

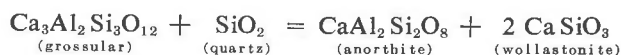
The effect of reduced activity of anorthite on the reaction grossular + quartz = anorthite + wollastonite: a model for plagioclase in the earth's lower crust and upper mantle

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Abstract

The reaction



was investigated at 1100°C, using intermediate-composition plagioclase to determine the shift of the equilibrium pressure as a function of composition at pressure and temperature conditions representative of the earth's lower crust and upper mantle. For compositions within the range An_{80–100}, activity of the anorthite component is equal to its mole fraction. For compositions more albitic than about An₇₀, the activity of the anorthite component equals its mole fraction multiplied by a constant factor of 1.2. This latter behavior is interpreted as a result of anorthite-like domains being in an energetically unfavorable environment for these compositions.

Application of the data obtained from subsolidus experiments to melting behavior indicates that plagioclase liquids do not obey Raoult's Law, but have an activity coefficient similar to crystalline plagioclase. This hypothesis is supported by high-pressure melting experiments for both anhydrous and hydrous systems.

In parts of the lower crust composed of basic rock (*e.g.* gabbro), the calcic plagioclase will be consumed at relatively shallow levels and over a narrow (2–3 km) depth interval. On the other hand, plagioclase in regions consisting of intermediate (*e.g.* andesitic) compositions will persist to greater depths, and the reactions will occur over relatively wide depth intervals. This contention is supported by the nonuniformity of some seismic discontinuities in the lower crust.

Introduction

Plagioclase comprises the largest volume of any mineral group in the crust of the earth (Ronov and Yaroshevsky, 1969) and occurs as a primary phase in a wide variety of igneous and metamorphic rocks. Among these are the granulites, amphibolites, andesites, anorthosites, and gabbros, all of which are possible candidates for the lower crust. However, plagioclase is unstable at high pressures, reacting with other minerals to form a higher-density aluminous phase (garnet, spinel, kyanite, *etc.*) plus other phases such as quartz and clinopyroxene (*e.g.*, Kushiro and Yoder, 1966; Green and Hibberson, 1970; Akella and Kennedy, 1971; Boettcher, 1970, 1971). Thus, if we

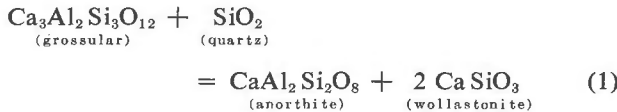
are ever to fully understand the nature of the lower crust and upper mantle, we must determine the behavior of plagioclase at pressure and temperature conditions representative of this region.

Numerous reactions involving the end-members albite (NaAlSi₃O₈) and anorthite (CaAl₂Si₂O₈) have been investigated (*e.g.*, Newton, 1966; Kushiro and Yoder, 1966; Newton and Smith, 1967; Hays, 1967; Hariya and Kennedy, 1968; Boettcher and Wyllie, 1968; Boettcher, 1970; Akella and Kennedy, 1971). In addition, selected intermediate compositions have been studied (*e.g.*, Green and Hibberson, 1970). Various models for activity-composition relations of plagioclase at pressures and temperatures corresponding to the upper crust have also been proposed (Orville, 1972; Saxena and Ribbe, 1972; Kerrick and Darken, 1975). However, there exists no comprehen-

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sive study for a wide range of plagioclase compositions at pressures and temperatures representative of the lower crust and upper mantle.

The purpose of the present study is to provide experimental data that will permit us to formulate a model that can be used to predict the behavior of plagioclase in both synthetic and natural assemblages at high pressures and temperatures. To obtain this information, the reaction



was investigated using intermediate plagioclase compositions. This reaction was chosen primarily because no solid-solutions other than plagioclase occur with the addition of Na₂O component, thus permitting the isolation of plagioclase behavior.

Abbreviations and symbols used in text

- P* = pressure
T = temperature (Kelvin unless otherwise stated)
V = volume
S = entropy
G = Gibbs' free energy
R = gas constant
a = activity
X = mole fraction

subscript *r* = quantity for a reaction
 superscript 0 = standard state conditions

- Δ = change in a parameter
 γ = activity coefficient
 α = a phase
i = component in a phase

- Qz = quartz
 Gr = grossular
 Wo = wollastonite
 An = anorthite
 Ab = albite
 Pl = plagioclase
 Alm = almandine
 Fs = ferrosilite

Experimental approach

The quantitative determination of the effect of independently changing any of the parameters of state, *P*, *T*, or *X*, on ΔG_r for any reaction in a multi-component system is given by

$$\begin{aligned} d\Delta G_r = & \left(\frac{\partial \Delta G_r}{\partial P} \right)_{T, X_i} dP + \left(\frac{\partial \Delta G_r}{\partial T} \right)_{P, X_i} dT \\ & + \sum \left(\frac{\partial \Delta G_r}{\partial X_i} \right)_{P, T, X_j, \dots} dX_i \quad (2). \end{aligned}$$

Since

$$\begin{aligned} \left(\frac{\partial \Delta G_r}{\partial P} \right)_{T, X_i} &= \Delta V_r; & \left(\frac{\partial \Delta G_r}{\partial T} \right)_{P, X_i} &= -\Delta S_r; \\ \left(\frac{\partial \Delta G_r}{\partial X_i} \right)_{P, T, X_j, \dots} &= RT \left(\frac{\partial \ln a_i}{\partial X_i} \right)_{P, T, X_j, \dots} dX_i \end{aligned}$$

then,

$$\begin{aligned} d\Delta G_r = & \Delta V_r dP - \Delta S_r dT \\ & + \sum RT \left(\frac{\partial \ln a_i}{\partial X_i} \right)_{P, T, X_j, \dots} dX_i^2 \quad (3). \end{aligned}$$

For conditions of constant *T* and unit activities of all components (*i.e.*, pure solid phases),

$$d\Delta G_r = \Delta V_r dT \quad (4).$$

Therefore, assuming ΔV_r constant between *P*⁰ and *P*,

$$(\Delta G_r)_{P, T^0, X_i^0} = (\Delta G_r^0)_{P^0, T^0, X_i^0} + \Delta V_r(P - P^0) \quad (5).$$

For conditions of constant *T* and unit activities of all components except *i*,

$$d\Delta G_r = \Delta V_r dP + RT \left(\frac{\partial \ln a_i}{\partial X_i} \right)_{P, T, X_j, \dots} dX_i \quad (6)$$

Therefore,

$$\begin{aligned} (\Delta G_r)_{P, T^0, X_i} &= (\Delta G_r^0)_{P^0, T^0, X_i^0} \\ &+ \Delta V_r(P - P^0) + RT \ln(a_i/a_i^0) \quad (7) \end{aligned}$$

where *a_i* = activity of component *i* at *X_i* and *a_i*⁰ = activity of component *i* at *X_i*⁰ = 1.

The present study is designed to determine the change in equilibrium pressure caused by a change in the plagioclase composition. Therefore,

$$(\Delta G_r)_{P, T^0, X_i} = 0$$

and

$$(\Delta G_r^0)_{P^0, T^0, X_i^0} = 0.$$

Consequently, equation (7) reduces to

$$(P - P^0) = \left(\frac{-RT \ln a_{\text{An}}^{\text{Pl}}}{\Delta V_r} \right) \quad (8).$$

² Equation 3 is a general form for the treatment of any equilibria as a function of *P*, *T*, or *X*. It is implicitly assumed that, where data are available, ΔV_r and ΔS_r include appropriate mixing terms.

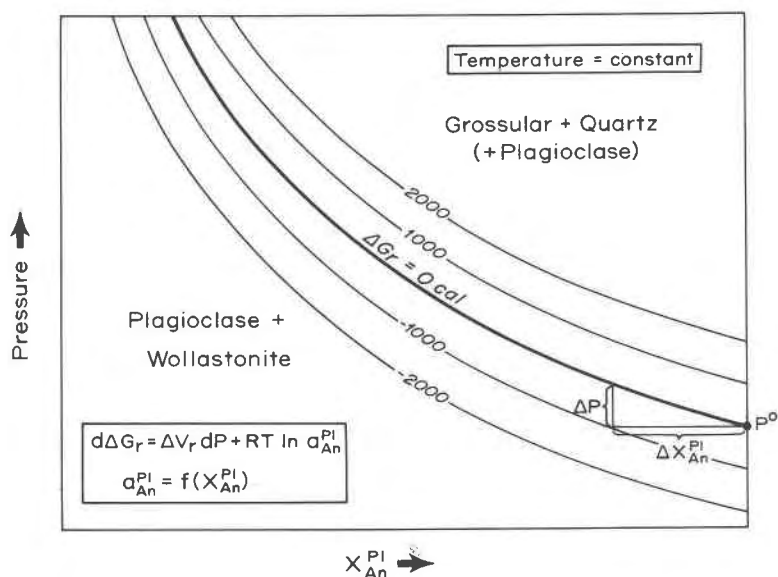


FIG. 1. Schematic pressure-composition diagram illustrating the effect of changes in plagioclase composition on the equilibrium pressure for reaction (1).

Activity-composition relations for solutions are given by the equation

$$a_i^\alpha = X_i^\alpha \gamma_i^\alpha \quad (9)$$

For solutions that obey Raoult's law, $\gamma = 1$. Solutions in which $\gamma > 1$ are said to have a positive deviation from Raoult's law and show a tendency toward unmixing, whereas those in which $\gamma < 1$ have a negative deviation and tend to form stoichiometric intermediate compounds.

Substitution of equation 9 into equation 8 yields

$$(P - P^0) = \frac{-RT \ln (X_{An}^{Pl} \gamma_{An}^{Pl})}{\Delta V_r} \quad (10)$$

It is now possible to determine γ_{An}^{Pl} , and thus a_{An}^{Pl} , by experimentally determining P^0 (equilibrium pressure for An_{100} composition) and the value of P for different plagioclase compositions under isothermal conditions.

The arguments presented above are schematically illustrated in Figure 1. Contours of ΔG_r are shown with the contour labeled $\Delta G_r = 0$ representing the equilibrium curve. An assemblage containing grossular, quartz, wollastonite, and An_{100} is in equilibrium only at pressure P^0 for the temperature represented here. A shift in the plagioclase composition causes a reduction in the activity of the anorthite component and results in disequilibrium of the assemblage. For example, a compositional change corresponding to ΔX_{An}^{Pl} of Figure 1 results in the assemblage being

out of equilibrium by an absolute amount of 1000 calories. Thus, a change of pressure (ΔP) is required for this assemblage to equilibrate.

Experimental methods

Gels of plagioclase compositions ranging from An_{30} to An_{100} in 10 mole percent increments were prepared following a procedure similar to that of Luth and Ingamells (1965). These gels were hydrothermally crystallized in cold-seal pressure vessels (Tuttle, 1949) at approximately 800°C and 20,000 p.s.i. for 14 days. The structural state of these feldspars was determined by G. A. Furst (The Pennsylvania State University, personal communication, 1974) to be approximately 80 percent disordered for structures crystallizing in a 7Å cell. In addition to the synthetic plagioclase, a natural sample (Lake County plagioclase, An_{67} ; Stewart *et al.*, 1966) was used in some experiments.

Starting mixes were prepared from a given plagioclase composition together with natural grossular ($Gr_{95}Alm_5$; $SiO_2 = 39.2$, $Al_2O_3 = 21.8$, total Fe as FeO = 1.91, MnO = 0.63, CaO = 35.5, in weight percent³), quartz, and wollastonite (0.75 percent Fe as Fe_2O_3 ; Boettcher, 1970, p. 341), then homogenized for one minute in a Spex mixer.

³ K. Jensen, analyst, Argonne National Laboratory. Sample kindly supplied by Dr. E. Olsen, Field Museum of Natural History, Chicago, Illinois.

A sample of the dried starting material was weighed into a platinum capsule that had been welded closed at one end. The capsule plus sample was then heated for approximately two minutes in a Bunsen-burner flame and the other end welded immediately after removal from the flame. One to three capsules were loaded into a 25.4-mm furnace assembly (Fig. 2). Boron nitride, fired for 24 hours at 800°C, immediately surrounded the capsule(s). A Pyrex cylinder separated the talc from the graphite to maintain anhydrous conditions and prevent incipient melting of the charge. Without these precautions, trace amounts of glass (quenched liquid) appeared in all runs.

All experiments were performed in piston-cylinder apparatus similar to that described by Boyd and England (1960). Each run was pressurized to approximately 6 percent below the final pressure and then brought to temperature. Run pressure was then obtained by increasing ram pressure to the desired reading, the true value of which was calculated using a -6 percent friction correction.

A temperature of 1100°C was maintained for all runs because it is representative of temperatures in the region of interest. In addition, reaction rates are too slow at lower temperatures, and melting occurs at

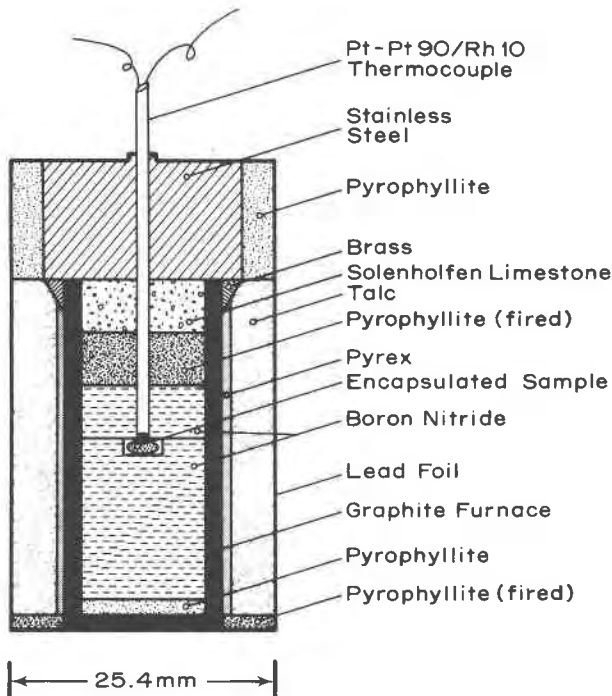


FIG. 2. Cross-sectional view of solid-media furnace assembly used in experiments.

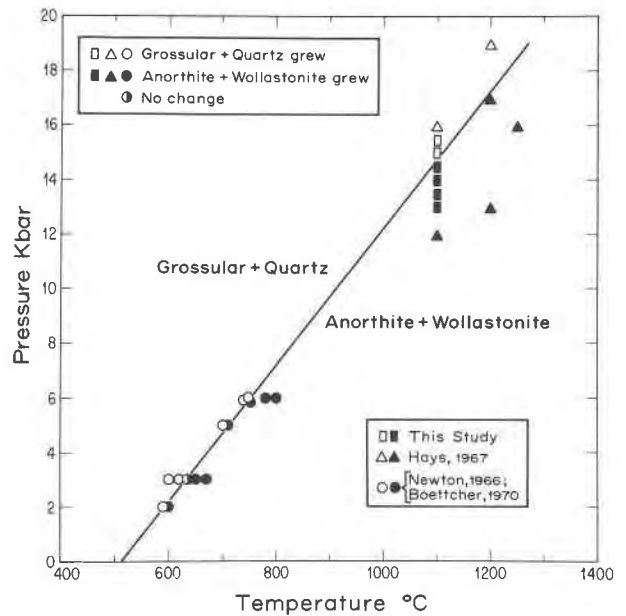


FIG. 3. Pressure-temperature diagram comparing the results obtained in this study for $Gr + Qz = An_{100} + Wo$ with results of Newton (1966), Hays (1967), and Boettcher (1970).

slightly higher temperatures for assemblages containing more albitic plagioclase.

Each starting mix was X-rayed using both a Nor-elco diffractometer and Guinier powder camera, and the peaks were indexed. Each run product was also X-rayed using both techniques, and the relative intensities were compared with those of the starting material. Replicates of certain runs, as well as duplicate runs, were made to check for reproducibility. In all instances, reproducibility was attained within ten percent change for all phases, a value taken as the limit for detectable reaction.

Attempts to analyze the plagioclase from various runs using the electron microprobe were unsuccessful because of the small grain size (1-10 μ m) and the intimate mixture with the other phases. Scanning electron microscopy was also tried, to determine if reaction direction could be detected from morphological changes in the various phases. No conclusive results were obtained using this approach.

Experimental Results

A comparison of our data for An_{100} composition with previous results is shown in Figure 3. Based on these data, a value of $P^0 = 14.8 \pm 0.3$ kbar is taken as the equilibrium pressure at 1100°C. The results of the present study are shown in Table 1 and Figure 4.

Uncertainties in our data may arise from the fol-

lowing sources: (1) Uncertainties in experimental technique—based on duplicate runs and past experience with the apparatus used in these experiments (see Johannes *et al.*, 1971), experimental uncertainties are believed to be within $\pm 10^\circ\text{C}$ and ± 300 bars. (2) Reaction kinetics—it was found that the reaction rate is not symmetrical about the equilibrium curve. Starting mixes of 50 weight percent products, 50 weight percent reactants for An_{100} composition resulted in essentially complete reaction for runs at pressures lower than the equilibrium curve, whereas runs of equal duration at pressures a comparable distance above the equilibrium curve did not go to completion, although enough reaction occurred to indicate the sense of reaction. It is probable that these relative reaction rates occurred for the other plagioclase compositions as well. (3) The equilibrium P - X curve is not strictly univariant because of impurities in the grossular and wollastonite. These impurities are minor, and they probably do not significantly affect equilibrium.

Uncertainties in determining reaction direction may also arise because of a buffering effect on the plagioclase composition in equilibrium with grossular, quartz, and wollastonite. The equilibrium condition for An_{100} is isothermally invariant, and complete reaction to either products or reactants is possible as a result of a change in pressure. This is not the case for plagioclase that is not pure anorthite, because the addition of Na_2O increases the variance by 1, creating an isothermally univariant equilibrium curve. Thus, for a P - $X_{\text{An}}^{\text{Pl}}$ condition not at equilibrium, reaction will occur causing the plagioclase to become either more albitic ($\Delta G_r > 0$), or more anorthitic ($\Delta G_r < 0$), or until one of the other phases is consumed. This means that for initial conditions near equilibrium where the absolute value of ΔG_r is small, only a minor amount of reaction will occur before the plagioclase composition is adjusted to near the equilibrium value and perceptible reaction ceases. For this reason it is difficult to unequivocally determine the sense of reaction of runs near the equilibrium curve because of the insensitiveness of X-ray patterns to small changes ($< \sim 10$ percent) in the proportions of phases.

TABLE 1. Results of experiments at 1100°C

$X_{\text{An}}^{\text{Pl}}$ (mole percent)	Pressure (kbar)	Run no.	Time (hours)	Results
100	13.0	122	24	products grew
100	13.5	123	24	products grew
100	14.0	124	48	products grew
100	14.5	125	24	products grew
100	15.0	135	65	reactants grew
100	15.5	136	72	reactants grew
90	15.0	138	72	products grew
90	15.5	139	72	reactants grew
80	15.0	141	72	products grew
80	15.5	142	72	products grew
80	16.0	143	72	reactants grew
70	15.0	131	65	products grew
70	15.5	132	72	no change
70	16.0	133	72	reactants grew
67	14.0	54	44	products grew
67	15.0	58	24	products grew
67	15.5	56	24	no change
67	16.5	57	24	reactants grew
60	15.5	145	72	products grew
60	16.0	146	72	no change
60	16.5	147	72	no change
60	17.0	148	72	reactants grew
50	15.5	128	24	products grew
50	16.0	156	72	products grew
50	16.5	157	72	no change
50	17.0	158	72	reactants grew
50	17.5	159	72	reactants grew
40	16.5	150	72	products grew
40	17.0	151	72	products grew
40	17.5	152	72	products grew
40	18.0	153	72	no change
40	18.5	154	72	no change
40	19.0	155	72	reactants grew
30	17.5	79	24	products grew
30	18.0	162	72	products grew
30	18.5	163	72	no change
30	19.0	164	72	no change
30	19.5	126	24	reactants grew

The solid curve shown in Figure 4 is our interpretation of the best fit for these data. From this curve, values of $\gamma_{\text{An}}^{\text{Pl}}$ can be calculated, assuming the value for ΔV_r is known. We have attempted to correct this volume term for the effect of thermal expansion and compressibility using available data and extrapolating where necessary. Thermal expansion data for plagioclase ($\text{An}_{95}\text{Ab}_5$) and β -quartz up to 1000°C , and for grossular up to 800°C , were taken from Skinner (1966) and extrapolated to 1100°C . No data for wollastonite were found in the literature. However, it is possible to model wollastonite using minerals with similar structures. Thermal expansion for wollastonite was obtained by extrapolating values for $\text{Wo}_{46}\text{-Fs}_{55}$ and $\text{Wo}_{69}\text{-Fs}_{31}$ (Skinner, 1966) from 600°C to 1100°C , then extrapolating these values to Wo_{100} composition. Compressibility data for wollastonite and quartz are from Vaidya *et al.* (1973). Compressibility data for grossular and labradorite (An_{52}) are from Birch (1966). Table 2 lists the values used for thermal expansion and compressibility and the molar volumes of each phase at 1100°C and 15 kbar. Isothermal compressibilities from 15 kbar to 20 kbar are small and are neglected. Volume changes resulting from changes in the composition of plagioclase are also neglected (see Figure 7-41 of Smith, 1974). The data in Table 2 yield a value $\Delta V_r = 0.70534$ cal/bar at 1100°C and 15 kbar. Using this

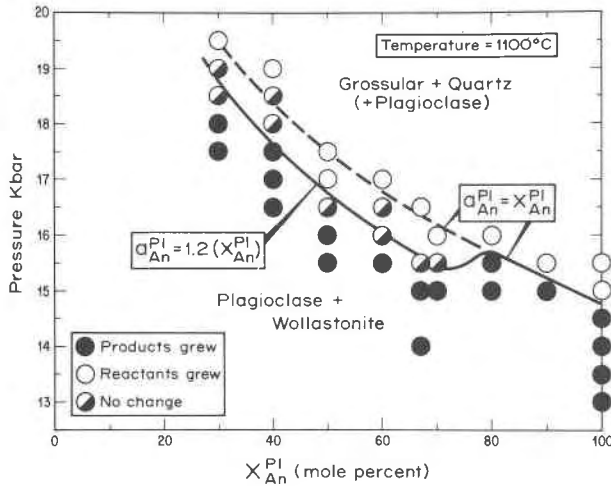


FIG. 4. Pressure-composition diagram showing experimentally determined points and our interpretation of the best fit for these data (solid curve). The dashed curve was calculated using $a_{An}^{PI} = X_{An}^{PI}$.

value and solving equation 10 for the curve in Figure 4 yields values of $\gamma_{An}^{PI} = 1.0$ for the composition range An_{80-100} and $\gamma_{An}^{PI} = 1.2$ for the range An_{30-70} . The dashed curve in Figure 4 was calculated for $a_{An}^{PI} = X_{An}^{PI}$; it does not satisfy the experimental data for compositions more albitic than An_{80} . Hence, compositions in the range An_{30-70} show a positive deviation from Raoult's law. This composition range probably extends to pure albite, based on arguments discussed in the next section.

Discussion and conclusions

The positive deviation from Raoult's law of γ_{An}^{PI} values for plagioclase more albitic than about An_{80} at the conditions of our experiments indicates a tendency to separate into two structural entities. A separation of this nature does occur at lower temperatures

as the structures become more ordered, as evidenced by the occurrences of various solvi below about 500°C (for a review, see Smith, 1974). At higher temperatures, the structures become more disordered and the solvi close. Smith and Ribbe (1969) have proposed the existence of unit-cell intergrowths in the plagioclase structure at temperatures above the crests of the various solvi, but below the solidus. In these structures, there is continuity of the aluminosilicate framework with both anorthite-like and high albite-like domains occurring within this framework on the scale of a few unit cells. Compositions in the range An_{100} to about An_{70-80} are ordered on tetrahedral sites and occur as structures with the c axis $\approx 14\text{\AA}$. Compositions more albitic than about An_{70} occur in structures resembling high albite with $c \approx 7\text{\AA}$.

We interpret the results obtained in the present study as a reflection of this domain assemblage in the plagioclase structure. For compositions in the range An_{100} to about An_{80} , the plagioclase unit-cell is interpreted as having a 14\AA c axis with the anorthite-like domains being dominant. For these compositions, $\gamma_{An}^{PI} = 1.00$. For compositions more albitic than about An_{80} , the structure is not energetically favorable for the large 14\AA anorthite-like domains, and thus they tend toward unmixing, resulting in a positive deviation from Raoult's law.

Orville (1972) obtained similar results for plagioclase at 700°C and 2000 bars. He interpreted his results as "ideal solution" ($\gamma_{An}^{PI} = 1.00$) between "real" and "fictive" end-member compositions. We feel that the use of fictive end-members is not warranted, especially in the light of the domain theory for plagioclase solutions.

The positive sign of dP/dX between An_{70} and An_{80} is speculative. It implies the coexistence of two plagioclase phases, having different compositions but the same activity at a given temperature and pressure.

TABLE 2. Thermal expansion and compressibility data used in calculations

Phase	Thermal expansion at 1100°C (percent V increase)	Compressibility at 15 kbar ($(V_0 - V)/V_0$)	Molar volume at 1100°C and 15 kbar (cal/bar)**
Anorthite	1.63	0.0223	2.3985
Wollastonite	1.55*	0.0214	0.94869
Grossular	2.70	0.00947	3.0464
Quartz	4.18	0.0368	0.54414

* Data obtained by extrapolating data for Wo-Fs solid-solutions.

** Determined by applying thermal expansion and compressibility data to 1 atm, 25°C molar volume data given in Robie and Waldbaum (1968).

The hypothetical one-atmosphere phase diagram of Smith (1974, p. 6) shows both a solvus and a hanging binary loop, each covering the composition range An_{70-80} at temperatures near 1100°C. This phase diagram does not constitute proof of a two-phase region at 15 kbar pressure, but does lend support to this possibility.

The results obtained in subsolidus studies have implications regarding melting phenomena of plagioclase. The similarity between our results and those of Orville (1972) indicates a large pressure-temperature region over which plagioclase exhibits a positive deviation from Raoult's Law. Based on one-atmosphere experiments, Bowen (1913) concluded that the melting behavior of plagioclase obeys Raoult's Law; his conclusion has been confirmed by C. Wayne Burnham (The Pennsylvania State University, personal communication, 1975). This difference in behavior cannot be solely attributed to either a change in temperature or in pressure because the melting curves for plagioclase + H₂O at 5 kbar (Yoder *et al.* 1956) and at 10 kbar (Furst and Boettcher, 1972), determined at temperatures and pressures below those of our experiments yet above those of Orville (1972), appear to obey Raoult's Law. Further, the proposed phase diagram of Smith (1974) shows a field for a nonquenchable monoclinic structure (monalbite) for albite-rich compositions at solidus temperatures. Consequently, increased temperature does not result in a continuous isomorphous solid solution series, but rather the occurrence of three separate structures, *i.e.*, a 7Å monoclinic structure for compositions rich in albite, a 7Å triclinic structure for compositions between about An_{15} and An_{80} , and a 14Å triclinic structure for anorthite-rich compositions. One reasonable explanation for the apparent Raoult's Law behavior of melting phenomena is that the activity coefficients of the liquid are similar to those of the solid, thus cancelling each other. This implies short-range order in the liquid and a tendency for the liquid to separate into two phases (although not necessarily two liquids). Interestingly, this possibility was alluded to by Bowen (1913, p. 594).

Some experimental data support the hypothesis of positive deviation from Raoult's Law for plagioclase liquids. Anorthite-rich compositions have been shown to melt incongruently to corundum + liquid at pressures above about 7.5 kbar for both anhydrous (Lindsley, 1967) and hydrous (Boettcher, 1970) systems. Albite-rich compositions melt incongruently to jadeite + liquid at pressures above about 32 kbar in the anhydrous system (Bell and Roseboom, 1969)

and pressures above about 17 kbar in the hydrous system (Boettcher and Wyllie, 1968).

Information regarding plagioclase behavior obtained from the study of reaction 1 can be applied to the more complex, natural assemblages that contain plagioclase.

As a result of the inflections at compositions An_{70} and An_{80} (Figure 4), the beginning of reaction for plagioclase compositions in the range An_{60} to An_{90} is within a pressure interval of only about 1000 bars. The actual pressure interval is different for different reactions and is a function of ΔV_r . The interval is also temperature-dependent, probably widening with increasing temperature for a given reaction. Thus, comparable mineralogical assemblages containing plagioclases that range from calcic-labradorite to anorthite will all begin to react within a zone on the order of 2–3 km thick. Conversely, assemblages containing more sodic plagioclase (oligoclase, andesine) will persist to higher pressures and will begin to react over a rather wide pressure interval because of the steepening of the equilibrium curve for the beginning of reaction.

Based on these observations, a possible explanation is given for the existence of seismic discontinuities (*e.g.*, the Conrad discontinuity) in certain parts of the lower crust, whereas other parts show no evidence of such a discontinuity. If large areas of the lower crust are composed of basic rock (*e.g.* gabbro) containing calcic plagioclase, these rocks will undergo plagioclase-consuming reactions at relatively shallow levels. These reactions would all occur within a zone of approximately 2–3 km thick and may be seismically detectable if the region is large. Conversely, areas composed of rocks (*e.g.*, andesite) containing plagioclase within the range oligoclase to andesine will not be involved in plagioclase-consuming reactions until much higher pressures, and the pressure interval over which these reactions begin will be much greater. Thus, no sharp break will occur and no seismically detectable layer will be formed.

Acknowledgments

Discussions with D. M. Kerrick and C. Wayne Burnham regarding crystalline solutions and with D. K. Smith regarding plagioclase structure contributed to the manuscript. R. Z. Small fabricated furnace parts and maintained the laboratory equipment. This research was supported by the Earth Sciences Section, National Science Foundation, NSF Grant DES73-00220 A01.

References

- AKELLA, J. AND G. C. KENNEDY (1971) Studies on anorthite + diopside₅₀-hedenbergite₅₀ at high pressures and temperatures. *Am. J. Sci.* **270**, 155–165.

- BELL, P. M. AND E. H. ROSEBOOM, JR. (1969) Melting relationships of jadeite and albite to 45 kilobars with comments on melting diagrams of binary systems at high pressures. *Mineral. Soc. Am. Spec. Paper* 2, 151-161.
- BIRCH, F. (1966) Compressibility; elastic constants. In, S. P. Clark, Jr., Ed., *Handbook of Physical Constants. Geol. Soc. Am. Mem.* 97, 97-173.
- BOETTCHER, A. L. (1970) The system $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ at high pressures and temperatures. *J. Petrol.* 11, 337-379.
- (1971) The nature of the crust of the Earth with special emphasis on the role of plagioclase. In, J. G. Heacock, Ed., *The Structure and Physical Properties of the Earth's Crust. Am. Geophys. Union Monograph* 14, p. 261-277.
- AND P. J. WYLLIE (1968) Jadeite stability measured in the presence of silicate liquids in the system $\text{NaAlSi}_3\text{O}_8\text{-SiO}_2\text{-H}_2\text{O}$. *Geochim. Cosmochim. Acta*, 32, 999-1012.
- BOWEN, N. L. (1913) The melting phenomena of the plagioclase feldspars. *Am. J. Sci.* 35, 577-599.
- BOYD, F. R. AND J. L. ENGLAND (1960) Apparatus for phase-equilibrium measurements at pressures up to 50 kilobars and temperatures up to 1750°C. *J. Geophys. Res.* 65, 741-748.
- FURST, G. A. AND A. L. BOETTCHER (1972) Stability of plagioclase at high temperatures and pressures. [abstr.] *Annu. Meet. Geol. Soc. Am., Abstracts with Programs*, 4, 514.
- GREEN, D. H. AND W. HIBBERSON (1970) The instability of plagioclase in peridotite at high pressure. *Lithos*, 3, 209-221.
- HARIYA, Y. AND G. C. KENNEDY (1968) Equilibrium study of anorthite under high pressure and high temperature. *Am. J. Sci.* 266, 193-203.
- HAYS, J. F. (1967) Lime-alumina-silica. *Carnegie Inst. Wash. Year Book*, 65, 234-239.
- JOHANNES, W., P. M. BELL, H. K. MAO, A. L. BOETTCHER, D. W. CHIPMAN, J. F. HAYS, R. C. NEWTON AND F. SEIFERT (1971) An interlaboratory comparison of piston-cylinder pressure calibration using the albite-breakdown reaction. *Contrib. Mineral. Petrol.* 32, 24-38.
- KERRICK, D. M. AND L. S. DARKEN (1975) Statistical thermodynamic models for ideal oxide and silicate solid solution, with application to plagioclase. *Geochim. Cosmochim. Acta*, 39, 1431-1442.
- KUSHIRO, I. AND H. S. YODER, JR. (1966) Anorthite-forsterite and anorthite-enstatite reactions and their bearing on the basalt-eclogite transformation. *J. Petrol.*, 7, 337-362.
- LINDSLEY, D. H. (1967) Melting relations of plagioclase at high pressures. *Carnegie Inst. Wash. Year Book*, 65, 204.
- LUTH, W. C. AND C. O. INGAMELLS (1965) Gel preparation of starting materials for hydrothermal investigation. *Am. Mineral.* 50, 255-258.
- NEWTON, R. C. (1966) Some calc-silicate equilibrium relations. *Am. J. Sci.* 264, 204-222.
- AND J. V. SMITH (1967) Investigations concerning the breakdown of albite at depths in the earth. *J. Geol.* 75, 268-286.
- ORVILLE, P. M. (1972) Plagioclase cation exchange equilibria with aqueous chloride solution: results at 700°C and 2000 bars in the presence of quartz. *Am. J. Sci.* 272, 234-272.
- ROBIE, R. A. AND D. R. WALDBAUM (1968) Thermodynamic properties of minerals and related substances at 298.15°K (25.0°C) and one atmosphere (1.013 bars) pressure and at higher temperatures. *U.S. Geol. Surv. Bull.* 1259, 256 p.
- RONOV, A. B. AND A. A. YAROSHEVSKY (1969) Chemical composition of the Earth's crust. In, P. J. Hart, Ed., *The Earth's Crust and Upper Mantle. Am. Geophys. Union Monograph* 13, p. 37-57.
- SAXENA, S. K. AND P. H. RIBBE (1972) Activity-composition relations in feldspars. *Contrib. Mineral. Petrol.* 37, 131-138.
- SKINNER, B. J. (1966) Thermal expansion. In, S. P. Clark, Jr., Ed., *Handbook of Physical Constants. Geol. Soc. Am. Mem.* 97, p. 75-96.
- SMITH, J. V. (1974) *Crystal Structure and Physical Properties. Feldspar Minerals*. Vol. 1. Springer-Verlag, New York. 627 p.
- AND P. H. RIBBE (1969) Atomic movements in plagioclase feldspar: kinetic interpretation. *Contrib. Mineral. Petrol.* 21, 157-202.
- STEWART, D. B., G. W. WALKER, T. L. WRIGHT AND J. J. FAHEY (1966) Physical properties of calcic laboradorite from Lake County, Oregon. *Am. Mineral.* 51, 177-197.
- TUTTLE, O. F. (1949) Two pressure vessels for silicate-water studies. *Bull. Geol. Soc. Am.* 60, 1727-1729.
- VAIDYA, S. N., S. BAILEY, T. PASTERNAK AND G. C. KENNEDY (1973) Compressibility of fifteen minerals to 45 kilobars. *J. Geophys. Res.* 78, 6893-6898.
- YODER, H. S., JR., D. B. STEWART AND J. R. SMITH (1956) Ternary feldspars. *Carnegie Inst. Wash. Year Book*, 55, 190-194.

Manuscript received, November 14, 1975; accepted for publication, April 28, 1976.