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Thermodynamic calibration of geobarometers based on the assemblages garnet-plagioclase-orthopyroxene (clinopyroxene)-quartz[1]

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Abstract

Two mineralogic geobarometers based on the assemblage garnet-plagioclase-pyroxene-quartz, common in granulite-grade quartzofeldspathic and basic lithologies, have been calibrated almost entirely from measured thermodynamic quantities, especially enthalpy of solution and heat capacity measurements. For the continuous reaction:

$$\underset{\text{(plagioclase)}}{CaAl_2Si_2O_8} + \underset{\text{(opx)}}{Mg_2Si_2O_6} = \underset{\text{(garnet)}}{1/3Ca_3Al_2Si_3O_{12} + 2/3Mg_3Al_2Si_3O_{12}} + \underset{\text{(quartz)}}{SiO_2} \qquad \text{(A)}$$

the resulting geobarometric expression is:

$$P_{\text{Opx}}\ \text{(bars)} = 3944 + 13.070T\text{(K)} + 3.5038T\ln K_{\text{A}} \qquad (1)$$

where $K_{\text{A}} = \dfrac{(a_{\text{Ca}} \cdot a_{\text{Mg}}^2)^{\text{Gt}}}{(a_{\text{Ca}}^{\text{Pl}})(a_{\text{Mg}_2}^{\text{Opx}})}$.

The pressure uncertainty is ±1500 bars, mainly from the calorimetric uncertainty in $\Delta G^\circ_{\text{A}}$. For the reaction

$$\underset{\text{(plagioclase)}}{CaAl_2Si_2O_8} + \underset{\text{(cpx)}}{CaMgSi_2O_6} = \underset{\text{(garnet)}}{2/3Ca_3Al_2Si_3O_{12} + 1/3Mg_3Al_2Si_3O_{12}} + \underset{\text{(quartz)}}{SiO_2} \qquad \text{(B)}$$

the expression is:

$$P_{\text{Cpx}} = 675 + 17.179T + 3.5962T\ln K_{\text{B}} \qquad (2)$$

where $K_{\text{B}} = \dfrac{(a_{\text{Ca}}^2 \cdot a_{\text{Mg}})^{\text{Gt}}}{(a_{\text{Ca}}^{\text{Pl}})(a_{\text{CaMg}}^{\text{Cpx}})}$.

The uncertainty is ±1600 bars. The activity expressions are simple formulae based on calorimetry, except for those of the pyroxene components, which are based on the "ideal two-site" model.

A literature survey of analyzed occurrences of the above assemblages shows that they can be classified into (1) thermal aureoles, (2) transitional granulite terranes, (3) massif granulite terranes, (4) tectonically uplifted deep crustal granulites and (5) deep crustal granulite exotics in explosive igneous pipes. Characteristic pressure ranges for each class were found with the present geobarometers. Thermal aureoles in the Nain (Labrador) province and the Scottish Dalradians show 1–4 kbar; massif granulite terranes show a notable cluster in the range 8.9±1.5 kbar, transitional granulite terranes fall at lower pressures, as well as lower temperatures, than the massif granulites, and the highest pressures are registered by the deep crustal uplifts, such as the Ronda (Spain) peridotite aureole and the Doubtful Sound, New Zealand, mafic granulites. Pressures of up to 12.5 kbar for the Doubtful Sound granulites confirms their deep-crustal character.

The consistent 8 kbar pressures of many granulite terranes could correspond to the base

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of a 30–40 km-thick continent, which provides evidence that continental-scale overthrusting, such as that postulated to be currently in progress under the Tibetan Plateau, could be the principal tectonic mechanism of ancient granulite metamorphism.

Introduction

Geobarometry of garnetiferous crustal rocks

In recent years several mineralogic geobarometers for metamorphic rocks have been proposed which make use of the common coexistence of garnet with less dense aluminous minerals such as cordierite, plagioclase, or aluminous pyroxenes. Simple reactions relating garnet to the less dense minerals form the basis of geobarometric equations. The reactions are of high variance in natural compositions, so that the corresponding thermodynamic equations are sliding-scale, or continuous, pressure indicators. A simple example is the reaction of $Mg_3Al_2Si_3O_{12}$ (pyrope) to $Mg_2Si_2O_6$ (enstatite) and $MgAl_2SiO_6$ (MgTs), first calibrated from experimental phase equilibrium studies as a geobarometer by Wood and Banno (1973). The garnet–orthopyroxene barometer was originally intended for garnet peridotites of subcrustal origin, but has also been applied numerous times to high-grade crustal rocks (Weaver *et al.* 1978; Wells, 1979; Hörmann *et al.*, 1980). This barometer has some severe limitations in the crustal application, mainly arising from inadequate experimental calibration for the crustal ranges of temperature, pressure, and mineral compositions. The association garnet–plagioclase–Al_2SiO_5–quartz in high-grade pelitic rocks is the basis of another widely-used geobarometer. The calibration, based on experimental phase equilibrium work (Goldsmith, 1980) and measured thermodynamic properties of garnet and plagioclase (Newton and Haselton, 1981), is fairly precise, and the volume change of the reaction is large, which is a prerequisite of an accurate geobarometer. The main disadvantage is comparative rarity of pelitic compositions yielding the four-phase assemblage in some high-grade terranes. A third widely-used geobarometer is based on the reaction of Mg-cordierite to pyrope, sillimanite and quartz. The volume change of reaction is very large, and the requisite four-phase assemblage has been reported from many terranes. Experimental calibrations based on attempted direct equilibration of garnet and cordierite are in some conflict (Hensen and Green, 1971; Currie, 1971), as are semiempirical theoretical calibrations (Thompson, 1976; Perchuk *et al.*, 1981). One problem stems from the poorly-known effect of molecular H_2O in the cordierite structure (Newton and Wood, 1979). Another problem is the limited pressure range over which garnet and cordierite coexist, which is probably only 3–4 kbar in many rock compositions.

Quartzo-feldspathic lithologies are the dominant components of many granulite-facies terranes. Pyroxene-bearing gneisses, or charnockites, commonly contain garnet, including the type charnockite found near Madras (Pichamuthu, 1970). Basic granulites are ubiquitous and abundant in all gneiss terranes as lenses, enclaves, and, sometimes, thick bodies of supracrustal or plutonic origin. Clinopyroxene or orthopyroxene or both are often accompanied by garnet and quartz. The mineralogy of charnockites and basic granulites suggests the possibility of geobarometers based on the reactions:

$$\underset{\substack{\text{anorthite}\\ \textit{in}\\ \text{plagioclase}}}{CaAl_2Si_2O_8} + \underset{\substack{\text{enstatite}\\ \textit{in}\\ \text{orthopyroxene}}}{Mg_2Si_2O_6} = \underset{\substack{\text{grossular}\\ \textit{in}\\ \text{garnet}}}{1/3Ca_3Al_2Si_3O_{12}} + \underset{\substack{\text{pyrope}\\ \textit{in}\\ \text{garnet}}}{2/3Mg_3Al_2Si_3O_{12}} + \underset{\text{quartz}}{SiO_2} \qquad \text{(A)}$$

$$\underset{\substack{\text{anorthite}\\ \textit{in}\\ \text{plagioclase}}}{CaAl_2Si_2O_8} + \underset{\substack{\text{diopside}\\ \textit{in}\\ \text{clinopyroxene}}}{CaMgSi_2O_6} = \underset{\substack{\text{grossular}\\ \textit{in}\\ \text{garnet}}}{2/3Ca_3Al_2Si_3O_{12}} + \underset{\substack{\text{pyrope}\\ \textit{in}\\ \text{garnet}}}{1/3Mg_3Al_2Si_3O_{12}} + \underset{\text{quartz}}{SiO_2} \qquad \text{(B)}$$

These reactions have large volume changes and are thus suitable in principal for accurate geobarometry. They are of high variance in crustal rocks, however, and therefore are less amenable to direct experimental calibrations.

Thermodynamic formulation of the barometers

The equilibrium condition for any reaction is that the Gibbs energy difference, ΔG, vanish at a given temperature, T, and pressure, P:

$$\Delta G(T, P, X_i^{\beta}) = 0 \qquad (1)$$

X_i represents the mole fractions of the components, i, in the participating phases, β. Equation (1) may be expanded for reactions (A) and (B):

$$\frac{-\Delta H^{\circ}_{A}}{RT} + \frac{\Delta S^{\circ}_{A}}{R} \cong \ln \frac{(a^{Gt}_{Mg})^2 \cdot a^{Gt}_{Ca}}{a^{Opx}_{En} \cdot a^{Pl}_{An}} + \frac{P\Delta \bar{V}_{A}}{RT} \qquad (2)$$

$$\frac{-\Delta H^{\circ}_{B}}{RT} + \frac{\Delta S^{\circ}_{B}}{R} \cong \ln \frac{a^{Gt}_{Mg} \cdot (a^{Gt}_{Ca})^2}{a^{Cpx}_{Di} \cdot a^{Pl}_{An}} + \frac{P\Delta \bar{V}_{B}}{RT}$$

where ΔH° and ΔS° denote, respectively, the standard enthalpy and entropy changes of the reactions, $\Delta \bar{V}$ the partial molal volume differences, a the activities at one bar, and R is the gas constant. The approximation sign is used because of neglect of differences in compressibilities. The subscripts Mg, Ca, En, Di and An denote, respectively, the components $MgAl_{2/3}SiO_4$, $CaAl_{2/3}SiO_4$, $Mg_2Si_2O_6$, $CaMgSi_2O_6$, and $CaAl_2Si_2O_8$, and the superscripts Gt, Opx, Cpx, and Pl denote, respectively, the phases garnet, orthopyroxene, clinopyroxene and plagioclase.

Equations (2) define P in terms of T and the compositions of the phases provided that the activities and partial molar volumes are known as functions of composition and T and that the standard Gibbs energy changes, which are the left-hand sides of equations (2), are known as functions of T. The activities may be determined by calorimetric measurements on solid solutions and by modelling of phase equilibrium data. The partial molar volumes are determined by X-ray diffraction data for the solid solutions. The standard Gibbs energies for reactions (A) and (B) may not be deduced directly and accurately from phase equilibrium data because the reactions are not univariant and because relevant experimental phase equilibrium data (Kushiro and Yoder, 1966; Hensen, 1976) do not define closely enough the compositions of coexisting garnets and pyroxenes. However, enthalpy of solution and heat capacity measurements on the end-member substances allow purely thermodynamic determination of ΔG°_{A} and ΔG°_{B}.

Previous calibrations

Wood (1975) first used reaction (A) in geobarometric calculations of the South Harris (Scotland) Archaean charnockites and metagabbros. He evaluated ΔG°_{A} from phase equilibrium data of Kushiro and Yoder (1966), which required a long temperature extrapolation of the data, obtained mostly above 1200°C. Moreover, compositions of the phases in their reactions were not accurately determined. Activities of garnet components were taken from phase equilibrium reductions of Hensen *et al.* (1975a) and plagioclase activities were based on the phase equilibrium data of Orville (1972). Wood found maximum pressures of 11–13 kbar at plausible granulite temperatures of 700–900°C. These pressures seem rather high considering that the South Harris charnockites do not actually contain garnet. Wells (1979) deduced pressures of 9.1–11.4 kbar (mean of 10.5 kbar) for basic granulites of the Buksefjorden region, SW Greenland, from the same geobarometer and assuming a temperature of 800°C. He used more recent phase equilibrium data (Hensen, 1976) to evaluate ΔG°, and nearly the same activity assumptions used by Wood (1975). The Hensen (1976) equilibrium curves also require long extrapolations to crustal conditions, and the compositions of phases along them were not well-determined. Perkins (1979) calibrated geothermometers based on reactions (A) and (B) for rocks of a transitional amphibolite-granulite terrain in the Otter Lake, S. Quebec, region. He used experimental phase equilibrium work on plagioclase, pyroxenes, garnet and quartz of Kushiro (1969) and Kushiro and Yoder (1966) to evaluate the ΔG°'s, and summarized available measurements, both calorimetric and experimental, to define the activity-composition relations of Ca–Mg–Fe garnets. Indicated pressures of the Otter Lake rocks were zero to negative kilobars. The inconsistencies were traced to the dubious nature of the ΔG's derived from phase equilibrium data.

Newton (1978) recalibrated the reaction (A) barometer using recent heat of solution data for ΔH° and entropy measurements for ΔS°. Activity relations were taken largely from deductions from natural parageneses of Ganguly and Kennedy (1974), together with experimental phase equilibrium measurements of Ca–Mg garnet mixing of Hensen *et al.* (1975b), based on the anorthite–garnet–Al_2SiO_5–quartz reaction. Recomputed pressures of the South Harris terrane were 3–4 kbar lower than found by Wood (1975) at the same assumed temperatures. The mixing properties of garnets used by Newton (1978) have been superceded by recent phase equilibrium and calorimetric measurements.

Scope of the present work

In this paper we calibrate the two garnet–pyroxene–plagioclase–quartz geobarometers based on reactions (A) and (B) using recently determined thermodynamic data and discuss the uncertainties in pressure indication. Various parageneses of the four-phase assemblages in charnockites and basic granulites are tabulated from the literature, and apparent pressures of crystallization are calculated. The survey, although not exhaustive, shows patterns which suggest new interpretations about various kinds of granulites, as discussed in subsequent sections.

Thermodynamics of the barometric reactions

Enthalpy of reaction

Table 1 lists enthalpy of formation data at 970 K determined by oxide melt calorimetry for the phases anorthite (Newton et al, 1980), diopside and grossular (Charlu *et al.*, 1978) and enstatite and pyrope (Charlu *et al.*, 1975). The data of Table 1 lead to the following enthalpies of reaction at 970 K, taken as the differences in the enthalpies of formation of the reacting phases:

$$\Delta H^\circ_A = 2237 \pm 570 \text{ cal}$$
$$\Delta H^\circ_B = 373 \pm 650 \text{ cal} \tag{3}$$

The error limits are taken as the square roots of the sums of the squares of the uncertainties in the enthalpies of formation in reactions (A) and (B) and are certainly overestimates, in that the uncertainties in the actual enthalpy of solution measurements have entered twice (Anderson, 1977) in the error assessment. High temperature heat capacity data (Holland, 1981) are given in Table 1 to correct ΔH° from 970 K to any temperature in the crustal range. The corrections for $900 \text{ K} < T < 1150 \text{ K}$ are very small and may be neglected.

Entropies of reaction

Table 1 lists entropy data at 1000 K for the six substances of reactions (A) and (B). The most important recent data are those of Haselton (1979) for pyrope and grossular which include both high-accuracy, low-temperature adiabatic heat capacity measurements and heat content measurements on the same samples at high temperatures. Krupka *et al.* (1979a) measured the low-temperature heat capacity of synthetic $Mg_2Si_2O_6$ enstatite and heat capacities to 1000 K by differential scanning calorimetry (DSC). Haselton (1979) made drop calorimetry measurements on synthetic enstatite at 973, 1173 and 1273 K and fitted a high-temperature heat capacity equation to his and Krupka *et al.*'s (1979a) data. Robie et al. (1978) made precise low-temperature heat capacity measurements on synthetic anorthite, and Krupka *et al.* (1979b) added DSC measurements to supplement earlier drop calorimetry. According to Haselton (1979) and Perkins *et al.* (1980), a configurational entropy of about 1.0 cal/K due to partial Al,Si disordering of anorthite is consistent with phase equilibrium data of anorthite and other minerals with well-measured parameters. X-ray diffraction data also require a small amount of tetrahedral disorder (Smith, 1974). For these reasons, a configurational entropy of 1.0 cal/K is added to the Third Law entropy of anorthite in Table 1. The uncertainty of this term, probably no more than ±0.5 cal/K, is one of the largest sources of uncer-

Table 1. Heats of formation, entropies, volumes, and heat capacities

	$\Delta H^\circ_{f,1000}$ (kcal/mol)	S°_{1000} (cal/o-mol)	V°_{298} (cm³/mol)	Heat Capacity Coefficients (cal/o-mol)			
				a	$b \times 10^{-3}$	$c \times 10^{6}$	$d \times 10^{3}$
anorthite	-24.06±.31	127.78	100.93	93.55	3.001	-.7257	-.6174
enstatite	-17.62±.34	93.51	62.66	82.68	-.0743	-.3387	-.6843
diopside	-34.99±.41	96.01	66.08	78.44	.451	-.3349	-.6021
pyrope	-20.21±.38	185.83	113.13	130.25	4.943	-1.9912	-.5457
grossular	-77.91±.67	187.10	125.23	130.26	5.695	-2.2006	-.4781
quartz	0	27.62	22.69	25.179	1.451	.0082	-.226

ΔH°_A (1000) = 2.237 ± .57 kcal ΔS°_A = -7.417 ± 0.64 cal/K ΔV°_A = -23.73 cm^3

ΔH°_B (1000) = 0.373 ± .65 kcal ΔS°_B = -9.493 ± 0.64 cal/K ΔV°_B = -23.12 cm^3

Sources given in text.

tainty in $\Delta G°$. The standard entropies of reaction at 1000 K are:

$$\Delta S_A^\circ = -7.417\pm0.64 \text{ cal/K}$$
$$\Delta S_B^\circ = -9.493\pm0.64 \text{ cal/K} \quad (4)$$

These values may be corrected to any temperature by the heat capacity data of Table 1; however, they may be taken as virtual constants in the temperature range of 850–1150 K.

Partial molar volumes

Haselton and Newton (1980) showed that the nonsymmetric partial molar volume function of grossular has a significant effect on its activity coefficient in Ca–Mg–Fe garnets in the range $0.05 \leq X_{Ca} \leq 0.20$, and that the partial molar volume versus X_{Ca} function could be represented by a relatively simple numerical expression which is almost independent of Mg/Fe ratio. Unfortunately, this cannot be done for the partial molar volume of pyrope, because the molar volumes of Fe–Mg garnets have not been carefully measured yet. Therefore, the $\Delta\bar{V}$ terms in equations (2) have been approximated by $\Delta V°$, the 298 K, one bar volume change. These are -23.73 cm^3 for reaction (A) and -23.12 cm^3 for reaction (B). Trial replacement of $\bar{V}_{Ca}$ for V_{Ca} in a few calculated pressures shows that the substitution results in very small pressure changes. Thermal expansion effects on the ΔV's are negligible.

Activities of garnet components

The activity coefficient, γ, which is multiplied by the mole fraction of a garnet component to give the activity, can be expressed over a limited range of composition by the formula:

$$\ln\gamma = \frac{W(1-X)^2}{RT} \quad (5)$$

where X is the mole fraction of the component in a binary solution and W is a constant. Most solid solutions whose properties have been measured do not obey this "symmetrical solution" formulation over the complete range of compositions. The fact that pyrope and grossular components of typical granulite garnets are usually restricted to the range $0.05 \leq X \leq 0.40$ allows the application of (5).

Enthalpy of solution measurements on several synthetic garnets of the pyrope-grossular series (Newton *et al.*, 1977), together with heat capacity measurements on synthetic pyrope, grossular, and $Py_{.6}Gr_{.4}$ (Haselton and Westrum, 1980), define the one bar activities in the join by (5) and:

$$W_{CaMg} = 3300 - 1.5T(\text{K}), \text{ calories/mole} \quad (6)$$

which applies to all except very Ca-rich compositions (Newton and Haselton, 1981). The coefficient of the temperature term is the excess entropy parameter, W_S, the existence of which was predicted by the high temperature, high pressure phase equilibrium data of Hensen *et al.* (1975b). Haselton and Newton (1980) showed that expression (6), based on calorimetry, is in good agreement with the Hensen *et al.* (1975b) data when the peculiar shape of the grossular-pyrope molar volume curve, and its effect on activities at high pressures, are taken into account.

Cressey *et al.* (1978) derived the Gibbs energies of mixing of synthetic Ca–Fe garnets from phase equilibrium measurements based on the anorthite breakdown reaction in the system FeO–CaO–Al_2O_3–SiO_2. The mixing energy is temperature-dependent and depends on composition in a complex way. However, the excess Gibbs energy of mixing is very small for $X_{Ca} \leq 0.30$, at least at temperatures down to 900°C, and, within the accuracy of their measurements, may be taken as zero. Deductions based on the compositions of coexisting natural phases yield W_{CaFe} values of -1000 to 1000 cal/mole for small grossular contents (Ganguly and Kennedy, 1974; Ghent, 1976). The value of zero is taken here as the simplest assumption compatible with the experimental evidence, for the compositions of most of the garnets considered here.

The value of W_{FeMg} is still subject to debate. Earlier deductions from natural parageneses resulted in a value of 2900 cal/mole (Ganguly and Kennedy, 1974) but later workers using the same method have found much smaller values (Kawasaki and Matsui, 1977; Dahl, 1980). The latter reference gives the value of 1390±1160 cal/mole. O'Neill and Wood (1979) determined that Fe,Mg mixing in garnet is more ideal at 1000°C and above by several hundred cal/mole than is olivine at the same conditions from their experimental Fe,Mg distribution isotherms at high pressures. Wood and Kleppa (1981) found, by enthalpy of solution measurements on synthetic olivines, a non-ideality which would correspond to a W of about 1200 cal/mole in the Fe-rich range. This implies a W_{FeMg} of garnet of about 600 cal/mole. Sack (1980) concluded, after a considerable review of available experimental work, that W for olivine is probably less than about 800 cal/

mole, which suggests that W_{FeMg} for garnet is negligible. A value of zero is taken in this work, which is probably a lower limit of values compatible with currently-available evidence.

There is little experimental work available to determine the mixing properties of spessartine with other garnet components. Hsü (1980) experimentally found a stable join spessartine-grossular down to at least 400°C at 2 kbar, and spessartine-grossular garnets are characteristic of low-temperature blueschist terranes (*e.g.* Hashimoto, 1968), which suggests a very small Ca–Mn interaction energy. The mixing of Mn with Fe^{2+} and, especially, with Mg may be substantially non-ideal, however. This uncertainty rules out use of Mn-rich garnets with the geobarometers considered here. This is unfortunate, since some high grade terranes have abundant manganiferous quartzites with barometrically diagnostic assemblages (*e.g.* Janardhan and Srikantappa, 1975). In the present study we exclude any assemblages from consideration where the garnets have $Mn \geq Mg/3$, which insures that Ca interactions with Mg and Fe far outnumber interactions with Mn.

The activity coefficient of grossular in ternary garnets may be approximated by the following expression, due to Prigogine and DeFay (1954) and used by Ganguly and Kennedy (1974):

$$RT\ln\gamma_{Ca} \cong W_{CaFe}X_{Fe}^2 + W_{CaMg}X_{Mg}^2 + (W_{CaFe} - W_{FeMg} + W_{CaMg})X_{Fe}X_{Mg} \qquad (7)$$

A corresponding expression exists for the pyrope component. The activity coefficients of grossular and pyrope are, with the parameters adopted above:

$$\begin{aligned} RT\ln\gamma_{Ca} &= (3300-1.5T)(X_{Mg}^2+X_{Mg}X_{Fe}) \\ RT\ln\gamma_{Mg} &= (3300-1.5T)(X_{Ca}^2+X_{Ca}X_{Fe}) \end{aligned} \qquad (8)$$

Plagioclase activities

Enthalpy of solution measurements at 1000 K on many synthetic high-structural state plagioclases, together with the theoretical entropy of mixing given by the "Al-avoidance" model of Kerrick and Darken (1975), lead to the following expressions for the activity coefficient of anorthite (Newton *et al.*, 1980):

$$\begin{aligned} RT\ln\gamma_{An} &= X_{Ab}^2[W_{An}+2X_{An}(W_{Ab}-W_{An})] \\ W_{An} &= 2025 \text{ cal} \\ W_{Ab} &= 6746 \text{ cal} \end{aligned} \qquad (9)$$

The activity of anorthite is then determined by:

$$a_{An} = \gamma_{An} \cdot \frac{X_{An}(1+X_{An})^2}{4} \text{ (Al-avoidance model)} \qquad (10)$$

It is not yet established that plagioclase crystallizes in granulite metamorphism in the high structural state. Ordering of Si and Al could have some effect in changing the anorthite activity from expressions (9) and (10). It is likely, however, that Al-avoidance (*i.e.*, avoidance of adjacent Al-filled tetrahedra in the framework structure) gives an adequate account of the solid solution energetics at least above 700°C and for $X_{An} \leq 0.25$.

Enstatite and diopside activities

Ferrous iron is the main substituent in enstatite and diopside. There are currently no thermochemical data for these solid solutions; however, a number of authors (*e.g.* Saxena, 1973; Sack, 1980) have concluded that $Fe_2Si_2O_6$ and $Mg_2Si_2O_6$ are virtually ideal orthopyroxene substituents at temperatures above 700°C, and Bishop (1980) and Oka and Matsumoto (1974) concluded that $CaMgSi_2O_6$ and $CaFeSi_2O_6$ solid solution is attended by a W of, at most, 2.5 kcal. Wood and Banno (1973) and Wood (1979) have shown, by phase equilibrium deductions, that the aluminous pyroxene molecules $MgAl_2SiO_6$ and $CaAl_2SiO_6$, in enstatite and diopside respectively, are virtually ideal substituents, and Ganguly (1973) found, also from phase equilibrium work, that $NaAlSi_2O_6$ (jadeite) forms a nearly ideal solid solution with diopside. These considerations lead to, and justify, the "ideal two-site" pyroxene mixing model (Wood and Banno, 1973; Wells, 1977) expressed as:

$$\begin{aligned} a_{En} &= X_{Mg}^{M2} \cdot X_{Mg}^{M1} \text{ in orthopyroxene} \\ a_{Di} &= X_{Ca}^{M2} \cdot X_{Mg}^{M1} \text{ in clinopyroxene} \end{aligned} \qquad (11)$$

where M2 denotes the larger structural site containing divalent and monovalent cations and M1 the smaller site. These formulations are only approximations; intercationic substitutions are generally attended by some non-ideality (excess Gibbs energy of solid solution). However, it is fortunate that the mole fractions of enstatite and diopside in orthopyroxene and clinopyroxene, respectively, are usually high, so that effects of non-ideal mixing are minimized. The largest departure from the system $CaO–MgO–Al_2O_3–SiO_2$ in granulite pyroxenes is

$Fe_2Si_2O_6$ substitution in orthopyroxene, which has been shown to be nearly ideal. Thus, the ideal two-site model should give good results in many applications. The cation-site assignments for clinopyroxene followed here are: Ca, Na, Mn and Fe^{2+} in M2 and Mg, Fe^{3+}, Ti, Al and the remaining Fe^{2+} in M1. Mg and Fe^{2+} are equipartitioned between M1 and M2 in orthopyroxene (Wood and Banno, 1973).

Geobarometric expressions

The numerical geobarometric expressions based on equations 2) and with the foregoing input data and T in K are:

$$P(\text{bars}) = 3944 + 13.070T + 3.5038T\ln\frac{(a_{\text{Ca}}^{\text{Gt}})(a_{\text{Mg}}^{\text{Gt}})^2}{a_{\text{An}}^{\text{Pl}}\cdot a_{\text{En}}^{\text{Opx}}} \qquad (12)$$

for opx–garnet–plagioclase–quartz

and

$$P = 675 + 17.179T + 3.5962T\ln\frac{(a_{\text{Ca}}^{\text{Gt}})^2(a_{\text{Mg}}^{\text{Gt}})}{a_{\text{An}}^{\text{Pl}}\cdot a_{\text{Di}}^{\text{Cpx}}}$$

for cpx–garnet–plagioclase–quartz.

The activities at a temperature are evaluated from compositions of the phases as outlined in the preceding section. Although the choice of temperature depends on mineralogic geothermometry, with its inherent uncertainties, it turns out that the barometric indicators are quite insensitive to temperature uncertainties: a temperature error of ±100°C introduces pressure errors of only a few to several hundred bars. The major pressure uncertainty lies in $\Delta G°$ of the reactions. The combined uncertainties in thermochemistry lead to uncertainties of ±1500 bars for reaction (A) and ±1700 bars for reaction (B) in evaluating the errors in $\Delta G°$ as the square roots of the sums of the squares of the individual uncertainties in the $\Delta H°$ and $T\Delta S°$ terms at 1000 K. Uncertainties in the volume terms introduce much smaller errors. The combined uncertainties resulting from errors in the activity expressions are difficult to assess. However, calculation of pressures from many different terranes, to be presented, affords considerable insight into the accuracy problem, particularly where comparison of the two barometers in the same terrane or, in many cases, the same rock, is possible.

Selection of analytic data

Criteria for selection

The requirements for a valid pressure calculation are textural evidence of four-phase equilibrium, reliable analyses of the minerals, and an independent temperature estimate. The first criterion may consist of contact or close local association of unzoned minerals, or compositional "plateaus" in cores of coarse mineral grains. Many granulites show evidence of polymetamorphism in the form of corona assemblages around garnet rims, containing pyroxenes and plagioclases of sharply different compositions from those of the broad plateaus, and the garnets may be strongly zoned with rim compositions approximating local equilibrium with the corona assemblages, or, there may be a discrete second generation of garnet. In such cases two distinct pressure indications, one for the primary or core compositions and one for the corona and rim compositions may be obtained, which may afford an interpretation about uplift from deepseated conditions or later regional retrogression. The common pattern is more calcic plagioclase, less aluminous pyroxene (frequently orthopyroxene rather than clinopyroxene) and less pyropic garnet rims in the corona assemblage than in the primary assemblage. Wet chemical analyses of garnets may fail to distinguish garnet and plagioclase cores and rims that microprobe analyses can resolve. It is very important in the temperature estimates to distinguish primary from secondary assemblages. For instance, retrograde biotite replacing garnet may not yield a valid temperature estimate with garnet cores. It is frequently hard to decide if biotite and hornblende are primary or retrogressive.

Compilation of data

The literature of petrology abounds in descriptions of the assemblage pyroxene–garnet–plagioclase–quartz. A disappointingly small fraction of the reports satisfy the above criteria, however. Electron microprobe analyses have become abundant since about 1965, but some authors have presented only representative analyses of minerals from different rocks. Frequently, plagioclase analyses are not presented, and plagioclase is characterized only as "oligoclase," for instance, or a broad range of An contents may be given. In the older literature, some minerals from a rock may have been analyzed by wet chemistry, while compositions for the others may only have been estimated from optical properties. In some descriptions, it is not clear whether quartz is part of the equilibrium assemblage. Table 2 lists the suitable described parageneses which were found after a considerable search. Some well-described parageneses have undoubtedly been overlooked. The occurrences fall naturally into a few categories: low-pressure thermal aureoles (pyroxene hornfels facies), transitional granulite terranes, regional granulite terranes, granulite exposures of very deep-seated origin in modern uplift areas, and deep-crustal granulite exotics from explosive volcanic pipes. The temperature estimates for each locality are generally those preferred by the authors of the mineral analyses, except where noted in the following discussions. Temperatures are based on quantitative mineralogic geothermometry.

Results of calculations

Table 2 gives the calculated pressures of the assemblages using the given compositional data and the temperature estimates. It is seen that the calculated pressures span almost the entire crustal range of pressure, from about 2 kbar for andalusite–sillimanite bearing migmatite terranes of the Scottish Dalradians, to about 12.5 kbar for the deepest crustal samples, the mafic granulites from Doubtful Sound, New Zealand. The clinopyroxene barometer, based on reaction (B), consistently yields pressures which average two kbar lower than those from the orthopyroxene, or reaction (A), barometer. Although this discrepancy is within the combined uncertainties in the ΔG° values of reactions (A) and (B), other possible interpretations will be discussed. The average spread of the calculations for a given terrane is about ±850 bars for each barometer. Details of the results for a large number of individual terranes, given in subsequent sections, afford insight into the problems of the precision, accuracy, and validity of the pressure calculations.

Thermal aureoles

Results for the granulite aureole of the *Nain*, Labrador, anorthosite complex are given in Table 2. Calculations for two orthopyroxene-bearing granulites are complicated somewhat by zoned garnets and variable plagioclase compositions, probably resulting from reequilibration during uplift of the anorthosite mass. The garnet cores and most sodic plagioclases in each rock yield an average of 3700 bars, which is considerably lower than Berg's (1977) assessment based on the garnet–cordierite–hypersthene–quartz barometer (Hensen and Green, 1973) and earlier calibrations of the orthoferrosilite–fayalite–quartz barometer (Smith, 1972), but is in good agreement with the value of 3.2 kbar calculated for the Nain aureole by Bohlen and Boettcher (1981) based on their accurate experimental work on the compositions of coexisting orthopyroxene and olivine in the presence of quartz. A combination of the most calcic plagioclase and garnet rim in one rock (NAR-2893 R) yields only 1100 bars, which may represent a late, very shallow reequilibration.

The garnet–orthopyroxene assemblage is developed in the *Huntley–Portsoy* area of the Buchan zone of the Dalradians, and in the *Lochnagar* area of the Central Dalradians, Scottish Highlands (Ashworth and Chinner, 1978), as aluminous-basic restites of anatectic migmatites developed in the aureoles of the Newer Intrusives. Both occurrences are in metamorphic terranes containing andalusite as the regional Al_2SiO_5 polymorph, and both have sillimanite in the thermal aureole. If, as seems probable, the aureoles reflect nearly isobaric heating, the pressures should be at least as low as the Al_2SiO_5 triple-point. The calculated average pressures of 3880 bars for the Huntley–Portsoy area and 2700 bars for the Lochnagar aureole satisfy this condition for the Holdaway (1971) triple-point within the experimental uncertainty. Pressures calculated for the aureole localities using the Thompson (1976) garnet–cordierite–sillimanite–quartz barometer are about two kbar higher.

Precambrian granulite massifs

Published mineral analyses suitable for geobarometric calculations using reactions (A) and (B) were found for twenty Precambrian localities in the present survey. Of these, ten were from large granulite tracts, most of which show the definitive features of uniformly high grade mineralogy and pronounced depletion of large-ion lithophile elements (Newton and Hansen, 1981).

Six suitable metabasites and charnockites from the *Adirondack Highlands*, northern New York, contain both pyroxenes in addition to plagioclase, garnet and quartz. Garnet and clinopyroxene analyses are from Bohlen and Essene (1980), orthopyroxene analyses from Bohlen and Essene (1979), and plagioclases and confirmation of quartz were provided by S. R. Bohlen (written communication).

Table 2. Calculated pressures of various granulites

CLASS	LOCALITY	DESCRIPTION	SOURCE OF DATA	I.D. NUMBERS	ESTIMATED TEMPERATURES °C	ORTHOPYROXENE PRESSURES BARS	CLINOPYROXENE PRESSURES BARS
Low-pressure Thermal aureoles	Main Complex, Labrador	Granulite aureoles of anorthosite	Berg (1977)	NAK-3909C, -2893C, -2893R	800, 750 750	3798, 3664 1083	
	Huntley-Portsoy, Scotland	Migmatites, aureoles of Newer Intrusives	Ashworth and Chinner (1978)	10557	690	3876	
	Lochnagar, Scotland			82891	780	2702	
Massif Granulite Terranes	Adirondack Highlands, New York	Charnockites and metagabbros	Bohlen and Essene (1980); (1979)	AD-AS3, -ET1, -ET24, -IN11, -SL5, -N3	700, 750, 750, 725, 775, 750	8794, 9782, 9325, 8541, 9851, 9913	5913, 7312, 7366, 7005, 7255, 6971
	Sittampundi Complex, S. India	Mafic granulite (P) and corona assemblage (S)	F.C. Bishop and J.V. Smith, unpub. data., 1976	SITM-92P, -92S,	830, 725		7993, 3406
	Nilgiri Hills, S. India	Charnockites	Janardhan et al (1981)	5-2, 11-1 11-3E, GN-4A	820, 760 850, 880	9493, 7416, 8255, 9488	6530, 6209, 6124, 7153
	Labwor Hills, Uganda	Metapelite	Nixon et al (1974)	AR 51	950	8087	
	Scourie Complex, Scotland	Metagabbros	Rollinson (1981a)	200, 275	840, 840	8456	7117
	Bagla Hill, Sierra Leone	Mafic granulite	Rollinson (1981b)	219	770	6784	
	Furua Complex, Tanzania	Acid, intermediate and basic granulites	Coolen (1980)	MF-283.2, -286.1, WE-322.3, ZC-8, DMa-40 C-247.1, -311.1, -352.2	800, 800, 800, 800, 800, 800, 800, 800	10261, 10534, 9493, 10158, 11040, 10614,12723	8233, 7962, 7277, 7016, 8500, 8144, 9299
	Qianxi Complex, N.E. China	Basic granulite	Zhang and Cong (1981)	T_{1-1}	825	10649	8889
	Isortoq Complex, W. Greenland	Granulite metadolerites	Glassley and Sorenson (1980)	88589, 91141	875, 875	7568, 8252	5461, 5768
	Akilia Association, W. Greenland	Metabasites	Griffin et al (1980)	152735, 152765	700, 700	6877, 8796	4881, 6668

Table 2. (continued)

Class	Locality	Description	Source of data	I.D. numbers	Estimated temperatures °C	Orthopyroxene pressures bars	Clinopyroxene pressures bars
Transitional Granulite Terranes	Adirondack Lowlands, N.Y.	Semipelites and amphibolites	Stoddard (1976)	74-C-248A, -248B, -252, -253E	730, 730, 730, 730	6647, 6084, 5631, 6343	4221
	Otter Lake Area, S. Quebec	Acid and basic granulites	Perkins (1979)	RK-2, DD-2, DD-11, DD-17, A-11, A-12, A-13, DL-2, M1-11	675, 675, 675, 675, 675, 675, 675, 675, 675	5205, 7426, 6903, 6591, 8094	5362, 4684, 5262, 5018, 5102, 5574, 4350
	Buksefjorden Area, S.W. Greenland	Basic granulites	Wells (1979)	174087, 174102	800, 800	7599, 7475	5576, 4476
	Inarijärvi Area, N. Finland	Basic granulites	Hörmann et al (1980)	47-III	740	7284	5166
	Madras (Pallavaram), S. India	Charnockites	Weaver et al (1978)	MP-44, -72	790, 790	7065, 7747	
	W. Sargurs, S. India	Basic granulites	Rollinson et al (1981)	2-07, 3-01, 12-03, 12-11	750, 750, 750, 750	7778	6512, 6585, 5591
	Ruby Range, Montana (Kelly Mine)	Fe-rich metapelites	Dahl (1980)	RMK-57, -27_3	745, 745	7617, 7978	
	Ruby Range, Montana (S-locality)	Fe-rich metapelites	Dahl (1980)	RMS-22	745	5740	
Deep Crustal Granulites	Doubtful Sound, New Zealand	Deep crustal mafic granulites	Oliver (1977)	36453, 36457, 36460, 36461, 36468	750, 750, 750, 750, 750	12427	8927, 11796, 11001, 12076, 11053
	Ronda Complex, S. Spain	Mafic granulites, primary (P) and corona (C) assemblages	Loomis (1979)	R-208A (P), -208A (C)	800, 800		11100, 6482
	Cone Peak, California	Granulite veins in amphibolites	E.C. Hansen, unpub. data	H-3	750	8704	5954
	Kristiansund Area, S.W. Norway	Norwegian Basal Gneisses (core analyses)	Krogh (1980)	MA-1, MA-2, KV-1	750, 750, 750		12948, 11570, 9445
Granulites in Volcanic Pipes	Letseng-la-Terae kimberlite, Lesotho	Deep crustal mafic granulite	Griffin et al (1979)	LT-2	680	10144	7430
	The Thumb minette, New Mexico	Deep crustal acid (225) and mafic (253) granulites	Ehrenberg and Griffin (1979)	225, 253	650, 650		7686, 6564

The I.D. numbers, estimated temperatures, orthopyroxene pressures and clinopyroxene pressures are arranged in corresponding column and row positions.

Temperatures for pressure calculations were taken from the regional isotherm map of Bohlen *et al.* (1980). Calculated pressures with the orthopyroxene barometer average 9.2 kbar, and, with the clinopyroxene barometer, 7.0 kbar. Some of the scatter in the calculated pressures may be due to real variations over the Adirondack terrane. The orthopyroxene mean pressure is somewhat higher than the assessment of 8.0 ± 1.0 kbar for the Adirondack Highlands of Bohlen *et al.* (1980) based mainly on a few occurrences of orthoferrosilite–fayalite–quartz associated with the Adirondack anorthosite.

The average discrepancy between the orthopyroxene and clinopyroxene pressure indications in the same rock for the 6 Adirondack Highlands rocks is 2.3 kbar, close to the average discrepancy of 2.2 kbar for all rocks in Table 2 with both pyroxenes. This figure may be used in an empirical readjustment of the geobarometers, to be discussed below.

The *South Indian Highlands* granulite massif areas yield pressures of 7–10 kbar. These localities represent the culmination of progressive metamorphism across 200 km in southern Karnataka (Pichamuthu, 1965). Of particular interest are the Sittampundi garnet granulites (Subramaniam, 1956), which show a primary association (92P) with clinopyroxene and a secondary, or corona assemblage (92S) with a distinctly different plagioclase and clinopyroxene. The primary assemblage crystallized at 8.0 kbar, according to the barometer of reaction (B) and the retrogressive assemblage at 3.4 kbar. The secondary assemblage represents a distinct and probably much younger regional metamorphism in the contact zone of the Tiruchengodo granite (Naidu, 1963).

The Archaean high-grade terranes of the *Labwor Hills*, Uganda (Nixon *et al.* 1974) and *Enderby Land*, Antarctica (Grew, 1980) are higher temperature terranes than many granulite areas, as evidenced by regional development of sapphirine–quartz, and in the latter area, osumilite. The very high temperatures account for the presence of cordierite even at the elevated pressures. Garnet metabasites from Enderby Land were not described by Grew (1980). Newton and Haselton (1981) calculated a pressure of 7.0±0.3 kbar for Grew's rocks based on the garnet–plagioclase–sillimanite–quartz assemblage.

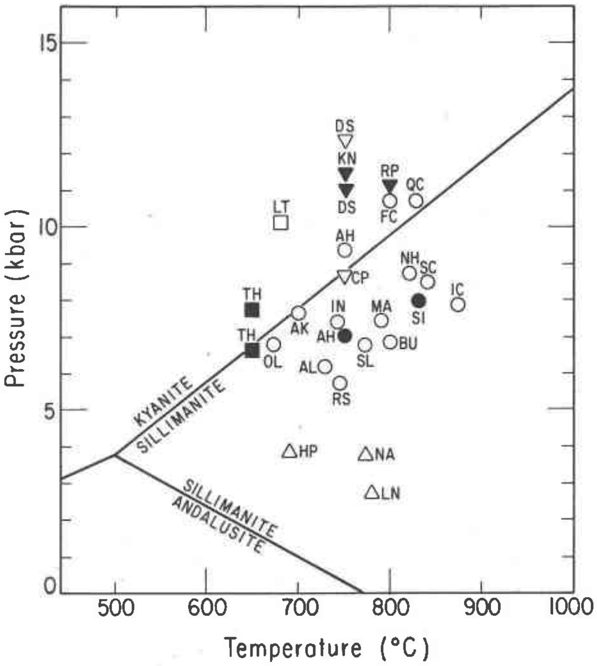

Fig. 1. Calculated pressures for various granulites. *Triangles*: thermal aureole granulites. *Circles*: Precambrian shield granulites. *Inverted triangles*: uplifted deep-crustal sections. *Squares*: exotic granulites in explosive pipes. *Open symbols*: orthopyroxene (reaction A) barometer. *Filled symbols*: clinopyroxene (reaction B) barometer. Al_2SiO_5 (kyanite, sillimanite, andalusite) stability relations from Holdaway (1971). *Localities*: LN = Lochnagar, HP = Huntley-Portsoy, NA = Nain, RS = Ruby Range (S), AL = Adirondack Lowlands, OL = Otter Lake, SL = Sierra Leone, BU = Buksefjorden, AH = Adirondack Highlands, SI = Sittampundi, MA = Madras, AK = Akilia, IN = Inarijärvi, NH = Nilgiri Hills, SC = Scourie, IC = Isortoq, TH = The Thumb, LT = Letseng-le-Terae, CP = Cone Peak, FC = Furua, QC = Qianxi, DS = Doubtful Sound, RP = Ronda, KN = Kristiansund.

The *Furua*, Tanzania, *Complex* (Coolen, 1980) and the *Qianxi Complex*, northeastern China (R. Zhang and B. Cong, unpublished data) are high-grade massifs where kyanite is the regional Al_2SiO_5 polymorph, rather than the more usual sillimanite. The calculated pressures, at the estimated temperatures of ~800°C in both regions, are compatible with the experimental Al_2SiO_5 diagram (Holdaway, 1971), as shown in Figure 1. The Qianxi Complex, dated at 3675 m.y., is the oldest very high grade area known, and the 10+ kbar pressure shows that the early Archaean crust was, locally at least, very thick. The early Archaean Akilia metabasites (Griffin *et al.*, 1980) yield the same information (Table 2).

The *Scourie Complex*, northwestern Scotland, is one of the most intensely-studied Archaean terranes. Only recently, however, have mineral analyses been forthcoming sufficient to characterize the temperatures and pressures of metamorphism (Rollinson, 1980; 1981a). The pressures of 7–8.5 kbar for Rollinson's (1981a) basic granulites yielded by the present pressure method are somewhat less than the 10.5 kbar calculated by him by the aluminous enstatite–garnet method (Wood, 1974), and much less than the 15±3 kbar estimated by O'Hara and Yarwood (1978) based on experimental phase relations of garnetiferous gabbros. The latter estimate contradicts the presence of sillimanite and absence of kyanite throughout the Scourie terrane.

Transitional granulite terranes

Pressures calculated for those regions, all Precambrian, where amphibolite facies gneiss terranes give way to granulite facies, are given in Table 2. The Madras type charnockite locality is classified as transitional on the basis of variable minor element depletion and migmatitic-metasomatic aspect (Weaver, 1980). Several of the published mineralogical descriptions of the transition localities have been supplemented by personal communications to the authors.

Pressures, as well as temperatures, are generally lower in the transitional regions than in the massif areas. Of course, the compilation does not take into account transitional areas where the pressures of crystallization were too low to produce garnet in ordinary basic and intermediate compositions, and the pressures in Table 2 should be considered only as the higher pressure range of transitional granulites.

All of the transitional granulite terranes in Table 2 lie in well-defined gradational zones adjacent to amphibolite-grade tracts except for the *Ruby Range, Montana,* granulites (Dahl, 1980), which are isolated cordilleran "core complex" exposures. For this reason they could conceivably be classified with the isolated granulite exposures in strong uplift areas described in the next subsection.

Granulites in young uplift areas

Several high pressure granulite terranes are exposed in areas of strong modern uplift, typically at continental margins. These include the Precambrian Basal Gneisses of southwestern Norway (*Kristiansund area*) (Krogh, 1980), the *Doubtful Sound* mafic granulites of the southwestern New Zealand Fiordland (Oliver, 1977), the mafic granulites of the Inner Aureole, *Ronda Complex*, southern Spain, the *Cone Peak* granulites of the Big Sur area, central California (Compton, 1960), and, perhaps, the *Ivrea Zone* granulites, northern Italy (Mehnert, 1975). The latter are part of an isolated exposure of progressive amphibolite-to-granulite progression (Schmid and Wood, 1976), and perhaps should be classified in the preceeding section.

The *Doubtful Sound* granulites give very high pressures of 9–12.4 kbar. The granulites are garnet, two-pyroxene rocks in vein complexes in mafic garnet-clinopyroxene amphibolites. Sulfate-carbonate scapolite is well developed in the Fiordland area (Blattner, 1976). In the mafic character and presence of scapolite these granulites greatly resemble the lower-crustal granulite exotics of explosive volcanic pipes in southeastern Australia (Irving, 1974) and southern Africa (Rogers and Nixon, 1975). Gravity surveys over the Fiordland show that the uppermost mantle lies only a few kilometers below the granulite exposures (Oliver, 1980). It seems quite probable from these lines of evidence that an actual section of lowermost continental crust is exposed in the New Zealand Fiordland.

The *Ronda Complex* is believed to be a mass of upper mantle peridotite which has been, for some reason, lifted to crustal levels during the Mid-Tertiary orogeny of the Betic Cordillera (Obata, 1980). The inner thermal aureole contains mafic granulites with a primary garnet–clinopyroxene–plagioclase–quartz assemblage and a corona assemblage with different plagioclase, clinopyroxene and garnet (Loomis, 1977). These granulites are believed to have been dragged up from the deeper crust by the peridotite mass (Loomis, 1972). The clinopyroxene barometer gives 11.1 kbar for the primary assemblage and 6.5 kbar for the corona assemblage, at the temperature of about 800°C for both assemblages suggested by Loomis (1977). These estimates correspond closely to the temperatures and pressures deduced by Obata (1980) for two equilibration stages of the peridotite mineralogy, presumably during a prolonged sojourn of the rising mass at two discrete levels.

Eclogite and garnetiferous peridotite masses exposed in the Norwegian fiord country have long been considered to be of subcrustal origin, incorporated into the crust tectonically (*e.g.*, O'Hara and Mercy, 1963). Recent reappraisal (Krogh, 1977; Carswell and Gibb, 1980) concludes that the high pressure mafic and ultramafic rocks were metamorphosed along with their enveloping crustal gneisses at pressures estimated by Krogh (1980) at 18±3 kbar during a mid-Proterozoic very high pressure event, perhaps continental collision. Garnet-clinopyroxene assemblages in acid gneisses analyzed by

Krogh (1980) give pressures as high as 13 kbar from the reaction (B) barometer. If, as is likely, currently-used geobarometers for peridotites and eclogites somewhat overestimate pressures, and if the reaction (B) barometer somewhat underestimates pressures, as will be discussed in the next section, it may well be that the eclogite pressure indication and that of the enclosing gneisses converge, supporting the view that they were metamorphosed together, rather than mechanically juxtaposed during post-metamorphic times.

The Cone Peak, California granulites are a vein-complex in amphibolites in a coastal terrane of precipitous relief. The Cretaceous radiometric age of a nearby charnockite body (Mattinson, 1978) supports the belief (Aitken, 1979) that the granulites are the uplifted root zones of the Mesozoic Salinia block batholiths. The pressure of 8.7 kbar deduced here (reaction (A) barometer) is in contrast with the high level of emplacement of most of the California mesozoic batholiths.

Granulites of the Ivrea Zone are considered by some (*e.g.* Mehnert, 1975) to represent uplifted lowermost crust, and a large positive gravity anomaly across the zone supports this conjecture. However, the pressures calculated from the assemblage garnet–plagioclase–sillimanite–quartz by Newton and Haselton (1981) are only 6.0±0.5 kbar for the highest grade rocks, and this makes it seem doubtful that the Ivrea Zone is as representative of the lower continental crust as the Doubtful Sound granulites. Although the garnet–pyroxene–plagioclase–quartz assemblage exists in Ivrea Zone mafic granulites, analyses satisfactory for geobarometry are not yet available.

Exotic fragments from volcanic pipes

Various granulites from explosive alkali basalt and kimberlite pipes have been reported recently. A large number of granulite fragments of undoubted crustal origin from the Lesotho kimberlites were analyzed by Griffin *et al.* (1979). Complete data exist for one specimen (LT-2) from the Letseng-la-Terae pipe, which yielded an orthopyroxene pressure of 10.1 kbar at the estimated temperature of 680°C. This specimen is of particular value in providing the only example we have of a quenched two-pyroxene granulite with which to investigate the possibility of clinopyroxene reequilibration during slow uplift of granulite terranes, as discussed below.

The minette pipe, The Thumb, and many similar tertiary occurrences in the Four Corners area, western United States, contain suites of lower crustal granulites. Two specimens from The Thumb described by Ehrenberg and Griffin (1979) yielded clinopyroxene pressures of 7700 and 6600 bars at the authors' preferred temperature of 650°C, confirming the deep-crustal interpretation. Although one is mafic (THM 253) and the other granitic (THM 223), and although they have quite different garnets and plagioclases, the similarity of the pressures calculated for the two specimens indicates that they were quarried from nearly the same level on the sub-Colorado Plateau geotherm. The garnet–clinopyroxene temperature for both of 650°C is somewhat high for a 20–35 km depth, particularly since the garnet–clinopyroxene temperature scale almost always yields lower temperatures than the two-pyroxene scale where they can be compared in a single rock. In view of the difficulty of reequilibration of silicate mineral compositions by diffusion in dry rocks below 800°C (Ahrens and Schubert, 1975), 650°C may be a temperature below which readjustment of mineralogic thermometers does not take place even for long time scales.

Interpretations and conclusions

Accuracy of the barometers

Some idea of the potential accuracy of the two geobarometers may be acquired from ancillary field and experimental information on the localities studied here. The pressures of the Nain anorthosite aureole from reaction (A) agree with those obtained from the recent revision of the ferrosilite–fayalite–quartz barometer (Bohlen and Boettcher, 1981). The two Scottish localities where the apparent andalusite to sillimanite transition is recorded in thermal aureoles give orthopyroxene pressures at or less than the Holdaway (1971) Al_2SiO_5 triple-point. The Furua, Tanzania, and Qianxi, northeastern China, terranes contain kyanite as the regional Al_2SiO_5 polymorph, and the reaction (A) pressures satisfy this condition with respect to the experimental Al_2SiO_5 diagram (Fig. 1). All of the other large Precambrian granulite terranes investigated have sillimanite. The Adirondack localities plot a short distance into the kyanite field, but the Bohlen *et al.* (1980) temperatures for these localities were based on two-feldspar and Fe–Ti oxide thermometry, which methods have been criticized (Stoddard, 1980) as yielding temperatures somewhat too low.

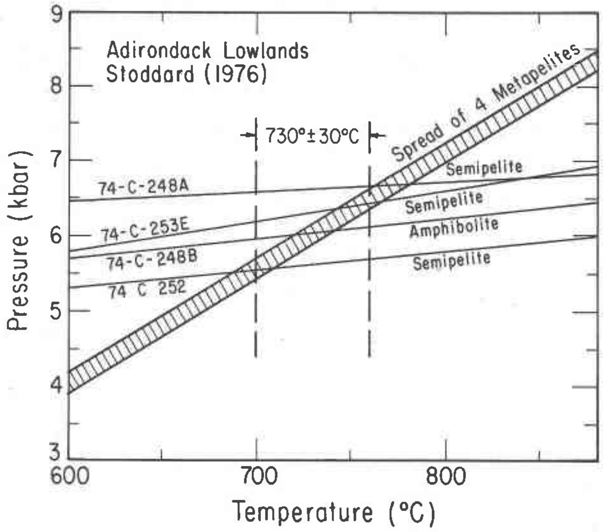

Fig. 2. Calculated pressures of four orthopyroxene–garnet–plagioclase–quartz assemblages in basic rocks from the Adirondack Lowlands, analyzed by Stoddard (1976), as functions of assumed temperature. Note the slight dependence on temperature. The pressure band width for four interbedded metapelites, containing garnet–sillimanite–plagioclase–quartz, analyzed by Stoddard (1976), were calculated by the method of Haselton and Newton (1981). The crossing area of the bands defined by the two barometers is consistent with the estimate of 730°±30°C of Stoddard (1976) for the metamorphism.

Also, a kyanite locality in the central Adirondacks (Boone, 1978) indicates that the kyanite field was approached during metamorphism.

In several areas the orthopyroxene barometer of reaction (A) can be compared with the metapelite barometer based on garnet–plagioclase–sillimanite–quartz calibrated by Newton and Haselton (1981). Figure 2 shows the dP/dT lines generated by the latter and the reaction (A) barometers for several rocks from the Adirondack Lowlands (Stoddard, 1976; 1980). These are all of the suitable rocks analyzed by Stoddard (1976) except for a fifth metapelite, #75-C-74, which plots about one kbar lower than the others, and is thought to be anomalous. The near temperature independence of the reaction (A) barometer is evident. The two barometers give consistent pressures of 5.5–6.5 kbar in the temperature range 730°±30°C judged appropriate on the basis of eight geothermometers by Stoddard (1980). The migmatitic character of the Adirondack Lowlands rocks is consistent with the experimentally-determined temperature of the beginning of melting of the assemblage biotite–K-feldspar–quartz in the presence of H_2O–CO_2 vapors (Wendlandt, 1981), which is about 740°C at 5–6 kbar. Table 3 gives comparisons of the average reaction (A) pressures for several localities with the Newton-Haselton barometer. The agreement seems to be good.

In summary, the calculated pressures of the orthopyroxene barometer appear to be consistent with most of the independent information for the localities where comparisons are possible.

The clinopyroxene or reaction (B) barometer consistently yields pressures two kbar lower than the reaction (A) barometers for rocks that contain both pyroxenes. Some of the reaction (B) pressures would not be in good agreement with the Al_2SiO_5 experimental diagram or other reliable barometers. For instance, amphibolite 74-C-2488B of the Adirondack Lowlands transitional granulite region yields a reaction (B) pressure of 4.2 kbar, which is considerably lower than pressures for this locality calculated from the other barometers. This lack of agreement indicates that the reaction (A) barometer is of superior accuracy.

Table 3. Comparison of the reaction (A) and Newton–Haselton barometers

Locality	Source	Estimated T °C	Opx-Gar-Plag-Qz		Gar-Sill-Plag-Qz	
			No. of rocks	Calc. P (bars) avg.	No. of rocks	Calc. P (bars) avg.
Western Sargurs, S. India	Rollinson et al (1981)	750	1	7772	2	7674
Adirondack Lowlands, New York	Stoddard (1976)	730	4	6176	5	5823
Ruby Range (Kelly Mine), Montana	Dahl (1980)	745	2	7798	1	8177
Otter Lake, S. Quebec	Perkins (1979)	675	5	6844	3	5933*

* *Neglects one rock with a calculated pressure of 10.3 kbar*

Precision of the barometers

The orthopyroxene pressures for the six Adirondack Highlands rocks show a standard deviation of ±600 bars, and those of the Otter Lake area of ±1100 bars. These figures might indicate the precision of the method were it not for the possibility that some of the apparent scatter is actually real variation of the crystallization pressure. This possibility may be explored with samples having the requisite assemblage but many different bulk compositions, gathered from closely-spaced localities which appear to be structurally contiguous. Data this comprehensive are not yet available from any of the granulite localities.

Closure problem

Another possible reason for the discrepancy between barometers (A) and (B) is preferential clinopyroxene reequilibration to lower pressures en route to the surface. Evidence on this is provided by the two-pyroxene garnet granulite LT-2 from the Letseng-la-Terae kimberlite, Lesotho (Griffin *et al.*, 1979). This is a "quenched" sample; that is, the travel time to the surface is negligible on a geological time scale. The reaction (A) and (B) barometers show, nevertheless, the discrepancy characteristic of the Precambrian massif two-pyroxene garnet granulites (Table 2). This would seem to indicate that the discrepancy lies in the thermodynamic formulation or input parameters, rather than in real differences in pressure indication. Lines of evidence that the geobarometric minerals commonly retain their peak metamorphic compositions through the slow ascent to the surface are the usual lack of zonation of pyroxenes, plagioclase, and, often, of garnets, and the indication that when reequilibration at lower pressures does occur, the result is usually symplectites or coronas of pyroxenes, plagioclase, and, sometimes, garnets of compositions greatly different from the primary assemblage.

Readjusted geobarometer expressions

Evidence has been presented that the difference in pressure indication of the reaction (A) and (B) barometers is not due to real pressure differences of final equilibration before closure of individual minerals. The possibility is strong that the discrepancy has its source in the thermodynamics of expressions (12), either in the magnitudes of the ΔG° quantities or in the validities of the activity expressions. The lack of correlation of the amount of pressure discrepancy with compositions of the minerals argues against the latter possibility. The average pressure discrepancy is thus in the ΔG°'s. The estimated uncertainties of the two barometers due to ΔG° uncertainties are ±1500 bars for the orthopyroxene barometer and ±1600 bars for the clinopyroxene barometer, and these ΔG° uncertainities are almost equally distributed between ΔH° and ΔS° factors in the neighborhood of 1000 K.

In order to arrive at an unbiased pressure estimate based on the reaction (A) and (B) barometers for rocks containing both pyroxenes one could simply average the two independent calculations. This would result in a pressure that is usually within 1.2 kbar of each individual calculation. Since the orthopyroxene (reaction A) pressures seem to agree with most other independent evidence, one could weight the average by raising the reaction (B) pressure to the limit of the $\Delta G^{\circ}_{\mathrm{B}}$uncertainty and by lowering the reaction (A) pressure a small amount. The two barometers would read the same pressure, on the average, for two-pyroxene rocks if 1600 bars are added to expression (12) (cpx) and 600 bars are subtracted from expression (12) (opx). However, such adjustments are empirical and necessarily subjective, and are left to the reader's discretion.

Geological applications

Classes of granulites

The five-fold classification of granulite localities adopted here is supported by the more or less characteristic pressure ranges found for each class. The aureole granulites are of shallow origin and perhaps should be considered in the pyroxene hornfels facies, rather than the granulite facies. The low pressures found for the Nain anorthosite aureole confirm the model of Berg (1977) and Emslie (1978), who advocated a high-level emplacement for the Labrador and Grenville magmatic complexes, followed by a high pressure metamorphic overprint for the complexes within the Grenville belt. The granulite terranes classified as transitional between amphibolite facies and granulite facies give somewhat lower pressures than the granulite massif areas, which cluster in the range 8.9±1.5 kbar. The regions of strong modern uplift, such as Doubtful Sound, New Zealand, and the aureole of the Ronda Complex, Spain, give very high pressures which correspond to the base of the continental crust. The volcanic pipe exotics display a range of high pres-

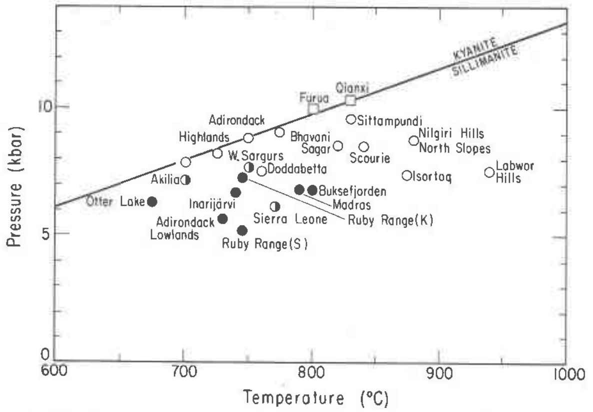

Fig. 3. Pressures for nineteen Precambrian granulite terranes. Plotted points are the weighted averages of all calculated reaction (A) and reaction (B) pressures for each locality (see text). *Circles*: sillimanite-bearing terranes. *Squares*: kyanite-bearing terranes. *Open symbols*: massif granulites. *Filled symbols*: transitional granulite terranes. *Half-filled symbols*: indeterminate granulite status. *Bhavani Sagar, Doddabetta,* and *North Slopes* are individual localities within the Nilgiri Hills, S. India massif. Other localities explained in Table 2. Kyanite-sillimanite relations from Holdaway (1971).

sures, the highest being possibly subcrustal. The pressure–temperature indications of these cannot together be interpreted as describing a Phanerozoic continental geotherm since some of them are from areas of abundant magmatism where geotherms are likely to be perturbed, and some of the samples may actually be magmatic cognates. Also, the cut-off temperatures below which granulite samples may continue to reequilibrate may be higher than the present normal sub-continent geothermal curve, in which case temperature-pressure indications of some deep-crustal exotics may be fossilized from earlier times.

Transitional granulite terranes

Figure 3 shows weighted average pressures of regional Precambrian granulite terranes, with 600 bars subtracted from equation (12) (opx) and 1600 bars added to equation (12) (cpx). Although this adjustment is arbitrary, it allows data for both reactions (A) and (B) to be used in a mutually consistent way. The pressures, as well as the temperatures, of the granulite terranes classified as transitional average lower than those of the massifs (homogeneous high grade areas). This enhances the hypothesis that the granulite terranes are related to lower grade terranes by overprinted progressive metamorphism, rather than by initial differences, magmatic fractionation, or mobilizate and restite fractions of partial melting, as other current hypotheses propose. An average Precambrian geotherm might be constructed by drawing a P–T line between the centroids of the transitional granulites and the massif granulites in Figure 3. However, the relationship between transitional granulite terranes and massifs may be something other than a simple depth-zone arrangement. A model commonly proposed for metamorphism in the Adirondacks is continental collision and crustal doubling (*e.g.* McLelland and Isachsen, 1980). For this model strong lateral temperature and pressure gradients may be expected in the vicinity of the ancient suture zone.

Granulite massifs

The origin of ancient granulite terranes has long been a subject of speculation and controversy. A new aspect of the problem is provided by the narrow spread of pressure calculations (8.9±1.5 kbar) for twelve different massif localities. The nearly constant pressures cannot simply be the result of progressive excavation over time by deep erosion in shield areas to expose a "granulite level" at the present time, for several reasons. One is that the high-grade rocks are often demonstrably metasedimentary and thus went through an upper crustal history prior to being buried to some thirty kilometers. Some explicit tectonic mechanism must be invoked to explain this great burial. The second is that the terranes considered here span the time interval from 3675 m.y. (Qianxi Complex) to 1000 m. y. (Adirondack Highlands). There is no apparent relation between depth of metamorphism and antiquity which would be implied by the progressive excavation theory. Instead, the strong implication is that a specific tectonic mechanism of metamorphism was operative in the Precambrian which still may be operative today but whose effects may be somewhat different than in the past because of reduced geothermal gradients or reduced intensity of action. Such a mechanism is continental overriding during collision, as has been proposed for the apparently double crustal thickness at the juncture between Asia and the Indian subcontinent (Powell and Conaghan, 1975) and for high pressure metamorphism in the Alps (Richardson and England 1979). This hypothesis explains the repeated 7-10 kbar pressures as the result of effectively instantaneous loading of a continental margin with a 30-km thickness of another continent. Continental shelf sedimentary facies, recumbent overfolding and subhorizontal foliations, and CO_2 fluid inclusions (from destruction of shelf carbonates), all nearly ubiquitous characteristics of ancient granulite terranes, are explainable by this mechanism (Newton and Hansen, 1981).

Nature of the lower continental crust

Speculation about the lower continental crust has focussed on certain exposed granulite terranes as possible actual lower crustal sections, tectonically uplifted. The ancient granulite massifs have been put forward as a model largely because of their low intrinsic heat production, which is a necessary condition for the low heat-flow shield terranes (Heier, 1973). However, it seems unlikely that this is a generally valid model because of the ubiquitous supracrustal rocks, which are found in all Precambrian granulite terranes, sometimes as dominant components, as in the Sri Lanka Highland Series (Cooray, 1962). The interbanded pelitic granulite-mafic granulite sequence of the Ivrea Zone, northern Italy, has also been regarded as an actual deep-crustal section (Mehnert, 1975). A strong positive gravity anomaly over the granulites has been cited as evidence of near-surface upper mantle, but the anomaly could also be explained by a large gabbro intrusion under the granulite sequence (Schmid and Wood, 1976). The low pressures of 6.0±0.8 kbar computed by Newton and Haselton (1981) from the assemblage garnet–plagioclase–sillimanite–quartz in Ivrea Zone metapelites indicates that the exposure is not the basal section of a crust of normal thickness. A third model is the mafic granulite tract of the Doubtful Sound area, New Zealand (Oliver, 1976). In addition to being petrologically similar to the mafic granulites of explosive pipe nodule suites, commonly of plagioclase–clinopyroxene–garnet–hornblende±scapolite±quartz mineralogy (*e.g.* Rogers and Nixon, 1975), the pressures calculated here for the Doubtful Sound rocks are equivalent to approximately 40 km depth in a crust of average density 2.8 gm/cm^3. This fact, together with the profound gravity high over the area, suggests strongly that the Doubtful Sound granulites are indeed an actual deep-crustal array. The mechanisn of modern strong uplift, exhibited in some granulite terranes, which elevates a lower crustal section, or, in the case of the Ronda peridotite, a subcrustal sequence, remains obscure.

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