

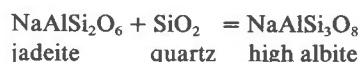
The reaction albite = jadeite + quartz determined experimentally in the range 600–1200°C

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Abstract

The reaction



has been determined by direct experiment in the temperature range 600–1200°C, and the P - T line can be described by the equation

$$P = 0.35 + 0.0265 T (^\circ\text{C}) \pm 0.50 \text{ kbar}$$

The brackets, when compared with the gas-apparatus determinations of this reaction by Hays and Bell (1973) and by Birch and LeComte (1960), show clearly that pressure corrections are vanishingly small when the NaCl pressure cell is used with the piston-cylinder device if piston-out methods are used. The slope ($dP/dT = 26.5 \text{ bar } ^\circ\text{C}^{-1}$), in conjunction with tabulated entropies for quartz and jadeite, leads to a value for the entropy of synthetic high albite. The disordering entropy of albite is ($14.2 \pm 2.4 \text{ J K}^{-1} \text{ mol}^{-1}$), and the enthalpy is ($12950 \pm 3320 \text{ J mol}^{-1}$). The disordering enthalpy is in excellent agreement with recent calorimetric measurements on Amelia albite and its heat-treated modification. The best values from phase equilibria for the 298 K, 1 bar, thermochemical data for synthetic high albite are

$$\Delta_f H_{298, 1 \text{ bar}}^\circ = -3922170 \pm 4300 \text{ J mol}^{-1}$$

$$S_{298, 1 \text{ bar}}^\circ = 221.6 \pm 2.5 \text{ J K}^{-1} \text{ mol}^{-1}$$

The lack of curvature of the reaction in the P - T plane implies that high albite does not undergo ordering down to 600°C, at least within the duration time of the experiments. This is also confirmed by the X-ray patterns of albites from runs at 600°C.

Introduction

The stability of the end-member feldspars is of fundamental importance to petrology, yet considerable uncertainty exists as to the P - T location of the albite to jadeite + quartz curve at high temperatures.

In the temperature range 500–600°C the experimental location is precise (Newton and Smith, 1967; Johannes *et al.*, 1971; Hays and Bell, 1973), but at higher temperatures the slope and position of the curve are only loosely constrained by the reversal intervals determined by Birch and LeComte (1960) and Bell and Roseboom (1969). Boettcher and Wyllie (1968) published brackets at 600°C and 800°C which demand a lower dP/dT slope ($19.5 \text{ bar deg}^{-1}$) than expected for the breakdown of disordered albite, for

which high-temperature calorimetry (Holm and Kleppa, 1968) predicts a slope of $27.6 \text{ bar deg}^{-1}$, as shown later.

The importance of this reaction to petrology cannot be overstated, as it forms the basis for a number of geobarometric inferences on the stability of plagioclase-bearing assemblages at depth (Boettcher, 1971).

This study defines closely the P - T stability of high albite relative to jadeite and quartz, using the precise pressure control afforded by the low-friction NaCl pressure cell with the piston-cylinder apparatus. The precision made possible by this technique allows accurate determination of the standard thermodynamic properties of high albite.

Starting materials and experimental technique

High albite was synthesized hydrothermally at 750°C, 2 kbar, from a mixture of natural vein quartz and NaAlSi₃O₆ glass (prepared by P. A. M. Anderson) in a 1:1 molar ratio. The X-ray pattern is that of high albite, with $\Delta 2\theta$ (CuK α) = 1.90° for (131)–(1 $\bar{3}$ 1) (Goldsmith and Laves, 1954). Natural white jadeite from a vein in serpentinite, donated to R. C. Newton by R. G. Coleman, was used; it contains as principal impurities 0.13 weight percent CaO, 0.12 weight percent MgO, and 0.45 weight percent Fe₂O₃ (Coleman, 1961).

An end-loaded piston-cylinder apparatus with a 0.75" diameter cylindrical pressure chamber and NaCl pressure medium was used for all runs. The chamber contained a smooth, but not polished, steel liner and was lubricated by dry MoS₂ powder. Piston-out type runs were made, using pistons with bevelled tops capped with pyrophyllite sealing gaskets as described in Holland (1979a), by the following procedure. The cold assembly was brought up to a predetermined pressure of 3.5 kbar or more below the final desired run pressure and was then heated to the required temperature for the run. The large thermal expansion of the NaCl assembly during heating, a pre-calibrated function of temperature and final run

pressure, ensures initiation of the run under conditions of retreating piston. Occasionally it was necessary to bleed off a little oil pressure during the final stages of heating to prevent pressure overshoot.

Chromel–alumel thermocouples, in AlSiMag sleeves, with the junctions protected by a layer of alundum cement, were used to measure temperatures. No pressure correction was applied to the thermocouple readings. The reversal mixture was made up of the crystalline starting materials high albite, jadeite, and quartz in reacting proportions. The mixture was ground repeatedly under acetone to thoroughly homogenize the reactants, and was then baked at 350°C overnight to burn off any organic residue from the acetone. Following Boettcher and Wyllie (1968) in the successful use of interstitial melt as a flux, the charge was moistened by breathing on the powder before sealing in platinum capsules. The small amount of interstitial water-undersaturated melt was found sufficient to produce 100 percent reaction in many runs. Direction of reaction was detected by changes of more than 15 percent in relative peak intensities on the diffractometer trace. Runs at 600°C (from Holland, 1979a) were conducted under H₂O-excess conditions.

Results

Kinetics of the albite to jadeite + quartz reaction in the presence of small amounts of melt are such that complete reaction occurred in less than 3 hours at 1200° and 24 hours at 800°C. Runs at and above 1100°C cannot be considered reversed, as the albite breaks down to jadeite + quartz during the approach to the final *P*–*T* conditions (Table 1). However, growth of albite is extremely rapid (Newton, in Johannes *et al.*, 1971) and the results certainly represent equilibrium. Table 1 and Figure 1 display the experimental results. The best straight-line fit (by eye) through the brackets can be described by P (kbar) = $0.0265T^{\circ}\text{C} + 0.35 \pm 0.50$.

Discussion

Pressure calibration of piston cylinder apparatus

The use of the NaCl pressure medium in recent years has significantly improved the pressure determination in piston-cylinder experiments (Johannes *et al.*, 1971; Mirwald *et al.*, 1975; Johannes, 1978; Danckwerth and Newton, 1978; Holland, 1979a). It is instructive to compare the present results at 600°C with the gas-apparatus determination by Hays and Bell (1973) and in the range 800–1000°C with the de-

Table 1. Experimental results on the reaction jadeite + quartz = high albite

Run no.	T °C	P kb	Time (hours)	Result*
4	600	16.0	24.0	A
6	600	16.5	8.0	JQ
24	800	21.0	13.25	A
23	800	22.0	23.75	JQ
28	900	23.5	23.5	A
25	900	24.25	22.75	NR
27	900	25.0	21.50	JQ
18	1000	26.0	23.25	A
22	1000	27.5	22.75	JQ
13	1100	28.0	3.25	A
14	1100	29.0	5.2	A
10	1100	30.0	0.2	JQ
11	1100	30.0	—**	JQ
15	1200	31.0	3.3	A
16	1200	32.0	5.4	NR
17	1200	33.0	4.25	JQ

* A - albite growth; JQ - jadeite + quartz growth; NR - no reaction.

** Run was quenched as soon as desired *P*, *T* conditions had been reached.

termination by Birch and LeComte (1960), also performed with gas pressure medium. At 600°C the pressures obtained in this study, 16.0–16.5 kbar, agree well with the Hays and Bell value (16.4±0.5 kbar). The brackets in the range 800–1000°C all lie within the reversal interval of Birch and LeComte and can be regarded as a refinement of their results. Although Birch and LeComte used natural low albite in their starting material, the product albite which was nucleated and/or grown in their runs was without doubt disordered high albite. On the other hand the less stable low albite in their runs probably broke down to jadeite + quartz at slightly lower pressures than those required for the breakdown of high albite. The equilibrium curve for high albite = jadeite + quartz should therefore be expected to lie within or at marginally higher pressures than the Birch and LeComte reaction brackets. The fact that the present results all lie within the Birch and LeComte intervals indicates that the pressures determined with the NaCl cell, as used here, are not overestimates, and that subtractive friction corrections are vanishingly small. Indeed, any correction due to friction would be much less at these higher temperatures (800–1200°C) than at 600°C, where it was shown to be negligible (this work; Hays and Bell, 1973; Johannes *et al.*, 1971). Johannes (1978) reported a pressure of less than 16 kbar for a piston-out reversal at 600°C, in contrast to the 16.25±0.25 kbar reported here. Although both studies used the NaCl pressure medium, the methods of arrival at the final pressure and temperature differed. It is apparent that with this method no pressure correction is necessary, and this redetermination is sufficiently precise to be used as a pressure calibration for alternative pressure cells such as Pyrex, talc, or soft glass. Results in this laboratory suggest that the 7–10 percent subtractive correction commonly applied to Pyrex-talc assemblies above 1100°C with piston-in runs is valid.

Thermodynamic considerations

The slope for the reaction between albite and jadeite + quartz can be readily calculated from high-temperature oxide melt solution calorimetry. For low albite, the data of Hlabe and Kleppa (1968) yield $\Delta H_{964\text{K}} = -2385 \pm 2090$ J, for the reaction from jadeite + quartz. Recent measurements (R. C. Newton, personal communication) on the enthalpy difference between low albite and albite heat-treated at 20 kbar, 1200°C yield $\Delta H_{\text{disorder}} = 14580 \pm 1660$ J mol⁻¹ at 970 K. Taking account of the α - β quartz transition by

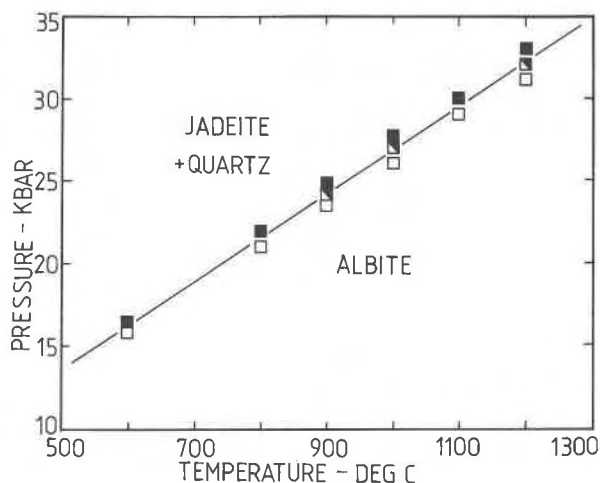


Fig. 1. P, T brackets on the jadeite + quartz to albite reaction. Filled squares denote growth of jadeite + quartz, open squares denote growth of albite, and partially-filled squares denote no apparent reaction.

extrapolating the α -quartz heat content data in Robie *et al.* (1978), the one-bar enthalpy for the reaction jadeite + quartz = albite, involving α -quartz and high albite, becomes 11405 ± 2670 J at 964 K. With mean thermal expansions and compressibilities from Table 2 and the equilibrium pressure of 18.7 kbar, the slope may be calculated from:

$$dP/dT = \left[\Delta H_{1 \text{ bar}} + \int_1^P [\Delta V - T\Delta(\alpha V)] dP \right] / T\Delta V$$

The result, 27.6 ± 1.5 bar °C⁻¹, is in good agreement with the measured slope, 26.5 ± 1.5 bar °C⁻¹.

The entropy of synthetic high albite may be calculated from the experimental brackets, using the measured volumes and heat capacities (in Robie *et al.*,

Table 2. Standard thermodynamic properties for jadeite, albite and quartz

	V_{298}^0 cm ³	S_{298}^0 J K ⁻¹ mol ⁻¹	$\Delta_f H_{298}^0$ J mol ⁻¹	$\alpha V^0 \times 10^5$ J bar ⁻¹ K ⁻¹	$\beta V^0 \times 10^6$ J bar ⁻²
Jadeite	60.4 ±0.1	133.47 ±1.25	-3024270 ±4180	17.15	4.52
High albite	100.43 ±0.09	221.6 ±2.5	-3922170 ±4300	27.21	15.94
Low albite	100.07 ±0.13	207.40 ±0.40	-3935120 ±3415	27.21	15.94
Quartz	22.688 ±0.001	41.46 ±0.20	-910700 ±1000	12.15	5.18

Thermal expansion data taken from Skinner (1966), compressibility data taken from Birch (1966). All thermodynamic data are from Robie *et al.* (1978) except for high albite and jadeite data which are from this study.

1978), thermal expansion and compressibility data (Table 2). Solving the relation:

$$\Delta H_{298,1} - T\Delta S_{298,1} = - \left[\int_{298}^T \Delta C_p dT - T \cdot \int_{298}^T \frac{\Delta C_p}{T} dT + \int_1^P \Delta V dP \right]$$

by plotting the right side against absolute temperature yields $\Delta S_{298,1}$ as slope and $\Delta H_{298,1}$ as intercept. The derived entropy of albite is $221.6 \pm 2.5 \text{ J K}^{-1} \text{ mol}^{-1}$. Comparing this value with that for low albite gives the disordering entropy as $14.2 \pm 2.4 \text{ J K}^{-1}$ per mole of albite, which is somewhat lower than the maximum configurational term $-4R (0.25 \ln 0.25 + 0.75 \ln 0.75) = 18.7 \text{ J K}^{-1} \text{ mol}^{-1}$. X-ray crystallographic site-occupancy studies show that natural low albite is not fully ordered and that high albite may not be completely disordered (Holm and Kleppa, 1968). From the observed distribution of Al and Si on the tetrahedral sites in low and heat-treated albite, the configurational disordering entropy is calculated as $16.0 \text{ J K}^{-1} \text{ mol}^{-1}$ (Holm and Kleppa, 1968). The agreement with the value, $14.2 \pm 2.4 \text{ J K}^{-1}$, derived from the slope of the experimental study is encouraging.

By comparing the derived $\Delta H_{298,1}$ for the reaction ($12800 \pm 2580 \text{ J}$) obtained from the experimental brackets with that for the reaction involving low albite ($-150 \pm 2090 \text{ J}$) calculated from the data of Hlabse and Kleppa (1968) with the help of the high-temperature heat contents (Robie *et al.*, 1978), we can estimate the disordering enthalpy of albite. This estimate, $12950 \pm 3320 \text{ J}$, can be compared with the measured enthalpies of disorder $11015 \pm 840 \text{ J mol}^{-1}$ (Waldbaum and Robie, 1971), 9640 J mol^{-1} (Kracek and Neuvonen, 1952), and $14220 \pm 1660 \text{ J mol}^{-1}$ (R. C. Newton and T. V. Charlu, unpublished data). This last value was determined from the difference in heats of solution at 970 K of Amelia albite and high albite crystallized from Amelia albite glass at 20 kbar, 1200°C , and should represent maximum disordering enthalpy for albite. All enthalpies, unless otherwise stated, are given corrected to 298 K for ease of comparison. The high-temperature calorimetric measurements of Holm and Kleppa (1968) on albites heat-treated for times of the order of one month at 1050°C yielded a disordering enthalpy of $14230 \pm 1050 \text{ J mol}^{-1}$ at 971 K, which is equivalent to $13870 \pm 1050 \text{ J mol}^{-1}$ at 298 K. It may be (R. C. Newton, personal communication) that albite does not disorder fully at 1050°C under atmospheric pressure

in times of the order of three weeks. Note that the low-temperature acid calorimetric results (Waldbaum and Robie, 1971; Kracek and Neuvonen, 1952) yield somewhat low enthalpies of disorder.

Applications

The improved precision in the location of the albite breakdown curve to high temperatures allows for more reliable geobarometry of sodic pyroxenes than was possible before. An important application is in the estimation of the stability of jadeitic pyroxenes coexisting with quartz in natural rocks. As an example we consider the metamorphic rocks of the Sezia-Lanzo zone of the Western Alps, and in particular the assemblage pyroxene + quartz, described by Reinsch (1977). Reinsch estimated 680°C as an appropriate temperature for the equilibration of the pyroxene, which contained 81 percent of the jadeite end-member. Direct application of the present results yield a pressure of 18.4 kbar below which pure jadeite + quartz would break down. However, the effects of 19 percent diluent in the natural pyroxene can be calculated and will result in a destabilization of the quartz + pyroxene assemblage by an amount

$$\Delta P \approx -(RT/\Delta V^\circ) \ln \alpha_{jd}$$

where R is the gas constant, T the absolute temperature, ΔV° the volume change for the reaction jadeite + quartz = high albite, and α_{jd} the activity of jadeite in the pyroxene. The experimental work of Holland (1979b) on the activity-composition relationships for the join jadeite-diopside at 600°C showed that the activity of jadeite can be expressed as

$$\alpha_{jd} = X_{jd}^2 \gamma_{jd}$$

where X_{jd} and γ_{jd} are the mol fraction and the activity coefficient of jadeite respectively. γ_{jd} was determined (Holland, 1979b) as

$$\gamma_{jd} = \exp [(W/RT) (1 - X_{jd})^2]$$

where the interaction energy, W , was found to be 24 kJ . For Reinsch's pyroxene we find $\gamma_{jd} = 1.12$ and $\alpha_{jd} = (0.81)^2 (1.12) = 0.73$ at 680°C , which leads to a destabilization of $\Delta P = 1.4 \text{ kbar}$, and an estimate of a minimum pressure of 17 kbar for the assemblage.

The quantitative interpretation (Ganguly, 1973) of the experiments of Kushiro (1969) on the join diopside-albite was hampered by lack of data for the albite breakdown curve at the high temperatures involved. Application of the mixing relations discussed above to Kushiro's data shows that predictions based

upon the location of the albite breakdown curve together with the activity-composition relations determined at 600°C are in good agreement with the experiments of Kushiro. The agreement is particularly gratifying because Kushiro's work was performed at temperatures (1050–1250°C) far removed from those at which the mixing relations were determined.

The results on the albite breakdown curve can be used together with the recent determination of the anorthite breakdown curve to grossular + kyanite + quartz (Goldsmith, 1979) to predict the maximum stability pressures for plagioclase feldspars in the lower crust. Reliable estimates for these limits await accurate determination of the mixing relations in plagioclase feldspar.

Conclusions

The experimental determination of the jadeite + quartz = albite reaction represents a considerable improvement in location of the curve as well as an extension of the measurements to higher temperatures. This study demonstrates that the *P-T* line shows no curvature, at least in the range 600–1200°C, and hence that albite does not undergo Al-Si ordering in the experimental runs.

The location of the curve agrees precisely with both pre-existing gas-apparatus determinations (Birch and LeComte, 1960; Hays and Bell, 1973) and demonstrates the reliability of the NaCl pressure medium in piston-cylinder experiments. No pressure correction need be applied for such determinations with the experimental technique used in this study.

The slope of the reaction as experimentally determined is consistent with recent high-temperature calorimetry and yields an entropy of disordering which is in accord with predictions based upon site occupancy studies on natural and heat-treated albites. The enthalpy of disordering in albite can be similarly determined from the experimental brackets and is also in agreement with thermochemical measurements. Thermodynamic data derived for hydrothermally crystallized synthetic high albite are tied to the entropy and enthalpy of low albite given in Robie *et al.* (1978) and form part of a self-consistent set which describes accurately all the measured reactions among albite, paragonite, kyanite, andalusite, jadeite, quartz, corundum, and water (Holland, 1979a).

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