\text{ex}} \simeq 0$. Further, since all the octahedral sites in the garnet structure are symmetrically equivalent, the distribution of the Y^{3+} ions in these sites should be expected to be random, or nearly so, and hence $\Delta S^{\text{ex}} \simeq 0$. W_{12} should thus be expected to be fairly insensitive to both temperature and pressure changes. Also, we shall have

$$\Delta H^{\text{mix}} \simeq \Delta G^{\text{ex}} = W_{12} X_1 X_2 \quad (1.4)$$

From a crystal-chemical point of view, we may consider, as a first approximation, that

$$\Delta H^{\text{mix}} \simeq \Delta H_{\text{Est}}^{\text{mix}} + \Delta H_{\text{Cov}}^{\text{mix}} + \Delta H_{\text{Dis}}^{\text{mix}} + \Delta \text{CFSE}^{\text{mix}} \quad (2)$$

where $\Delta H_{\text{Est}}^{\text{mix}}$ represents the heat of mixing owing to the changes in the electrostatic interaction between the cation and neighboring anions, $\Delta H_{\text{Cov}}^{\text{mix}}$ represents that due to changes in the covalent (or ionic) character of the bonding, $\Delta H_{\text{Dis}}^{\text{mix}}$ is the heat of mixing arising from distortion of the lattice caused by the substitution of ions of different size and shape, and $\Delta \text{CFSE}^{\text{mix}}$ is the change in the crystal field stabilization energy when the substitution involves transition metal ions. Although the CFSE results from electrostatic effect, it is convenient for the present purpose to treat it separately.

Solid Solution of Grossularite and Andradite

There are no available data which could be directly related to the mixing properties of grossularite and andradite. However, the distribution of Al and Fe^{3+} between the tetrahedral (T) and octahedral (O) sites of synthetic yttrium garnets, $\text{Y}_3\text{Al}_t\text{Fe}_{5-t}^{3+}\text{O}_{12}$, as studied by Czerlansky and MacMillan (1970) by Mössbauer spectroscopy for several compositions at 1,000° C, permit deduction of the mixing property of these cations in both sites of the yttrium garnets. The yttrium garnet

and the silicate garnet have the same fundamental crystal structure. Also, according to the data of Novak and Gibbs (1971, Table 9) and of Euler and Bruce (1965, Table 4), the octahedral Fe^{3+} -O and Al-O distances are very similar in both garnets. It is, therefore, reasonable to suggest that the energetic environment of the octahedrally coordinated cations in the yttrium and calcium silicate garnets are quite similar. Thus, the mixing of Al and Fe^{3+} in the octahedral site of yttrium garnet should not be expected to differ significantly from that in the calcium silicate garnet. Following Borghese (1967), the site occupancies of Al and Fe^{3+} in yttrium garnet be written as $\text{Al}(\text{T})=t-x$, $\text{Al}(\text{O})=x$, $\text{Fe}^{3+}(\text{T})=2+x-t$ and $\text{Fe}^{3+}(\text{O})=3-x$, which leads to a unit formula of $\text{Y}_3(\text{Fe}_{3-x}\text{Al}_x)^{\text{O}}(\text{Fe}_{2-t+x}\text{Al}_{t-x})^{\text{T}}\text{O}_{12}$ for the yttrium garnet. For the intracrystalline ion exchange equilibrium



we can, thus, write an expression of equilibrium analogous to equilibrium constant for heterogeneous ion exchange reaction as follows.

$$K(P, T) = \left[\frac{(x)(2+x-t)}{(t-x)(3-x)} \right] \left[\frac{\gamma_{\text{Al}(\text{O})}\gamma_{\text{Fe}^{3+}(\text{T})}}{\gamma_{\text{Al}(\text{T})}\gamma_{\text{Fe}^{3+}(\text{O})}} \right] \quad (3)$$

where γ represents what may be called the partial or site activity coefficient of the specified ion. We call the ratios of ionic concentrations and of site activity coefficients, K_D and K_γ , respectively. Assuming now that the mixing in the individual sites conforms to the "simple mixture" behavior, we can write the following expressions for the site activity coefficients of the different ions.

$$RT \ln \gamma_{\text{Al}}^{\text{O}} = W^{\text{O}}(1-x_{\text{Al}}^{\text{O}})^2 = \frac{W}{9}(3-x)^2 \quad (4.1)$$

and similarly

$$RT \ln \gamma_{\text{Al}}^{\text{T}} = \frac{W^{\text{T}}}{4}(2+x-t)^2 \quad (4.2)$$

$$RT \ln \gamma_{\text{Fe}^{3+}}^{\text{T}} = -\frac{W^{\text{T}}}{4}(t-x)^2. \quad (4.3)$$

Combining (3) and (4), and rearranging terms,

$$\ln K_D = \ln K + \frac{W^{\text{T}}}{4RT} [(2+x-t)^2 - (t-x)^2] + \frac{W^{\text{O}}}{9RT} [x^2 - (3-x)^2] \quad (5.1)$$

or,

$$\ln K_D = \ln K + \frac{W^{\text{T}}}{RT}(1+x-t) + \frac{W^{\text{O}}}{3RT}(2x-3). \quad (5.2)$$

Regression analysis of the data of Czerlansky and MacMillan in terms of the above equation yields

$$\begin{aligned} \ln K_D = & 0.9511 (\pm 0.0723) - 0.1618 (\pm 0.2160)(1+x-t) \\ & - 0.2036 (\pm 0.0796)(2x-3) \end{aligned} \quad (6)$$

where the uncertainties, as also elsewhere in the paper, are twice the standard deviation, and thus define 95% confidence interval. Comparing (5.2) and (6),

we have

$$K(1 \text{ atm}, 1,000^\circ \text{ C}) = 2.588 (\pm 0.20) \quad (7.1)$$

$$W^T(1 \text{ atm}, 1,000^\circ \text{ C}) = -408 \pm 544 \text{ cal/mol} \quad (7.2)$$

$$W^O(1 \text{ atm}, 1,000^\circ \text{ C}) = -1,539 \pm 576 \text{ cal/mol.} \quad (7.3)$$

Thus, considering the uncertainties of the experimental data, the mixing of Fe^{3+} and Al conforms to ideal solution behavior in the tetrahedral site, but shows a small negative departure from ideality in the octahedral site of the yttrium garnet solid solution. The latter result can be compared with the inferred ideal mixing of Fe^{3+} and Al in the octahedral site in acmite-jadeite solid solution (Newton and Smith, 1967; Popp and Gilbert, 1972). As discussed earlier, W -s are expected to respond very weakly to temperature and pressure changes.

Solid Solution of Uvarovite with Andradite and Grossularite

With regard to the mixing of uvarovite with andradite and grossularite, we would first try to calculate $\Delta\text{CFSE}^{\text{mix}}$, and then consider the possible modifying effects of other contributions to ΔH^{mix} as expressed in the Eq. (2). Most ions of the first transition series have high spin configuration in silicate structure, at least at atmospheric to moderate pressures (cf. Burns, 1970, p. 18). Consequently, we need to concern ourselves only with the CFSE of $\text{Cr}^{3+}(t_{2g}^3)$, since Fe^{3+} has zero CFSE in high spin configuration ($t_{2g}^3 e_g^2$). The CFSE of Cr^{3+} in an octahedral field is given by $3(-\frac{2}{5}\Delta)$ or $3(-\frac{2}{5}\Delta) \cdot 2.859 \text{ Cal/mole}$, where Δ is the crystal field splitting between the e_g and t_{2g} orbitals. Hence $\Delta\text{CFSE}^{\text{mix}}$ of Cr^{3+} involved in the formation of a solid solution with mole fraction X of uvarovite (e.g. $(1-X)\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12} + X\text{Ca}_3\text{Cr}_2^3+\text{Si}_3\text{O}_{12} \rightarrow \text{Ca}_3(\text{Al}_{1-X}\text{Cr}_X^3+)\text{Si}_3\text{O}_{12}$) is given by

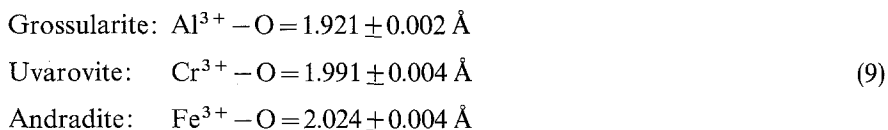
$$\Delta\text{CFSE}^{\text{mix}}(X) = X(\frac{6}{5})[\Delta_0 - \Delta(X)] (2.859) \text{ Cal/mole} \quad (8.1)$$

where Δ_0 and $\Delta(X)$ represent the crystal field splitting of e_g and t_{2g} orbitals of Cr^{3+} in pure uvarovite and in the garnet solid solution, respectively. The absorption spectra of Cr^{3+} in a natural uvarovite, as determined by Neuhaus (1960), shows the crystal field splitting to be $16,600 \text{ cm}^{-1}$ (see also Manning, 1969; Burns, 1970). The uvarovite has a Cr_2O_3 content of 20 wt% as compared to the ideal of 24.6%. If we assume the effect of the small amount of impurity to be negligible, then $\Delta_0 = 16,600 \text{ cm}^{-1}$. Since for a given transition metal-ligand pair, $\Delta \propto R^{-5}$, where R is the metal-ligand distance, $\Delta(X)$ is given by

$$\Delta(X) = 16,600 \left(\frac{R_0}{R(X)} \right)^5 \text{ cm}^{-1}. \quad (8.2)$$

According to Novak and Gibbs (1971), $\text{Y}^{3+} - \text{O}$ distance in the calcium silicate garnets varies linearly with the mean Y^{3+} radius as computed from Shannon and Prewitt's (1960) data of effective ionic radii in octahedral coordination. From the data of Novak and Gibbs (Table 3), one can therefore easily derive the following values of $\text{Y}^{3+} - \text{O}$ distances in the end-member components, and then obtain

$R(X)$ by linear interpolations between the appropriate end-member data.



We can now solve for expression (8). Fig. 1 shows the calculated $\Delta\text{CFSE}^{\text{mix}}$ for the binary solid solutions uvarovite-andradite and uvarovite-grossularite, along with ΔH^{mix} for grossularite-andradite solid solution, as derived from (1.4) and (7.3), as functions of composition. The extreme values, at $X = 0.5$, are

$$\begin{aligned}\Delta\text{CFSE}^{\text{mix}}(\text{Uvar}_{50}\text{And}_{50}) &= -1,151 (\pm 412) \text{ cal/mol} \\ \Delta\text{CFSE}^{\text{mix}}(\text{Uvar}_{50}\text{Gross}_{50}) &= -2,640 (\pm 390) \text{ cal/mol} \\ \Delta H^{\text{mix}}(\text{And}_{50}\text{Gross}_{50}) &= -384 (\pm 144) \text{ cal/mol}\end{aligned}\quad (10)$$

It is impossible at this stage to determine the separate contributions of distortion, covalent, and electrostatic effects towards ΔH^{mix} of the solid solutions of uvarovite. However, we may develop certain approximate ideas of the net contributions of these effects through crystal-chemical considerations as follows. The crystal-chemical properties of the end-member components, which seem pertinent in this respect, are shown below.

	Cell edge of end-members, Å	Ionic radius, Å	Electro- negativity	Preferred covalent coordination	Preferred ionic coordination
Al^{3+}	11.851 ± 0.001	0.54 ± 0.002	1.5	4(SP^3)	4,6
Cr^{3+}	12.000 ± 0.001	0.61 ± 0.004	1.6	6($d^2 SP^3$)	4,6
Fe^{3+}	12.048 ± 0.001	0.64 ± 0.004	1.8	6($d^2 SP^3$)	4,6

The values for the cell edge of grossularite and andradite are taken from Skinner (1956), and that for uvarovite is from Geller and Miller (1959). The ionic radii are derived from (9) on the basis of tetrahedral oxygen radius of 1.38 Å. The electronegativity values are from Pauling (1960). It is clear that Al^{3+} and Fe^{3+} constitute the most unlike pair of ions in terms of the crystal-chemical properties tabulated above. It then seems likely that ΔH^{mix} of grossularite and andradite, which is completely due to non-crystal field effects

$$(\Delta H^{\text{mix}}(\text{Gross-And}) \simeq \Delta H_{\text{Est}}^{\text{mix}} + \Delta H_{\text{Cov}}^{\text{mix}} + \Delta H_{\text{Dis}}^{\text{mix}}),$$

would provide an approximate upper limit to the net non-crystal field contributions in the other binary joins in the calcium silicate garnet system, namely uvarovite-andradite, and uvarovite-grossularite. It is not impossible, however, that there is significant cancellation among $\Delta H_{\text{Est}}^{\text{mix}}$, $\Delta H_{\text{Cov}}^{\text{mix}}$, and $\Delta H_{\text{Dis}}^{\text{mix}}$, so that although each of these terms has a smaller magnitude for the solid solutions of uvarovite relative to that between grossularite and andradite, as seem likely in view of the crystal-chemical data, the residual magnitudes bear reverse relations;

that is, although

$$|\Delta H_{\text{Est}}^{\text{mix}}|_{\text{Uvar-And/Gross}} < |\Delta H_{\text{Est}}^{\text{mix}}|_{\text{Gross-And}},$$

and so on,

$$|\Delta H_{\text{Est}}^{\text{mix}} + \Delta H_{\text{Cov}}^{\text{mix}} + \Delta H_{\text{Dis}}^{\text{mix}}|_{\text{Uvar-And/Gross}} > |\Delta H_{\text{Est}}^{\text{mix}} + \Delta H_{\text{Cov}}^{\text{mix}} + \Delta H_{\text{Dis}}^{\text{mix}}|_{\text{Gross-And}} \simeq \Delta H_{\text{Gross-And}}^{\text{mix}}.$$

Even then, it seems reasonable to assume that the net non-crystal field contributions to the ΔH^{mix} of the solid solutions of uvarovite does not exceed, at least significantly, ΔH^{mix} (Gross-And). It may now be noted from Figure 1 that the magnitude of the latter term is approximately of the same order as the uncertainty of $\Delta \text{CFSE}^{\text{mix}}$ of the solid solutions of uvarovite. This suggests that within the limits of their uncertainties, the inferred values of $\Delta \text{CFSE}^{\text{mix}}$ of the solid solutions of uvarovite in the calcium silicate garnet system are unlikely to differ significantly from the respective heats of mixing. At any rate, it seems reasonably certain that the solid solution of uvarovite with andradite and grossularite involves positive and negative heat, or excess free energy of mixing. This conclusion is compatible with the observational data in that natural calcium silicate garnet solid solutions exhibit large compositional gap relative to their Fe^{3+} and Cr^{3+} content, but show Al^{3+} and Cr^{3+} almost in any proportion (cf. Deer *et al.*, 1962).

It should be noted in Fig. 1 that the $\Delta \text{CFSE}^{\text{mix}}$ of the solid solutions of uvarovite, which has been calculated without recourse to any solution model, is almost perfectly symmetrical to composition. Thus, if indeed $\Delta \text{CFSE}^{\text{mix}}$ constitutes the most dominant contribution to the ΔH^{mix} of the solid solutions of uvarovite, then this observation provides a *posteriori* justification of our choice of a symmetrical thermodynamic solution model.

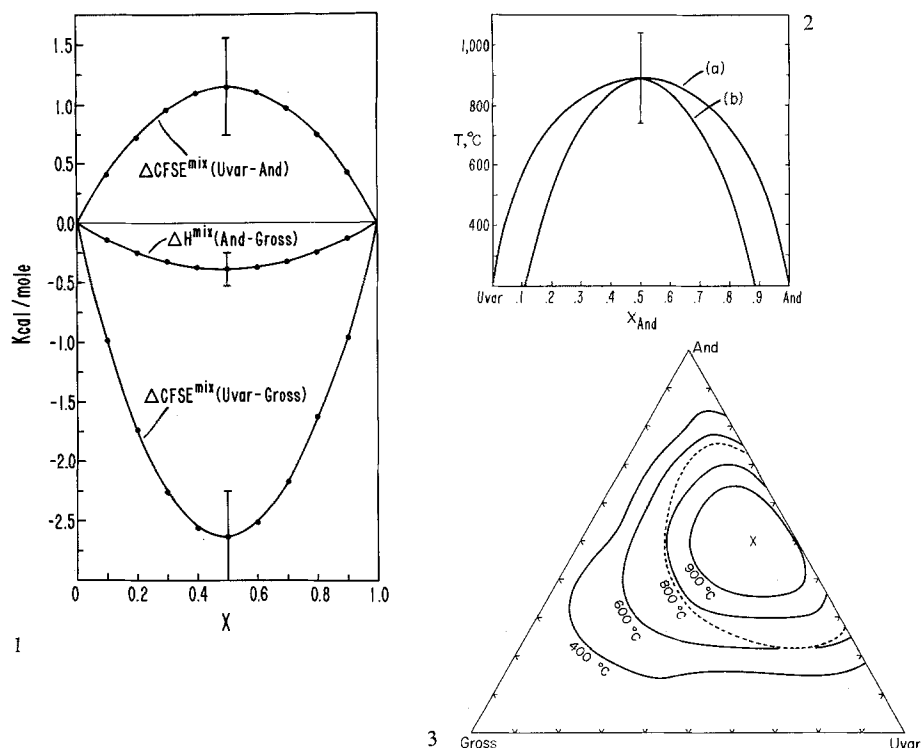
Stability of the Solid Solution with Respect to Phase Separation

If it could be assumed, in view of the above discussion, that within the limits of its uncertainty the $\Delta \text{CFSE}^{\text{mix}}$ (Uvar-And/Gross) $\simeq \Delta H^{\text{mix}}$ (Uvar-And/Gross), then we have the following values of the "simple mixture" interaction parameters for the binary joins of the calcium silicate garnets (see expression (1.4)).

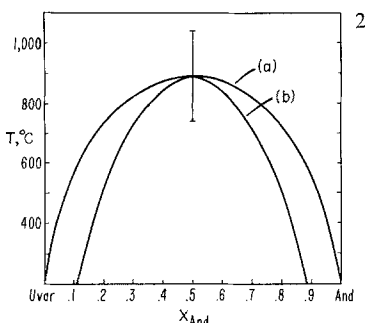
$$\begin{aligned} W(\text{Uvar-And}) &= 4,604 \pm 1,648 \text{ cal/mol} \\ W(\text{And-Gross}) &= -1,536 \pm 576 \text{ cal/mol} \\ W(\text{Uvar-Gross}) &= -10,560 \pm 1,560 \text{ cal/mol} \end{aligned} \quad (11)$$

Evidently, the binary solid solutions of grossularite are *intrinsically* stable for all compositions, whereas the uvarovite-andradite join would be unstable with respect to phase separation below certain critical temperature, T_c , given by $T_c = W/2R \simeq 1,163 \pm 413 \text{ K}$ or $890 \pm 140^\circ \text{ C}$.

The large negative deviation from ideality of the grossularite-uvarovite join, if true, implies that Al and Cr^{3+} would probably tend to be ordered in the octahedral site of garnet of intermediate composition (cf. Guggenheim, 1952, p. 101; also Grover, 1974).



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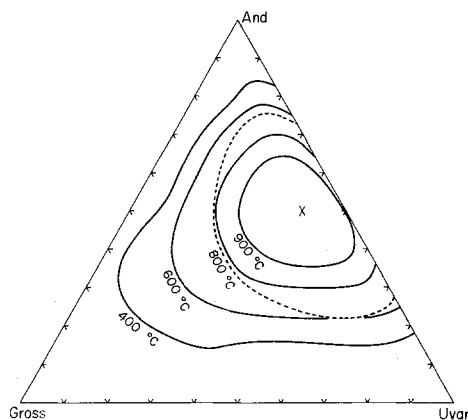


Fig. 1. Calculated heat of mixing, ΔH^{mix} , and crystal field stabilization energy of mixing, $\Delta \text{CFSE}^{\text{mix}}$, in the different binary joins of calcium silicate garnets as functions of composition. Vertical bars are uncertainties, $\pm 2\sigma$, where σ is the standard deviations

Fig. 2. Calculated solvus (a) and spinodal (b) in the uvarovite-andradite join. Vertical bar is uncertainty of the critical temperature

Fig. 3. Intrinsic stability of the solid solution in the ternary system grossularite-uvarovite-andradite. Solid lines are calculated spinodals. Broken curve is the approximate position of the solvus at 800°C (others can be drawn in analogous manner on the basis of the respective spinodals). The cross is the summit point, T_s , or ternary critical temperature at $\sim 1,000 \pm 100^{\circ}\text{C}$. The tie lines will rotate clockwise, and intersect the and-uvar join to the side of the andradite corner within $X_{\text{And}} = 1$. It is assumed that for the binary solid solutions of uvarovite, $\Delta \text{CFSE}^{\text{mix}} \approx H^{\text{mix}}$ within the limits of its uncertainty (see text)

The solvus and the spinodal curve in the uvarovite-andradite join have been calculated according to the equations given in Prigogine and Defay (1954, p. 248–249), and are shown in Fig. 2. The splitting of the X-ray reflections due to the predicted unmixing of uvarovite-andradite solid solution below the critical temperature can be easily calculated from the elementary diffraction theory. It turns out that the unit-cell dimension of the end-members are so close that the splitting of the prominent X-ray reflections due to unmixing at temperatures down to 700°C are less than the measured half-width of the reflections. Thus no attempt was made to experimentally verify the predicted solvus in the uvarovite-andradite join.

With respect to the ternary system, we first note that the absolute magnitude of the difference between the interaction parameters of the binary joins involving grossularite is likely to be greater than $W(\text{Uvar-And})$. Thus, addition of grossularite would probably raise the critical solution temperature, or reduce the mutual solubility, of uvarovite and andradite in the immediate neighborhood of this binary join (cf. Meijering, 1950, p. 341). However, the critical temperature must pass through a maximum or a summit point, T_s , since every isothermal section of the ternary system must contain a critical condition owing to the intrinsic stability of the binary solid solutions of grossularite at all temperatures. This would lead to the appearance of *isolated* miscibility gap in the ternary system at temperatures between the binary critical temperature and T_s . Thus, with increasing temperature, the immiscibility gap in the ternary calcium silicate garnet solid solution may be expected to disappear at a ternary critical temperature, T_s , rather than at the binary critical temperature at the uvarovite-andradite join. The coordinates of the ternary critical point, calculated according to Meijering (1950), are as follows:

$$\begin{aligned} T_s &\approx 1,000 \pm 100^\circ \text{C} \\ X_{\text{uvar}} &\approx 0.50 \\ X_{\text{And}} &\approx 0.40. \end{aligned} \tag{12}$$

The spinodal line for the ternary solid solution of calcium silicate garnets has been calculated for several temperatures by solving the equation for spinodal derived by Scott (1949), Haase (1950), and Meijering (1950), and given in Prigogine and Defay (1954, p. 261). The results are illustrated in Fig. 3. The approximate position of the solvus in the ternary field, which must be tangent to the corresponding spinodal at critical conditions, can be drawn, as illustrated for 800°C , by following the general form of the spinodal. Since $W(\text{Gross-And}) > W(\text{Gross-Uvar})$, the tie lines would intersect uvarovite-andradite join to the side of the andradite corner, that is rotate clockwise. Also, since the absolute magnitude of the difference between these interaction parameters is greater than $W(\text{Uvar-And})$, the intersections would lie between $X_{\text{Uvar}} = 1.0$ and $X_{\text{And}} = 1.0$ and not on the extension of the join (cf. Meijering, 1951, p. 186–187).

Multicomponent Natural Garnet Solid Solution

In terms of the “ionic solution” model, which has so far been applied with great success in the thermodynamic analysis of inorganic crystalline solution (cf. Mueller, 1962, 1972; Saxena, 1973), we can express activity of a component, such as $\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12}$, in a multicomponent garnet solid solution, $[\text{X}_3^{2+}]^{\text{VIII}}[\text{Y}_2^{3+}]^{\text{VI}}\text{Si}_3\text{O}_{12}$, as follows.

$$\begin{aligned} a_{\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12}}^{\text{Gt}} &= (a_{\text{Fe}}^{\text{VIII}})^3 (a_{\text{Al}}^{\text{VI}})^2 \\ &= (X_{\text{Fe}}^{\text{VIII}})^3 (X_{\text{Al}}^{\text{VI}})^2 (\gamma_{\text{Fe}}^{\text{VIII}})^3 (\gamma_{\text{Al}}^{\text{VI}})^2 \end{aligned} \tag{13}$$

where $a_{\text{Fe}}^{\text{VIII}}$ denotes the activity of Fe^{2+} in the eight coordinated site of garnet, and so on. There is, in principle, a cooperative effect of the cation substitution in one site on the activity-composition relation in another site. Thus, in general,

$$\begin{aligned} (\gamma_{\text{Fe}}^{\text{VIII}})\text{X}_3^2 + \text{Y}_2^3 + \text{Si}_3\text{O}_{12} &\neq (\gamma_{\text{Fe}}^{\text{VIII}})\text{X}_3^2 + \text{Al}_2\text{Si}_3\text{O}_{12} \\ (\gamma_{\text{Al}}^{\text{VI}})\text{X}_3^2 + \text{Y}_2^3 + \text{Si}_3\text{O}_{12} &\neq (\gamma_{\text{Al}}^{\text{VI}})\text{Ca}_3\text{Y}_2^3 + \text{Si}_3\text{O}_{12} \end{aligned} \quad (14)$$

However, considerable uncertainties are associated with the inferred mixing properties of X^{2+} cations in the eight coordinated site of the aluminosilicate garnet, and of Y^{3+} cations in the six coordinated site of the calcium silicate garnet solid solutions. We would probably introduce little error beyond these uncertainties if we replace at the present stage the above inequalities by approximate equalities. This seems all the more likely in view of the compositional data of natural garnets summarized by Deer *et al.* (1962). These data show that by far the most natural aluminosilicate garnets have Fe^{3+} , which seems to mix with Al^{3+} with little or very small deviation from ideality, as the only significant extraneous ion in the six coordinated site, whereas nearly all calcium silicate garnets may be represented practically within the compositional space defined by the three end-member components grossularite, uvarovite, and andradite. We can then find, using the "simple mixture" model and values of the interaction parameters derived above and elsewhere (Ganguly and Kennedy, 1974), approximate solution for the activitycomposition relation embodied in the expression (13) for most natural garnet solid solutions.

The composition of multicomponent natural garnets has often been displayed in published literature in a ternary plot using *gross + and*, *almandine + spessartite*, and *pyrope* apices. Coleman *et al.* (1965) have, in particular, displayed the composition of garnets from various different types of eclogite in such a ternary plot, and discovered significant correlation of the garnet composition and the groups of eclogite classified on the basis of mode of occurrence. This representation of the composition of natural garnets in terms of a quasi-ternary system of *gross + and*, *almandine + spessartite*, and *pyrope* is justified in terms of the solid solution property derived in this and in the previous work (Ganguly and Kennedy, *op. cit.*) in that grossularite and andradite, as well as almandine and spessartite have been found to mix without very significant deviation from ideality.

In conclusion, it should be emphasized that in accepting and applying the above results, one should bear in mind the tenuous approximations involved in deriving the interaction parameters relating to the binary solid solutions of uvarovite. Certain aspects of the model, such as the presence of a ternary critical temperature in the calcium silicate garnet system, might as well be artifacts of these approximations. Comparison of the mixing properties of the binary calcium silicate solid solutions of uvarovite via phase equilibrium studies or calorimetric measurements with those derived above might provide interesting insight as to the effect of different crystal-chemical or *microscopic* interactions on the macroscopic solid solution property of silicates.

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