

The ΔH of reaction and recalibration of garnet-pyroxene-plagioclase-quartz geobarometers in the CMAS system by solution calorimetry

JAMES O. ECKERT, JR.,* R. C. NEWTON

Department of the Geophysical Sciences, University of Chicago, 5734 South Ellis Avenue, Chicago, Illinois 60637-1434, U.S.A.

O. J. KLEPPA

James Franck Institute, University of Chicago, 5640 South Ellis Avenue, Chicago, Illinois 60637-1434, U.S.A.

ABSTRACT

Two of the potentially most useful barometers for the granulite facies are based on the following reactions:



Enthalpy of reaction (ΔH_R) is one of the major sources of uncertainty in the calibration of these geobarometers. Solution calorimetry of stoichiometric mixes of synthetic phases from each side of each reaction provides an improved method for determination of the enthalpies of reaction. Our results at 973 K are $\Delta H_A = 8.23 (\pm 2.52)$ kJ/mol and $\Delta H_B = 6.02 (\pm 3.47)$ kJ/mol. These values discriminate among various ΔH_R values compiled from previous solution calorimetry and from internally consistent datasets. For the GAPES reaction there is agreement (though marginal) with all of the derived ΔH_R values, but for the GADS reaction, only the ΔH_R value compiled from the data of Holland and Powell (1985) is within the calorimetric uncertainty.

The resultant geobarometric equations, retaining entropy and volume data from Newton and Perkins (1982), are (P in kbar, T in K)

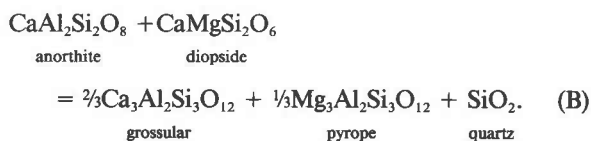
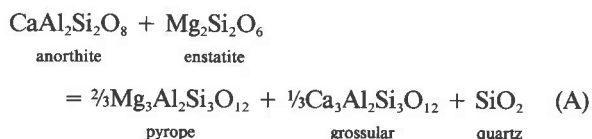
$$\text{GAPES reaction: } P = 3.47 + 0.01307T + 0.003504T \ln K_A \quad (\pm 1.55 \text{ kbar}) \quad (8)$$

$$\text{GADS reaction: } P = 2.60 + 0.01718T + 0.003596T \ln K_B \quad (\pm 1.90 \text{ kbar}). \quad (9)$$

A practical field test of these equations, for a well-characterized granulite facies area in southwestern North Carolina, indicates internal consistency for two-pyroxene-garnet granulites and consistency with the experimental Al_2SiO_5 diagram compared to a regional kyanite-sillimanite isograd. The empirical adjustments of Newton and Perkins (1982), which subtracted 600 bars from the Reaction A scale and added 1600 bars to the Reaction B scale, are consistent with our calculations with no adjustment. Thus, previous barometric calculations using their adjusted formulae, and tectonic interpretations based on those pressures, should require little revision.

INTRODUCTION

Several mineralogical geobarometers applicable to granulite facies rocks are based on reactions among end-member substances of coexisting minerals. Two of the potentially most useful barometers are based on the following reactions:



Anorthite (An), enstatite (En), and diopside (Di) are, respectively, principal components of plagioclase, orthopyroxene, and clinopyroxene, and pyrope (Py) and grossular (Gr) are principal components of garnet. Quartz (Qz) is essentially pure SiO_2 .

Apparent metastable persistence of An + pyroxene assemblages complicated previous attempts to determine stabilities of these reactions by phase-equilibrium experiments. All pyroxenes in these previous attempts were not end-member compositions, but contained Al (as well

* Present address: Department of Geological Sciences, University of Tennessee, Knoxville, Tennessee 37996-1410, U.S.A.

as Ca in orthopyroxene) substitution (Perkins, 1983). Three of nine experiments attempting to determine the stability of Reaction A, though using garnets more Py rich than would be stoichiometric, produced clinopyroxene at pressures > 17.3 kbar with garnet compositions of Py_{85} ; for both Reactions A and B, equilibrium pressures determined were strongly dependent on garnet composition (Perkins, 1983, Table 2). An attempt to evaluate ΔG values and pressures, using compiled phase-equilibrium work on these reactions, produced calculated pressures from the Otter Lake, Quebec region which ranged from zero to negative values, indicating a fundamental problem with those phase-equilibrium data (Newton and Perkins, 1982, p. 205). Thus, direct investigation by high-temperature, high-pressure experiments is not feasible. However, measured thermodynamic data may be used to calibrate the geobarometer reactions, based on the equation of equilibrium

$$\Delta G_R = \Delta H_R^\circ - T\Delta S_R^\circ + P\Delta V_R^\circ + RT \ln K_{eq} = 0. \quad (1)$$

Here, ΔG_R , ΔH_R° , ΔS_R° are, respectively, the free energy, standard enthalpy, standard entropy, and standard volume change of the reaction at 1 bar, T , K_{eq} is the equilibrium constant, defined for Reactions A and B by:

$$K_A = \frac{\alpha_{\text{Py}}^2 \cdot \alpha_{\text{Gr}} \cdot \alpha_{\text{Qz}}}{\alpha_{\text{An}} \cdot \alpha_{\text{En}}} \quad K_B = \frac{\alpha_{\text{Py}} \cdot \alpha_{\text{Gr}}^2 \cdot \alpha_{\text{Qz}}}{\alpha_{\text{An}} \cdot \alpha_{\text{Di}}} \quad (2)$$

Activities of Py (Reaction A) and Gr (Reaction B) are squared, as those components have coefficients of $\frac{2}{3}$ in these reactions, and activities of garnet end-member components are cubed because mixing occurs among three sites. This is analogous to defining the garnet components as $\frac{1}{3}$ of the formula units shown in Reactions A and B. The activities (α) are related directly to the concentrations of the components of the solid solution phases; α_{Qz} is effectively unity. Knowledge or assumption of activity-concentration relations is necessary to formulate K_{eq} for complex rock systems. The other terms can be evaluated by X-ray diffraction (for ΔV_R°), heat capacity measurements (for ΔS_R°), and enthalpy of solution measurements (for ΔH_R°). The first two standard quantities may be compiled from existing data based on precise measurements and, in general, do not contribute major uncertainties to the geobarometer calibrations. The enthalpy of solution measurements are less precise; moreover, relatively few measurements, especially duplicate studies of the important rock-forming end-member minerals, have been made using high-temperature oxide melt calorimetry. Input of the measured thermodynamic quantities into Equation 1 defines implicitly the pressure (P) of recrystallization of a garnet granulite, subject to an independently estimated temperature (T) and to the assumption or documentation that the minerals have not been reequilibrated subsequently.

The geobarometer Reactions A and B, which may be called, respectively, GAPES (grossular-anorthite-pyroxene-enstatite-silica) and GADS (garnet-anorthite-diopside-

silica), were calibrated from thermodynamic data by Perkins and Newton (1981). Except for uncertainty regarding a small configurational entropy term for anorthite, the entropies, heat capacities, and volumes of the substances are well constrained. The provisional calibrations also were based on enthalpy of formation values derived from enthalpy of solution data available only since 1975–1980, and on simple activity-composition models based in part on enthalpy of solution measurements on garnet, plagioclase, and pyroxene solid solutions. Newton and Perkins (1982) showed that their adjusted calibrations of the barometers produced paleopressures for a wide variety of granulite-facies occurrences that generally were consistent with alternative pressure estimates. Their GAPES barometer yielded pressures consistently about 2 kbar higher than their GADS barometer for two-pyroxene granulites, and they considered that the former scale was more accurate than the latter. Accordingly, to produce agreement of the two scales, empirical adjustments of –500 bars for the GAPES scale and +1500 bars for the GADS scale (Perkins and Newton, 1981, Eqs. 9), and of –600 bars (GAPES) and +1600 bars (GADS) (Newton and Perkins, 1982, p. 217), were suggested.

The calibrations of Newton and Perkins used calorimetric determinations of the enthalpies of formation for the individual minerals by Charlú et al. (1975, 1978) and Newton et al. (1977, 1980). These results were produced in three different batches of $\text{Pb}_2\text{B}_2\text{O}_5$ calorimeter solvent over a period of five years; the possibility exists of substantial variation of results from one melt batch to another. Also, since boric acid was used to prepare the solvent, there were small, variable amounts of H_2O in the solvent. Possibly because of errors arising from these factors, the formation enthalpy for enstatite of Charlú et al. (1975) later was recognized to be incompatible with phase equilibrium measurements (Perkins et al., 1981). More recent calorimetric work of Brousse et al. (1984) used an alkali borate solvent and confirmed that the earlier result of Charlú et al. was too negative by almost 6 kJ/mol. Moreover, internally consistent thermodynamic datasets derived from experimental phase equilibria (Holland and Powell, 1985, 1990; Berman, 1988) agree that the $\Delta H_{f,970}^\circ$ of pyrope reported by Charlú et al. (1975) is too negative by about 6–13 kJ/mol. Conflicts of smaller magnitude also exist between the measured ΔH_f° of anorthite, diopside, and grossular and deductions from phase equilibria (Newton, 1987). These inconsistencies erode confidence in the earlier geobarometer calibrations and indicate that a redetermination of the enthalpies of Reactions A and B is needed.

This study redetermines ΔH_R of the geobarometer Reactions A and B by solution calorimetry. Dissolution of the left-hand-side (LHS) or reactant assemblage and of the right-hand-side (RHS) or product assemblage gives ΔH_R directly by subtraction. This method was used by Newton et al. (1974) to define the dP/dT slopes of the high-pressure breakdown reactions of anhydrous magnesian cordierite and may be applied to any reaction,

stable or metastable, whose reactant and product assemblages dissolve congruently, and without effects of solute concentration, in the calorimeter solvent.

The calorimetric measurements reported here overcome several shortcomings of previous oxide-melt calorimetry on the individual phases, in terms of establishing ΔH_R . These improvements include:

1. A single master batch of $\text{Pb}_2\text{B}_2\text{O}_5$ melt was used in order to eliminate errors arising from batch-to-batch variation.
2. The B_2O_3 used to prepare the oxide melt was obtained in fused anhydrous disks that contained reported H_2O contents of less than 230 ppm, thus greatly reducing problems of solute interaction with H_2O . This could be a major source of error in dissolving the basic oxides CaO and MgO.
3. Measurements of heats of solution were made only on the phases involved in the reaction, mixed in reaction proportions. Thus, this method involves no accrued inaccuracies associated with heats of solution of the individual oxides, which, especially for MgO and CaO, could result in systematic inaccuracies of several kJ/mol. The stoichiometry (fixed bulk composition) maintained in the dissolution experiments should minimize effects of melt interactions resulting from nonstoichiometry.
4. To maintain an inert atmosphere, dissolution events were undertaken, and the calorimeter solvent between experiments was maintained, under a slight flow of Ar.
5. Additional improvements in technique include the use of a digitally integrated (rather than manually integrated) temperature-time curve to establish the heat effect, and the accumulation of more measurements than were used in previous work on any one bulk composition.

The larger number of measurements gathered here, though apparently not improving precision, should produce more accurate mean values for the enthalpies of solution. Improvement of accuracy neither implies nor requires improved precision.

EXPERIMENTAL METHODS

Starting materials

All phases used for calorimetry, except quartz and enstatite, were synthesized from glasses made from stoichiometric mixtures of reagent-grade oxides. Puratronic $\gamma\text{-Al}_2\text{O}_3$ (99.99%) and MgO (99.998%) and Alfa Co. SiO_2 (99.999%) were fired at $\sim 1400^\circ\text{C}$ for 4–7 h prior to preparing the stoichiometric oxide mixes for glasses. The weight of MgO was corrected empirically for weight gain from adsorption of atmospheric H_2O . In addition, Baker Ultrex CaCO_3 , dried at $\sim 300^\circ\text{C}$ for several hours, was weighed into the stoichiometric oxide mixes for diopside, grossular, and anorthite; these mixes then were fired at $\sim 830^\circ\text{C}$ until decarbonation was complete, as indicated

by weight loss. The stoichiometric oxide mixes were melted, quenched to glass, then ground and remelted for homogenization, and again quenched.

Anhydrous mineral syntheses at high pressure were made with the $\frac{3}{4}$ " piston-cylinder apparatus in graphite capsules of ~ 150 -mg yield (except for most grossular) that were surrounded by an AlSiMg-ceramic inner assembly, graphite-sleeve heater, soft glass, and a talc outer sleeve. Dry synthesis of most grossular was accomplished in graphite capsules, of ~ 600 -mg yield, which formed part of the graphite heater; this assembly was surrounded by soft glass and a talc outer sleeve. Nucleation in dry syntheses of garnets was assisted by mixing in small amounts of seeds with ground glass. These garnet seeds were grown in hydrothermal syntheses from ground glass, sealed in Au capsules with ~ 20 mg of deionized H_2O , in the $\frac{3}{4}$ "-diameter piston-cylinder apparatus with NaCl pressure medium. Hydrothermal experiments at 1000°C used chromel-alumel thermocouples. Dry-synthesis experiments used 25% Re-W/W-3%-Re thermocouples. Conditions and durations of anhydrous syntheses are listed in Table 1.

After opening the graphite sample capsules and burning off excess graphite at $\sim 830^\circ\text{C}$, all minerals synthesized were inspected for purity under immersion oils. Experimental products estimated optically to contain more than trace quantities of impurities were rejected. No spurious peaks appeared in X-ray diffraction powder patterns. Unit-cell values were determined by scanning at $\frac{1}{8}^\circ 2\theta/\text{min}$ ($\text{CuK}\alpha$) with an annealed corundum internal standard. Ten to 12 peaks of each substance were used in least-squares refinement of the unit-cell values listed in Table 1. Unit-cell indexing was accomplished using a program from the National Bureau of Standards. Additional synthesis details follow.

Anorthite. $\text{CaAl}_2\text{Si}_2\text{O}_8$ glass was obtained by melting the stoichiometric oxide mixture in a DelTech vertical-tube molybdenum-silicide furnace at 1600°C in a Pt crucible. Melts were drop-quenched into H_2O . This glass was crystallized in a Global silicon carbide furnace at 1450°C for 160 h. X-ray diffraction powder patterns showed only anorthite peaks.

Diopside. $\text{CaMgSi}_2\text{O}_6$ glass was obtained by melting the stoichiometric oxide mixture in the Global furnace at 1480°C , then drop-quenched into H_2O . This glass was crystallized in the Global furnace at 1285°C for 168 h. X-ray diffraction powder patterns showed only diopside peaks.

Enstatite. Attempts to make MgSiO_3 glass in the DelTech furnace at 1570°C and at 1600°C (drop-quenched into H_2O) failed to eliminate quench crystals of forsterite, even for melting times exceeding 30 min. Thus, stoichiometric oxide mixes of MgSiO_3 composition were reacted in pressed pellets to a mixture of protoenstatite and clinoenstatite in a procedure similar to that of Brousse et al. (1984). Sintering conditions in the Global furnace were $1300\text{--}1400^\circ\text{C}$. After five sintering cycles, each of 24 to 161 h duration, interspersed with grinding

TABLE 1. Characteristics of synthetic minerals used for calorimetry

Mineral	Synthesis conditions (kbar, °C, h)			Unit cell constants (Å, degree, cm³)						
	Pressure	Temperature	Time	<i>a</i>	<i>b</i>	<i>c</i>	α	β	γ	<i>V</i>
Diopside CaMgSi ₂ O ₆	0.001	1285	168	9.744(1)	8.927(1)	5.248(2)	105.88(1)			66.11(2)
Enstatite Mg ₂ Si ₂ O ₆	15–17	1400	41–118	18.214(2)	8.824(2)	5.171(1)				62.57(1)
Anorthite CaAl ₂ Si ₂ O ₈	0.001	1450	160	8.176(3)	12.862(3)	14.166(5)	93.14(2)	115.78(2)	91.24(1)	100.70(1)
Grossular Ca ₃ Al ₂ Si ₃ O ₁₂	25–26	1200	42–170	11.851(1)						125.30(2)
Pyrope Mg ₃ Al ₂ Si ₃ O ₁₂	30	1200	91–142	11.455(1)						113.16(1)
<i>Note:</i> All minerals crystallized from glass except enstatite (see text); garnets crystallized from glass + seeds (see text). Numbers in parentheses refer to one standard deviation (sample s.d.) in the last digit.										

Note: All minerals crystallized from glass except enstatite (see text); garnets crystallized from glass + seeds (see text). Numbers in parentheses refer to one standard deviation (sample s.d.) in the last digit.

and repelletizing, no forsterite peaks were evident in X-ray diffraction patterns, which showed only peaks corresponding to protoenstatite and clinoenstatite. This material was converted to orthoenstatite at high pressure in the piston-cylinder apparatus in graphite containers. X-ray diffraction powder patterns showed only orthoenstatite peaks.

Pyrope. Mg₃Al₂Si₃O₁₂ glass was obtained by melting, grinding, and remelting the stoichiometric oxide mixture in the DelTech furnace at 1600 °C. Melts were drop-quenched into H₂O. The glass was free of crystals. A portion of the glass was ground and crystallized to seed crystals in hydrothermal experiments at 1000 °C, 25 kbar for 5.5–7.4 h. The seed crystals then were mixed with ground glass in dry synthesis experiments. Seed crystals composed 12.5% by weight of these dry synthesis experiments. X-ray diffraction patterns showed only pyrope peaks.

Grossular. Ca₃Al₂Si₃O₁₂ glass was obtained by melting, grinding, and remelting the oxide mixture in the Global furnace at 1440 °C. Melts were drop-quenched into H₂O. Seed crystals were obtained by crystallizing this glass in hydrothermal experiments at 1000 °C, 24 kbar for 3–5 h. These seed crystals were mixed with ground glass in dry synthesis experiments and composed 9.1% by weight of the dry syntheses. X-ray diffraction patterns showed only grossular peaks.

Quartz. The quartz used is a natural sample from Lisbon, Maryland, which was purified by leaching.

Calorimetric technique

The oxide-melt calorimeter used is the Ni-block, twin Calvet-type apparatus first described with an Al block by Kleppa (1960). Later modifications to this heat-flow calorimeter, including the replacement of the Al block with a Ni block, were described by Kleppa (1972) and by Kleppa and Newton (1975). Our measurements were made with this calorimeter operating at 700 (±3) °C (973 K).

Calibration was accomplished by the Pt-drop method, whereby a length of Pt wire was dropped from room tem-

perature (25 °C) into the solvent, and the heat effect was calculated using known values for the heat contents of Pt. Calibration was repeated for each set of measurements of melt, about 30 g in a single crucible. Each calibration constant was determined using three to five consistent drops. The standard deviation (sample S.D. or "S") of a set of calibration experiments was ±0.21% to ±0.97% of the mean calibration value.

The schematic diagram of Kleppa and Newton (1975, Fig. 1) shows a cutaway view of this calorimeter, including fused silica liners in which the dissolutions occur. Inside the fused silica liners, dissolutions occur within a Pt crucible containing ~30 g of Pb₂B₂O₅ solvent. These silica liners were flushed with dry Ar throughout and between each experiment to maintain an inert atmosphere. The sample powder occupying the sample container was a mixture of phases for the LHS or RHS in stoichiometric proportions. The sample container is attached to the bottom of a thin fused silica tube passing through the center of the liner. This thin silica tube is the means by which the sample container is moved in and out of the oxide melt to insure that the powder is clear of the container when dissolving. This stirring was performed in an identical manner for each experiment; at each of the first four 60-s intervals of each experiment the stirring tube was moved up and down (sample container in and out of the solvent) 20 times. After most individual dissolution experiments, a separate experiment was made to evaluate any heat effect associated with the stirring procedure for the exact geometry of that particular experiment. Heat effects indicated by these stirring-effect experiments ranged from exothermic to endothermic and were equivalent to 1.1% to 3.4% of the total heat signal in any given experiment. During several stirring-effect experiments, both endothermic and exothermic values were reported by the integrator over the course of a single experiment. As these effects were inconsistent, no stirring correction was applied to any of the reported heat of solution values.

The calorimeter solvent was mixed in a master batch of Pb₂B₂O₅ from Aesar (99.99%) PbO powder and Pura-tronic, anhydrous B₂O₃ (99.9995%) fused disks. Four in-

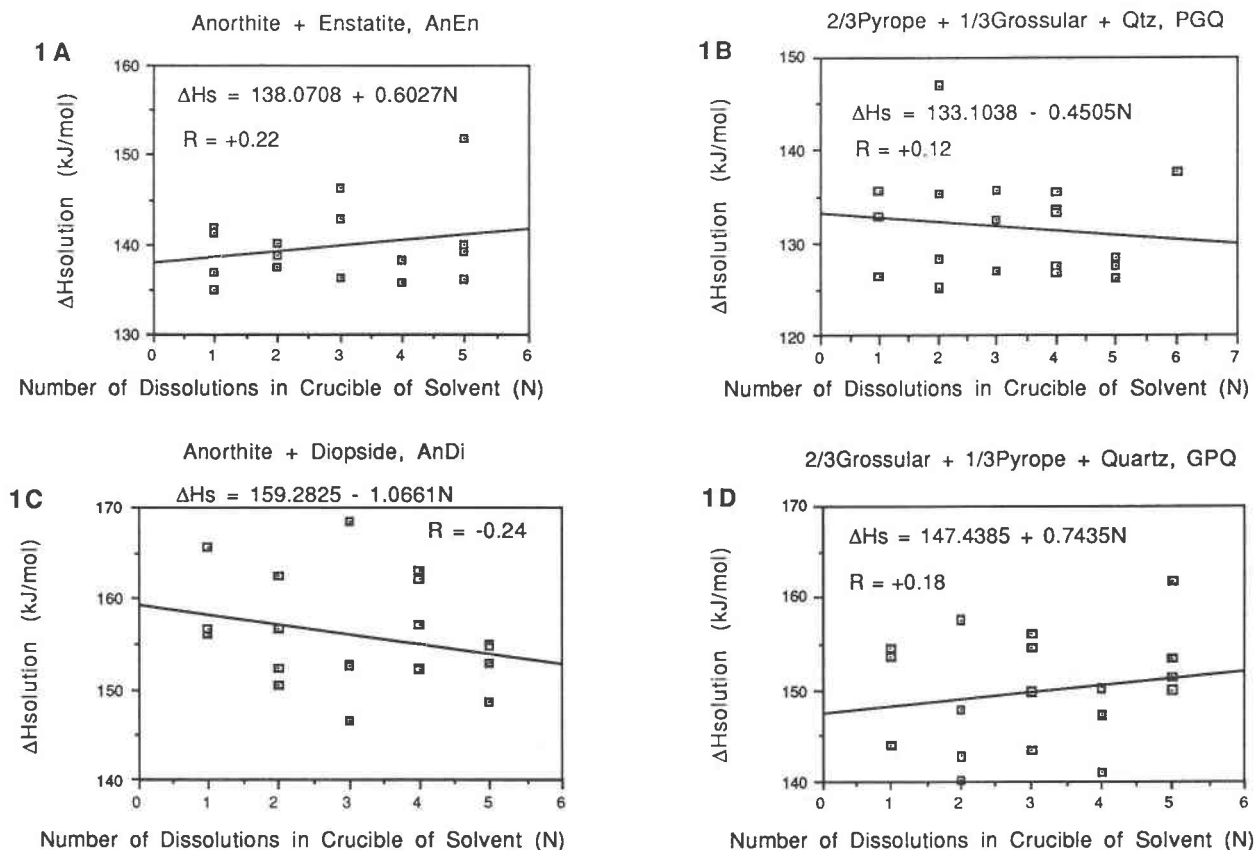


Fig. 1. Data for heats of solution are plotted vs. the corresponding dissolution event in a particular crucible of solvent, for each stoichiometric mixture of phases: anorthite + enstatite, AnEn (A), $\frac{2}{3}$ pyrope + $\frac{1}{3}$ grossular + quartz, PGQ (B), anorthite + diopside, AnDi (C), and $\frac{2}{3}$ grossular + $\frac{1}{3}$ pyrope + quartz, GPQ (D). Heat of solution values are plotted on the vertical axis; the

dissolution event in the oxide-melt batch, which corresponds to each heat-of-solution value, is plotted on the horizontal axis. Very slight slopes and very low correlation coefficients result from linear regression of these data. The absence of significant trends for solution values with successive measurements confirms that the assumption of infinite dilution of the solvent is justified.

dividual subbatches of 400 g each were melted at $\sim 850^\circ\text{C}$, then each subbatch was split into three approximately equal portions. Three subsets of the master batch were formed by combining one portion from each of the four subbatches. Each of these three subsets was remelted for ≥ 30 min and was stirred to insure homogenization. Each set of calibrations and five dissolutions was accomplished in a single crucible filled with 30 g of solvent.

Products of successful mineral syntheses were ground under acetone and sized to -200 to -325 mesh (45 – 75 μm). Extraneous organic materials were burned off from these sized fractions at $\sim 830^\circ\text{C}$, then these fractions were hand picked under the binocular microscope at 15 – $40\times$ until purity was estimated visually to be essentially 100%. The purified, sized fractions were used for the calorimetry. Total powder sample (LHS or RHS) was 30 – 40 mg. Individual mineral powders were weighed directly into the calorimeter sample container preparatory to a solution experiment. Extreme care was exercised during the weighing of these mixtures. The individual weight of each phase was reproduced to 0.01 mg by two successive lift-

ings of the balance pan. Zero on the balance was inspected after each weighing and the drift from zero was recorded. The maximum drift observed was less than 0.3 mg, and the drift was typically less than 0.1 mg. This maximum zero-drift corresponds to a worst-case weighing precision of $<1\%$.

Samples were thermally equilibrated in the calorimeter from 1.5 to 3 h before beginning dissolution; equilibration was confirmed by steady background readings on the integrator. The background assigned by the integrator is the average of the last three background readings, each of which is counted over a 60 -s interval (Dickens et al., 1980). The maximum of six (five in all but one) sample dissolutions in a given crucible filled with 30 g of solvent insured that melt solutions were always very dilute. No significant trends of measured heats of solutions with successive measurements are indicated by the data (Fig. 1). The absence of a significant trend for heats of solution with successive measurements indicates negligible concentration-dependent heat effects.

The heat effects of all dissolutions decayed to the cal-

TABLE 2. Heat of solution values (kJ/mol) from individual dissolution experiments

Mineral mix: anorthite + enstatite (AnEn)										
Experiment	1	2	3	4	5	6	7	8	9	10
$\Delta H_{\text{solution}}$	141.78	146.15	139.90	141.20	142.77	[151.86]	140.19	138.16	134.99	139.24
Time of experiment	40	37	52	44	47	51	41	38	34	40
Experiment	11	12	13	14	15	16				
$\Delta H_{\text{solution}}$	137.41	135.77	136.80	136.36	136.16	138.72				
Time of experiment	36	41	40	36	40	43				
Mineral mix: 2/3pyrope + 1/3grossular + quartz (PGQ)										
Experiment	1	2	3	4	5	6	7	8	9	10
$\Delta H_{\text{solution}}$	135.32	135.51	137.49	[146.95]	133.63	135.67	132.38	126.15	128.13	133.27
Time of experiment	38	38	46	46	39	43	42	36	37	37
Experiment	11	12	13	14	15	16	17	18	19	
$\Delta H_{\text{solution}}$	132.80	126.83	128.50	125.25	126.68	126.30	135.74	127.39	127.52	
Time of experiment	36	48	37	38	38	52	43	42	38	
Mineral mix: anorthite + diopside (AnDi)										
Experiment	1	2	3	4	5	6	7	8	9	10
$\Delta H_{\text{solution}}$	[168.66]	163.11	156.09	156.65	162.26	150.94	146.58	148.56	152.41	152.39
Time of experiment	49	41	45	39	39	41	41	40	38	44
Experiment	11	12	13	14	15	16	17	18	19	20
$\Delta H_{\text{solution}}$	156.56	152.72	154.91	150.59	156.94	165.72	152.61	153.00	162.56	152.21
Time of experiment	39	42	39	47	47	44	45	50	48	53
Mineral mix: 2/3grossular + 1/3pyrope + quartz (GPQ)										
Experiment	1	2	3	4	5	6	7	8	9	10
$\Delta H_{\text{solution}}$	143.73	157.56	153.42	154.49	147.02	140.18	140.90	156.09	151.19	147.86
Time of experiment	46	42	40	42	45	44	48	49	40	48
Experiment	11	12	13	14	15	16	17	18	19	
$\Delta H_{\text{solution}}$	147.35	154.60	143.16	149.85	142.60	150.17	153.50	149.72	[161.81]	
Time of experiment	42	38	49	51	54	38	50	46	47	

Note: Time of experiment is the time elapsed (in minutes) until background readings returned to or near the original baseline value. Values in brackets denote the values for each suite of experiment excluded in the calculations. (See additional discussion in text.)

orimeter baseline values within 35 to 54 min after immersion of a sample (Table 2). The digital integrator prints values for peak and for background at 60-s intervals. Experiments were considered complete, and averaging of the digitally integrated values was terminated, within 15 min after the temperature-time curve was restored to within 0.15% of the baseline value relative to the background signal. Only one experiment of the entire operation failed to restore to this level; this experiment was discarded. For each suite of experiments (e.g., experiments on the LHS assemblage of Reaction A, AnEn), high or low outliers were omitted (see below), the mean values were calculated from the remaining experiments, and values of δ ("twice the standard deviation of the mean") (Robie et al., 1979) were computed. This criterion is given by

$$\delta = 2 \sqrt{\frac{\sum(\bar{x} - x_i)^2}{n(n-1)}} \quad (3)$$

where $\bar{x}$ is the mean of measured values, x_i are the individual measurements, and n is the number of measurements. These δ values have been recommended by calorimetry experts as the precision standard for calorimetry (Rossini, 1956, p. 319; Robie et al., 1979, p. 11). For sample standard deviation S , $\delta = 2S\sqrt{n}$.

RESULTS OF CALORIMETRY

The individual enthalpy of solution measurements are listed in Table 2. Measurements enclosed in brackets were not used in the averages. These omitted high or low values from a suite of measurements, which were considered

outliers, deviated by more than 1.5% of the mean value for the suite from the next highest or lowest measurement, respectively. Possible sources of the spread of values in Table 2 include (but are not limited to) variations in solution-time characteristics or dissolution kinetics (giving rise to somewhat different temperature-time curves), uncorrected-for departure from perfect background restoration and background drift during an experiment, possible slight variation in the master batch of calorimeter solvent, and weighing errors of the mineral mixtures for dissolution. Application to each value of a correction for the heat effect of stirring would increase the scatter of the data. Some portion of this variation likely is produced as an artifact of calorimeter design and sample arrangement; however, the magnitude of these effects cannot be quantified at present. Further discussion of this problematic precision is beyond the scope of this paper.

As a result of these uncertainties (and perhaps others), the relative precision (δ) for the individual suites ranges from 1.1% to 1.7%. This is near the best precision realizable by high-temperature solution calorimetry. The analytical precision reported by Charlú et al. (1975, 1978), when calculated for the geobarometer reactions (propagated as the square root of the sum of the squares of the standard deviations for the solution enthalpies of individual phases; Newton and Perkins, 1982), appears better than that of our measurements. However, many solution experiments were omitted from those results as presented, and the apparent standard deviations for the geobarometer reactions are decreased more by the method of propagating a greater number of sets of measurements

TABLE 3. Enthalpies of solution (kJ/mol) of individual minerals and of assemblages and enthalpies of reaction from calorimetry and internally consistent datasets

Substance:	Anorthite	Enstatite	Diopside	Pyrope	Grossular	Quartz
$\Delta H_{\text{soln}}^{\circ}$ (970)	67.91	73.47	85.90	116.27	177.44	-5.15
σ_H	0.96	1.09	1.05	1.34	1.72	0.29
Reference	4	1	2	1	3	1
Assemblage:	AnEn	PGQ	AnDi	GPQ		
$\Delta H_{\text{soln}}^{\circ}$ (Refs. 1-4)	141.38	131.52	153.80	151.90		
σ_H	1.45	1.10	1.42	1.26		
$\Delta H_{\text{soln}}^{\circ}$ (present)	139.04	130.81	155.09	149.08		
δ_H	1.57	1.97	2.38	2.52		
Source of ΔH_R° :	Refs. 1-4	Present	H-P(85)	RGB	H-P(90)	
ΔH_A° (973)	9.77*	8.23	11.16	5.14	8.49**	
σ_H	1.82	2.52	2.68			
ΔH_B° (973)	1.76*	6.02	5.06	1.02	1.61**	
σ_H	1.90	3.47	2.86			

Note: Assemblages: AnEn = anorthite + enstatite. PGQ = $\frac{2}{3}$ pyrope + $\frac{1}{3}$ grossular + quartz. AnDi = anorthite + diopside. GPQ = $\frac{2}{3}$ grossular + $\frac{1}{3}$ pyrope + quartz. References: 1 = Charlu et al. (1975); 2 = Newton et al. (1977); 3 = Charlu et al. (1978); 4 = Newton et al. (1980); H-P(85) = Holland and Powell (1985); H-P(90) = Holland and Powell (1990); RGB = Berman (1988). Heat contents (298–973 K) calculated from parameters in H-P(85), H-P(90), and RGB for the relevant reference. Corrections for 1–4 (970–973 K) use tabulated values for pyrope and enstatite of Haselton (1979) and those of Robie et al. (1979) for other phases.

* Values from references 1–4 at 970 K = 9.87 (GAPES) & 1.91 (GADS).

** Heat capacity corrections use the H-P(85) value for quartz.

(five per reaction) than are the standard deviations calculated from our results (two sets per reaction).

Table 3 compares our enthalpies of solution for the four assemblages to the composite enthalpies predicted by compilation from four previous studies of the individual minerals. The agreement appears reasonably good: all of the compiled ΔH of solution values (within uncertainty) are within the precision limits of this study. Apparently, systematic errors in the previously reported solution values for the individual phases, though producing composite solution enthalpies for each assemblage that overlap, within precision, our measured values, created systematic shifts in the mean values for each assemblage (see Table 3). Small relative differences in ΔH of solution for each assemblage are magnified in calculating ΔH_R . Similarity of ΔH_A from the previous measurements to the present value suggests that compensating errors for enthalpies of the predominating Mg phases on each side of the reaction (En and Py) produced a previous value that was reasonable. Discrepancies between the measured enthalpies of formation and phase equilibrium deductions may have arisen, in part, from problems in determining enthalpies of solution of the component oxides CaO, MgO, Al_2O_3 , and SiO_2 . These oxides were measured separately, rather than together in proportions of the reactions, and there may have been specific concentration-dependent heat effects violating the limiting dilution law. The formation enthalpies of the individual phases, where possible, should be remeasured by dissolution of stoichiometric oxide mixes, with or without other anchor phases.

Table 3 also lists ΔH_R for Reactions A and B from our work, along with those derived from solution values of the individual minerals and from the internally consistent datasets of Holland and Powell (1985, 1990) and of Berman (1988). The latter three values were corrected to 973 K using the heat-capacity corrections presented by the

respective authors. For each ΔH_R value derived from solution calorimetry, the uncertainty is listed as the square root of the sum of the squares of the two δ -values. Our value of ΔH_A° at 973 K is marginally compatible with the value compiled from earlier calorimetry, is very near the value calculated from the dataset of Holland and Powell (1990), and lies midway between the values obtained from the datasets of Holland and Powell (1985) and Berman (1988), marginally compatible with both. Our value of ΔH_B° is marginally compatible with that of Holland and Powell (1985) but excludes the value compiled by Newton and Perkins (1982) and the values of Berman (1988) and Holland and Powell (1990), being 4–5 kJ larger than these other values. Our work supports generally the ΔH_A° compiled by Newton and Perkins (1982) but indicates that their ΔH_B° is roughly 4.5 kJ too negative. The revision of ΔH_B° is of the correct sign and magnitude to obtain reasonable agreement between pressure values calculated from Reactions A and B for two-pyroxene granulites without empirical adjustments, as demonstrated in the next section.

Although the precision of our results does not appear improved over those reported previously, the larger number of measurements and improvements in technique suggest that our results may be more accurate.

APPLICATION TO GEOBAROMETRY

The calorimetric results reported here define ΔH_R° of the GAPES and GADS Reactions A and B. For purposes of evaluating explicitly the effect of this work on the geobarometer calibrations, pressure calculations are presented (Table 4) which were made by replacing only the ΔH_R term in the pressure equations of Newton and Perkins (1982). Prior to comparison of these calculations, some discussion is necessary of the other terms in Equations 1 and 2.

TABLE 4. GAPES and GADS pressures (kbar) for two-pyroxene-garnet and selected one-pyroxene-garnet granulites, southwest North Carolina

Sample	GAPES					GADS				
	P-N	Present	Present*	P-H	RGB	P-N	Present	Present*	P-H	RGB
FQ42E-AA	8.46	8.49	8.93	8.51	7.80	8.40	8.81	9.16	7.70	8.40
WB1866E-A	7.62	7.65	8.04	7.62	6.92	—	—	—	—	—
WB1866E-F	7.19	7.22	7.59	7.16	6.46	—	—	—	—	—
FQ50E	7.82	7.85	8.25	7.83	7.13	8.03	8.44	8.78	7.31	8.01
WB1575E	7.43	7.46	7.84	7.42	6.72	7.23	7.64	7.94	6.46	7.17
FQ75E	7.83	7.86	8.26	7.84	7.14	8.04	8.45	8.78	7.31	8.01
FQ107E	8.28	8.31	8.73	8.32	7.61	—	—	—	—	—
FQ106E	—	—	—	—	—	8.03	8.44	8.77	7.31	8.01
WB1120E	8.56	8.59	9.03	8.62	7.91	—	—	—	—	—
WB1116E	8.87	8.90	9.36	8.96	8.24	—	—	—	—	—
WB1762E	—	—	—	—	—	7.16	7.57	7.87	6.38	7.10
FQ88E	—	—	—	—	—	7.87	8.28	8.61	7.14	7.84

Note: Pressures calculated at 750 °C. Present calculations are from Equations 8 and 9. Present* calculations use the present results (ΔH_r) combined with the ΔV_r calculated at 1023 K (750 °C), 3.5 kbar, using the expansivity and compressibility parameters in Holland and Powell (1985). P-N = adjusted formulation of Perkins and Newton (1981). P-H = linearized formulation of Powell and Holland (1988). RGB = formulation using the Berman (1988) internally consistent dataset corrected to 1023 K (750 °C), 3.5 kbar (see text). WB1866E-A and WB1866E-F are amphibolitic and felsic gneisses from a single thin section. FQ107E and FQ106E are GAPES and GADS assemblages separated by less than 200 m. All data are from Eckert (1988); the last three samples and WB1575E are also in Eckert et al. (1989).

The ΔS_r term

The entropy changes of the reactions, ΔS_r , are based on very precise low-temperature heat capacity measurements to establish the 298 K entropies of the substances and also on quite precise high-temperature heat-content measurements to establish ΔS_r at elevated temperatures. The maximum uncertainty in ΔS_r for both reactions is ± 2.68 J/K at 1000 K (see Newton and Perkins, 1982, for sources of data). Some disagreement remains about a possible configurational entropy term for anorthite resulting from tetrahedral Al-Si disorder. According to the phase equilibrium deductions of Koziol and Newton (1988), Gasparik (1986), and Wood (1988), all based on experimental reactions involving anorthite, a mean configurational entropy of 3.3 J/K (range: 1.3–7.7 J/K), corresponding to 4% (range: 1.4–12%) disorder, is indicated (Koziol and Newton, 1988). The internally consistent datasets of Holland and Powell (1985) and Berman (1988) use much smaller values (1.3 J/K and 0.5 J/K, respectively). Inasmuch as larger values seem in accord with the phase equilibrium data and heat capacity data for synthetic anorthite and grossular, and since these synthetic phases were used in our calorimetry, configurational entropy of 4.18 J/K is retained as in Newton and Perkins (1982, p. 206, Table 1, Eqs. 12).

The ΔV_r term

Newton and Perkins (1982) used the 298 K, 1 bar volumes of the phases to calculate ΔV_r , and chose to ignore thermal expansivities and compressibilities. The uncertainties in the 298 K, 1 bar volumes measured by X-ray diffraction contribute negligible error (Table 1). A slight improvement of the calibration might be obtained by taking the ΔV_r 's calculated for 1000 K and 3.5 kbar (for 7 kbar paleopressure), conditions representative for granulite facies calculations. The pressure of 3.5 kbar is as-

signed for 7-kbar pressures by evaluating the volume correction as a definite integral from 1 bar to 7 kbar $\{\int_{0.001}^7 dVdP = [(V)^7 - (V)^{0.001}]/2 = \sim (V)^{3.5}\}$. This correction decreases ΔV_r 's by about 4–5%, and raises calculated pressures by 300–350 bars (GADS) and 370–460 bars (GAPES), as shown in Table 4 for corrections of Holland and Powell (1985). However, replacement of α by β quartz at 298 K, 1 bar (calculated from Berman, 1988), results in ΔV_r 's that differ by $\sim 3\%$ from values calculated with no expansivity or compressibility corrections. At 750 °C, α quartz would be stabilized above ~ 8.45 kbar (Berman, 1988, Table 3b, Fig. 4), so the choice of quartz polymorph will have a significant effect on volume calculations at higher pressures. Substituting the volume of β -quartz for α -quartz constitutes most of the difference among calculated values of ΔV_r at 1 bar, 298 K and, given this and other uncertainties regarding volume corrections, may be a more straightforward approach. However, to emphasize comparison to the Newton and Perkins calibrations by replacing only the ΔH_r terms, calculations presented here retain the 298 K, 1 bar volumes using α quartz.

Activity-composition relationships

An uncertainty of unknown magnitude that affects all thermodynamically based geothermometers and geobarometers arises from uncertainties in the activity-concentration relations used to calculate the equilibrium constant (Eq. 2). The activity-composition relations in use involve a certain number of measured data together with a considerable amount of crystal-chemical interpretation and empirical adjustment based on natural parageneses. The equilibrium constant is therefore the least-constrained parameter in Equation 1.

For garnet components, simple activity expressions used by Newton and Perkins (1982) are of the following form:

$$\alpha_{Gr} = X_{Ca} \exp \left[\frac{W_{CaMg}}{RT} (X_{Mg}^2 + X_{Mg} X_{Fe}) \right] \quad (4)$$

$$\alpha_{Py} = X_{Mg} \exp \left[\frac{W_{CaMg}}{RT} (X_{Ca}^2 + X_{Ca} X_{Fe}) \right] \quad (5)$$

where X is the atomic fraction in a ternary (Ca,Mg,Fe) garnet and W_{CaMg} is a grossular-pyropite binary interaction parameter evaluated as $13.807 - 0.0063T$ kJ (for four O atoms), independent of composition (Newton and Haselton, 1981). These expressions are of the type for multicomponent regular solutions used by Ganguly and Kennedy (1974) and originally from Prigogine and Defay (1954), in which the assumption is made that the other binary interaction parameters W_{CaFe} and W_{MgFe} , and a second-order term from ternary interactions, are negligible. The expressions follow from more general equations for subregular multicomponent solutions by assuming that, over a restricted compositional range, the garnets behave approximately as regular solutions. The binary parameter W_{CaMg} may be split into enthalpic and entropic parts:

$$W_{CaMg} = W_{CaMg}^H - TW_{CaMg}^S \quad (6)$$

The enthalpic term W_{CaMg}^H (excess enthalpy parameter) was evaluated using the solution calorimetry measurements of Newton et al. (1977) on synthetic pyrope-grossular garnets, and the entropic term W_{CaMg}^S (excess entropy parameter) was evaluated using the heat capacity measurements of Haselton and Westrum (1980) on synthetic pyrope, grossular, and a pyrope₆₀-grossular₄₀ solid solution. Recent phase equilibrium work on pyrope-grossular solid solutions by Wood (1988) upholds the general magnitude of W_{CaMg} expressed by the Newton and Perkins formula but indicates that the excess entropy term may be somewhat dependent on composition and may not be symmetric as assumed here.

Bohlen et al. (1983a) and Ganguly and Saxena (1984) found reasons from experimental phase equilibria and natural parageneses to infer that the binary Mg-Fe interaction may not be negligible. They suggested that the interaction parameter was asymmetric and particularly significant near the Fe end-member. This conjecture was supported by the enthalpy of solution measurements on almandine-pyrope garnets by Geiger et al. (1987) and by deductions based partially thereon by Sack and Ghiorso (1989). However, standard deviations of the measurements of Geiger et al. (1.81–7.15 kJ/mol) are large relative to their derived excess enthalpy [~ 3 kJ/mol at Mg/(Mg + Fe) = 0.25]. In contrast, recent deductions from experimental Fe-Mg exchange between garnet and olivine by Hackler and Wood (1989), as well as deductions from phase equilibria and natural parageneses by Berman and Brown (1988), indicate much smaller, perhaps negligible, Fe-Mg nonideality. Most recently, experimental measurements at 1000 °C on the displacement of the GRAIL equilibrium indicate nearly ideal Fe-Mg mixing for Fe-rich garnets (Kozior and Bohlen, 1990).

Solution calorimetry by Geiger et al. (1987) on Ca,Fe garnets and phase equilibrium measurements in the same join by Kozior (1990) indicate negligible Ca-Fe interactions; this has been verified for ternary Ca,Mg,Fe garnets in the Fe-rich (almandine-dominated) range with about 20 mol% grossular by the phase equilibrium measurements of Kozior and Newton (1989). These recent observations tend to justify the selection of interaction parameters made by Newton and Perkins (1982). For comparison to previous calculations, the barometer calibrations presented here employ the garnet solution parameters used by Newton and Perkins (1982).

The pyroxene activity models used in the Newton and Perkins (1982) geobarometer calibrations (and most others) are essentially the two-site ideal models of Wood and Banno (1972). In these models, the activity of $Mg_2Si_2O_6$ in orthopyroxene is given by $X_{Mg}^{M1} \cdot X_{Mg}^{M2}$, where each X is the fraction of Mg atoms on each of the two octahedral M sites. The presence of nonquadrilateral components (Al,Mn,Ti) in natural pyroxenes prevents the application of macroscopic components and requires calculations employing the two M sites. Solid-state emf measurements of orthopyroxenes (Sharma et al., 1987) suggested substantial positive excess free energy, in contrast to recent theoretical studies (Sack and Ghiorso, 1989; Davidson and Lindsley, 1985) that predict small or even slightly negative excess free energy. Thus, apparently there is no irrefutable reason at present to defer to a model more complex than that of Wood and Banno (1972). Deductions based on experimental Fe-Mg exchange between ilmenite and clinopyroxene (Bishop, 1980) and on modeling of experimental data on the quadrilateral pyroxene solvus (Saxena et al., 1986) show substantial nonideality of diopside-hedenbergite clinopyroxenes, with a maximum excess free energy of about 2 kJ at intermediate compositions. However, modeling of the experimental Fe-Mg distribution between garnet and clinopyroxene (Pattison and Newton, 1989) indicated nearly ideal clinopyroxene, or even slightly negative deviations from ideality, in the Mg-rich range of most granulite clinopyroxenes, regardless of whether an ideal or a nonideal garnet is assumed. Thus, uncertainty remains as to whether any improvement in clinopyroxene component activities is achieved by adopting a model more complex than the ideal two-site model. For comparison to previous results, pressure calculations using the present calibrations employ these same ideal two-site models for pyroxene.

There is also some uncertainty in plagioclase activity models. The Al avoidance model of Newton et al. (1980) is based on solution calorimetry of plagioclase in the high structural state synthesized at 1200 °C in conjunction with the entropy-of-mixing model of Kerrick and Darken (1975). The activity of $CaAl_2Si_2O_8$ is given by

$$\alpha_{An} = \frac{X_{An}(1 + X_{An})^2}{4} \exp \left(\frac{1032 + 4726X_{An}}{T} \right) \quad (7)$$

This formula reproduces rather closely the activities found by Orville (1972) in his aqueous alkali chloride exchange experiments with plagioclase at 700 °C and 2 kbar in the composition range An₂₀–An₅₀. At higher anorthite contents there may be a slight discontinuity in the activity at the transition from the face-centered to the body-centered structures (Carpenter and Ferry, 1984). At compositions below An₂₀ and temperatures below 600 °C, Equation 7 probably underestimates the anorthite activity (Ashworth and Evirgen, 1985). In the temperature-composition range of recrystallization of most intermediate and mafic granulites, Expression 7 may be adequate; it also has been incorporated into several general ternary feldspar models (Haselton et al., 1983; Ghiorso, 1984; Fuhrman and Lindsley, 1988). For comparison to previous calculations, Expression 7 is retained in the calculations of pressure given herein.

At present the net errors in geobarometry contributed by all of the uncertainties in activity-composition relations cannot be evaluated precisely. A worst-case estimate formulated by Hodges and McKenna (1988) concluded that the accuracy of the most commonly used geobarometer formulations applicable to crustal rocks is likely to be $\pm \sim 5$ kbar, which would make most of the barometer scales virtually useless on an absolute basis. Nevertheless, several barometers have proven to be generally consistent with geologic criteria in various metamorphic belts and to provide useful information when used in a relative sense to distinguish pressure variation in individual metamorphic progressions [see Newton (1983) and Bohlen et al. (1983b) for summaries].

Reformulation of the barometers

Equations for geobarometry may be reformulated with the new ΔH_R values and otherwise the same input terms as those used by Newton and Perkins (1982); this allows direct comparison of the effect of replacing only ΔH_R . The revised equations are (P in kbar, T in K)

GAPES reaction:

$$P = 3.47 + 0.01307T + 0.003504T \ln K_A \quad (\pm 1.55 \text{ kbar}) \quad (8)$$

GADS reaction:

$$P = 2.60 + 0.01718T + 0.003596T \ln K_B \quad (\pm 1.90 \text{ kbar}). \quad (9)$$

Uncertainty for each reaction is propagated as the square root of the sum of the squares of the standard deviations of the enthalpy and entropy terms (Newton and Perkins, 1982), scaled to the pressure calculation by dividing by ΔV_R .

Equations were derived by linear regression to establish the variation of pressure as a function of pyrope content (X_{Py}) in garnet, using the experimental results of Perkins

(1983) at 1300 °C, on Reactions A and B. These equations are (P in kbar)

$$P = 48.22 - 0.318X_{Py}, \quad R = -0.9997 \quad (\text{GAPES}) \quad (10)$$

and

$$P = 40.13 - 0.235X_{Py}, \quad R = -0.6194 \quad (\text{GADS}). \quad (11)$$

For the stoichiometric garnet compositions of Reactions A and B, at 1300 °C, equilibrium pressures of 25.00 (A) and 32.29 (B) kbar were calculated. Pressures calculated from Equations 8 and 9 for end-member compositions in Reactions A and B (all $\alpha = 1$), at 1300 °C, are 24.03 (A) and 29.62 (B) kbar, in reasonable agreement despite the inherent uncertainties and the problems of metastability in the phase equilibrium results.

An evaluation of the present calorimetric results and their contribution to the geobarometer calibrations is attempted below, in spite of the intrinsic uncertainties involved. The test is based on the consistency of the two barometers for pyroxene-garnet granulites from a well-characterized and well-mapped metamorphic area.

Pressure calculations for southwestern North Carolina

Comparative pressure calculations were made for a granulite-facies core of Paleozoic metamorphism in the Blue Ridge province of the North Carolina Appalachians (Fig. 2) (Eckert et al., 1989). Structural, petrologic, and stratigraphic evidence indicates a continuous metamorphic progression from the staurolite zone to the hornblende granulite subfacies of the granulite facies (Eckert, 1988; Eckert and Mohr, 1988; Eckert et al., 1989). GADS assemblages, with or without GAPES assemblages, occur in the granulite-facies area of Figure 2 in mafic (amphibolitic) rocks; GAPES assemblages also occur alone in felsic (tonalitic) gneisses.

GAPES and GADS pressures, using five different formulations for each barometer, were calculated from the compositional data in Eckert et al. (1989) and Eckert (1988), at an inferred temperature of 750 °C. All calculations were made with the activity models used by Newton and Perkins (1982) as discussed above. Pressures listed in Table 4 were calculated (1) with the adjusted formulation of Perkins and Newton (1981), (2) with Equations 8 and 9 of this study which apply our new ΔH_R values, (3) with Equations 8 and 9 and ΔV_R corrected to 750 °C and 3.5 kbar (parameters in Holland and Powell, 1985), (4) with the linearized formulation of Powell and Holland (1988) (which is based on the internally consistent dataset of Holland and Powell, 1985), and (5) with an equation derived from the internally consistent dataset of Berman (1988), corrected to 750 °C, 3.5 kbar. Pressures calculated for two-pyroxene + garnet assemblages

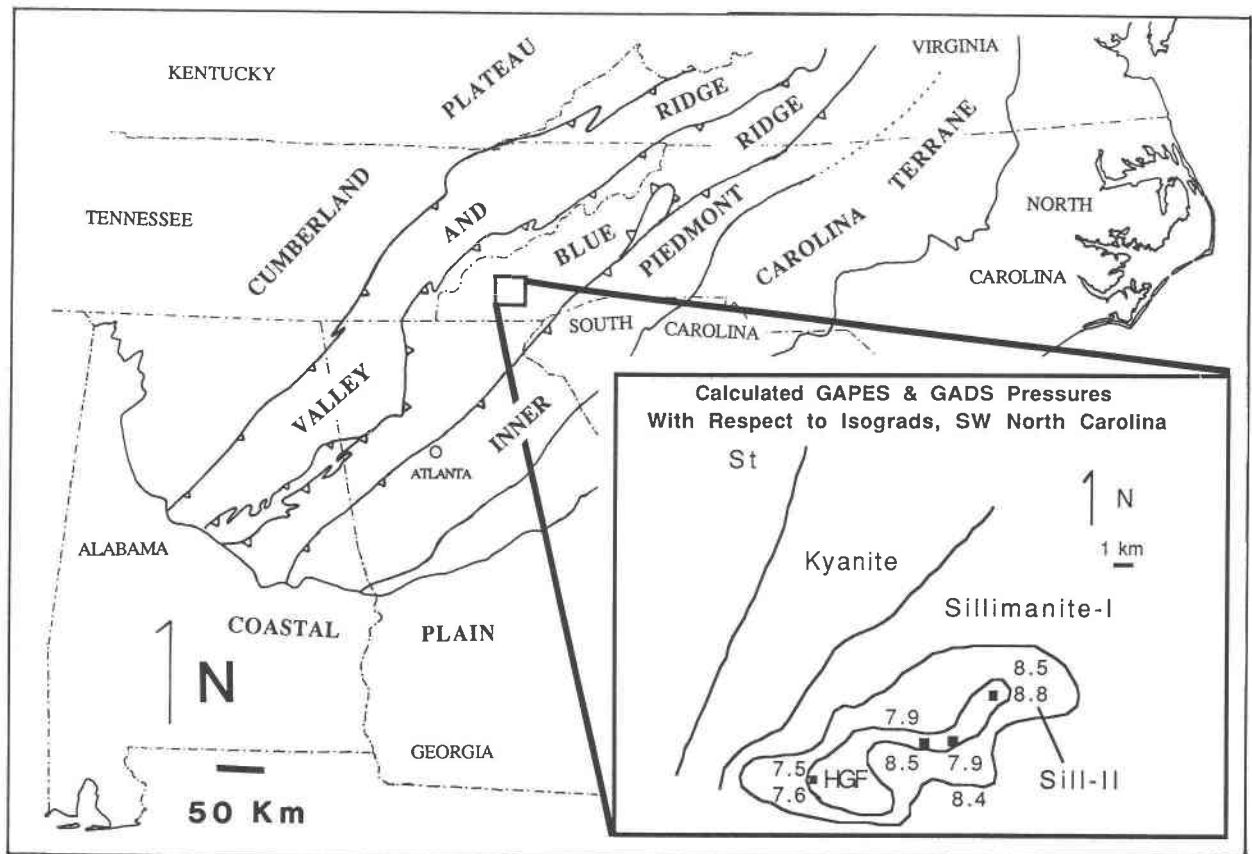


Fig. 2. Map relationships of GAPES and GADS pressures calculated (using Equations 8 and 9) for two-pyroxene + garnet assemblages in western North Carolina (Table 4). In the small-scale map, major subdivisions of the southern Appalachians are shown (simplified after Hatcher, 1987). The inset shows isograds in the Noland Creek–Wayah amphibolite/granulite transition (Eckert and Mohr, 1988; Eckert, 1988) and pressures calculated using our formulations of the GAPES and GADS barometers.

Metamorphic zones: staurolite (St), staurolite-kyanite + kyanite-almandine (Kyanite), sillimanite-muscovite (Sillimanite-I), sillimanite-orthoclase (Sill-II), and the hornblende granulite subfacies of the granulite facies (HGF). For each locality, the GAPES pressure is positioned above the GADS pressure. Data are from Eckert (1988); data from the southwesternmost locality (WB1575E) are also in Eckert et al. (1989).

(both GAPES and GADS) are plotted by sample locality in Figure 2.

All of the GAPES calculations are in reasonable to good agreement, and indicate that the pressures fall in the sillimanite field of the experimental Al_2SiO_5 diagram (Fig. 3), consistent with the kyanite-sillimanite isograd (Fig. 2) and with the presence of peak-metamorphic sillimanite in nearby metapelites. The smaller ΔH_A from the Berman (1988) dataset (Table 3) contributes to lower pressures from his calibration. Calculated pressures of 7.5–8.5 kbar at 750 °C are in the range expected if there is a generally coherent increase of temperature and pressure from inside the kyanite field to the granulite facies, across the kyanite-sillimanite isograd (compare Figs. 2 and 3).

The GADS calculations, based on our calorimetry, agree reasonably well with the GAPES pressures from the same rock or adjacent outcrops, although GADS pressures are systematically higher than GAPES by 130–590 bars (Table 4). The agreement suggests that the activity models

pertinent to the two equilibrium constants, which involve mostly the same components, either are reasonable or have comparable errors, at least in the composition ranges considered. This agreement implies further that the assumption of frozen-in paleopressures is valid. A small empirical pressure adjustment of –350 bars could be applied to GADS calculations; this would force agreement of the two scales, on average. Such a small empirical adjustment would be well within the calorimetric uncertainties but is not required and remains a matter of individual preference. The Powell and Holland (1988) GADS pressures are substantially (1.1–1.2 kbar) below those calculated with Equation 9; this results largely from the smaller value of ΔH_b employed (Table 3). Although the small ΔH_b of Berman (1988) (Table 3) should lower calculated pressures, the larger ΔS calculated from that dataset contributes an upward shift to calculated GADS pressures. Pressures calculated from the Berman (1988) dataset agree reasonably well with our values and ex-

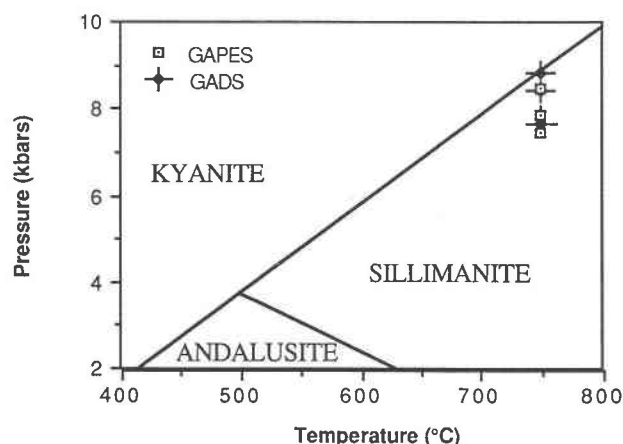


Fig. 3. GAPES and GADS pressures calculated (using Equations 8 and 9), for two-pyroxene + garnet assemblages in the area of Figure 2, are plotted in P - T space relative to the aluminum silicate diagram of Holdaway (1971). All pressures are calculated at 750 °C. Symbols for GAPES pressures are open squares; those for GADS are filled symbols with crosses. Four pressures are plotted each for GAPES and for GADS, but the essentially identical pressures for FQ75E and FQ50E (Table 4) cannot be resolved as distinct symbols.

tremely well with the adjusted values of Perkins and Newton (1981, Table 4).

Previously calculated GAPES pressures using the adjusted Perkins and Newton (1981) formulae were shown to compare favorably to pressures calculated from nearby metapelitic rocks using the Newton and Haselton (1981) garnet- Al_2SiO_5 -plagioclase-quartz (GASP) barometer (Eckert, 1988; Eckert et al., 1989). The pressure spread of the present GAPES and GADS calculations, to some extent, may reflect real pressure variations, notably an eastward pressure increase (Fig. 3) which is similar to a trend indicated by pressure calculations from nearby metapelites using the Newton and Haselton (1981) GASP barometer (Eckert, 1988).

CONCLUSIONS

1. Results from solution calorimetry of reaction assemblages define the possible ranges of the enthalpy changes of two geobarometer reactions important to the granulite facies and discriminate among various ΔH_r values compiled from previous solution calorimetry and internally consistent datasets.

2. The ΔH_r values determined at 973 K for the GAPES and GADS reactions are, respectively, $8.23 (\pm 2.52)$ and $6.24 (\pm 3.47)$ kJ/mol.

3. A practical field test of resultant equations indicates internal consistency for two-pyroxene-garnet granulites and consistency with kyanite-sillimanite phase relationships.

4. Solution calorimetry of reaction assemblages is a potentially important technique for calibrating geothermometer and geobarometer scales and may prove valu-

able in future work to improve measurement of enthalpies of formation of silicates.

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REFERENCES CITED

- Ashworth, J.R., and Evirgen, M.M. (1985) Plagioclase relations in pelites, central Menderes Massif, Turkey. II. Perturbation of garnet-plagioclase geobarometers. *Journal of Metamorphic Geology*, 3, 219–229.
- Berman, R.G. (1988) Internally-consistent thermodynamic data for minerals in the system Na_2O - K_2O - CaO - MgO - FeO - Fe_2O_3 - Al_2O_3 - SiO_2 - H_2O - CO_2 . *Journal of Petrology*, 29, 445–522.
- Berman, R.G., and Brown, T.H. (1988) A general method for thermobarometric calculations, with a revised garnet solution model and geologic applications. *Geological Society of America Abstracts with Programs*, 20, A98.
- Bishop, F.C. (1980) The distribution of Fe^{2+} and Mg between coexisting ilmenite and pyroxene with applications to geothermometry. *American Journal of Science*, 280, 46–77.
- Bohlen, S.R., Wall, V.J., and Boettcher, A.L. (1983a) Experimental investigations and geological applications of equilibria in the system FeO - TiO_2 - Al_2O_3 - SiO_2 - H_2O . *American Mineralogist*, 68, 1049–1058.
- (1983b) Experimental investigation and application of garnet granulite equilibria. *Contributions to Mineralogy and Petrology*, 83, 52–61.
- Brousse, C., Newton, R.C., and Kleppa, O.J. (1984) Enthalpy of formation of forsterite, enstatite, akermanite, monticellite and merwinite at 1073 K determined by alkali borate solution calorimetry. *Geochimica Cosmochimica Acta*, 48, 1081–1088.
- Carpenter, M.A., and Ferry, J.M. (1984) Constraints on the thermodynamic mixing properties of plagioclase feldspars. *Contributions to Mineralogy and Petrology*, 87, 138–148.
- Charlu, T.V., Newton, R.C., and Kleppa, O.J. (1975) Enthalpies of formation at 970 K of compounds in the system MgO - Al_2O_3 - SiO_2 from high temperature solution calorimetry. *Geochimica Cosmochimica Acta*, 39, 1487–1497.
- (1978) Enthalpy of formation of some lime silicates by high-temperature solution calorimetry, with discussion of high pressure phase equilibria. *Geochimica Cosmochimica Acta*, 42, 367–375.
- Davidson, P.M., and Lindsley, D.H. (1985) Thermodynamic analysis of quadrilateral pyroxenes. Part II: Model calibration from experiments and applications to geothermometry. *Contributions to Mineralogy and Petrology*, 91, 390–404.
- Dickens, K.J., Kleppa, O.J., and Yokokawa, H. (1980) Microcomputer controlled integrator for Calvet-type twin calorimeters. *Reviews of Scientific Instruments*, 51, 675–677.
- Eckert, J.O., Jr. (1988) Petrology and tectonic implications of the metamorphic transition from the staurolite-kyanite zone to the Wayah granulite-facies metamorphic core, southwest North Carolina Blue Ridge: Including quantitative analysis of mineral homogeneity, 337 + xii p. Ph.D. thesis, Texas A&M University, College Station, Texas.
- Eckert, J.O., Jr., and Mohr, D.W. (1988) Conditions in the metamorphic transition from the staurolite-kyanite zone to the hornblende granulite facies core near Franklin, North Carolina: Petrologic evidence for a continuous Paleozoic progression. *Geological Society of America Abstracts with Programs*, 20, 262.

- Eckert, J.O., Jr., Hatcher, R.D. Jr., and Mohr, D.W. (1989) The Wayah granulite-facies metamorphic core, southwestern North Carolina: High-grade culmination of Taconic metamorphism in the southern Blue Ridge. *Geological Society of America Bulletin* 101, 1434–1447.
- Fuhrman, M.L., and Lindsey, D.H. (1988) Ternary-feldspar modeling and thermometry. *American Mineralogist*, 73, 201–215.
- Ganguly, J., and Kennedy, G.C. (1974) The energetics of natural garnet solid solution. I. Mixing of the aluminosilicate endmembers. *Contributions to Mineralogy and Petrology*, 48, 137–148.
- Ganguly, J., and Saxena, S.K. (1984) Mixing properties of aluminosilicate garnets: Constraints from natural and experimental data, and applications to geothermo-barometry. *American Mineralogist*, 69, 88–97.
- Gasparik, T. (1986) Experimental study of subsolidus phase relations and mixing properties of pyroxene in the system $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$. *Geochimica Cosmochimica Acta*, 48, 2537–2545.
- Geiger, C.A., Newton, R.C., and Kleppa, O.J. (1987) Enthalpy of mixing of synthetic almandine-grossular and almandine-pyroxene garnets from high-temperature solution calorimetry. *Geochimica Cosmochimica Acta*, 51, 1755–1763.
- Ghiorso, M.S. (1984) Activity/composition relations in the ternary feldspars. *Contributions to Mineralogy and Petrology*, 87, 282–296.
- Hackler, R.T., and Wood, B.J. (1989) Experimental determination of Fe and Mg exchange between garnet and olivine and estimation of Fe-Mg mixing properties in garnet. *American Mineralogist*, 74, 994–999.
- Haselton, H.T., Jr. (1979) Calorimetry of synthetic pyroxene-grossular garnets and calculated stability relations, 98 p. Ph.D. thesis, University of Chicago, Chicago, Illinois.
- Haselton, H.T., Jr., and Westrum, E.F. (1980) Low-temperature heat capacities of synthetic pyroxene, grossular, and pyroxene-grossular. *Geochimica Cosmochimica Acta*, 44, 701–709.
- Haselton, H.T., Jr., Hovis, G.L., Hemingway, B.S., and Robie, R.A. (1983) Calorimetric investigation of the excess entropy of mixing in analbite-sanidine solid solutions: Lack of evidence for Na,K short-range order and implications for two-feldspar thermometry. *American Mineralogist*, 68, 398–413.
- Hatcher, R.D., Jr. (1987) Tectonics of the southern and central Appalachian internides. *Annual Reviews of Earth and Planetary Science*, 15, 337–362.
- Hodges, K.V., and McKenna, L.W. (1988) Accuracy versus precision in locating reaction boundaries: Implications for the garnet-plagioclase-aluminum silicate-quartz geobarometer. *American Mineralogist*, 73, 1205–1208.
- Holdaway, M.J. (1971) Stability of andalusite and the aluminum silicate phase diagram. *American Journal of Science*, 271, 97–131.
- Holland, T.J.B., and Powell, R. (1985) An internally consistent thermodynamic dataset with uncertainties and correlations: 2. Data and results. *Journal of Metamorphic Geology*, 3, 343–370.
- (1990) An enlarged and updated internally consistent thermodynamic dataset with uncertainties and correlations: The system $\text{K}_2\text{O-Na}_2\text{O-CaO-MgO-MnO-FeO-Fe}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-TiO}_2\text{-SiO}_2\text{-C-H}_2\text{O}$. *Journal of Metamorphic Geology*, 8, 89–124.
- Kerrick, D.M., and Darken, L.S. (1975) Statistical thermodynamic models for ideal oxide and silicate solid solutions, with application to plagioclase. *Geochimica Cosmochimica Acta*, 39, 1431–1442.
- Kleppa, O.J. (1960) A new twin high temperature reaction calorimeter. The heats of mixing in liquid-potassium nitrates. *Journal of Physical Chemistry*, 64, 1937–1940.
- (1972) Oxide melt solution calorimetry. *International Symposium on Thermochemistry* (Marseilles, France), no. 201. *Thermochimie*, 119–127.
- Kleppa, O.J., and Newton, R.C. (1975) The role of solution calorimetry in the study of mineral equilibria. *Fortschritte Mineralogie*, 52, 3–20.
- Koziol, A.M. (1990) Activity-composition relationships of binary Ca-Fe and Ca-Mn garnets determined by reversed, displaced equilibrium experiments. *American Mineralogist*, 75, 319–327.
- Koziol, A.M., and Bohlen, S.R. (1990) Almandine-pyroxene solution properties determined by displaced equilibrium experiments. *Eos*, 71, 660.
- Koziol, A.M., and Newton, R.C. (1988) Redetermination of the anorthite breakdown reaction and improvement of the plagioclase-garnet- Al_2SiO_5 -quartz geobarometer. *American Mineralogist*, 73, 216–233.
- (1989) Grossular activity-composition relationships in ternary garnets determined by reversed displaced-equilibrium experiments. *Contributions to Mineralogy and Petrology*, 103, 423–433.
- Newton, R.C. (1983) Geobarometry of high-grade metamorphic rocks. *American Journal of Science*, 283-A, 1–28.
- (1987) Thermodynamic analysis of phase equilibria in simple mineral systems. In I.S.E. Carmichael and H.P. Eugster, Eds., *Thermodynamic modeling of geological materials: Minerals, fluids and melts*. Mineralogical Society of America, Reviews in Mineralogy, 17, 1–33.
- Newton, R.C., and Haselton, H.T., Jr. (1981) Thermodynamics of the garnet-plagioclase- Al_2SiO_5 -quartz geobarometer. In R.C. Newton, A. Navrotsky, and B.J. Wood, Eds., *Thermodynamics of minerals and melts*, p. 129–145. Springer-Verlag, New York.
- Newton, R.C., and Perkins, D., III (1982) Thermodynamic calibration of geobarometers based on the assemblages garnet-plagioclase-orthopyroxene (clinopyroxene)-quartz. *American Mineralogist*, 67, 203–222.
- Newton, R.C., Charlu, T.V., and Kleppa, O.J. (1974) A calorimetric investigation of the stability of anhydrous cordierite with application to granulite facies metamorphism. *Contributions to Mineralogy and Petrology*, 44, 295–311.
- (1977) Thermochemistry of high pressure garnets and clinopyroxenes in the system $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$. *Geochimica Cosmochimica Acta*, 41, 369–377.
- (1980) Thermochemistry of the high structural state plagioclases. *Geochimica Cosmochimica Acta*, 44, 933–941.
- Orville, P.M. (1972) Plagioclase cation exchange equilibria with aqueous chloride solution: Results at 700 °C and 2000 bars in the presence of quartz. *American Journal of Science*, 272, 234–272.
- Pattison, D.R.M., and Newton, R.C. (1989) Reversed experimental calibration of the garnet-clinopyroxene Fe-Mg exchange thermometer. *Contributions to Mineralogy and Petrology*, 101, 87–103.
- Perkins, D., III (1983) The stability of Mg-rich garnet in the system $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$ at 1000–1300 °C and high pressure. *American Mineralogist*, 68, 355–364.
- Perkins, D., III, and Newton, R.C. (1981) Charnockite geobarometers based on coexisting garnet-pyroxene-plagioclase-quartz. *Nature*, 292, 144–146.
- Perkins, D., III, Holland, T.J.B., and Newton, R.C. (1981) The Al_2O_3 contents of enstatite in equilibrium with garnet in the system $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$ at 15–40 kbar and 900–1600 °C. *Contributions to Mineralogy and Petrology*, 78, 99–109.
- Powell, R., and Holland, T.J.B. (1988) An internally consistent dataset with uncertainties and correlations: 3. Applications to geobarometry, worked examples and a computer program. *Journal of Metamorphic Geology*, 6, 173–204.
- Prigogine, L., and Defay, R. (1954) *Chemical thermodynamics*, 543 p. Longmans, London.
- Robie, R.A., Hemingway, B.S., and Fisher, J.R. (1979) Thermodynamic properties of minerals and related substances at 298.15 K and 1 bar (10^5 Pascals) pressure and at higher temperatures. *U.S. Geological Survey Bulletin* 1452, 456 p.
- Rossini, R.D. (1956) Assignment of uncertainties to thermochemical data. In F.D. Rossini, Ed., *Experimental thermochemistry*, p. 297–320. Interscience, New York.
- Sack, R.O., and Ghiorso, M.S. (1989) Importance of considerations of mixing properties in establishing an internally consistent thermodynamic database: Thermochemistry of minerals in the system $\text{Mg}_2\text{SiO}_4\text{-Fe}_2\text{SiO}_4\text{-SiO}_2$. *Contributions to Mineralogy and Petrology*, 102, 41–68.
- Saxena, S.K., Sykes, J., and Eriksson, G. (1986) Phase equilibria in the pyroxene quadrilateral. *Journal of Petrology*, 27, 843–852.
- Sharma, K.C., Agrawal, K.C., and Kapoor, M.L. (1987) Determination of thermodynamic properties of (Fe,Mg)-pyroxenes at 1000 K by the EMF method. *Earth and Planetary Science Letters*, 85, 302–310.
- Wood, B.J. (1988) Activity measurements and excess entropy-volume relationships for pyroxene-grossular garnets. *Journal of Geology*, 96, 721–729.
- Wood, B.J., and Banno, S. (1972) Garnet-orthopyroxene and orthopyroxene-clinopyroxene relationships in simple and complex systems. *Contributions to Mineralogy and Petrology*, 42, 109–124.