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# Al zoning in pyroxene and plagioclase: Window on late prograde to early retrograde *P-T* paths in granulite terranes

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## ABSTRACT

Little information on prograde *P-T* paths in granulites is generally preserved because cation diffusion in most mineral species is relatively rapid above 700 °C. A knowledge of part of the prograde path is, however, critical to understanding the tectonics of granulite-forming processes. Clino- and orthopyroxenes in granulites commonly show significant Al zoning typified by Al-rich cores and Al-poor rims. Zoning-relaxation calculations suggest that relaxation of Al growth zoning in pyroxenes and plagioclases during peak metamorphism is minor. Thus, Al-zoning data may be used to examine that part of the granulite *P-T* path along which pyroxene grew. The slope of the log *K* curves for the reaction CaTs + quartz = anorthite is negative below 20 kbar whereas that for jadeite + quartz = albite is positive, and the two may be combined to yield both pressure and temperature. A subregular quaternary activity model for the system CaTs-jadeite-diopside-hedenbergite was fitted for these calculations.

Data for four granulite terranes were examined. Calculations for the Grenville Province, Ontario, yield decreasing pressures and temperatures and an average d*P*/d*T* of 54 bars/°C. The average rim results (10.1 kbar, 860 °C) agree well with peak *P-T* values (10 kbar, 800–850 °C) obtained by other methods. Average core results (12.8 kbar, 910 °C) are significantly higher and suggest prepeak unloading. Data from the Furua Complex, Tanzania, are similar to those from the Grenville (core = 13.7 kbar, 930 °C; rim = <11.6 kbar, <845 °C) but yield only limits for the rim *P-T* because plagioclase rim compositions were not obtained. In the Fiordland complex, both Fe-Mg and Al zoning (core = 6.7 kbar, 650 °C; rim = 14.8 kbar, 810 °C) are in reasonable agreement and suggest an increase in *P*. Results from the Pikwitonei area, Manitoba, yield retrograde *P-T* paths (core = 6.7 kbar, 830 °C; rim = 3.3 kbar, 670 °C; 21 bars/°C), and zoning patterns in the feldspar suggest that plagioclase may have grown during retrogression.

## INTRODUCTION

Recent work by a number of authors has established that many granulite terranes cool isobarically during the initial stages of retrogression (cf. Bohlen, 1987; Harley, 1989; Anovitz and Essene, 1990). Thermal modeling (England and Thompson, 1984) suggested, however, that if the pressures and temperatures recorded by thermobarometry are near the maximum values attained in the terrane, the initial retrograde path in a continent to continent collision should be nearly isothermal, and the direction of the overall path in *P-T* space is clockwise. Interpretation of isobaric cooling in terms of tectonics of the formation of granulite terranes has, therefore, led to significant discussion.

Assuming that isobaric cooling represents a real portion of the *P-T* path in granulites (cf. Frost and Chako, 1989; Anovitz and Essene, 1990; Bohlen, 1990), two explanations for this process have been suggested. Bohlen (1987) and Mezger et al. (1990) combined these data with textural evidence to suggest that the overall *P-T* path was counterclockwise and that granulites may not be the product of continent to continent collisions but are caused by magmatic underplating, possibly in the roots of island arcs. In this model, the exhumation of the terrane would be due to a later, possibly unrelated event.

Alternatively, nearly isobaric cooling can be achieved if the pressures recorded by the thermobarometers currently in use do not record the maximum pressures attained during the metamorphism. Anovitz and Chase (1990) noted that there are three types of data on retrograde *P-T-t* paths that must be satisifed by any model for the formation of granulites: isobaric cooling, unbundling (parallelism of initial retrograde paths at different depths as observed in the Grenville Province, Ontario), and $^{40}$Ar/$^{39}$Ar data on the rates of cooling of the terrane. The only simple tectonic model that fits all these data involves a collisional model with an episode of possibly extension-related tectonic exhumation near the peak of the metamorphism. Simple underplating models cannot account for these data, but available data are insufficient to rule out counterclockwise paths generated by a combination of collision and underplating. Evaluation of the overall

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sense of the *P-T* path therefore requires constraints on an earlier portion of the path than is recorded by standard thermobarometry.

The availability of data on early portions of the *P-T* path for granulites is strongly limited by the high temperatures of granulite metamorphism. In the temperature range of 700–900 °C observed in most granulites, reaction and diffusion rates in most minerals are sufficiently fast that relicts of cooler, prepeak conditions are seldom preserved (Essene, 1982; Bohlen et al., 1983a; Lasaga, 1983; Loomis, 1983). Several authors (Phillips, 1980; Phillips and Wall, 1981; Bohlen et al., 1986; Mezger et al., 1990) have used textural data to constrain the prograde path. Unfortunately, textural data are often either lacking or are difficult to interpret. One must prove that no other interpretations of a given texture are reasonable and explain why a particular prograde texture is preserved when so many others are not. It is therefore important to find a quantitative approach to constraining prepeak portions of the *P-T* path for granulites.

This paper will consider the possibility that Al zoning in pyroxene and plagioclase formed during the prograde part of the *P-T* cycle and can be used to refine our knowledge of the *P-T* path for granulites. To do so, it is necessary to show that the rate of diffusion of Al in pyroxenes and plagioclase is slow enough that growth zoning will be preserved, to provide a calibration based on Al-Si exchange between plagioclase and pyroxene, and to apply the result to available zoning data.

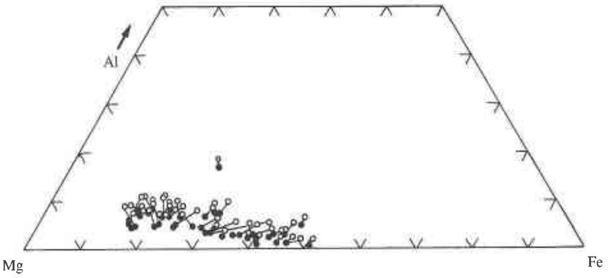

Fig. 1. Zoning of Al, Mg, and Fe in orthopyroxene plotted as mole percent of the three elements normalized to 100%. Core analyses are shown as open circles, rim analyses as filled circles. Data were obtained from the Grenville Province, Ontario (Anovitz, 1987; Moecher, 1988; Anovitz and Essene, 1990); the Furua Complex, Tanzania (Coolen, 1980); Enderby Land, Antarctica (Harley, 1984, 1985, 1987, 1988); Molodezhnaya Station, Antarctica (Grew, 1981); the Minnesota River Valley (Moecher et al., 1986); and the Gruf Complex, Italy (Droop and Bucher-Nurminen, 1984).

## RATES OF Al DIFFUSION IN CLINOPYROXENES AND PLAGIOCLASES

Calculations of retrograde *P-T* paths for granulites are often based on zoning of elements such as Ca, Fe, and Mg in garnet and pyroxene for which exchange does not require major changes in the structural frameworks of the minerals involved. Diffusion during charge-coupled exchanges is usually significantly slower than in simple exchanges. For instance, the Ca-Na exchange in plagioclase involves the charge balanced exchange NaSi = CaAl, which requires rearrangement of the Al-Si feldspar framework. Exchange of Na and K, however, does not require rearrangement of the feldspar structure, and one would predict a priori that Ca-Na diffusion in feldspar is significantly slower than Na-K diffusion (cf. Morse, 1984). This is confirmed by available experimental data (e.g., Bailey, 1971; Foland, 1974; Giletti et al., 1974; Kasper, 1974; Brady and Yund, 1983; Christoffersen et al., 1983; Yund, 1983, 1986; Snow, 1987; Yund and Snow, 1989). For example, in a $H_2O$-free environment at 800 °C, 1 bar the diffusional coefficients for the Ca-Na and Na-K exchanges are approximately $3.2 \times 10^{-26}$ and $8 \times 10^{-18}$ $m^2/s$, respectively (Yund, 1986). The diffusional coefficient for Ca-Na exchange in plagioclase is also significantly slower than that for Ca-Fe-Mg-Mn zoning in garnets ($2.1 \times 10^{-21}$ $m^2/s$ for Fe tracer diffusion in almandine-rich garnet at 800 °C, 8.5 kbar, Loomis et al., 1985). As garnets preserve compositions attained at or near the thermal maximum of granulite metamorphism up to 750–850 °C (cf. Essene, 1982; Lasaga, 1983; Chakraborty and Ganguly, 1990), plagioclase may preserve growth zoning during granulite facies metamorphism.

Ortho- and clinopyroxenes in granulite facies rocks often show significant Al zoning (Coolen, 1980; Grew, 1981; Droop and Bucher-Nurminen, 1984; Harley, 1984, 1985, 1987, 1988; Moecher et al., 1986; Anovitz, 1987; Warren et al., 1987; Bingen et al., 1988; Bradshaw, 1989). Unfortunately, relatively few pairs of core and rim analyses and even fewer complete zoning profiles of pyroxenes are available (Figs. 1 and 2). However, a pattern is apparent in the available data. With the exception of pyroxenes from the Fiordland complex of New Zealand (Bradshaw, 1989), all available profiles show Al-rich cores and Al-

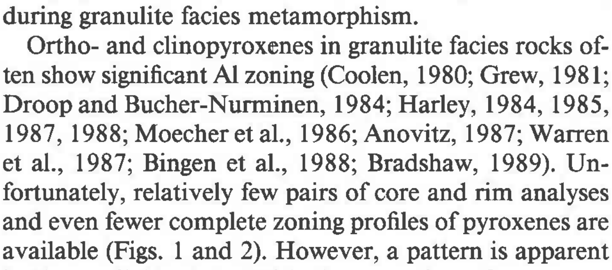

Fig. 2. Zoning of Al, Mg, and Fe in clinopyroxene plotted as mole percent of the three elements normalized to 100%. Core analyses are shown as open symbols, rim analyses as filled symbols. Data were obtained from the Grenville Province, Ontario (Anovitz, 1987; Moecher, 1988; Anovitz and Essene, 1990); the Furua Complex, Tanzania (Coolen, 1980); Enderby Land, Antarctica (Harley, 1984, 1985, 1987, 1988); the Arunta Block, Australia (Warren et al., 1987); western Fiordland, New Zealand (triangles, Bradshaw, 1985, 1989, personal communication); and the Pikwitonei terrane, Manitoba (Mezger et al., 1990, this study). Note that only the Fiordland samples show inverse Al zoning.

poor rims. Clinopyroxene core compositions have up to 12 wt% $Al_2O_3$ (Coolen, 1980), and orthopyroxenes in general have lower Al contents than coexisting clinopyroxenes. In addition, complete zoning profiles (Moecher et al., 1986; Anovitz, 1987; Anovitz and Essene, 1990) show that zoning is relatively smooth, suggesting no change in the reactions controlling growth zoning (Crawford, 1977).

The nature of Al zoning in pyroxenes suggests that Al diffusion may be slower than Fe-Mg exchange (cf. Herzberg and Chapman, 1976). The Tschermak's exchange

$$R^{2+}_{M1}Si_T = Al_{M1}Al_T \tag{1}$$

requires restructuring of the tetrahedral chains in the mineral. While the jadeite exchange

$$R^{2+}_{M1}R^{2+}_{M2} = R^{1+}_{M1}R^{3+}_{M2} \tag{2}$$

does not, it does involve a charge-coupled two-site exchange and significant site distortion. Thus, Al diffusion may be expected to be slower than in uncoupled exchanges such as Ca-Mg-Fe. Sautter and Harte (1988) examined garnet exsolution in eclogite xenoliths from the Roberts Victor kimberlite pipe and noted that even though Fe-Mg diffusion stopped at approximately 1000 °C, Al diffusion had stopped at significantly higher temperatures. Even though cooling rates in xenoliths are faster than in regional metamorphic terranes, and reequilibration will therefore continue to lower temperatures in pyroxenes from granulites, these data support the argument that Al diffusion in pyroxene is significantly slower than Ca-Mg-Fe diffusion.

On the basis of diffusion profiles in coexisting garnet-clinopyroxene pairs, Anovitz (1987) estimated that in the temperature range 600–800 °C Ca-Mg-Fe diffusion in pyroxenes is approximately 1 order of magnitude slower than that in garnet, which agrees qualitatively with existing experimental data (Ross et al., 1973; Huebner et al., 1975; Huebner, 1976; Miyamoto and Takeda, 1977; McCallister et al., 1979; Sanford and Huebner, 1979, unpublished data; Brady and McCallister, 1980, 1983; McCallister, 1980; Ross and Huebner, 1980; Freer et al., 1982; Wilson, 1982; Reitmeijer, 1983; Huebner and Voigt, 1984) and with an estimate based on ordering kinetics (Ganguly and Chakraborty, 1990). Ca-Mg-Fe zoning profiles in pyroxenes from granulites suggest that many retain their high temperature core compositions. If Al diffusion is significantly slower than Ca-Mg-Fe diffusion, Al zoning in pyroxenes may be a relic of mineral growth zoning. As metamorphic pyroxenes probably grow under amphibolite and granulite facies conditions (cf. Turner, 1981), *P-T* results obtained from these data should reflect a high-grade portion of the *P-T* path.

To evaluate the possibility that pyroxenes and plagioclase retain growth zoning during high-grade metamorphism, it is necessary to know Al-Si interdiffusion rates in both phases and to model diffusional relaxation. Three such models are available (Muncill and Chamberlain, 1988; Spear, 1988; Florence and Spear, 1989; Chakraborty and Ganguly, 1988, 1990). While these models are for spherical geometries, models for rhombic geometries simply require replacement of half-width terms for radial terms (Chakraborty, personal communication). As both the Muncill and Chamberlain and the Chakraborty and Ganguly models present analytical solutions to the relaxation problem, the numerical Florence and Spear model was not considered. The Chakraborty and Ganguly (1988, 1990) model was adopted because it allows both increasing and decreasing temperatures to be considered.

Application of diffusion data to relaxation of Al zoning in plagioclase and pyroxene requires that the effects of both temperature and $H_2O$ pressure be evaluated, as the presence of $H_2O$ enhances diffusion rates in feldspars (cf. Yund and Tullis, 1980; Yund, 1983, 1986). Given the similarity of the anorthite-albite and Tschermak's exchanges, Al diffusion in pyroxenes could be similarly affected. Several sets of experimental data (Grove et al., 1984; Yund, 1986; Yund and Snow, 1989) suggest that this enhanced diffusion is primarily a factor of $H_2O$ pressure (rather than lithostatic pressure) and $f_{O_2}$ and is probably controlled by H ion concentration (Goldsmith, 1987, 1988; Yund and Snow, 1989).

This paper uses an Arrhenius equation to describe the variation of the diffusion coefficient with temperature. For plagioclase, it is assumed that the activation energy for NaSi and CaAl diffusion is a linear function of $H_2O$ pressure between the anhydrous experiments of Grove et al. (1984) and the hydrous experiment (15 kbar $H_2O$) of Yund (1986), as only these two data are available; however, Yund's experiment was unbuffered and thus may be slightly in error (Yund, personal communication). The data of Yund were obtained on a sample of composition $An_{0-26}$, and those of Grove et al. were for $An_{70-90}$. Thus, it is possible that part of the difference between them reflects a compositional dependence of the diffusion coefficient. An experiment by Yund on the $An_{0-26}$ composition dry at 1 atm, however, yields a limit consistent with the data of Grove et al., and thus it is reasonable to assume little or no compositional dependence. Yund and Snow (1989) showed that the diffusion coefficient is dependent on $f_{O_2}$. Their data at a constant $f_{H_2}$ of 1 bar are used here to constrain the value of the preexponential factor. Thus, this equation does not account for the effects of variations in $f_{O_2}$, but represents an $f_{O_2}$ slightly below the hematite-magnetite buffer (Yund and Snow, 1989). This yields

$$\begin{aligned} \ln D = {} & 8.358 - 1.739 \cdot 10^{-2} \cdot P_{H_2O} \\ & - 2.831 \cdot 10^{-2} \cdot P^2_{H_2O} \\ & - \frac{123\,400 + 1760 \cdot P_{H_2O}}{RT} \end{aligned} \tag{3}$$

where $P_{H_2O}$ is the water pressure in kilobars, $T$ is the temperature in kelvins, R is the gas constant in cal/mol·K, and $D$ is the diffusion coefficient in $cm^2/s$.

Only a single datum on Al diffusion in pyroxenes is available (Sautter et al., 1988; Jaoul et al., 1990): $D = 3.7 \cdot 10^{-17}$ cm²/s at 1180 °C; this is 2–7 orders of magnitude below the data for Ca-Mg-Fe diffusion in pyroxenes (excepting a single measurement by Miyamoto and Takeda, 1977), approximately 1.5 log units below that for CaAl-NaSi diffusion in plagioclase at 1 bar $f_{H_2}$ ($D = 1.18 \cdot 10^{-15}$ cm²/s; Yund and Snow, 1989), and slightly faster than that at 1 bar of air ($D = 3.04 \cdot 10^{-18}$ cm²/s, Grove et al., 1984) at the same temperature. Jaoul et al. note that experiments in progress at 1000 °C suggest that "Al diffusion in diopside is very unlikely in dry rocks over geological time scales." Unfortunately, no data are available on the temperature dependence of Al diffusion in pyroxenes nor on the isothermal effects of increased water pressure.

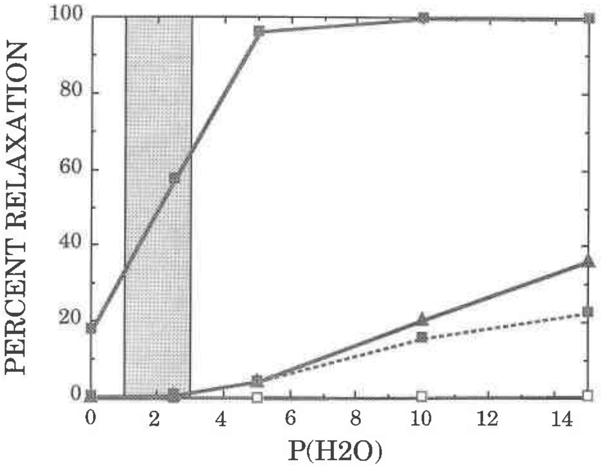

Fig. 3. Relaxation of growth zoning of Al in plagioclase using the model of Chakraborty and Ganguly (1988, 1990). All calculations assume 100 m.y. at peak temperatures. Solid lines are for 1-mm plagioclase grains, and dashed lines are for 1-cm plagioclases; solid squares are at 900 °C, solid triangles are at 800 °C, open squares are at 700 °C. The shaded region shows typical $H_2O$ activities for a 10 kbar granulite.

Figure 3 shows calculated relaxations for plagioclase assuming an initially sinusoidal profile. The operative variable in this model, $\phi$, is defined as

$$\phi = \frac{\Pi^2 Dt}{a^2} \qquad (4)$$

and percent relaxation is defined as

$$\mathrm{abs}\{[C_0(t) - C_s]/[C_s - C_0(0)]\} \times 100 \qquad (5)$$

where $C_s$ is the surface concentration, $C_0(0)$ is the initial core composition, and $C_0(t)$ is the core concentration at time *t*.

Three additional values are needed to calculate relaxation of growth-zoning profiles: time (*t*), temperature (*T*), and grain size (*a*). The temperature represents either an isothermal heating period or a characteristic temperature for a prograde to retrograde *T-t* cycle. Relaxations have been calculated (Fig. 3) assuming 100 m.y. of peak metamorphism. This is significantly longer than most thermal models suggest is reasonable for granulites to be at peak temperatures (e.g., England and Thompson, 1984) and $^{40}Ar/^{39}Ar$ data (e.g., Cosca et al., 1987, 1991). Thus, the predicted relaxation will be a maximum value for reasonable geologic events. Relaxations were calculated at 700, 800, and 900 °C, which represent a range of potential granulite temperatures, and for grains with a radius of 1 mm and 1 cm.

At 700 °C, Al zoning in plagioclase will remain essentially unrelaxed (<5% relaxation) even for a 1-mm grain at 15 kbar $P_{H_2O}$ over 100 m.y. As conditions other than the temperature exceed the typical values for metamorphism of granulites, plagioclase metamorphosed at this temperature should retain nearly all its original Al-growth zoning. At 800 °C and higher $P_{H_2O}$, plagioclase grains experience significant relaxations (36% at 15 kbar $P_{H_2O}$). At 900 °C, significant relaxations (arbitrarily >20%) occur for 1-mm plagioclase grains in 100 m.y. at $P_{H_2O}$ greater than 0.5 kbar. For 1-cm grains, plagioclase does not experience significant relaxation at $P_{H_2O}$ less than 12–14 kbar.

It is not possible to extend directly the above analysis to relaxation of Al zoning in pyroxenes, as only a single datum is available. However, if the 1.5 log unit difference between the rates of Al diffusion in pyroxenes and plagioclase at 1180 °C remains relatively constant or increases at lower temperatures and as a function of water pressure, Al zoning in pyroxenes of greater than 1-mm radius remains essentially unrelaxed under most geological conditions up to 900 °C.

Finally, it is necessary to evaluate whether the temperature and $P_{H_2O}$ conditions examined apply to metamorphism of granulites. Available data (Wells, 1979; Phillips, 1980; Valley et al., 1983; Newton, 1986) suggest that average $H_2O$ activities in granulites are no greater than 0.1 to 0.3 at lithostatic pressures ranging from 6 to 12 kbar. There are two possible explanations for these results. Either granulites are metamorphosed in the absence of a vapor phase or the $H_2O$ in the fluid is strongly diluted, possibly by $CO_2$ (Condie et al., 1982; Janardhan et al., 1982; Valley and O'Neil, 1984; Valley, 1985; Newton, 1986). As the increase in diffusion rates in the presence of $H_2O$ results from H, $CO_2$ is unlikely to influence the diffusion rate of Al in either pyroxenes or plagioclase unless large amounts of H are dissolved in the vapor. Thus, the appropriate $P_{H_2O}$ to use in calculating relaxation of growth zoning in minerals from granulites is no greater than 10–30% of the lithostatic pressure. This yields a maximum $P_{H_2O}$ of 3.6 kbar for very high-pressure granulites such as parts of the Grenville Province (Anovitz, 1987; Anovitz and Essene, 1990; Indares and Martignole, 1984) and the Furua Complex, Tanzania, (Coolen, 1980); maximum $P_{H_2O}$ is 1.5 to 2.5 kbar for intermediate pressure granulites such as the Adirondacks of New York, Pikwitonei, Manitoba (cf. Bohlen, 1987), and the Fiordland complex, New Zealand (Bradshaw, 1989).

**TABLE 1.** Entropy, heat capacity, and Gibbs energy data

| Phase | Formula | $S^0_{298}$ (J/mol·K) | *a* | *b* (J/mol·K) | *c* | *d* | $\Delta G^0_{298}$ (kJ/mol) |
|---|---|---|---|---|---|---|---|
| CaTs | $CaAl_2SiO_6$ | 142.76 (A) | 322.150 | 1.47E−3 | −21.656 | −27.642 (A) | −3122.88 (A) |
| Jadeite | $NaAlSi_2O_6$ | 133.47 (B) | 301.154 | 10.132 | −20.556 | −22.383 (B) | −2851.77 (I) |
| Albite | $NaAlSi_3O_8$ | 225.70 (C) | 486.742 | −25.700 | −46.829 | −2.959 (B) | −3706.30 (D) |
| Anorthite | $CaAl_2Si_2O_8$ | 199.27 (A) | 116.967 | 105.943 | 33.672 | −120.829 (A) | −4010.21 (E) |
| α-quartz | $SiO_2$ | 41.46 (A) | 66.501 | 31.057 | −4.673 | −3.656 (F) | −856.29 (F) |
| α-quartz* | $SiO_2$ | 41.46 (A) | 145.299 | −20.897 | −16.818 | 2.218 (A) | −856.29 (F) |
| β-quartz | $SiO_2$ | 37.44 (G) | 59.296 | 9.933 | −8.951E−2 | 0.152 (A) | −855.89 (H) |

*Note:* $C_P = a + b \times 10^{-3} \times T + c \times 10^2 \times T^{-1/2} + d \times 10^{-5} \times T^{-2}$ ($T$ in K). (A) Robinson et al. (1982), (B) Robie et al. (1979), (C) Haselton et al. (1983), (D) Anovitz et al. (1987), (E) Essene et al. (in preparation), Anovitz and Essene (1987), (F) Hemingway (1987), (G) Fitting coefficient for high temperature data, (H) fitted to α/β transition, (I) this study.

* For $T > 573$ °C.

Maximum temperatures in granulite terranes vary widely. A variety of geothermometers yield maximum temperatures for most between 700 and 800 °C in many terranes. It remains unclear, however, to what extent these temperatures may have reset during cooling. In addition, evidence has been presented that at least one granulite terrane (Enderby Land, Antarctica) reached temperatures of 900–980 °C at pressures of 7–10 kbar (Ellis, 1980; Ellis et al., 1980; Harley, 1983, 1985, 1987; Ellis and Green, 1985).

Comparison of calculated temperatures and $H_2O$ pressures in granulites with Al-diffusion data for plagioclase and pyroxene suggests that under most metamorphic conditions, little or no relaxation of Al-zoning profiles will occur, although very high temperature metamorphism of small grains can allow significant resetting. Therefore, for most metamorphic rocks, observed Al zoning in pyroxenes and plagioclase is a reasonable representation of the growth zoning of these minerals, which has been little affected by either the peak metamorphic conditions or retrogression. These data may be used to examine that section of the metamorphic *P-T* paths where this growth occurred.

## CALIBRATION OF CLINOPYROXENE-PLAGIOCLASE-QUARTZ THERMOBAROMETRY

In order to use Al-zoning data to constrain *P-T* paths, reactions controlling these concentrations must be calibrated. As the Al content in most orthopyroxene from granulites is relatively low, this paper will concentrate on reactions involving clinopyroxene. Two reactions that describe the Al concentration in clinopyroxene are

$$\text{albite} = \text{jadeite} + \text{quartz}$$

$$NaAlSi_3O_8 = NaAlSi_2O_6 + SiO_2 \tag{6}$$

and

$$\text{anorthite} = \text{Ca-Tschermak's pyroxene (CaTs)} + \text{quartz}$$

$$CaAl_2Si_2O_8 = CaAl_2SiO_6 + SiO_2. \tag{7}$$

These reactions may also be combined into an exchange reaction:

$$\text{albite} + \text{CaTs} = \text{anorthite} + \text{jadeite}$$

$$NaAlSi_3O_8 + CaAl_2SiO_6 = CaAl_2Si_2O_8 + NaAlSi_2O_6. \tag{8}$$

Tables 1 and 2 list the thermodynamic data used for these calculations, and Figures 4 and 5 show the contours of $\log_{10}K$ for each as a function of pressure and temperature. All calculations were performed using the Thermo soft-

**TABLE 2.** Volumetric data

| Phase | $V^0_{298}$ | *a* | *b* (cc/mol) | *c* | *d* |
|---|---|---|---|---|---|
| CaTs | 63.58 (A) | 2.369 | 2.933 (A) | 0.799 | −3.041 (A) |
| Jadeite | 60.40 (B) | 2.080 | 4.963 (C) | 0.747 | −2.100 (D) |
| Albite | 100.43 (B) | 2.631 | 3.207 (E) | 1.945 | −4.861 (F) |
| Anorthite | 100.73 (A) | 1.264 | 0.0348 (A) | 1.087 | −12.522 (G) |
| α-quartz | 22.69 (A) | 0.420 | 112.926 (B) | 2.258 | −7.469 (H) |
| α-quartz* | 23.24 (I) | 3.265 | −14.715 (I) | 2.258 | −7.469 (H) |
| β-quartz | 23.74 (J) | 0.368 | −3.275 (B) | 2.258 | −7.469 (H) |

*Note:* Percent expansion = $a \times 10^{-3} \times (T - 293) + b \times 10^{-7} \times (T - 293)^2$; ($T$ in K). Percent compressibility = $c \times 10^{-1} \times P + d \times 10^{-4} \times P^2$; ($P$ in kbar). (A) Robinson et al. (1982), (B) Robie et al. (1979), (C) Cameron et al. (1973), (D) Birch (1966), (E) Winter et al. (1979), (F) Yoder and Weir (1951), (G) Vaidya et al. (1973), Lieberman and Ringwood (1976), (H) Olinger and Halleck (1976), (I) fitted to α/β transition, (J) fitting coefficient for high temperature data.

* For $T > 573$ °C.

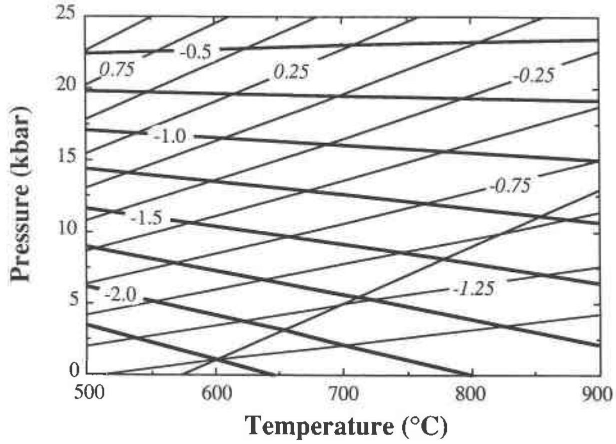

Fig. 4. Contours of $\log_{10}K$ for reactions albite = jadeite + quartz (light lines) and anorthite = CaTs + quartz (heavy lines).

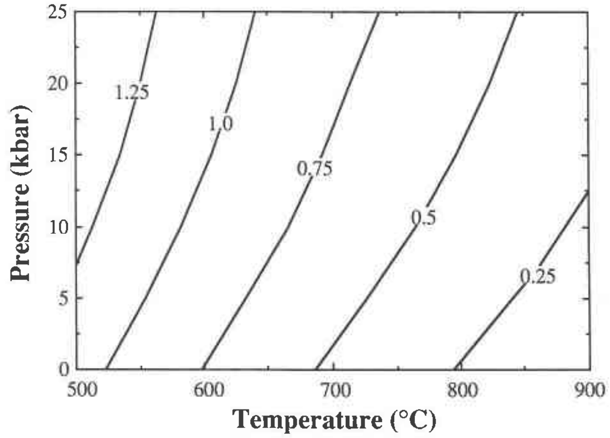

Fig. 5. Contours of $\log_{10}K$ for the exchange reaction albite + CaTs = anorthite + jadeite.

ware of Perkins et al. (1987). Sources of data for albite, anorthite, and quartz are discussed elsewhere (Anovitz et al., 1987; Anovitz and Essene, 1987; Essene et al., in preparation).

Studies of Reaction 6 have been completed by a number of researchers (Johannes et al., 1971; Essene et al., 1972; Hays and Bell, 1973; Holland, 1980; Gasparik, 1984). Fitting these data yields $\Delta G^0_{298}$ for jadeite of −3122.88 kJ/mol, in reasonable agreement with the value of −3122.31 derived by Berman (1988). At 800 °C and 5–15 kbar, $\log_{10}K$ for this reaction changes 0.076 log units per kilobar for 1 mol of quartz and feldspar. This is at the low end of the range displayed by other commonly used geobarometers (GRAIL, 0.064/mole garnet; GASP, 0.087/mole feldspar; GAFS, 0.124/mole feldspar or garnet, cf. Bohlen et al., 1983a, 1983b, 1983c; Anovitz and Essene, 1987; Koziol and Newton, 1988), but is not unreasonable if suitable activity models are available.

Data for CaTs pyroxene were obtained from the thermodynamic data set of Robinson et al. (1982), derived from the experimental data of Hays (1966), Charlu et al. (1978), and Gasparik (1981), and the heat capacity and volume data of Thompson et al. (1978) and Haselton (unpublished data). The change in $\log_{10}K$ for Reaction 7 at 800 °C between 5 and 15 kbar is 0.065 per kbar for 1 mol of quartz and feldspar. This is within a reasonable range for a geobarometer. Below 20 kbar, the $\log_{10}K$ contours for this reaction have a negative slope (cf. Herzberg, 1979). Thus, the intersections of its $\log_{10}K$ contours with those of Reaction 6, which have a positive slope, will be at a relatively high angle, and $\log_{10}K$ contours for Reaction 8 will be known with fair accuracy, although this reaction has not been studied experimentally. The $\log_{10}K$ contours for Reaction 8 are, however, relatively widely spaced (approximately 380 °C per $\log_{10}$ unit at 5 kbar, 550–850 °C). Temperatures calculated in this manner will thus be sensitive to analytical imprecision or errors in activity models.

## ACTIVITY-COMPOSITION MODELS FOR ALUMINOUS CLINOPYROXENES

Application of Reactions 6–8 to thermobarometry requires activity models for both plagioclase and aluminous clinopyroxenes. The model of Newton et al. (1980) was used for plagioclase activities. Usable models for jadeite and CaTs activities were, however, more difficult to obtain. Cohen (1986) modeled the joins diopside-jadeite, jadeite-CaTs, and diopside-CaTs. Unfortunately, with the exception of the diopside-CaTs join, all of Cohen's models utilize a three-parameter Redlich-Kister equation. Although such an equation is satisfactory for binary studies, no ternary or quaternary formulations exist to extend Cohen's binary models to multicomponent clinopyroxenes. Consequently, mixing data for these joins were refitted to a two-parameter, pressure- and temperature-dependent, subregular Margules formulation (Table 3).

To apply these data, a quaternary activity model must be formulated to account for the large hedenbergite com-

**TABLE 3.** Margules parameters for the quaternary pyroxene system jadeite-CaTs-diopside-hedenbergite

| | $W_H$ (J/mol) | $W_S$ (J/mol·K) | $W_V$ (J/mol·bar) |
|---|---|---|---|
| CaTs-Jd | −16132.8 | −13 | 0.0 |
| Jd-CaTs | −2467.15 | −13 | 0.0 |
| CaTs-Di | 8889 | 2.147 | −0.11 |
| Di-CaTs | 29959 | 2.147 | −0.03 |
| Jd-Di | 28153 | 2.20788 | 0.0 |
| Di-Jd | 8953.14 | −15.9921 | 0.0 |
| CaTs-Hd | 8889 | 2.147 | −0.11 |
| Hd-CaTs | 29959 | 2.147 | −0.03 |
| Jd-Hd | 28153 | 2.20788 | 0.0 |
| Hd-Jd | 8953.14 | −15.9921 | 0.0 |
| Di-Hd | 0.0 | 0.0 | 0.0 |
| Hd-Di | 0.0 | 0.0 | 0.0 |

*Note:* $W_G(J) = W_H - TW_S + PW_V$ ($T$ in K, $P$ in bars). For calculation of quaternary coefficient, CaTs = 1, Jd = 2, Di = 3, Hd = 4.

ponent of most clinopyroxenes. Ganguly (1973) noted that to calculate the activities of jadeite, CaTs, and acmite the system may be reduced to one involving CaTs, acmite, diopside, and hedenbergite and also that diopside and hedenbergite may be grouped into a single component. As acmite activities are not of interest in this study, the quaternary system jadeite-CaTs-diopside-hedenbergite was modeled.

Few data are available for the hedenbergite-bearing joins. Wood (1976, 1979) performed a few experiments along the hedenbergite-CaTs join for compositions $0.86 \leq X_{Fe} \leq 0.93$ at 900–1100 °C as part of a study on the diopside-CaTs join. For this range of compositions, he concluded that at 1100 °C clinopyroxenes show a slight negative deviation from ideality ($0.89 \leq \gamma \leq 0.95$), whereas activity coefficients for diopside are slightly positive ($1.06 \leq \gamma \leq 1.37$). Cohen (1986) concluded, however, that uncertainties in Wood's analyses of very small samples (<5 μm) prevent these data from being quantitatively useful. At 1100 °C, assuming that mixing properties on the hedenbergite-CaTs join are the same as those on the diopside-CaTs join yields $a_{CaTs} = 0.08$ for $X_{CaTs} = 0.1$ and $a_{CaTs} = 0.18$ for $X_{CaTs} = 0.15$, as compared with activities of 0.095 and 0.134, respectively, suggested by Wood. These differences are probably within the errors of the experiment, and thus Wood's data have not been incorporated into the model. As no other data are available, mixing properties along the hedenbergite-jadeite and hedenbergite-CaTs joins are assumed to be the same as those for the analogous diopside-bearing joins. Mixing on the diopside-hedenbergite join is therefore assumed to be ideal, and a subregular quaternary mixing model (cf. Ganguly and Saxena, 1984) was used to obtain activities for pyroxenes in this system.

To apply this model to natural pyroxenes, activity coefficients were obtained for a system in which the mole fractions of the four components are normalized to 100%. Analyses of natural pyroxenes were examined and site partitionings and end-member mole fractions estimated; activities were calculated for the real pyroxenes using a site-based model. Details of this mixing model are given in Appendix 1.

The normalization and partitioning procedure used here is largely arbitrary and ignores important factors such as Mg-Fe and Al-$Fe^{3+}$ ordering. For instance, Rossman (1989) showed that in some clinopyroxenes significant $Fe^{3+}$ is present in the tetrahedral site, whereas Cosca and Peacor (1987) found that in esseneite, a phase formed in paralavas, all the $Fe^{3+}$ was in the M1 site. Other normalization schemes are possible and may lead to different activities, but the approach used here provides a uniform treatment of all analyses. Improved models require mathematical formulations involving several additional end-members and the ordering state of each sample. Because the mole fractions of jadeite and CaTs in most clinopyroxenes from granulites are small, small changes in mixing parameters may cause large changes in calculated activities, and the absolute pressures calculated here are therefore semiquantitative. Relative changes in pressure should be less affected by changes in the activity models, however, and Reactions 6–8 remain useful for determining the relative changes in pressure and possibly temperature during pyroxene and plagioclase growth.

## APPLICATIONS TO REGIONAL GRANULITE TERRANES

The above discussions have shown that growth zoning of Al in pyroxenes and plagioclase is largely preserved during granulite facies metamorphism; they have also presented the reactions and the activity-composition models necessary to calculate pressures and temperatures. These models may be applied to available data from granulites to ascertain whether constraints can be placed on the sign (clockwise vs. counterclockwise) of the overall *P-T* path during granulite metamorphism. Calculation of pressures and temperatures at two points along the *P-T* path requires that core and rim analyses be available for both plagioclase and pyroxene grains. Unfortunately, complete data are available for only three terranes: the Grenville Province of Ontario (Anovitz, 1987; Moecher, 1988), the Pikwitonei area, Manitoba (samples provided by K. Mezger), and the Fiordland complex (Bradshaw, personal communication). Of the other localities where clinopyroxene-zoning data are available, only plagioclase core analyses are available for the Furua Complex, Tanzania (Coolen, 1980), and other authors have not provided data on plagioclases coexisting with pyroxenes. Available data show that plagioclase zoning patterns are, in most cases, similar to those in coexisting clinopyroxenes. Thus, the Furua data may be used to limit rim conditions and to constrain the direction of the *P-T* path vector but not to calculate $\Delta P$ and $\Delta T$ values.

Selected analyses used in these calculations are summarized in Tables 4 and 5; results in Table 6 and Figure 6. To minimize uncertainties related to the pyroxene activity model and projection scheme, only samples containing greater than 2.5 wt% $Al_2O_3$ were considered. Qualitative results from each terrane are remarkably consistent. In all cases, the sign of $\Delta P$ and, in most cases, the sign of $\Delta T$ are the same for all samples from each terrane. Thus, regardless of the absolute error in pressure, this approach qualitatively yields the direction of the late prograde or early retrograde *P-T* path. In addition, the scatter in $\Delta P$ between core and rim values of individual grains is small, less than ±1 kbar, although there is greater scatter in absolute pressure, ±1.5–2 kbar. Thus, Al-zoning calculations may yield reasonable constraints on the amount of prepeak unloading. One should, however, be careful about using these reactions for quantitative thermobarometry.

The largest number of available analyses is from the Grenville Province. All Grenville samples show significant pressure decreases from core to rim, and most suggest that some cooling occurred during this unloading. The observed scatter probably results from the low Al content of the clinopyroxenes and from the large lateral distances between some of the sample localities (up to 125

**TABLE 4.** Selected plagioclase analyses

| | 85 DMP 174 Δ1a core | 85 DMP 174 Δ1a rim | Pik 365-1 core | Pik 365-1 rim | FL 51126 core | FL 51126 rim | Furua 55 core |
|---|---|---|---|---|---|---|---|
| $SiO_2$ | 58.67 | 60.67 | 49.37 | 46.95 | 60.40 | 60.52 | 59.99 |
| $Al_2O_3$ | 24.98 | 24.22 | 31.93 | 32.90 | 25.10 | 24.95 | 25.27 |
| $Fe_2O_3$ | 0.00 | 0.09 | 0.10 | 0.29 | 0.00 | 0.00 | 0.00 |
| MgO | 0.00 | 0.02 | 0.00 | 0.02 | 0.00 | 0.00 | 0.00 |
| CaO | 7.26 | 6.14 | 14.42 | 16.81 | 6.88 | 6.46 | 6.85 |
| $Na_2O$ | 6.98 | 7.23 | 3.42 | 2.23 | 7.98 | 7.94 | 7.59 |
| $K_2O$ | 0.29 | 0.40 | 0.03 | 0.03 | 0.14 | 0.12 | 0.30 |
| Total | 98.17 | 98.78 | 99.27 | 99.23 | 100.50 | 100.00 | 100.00 |
| Si | 2.6718 | 2.7471 | 2.2609 | 2.1669 | 2.6725 | 2.6920 | 2.6730 |
| Al | 1.3407 | 1.2923 | 1.7232 | 1.7894 | 1.3089 | 1.3080 | 1.3270 |
| $Fe^{3+}$ | 0.0000 | 0.0030 | 0.0033 | 0.0099 | 0.0000 | 0.0000 | 0.0000 |
| Mg | 0.0000 | 0.0011 | 0.0000 | 0.0016 | 0.0000 | 0.0000 | 0.0000 |
| Ca | 0.3541 | 0.2981 | 0.7075 | 0.8309 | 0.3262 | 0.3080 | 0.3270 |
| Na | 0.6166 | 0.6351 | 0.3034 | 0.1995 | 0.6846 | 0.6850 | 0.6560 |
| K | 0.0168 | 0.0233 | 0.0017 | 0.0018 | 0.0079 | 0.0070 | 0.0170 |
| O | 8.0000 | 8.0000 | 8.0000 | 8.0000 | 8.0000 | 8.0000 | 8.0000 |
| Orthoclase | 0.0171 | 0.0244 | 0.0017 | 0.0017 | 0.0078 | 0.0070 | 0.0170 |
| Albite | 0.6244 | 0.6640 | 0.2996 | 0.1933 | 0.6721 | 0.6850 | 0.6560 |
| Anorthite | 0.3586 | 0.3116 | 0.6987 | 0.8050 | 0.3202 | 0.3080 | 0.3270 |

*Note:* 85 DMP 174 Δ1a—sample from Grenville Province, Ontario provided by D.P. Moecher, analysis this study. Pik 365—sample from Pikwitonei area, Manitoba provided by K. Mezger, analysis this study. FL 51126—from Fiordland, New Zealand. Analysis provided by J. Bradshaw, renormalized this study. Furua 55—from Furua Complex, Tanzania. Analysis from Coolen (1980), renormalized this study. Rim analysis for FL 51126 and core analysis for Furua 55 were obtained as normalized percentages of end-member components, and oxide analyses have been recalculated normalized to 100%.

km). These calculations yield average core conditions of 12.8 kbar, 915 °C, rim conditions of 10.1 kbar, 865 °C, and d*P*/d*T* slopes of 54 bars/°C. The rim conditions are in good agreement with other calculated peak conditions for the Parry Sound and Mattawa areas (10–10.5 kbar, 800–850 °C, Anovitz and Essene, 1990). Field evidence is also available to support a high-pressure prepeak metamorphism. Davidson (1990) has found evidence of retrograded eclogites in the Ontario Grenville, suggesting that the terrane was subjected to high pressures during prograde metamorphism, and Grant (1989) used sapphirine-bearing assemblages to obtain evidence of high-pressure metamorphism at 14–16 ± 1–2 kbar, 775–860 ± 50 °C.

Results from the Furua Complex also suggest significant unloading during the high-grade section of the *P-T* path. Peak conditions for this terrane are 9.6–10.4 kbar, 800 °C (Coolen, 1980; Bohlen, 1987). All the samples for

**TABLE 5.** Selected pyroxene analyses

| | 85 DMP 174 Δ1a core | 85 DMP 174 Δ1a rim | Pik 365-1 core | Pik 365-1 rim | FL 51126 core | FL 51126 rim | Furua 55 core | Furua 55 rim |
|---|---|---|---|---|---|---|---|---|
| $SiO_2$ | 50.51 | 51.91 | 48.55 | 49.58 | 52.70 | 53.00 | 51.44 | 51.62 |
| $TiO_2$ | 0.37 | 0.20 | 0.22 | 0.15 | 0.06 | 0.10 | 0.36 | 0.29 |
| $Al_2O_3$ | 4.29 | 2.96 | 2.53 | 1.60 | 2.01 | 4.38 | 4.05 | 3.52 |
| $Cr_2O_3$ | 0.00 | 0.03 | 0.08 | 0.02 | 0.00 | 0.00 | 0.00 | 0.00 |
| $Fe_2O_3$ | 2.91 | 2.67 | 1.20 | 0.50 | 0.59 | 2.28 | 1.58 | 2.17 |
| FeO | 7.90 | 6.50 | 15.94 | 15.30 | 10.27 | 6.10 | 8.86 | 6.76 |
| MnO | 0.19 | 0.15 | 1.70 | 1.31 | 0.65 | 0.24 | 0.27 | 0.16 |
| MgO | 11.28 | 12.66 | 6.41 | 7.22 | 12.6 | 12.4 | 11.57 | 12.55 |
| CaO | 21.23 | 22.16 | 21.53 | 22.16 | 18.9 | 20.2 | 20.84 | 21.75 |
| $Na_2O$ | 1.15 | 1.00 | 0.34 | 0.33 | 1.18 | 1.97 | 1.16 | 1.04 |
| Total | 99.83 | 100.25 | 98.50 | 98.17 | 98.96 | 100.67 | 100.13 | 99.87 |
| Si | 0.9477 | 0.9639 | 0.9641 | 0.9816 | 0.9942 | 0.9707 | 0.9603 | 0.9609 |
| Ti | 0.0052 | 0.0028 | 0.0033 | 0.0022 | 0.0009 | 0.0014 | 0.0051 | 0.0041 |
| Al | 0.0949 | 0.0648 | 0.0592 | 0.0373 | 0.0447 | 0.0945 | 0.0891 | 0.0772 |
| Cr | 0.0000 | 0.0004 | 0.0013 | 0.0003 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| $Fe^{3+}$ | 0.0411 | 0.0374 | 0.0179 | 0.0074 | 0.0084 | 0.0314 | 0.0222 | 0.0305 |
| $Fe^{2+}$ | 0.1239 | 0.1010 | 0.2648 | 0.2534 | 0.1619 | 0.0935 | 0.1383 | 0.1053 |
| Mn | 0.0030 | 0.0024 | 0.0286 | 0.0220 | 0.0104 | 0.0037 | 0.0043 | 0.0025 |
| Mg | 0.3155 | 0.3505 | 0.1898 | 0.2131 | 0.3544 | 0.3386 | 0.3220 | 0.3483 |
| Ca | 0.4268 | 0.4408 | 0.4581 | 0.4701 | 0.3820 | 0.3964 | 0.4168 | 0.4338 |
| Na | 0.0418 | 0.0360 | 0.0131 | 0.0127 | 0.0432 | 0.0700 | 0.0420 | 0.0375 |
| O | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 |

*Note:* 85 DMP 174 Δ1a—sample from Grenville Province, Ontario provided by D.P. Moecher, analysis this study. Pik 365—sample from Pikwitonei area, Manitoba provided by K. Mezger, analysis this study. FL 51126—from Fiordland, New Zealand. Analysis provided by J. Bradshaw, renormalized this study. Furua 55—from Furua Complex, Tanzania. Analysis from Coolen (1980), renormalized this study.

**TABLE 6.** Core and rim pressures and temperatures derived from Al zoning

| | Nonideal pyroxene mixing | | | | Ideal pyroxene mixing | | | |
|---|---|---|---|---|---|---|---|---|
| | Core | | Rim | | Core | | Rim | |
| Sample | *P* (kbar) | *T* (°C) | *P* (kbar) | *T* (°C) | *P* (kbar) | *T* (°C) | *P* (kbar) | *T* (°C) |
| **Grenville** | | | | | | | | |
| MAT 83C 2 | 14.8 | 980 | 11.5 | 910 | 13.7 | 1105 | 10.8 | 1130 |
| S3B DPM | 10.4 | 790 | 6.8 | 800 | 10.1 | 880 | 7.9 | 1035 |
| PS86E6B | 12.9 | 1080 | 11.6 | 990 | 11.3 | 1130 | 10.8 | 1100 |
| S86E41 | 11.8 | 810 | 10.7 | 800 | 10.8 | 900 | 10.0 | 865 |
| 85 DMP 174 Δ1A | 14.0 | 910 | 10.1 | 825 | 12.6 | 1010 | 10.0 | 980 |
| Average | 12.8 | 915 | 10.1 | 865 | 11.7 | 1005 | 9.9 | 1020 |
| Difference | 2.7 | 50 | slope (bars/°C) | 54 | 1.8 | −18 | slope (bars/°C) | 100 |
| **Fiordland** | | | | | | | | |
| 51068 | 9.9 | 740 | 17.8 | 870 | 9.7 | 860 | 15.7 | 935 |
| 51126 | 5.4 | 550 | 12.8 | 730 | 5.8 | 585 | 11.8 | 795 |
| 51229 | 4.7 | 650 | 13.9 | 830 | 5.9 | 825 | 12.9 | 975 |
| 51112 | 5.0 | 645 | 13.9 | 740 | 6.2 | 900 | 12.5 | 800 |
| Average | 6.2 | 650 | 14.6 | 790 | 6.9 | 790 | 13.2 | 875 |
| Difference | 8.4 | 140 | slope (bars/°C) | 60 | 6.3 | 85 | slope (bars/°C) | 75 |
| **Furua** | | | | | | | | |
| 55 | 13.4 | 905 | <11.7 | <865 | 12.4 | 960 | <11.2 | <975 |
| 94 | 12.9 | 945 | <11.8 | <845 | 12.3 | 1005 | <11.1 | <980 |
| 48* | 17.3 | 1035 | <13.1 | <880 | 13.8 | 1030 | <11.7 | <940 |
| 17 | 14.7 | 940 | <11.3 | <825 | 13.7 | 1010 | <11.2 | <950 |
| Average | 13.7 | 930 | <11.6 | <845 | 12.8 | 990 | <11.2 | <970 |
| Difference | >2.1 | >85 | | | >1.6 | >20 | | |
| **Pikwitonei** | | | | | | | | |
| 363 | 5.4 | 890 | 1.5 | 770 | 6.8 | 1010 | 4.3 | 860 |
| 365-1** | 7.7 | 825 | 3.9 | 630 | 7.8 | 910 | 6.1 | 690 |
| 365-3** | 7.7 | 740 | 3.2 | 630 | 8.7 | 770 | 6.4 | 650 |
| 365-4** | 6.0 | 870 | 4.5 | 635 | 7.4 | 935 | 6.4 | 705 |
| Average | 6.7 | 830 | 3.3 | 670 | 7.7 | 905 | 5.8 | 725 |
| Difference | 3.4 | 160 | slope (bars/°C) | 21 | 1.9 | 180 | slope (bars/°C) | 10.5 |

* Ligamba-type, not included in average.

** Three results from different in-contact pairs from the same sample.

which Al equilibration pressures and temperatures have been obtained yield significantly higher core pressures and temperatures. As the Ligamba-type granulites (sample 48) have mantle affinities (Coolen, 1980), it is not reasonable to average this sample with the rest. The remaining samples yield average core conditions of 13.7 kbar, 930 °C and rim condition limits of <11.6 kbar, <840 °C, in reasonable agreement with peak conditions and again suggesting significant unloading during the high *P-T* part of the path.

Data from both the Grenville Province in Ontario and the Furua Complex suggest that a significant period of unloading occurred prior to the peak of metamorphism recorded by other thermobarometers: prior to the isobaric cooling part of the retrograde path. Thus, both granulite-facies terranes appear to have experienced clockwise overall *P-T* paths if such paths can be described by simple loops. The calculations of England and Thompson (1984) and those of Anovitz and Chase (1990) suggest that this type of *P-T* path is consistent with Himalayan-type tectonics, as both data sets suggest cooling during unloading. If results obtained from Al zoning are real, however, they imply that standard geothermometers may not record peak temperatures above 800 to 900 °C. This is supported by available diffusion data (Chakraborty and Ganguly, 1990) and by the observation from the Grenville that temperatures obtained from standard geobarometers are nearly independent of pressure in this temperature range. A much larger data set and possibly an experimental calibration of Reaction 8 are needed, however, to determine whether the observed pressure and temperature trends obtained from Al zoning are quantitatively accurate.

The observation that Al zoning in pyroxene and plagioclase yields higher core temperatures than standard thermometers presents a terminology problem. If the temperatures obtained from the Al-zoning data are accepted, pressures and temperatures obtained from standard thermobarometers should not be referred to as "peak," as they are lower in many cases than those obtained from core Al concentrations. Because of the uncertainties in this interpretation, however, this paper will retain the standard terminology in order to remain consistent with common usage, and the term "peak metamorphism" will refer to the maximum pressures and temperatures recorded by standard thermobarometers.

Results from the Fiordland and Pikwitonei terranes differ from those obtained in the Grenville Province and Furua Complex. In the Fiordland samples, clinopyroxenes show inverse Al zoning (Fig. 2). Qualitatively, therefore, these samples suggest a pressure increase during prograde metamorphism, and calculations confirm this hypothesis. On the basis of mineral zoning and textural studies, Bradshaw (1989) suggested that Fiordland experienced an episode of high-temperature and low-pressure metamorphism accompanying intrusion of anhydrous magmas (4–8 kbar, 650–750 °C) followed by a later high-pressure metamorphism (12–13 kbar, 650–700 °C) associated with overthrusting of a 20 km thick slab. The average core pressures and temperatures (core = 6.7 kbar, 650 °C; rim = 14.8 kbar, 810 °C) agree reasonably well with Bradshaw's results. The rim temperature, however, is significantly higher. This may simply reflect imprecision in the Al-based temperature calculation. It is also possible, however, that the suggested temperature increase is real. If the overthrust plate contains even average crustal levels of radioactive elements, some temperature increase related to overthrusting is likely unless unloading following thrusting is extremely rapid. Thus, as Bradshaw's rim temperatures were based on touching garnet-clinopyroxene and garnet-biotite pairs, the lower rim temperatures obtained by Bradshaw may reflect partial resetting of the thermometers during retrogression.

Two samples containing the assemblage garnet + clinopyroxene + plagioclase + quartz from the Cauchon Lake region of the Pikwitonei terrane, Manitoba, were also examined. The Al content of pyroxenes in one of the samples was very low, and no calculations were attempted. In the other, rim compositions were below the assumed minimum of 2.5 wt% $Al_2O_3$, but pyroxenes showed normal Al zoning. Mezger et al. (1990) obtained a peak *P-T* for this region of 6.9–7.5 kbar, 700–750 °C and suggested that the initial retrograde path was close to isobaric on the basis of garnet zoning. They also observed that in a lower grade part of the terrane (Utik Lake), sillimanite in some samples appears to replace andalusite, and at Cauchon Lake apparent pseudomorphs of sillimanite after andalusite occur. This suggested that the terrane may have followed a narrow, counterclockwise *P-T* path. No quantitative data are available, however, to support this assertion, and results obtained from Al zoning in clinopyroxenes could therefore be quite significant. Unfortunately, data from Al zoning in the two clinopyroxene-plagioclase pairs from the Pikwitonei terrane examined in this study neither support nor disprove the overall *P-T* path suggested by Mezger et al. (1990). The average core *P-T* obtained (6.7 ± 1 kbar, 830 ± 90 °C) is quite close to that obtained by Mezger et al., and the rim *P-T* (3.3 ± 1.5 kbar, 660 ± 110 °C) yields a retrograde path with a slope (20.7 bars/°C), slightly steeper than the retrograde path they suggested but within the range of calculated retrograde paths obtained by Anovitz and Essene (1990) for the Grenville Province in Ontario.

The explanation of the results from Pikwitonei is unclear. The Pikwitonei data are unusual among the data analyzed in two ways. First, the concentration of $Al_2O_3$ in these pyroxenes is very low, a maximum of 2.66 wt%. Although all pyroxenes showed normal Al zoning, the concentrations are so low that calculated jadeite and CaTs activities are uncertain. Second, pyroxenes and plagioclase show opposite zoning trends, as plagioclase is reversely zoned. Thus, the assumption that the cores and

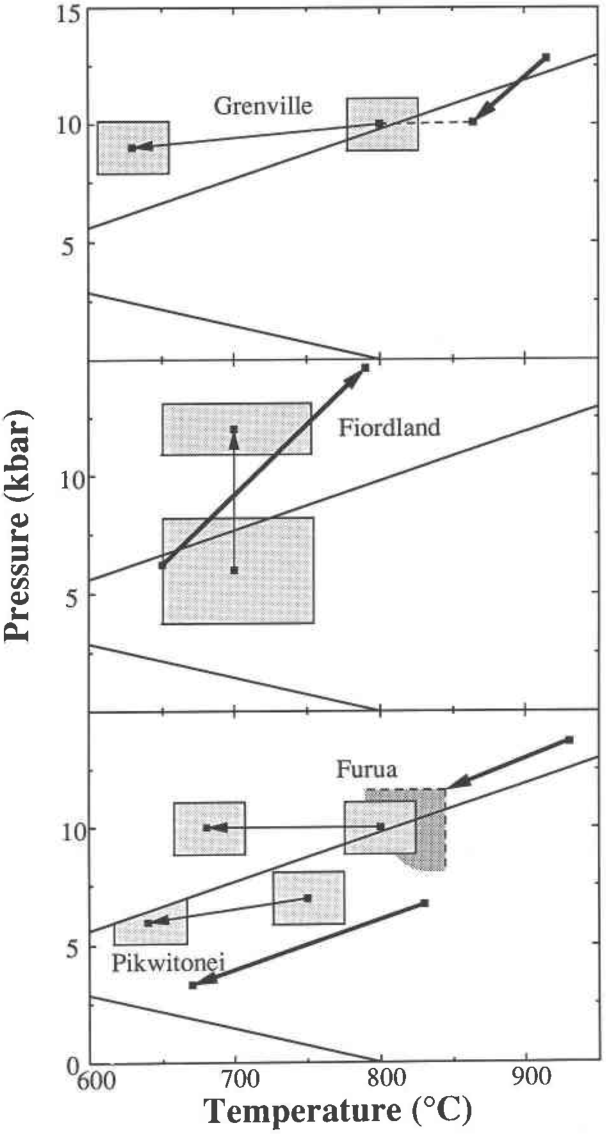

Fig. 6. Average results of the Al-zoning calculations and initial retrograde paths for the four terranes examined. Heavy arrows connect the core and rim *P-T* values obtained from the Al-zoning data, and light arrows show the retrograde *P-T* paths obtained from standard thermobarometry. Light shaded areas are estimates of the uncertainties in the standard thermobarometry. Initial retrograde data were obtained from the work of Bohlen (1987), Anovitz and Essene (1990), and Mezger et al. (1990). Late prograde data for the Fiordland complex are from Bradshaw (1989). Only limiting values for rim conditions are available from the Al-zoning data from Furua, as plagioclase rim compositions were not obtained; the dark hatched area shows part of the allowed *P-T* range. If final average results from Al-zoning calculations differ slightly from suggested peak pressures and temperatures, the two are connected by a dashed line. This may represent either uncertainties in the results or an unrecorded part of the *P-T* path. The reactions andalusite = sillimanite and sillimanite = kyanite are also shown for reference.

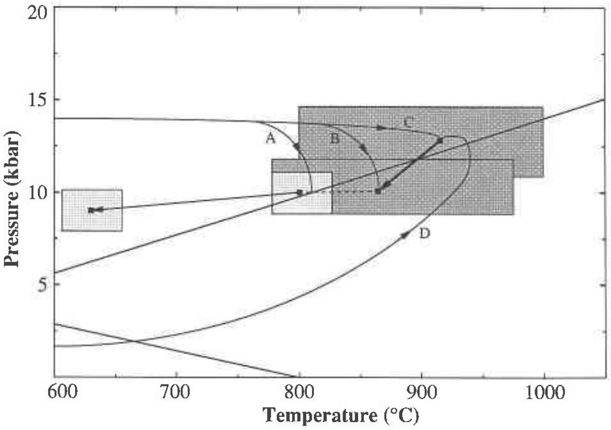

Fig. 7. Qualitative analysis of possible overall *P-T* paths for the Grenville Province, Ontario, given available *P-T*-path data. The heavy arrow is the average result from the Al-zoning data, and the dark shaded areas are estimates of the uncertainties in these values. The light arrow and lighter error boxes are the peak pressure and temperature and the retrograde *P-T* path obtained by Anovitz and Essene (1990). Lighter arrows show potential *P-T* paths that are consistent with the data. Paths A, B, and C are clockwise and show that either heating or cooling during unloading is permissible given the precision in the thermobarometry and that the implied 50 to 75 °C extension to the isobaric cooling path is possible but unproven. Path D is counterclockwise and shows that a tectonic model involving initial magmatic heating followed by underthrusting and rapid erosion or tectonic denudation may also explain the observed *P-T* path. The *T-t* implications of such a path, however, remain uncertain.

rims of the plagioclase and pyroxene grains were in equilibrium may be incorrect. It is unlikely that pyroxene either grew or reequilibrated during retrogression, but either process may have affected plagioclase, especially if values of $f_{H_2O}$ were locally raised. It may be unreasonable, therefore, to use these values to calculate *P-T* paths, despite the good agreement between the core results and those obtained by Mezger et al. (1990). Crawford (1977) noted that, if zoning in two minerals in equilibrium is controlled by the overall availability of an element such as Al to the growing crystals, zoning in the two minerals will follow the same trend. If, however, the amount of Al in the two samples is fixed, zoning is controlled by an exchange equilibrium such as Reaction 8, and zoning patterns in the two phases will be antithetic, as observed in the Pikwitonei samples. Additional samples and complete zoning profiles of pyroxene-plagioclase pairs from this terrane need to be examined if the Pikwitonei results are to be understood.

Because of the necessary assumptions included in the activity-composition model for aluminous pyroxenes used for these calculations, it is reasonable to examine the results obtained using an ideal mixing model. Ideal activities of CaTs and jadeite were calculated using the equations for the mole fractions of these phases given in Appendix 1. The model of Newton et al. (1980) was again used to obtain the activity of anorthite. In most cases (Table 6), these calculations yielded lower pressures, higher temperatures, and smaller average pressure and temperature differences between core and rim results. In the Grenville and Fiordland terranes, steeper average *P-T* paths were obtained. The exception is again Pikwitonei, where both average pressures and temperatures increased, and the average *P-T* path obtained was flatter. Although the available activity-composition data suggest that mixing properties of aluminous pyroxenes are not ideal, these calculations emphasize that the results obtained are semiquantitative, as uncertainties in calculated activities can yield large changes in calculated results. The qualitative results, however, especially for pressure, are much more robust, and strong evidence remains for an episode of high pressures in the Grenville and Furua prior to the peak pressures and temperatures recorded by standard thermobarometry, and for the on-loading event in Fiordland.

Of the four terranes examined, only results from Fiordland appear to be prograde. Average results from the Grenville, Furua, and Pikwitonei provinces (Fig. 6) suggest cooling during unloading and thus appear to be early retrograde rather than late prograde *P-T* paths. This implies that pyroxenes did not grow during prograde metamorphism, that recrystallization during the high-pressure part of the *P-T* path has destroyed any preexisting zoning, or that there are systematic errors in the calculated temperatures. Given the relatively flat slope (20 bars/°C for the end-member reaction, 11 bars/°C for $P = 8–12$ kbar, $T = 550–900$ °C) of reactions such as (cf. Moecher et al., 1988)

$$\begin{aligned} &2 \text{ grossular} + \text{pyrope} + 3 \text{ quartz} \\ &\quad = 3 \text{ diopside} + 3 \text{ anorthite} \qquad (9) \end{aligned}$$

pyroxene may grow from garnet and quartz-bearing assemblages in response to significant unloading; however, it is probably not reasonable for growth to occur only during cooling. Figure 7 shows several possible *P-T* paths for the Grenville results. Paths A, B, and C are possible clockwise paths given the errors in the clinopyroxene + plagioclase + quartz thermobarometry. While cooling during unloading is suggested by the average path, uncertainties in temperature make prograde paths (A, B) possible. In addition, if more complex paths are envisioned (D), the data do not rule out the possibility of counterclockwise *P-T* paths.

## CONCLUSIONS

These research results suggest that different granulite terranes may form by different processes and follow different overall *P-T* paths. In some granulites, such as the Grenville Province in Ontario and the Furua Complex, the *P-T* path appears to be the result of a crustal thickening event that yields a clockwise *P-T* path (in standard *P-T* space) described mathematically by several models (e.g., England and Thompson, 1984; Anovitz and Chase, 1990), if it is assumed that the overall *P-T* path can be described by a simple loop. The presence of a prepeak high-pressure episode fits well with the prediction by Anovitz and Chase (1990) that prepeak unloading is necessary to generate initial retrograde paths that are unbundled and isobaric and cooling rates that agree with the available $^{40}Ar/^{39}Ar$ data. In terranes such as Fiordland, however, early phases of the metamorphic event appear to be dominated by an influx of heat, possibly of magmatic origin. Additional pressure increases resulting from tectonic activity may or may not be involved, and the processes that bring sediments into the middle or lower crust before metamorphism and then uplift the terrane to the surface may be unrelated to the main metamorphic event. Such *deus ex machina* arguments are unsatisfactory, however, and evidence needs to be sought to explain these factors. Overall *P-T* paths in this case may vary. Anovitz and Chase (1990) showed that simple underplating generates a clockwise path with an uplift approximately ⅔ that obtained from a slab of crustal material of thickness similar to the underplating magma body; thus, counterclockwise paths appear to require a combination of underplating and crustal thickening.

The possibility that overall *P-T* paths do not necessarily form simple loops should also be considered (cf. Mezger et al., 1989). One possible, more complex scenario involves burial of the terrane after a significant input of magmatic heat, possibly resulting from the addition of a cold slab on top of the original terrane (cf. Bradshaw, 1985, 1989). In this case, however, the terrane heats again after thrusting because of burial and heat input from radiogenic elements in the upper plate; this heating should occur unless subsequent unroofing is quite rapid (Anovitz and Chase, unpublished data). No model has yet been proposed that generates a counterclockwise path without a significant input of magmatic or possibly volatile-derived heat (Ganguly and Singh, 1988). The overall tectonics necessary to generate a path such as D in Figure 7, however, remain unclear but may involve rapid tectonic denudation soon after burial. Polymetamorphic terranes should also exhibit complex *P-T* paths.

Several factors influence interpretation of the results obtained from Al zoning in pyroxenes. The absolute pressures and temperatures obtained are relatively imprecise. Relative $\Delta P$ and $\Delta T$ values appear to be much more consistent but should be used with caution, especially if Al contents are low, because of uncertainties in the available mixing models. Qualitatively, however, all samples examined from each terrane yielded the same direction of change in pressure, and most gave similar results for temperature. Thus examination of Al-zoning profiles in coexisting pyroxenes and plagioclases appears to be a useful approach for obtaining prepeak segments of *P-T* paths in granulites.

This analysis has assumed that plagioclase and pyroxene grains grew at approximately the same time and thus that the cores and rims of the two grains were in equilibrium at some time during the metamorphic cycle. It is possible that plagioclase existed in these rocks prior to growth of clinopyroxene under upper amphibolite or granulite facies conditions or conversely that clinopyroxene grew before plagioclase, possibly under eclogite facies conditions. If only core and rim compositions are given, zoning changes are also assumed to be smooth and continuous. These assumptions need to be tested. Careful analysis of variations in plagioclase compositions in pyroxene-bearing rocks and more complex modeling of mineral growth and $f_{H_2O}$ changes with time could suggest whether such relicts exist in granulites and, if so, how to correlate pyroxene and plagioclase zoning profiles for more accurate thermobarometry.

The discussion also assumes that the differences between the retrograde *P-T* paths obtained from other approaches and the late-prograde or early-retrograde paths obtained from Al zoning are significant. Agreement between the average *P-T* values from the Grenville Province and Furua Complex obtained from Al zoning of the mineral rims and the peak *P-T* values obtained from other thermobarometers suggests this is reasonable; however, relatively large error brackets suggest that caution is appropriate. Resolution of this uncertainty requires both a much larger data base of pyroxene + plagioclase + quartz assemblages from a number of granulite terranes and improved reaction calibrations and activity models.

Finally, the tectonic interpretations of the processes that form granulites presented here assume that isobaric retrograde *P-T* paths are real (cf. Ellis, 1980; Ellis and Green, 1985; Harley, 1989; Bohlen, 1987; Anovitz and Essene, 1990). Combination of the Al-zoning results with isobaric initial retrograde paths and available data on the later parts of the cooling histories of granulite terranes (van der Pluijm and Carlson, 1989; Lamb et al., 1991) strongly constrains the details of much of the *P-T* history of a given area and therefore the processes by which it may have formed. If, as has recently been claimed (Frost and Chako, 1989), isobaric cooling is an artifact of differential closure temperatures of thermobarometric reactions, this may alter the tectonic interpretations presented. It will not, however, affect the usefulness of Al-zoning studies in the interpretation of parts of the *P-T* paths of granulites.

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## APPENDIX 1.

Site partitionings were determined using the following assumptions:

1. Pyroxenes are normalized to two cations and charge balanced to three O atoms by varying the $Fe^{2+}/Fe^{3+}$ ratio.
2. All Na and Ca go into the M2 site.
3. Al and $Fe^{3+}$ partition equally into the tetrahedral site as a function of their concentrations

$$X^{\mathrm{T}}_{\mathrm{Al}} = (1 - X_{\mathrm{Si}})\cdot\left(\frac{X_{\mathrm{Al}}}{X_{\mathrm{Al}} + X_{\mathrm{Fe^{3+}}}}\right)$$

$$X^{\mathrm{T}}_{\mathrm{Fe^{3+}}} = (1 - X_{\mathrm{Si}})\cdot\left(\frac{X_{\mathrm{Fe^{3+}}}}{X_{\mathrm{Al}} + X_{\mathrm{Fe^{3+}}}}\right).$$

4. All remaining Al and $Fe^{3+}$ goes into the M1 site.
5. Mg and $Fe^{2+}$ are equally partitioned into the remaining space in the M2 site as a function of their concentrations

$$X^{\mathrm{M2}}_{\mathrm{Mg}} = \left(\frac{X_{\mathrm{Mg}}}{X_{\mathrm{Mg}} + X_{\mathrm{Fe^{2+}}}}\right)\cdot(1 - X^{\mathrm{M2}}_{\mathrm{Ca}} - X^{\mathrm{M2}}_{\mathrm{Na}})$$

$$X^{\mathrm{M2}}_{\mathrm{Fe^{2+}}} = \left(\frac{X_{\mathrm{Fe^{2+}}}}{X_{\mathrm{Mg}} + X_{\mathrm{Fe^{2+}}}}\right)\cdot(1 - X^{\mathrm{M2}}_{\mathrm{Ca}} - X^{\mathrm{M2}}_{\mathrm{Na}}).$$

6. All remaining Mg and $Fe^{2+}$ goes into the M1 site.

End-member mole fractions were calculated as

$$X_{\mathrm{Jd}} = X^{\mathrm{M2}}_{\mathrm{Na}}\cdot\left(\frac{X^{\mathrm{M1}}_{\mathrm{Al}}}{X^{\mathrm{M1}}_{\mathrm{Al}} + X^{\mathrm{M1}}_{\mathrm{Fe^{3+}}}}\right)$$

$$X_{\mathrm{CaTs}} = X^{\mathrm{T}}_{\mathrm{Al}}$$

$$X_{\mathrm{Di}} = 2\cdot(X^{\mathrm{M1}}_{\mathrm{Mg}} - X_{\mathrm{Mg}})$$

$$X_{\mathrm{Hd}} = 2\cdot(X^{\mathrm{M1}}_{\mathrm{Fe^{2+}}} - X_{\mathrm{Fe^{2+}}})$$

and final activities were calculated as

$$a(\mathrm{Jd}) = X^{\mathrm{M2}}_{\mathrm{Na}}\cdot X^{\mathrm{M1}}_{\mathrm{Al}}\cdot(X^{\mathrm{T}}_{\mathrm{Si}})^2\cdot\gamma_{\mathrm{Jd}}$$

$$a(\mathrm{CaTs}) = X^{\mathrm{M2}}_{\mathrm{Ca}}\cdot X^{\mathrm{M1}}_{\mathrm{Al}}\cdot(2\cdot X^{\mathrm{T}}_{\mathrm{Al}})\cdot(2\cdot X^{\mathrm{T}}_{\mathrm{Si}})\cdot\gamma_{\mathrm{CaTs}}$$

$$a(\mathrm{Di}) = X^{\mathrm{M2}}_{\mathrm{Ca}}\cdot X^{\mathrm{M1}}_{\mathrm{Mg}}\cdot(X^{\mathrm{T}}_{\mathrm{Si}})^2\cdot\gamma_{\mathrm{Di}}$$

$$a(\mathrm{Hd}) = X^{\mathrm{M2}}_{\mathrm{Ca}}\cdot X^{\mathrm{M1}}_{\mathrm{Fe}}\cdot(X^{\mathrm{T}}_{\mathrm{Si}})^2\cdot\gamma_{\mathrm{Hd}}.$$

As noted by Ganguly and Saxena (1984), different ordering of these components changes the sign of the Wohl estimation of the ternary mixing coefficient (*C*). The order used here was CaTs(1), Jd(2), Di(3), Hd(4). Trial experiments with alternate orders yielded only slight variations (<0.5 kbar) in calculated pressures.