

## Dry melting of high albite

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### ABSTRACT

The properties of albitic melts are central to thermodynamic models for synthetic and natural granitic liquids. We have analyzed published phase-equilibrium and thermodynamic data for the dry fusion of high albite to develop a more accurate equation for the Gibbs free energy of this reaction to 30 kbar and 1400 °C. Strict criteria for reaction reversal were used to evaluate the phase-equilibrium data, and the thermodynamic properties of solid and liquid albite were evaluated using the published uncertainties in the original measurements. Results suggest that neither available phase-equilibrium experiments nor thermodynamic data tightly constrain the location of the reaction. Experimental solidus temperatures at 1 atm range from 1100 to 1120 °C. High-pressure experiments were not reversed completely and may have been affected by several sources of error, but the apparent inconsistencies among the results of the various experimentalists are eliminated when only half-reversal data are considered. Uncertainties in thermodynamic data yield large variations in permissible reaction slopes. Disparities between experimental and calculated melting curves are, therefore, largely attributable to these difficulties, and there is no fundamental disagreement between the available phase-equilibrium and thermodynamic data for the dry melting of albite. Consequently, complex speciation models for albitic melts, based on the assumption that these discrepancies represent a real characteristic of the system, are unjustified at this time.

### INTRODUCTION

The albite-water system is of fundamental importance in igneous petrology. Like other parts of the haplogranodioritic system ( $\text{CaAl}_2\text{Si}_2\text{O}_8\text{-NaAlSi}_3\text{O}_8\text{-KAlSi}_3\text{O}_8\text{-SiO}_2\text{-H}_2\text{O}$ ), it provides valuable insights into the thermodynamics of synthetic and natural granitic liquids and the processes that form and modify granites.

Goranson (1936) published his seminal study of the albite-water system more than 60 years ago. Since that time, numerous authors have conducted phase-equilibrium, volumetric, calorimetric, spectroscopic, and theoretical evaluations of dry and hydrous albitic melts. Despite these efforts, many important measurements have not been made and discrepancies remain. For example, many phase-equilibrium studies have provided either no-reaction results, or poorly constraining half-reversals, and in some cases conclusions have been drawn on the basis of synthesis experiments alone. To date, however, no study has attempted to critically evaluate and integrate the data.

Despite the limitations in the database, many thermodynamic models have been proposed for the albite-water system (e.g., Wasserburg 1957; Kadik 1971; Burnham and Davis 1974; Burnham 1974, 1975, 1981; Stolper 1982; Silver and Stolper 1985; Burnham and Nekvasil 1986; Blencoe 1992; Blencoe et al. 1994; Wen and Nekvasil 1994; Zeng and Nekvasil 1996). Most are based on selected sets of phase-equilibrium and/or thermodynamic data, and several were developed in accordance

with hypothetical speciation schemes. In addition, each includes one or more simplifying assumptions concerning the activity/composition relations of the melt species (e.g., ideal mixing, Henry's Law, or regular solution behavior). None of the published models is, however, consistent with all the high-quality data for the system.

Therefore, in this paper and a companion study of hydrous albitic melts (Anovitz and Blencoe, in preparation), we evaluate the published phase-equilibrium, volumetric, and calorimetric data on the dry and wet melting of high albite. The primary objectives of this work are to: (1) identify the well-reversed phase-equilibrium data; (2) determine the extent to which these data constrain melting relations in  $P$ - $T$ - $X$  space; (3) evaluate the available thermodynamic data; and (4) combine the best phase-equilibrium and thermodynamic data into a consistent model for the melting of albite that properly accounts for the uncertainties.

### ANALYSIS OF EXPERIMENTAL DATA

Evaluation of phase-equilibrium data is never a completely unambiguous process. Discrepancies commonly occur among data sets for which there is no obvious explanation, and choices must be made. Nonetheless, several principles can be applied. The most significant is that only reversed experimental data should be accepted for locating phase boundaries (cf. Roedder 1959; Fyfe 1960; Holloway and Wood 1988; Anovitz and Essene 1987; Berman and Aranovich 1996). Whereas no-reaction and synthesis data can give correct results, they are commonly erroneous and nearly always ambiguous. This is as true for high-temperature and melt-bearing systems as it is for lower

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temperatures or for solid-solid reactions, regardless of the obvious benefits of increased reaction rates at high temperatures. Although it is also true that apparently reversed experiments can defy simple interpretations (cf. Goldsmith and Newton 1974; Perkins et al. 1981; Pattison 1994), this does not validate other, less rigorous approaches.

In this paper and its forthcoming companion study on the albite-water system, therefore, we rely on reversed experimental data to constrain the phase equilibria of the system albite-water. No-reaction data points are used only where absolutely necessary, and the ambiguities of such situations are carefully noted. This analysis shows that many of the apparent discrepancies between phase-equilibrium results disappear when the original data are evaluated properly.

### THE DRY MELTING OF HIGH ALBITE

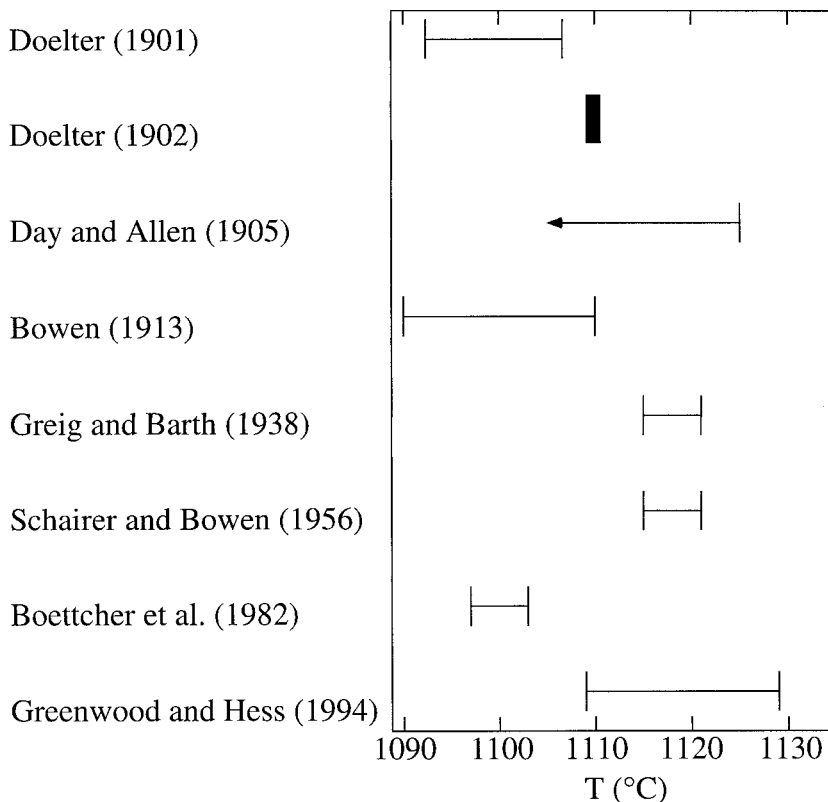
To determine the thermodynamic mixing properties of hydrous albite melts and more complex granite analogues, it is first necessary to understand the thermodynamics of the dry melting of high albite. This is because the Gibbs free energy of fusion of high albite ( $\Delta G_{\text{fus}}$ ), calculated from the dry melting reaction, and the activity of liquid albite in an albite-water melt determine the composition of the melt along the hydrous liquidus. Thus,  $\Delta G_{\text{fus}}$  must be known to develop a thermodynamic model for any multicomponent melt system that includes  $\text{NaAlSi}_3\text{O}_8$ . Unfortunately, there appear to be serious discrepancies among the phase-equilibrium data for the dry melting reaction and between the phase-equilibrium and thermodynamic data. The latter has led to several

theories concerning the structure of albitic melts (e.g., Boettcher et al. 1982, Wen and Nekvasil 1994; Zeng and Nekvasil 1996). It is therefore essential to assess properly the available data to determine whether these discrepancies are real, or functions of uncertainties in the data.

### Phase-equilibrium studies at 1 atm

At least eleven sets of data have been obtained that constrain the melting point of albite at 1 atm [Joly 1891 ( $1175 \pm 5$  °C); Cusack 1896 (1172 °C); Doelter 1901 ( $1099.5 \pm 7$  °C), Doelter 1902 (1110 °C); Day and Allen 1905 ( $<1125$  °C); Bowen 1913 ( $1100 \pm 10$  °C); Greig and Barth 1938 ( $1118 \pm 3$  °C); Schairer and Bowen 1956 ( $1118 \pm 3$  °C); Birch and LeComte 1960 (experimental limit  $<1135$ – $1154$  °C, fitted equation 1115 °C); Boettcher et al. 1982 ( $1100 \pm 3$  °C); Greenwood and Hess 1994 ( $1119 \pm 10$  °C); Fig. 1]. The reasons for the disagreement among these results are uncertain, but probably can be attributed to differences in experimental techniques, albite starting materials with differing compositions or degrees of Al-Si ordering, and possibly to the thermal history of the liquid. For instance, the early "meldometer" studies of Joly (1891) and Cusack (1896) probably suffered from poor temperature calibration, but the discrepancies among the remaining data are more difficult to explain.

The results occur in two clusters, both apparently reversed. The first, near 1100 °C, is supported primarily by the experiments of Bowen (1913) and Boettcher et al. (1982). The data of Doelter (1901) are similar. Day and Allen (1905) first worked



**FIGURE 1.** The melting temperature of high albite at 1 atm as determined by several investigators. The data of Joly (1891;  $1175 \pm 5$  °C), Cusack (1896; 1172 °C) and Birch and LeComte (1960) are not shown.

on a sample from Mitchell Co., North Carolina, which contained approximately 86.4 percent albite. This produced what may have been incipient melting at 1100 °C and definite melting at 1125 °C. Using Amelia albite "the effects noted above reappeared in the same order" (Day and Allen 1905, p. 121). Thus, Day and Allen also appear to have observed melting in Amelia albite at 1100 °C.

The second cluster of melting temperatures occurs near 1118 °C. This value is based primarily on the experiments of Greig and Barth (1938) and Schairer and Bowen (1956). Birch and LeComte (1960) give an equation that yields 1115 °C, although their only experiment at 1 bar constrains the temperature to less than 1135–1154 °C. The 1 bar value of Birch and LeComte (1960) may have been derived from the work of Grieg and Barth (1938). Greenwood and Hess (1994) determined melting rates at 1125, 1175, and 1200 °C, which they extrapolated to a melting temperature of  $1119 \pm 10$  °C. Unfortunately, descriptions of these experiments are available only in abstract form, and insufficient information is provided to properly evaluate the results.

Schairer and Bowen (1956) suggested that the thermal history of the liquid plays an important role in the crystallization of high albite. In their studies, liquids that formed at temperatures between 1500 and 1600 °C failed to crystallize at 1025 °C (well below the melting point), even after five years. This result clearly demonstrates the danger of using no-reaction data to determine the equilibrium temperature of a univariant reaction. When Schairer and Bowen (1956) annealed (acclimated) the same samples at progressively lower temperatures above the melting point for up to several months, albite began to grow in a few hours at 1050 °C. This result was reproduced by Boettcher et al. (1982), and both sets of investigators attributed it to changes in melt structure as annealing progressed, implying that the stable structure of the melt varies with temperature.

Boettcher et al. (1982) further argued that the use of high-temperature glasses can lead to metastable crystallization of albite under melt-stable conditions. A melt with a disequilibrium structure will have a higher (less-negative) Gibbs free energy than one with the stable melt configuration. Under these conditions, the apparent stability region of crystalline high albite will be extended to higher temperatures. Boettcher et al. (1982) noted that in the experiments of Schairer and Bowen (1956), the Gibbs energy available was too small for nucleation to occur, given the high viscosity of the melt. Thus, the apparent contradiction between the failure of the metastable melt to crystallize below the equilibrium melting point in the experiments of Schairer and Bowen (1956), and the metastable crystallization of such a melt above that temperature suggested by Boettcher et al. (1982), was probably due to the presence of submicroscopic albite nuclei in the latter. Boettcher et al. (1982) concluded that, because the experiments of Bowen (1913) and Day and Allen (1905) were conducted using only crystalline albite, whereas those of Greig and Barth (1938) and Schairer and Bowen (1956) used glasses seeded with albite, the results of the former, corroborated by Boettcher et al., are more likely to be correct.

This hypothesis, however, has been disputed by Navrotsky et al. (1982). These authors noted that Taylor and Brown (1979)

and Taylor et al. (1980) found that radial distribution functions from X-ray scattering data on three glasses (one quenched from 1800 °C one cooled from 1600 to 1118 °C over a period of 376 hours, and one formed from Amelia albite at 1180 °C) were essentially identical. The X-ray scattering data showed that the melting transition involved a change from a four-membered ring structure to one consisting of six-membered rings, but no observable repolymerization of the glass structure occurred during slow cooling.

It is also possible that the discrepancies between the different experiments were caused by compositional differences among the albite starting materials. The sources and compositions of the materials used in these studies are listed in Table 1. The exact compositions of some of the materials used in the early experiments are unknown, but the compositions of the remaining albites are similar. As shown below, these variations are insufficient to yield the necessary activity reductions. Thus, compositional variations do not appear sufficient to explain the differences among the melting temperatures.

Navrotsky et al. (1982) also considered the effects of composition on the crystallization behavior observed by Schairer and Bowen (1956) and Boettcher et al. (1982). They proposed that high albite occurs over a small but finite compositional range on the  $\text{SiO}_2\text{-NaAlSi}_3\text{O}_8$  join. They further suggested that the maximum melting temperature of this material need not fall at the composition of end-member albite, and presented a semiquantitative phase diagram where the peak fusion temperature of ~1140 °C occurs at an  $\text{Al}/(\text{Al}+\text{Si})$  approximately 1% higher than for  $\text{NaAlSi}_3\text{O}_8$ . Navrotsky et al. (1982) examined a sample of Tiburon albite, similar to that used by Boettcher et al., and found that it contained a small amount of quartz (<1%). They also suggested that the synthetic albite glass used by Boettcher et al. might be Si-rich due to alkali loss on heating. If so, the 1100 °C melting temperature observed by Boettcher et al. may apply to a slightly Si-rich albite. The crystallization of glasses formed at high temperatures and annealed just above the melting point could then be due to the formation during annealing of microcrystalline nuclei of the maximum melt composition. Unannealed glasses would fail to crystallize due to the absence of these nuclei.

There are, however, several difficulties with this hypothesis. First, as Navrotsky et al. (1982) noted, once the composition of albite is allowed to be bivariant, the compositions of the melt and remaining solids should differ. Although they attempted to verify this prediction analytically no such compositional inhomogeneities were found within an error of  $\pm 0.01$  in  $\text{Al}/(\text{Al} + \text{Si})$ . Second, it is unclear why the compositional variations in the synthetic glasses made by both Schairer and Bowen (1956) and Boettcher et al. (1982) should be so similar (to judge by the experimental results) to each other and to those in the natural starting materials. To begin with, simple addition of silica to albite cannot yield the same bulk composition as alkali loss, which does not change the  $\text{Al}/(\text{Al} + \text{Si})$  ratio. If small compositional variations have the large effects on melting temperatures that Navrotsky et al. (1982) propose, then these materials should have yielded very different melting temperatures. Finally, as discussed in greater detail below, it is unclear whether such large temperature shifts are thermodynamically reasonable.

**TABLE 1.** Sources of crystalline albite used for phase equilibrium experiments

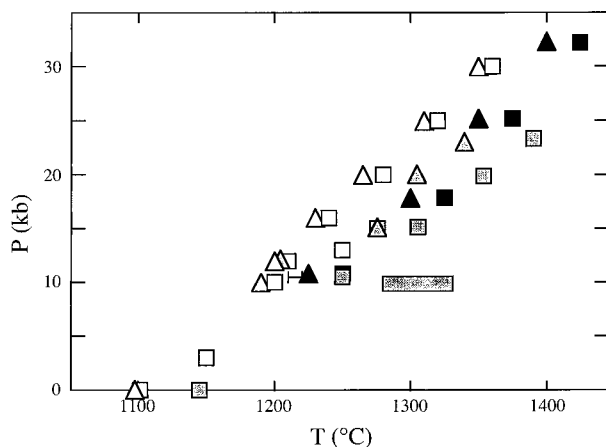
<b>1 atmosphere experiments</b>	
Joly (1891)	unknown
Cusack (1896)	Mourne Mountains, Ireland
Doelter (1901)	Pfitsch, Italy
Doelter (1902)	Pfitsch, Italy
Day and Allen (1905)	Mitchell Co., North Carolina and Amelia, Virginia
Bowen (1913)	Amelia, Virginia
Greig and Barth (1938)	synthetic albite in glass matrix
Schairer and Bowen (1956)	synthetic albite in glass matrix
Birch and LeComte (1960)	Amelia, Virginia or Varuträsk, Sweden
Boettcher et al. (1982)	synthetic and from Tiburon, California (disordered)
Greenwood and Hess (1994)	Amelia, Virginia
<b>High pressure experiments</b>	
Khitarov and Kadik (1973)	unknown
Birch and LeComte (1960)	Amelia, Virginia and Varuträsk, Sweden
Boyd and England (1963)	synthetic albite
Boettcher et al. (1982)	synthetic and from Tiburon, California (disordered)
Nekvasil (1992)	unknown
<b>Environments and approximate compositions of natural materials</b>	
Mourne Mountains albite – unknown	
Pfitsch albite – environment unknown; 0.32 wt% CaO	
Mitchell Co. – pegmatite; $\text{Na}_{0.85}\text{Ca}_{0.09}\text{K}_{0.04}\text{Fe}_{0.07}\text{Al}_{1.09}\text{Si}_{2.92}\text{O}_8$ (oligoclase; Day and Allen 1905; Deer et al. 1963)	
Varuträsk, Sweden – pegmatite; $\text{Na}_{0.988}\text{K}_{0.0045}\text{Ca}_{0.0125}\text{Li}_{0.0008}\text{Fe}_{0.0025}\text{Al}_{1.013}\text{Si}_{2.989}\text{O}_8$ (Deer et al. 1963)	
Tiburon, California – vein in glaucophane schist; $\text{Na}_{0.993}\text{K}_{0.001}\text{Al}_{0.989}\text{Si}_{3.000}\text{O}_8$ , Ti, Fe, Mg, Ca, and Ba undetectable by electron microprobe, $\text{Fe}_2\text{O}_3$ 0.07 wt. % by atomic absorption (Crawford 1966; Evans, personal communication.; Crawford, personal communication; A.A. analysis by K.V. Rogers)	
Amelia, Virginia – pegmatite; analyses vary significantly. May be compositionally zoned. Deer et al. (1963) give results ranging from $\text{Ab}_{92.2}$ to $\text{Ab}_{98.5}$ , with all but one greater than $\text{Ab}_{96.4}$ .	

The reasons for the observed discrepancies therefore remain uncertain. Despite the fact that the X-ray scattering data of Taylor and Brown (1979) and Taylor et al. (1980) revealed no differences between annealed and unannealed glasses, the results of Schairer and Bowen (1956) and Boettcher et al. (1982) are still suggestive that some significant difference exists. In addition, it remains possible that the discrepancies are simply due to uncertainties in temperature calibrations. Further work is needed to resolve these inconsistencies and to clearly define the melting temperature of high albite at 1 bar.

Nonetheless, to develop a thermodynamic model for the dry melting of high albite, a choice must be made among the various discrepant sets of 1 atm results. Boettcher et al. (1982) partially melted both synthetic high albite and disordered Tiburon albite at 1101 °C in runs without any glass in the starting material. A synthetic albite sample that partially melted at 1104 °C crystallized at 1098 °C. These results do not suffer from the uncertainties inherent in data obtained using high-temperature melts. Assuming that all of the albite crystals in these experiments were completely disordered, or nearly so, and with no analytical data to support the hypothesis of Navrotsky et al. (1982), we use the results of Boettcher et al., which suggest that the fusion of high albite occurs at  $1100 \pm 3$  °C at 1 atm.

#### Phase-equilibrium studies at $P > 1$ atm

Four sets of phase-equilibrium data directly constrain the high-pressure melting of high albite (Birch and LeComte 1960; Boyd and England 1963; Boettcher et al. 1982; Nekvasil 1992). The  $P$ - $T$  location of the reaction also can be approximated by extrapolating the hydrous liquidus data of Khitarov and Kadik (1973) to anhydrous conditions. The results obtained by these investigators are shown in Figure 2. These include not only



**FIGURE 2.** Experimental phase-equilibrium data constraining the dry melting of high albite as presented by the original authors including no-reaction and other non-reversal experiments. Squares = melt field, triangles = high albite field. Shaded = Birch and LeComte (1960). Black = Boyd and England (1963). Open = Boettcher et al. (1982). Bracket = Nekvasil (1992).

half-reversals, but also no-reaction experiments and all other results assumed by the original authors to constrain the location of the melting reaction. Unfortunately, there are major discrepancies among the various results if the original interpretations of the authors are accepted. Boyd and England (1963) claimed that their data were in reasonable agreement with those of Birch and LeComte (1960) at pressures up to 18 kbar, but considered that their higher-pressure data indicated a

lower melting temperature. The data of Boettcher et al. (1982) suggest temperatures significantly lower than those determined by either of the previous experimentalists. To evaluate these data further, therefore, it is necessary to examine individual data points and determine which represent true half-reversals.

Birch and LeComte (1960) performed experiments on the dry melting of high albite from 1 bar to 25 kbar. As noted by Boettcher et al. (1982), the argon and nitrogen pressure media used in these experiments probably preclude contamination of Birch and LeComte's samples by H<sub>2</sub>O or H<sub>2</sub>, which would have lowered the melting temperatures, and may have been a problem in later work (see Kress et al. 1988). In addition, because these experiments were performed in a hydrostatic apparatus, no pressure correction due to friction is needed. In six of ten experiments, Birch and LeComte used paired capsules: one containing albite and the other albite glass. In seven of the ten, including the experiment at 1 bar, albite melted. Thus, these results constrain the maximum temperature at which the melting reaction can lie for the albite used in the experiments. Unfortunately, the ordering states of the albite samples from Amelia, Virginia, and Varuträsk, Sweden, used in these experiments were not reported. The metastable melting of low or intermediate albite should occur at temperatures below the equilibrium melting point of high albite, and the melting of high albite could, therefore, occur at temperatures above the albite-melting half-reversals obtained. Thus, the experiments of Birch and LeComte (1960) provide somewhat ambiguous constraints on the melting temperature of high albite.

In two paired-capsule experiments performed by Birch and LeComte (1960), at 11.76–12.24 kbar, 1198–1210 °C and 15.00–15.12 kbar, 1274–1279 °C, albite glass crystallized in one of the samples. Unfortunately, interpretation of these results is also somewhat ambiguous. First, Boyd and England (1963) reported that albite glass can crystallize during run-up, and Boettcher et al. (1982) suggested that albite melt can form quench crystals on cooling. In addition, in the second of the Birch and LeComte experiments, while albite glass crystallized in one of the capsules, albite melted in the other. This could be due to thermal gradients in the experimental apparatus, but it makes interpretation of the result difficult. Metastable crystallization may have occurred, or appeared to occur, if run-up or quench effects are a problem, under conditions where melt is stable. We have therefore chosen to ignore the crystallization results of Birch and LeComte (1960), although the 12 kbar datum is in good agreement with the results of Boettcher et al. (1982, Fig. 1).

Boyd and England (1963) performed experiments to constrain the dry melting of albite from 10.8 to 32.3 kbar using a piston-cylinder apparatus. As noted by Boettcher et al. (1982) and Kress et al. (1988), however, it is likely that hydrogen entered Boyd and England's charges as a result of the hydrous talc and pyrophyllite used in their furnace assemblies. There were also significant temperature gradients (~25 °C) across their capsules. Nevertheless, their results are similar to those of Birch and LeComte (1960).

As noted above, Boyd and England (1963) discovered that albite glass tended to crystallize during run-up. They therefore began their crystallization experiments by raising the tempera-

ture into the liquid field and holding it there briefly. These authors also suggested, however, that the duration of this pre-treatment may not have been sufficient to re-melt crystals formed during run-up. Unfortunately, except for a series of 25.1 kbar runs held at 1400 °C, 13 kbar, for 5 minutes, no details are provided concerning the pressures, temperatures and durations of this process. In addition, run times were short (<3 hours) and metastable crystallization may have occurred after the final *P-T* conditions were achieved. Because of these uncertainties, we have not used the crystallization data of Boyd and England (1963).

Boyd and England (1963) also performed two melting experiments in which albite crystallized hydrothermally from glass was used as a starting material. The first experiment, run for two hours at 1250 °C, 10.8 kbar, partially melted. The second, run for three hours at 1225 °C, 10.8 kbar, did not melt. The first result provides a half-reversal, as this synthetic material is undoubtedly high albite, but if water was present, the dry melting curve could still lie at higher temperatures than those observed. The second experiment provided only a no-reaction result, which does not limit the minimum temperature of the reaction. Because run times were short, lack of melting may have been controlled kinetically.

Boettcher et al. (1982) investigated the dry melting of albite in a piston-cylinder apparatus using salt-cell pressure media. All of their experiments above 1 atm started with either a natural albite from Tiburon, California, which had been heated to disorder it, or a synthetic albite. Therefore, melting of these materials establishes maximum dry melting temperatures. Unfortunately, Boettcher et al. (1982) only crystallized one melt-bearing sample to reverse the equilibrium at 1 atm. At higher pressures they concluded from experiments in which no melting was observed that crystalline albite was stable under those conditions. These are no-reaction experiments that do not unambiguously constrain the minimum melting temperature.

Analysis of the data of Boettcher et al. (1982) is further complicated by the possibility of water contamination, which would lower melting temperatures and affect the interpretation of their data. Boettcher et al. (1982) were aware of this problem, and took steps to avoid it. The furnace assemblies were carefully dried, and the samples shielded with hematite to prevent hydrogen from diffusing into the charge. In addition, firing the natural material to disorder it would also be likely to decrepitate any fluid inclusions it contained, and thus these are unlikely to be a major source of water. Nonetheless, subsequent spectroscopic examination (Fine and Stolper 1985; Kress et al. 1988) revealed that albite glasses produced using an apparatus similar to that of Boettcher et al. (1982) contained up to 0.86 wt% H<sub>2</sub>O. Thus, the melting temperatures obtained by Boettcher et al. (1982) may be slightly too low.

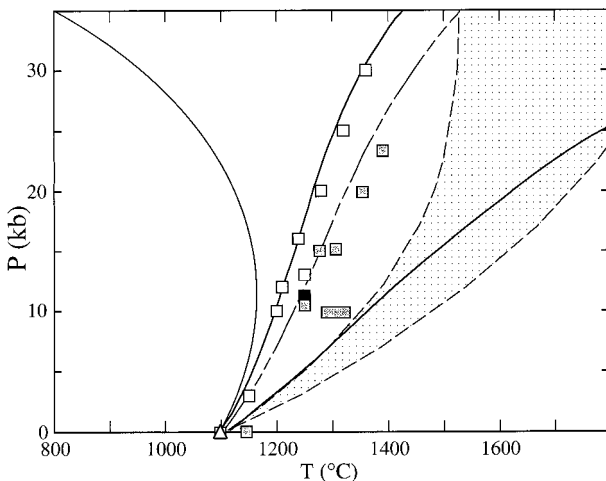
An additional constraint on the position of the melting reaction was reported by Nekvasil (1992) and Wen and Nekvasil (1994) at approximately 1210–1220 °C, 11 kbar. While generally consistent with results obtained in other studies, insufficient details are provided to allow the accuracy of this result to be assessed.

Finally, experiments on the hydrous fusion of high albite summarized by Khitarov and Kadik (1973) also can be used to con-

strain the dry melting of albite. Although their results do not directly apply to the anhydrous system, they can be extrapolated to the anhydrous boundary to obtain approximate melting temperatures for dry albite. Unfortunately, these data are only presented in graphical form, and are of uncertain quality because Khitarov and Kadik (1973) did not present a critical evaluation of the original experiments. Nonetheless, their diagram suggests temperatures that are only slightly higher than the results of Boettcher et al. (1982) and in reasonable agreement with results from other experimentalists, given a 10–20 °C uncertainty.

The foregoing analysis thus suggests that the reaction remains poorly constrained, despite the long history of experimental work on this system. Above 1 atm, even the best half-reversals are of uncertain reliability. Only the data of Birch and LeComte (1960) appear free from the uncertainties introduced by the possibility of water contamination, and these were performed with starting materials of uncertain ordering state and at best limit only the maximum temperature of the reaction.

If we ignore the effects of water contamination and ordering state, however, and compare only those experiments that otherwise are true half-reversals, it is apparent that many of the discrepancies among the high-pressure results are largely caused by overinterpretation of the data. When only the limits imposed by the half-reversal data are considered, the apparent inconsistencies are eliminated (Fig. 3). Unfortunately, the remaining data do not tightly constrain the  $P$ - $T$  conditions of the reaction, as all of the data available only limit the maximum reaction temperature.



**FIGURE 3.** The dry melting of high albite as a function of pressure and temperature. Only half-reversals (see text) are shown. High albite melting half-reversals: open squares = Boettcher et al. (1982), shaded squares = Birch and LeComte (1960), solid square = Boyd and England (1963). High albite crystallization half-reversals: Open triangle = Boettcher et al. (1982). The central solid curve represents our fit to the data of Boettcher et al. (1982), and the curve with two short dashes shows our fit to the data of Birch and LeComte (1960). The two outer solid curves indicate the range of permissible locations for the reaction calculated using the uncertainties in the available thermodynamic data. The stippled area bounded by dashed lines is the  $P$ - $T$  range of uncertainty calculated by Wen and Nekvasil (1994) using uncertainties provided by available thermodynamic databases.

Correction for the potential effects of water and ordering state is difficult. If the positions of the maximum temperature half-reversals have been shifted to lower temperatures (into the high albite field) by the presence of water in the experiments of Boettcher et al. (1982) and Boyd and England (1963), and by ordering in the experiments of Birch and LeComte (1960), there are essentially no experimental constraints on the position of the dry melting reaction above 1 bar. As the water contents and ordering states of the experimental run products were not measured, no quantitative correction can be made. If, however, the thermodynamics of the reaction are well known, it is possible to calculate melting temperatures and evaluate these uncertainties.

### THERMODYNAMIC DATA

Thermodynamic calculations provide a possible solution to the dilemma posed by the uncertainties in the experimental phase-equilibrium data. If high quality thermodynamic data are available for high albite and liquid albite, and if these data are consistent with constraints imposed by available phase-equilibrium experiments, then a more-accurate location for the dry melting reaction and more reliable estimates of the Gibbs free energy of fusion can be calculated.

Unfortunately, as noted by several authors (Birch and LeComte 1960; Burnham 1981; Boettcher et al. 1982; Navrotsky et al. 1982; Bottinga 1985; Burnham and Nekvasil 1986; Kress et al. 1988; Wen and Nekvasil 1994; Zeng and Nekvasil 1996), when the thermodynamic data are constrained to fit the experimental results at 1 atm, the calculated  $P$ - $T$  location of the melting reaction at higher pressures appears to lie at significantly higher temperatures than indicated by the phase-equilibrium data. The explanations offered for this include (1) uncertainties in the entropy or volume of the reaction at 1 atm, and/or in the compressibility of albitic liquid; (2) contamination of run products by water; and (3) pressure-dependent speciation in the liquid. Thus, there are either systematic errors in all of the phase-equilibrium data, significant uncertainties in the thermodynamic data (or both), or dramatic changes in the melt as a function of pressure, so that thermodynamic properties measured at 1 bar do not represent those at the conditions of the phase-equilibrium experiments (cf. Boettcher et al. 1982; Navrotsky et al. 1982; Bottinga 1985; Wen and Nekvasil 1994; Zeng and Nekvasil 1996).

To evaluate whether the differences between the thermodynamic and experimental approaches are within experimental uncertainty, it is necessary to examine the primary sources of the thermodynamic data. Assuming that the phase-equilibrium data at 1 atm can be used as a starting point, calculation of the  $P$ - $T$  curve requires data on entropy as a function of temperature, and volume as a function of pressure and temperature for both crystalline and liquid albite.

### Volume and structural data

Before discussing the thermodynamic properties of albite, its structural state must be considered. Several authors have suggested that high albite ( $C1$ ) transforms to monalbite ( $C2/m$ ) at high temperatures (e.g., Ribbe et al. 1969; Smith 1974; Prewitt et al. 1976; Winter et al. 1979). The temperature of this

transition appears to be a function of the ordering state of the initial sample, but the equilibrium inversion temperature may be as low as 930 °C (Winter et al. 1979). Bottinga (1985) suggested that the differences among the 1 atm melting temperatures could be due to this polymorphism, but noted that the possible differences in entropy and volume between high albite and monalbite are probably insufficient to account for the discrepancies between the phase-equilibrium data and thermodynamic calculations of the  $P$ - $T$  slope of the reaction. For this paper, therefore, we have assumed that the properties of high albite are the most appropriate for thermodynamic calculations. This is justified from two standpoints. First, available data (Winter et al. 1979) suggest that the properties of monalbite are similar to those of high albite and, second, insufficient data are available to treat monalbite directly.

The molar volume of high albite as a function of temperature has been measured three times (Grundy and Brown 1969; Prewitt et al. 1976; Winter et al. 1979). Whereas the volume vs. temperature slopes of data from these studies are similar, the results of Winter et al. (1979), obtained from 25 to 1080 °C, yield volumes that are 2–4 Å<sup>3</sup> per unit cell (0.38–0.58 cm<sup>3</sup>/mol) larger than those of Grundy and Brown (1969) or Prewitt et al. (1976). This difference is well outside the precision of the measurements (~0.1 Å<sup>3</sup>). Unfortunately, although the discrepancies with the data of Prewitt et al. (1976) were noted by Winter et al. (1979), they were not explained. Because the results of Prewitt et al. (their Fig. 4 and discussions) indicate that their sample may not have been fully disordered, and because additional disordering is likely to increase unit cell volume, we have adopted the data of Winter et al. for the volume and thermal expansivity of high albite. Fitting these results yields:

$$V_{298}^0 = 100.845 (\pm 0.03) \text{ cm}^3 \quad (1)$$

$$V_T^0 (\pm 0.0186) = V_{298}^0 + 1.22105 \times 10^{-3} (\pm 0.0637)T + 0.869711 \times 10^{-6} (\pm 0.0473) T^2 - 0.131265 \times 10^3 (0.0081)/T \quad (2)$$

where temperature is in Kelvins. The values in parentheses are 1  $\sigma$  standard deviations in the coefficients (to the same power of ten), independent of the uncertainty in  $V_{298}^0$ . The fit was obtained by least-squares regression. The standard deviations reflect the quality of this fit, but do not account for uncertainties in the individual measurements (0.03–0.045 cm<sup>3</sup>). Data for monalbite were not included. The fit is relatively stable to at least 1850 K (beyond the range of the experimental data shown in Fig. 4), but Equations 1 and 2 project an increase in  $dV/dT$  that occurs near the high-albite–monalbite transition to higher temperatures, which adds uncertainty to the calculations.

Yoder and Weir (1951) used a Bridgman-type dilatometry apparatus to measure the compressibility of albite from Varuträsk, Sweden (Weir 1950) between 2000 and 10 000 atm. Albite from Amelia County, Virginia, used for many of the phase-equilibrium experiments, was found unsuitable for measurement. From their data, Yoder and Weir (1951) developed the relation:

$$V^0(P) = V^0(1 \text{ atm}, T) - 2.123 \times 10^{-4} P + 2.17 \times 10^{-9} P^2 \quad (3)$$

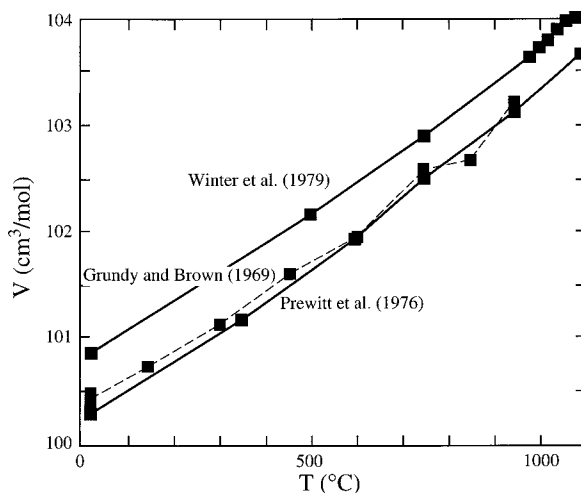


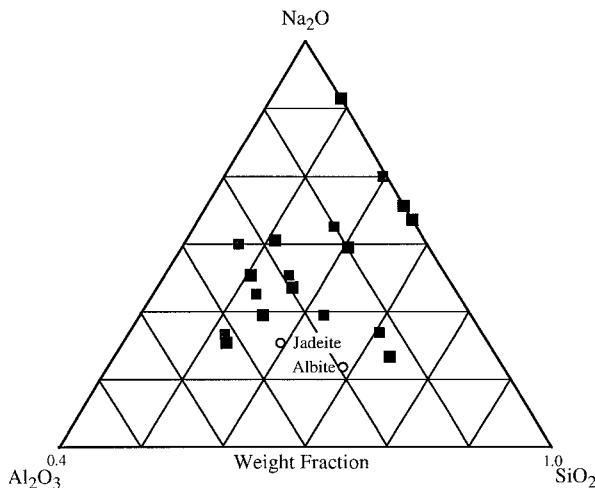
FIGURE 4. Measured molar volumes of high albite as a function of temperature. The smooth curve through the data of Winter et al. (1979) illustrates the fit provided by Equations 1 and 2 over the range of the experimental data. The dashed curve through the data of Grundy and Brown (1969) and the solid curve through the data of Prewitt et al. (1976) connect the data points from each set for clarity.

with pressure in atmospheres and volume in cm<sup>3</sup>/mol. Yoder and Weir (1951) provided no uncertainties for the coefficients in Equation 3, or the data on which it was based, but potentially significant sources of imprecision include: friction corrections, displacement uncertainties, and grain packing. In addition, neither the ordering state of the sample nor the temperature dependence of the compressibility was determined. Therefore, we have assumed that the compressibility of albite is independent of structural state and that  $d\beta/dT$  is negligible. The compressibilities calculated from this equation ( $\beta = 2.13/\text{Mbar}$  at 1 bar and  $2.02/\text{Mbar}$  at 4 kbar) are, in fact, somewhat larger than those calculated from velocity data by Birch (1961,  $\beta = 1.52/\text{Mbar}$  at 4 kbar) and Woeber et al. (1963,  $\beta = 1.33/\text{Mbar}$  at 1 bar).

The volumetric properties of liquid albite are less well known than those of crystalline albite. Stein et al. (1986) measured the densities of Na<sub>2</sub>SiO<sub>3</sub>-Al<sub>2</sub>SiO<sub>5</sub>-SiO<sub>2</sub> melts as a function of temperature using a double-bob Archimedean technique. These data were incorporated into the melt-density vs. composition model of Lange and Carmichael (1987). In all cases, however, the compositions used for these measurements are more sodic than albite, because of the high viscosity of molten albite (Fig. 5). Stein et al. (1986) fit their data to linear functions of Na<sub>2</sub>O, Al<sub>2</sub>O<sub>3</sub>, and SiO<sub>2</sub>, allowing calculation of density, and therefore molar volume, as a function of temperature for any composition of interest in the system. These equations yield:

$$V = 105.5 (\pm 0.7) + 5.00 (\pm 2.5) \times 10^{-3} T \text{ cm}^3/\text{mol} \quad (4)$$

for the thermal expansivity of liquid albite. The uncertainties quoted are large, and are probably minima, as values for liquid albite were extrapolated beyond the range of compositions over which the data were obtained. Although Stein et al. (1986) noted that their results are slightly different from those of Riebling



**FIGURE 5.** Compositions used to determine the expansivity and compressibility of melts in the system  $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ . Post-experiment compositions are plotted. Shaded squares = expansivity, Stein et al. (1986), samples 2, 8, 9, 10, 12, 15, A, and B; Solid squares = compressibility, Kress et al. (1988), samples 8, 9, 10, 12, 15, A, B, K, and R (sample R from Rivers and Carmichael 1987); Open circles = the compositions of albite and jadeite.

(1966), they also found that their estimate for liquid albite is close to that predicted by Mo et al. (1982) in a multicomponent model fitted to Riebling's data.

The scale of the uncertainty in our knowledge of the molar volume of liquid albite as a function of temperature is illustrated by comparing the results of Stein et al. (1986) to those of Arndt and Häberle (1973), who measured the thermal expansion of albite glass. At temperatures above the glass transition, the data of Arndt and Häberle (1973) yield:

$$V = 109.2 + 1.65 (\pm 0.27) \times 10^{-3} T \text{ cm}^3/\text{mol} \quad (5)$$

Whereas the volume calculated from this equation at 1100 °C (112.18 cm<sup>3</sup>/mol) is quite close to that from Stein et al. (112.37 cm<sup>3</sup>/mol), the values for the individual coefficients are quite different. Arndt and Häberle (1973) noted that their albite glass contained bubbles. Therefore, because Equation 5 was derived from measurements of linear thermal expansion ( $\alpha = 15 \pm 2.5 \times 10^{-6}/^\circ\text{C}$ ) and density ( $\rho = 2.382 \text{ gm}/\text{cm}^3$ ), it is likely that the absolute volumes derived from it are too high, and the agreement with Stein et al. at 1100 °C is probably fortuitous. The thermal expansion measured by Arndt and Häberle (1973) is close to that of Amelia albite glass measured by Vergano et al. (1967,  $\alpha = 20 \pm 2 \times 10^{-6}/^\circ\text{C}$ ), but significantly below the preferred value of Stein et al. (1986,  $\alpha = 47.4 \pm 23.7 \times 10^{-6}/^\circ\text{C}$ ) for liquid albite.

The compressibility of molten albite was measured ultrasonically by Kress et al. (1988) over a composition range (Fig. 5) similar to that examined by Stein et al. (1986). Their data yield the temperature dependence of the 1 atm compressibility:

$$\beta(T) = 5.78 \times 10^{-11} (32) - 2.6 \times 10^{-15} (5.6) T/\text{Pa} \quad (6)$$

( $T$  in K). The standard errors of the coefficients indicate large uncertainties, and the relation provides no estimate of the pressure dependence of the compressibility.

## Entropy and enthalpy

The entropy change of the high albite fusion reaction as a function of temperature can be derived from several sources. Hemingway et al. (1981) measured the heat capacity of analbite (high albite) from room temperature to 1000 K by differential scanning calorimetry and constrained their equation to 1400 K using the drop calorimetry results of Kelley (1960). This yielded:

$$C_p^0 = 671.4 - 0.1467 T + 3.659 \times 10^{-5} T^2 - 7974 T^{-1/2} + 3.174 \times 10^6 T^{-2} (\pm 0.3\%) \quad (7)$$

(J/mol·K,  $T$  in Kelvins). Haselton et al. (1983) measured the heat capacity of analbite from 5.77 to 371 K by adiabatic calorimetry, obtaining:

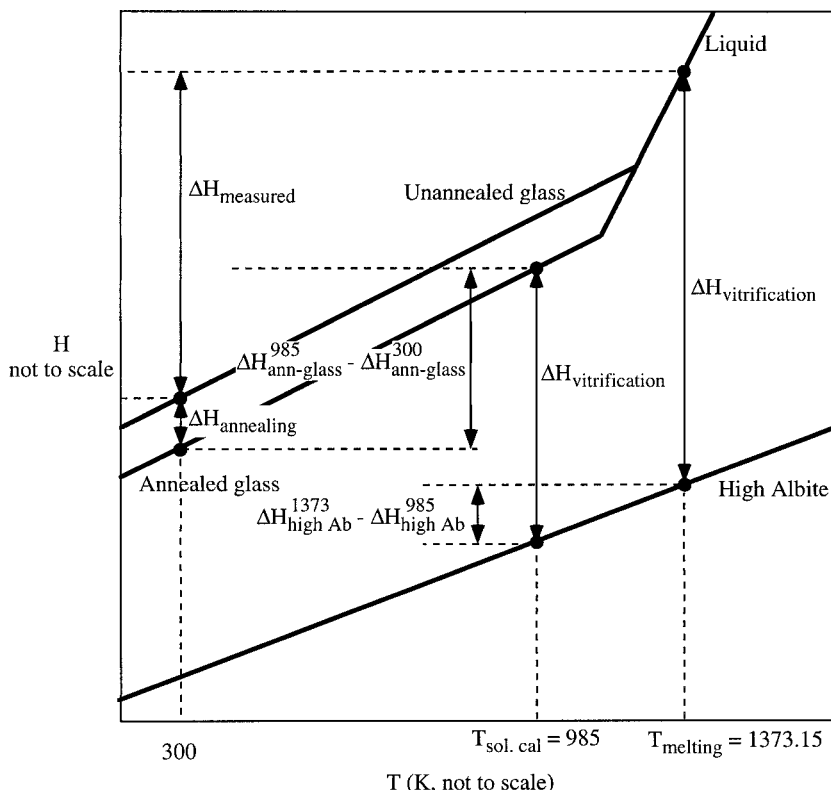
$$S_{298}^0 = 225.7 \pm 0.4 \text{ J/mol}\cdot\text{K} \quad (8)$$

which includes a zero-point entropy contribution for disorder (18.7 J/mol·K). These results are relatively precise, but must be extrapolated to higher temperatures to allow calculations over the entire temperature range of interest. The  $C_p$  vs.  $T$  function obtained by extrapolation is smooth and reasonable, but the extrapolation adds uncertainty to the calculation.

Stebbins et al. (1982, 1983) measured the enthalpy function of liquid albite by drop calorimetry from 1456.6 to 1809.5 K. Stebbins et al. (1983) applied several corrections to these data to obtain the enthalpy of fusion from their results, which are illustrated in Figure 6. During each measurement, the liquids quenched to an unannealed glass. Thus, the measured value is the difference between the enthalpy of the melt at high temperature and that of the unannealed glass at room temperature. To convert this to an enthalpy of fusion at the experimental temperature, or any temperature of interest within the range of the fitted equation given by Stebbins et al. (1983), the heat of annealing, obtained by drop calorimetry, is first added. This yields the difference between the enthalpy of the liquid at  $T$  and that of the annealed glass at room temperature.

The next correction is to add the heat of vitrification, the enthalpy difference between the annealed glass and solid albite. Several measurements have been made of this value (Kracek and Neuvonen 1952; Hlabse and Kleppa 1968; Holm and Kleppa 1968; Waldbaum and Robie 1971; Weill et al. 1980). Correcting for the heat of annealing where necessary, Stebbins et al. (1983) noted the similarity between the values of Weill et al. (1980) and Waldbaum and Robie (1971), and accepted the value of Weill et al. (1980). To utilize this value, the heat capacity of the annealed glass (Stebbins et al. 1982) is first used to calculate the change in enthalpy of the annealed glass between room temperature and the temperature at which the heat of vitrification is known ( $T_v$ ). This is subtracted from the total, and the heat of vitrification added. This yields the enthalpy difference between the melt at  $T$  and high albite at  $T_v$ . Finally, the enthalpy difference for high albite between  $T$  and  $T_v$  is subtracted from the total. This yields the heat of fusion at  $T$ . For this last calculation, the equation presented by Stebbins et al. (1983), a simplified version of that developed by Hemingway et al. (1981), was not used. Instead, we used the equation of Hemingway et al. (1981) to be consistent with other calcula-





**FIGURE 6.** Derivation of the enthalpy of fusion of high albite from the data of Stebbins et al. (1992, 1993). Corrections for annealing, changes in glass temperature, heat of vitrification, and changes in the temperature of crystalline albite are shown schematically. Neither the enthalpy nor the temperature axis is to scale.

tions in this paper. Fortunately, the differences are small. The enthalpy of fusion of high albite at 1100 °C so obtained is:

$$\Delta H_{\text{fus},1373.15}^0 = 62594.7 \text{ J/mol} \quad (9)$$

Several uncertainties are associated with the foregoing procedure. These include the precisions of the heats of annealing (approximately  $\pm 1$  kJ/mol) and vitrification (uncertain, assumed to be  $\pm 2$  kJ/mol); the enthalpy function for the glass ( $\pm 1.76$  kJ/mol); and the potential error resulting from extrapolation of the enthalpy of the solid from the highest temperature at which it was measured to that of the experiment (magnitude uncertain). The equation that Stebbins et al. (1983) fit to their uncorrected measurements of the enthalpy of the liquid-to-unannealed glass transition has a  $1\sigma$  fitting uncertainty of  $\pm 0.54$  kJ/mol. Thus, the enthalpy of fusion given by Stebbins et al. (1983) has a  $1\sigma$  uncertainty of at least  $\pm 3.3$  kJ/mol.

The purpose of calculating the enthalpy of fusion of high albite was not to calculate the location of the melting reaction at 1 atm because we have already concluded from available phase-equilibrium data that high albite melts at  $1100 \pm 3$  °C at 1 atm. Instead, the enthalpy equation was used to obtain the entropy of the melt as a function of temperature. Because the Gibbs free energy of fusion is zero at any equilibrium melting point, dividing the enthalpy of fusion by the absolute temperature (1373.15 K) yields the entropy of fusion at 1100 °C and 1 bar:

$$\Delta S_{\text{albite},\text{fus}}^0 = 45.961 \pm 2.4 \text{ J/mol}\cdot\text{K} \quad (10)$$

with the uncertainty derived from that of the enthalpy above. Combining this value with the temperature dependence of the

enthalpy of molten albite (Stebbins et al. 1982, 1983) and the entropy of high albite (Eq. 8) yields:

$$S_{\text{albite},\text{liq}}^0 = -1970.547 + 369.0 \ln(T) \text{ (J/mol}\cdot\text{K, } T \text{ in K)} \quad (11)$$

for the entropy of albite liquid. The uncertainty in this equation depends on the uncertainties in  $\Delta H_{\text{fus},1373.15}^0$  and both  $S_{298}^0$  and the heat capacity of high albite (Eqs. 7 and 8).

### THERMODYNAMIC UNCERTAINTIES

It is evident that large uncertainties remain in many of the thermodynamic quantities needed to calculate the melting relations of high albite. Some, such as the pressure dependence of the compressibility of molten albite, are unavailable. Others, including the thermal expansivity and 1 atm compressibility of molten albite and the heat capacity of high albite, either contain large errors or must be extrapolated beyond the temperatures at which they were measured. It is, however, possible to calculate the range of  $P$ - $T$  conditions for the reaction allowed by the data, and to determine whether a particular choice of thermodynamic data, within the estimated uncertainties, will fit the available half reversals.

The results of these calculations, shown in Figure 3, indicate that the fusion reaction for albite is as poorly known from a thermodynamic standpoint as it is from phase-equilibrium experiments. Because uncertainties cannot be established accurately for all the necessary thermodynamic quantities, the range of possible calculated positions for the reaction was estimated by varying the two parameters for the thermal expansivity

of the liquid (Eq. 4),  $d\beta/dP$  for the liquid, the constant in the liquid-glass enthalpy equation,  $V_{298}^0$ ,  $S_{298}^0$ , and the constant in the  $C_p$  equation for high albite. Each is independent, and was varied to the limits of the uncertainties given above, except for  $d\beta/dP$ , which was given a minimum value of zero, and a maximum equal to  $d\beta/dP$  for molten diopside (Rigden et al. 1989).

Figure 3 clearly shows that the range of uncertainty in the calculated location of the reaction resulting from uncertainties in the thermodynamic data overlaps the  $P$ - $T$  range of the phase-equilibrium data. Thus, no fundamental disagreement between the available phase-equilibrium and thermodynamic data for the dry melting of albite exists. The uncertainty we calculate in the pressure-temperature location of the albite melting curve is, however, significantly different from that calculated by Wen and Nekvasil (1994) using values from different thermodynamic databases. This implies that such a procedure may not always properly account for the actual imprecision in the original measurements.

### A THERMODYNAMIC MODEL

Because both the phase-equilibrium data and many of the thermodynamic quantities have relatively large uncertainties, several options can be explored in developing a consistent set of thermodynamic and phase-equilibrium data. To do so, we have first chosen to fit the thermodynamic data to the results of Boettcher et al. (1982). This was done for several reasons. To begin with, excluding the effects of water and ordering state, the half-reversals from all three sets of experiments are consistent with this choice. Second, whereas the results of Fine and Stolper (1985) suggest that water may have been present in the samples reacted by Boettcher et al. (1982), this has not been proven by direct analysis of the samples themselves. Therefore, as no clear proof exists that a correction is needed, and no data are available on which to base such a correction, we have used the melting experiments of Boettcher et al. (1982), but it should be recognized that the results obtained are relatively uncertain.

As noted above, however, the data of Boettcher et al. (1982) do not provide true half-reversals that constrain the minimum temperature of the reaction. Although the relative times and temperatures of the no-reaction experiments suggest that the reaction may not lie far below the upper half-reversals, no real constraints are available. Accordingly, we have assumed that the highest temperature no-reaction experiments of Boettcher et al. (1982) at each pressure approximate minimum temperature half reversals. This is in apparent contradiction to our assertion, made earlier in this paper, that only reversed data should be used to constrain phase equilibria. While this assertion remains true, we have made this assumption because some choice is required for modeling to proceed.

There are also several options in choosing which thermodynamic variables should be adjusted. We have arbitrarily chosen to fit the phase-equilibrium data by changing only three variables. Previous calculations of the dry melting of high albite (Birch and LeComte 1960; Burnham 1981; Boettcher et al. 1982; Navrotsky et al. 1982; Bottinga 1985; Burnham and Nekvasil 1986; Kress et al. 1988; Wen and Nekvasil 1994; Zeng and Nekvasil 1996) have all yielded 1 atm  $dP/dT$  slopes smaller

than those suggested by the lower-pressure phase-equilibrium data. This implies that the entropy and/or volume of the reaction at 1 atm are incorrect. As the volume of the liquid at 1 atm has the largest uncertainty among the various quantities, we have chosen to adjust it, lowering  $V^0$  by half the reported standard deviation, then lowering  $dV/dT$  until the appropriate initial slope was obtained. This procedure yielded:

$$V_{\text{liq}}^0 = 105.1 + 2.95 \times 10^{-3} T \text{ (cm}^3, \text{K)} \quad (12)$$

The volume of the liquid at 1100 °C calculated using Equation 12 is only 2.9% lower than that predicted by Equation 4. This is well within the uncertainties in the original measurements (Stein et al. 1986), and yields a thermal expansivity ( $\alpha = 28.1 \times 10^{-6}/^\circ\text{C}$ ) much closer to the values obtained by Vergano et al. (1967) and Arndt and Häberle (1973) on albite glasses at temperatures above the glass transition. The volume of the liquid would, however, need to be decreased by an additional 0.2–0.3% if the data on the volume of solid albite obtained by Grundy and Brown (1969) or Prewitt et al. (1976) were used instead of those of Winter et al. (1979).

To fit the higher pressure data, the change in the compressibility of the liquid with pressure was adjusted to fit the phase-equilibrium data of Boettcher et al. (1982), which place the reaction at, or slightly below, 1360 °C at 30 kbar. This yielded:

$$d\beta/dP = 1.515 \times 10^{-10}/\text{bar}^2 \quad (13)$$

and

$$dK/dP = (d\beta/dP)/(\beta^2) = 4.53 \quad (14)$$

where  $K$  is the bulk modulus. Although these values are larger than for most solids, they are close to those for other silicate liquids. Rigden et al. (1989) measured the high-pressure compressibilities of molten anorthite and diopside. Their  $dK/dP$  values, 5.3 and 6.9, respectively, are similar to that derived above (5.3 is equivalent to a  $d\beta/dP$  value of  $1.77 \times 10^{-10}/\text{bar}^2$  for albite), suggesting our estimate is reasonable.

The melting curve obtained from our calculations (Fig. 3) has a slightly sigmoidal shape. This is probably not correct, although it cannot be ruled out given the available data. The shape is probably caused by a combination of the uncertainties in the compressibility equation for liquid albite and the extrapolation of the volume and heat capacity data for high albite.

As noted above, the data of Fine and Stolper (1985) suggest that the samples reacted by Boettcher et al. (1982) contained some water, despite their efforts to assure dry experiments. If so, their melting half-reversals may be at temperatures below those of the true dry melting of albite. Alternatively, we can fit the data of Birch and LeComte (1960), although the ordering state of the albite used in their experiments is also uncertain. Examination of their half-reversal data (Fig. 3), however, shows that it is not distributed linearly. One experiment at 15.00–15.12 kbar lies at significantly lower temperatures than the trend of the remaining data. While this is also the paired experiment in which one sample melted and the other crystallized, it is the datum that best constrains the maximum temperature of melting.

Therefore, a second fit can be obtained, which is constrained by the data of Birch and LeComte (1960) at 15.00–15.12 kbar, 1274–1279 °C, again assuming that the reaction lies close to

this point. As their other data do not constrain the location of the reaction as tightly, we have chosen to represent their results by modifying the fit based on the data of Boettcher et al. (1982). The value of  $dV/dT$  for liquid albite was increased to obtain the appropriate slope, yielding:

$$V_{\text{liq}}^0 = 105.1 + 3.91 \times 10^{-3} T \text{ (cm}^3, \text{ K)} \quad (15)$$

The result of this calculation is shown in Figure 3. At 1100 °C, Equation 15 yields a molar volume for the liquid that is only 1.7% lower than that predicted by Equation 4, which is well within the uncertainties in the original measurements (Stein et al. 1986).

Finally, we can consider the effect of selecting the 1 bar melting temperature suggested by the work of Grieg and Barth (1938) and Schairer and Bowen (1956), rather than that obtained by Boettcher et al. (1982), i.e., 1118 °C instead of 1100 °C. This requires small additional changes in  $dV/dT$  and  $d\beta/dP$  for liquid albite to fit the high-pressure experimental data [ $2.48 \times 10^{-3}$  and  $1.64 \times 10^{-10}$  respectively for Boettcher et al. (1982), and  $3.43 \times 10^{-3}$  and  $1.64 \times 10^{-10}$  for Birch and LeComte (1960)]. At 1 bar, such a change increases the Gibbs free energy of the reaction at a given temperature by 815 J/mol.

## DISCUSSION

The discussions presented above suggest three important conclusions concerning the state of our knowledge of the dry melting of high albite. First, well-reversed phase-equilibrium experiments are critically important to accurate determination of crystal-melt phase relations. By applying standard reaction-reversal criteria to the high pressure melting data for high albite, most of the apparent discrepancies among the various data sets disappear. Second, once these criteria have been applied, our results indicate that the  $P$ - $T$  curve for the dry melting of high albite is poorly constrained by the available phase-equilibrium experiments, despite more than 60 years of investigation. Finally, consideration of the combined uncertainties in the available phase-equilibrium and thermodynamic data shows that there is no necessary disagreement between the two data sets. The range of possible reaction conditions allowed by uncertainties in the thermodynamic data includes the locations of all of the crystal-melt half reversals. Thus, there is currently no foundation for postulating complex changes in the microstructural properties of liquid albite at high pressures and temperatures.

Boettcher et al. (1982), Wen and Nekvasil (1994), and Zeng and Nekvasil (1996) used the differences between the calculated and experimentally determined melting relations of high albite to calculate a reduced activity of liquid albite along the experimentally located melting curve. Wen and Nekvasil (1994) and Zeng and Nekvasil (1996) suggest that the discrepancies are due to a measured compressibility for liquid albite that “does not reflect that of a structurally equilibrated melt and instead reflects the properties of a 1 atm melt configuration” (Zeng and Nekvasil 1996, p. 63). As noted above, however, the principal inconsistency between the thermodynamic calculations and phase-equilibrium data is the slope of the reaction at 1 bar. This is, therefore, independent of compressibility or any other pressure-dependent effect, and is solely a function of the change in entropy and volume of the reaction at 1 bar. Thus, pressure-dependent changes in the melt structure cannot explain much of the apparent incon-

sistency between the two sets of results. In addition, changes in melt structure with pressure must be reflected by changes in the thermodynamics of the bulk material. Thus, if the thermodynamic data were known completely, the calculated results would have to be consistent with the phase-equilibria experiments, assuming that the latter reflect the equilibrium state of the system. If both types of data are known with appropriate precision and accuracy, then they must agree, and no reduced activity will be indicated. Whereas reduced activities could be obtained by comparing high-pressure calculations based on 1 bar thermodynamic data with the actual equilibrium conditions, the meaningfulness of such results would be uncertain without direct structural determinations, as it is probable that several interpretations could account for the data.

The limitations in the available data thus call into question the current utility of complex microstructural models for the melting of high albite. Zeng and Nekvasil (1996) note that data necessary to constrain such models—direct measurements of the abundance of individual species or other descriptions of changes in melt structure as a function of pressure and temperature—are not yet available (however, see Stebbins and Sykes 1990; Sykes and Kubicki 1993). Thus, while microstructural models may eventually provide a framework for understanding the effects of microscopic states on macroscopic properties of albitic melts, neither the microscopic nor macroscopic data currently justify such modeling.

The thermodynamic data presented in this paper can also be used to evaluate the hypothesis of Navrotsky et al. (1982) that high albite melts over a range of compositions. If, as they propose, end-member high albite melts at 1105 °C, and the most stable low-silica albite at 1140 °C, then the Gibbs free energy difference between the two melting temperatures, calculated using the thermodynamic data presented above, is 1620.0 J/mol. This yields:

$$a(\text{Ab})_{\text{sol}}/a(\text{Ab})_{\text{liq}} = 0.871 \quad (16)$$

where  $a(\text{Ab})_{\text{sol}}$  is the activity of albite in the solid and  $a(\text{Ab})_{\text{liq}}$  is the activity of albite in the melt. Navrotsky et al. (1982) further suggested that the maximum melt has the approximate composition  $\text{Na}_{1.04}\text{Al}_{1.04}\text{Si}_{2.96}\text{O}_8$ . Defined relative to the albite-nepheline join, this composition corresponds to  $X_{\text{Ab}} = 0.96$ . As neither the melt nor the solid has the composition of end-member albite, the activity of albite in each is  $<1$ , but the maximum activity coefficient for the solid is 0.907, assuming that  $a(\text{Ab})_{\text{liq}} = 1$ . This negative deviation from ideality is unexpectedly large, and suggests that this hypothesis is unlikely to be completely correct.

Similarly, the difference in Gibbs free energy between 1100 and 1118 °C, the two suggested 1 atm melting temperatures, yields:

$$a(\text{Ab})_{\text{sol}}/a(\text{Ab})_{\text{liq}} = 0.930 \quad (17)$$

Although this value is within the extreme range of the compositions reported for Amelia albite (assuming ideal mixing and complete partitioning into the solid), it is unlikely for most of the experimental starting materials (Table 1). This result provides further confirmation that compositional variations are not likely to be the complete explanation for the differing experimental results.

Finally, whereas the thermodynamic quantities and equations presented in this paper reproduce the  $P$ - $T$  dependence of the dry melting of high albite within estimated uncertainties, their limitations should be carefully considered in any future applications. The available phase-equilibrium data have large uncertainties, and the adjustments made to fit the selected data are only one choice among many possibilities permitted by uncertainties in the original measurements. Thus, more precise and accurate data are needed to develop tightly constrained equations of state for high albite and dry albite melt.

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