

Redetermination of the anorthite breakdown reaction and improvement of the plagioclase-garnet- Al_2SiO_5 -quartz geobarometer

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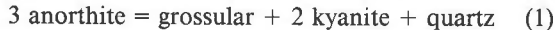
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ABSTRACT

The reaction $3 \text{ anorthite} = \text{grossular} + 2 \text{ kyanite} + \text{quartz}$ has been determined experimentally over the ranges $900\text{--}1250^\circ\text{C}$ and $19\text{--}28 \text{ kbar}$ in a piston-cylinder apparatus using a NaCl pressure medium. Two to four weight percent Li_2MoO_4 flux enabled reversal of the equilibrium 200°C lower than previously achieved. A point at 650°C , $13.5 \pm 0.6 \text{ kbar}$ was calculated from published studies of $4 \text{ zoisite} + \text{quartz} = 5 \text{ anorthite} + \text{grossular} + 2 \text{ H}_2\text{O}$ and $2 \text{ zoisite} + \text{kyanite} + \text{quartz} = 4 \text{ anorthite} + \text{H}_2\text{O}$, and the addition of this point constrains the equilibrium curve to $P \text{ (in kilobars)} = 22.80T \text{ (in }^\circ\text{C)} - 1093$. Use of this equation with the plagioclase-garnet- Al_2SiO_5 -quartz geobarometer results in reduction of the uncertainty of calculated pressures by a factor of two over previous calibrations. Calculated paleopressures are 400 bars higher for the assemblage with sillimanite than those given by Newton and Haselton (1981). Analysis of the data provides an estimate of the 1 bar, 298 K entropy of anorthite that is 3.3 J/K greater than the third-law entropy, implying 4% Al-Si disorder in anorthite.

INTRODUCTION

The reaction



forms the basis of an important geobarometer for metapelitic rocks. The assemblage garnet + plagioclase + (kyanite, andalusite, sillimanite) + quartz is common in medium- to high-grade metamorphic rocks over broad ranges of temperature and pressure. The principal sources of uncertainty in paleopressures calculated from this barometer are the P - T location of the end-member reaction (i.e., Reaction 1) and the activity-composition relationships of the garnet and plagioclase solid solutions.

Several experimental studies have been made of the end-member reaction, starting with Boyd and England (1961), who first identified the products of the breakdown of anorthite, and including Hays (1967), Hariya and Kennedy (1968), Schmid et al. (1978), Goldsmith (1980), and Gasparik (1984). Most of these experiments were conducted at pressures and temperatures well above crustal metamorphic conditions and required long extrapolation for geobarometry. Hodges and McKenna (1987) have pointed out that extrapolation of the equilibria, coupled with wide bracketing uncertainties and limited P - T ranges of experiments, contributes a large proportion of the uncertainty in any pressure estimate from this barometer. An additional complication is the uncertain pressure corrections in the different solid-media pressure devices used in the studies. These factors contribute to an uncertainty of at least 2 or perhaps 3 kbar in the P - T location of Reaction 1 in the temperature range $600\text{--}800^\circ\text{C}$. Large uncertainties have also been cited in various metamor-

phic studies (e.g., Lang and Rice, 1985; Hodges and Crowley, 1985).

We have undertaken a new experimental study of the anorthite breakdown reaction that reduces some of these uncertainties. Pressure cells of sodium chloride used in the piston-cylinder apparatus allowed greater accuracy in pressure determination. A nonaqueous molten flux, Li_2MoO_4 , was used to promote equilibration of the experimental charges, making it feasible to attain tightly bracketed reversals at lower temperatures. In addition, a bracket of the equilibrium curve at 650°C , $12.8\text{--}14.1 \text{ kbar}$, calculated from two zoisite-forming reactions precisely determined in gas-pressure apparatus at lower pressures, helps to constrain the curve in the P - T range of crustal metamorphism.

EXPERIMENTAL METHODS

All runs were performed in the piston-cylinder apparatus, using a $\frac{3}{4}$ in. (1.91 cm) diameter assembly with an NaCl pressure medium and WRe_3 - WRe_{25} thermocouples. Temperature uncertainties with these thermocouples are less than $\pm 5^\circ\text{C}$ (Perkins et al., 1981). The salt was partially molten in runs at 1250°C and $27.3\text{--}28 \text{ kbar}$ (Table 1) as inferred from large inward-growing quench crystals of salt next to the graphite furnace. The intersection of the melting curve of NaCl (Clark, 1959) with the anorthite breakdown curve just above 1275°C and 28 kbar limited the upper temperature range of this study.

The NaCl pressure medium with piston-out conditions requires very small pressure corrections (Johannes et al., 1971; Mirwald et al., 1975). However, a comparison of experimental reversals of the reaction $\text{anorthite} + \text{H}_2\text{O} = \text{zoisite} + \text{kyanite} + \text{quartz}$ in a gas-pressure vessel and with the $\frac{3}{4}$ in. (1.91 cm) NaCl piston-cylinder device by Jenkins et al. (1985) indicated that a 400-bar subtractive correction should be applied to piston-out

TABLE 1. List of experimental run conditions and results

Run	Treatment*	T (°C)	P (kbar)	Time (h)	Results
64	breathing	1250	28.0	9	gr growth; no zo
62	breathing	1250	27.3	20	strong an growth; no zo
50	breathing	1200	26.5	46	gr growth; trace zo
58	breathing	1200	26.0	46	an grew; no zo
45	2% Li_2MoO_4	1150	26.5	47	gr growth; zo present
47	<1% V_2O_5	1150	25.5	47	gr growth; zo present
44	2% Li_2MoO_4	1150	25.1	23	an grew
67	breathing	1150	25.0	43	an grew; no zo
21	2% Li_2MoO_4	1100	24.5	23	gr grew; tr. unknown
15	4% Li_2MoO_4	1100	24.0	22	no reaction; minor unkn.
19	4% Li_2MoO_4	1100	23.4	22	an grew; trace zo, unkn.
49	2% Li_2MoO_4	1050	23.4	66	gr grew; zo present
57	2% Li_2MoO_4	1050	23.0	116	an grew; zo present
72	4% Li_2MoO_4	1000	22.5	229	gr grew
39	4% Li_2MoO_4	1000	22.0	69	no reaction; minor zo, unkn.
75	4% Li_2MoO_4	1000	21.5	216	an grew
10	4% Li_2MoO_4	950	21.3	47	gr grew; minor zo, unkn.
60	2% Li_2MoO_4	950	21.0	264	no reaction; minor unkn.
30	4% Li_2MoO_4	950	20.5	137	no reaction; minor zo, unkn.
66	4% Li_2MoO_4	950	20.5	261	an grew, minor zo, unkn.
74	4% Li_2MoO_4	900	20.5	286	gr grew
70	4% Li_2MoO_4	900	19.0	238	an grew

Note: Pressures listed are uncorrected gauge pressures ($\sigma = \pm 0.5$ kbar). zo: zoisite. unkn.: unknown phase (see text).

* "Breathing" signifies breath-moistened charges. Values under "treatment" are in weight percent.

runs at temperatures near 600 °C and pressures near 10 kbar. The correction is certain to be smaller at the higher temperatures of our study, which approach the melting point of NaCl. The approach used here is to subtract 200 bars from the experimental gauge pressure and to add ± 200 bars to the pressure uncertainty. Total uncertainties in run pressure from friction correction and gauge drift is ± 540 bars.

Starting materials were a natural kyanite from Litchfield, Connecticut (FeO content = 0.16 wt%), a natural quartz from Lisbon, Maryland, and synthetic anorthite and grossular. Anorthite was made from an ultrapure oxide mixture by sintering at 1300 °C and 1 bar for 2 d, and then treated at 1000 °C and 16 kbar in a graphite capsule to standardize the material. Table 2 lists unit-cell parameters. Grossular ($a = 11.850 \pm 0.002$ Å) was synthesized from stoichiometric glass at 1200 °C and 26 kbar. Reversal mixes having nearly equal amounts of reactant and product phases were homogenized thoroughly under acetone in an agate mortar with small amounts of flux (see below), dried at 450 °C, and sealed in welded Pt capsules.

To reverse a reaction in reasonable laboratory times in the $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ system below 1200 °C, an intergranular fluid flux must be used in experimental runs. Water, an oxybate, and PbO have been used in the past (Goldsmith, 1980; Gasparik, 1984). However, water or oxybate produces excessive amounts of zoisite, which may obscure the anhydrous reaction (Reaction 1), and incorporation of Pb into the feldspar structure may bias the reaction.

Therefore, two molten oxide fluxes, Li_2MoO_4 (Ito, 1975) and V_2O_5 , were tested in this system. As little as 1 wt% V_2O_5 caused excessively large amounts of melting, with elimination of some of the reactants in some runs. This flux was discarded because of difficulty in controlling the amount of melting. Two to four weight percent of Li_2MoO_4 added to the reversal mix yielded better results. Runs without flux were successful at 1200 °C and 1250 °C (Table 1). At the temperature and pressure of most of the experiments, the Li_2MoO_4 dissolved some of the charge to

form about 20% of intergranular melt (Fig. 1). Extra kyanite and quartz were added to the reversal mixes to ensure that all four phases were present during the runs.

Reaction direction was determined by large (>30%) changes in the ratios of the strengths of anorthite and grossular X-ray diffraction peaks of quenched charges compared to the starting material. Starting mixes were X-rayed 5 to 6 times to character-

TABLE 2. Synthetic anorthite unit-cell data

	Anorthite sintered at 1300 °C, 1 bar	Anorthite (AK14)	Typical run product (no. 34)
A. Refined cell parameters			
a (Å)	8.180 \pm 0.003	8.179 \pm 0.013*	8.185 \pm 0.009
b (Å)	12.857 \pm 0.004	12.873 \pm 0.008*	12.866 \pm 0.006
c (Å)	14.175 \pm 0.006	14.168 \pm 0.026*	14.169 \pm 0.017
α (°)	93.333 \pm 0.026	93.047 \pm 0.082*	93.152 \pm 0.078
β (°)	115.781 \pm 0.023	115.895 \pm 0.106*	115.942 \pm 0.073
γ (°)	91.101 \pm 0.022	91.256 \pm 0.073*	91.145 \pm 0.059
V (Å ³)	1338.38 \pm 0.94	1338.31 \pm 5.14*	1338.13 \pm 3.43
B. X-ray diffraction data (hkl, d spacings, Δd) compared to anorthite sintered at 1300 °C, 1 bar			
202	4.0393	+0.0009**	-0.0055
130	3.7773	+0.0028**	+0.0049
130	3.6189	+0.0025**	-0.0014
114	3.3510	-0.0112**	—
220	3.2610	+0.0012**	+0.0012
220	3.1242	+0.0019**	+0.0011
132	3.0425	+0.0002**	+0.0035
042	2.9496	+0.0018**	—
132	2.8262	-0.0002**	-0.0015
134	2.6542	-0.0069**	—
242	2.5014	0.0**	-0.0011
060	2.1397	-0.0003**	+0.0003
208	1.7689	+0.0008**	+0.0005

* AK14 treated at 1000 °C, 16 kbar.

** Starting AK14.



Fig. 1. Backscattered-electron image (scale bar: 10 μm) of a quenched run product. Lightest-gray grains are grossular, medium-gray needlelike crystals are anorthite, darkest grains are kyanite or quartz. Medium-gray interstitial area is a mixture of aluminosilicate melt and tiny anorthite crystals. Small bright spots are bits of Li_2MoO_4 . Photo courtesy of John Laughlin.

ize variations in the peak intensities. The strong reflections of anorthite at $d = 3.18$ were compared to the (400) and (420) peaks of grossular, and the ($\bar{2}02$) and ($\bar{2}20$) peaks of anorthite were compared to the (422) and (431) peaks of grossular. Kyanite peak heights were not used because, as noted by Goldsmith (1980), natural kyanite shows strong preferred orientation that is diminished when it recrystallizes during the run.

Two extraneous phases were noted in some of the run products. Minor amounts of zoisite were present in some charges, as noted in Table 1, even though the capsules, reversal mixes, and salt assemblies were thoroughly dried previous to the run. Water may have been tenaciously adsorbed on the reversal mix, or H_2 generated from H_2O decomposition in the salt medium may have diffused through the Pt capsules (Goldsmith, 1986) during the run. In addition, an unknown phase was detected by a few very weak peaks in diffractograms of nearly all run products with 4 wt% Li_2MoO_4 and in a few of the runs with 2 wt% Li_2MoO_4 (noted as "unknown" in Table 1). This phase could not be detected optically with transmitted light, but polished charges under reflected light showed tiny acicular crystals in the intergranular melt patches, which could account for the unknown diffraction peaks. The unknown phase has d values of 3.420, 3.105, and 2.918, as determined by an X-ray diffraction pattern of a run with 8 wt% Li_2MoO_4 . That the unknown phase is not a polymorph or breakdown product of Li_2MoO_4 was determined by the X-ray pattern of a quenched charge of Li_2MoO_4 run at 1100 $^\circ\text{C}$ and 23 kbar. The diffractogram of this charge only had d values corresponding to Li_2MoO_4 . The unknown phase is probably a quench product of the aluminosilicate intergranular melt.

RESULTS OF EXPERIMENTS AND CALCULATIONS

Electron-beam microanalysis of the quenched charges confirmed that grossular, anorthite, kyanite, and quartz were all present during the runs. No Mo was detected in grossular or anorthite. Slow X-ray diffraction scans of several principal peaks of anorthite in quenched charges

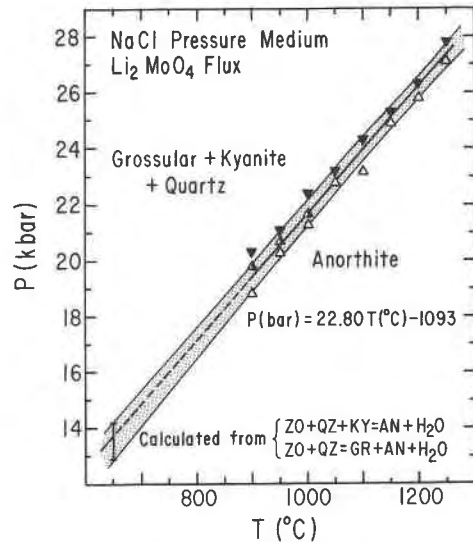


Fig. 2. Experimental data (corrected downward 200 bars in pressure) for the reaction 3 anorthite = grossular + 2 kyanite + quartz. Open symbols indicate that products grew, closed symbols that reactants grew. Half-filled symbols indicate no reaction. The curve plotted is a least-squares fit to the midpoints of the brackets. The bracket at 650 $^\circ\text{C}$, 12.8–14.14 kbar is calculated from two zoisite reactions (see text). The shaded area indicates the size of the uncertainty envelope as defined by the confidence limits of each reversal of Reaction 1 (see text). The area at $T < 900$ $^\circ\text{C}$ is extrapolated from the experimental data.

showed insignificant differences from the starting material anorthite (Table 2), indicating that Li did not enter the anorthite structure. Thus, the presence of Li_2MoO_4 should not have biased the P - T position of the reaction. This was confirmed by the consistency of the results of fluxed and unfluxed runs.

The eight reversal brackets (listed in Table 1) at 900–1250 $^\circ\text{C}$ and 19–28 kbar cover a wider P - T range and extend to lower temperatures and pressures than previous studies. The experimental points are plotted in Figure 2. Also plotted is a calculated bracket of the equilibrium curve at 650 $^\circ\text{C}$, discussed below. The straight line plotted is a least-squares fit to the midpoints of the experimental brackets and the bracket at 650 $^\circ\text{C}$. The univariant curve can be described by the equation P (in kilobars) = $22.80T$ (in $^\circ\text{C}$) - 1093.

The bracket at 650 $^\circ\text{C}$, 12.8–14.14 kbar was calculated thermodynamically on the basis of two zoisite-forming reactions:



The P - T conditions of these reactions, plotted in Figure 3, are well-constrained by several experimental studies, as cited in the caption. Each bracket, isobaric in the case of gas-apparatus runs and isothermal in the case of piston-cylinder runs, is shown by a cross, where the long arm represents the confidence interval calculated by the method of Demarest and Haselton (1981) and the short arm

the P or T uncertainty stated by the respective authors. The uncertainty envelope shown is a subjective estimate of what turns out to be an inconsistent data set. The calculated pressure of Reaction 1 at a given temperature depends only on the pressures of Reactions 2 and 3, the fugacity of H_2O in the pressure range between Reactions 2 and 3, and the volumes of the solids, all of which are well known. Details of the calculation are given in Appendix A. The uncertainties in the positions of the two zoisite reactions, which are smallest at 650°C , are the main sources of uncertainty in the calculated position of the anorthite-breakdown reaction at this temperature. The resulting bracket of maximum width (1.3 kbar at 650°C) takes account of uncertainties in all of the input quantities.

ERROR ANALYSIS

There has been much discussion of two problems of phase-equilibrium studies: first, of defining a "best" reaction curve (Chayes, 1968), and second, of determining the confidence limits of such a curve (Bird and Anderson, 1973; Zen, 1977; Demarest and Haselton, 1981; Hodges and McKenna, 1987). The position and limits directly affect the calculation and error estimation of derived thermodynamic data (Zen, 1977). Moreover, since many experimental studies are performed well above average metamorphic P - T conditions, extrapolation of equilibrium curves generates large uncertainties (Essene, 1982).

The importance of the anorthite breakdown curve, however, demands that a reasonable attempt be made at judging the slope and error. Demarest and Haselton (1981) have suggested that least-squares analysis is reasonable for phase-equilibrium brackets where the standard deviation of each point of a bracket is greater than the half-width of the bracket. They presented a statistically rigorous method for assigning errors to brackets where the standard deviation of each point in the pair is equal. Since the present tightly bracketed reversals meet their qualifications, we follow their method in this paper. We assume that the error in temperature is negligible and that the standard deviation in pressure measurement, including the 200-bar uncertainty of our pressure correction, is 540 bars. Taking the midpoint of the bracket as the putative position of the equilibrium curve, the standard deviation and confidence limit of each bracket are calculated from Equations 6a and 6c and Figure 4 of Demarest and Haselton (1981). The confidence limits are used to define an uncertainty envelope for the equilibrium curve (Fig. 1). This method is not as rigorous as that of Hodges and McKenna (1987), but results in a reasonable, if intuitive confidence interval. Lang and Rice (1985) have done an independent derivation of the P - T equation for Reaction 1 from the experimental studies of Hays (1967), Hariya and Kennedy (1968), and Goldsmith (1980) using linear programming. Their equation derived from ΔH^0 and ΔS^0 for Reaction 1 with kyanite is P (in bars) = $22.77 T$ (in kelvins) - 7111.9, with an uncertainty of ± 3 kbar at metamorphic P - T ranges. In our analysis, the slope can vary between the values 21.80 and 24.96 within the con-

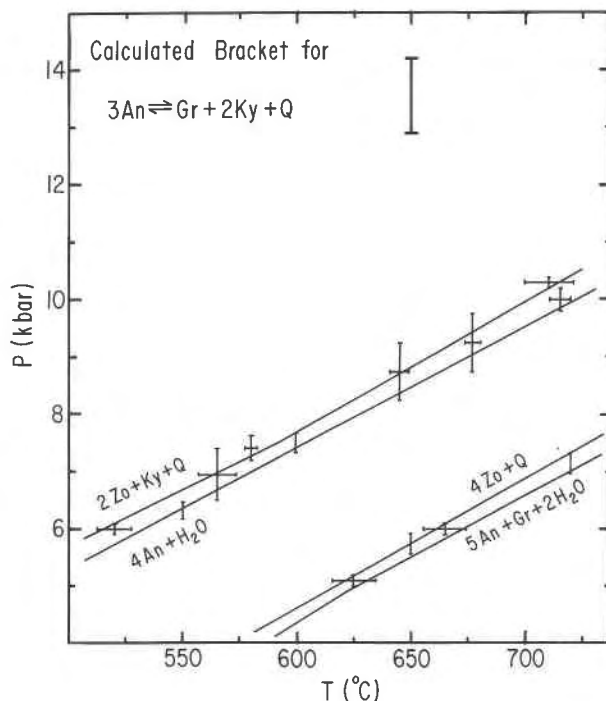


Fig. 3. Experimental data for the reactions $4\text{An} + \text{H}_2\text{O} = 2\text{Zo} + \text{Ky} + \text{Qz}$ (Chatterjee et al., 1984; Goldsmith 1981; Jenkins et al., 1985) and $5\text{An} + \text{Gr} + \text{H}_2\text{O} = 4\text{Zo} + \text{Qz}$ (Newton, 1966; Chatterjee et al., 1984) and a calculated bracket at 650°C for the reaction $3\text{An} = \text{Gr} + 2\text{Ky} + \text{Qz}$. Uncertainty envelopes for the two zoisite-forming reactions are also plotted. They were fit by eye to the confidence interval for each experimental reversal bracket (shown by crosses) as determined by the method of Demarest and Haselton (1981).

straints of the confidence interval. This is an important consideration for the precision of the geobarometer based on Reaction 1 and for calculation of the entropy of anorthite, discussed below.

APPLICATION TO GEOBAROMETRY

The present determination of the reaction of anorthite to grossular, kyanite, and quartz reduces the uncertainty in calibration of an important geobarometer for medium- to high-grade metamorphic rocks. Previous calibrations (Ghent, 1976; Ghent et al., 1979; Newton and Haselton, 1981; Ganguly and Saxena, 1984) made use of earlier determinations of the end-member reaction, a collection of which is shown in Figure 4. The most precise of these are the determinations of Goldsmith (1980) and Gasparik (1984). However, the study of Goldsmith (1980) included only two wide brackets determined with the NaCl pressure medium, and Gasparik's (1984) study used a glass-talc pressure medium and relied on experimentally fixed points of other equilibria, such as the albite-jadeite-quartz reaction (Holland, 1980) and the spinel peridotite-garnet peridotite boundary (Gasparik and Newton, 1984) for calibration. Gasparik (1984) also used a PbO flux which,

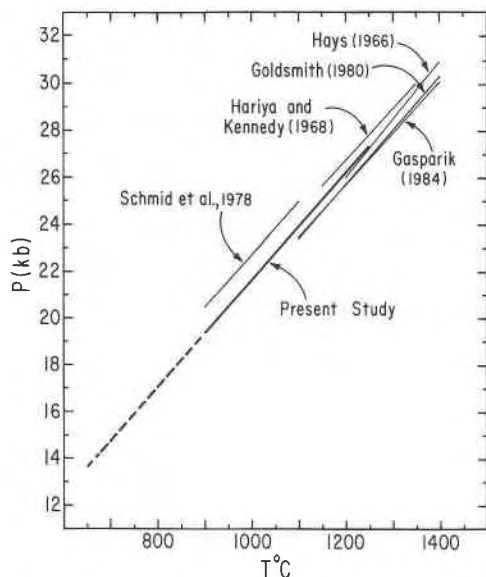


Fig. 4. Comparison of various experimental studies on the reaction $3\text{An} = \text{Gr} + \text{Ky} + \text{Qz}$. Length of line shows range of experiments. Dotted line shows the extension of the present study's results to a calculated bracket at 650 °C, 12.8–14.14 kbar.

in our experience, enters into solid solution with the feldspar.

For any temperature, Newton and Haselton (1981) have written the equation for the barometer as

$$-P^0\Delta V_1^0 + RT \ln(\alpha_{\text{gro}}/\alpha_{\text{an}})^3 + P\Delta\bar{V}_1 \approx 0, \quad (4)$$

where P^0 and ΔV_1^0 are the pressure and volume change, respectively, of the end-member reaction (1), α denotes the activity of grossular in garnet and anorthite in plagioclase, P is the estimated pressure of the assemblage, and $\Delta\bar{V}_1$ is the partial molal volume change at 1 bar. The approximation sign is used because of neglect of the effect of thermal expansion and compressibility on ΔV_1^0 and $\Delta\bar{V}_1$. Because considerable extrapolation from the experimental P - T ranges to metamorphic conditions of the equilibrium adds uncertainty to the P^0 term, the precision of the geobarometer calibration depends greatly on the P - T control of the experiments and the tightness of the experimental bracketing runs. A remaining source of error is the uncertainty inherent in the formulations of the gar-

net and plagioclase activities. Since the geobarometer has a considerable temperature dependence, accurate paleopressure determination depends on accurate knowledge of paleotemperatures through independent geothermometers.

Our experimental curve, determined with kyanite as the Al_2SiO_5 polymorph, was combined with the experimental expression of Holdaway (1971) for the kyanite = sillimanite reaction (see App. B for details), to obtain an expression with sillimanite as the polymorph. Our equations are (in °C, bars)

$$P_{1,\text{ky}} = 22.80T - 1093 \quad (5a)$$

$$P_{1,\text{sill}} = -0.0001872T^2 + 23.41T - 25. \quad (5b)$$

Equations 5a and 5b give pressures somewhat greater than the Newton and Haselton (1981) formulas, based upon the experimental work of Goldsmith (1980) (in °C, bars):

$$P_{1,\text{ky}} = 23.20T - 2100 \quad (6a)$$

$$P_{1,\text{sill}} = 23.60T - 600. \quad (6b)$$

The second formula is also based on the Holdaway (1971) kyanite-sillimanite curve and is in error by about +300 bars, as shown by E. Froese (cited in Ganguly and Saxena, 1984). The present formulas (Eqs. 5a and 5b) give pressures greater than the Newton and Haselton (1981) formulas by about 750 bars at 600 °C for the anorthite breakdown with kyanite and by about 400 bars for the reaction with sillimanite. Paleopressures calculated with the new formulas and using the same assumptions about grossular and anorthite activities as did Newton and Haselton (1981) will be higher by about these amounts. For example, Ghent (1976) estimated paleopressures at Esplanade Range, B.C., of about 8.6–9.0 kbar, whereas Newton and Haselton (1981) calculated 7.8–8.4 kbar and this study suggests 8.6–9.2 kbar.

Uncertainties in the paleopressures due to uncertainties in the location of the end-member curve are much reduced as a consequence of the new work, being ± 650 bars at 600 °C and ± 400 bars at 1000 °C. Further refinement of the geobarometer awaits clarification of the thermodynamic properties of the solid solutions.

ENTROPY OF ANORTHITE

Numerous authors have considered that the third-law entropy of anorthite should be supplemented with a con-

TABLE 3. Thermodynamic data used in entropy calculation

Phase	S^0	$a \times 10^{+2}$	$b \times 10^{-2}$	$c \times 10^{-6}$	$d \times 10^{+3}$	$e \times 10^{-5}$	V	$\alpha \times 10^5$	$\beta \times 10^7$
Anorthite (synthetic)	199.30	5.1683	-9.2492	-1.4085	-4.5885	4.1883	10.079	1.42	12.9
Grossular (natural)	255.50	16.333	-75.99	9.113	-20.873	26.690	12.530	2.39	6.3
Grossular (synthetic)	260.12	5.1633	3.2184	-9.9419	-1.4031		12.530	2.39	6.3
Kyanite	82.30	3.039	-1.339	-0.8952	-2.9043		4.415	2.54	4.3
Quartz	41.46	1.044	0.607	0.034	-1.070		2.269	5.91	22.9

Note: Third-law entropies (J/mol·K), heat-capacity coefficients (J/mol·K), volumes at 298 K and 1 bar (J/bar), thermal-expansion coefficients (deg⁻¹), and compressibilities (bar⁻¹).

$$C_p = a + bT + c/T^2 + d(T^{1/2}) + eT^2.$$

References: Anorthite—Robie et al. (1978), Krupka et al. (1979). Synthetic grossular—Haselton (1979). Natural grossular—Westrum et al. (1979), Krupka et al. (1979). Kyanite—Robie and Hemingway (1984). Quartz—Holland and Powell (1985). Volume parameters from Holland and Powell (1985).

figurational entropy, most plausibly of a small amount of tetrahedral Al-Si disorder. This would give an optimal fit to many experimental phase equilibria, including the anorthite breakdown reaction. X-ray diffraction studies of some natural high-temperature anorthite also indicate the existence of such disorder (Smith, 1974, p. 139). However, some recent thermodynamic summaries of many experimental equilibria involving anorthite suggest little (Wood and Holloway, 1984; Holland and Powell, 1985) or no (Halbach and Chatterjee, 1984; Robie et al., 1978) configurational entropy.

The present work allows an improved calculation of the thermodynamic properties of anorthite because high-quality measured heat-capacity data (Table 3) exist for all the participating phases. A fundamental ambiguity arises in the two conflicting heat-capacity and entropy data sets for grossular. Measurements on a natural, nearly pure end-member grossular (Westrum et al., 1979; Krupka et al., 1979) gave heat capacities and standard entropy values significantly smaller than measurements on a pure synthetic grossular sample (Haselton and Westrum, 1980). Estimates of a possible non-third-law entropy of anorthite based on Reaction 1 depend on which grossular data set is accepted. In spite of the uncertainties of the semi-empirical correction of the heat-capacity data for impurities (principally FeO and H_2O) in the natural grossular, several authors (e.g., Haas et al., 1981; Berman et al., 1985) have preferred this data set. Others (e.g., Halbach and Chatterjee, 1984; Wood and Holloway, 1984; Holland and Powell, 1985) have preferred the measurements on synthetic grossular.

The entropy of anorthite at 1000 K can be computed from the measured dP/dT slope of the anorthite breakdown reaction by the Clapeyron equation, $dP/dT = \Delta S/\Delta V$. A slope of 22.80 is our best experimental fit, but the slope can vary between 21.80 and 24.96, which adds a measure of uncertainty to the calculation. Details of the calculation, including error analysis, are in Appendix C. Our procedure is to compare the entropy of the reaction at 1000 K, 15.5 kbar as determined by the experimental data with the value calculated from the data in Table 3. Any discrepancy we assume to be due to configurational entropy in anorthite. If the data set for synthetic grossular is used, the configurational entropy of anorthite comes out to be, on average, 3.3 J/K (range: 1.3 to 7.7 J/K) at 1000 K. This is equivalent to 4% (range: 1.4 to 12.4%) tetrahedral Al-Si disorder. If, however, the C_p data for natural grossular are used, the amount of anorthite configurational entropy necessary to model the dP/dT slope of Reaction 1 is 0.07 J/K (range: -2.1 to 4.3 J/K), essentially zero.

The present experimental data cannot, of course, discriminate between these disparate results. Our preference is for the C_p data of the synthetic grossular and, therefore, the existence of some configurational entropy of anorthite. This is largely based on the fact that the Haselton and Westrum (1980) C_p data are more straightforward than the measurements on natural grossular, which re-

quire substantial corrections of unknown reliability for nonternary components. As a possible illustration of this, another set of measurements is available (Kolesnik et al., 1979) on a natural grossular with total impurities about a factor of two less than those in the grossular used by Westrum et al. (1979). The third-law entropy of this grossular is much closer to that of the Haselton and Westrum (1980) synthetic grossular, which may indicate that the effects of impurities are greater than allowed for by the correction procedures of Westrum et al. (1979).

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APPENDIX A

Note that two times Reaction 2 minus Reaction 3 will result in Reaction 1. Referring to Figure 3, at 650 °C, 5.55–5.75 kbar (P_3), $\Delta G_3 = 0$, but at 650 °C, 8.5–8.9 kbar (P_2), $\Delta G_2 = 0$ and $\Delta G_3 < 0$. The latter free-energy change can be expressed by

$$\Delta G_3 = +2RT \ln(f_2/f_3) + \Delta V_3(P_2 - P_3), \quad (\text{A1})$$

where f is the fugacity of water at the equilibrium pressures of Reaction 2 and Reaction 3, respectively. ΔV_3 is a characteristic volume change of the solids of Reaction 3 at 650 °C and can be closely approximated by the mean volume change over the pressure interval P_3 to P_2 . We used fugacity data from Burnham et al. (1969) and volume data (including α and β) from Holland and Powell (1985). The free-energy change is -27.85 kJ to -33.86 kJ.

The free-energy change of Reaction 1 at 650 °C and P_2 may be expressed as

$$-\Delta G_1 = \Delta G_3 - 2\Delta G_2 = \Delta G_3 - 0 = \int_{P_2}^{P_1} \Delta V_1 dP, \quad (\text{A2})$$

where ΔV_1 is the volume change of Reaction 1. From Equation A2, P_1 (the equilibrium pressure of the anorthite-breakdown reaction) may be obtained by iteration. Given the errors in the two lower curves, P_1 is between 12.8 and 14.14 kbar.

APPENDIX B

The standard free-energy change of Reaction 1 at a given temperature is obtained by multiplying a charac-

teristic volume change by the equilibrium pressure at this temperature. A volume change appropriate for the temperature range 600–1000 °C is that at 800 °C and 10 kbar; the equilibrium pressure times this ΔV differs negligibly from the integral of ΔV with respect to pressures from 1 bar to the equilibrium pressure over this temperature range. The thermal-expansion and compressibility data for the minerals of Reaction 1 compiled by Holland and Powell (1985) give $\Delta V = -6.210$ J/bar for the reaction with kyanite and -5.154 J/bar for the reaction with sillimanite. From the former value (in J, °C),

$$\Delta G_{1,\text{ky}}^0 = 141.59T - 6788. \quad (\text{B1})$$

The standard free-energy change of the anorthite-breakdown reaction with sillimanite is given by

$$\Delta G_{1,\text{sill}}^0 = \Delta G_{1,\text{ky}}^0 + 2\Delta G_{\text{ky}=\text{sill}}^0. \quad (\text{B2})$$

Using the experimental expression for the kyanite to sillimanite reaction of Holdaway (1971):

$$P_{\text{ky}=\text{sill}} = 20(T - 315) + 0.0009(T - 315)^2, \quad (\text{B3})$$

and a characteristic volume change of 0.536 J/bar at 800 °C and 5 kbar (Holland and Powell, 1985),

$$\Delta G_{\text{ky}=\text{sill}}^0 = -0.0004824T^2 - 10.414T + 3329, \quad (\text{B4})$$

from which

$$\Delta G_{1,\text{sill}}^0 = -0.0009648T^2 + 120.67T - 130. \quad (\text{B5})$$

The equilibrium pressure of Reaction 1 with sillimanite is then (in bars)

$$P_{1,\text{sill}} = \Delta G_{1,\text{sill}}^0 / -\Delta V_{1,\text{sill}}^0 = -0.0001872T^2 + 23.41T - 25. \quad (\text{B6})$$

APPENDIX C

For the reaction 3 anorthite = grossular + 2 kyanite + quartz, at 1000 K and 15.5 kbar, the volume change is -6.105 J/bar. Our experimental data indicate a dP/dT slope of 22.80 (range: 21.8–24.96). The change in entropy of this reaction (ΔS) is

$$\Delta S_{1,T} = \Delta S_{T,P} + \int_1^{15500} \Delta(\alpha V) dP, \quad (\text{C1})$$

where α is the thermal expansion, and this integral is approximated as $\alpha V(15500)$. The pressure correction is 3.545 J/K, so then $\Delta S_{1,T} = -135.65$. The data set listed in Table 3 is used to calculate ΔS at 1000 K, 1 bar by the equation

$$\Delta S_{1,T} = \Delta S_{298}^0 + \int_{298}^T \Delta C_p/T dT. \quad (\text{C2})$$

This value is -126.73 using the S^0 and C_p data for synthetic grossular and -135.87 for natural grossular. We assume that the discrepancy between the experimentally derived value and the thermodynamically derived value is non-third-law entropy in anorthite. Then the anorthite configurational entropy is 3.31 J/K (range: 1.3–7.7 J/K) using the synthetic grossular data set and 0.07 J/K (range: -2.1 – 4.3 J/K) using the natural grossular data set.