

Plagioclase-garnet-Al₂SiO₅-quartz: a potential geobarometer-geothermometer

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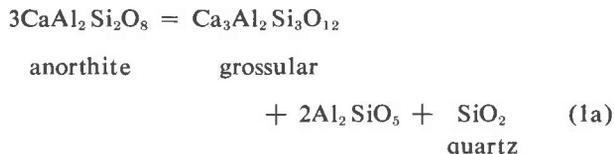
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Abstract

For the reaction $3\text{CaAl}_2\text{Si}_2\text{O}_8 = \text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12} + 2\text{Al}_2\text{SiO}_5 + \text{SiO}_2$, the logarithm of the apparent distribution coefficient (K_D) is $\log K_D = 3X_{\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}}^{\text{garnet}} - 3X_{\text{CaAl}_2\text{Si}_2\text{O}_8}^{\text{plagioclase}}$. Log K_D varies from -0.5 to -1.4 for kyanite-bearing assemblages and from -2.1 to -3.4 for sillimanite and/or andalusite-bearing assemblages. Using equilibrium constant equations derived from experimental data on pure phases and an ideal solution model for garnet and plagioclase solid solutions, individual P - T curves can be calculated for different values of log K_D . If P or T can be independently estimated, these curves can be used as either geothermometers or geobarometers. The degree of non-ideality of grossular solid solution in garnet can be estimated from calculations using the activity coefficients of anorthite in plagioclase and the kyanite-sillimanite P - T equilibrium curve as a limiting case for kyanite and sillimanite-bearing assemblages.

Introduction

Plagioclase, garnet, quartz, and an Al₂SiO₅ polymorph are a common assemblage in regionally metamorphosed pelitic rocks. Several workers, *e.g.*, Miyashiro (1953), Sturt (1962), have suggested that garnet compositions can be used as indicators of metamorphic grade. Other workers have noted a relationship between the CaO content of garnet, the anorthite content of plagioclase, and metamorphic grade (Kepzhinskas, 1973). Unless an appropriate mineral assemblage of low variance is chosen, however, the effects of bulk composition far overshadow the P - T significance of garnet and plagioclase compositional variability. In this note I will attempt to demonstrate that the reaction



provides data on the mineral assemblage plagioclase-garnet-Al₂SiO₅-quartz which is potentially useful in estimating pressures and temperatures of metamorphism (Ghent, 1975).

Reaction (1a) with kyanite as the Al₂SiO₅ polymorph has been studied experimentally at elevated pressure and temperatures by Hays (1967) and by Hariya and Kennedy (1968).

The equilibrium can be described by

$$0 = -\frac{3272}{T} + 8.3969 - \frac{0.3448(P - 1)}{T} \quad (1b)$$

where T is the temperature in degrees Kelvin and P is pressure in bars. The equation can be modified for the presence of sillimanite or andalusite as the Al₂SiO₅ polymorph by subtraction of equations of the form of (1b) for kyanite-sillimanite and kyanite-andalusite equilibria. Using the aluminum silicate diagram of Holdaway (1971) we obtain in place of equation (1b):

$$0 = -\frac{2551.4}{T} + 7.1711 - \frac{0.2842(P - 1)}{T} \quad (2)$$

where sillimanite is the Al₂SiO₅ polymorph and

$$0 = -\frac{2817.2}{T} + 7.4351 - \frac{0.2678(P - 1)}{T} \quad (3)$$

where andalusite is the Al₂SiO₅ polymorph.

Since the minerals are not pure phases we add terms for activity of anorthite solid solution in plagioclase and activity of grossular solid solution in garnet:

$$\begin{aligned}
 0 = & -\frac{3272}{T} + 8.3969 - \frac{0.3448(P - 1)}{T} \\
 & + \log a_{\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}}^{\text{garnet}} \\
 & - 3 \log a_{\text{CaAl}_2\text{Si}_2\text{O}_8}^{\text{plagioclase}} \quad (1c)
 \end{aligned}$$

For a discussion of the derivation of equilibrium constant equations, see Carmichael *et al.* (1974, p. 107 *et seq.*).

The activity of $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ in garnet can be expressed by $a_{\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}}^{\text{garnet}} = X_{\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}}^{\text{garnet}} \cdot \gamma_{\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}}^{\text{garnet}}$ where X = mole fraction and γ = activity coefficient, for random mixing on the three 8-fold coordinated sites in garnet. For the activity of $\text{CaAl}_2\text{Si}_2\text{O}_8$ in plagioclase, coupled substitution of $\text{CaAl} \rightleftharpoons \text{NaSi}$ is assumed and $a_{\text{CaAl}_2\text{Si}_2\text{O}_8}^{\text{plagioclase}} = X_{\text{CaAl}_2\text{Si}_2\text{O}_8}^{\text{plagioclase}} \cdot \gamma_{\text{CaAl}_2\text{Si}_2\text{O}_8}^{\text{plagioclase}}$ (See also Kerrick and Darken, 1975). Activity coefficients for $\text{CaAl}_2\text{Si}_2\text{O}_8$ have been reported by Orville (1972) and are used in the present study. Activity-composition relations in garnet solid solution have recently been discussed by Ganguly and Kennedy (1974). Their suggested model is evaluated in the following sections.

Applications

Applications of these relations will be illustrated by an example from the Esplanade Range, British Columbia. Garnet and plagioclase are chemically zoned, and rim compositions are inferred to have been in equilibrium with one another and with kyanite and quartz (Ghent, 1975). Recalculation of garnet electron microprobe analyses suggest a low Fe_2O_3 content and this is consistent with low f_{O_2} implied by coexisting ilmenite-graphite. The mole fraction of grossular is taken as $\text{mol CaO}/(\text{mol CaO} + \text{mol FeO} + \text{mol MnO} + \text{mol MgO})$. This calculation yields the *maximum* estimate of grossular component in garnet and consequently yields a *maximum* pressure estimate at a given temperature. Temperatures estimated by $\text{O}^{18}/\text{O}^{16}$ results on coexisting quartz-ilmenite and from experimental phase equilibria suggest that plagioclase-garnet-kyanite-quartz crystallized at a T near 540°C (O'Neil and Ghent, 1975).

The logarithm (to the base 10) of the distribution coefficient ($\log K_D = 3 \log X_{\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}}^{\text{garnet}} - 3 \log X_{\text{CaAl}_2\text{Si}_2\text{O}_8}^{\text{plagioclase}}$) for three samples ranges from -0.53 to -0.73 (Table 1). Assuming an ideal solution model, substitution of these values of $\log K_D$ and $T = 813^\circ\text{K}$ into equation (1c) yields pressures in the range 8600–9000 bars. An analytical uncertainty of 0.2 in $\log K_D$ leads to an uncertainty of about 400 bars in the estimate of pressure at constant temperature.

These results can be compared to data from other areas. Because of chemical zoning in garnet and plagioclase, only electron microprobe analyses of garnet and plagioclase rims have been selected. Kyanite-bearing assemblages from Encampment Creek,

British Columbia show a range in $\log K_D$ from -0.49 to -1.40 (Table 1, Fig. 1). The assemblage from western Maine contains sillimanite (Evans and Guidotti, 1966) and $\log K_D$ ranges from -2.73 to -2.83 (Table 1, Fig. 1). Andalusite \pm sillimanite assemblages from Mt. Raleigh, British Columbia, have $\log K_D$ ranging from -2.07 to -3.42 (Woodsworth, 1975, unpublished data). There is a clear separation of the values of the distribution coefficient from the different facies series of metamorphism (Fig. 1). For the ideal solution model these values of $\log K_D$ produce sets of P - T curves along which the given assemblages could have crystallized (Fig. 2).

The P - T curves must be modified for the effects of non-ideality of $\text{CaAl}_2\text{Si}_2\text{O}_8$ in plagioclase and $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ in garnet. The activity coefficient of $\text{CaAl}_2\text{Si}_2\text{O}_8$ for plagioclase in this composition range is taken as 1.276 (Orville, 1972). The garnet solid solution is treated as a simple binary solution of grossular with almandine. The effects of pyrope and spessartine on the activity of grossular in these garnet solid solutions are considered to be small and will be discussed in the sections below.

Synthetic almandine-grossular solid solutions show a very small $\Delta V_{\text{mixing}}^{\text{excess}}$ which can be safely neglected (Hariya and Nakano, 1972). Ganguly and Kennedy (1974), using data from natural materials, crystal chemistry and limited experimental synthesis estimate a small positive $\Delta G_{\text{mixing}}^{\text{excess}}$ for almandine-grossular solid solutions.

For a simple mixture model, the interaction parameter, W_{12} , for a binary mixture of components 1 and 2 is given by $\Delta G_{\text{mixing}}^{\text{excess}} = W_{12} X_1 X_2$. Ganguly and Kennedy (1974) estimate W for almandine-grossular (W_{AG}) is near $+1$ Kcal/mole. The expression relating the activity coefficient γ to W is

$$\ln \gamma_G = \frac{(1 - x_G)^2 W_{AG}}{RT} \quad (\text{Prigogine and Defay, 1954, p. 246})$$

Activity coefficients for $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ for garnet from the Esplanade Range are between 1.49 and 1.65 at 540°C . We can estimate the effects of neglecting the solid solution of pyrope and spessartine in grossular by using a modified version of Equation 2.1 of Ganguly and Kennedy (1974, p. 139). Using mole fractions of pyrope and spessartine in garnet solid solution and estimates of interaction parameters (W 's) for grossular-pyrope and grossular-spessartine (Ganguly and Kennedy, 1974), calculations indicate that γ differs by about 5 percent relative to γ calculated assuming a simple binary solution. Combined with $\gamma_{\text{CaAl}_2\text{Si}_2\text{O}_8}^{\text{plagioclase}} = 1.276$, calculations using activity

TABLE 1. Compositions of garnet and plagioclase rims and calculated apparent distribution coefficients

| Sample No. | Xan | Xgr | Xal | Xpy | Xsp | log $\frac{K_D}{K}$ | Al ₂ SiO ₅ phase | Source of data |
|------------|-----|-------|-------|-------|-------|------------------------|---|----------------------|
| CV-113 | .21 | .12 | .75 | .12 | .01 | -0.73 | K | 1 |
| CV-150 | .31 | .18 | .70 | .10 | .02 | -0.71 | K | 1 |
| CV-204 | .21 | .14 | .71 | .12 | .03 | -0.53 | K | 1 |
| 9 | .17 | .021 | .826 | .082 | .071 | -2.73 | S | 2 |
| 22 | .15 | .019 | .782 | .129 | .070 | -2.73 | S | 2 |
| 24 | .10 | .012 | .785 | .114 | .089 | -2.83 | S | 2 |
| 70-30492-4 | .15 | .0162 | .8473 | .0651 | .0714 | -2.90 | A | 3 |
| 71-40018-7 | .25 | .0180 | .8484 | .0787 | .0549 | -3.42 | S | 3 |
| 71-40198-1 | .15 | .0212 | .8905 | .0395 | .0488 | -2.55 | A | 3 |
| 71-40068-1 | .08 | .0073 | .9030 | .0697 | .0200 | -3.12 | A>S | 3 |
| 71-40060-8 | .19 | .0192 | .8608 | .0976 | .0224 | -3.05 | S | 3 |
| 71-40025-4 | .14 | .0276 | .7278 | .0519 | .1927 | -2.12 | A | 3 |
| 72-40001-1 | .17 | .0212 | .8905 | .0395 | .0488 | -2.71 | S>A | 3 |
| 72-40043-1 | .24 | .0255 | .7892 | .0838 | .1015 | -2.92 | S>A | 3 |
| 72-40141-2 | .44 | .0464 | .7948 | .0772 | .0816 | -2.93 | S | 3 |
| 72-40105-1 | .29 | .0301 | .8598 | .0282 | .0819 | -2.95 | A | 3 |
| 72-40142-3 | .26 | .0532 | .5879 | .0667 | .2922 | -2.07 | A | 3 |
| 72-40052-9 | .19 | .0179 | .9000 | .0335 | .0494 | -3.08 | S>A | 3 |
| 72-40094-3 | .37 | .0499 | .7690 | .0776 | .1035 | -2.61 | A | 3 |
| D | .12 | .076 | .771 | .146 | .007 | -0.60 | K | 4 |
| E | .46 | .184 | .652 | .150 | .013 | -1.19 | K | 4 |
| F | .23 | .088 | .738 | .163 | .010 | -1.25 | K | 4 |
| G | .21 | .098 | .718 | .167 | .016 | -0.99 | K | 4 |
| H | .36 | .122 | .746 | .132 | .001 | -1.41 | K | 4 |
| RM367 | .17 | .03 | .77 | .12 | .08 | -2.26 | S | 5 |
| GM-73-102 | .43 | .10 | .68 | .14 | .08 | -1.90 | K | 6 |
| JP-73-39 | .20 | .05 | .75 | .13 | .08 | -1.81 | S | 6 |

Xan = mol fraction of anorthite in plagioclase

Xgr = mol fraction of grossular in garnet

Xal = mol fraction of almandine in garnet

Xpy = mol fraction of pyrope in garnet

Xsp = mol fraction of spessartine in garnet

K = kyanite; S = sillimanite and/or fibrolite; A = andalusite,
> means one polymorph more abundant.

All samples from Woodsworth (1975) have the prefix RD.

Source of data: 1 - Ghent, 1975; 2 - Evans and Guodotti, 1966;
3 - Woodsworth, 1975, unpublished data; 4 - Robbins, 1975,
unpublished data, Encampment Creek, British Columbia; 5 - Ghent,
1975, unpublished data from Ruby Mountains, Nevada; 6 - Ghent,
1975, unpublished data from Mica Creek, British Columbia

coefficients derived for simple binary solutions yield a pressure estimate near 9500 bars. If the activity coefficients are calculated taking into account garnet end members other than grossular and almandine, the pressure estimate would be reduced by about 100 bars. Application of activity coefficients for grossular solid solution ($\gamma > 1.0$) to the data from other areas would also raise the P - T curves to higher pressures (Fig. 2).

Data presented in this paper can be used to set limits on the value of W_{AG} . Plagioclase-garnet-quartz-Al₂SiO₅ assemblages in the Mica Creek, Brit-

ish Columbia, area occur near the kyanite-sillimanite isograd (Table 1). The kyanite-sillimanite curve (Holdaway, 1971) can be used as a limiting case for assemblages occurring on either side of the isograd. Since P - T curves calculated from ideal solution models (Fig. 2) are not precisely parallel to the kyanite-sillimanite curve, estimates on the limits of W_{AG} will vary with P and T . Estimates of W_{AG} are near -460 cal at 501°C and 3760 bars, and near -320 cal at 810°C and 10,000 bars. These estimates are subject to a very large uncertainty.

In addition to analytical uncertainty and the uncer-

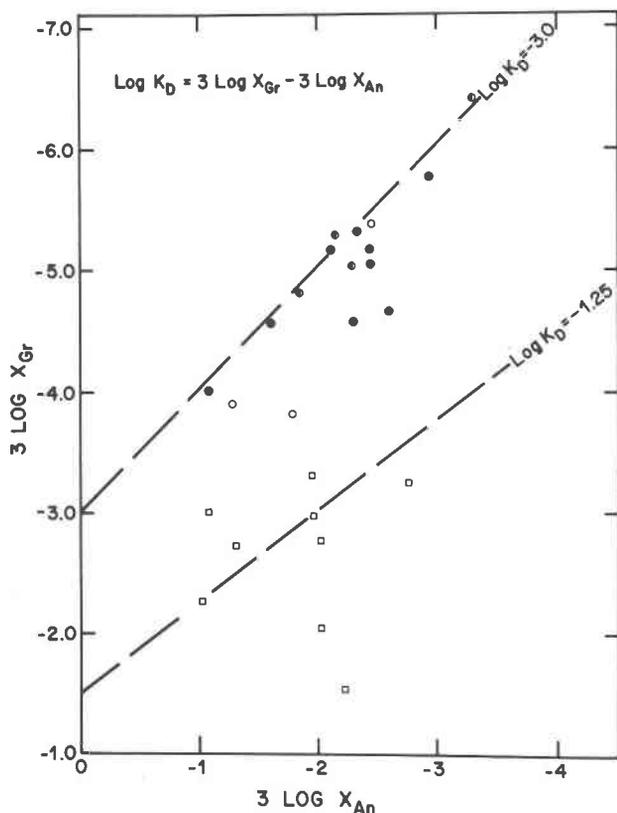


FIG. 1. Plot of $3 \log X_{Gr}$ against $3 \log X_{An}$ for samples from different metamorphic facies series. Symbols are: open squares = kyanite-bearing assemblages; open circles = andalusite-bearing assemblages; filled circles = sillimanite-bearing assemblages; half-filled circles = sillimanite and andalusite-bearing assemblages. Lines of constant $\log K_D$ are shown for reference. Data are tabulated in Table 1.

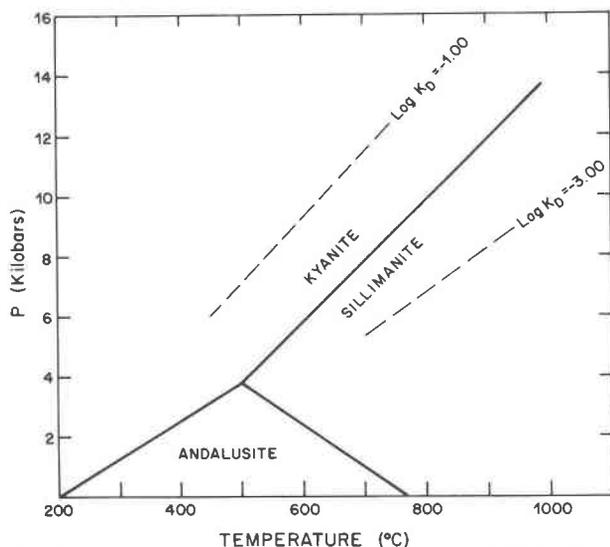


FIG. 2. Pressure-temperature diagram showing Al_2SiO_5 phase relationships after Holdaway (1971). P - T curves for $\log K_D = -1.00$ and -3.00 calculated from equations (1b) and (2) respectively, using an ideal solution model.

tainty introduced by approximation of a simple binary solution to the natural garnet solid solution, there is a possibility that the natural kyanite-sillimanite transition may be at variance with the experimental kyanite-sillimanite transition by as much as $100^\circ C$ (at constant pressure) e.g., Zen (1969), Greenwood (1972). Ganguly and Kennedy (1974) estimate $0 \leq W_{AG} \leq 1.355$ Kcal/mole. The constraint that $W_{AG} \geq 0$ was based on analogy with known mixing properties on the Ca-Fe joins in other systems and ionic size considerations.

Hensen *et al.* (1975) report a personal communication from Cressey that preliminary experiments suggest near-ideality for almandine-grossular solid solution. R. C. Newton (personal communication, 1975) is currently investigating thermochemical properties of almandine-grossular solid solutions.

The clear separation of K_D for garnet and plagioclase compositions in the assemblage plagioclase-garnet- Al_2SiO_5 -quartz from different facies series indicates the potential value of this equilibrium as a P - T indicator and should serve as encouragement to perform the critical experiments to provide accurate data on the activities of grossular in garnet solid solutions.

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