

The fusion curve of albite revisited and the compressibility of NaAlSi₃O₈ liquid with pressure

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ABSTRACT

The 1 bar, thermodynamic properties of crystalline and liquid NaAlSi₃O₈ are used to calculate the fusion curve of albite to 10 kbar. The calculated temperatures ($\pm 2\sigma$) of the melting reaction are 1152 (± 7) °C at 3 kbar and 1247 (± 24) °C at 10 kbar. The location of the calculated fusion curve to 10 kbar is in excellent agreement with phase-equilibrium constraints on the *maximum* and *minimum* temperatures of the fusion curve at 3 and 15 kbar, respectively. Calculation of the melting reaction at pressures >10 kbar requires that the pressure dependence of the liquid compressibility ($K'_0 = dK_{T,0}/dP$, where $K_{T,0} = 1/\beta_{T,0}$) be known. On the basis of five half-reversal, crystallization experiments in the literature, which collectively provide *minimum* temperatures of the fusion curve between 12 and 32 kbar, K'_0 (derived from the Birch-Murnaghan relation) is constrained to be ≥ 10 for liquid NaAlSi₃O₈. A comparison with other silicate liquids shows that there is a strong, positive correlation between the compressibility at one bar ($\beta_{T,0}$) and K'_0 . In addition, data on the water-saturated fusion curve of albite are used to quantify the effect of small amounts of H₂O (≤ 1 wt%) on lowering the melting temperature of albite (≤ 68 degrees).

INTRODUCTION

The melting curves of the end-member rock-forming minerals are an essential source of thermodynamic data, particularly for the liquid state. Typically, the one-bar thermodynamic properties of the crystal and liquid are well known, and it is the pressure dependence of the liquid compressibility ($K' = \partial K_0 / \partial P$, where K_0 is the bulk modulus at one bar) that may be derived (e.g., Rivers 1985). The example highlighted here is the equilibrium between crystalline NaAlSi₃O₈ (albite) and liquid of the same composition.

Over the last two decades, there have been numerous attempts to reconcile phase-equilibrium constraints with calculations of the albite fusion curve from thermodynamic property measurements (e.g., Boettcher et al. 1982; Navrotsky et al. 1982; Bottinga 1985; Burnham and Nekvasil 1986; Kress et al. 1988; Wen and Nekvasil 1994; Anovitz and Blencoe 1999). In general, the experiments and calculations do not agree well, owing partly to problems with the phase-equilibrium experiments [e.g., contamination by water, sluggish kinetics, unknown ordering state of the albite; see Kress et al. (1988) and Anovitz and Blencoe (1999) for discussions] and partly to problems with calculations of the fusion curve from available thermodynamic data in the literature. It is the initial slope of the fusion curve (<10 kbar) that has been the most controversial.

For example, Anovitz and Blencoe (1999) and Wen and Nekvasil (1994) calculated albite melting temperatures at 10 kbar (with no adjustments for hypothetical speciation effects in NaAlSi₃O₈ liquid; Nekvasil, personal communication) that differ from each other by >180 °C. Moreover, the error envelope for the calculated fusion curve in these two studies (based on a propagation of the errors in the thermodynamic properties

used to calculate each curve) show little overlap below 10 kbar. Anovitz and Blencoe (1999) presented an error envelope that spans ~200 °C at 10 kbar, whereas Wen and Nekvasil (1994) report one that spans ~120 °C at this pressure and is displaced ~100 °C higher than that given by Anovitz and Blencoe (1999). In Figure 3 of Anovitz and Blencoe (1999), the error envelopes of the two studies are illustrated; in combination, the lowest and highest temperatures permitted for the calculated fusion curve at 10 kbar differ by ~300 °C. Such large errors preclude any efforts to constrain the value of K' for NaAlSi₃O₈ liquid from phase-equilibrium experiments on the albite melting reaction at high pressure.

This study was prompted by these two most recent analyses of the albite fusion curve, and it is shown here that when the best available thermodynamic property measurements are employed, the error envelope (at the 95% confidence level) spans only 48 degrees at 10 kbar. The primary cause for the discrepancy in published fusion curves for albite (and the widely variable error envelopes) resides with the volume of NaAlSi₃O₈ liquid at one bar, which has been measured directly by Knoche et al. (1992) and Lange (1996), with experimental errors that are $\leq 0.4\%$. Surprisingly, the volume equations for liquid NaAlSi₃O₈ used by Anovitz and Blencoe (1999) and Wen and Nekvasil (1994) differ from each other by more than 8% and differ from the measured values by ~3 and ~5%, respectively. Although of smaller magnitude, modifications are also required for the volume of crystalline albite in these studies, owing to a misprint in the reported volume given by Winter et al. (1979) for high albite at 25 °C. It is thus demonstrated that without consideration of the best available thermodynamic data, conclusions regarding the location of the fusion curve, the precision to which it can be calculated, and implications for melt speciation require revision. Perhaps most important, constraints on K' for liquid NaAlSi₃O₈ become feasible within the smaller error envelope.

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As a consequence, an additional goal of this study is to re-evaluate phase-equilibrium experiments on the location of the albite fusion curve at pressures >10 kbar, in order to derive the K' of liquid $\text{NaAlSi}_3\text{O}_8$. The dramatic reduction in the melting temperature of albite under water-saturated conditions at low pressure (Tuttle and Bowen 1958) is used in this study to quantify the effect of small amounts of dissolved H_2O (<1 wt%) on the melting temperature of albite. This in turn is used to examine the cause of the discrepancy among the phase-equilibrium results of Birch and LeComte (1960), Boyd and England (1963), Boettcher et al. (1982), and Nekvasil and Carroll (1996) for the albite melting reaction. Utilization of the crystallization (and not melting) experiments of all four studies allows the minimum value of K' for $\text{NaAlSi}_3\text{O}_8$ liquid to be obtained.

CALCULATION OF THE FUSION CURVE TO 10 KBAR

The equation used to calculate the $\text{NaAlSi}_3\text{O}_8$ crystal-liquid equilibria as a function of temperature and pressure is:

$$\Delta H_{T_f} + \int_{T_f}^T \Delta C_p(T) dT - T \left(\Delta S_{T_f} + \int_{T_f}^T \frac{\Delta C_p(T)}{T} dT \right) = - \int_{T_f}^P \Delta V_T(P) dP \quad (1)$$

where T_f is the one-bar melting temperature of crystalline albite, ΔH_{T_f} is the enthalpy of the liquid minus that of the solid at T_f , ΔS_{T_f} is the entropy of the liquid minus that of the solid at T_f , $\Delta C_p(T)$ is the heat capacity of the liquid minus that of the solid, and $\Delta V_T(P)$ is the volume of the liquid minus that of the solid. The requisite data needed to calculate the fusion curve include: (1) the melting temperature of high albite at one bar; (2) the enthalpy of fusion at one bar (from which the entropy of fusion is derived); (3) the heat capacity of crystal and liquid; and (4) the volume, thermal expansion, and compressibility of crystal and liquid. For calculations below approximately 10 kbar, the effect of not including K' is negligible, whereas at pressures >10 kbar, K' is increasingly important.

Because there has been considerable controversy concerning the initial slope of the albite fusion curve, it is useful to begin at pressures <10 kbar. This has the advantage that the value of K' for the liquid, which has not been measured directly, can be neglected with negligible error. Thus all the thermodynamic data that are necessary to calculate the fusion curve at <10 kbar have been measured directly. A brief description of the thermodynamic data used in this study is given below, which is critical for the assessment of errors.

The melting temperature at one bar

An extensive review of the literature on the melting temperature of crystalline albite at one bar is given in Anovitz and Blencoe (1999). The most definitive and thorough experiments (fully reversed, replications, etc.) are those of Boettcher et al. (1982). They report a value of 1100 ± 3 °C, which contrasts with the mean value measured by Schairer and Bowen (1956) of 1118 °C. Moreover, as discussed below, the higher temperature of Schairer and Bowen is incompatible with the Modreski experiment at 3 kbar [details of this experiment are described in Boettcher et al. (1982)]. Therefore, in agreement with the value accepted by Anovitz and Blencoe (1999) and Wen and Nekvasil (1994), a one-bar melting temperature of 1100 °C (1373 K) is used in all the calculations given below.

The enthalpy and entropy of fusion at one bar

Two different values for the enthalpy of fusion of albite at 1373 K, ΔH_{T_f} , are reported in the literature: 62.8 ± 2.1 kJ/mol (Stebbins et al. 1983) and 64.3 ± 3.0 kJ/mol (Richet and Bottinga 1984). From the relationship:

$$\Delta H_{T_f} - T_f \Delta S_{T_f} = 0 \quad (2)$$

the values for the entropy of fusion at 1373 K (ΔS_{T_f}) obtained from the two studies are 45.74 and 46.83 J/(mol·K), respectively. It makes little difference to the location of the calculated fusion curve as to which of these two sets of values are used (~1 °C difference at 3 kbar and ~3 °C degree difference at 10 kbar). In the present study, the mean of the values given in the two aforementioned studies has been used [$\Delta H_{T_f} = 63.55$ kJ/mol and $\Delta S_{T_f} = 46.29$ J/(mol·K)]. A formal propagation of the reported errors for each measurement on the mean leads to an error of ± 1.8 kJ/mol. The effect of the two sigma error (± 3.6 kJ/mol) on the mean value for ΔH_{T_f} leads to an uncertainty in the temperature of the albite fusion curve of ± 3 °C at 3 kbar and ± 8 °C at 10 kbar.

The heat capacity of crystalline albite

Berman (1988) and Hemingway et al. (1981) each present a different form of the equation for the heat capacity of high albite as a function of temperature, although they are both based on nearly the same calorimetric data set (Openshaw et al. 1976; Hemingway et al. 1981; Kelley 1960). Berman (1988) additionally used the data from White (1919). The two forms of the equation are sufficiently similar that the calculated fusion curve is unaffected by the choice of heat capacity function. Nonetheless, because the equation of Berman (1988) is designed for extrapolation to high temperature, it is used in this study. It has the following form [units are J/(mol·K)]:

$$C_p = 393.64 - 2415.5 T^{-0.5} - 7892800 T^{-2} + 1070640000 T^{-3}. \quad (3)$$

The heat capacity of liquid albite

The heat capacity of liquid $\text{NaAlSi}_3\text{O}_8$ is constrained by the drop-calorimetric measurements of enthalpy between 1249 and 1486 K by Richet and Bottinga (1980) and those of Stebbins et al. (1982) between 1457 and 1810 K. The combined data of both studies (1249 to 1810 K) lead to a temperature-independent value for the heat capacity of liquid $\text{NaAlSi}_3\text{O}_8$ of 358 J/(mol·K), whereas that reported by Stebbins et al. (1983) is 369 J/(mol·K). This difference in the liquid heat capacity leads to <2 °C difference in the calculated fusion curve at 10 kbar. In this study, the value derived from the combined data is used.

The volume of crystalline albite

The volume equation for crystalline albite that is appropriate for the fusion curve calculation is that for fully disordered albite in monoclinic symmetry. Wruck et al. (1991) presented unit-cell volumes for various albite crystals with different Al/Si ordering states. The unit-cell volume of albite that is fully disordered ($Q_{od} = 0$, where Q_{od} is the ordering parameter that describes Al/Si order) at 25 °C is 667.86 \AA^3 ($100.57 \text{ cm}^3/\text{mol}$), which is higher than the value of 665.95 \AA^3 ($100.28 \text{ cm}^3/\text{mol}$) given in Prewitt et al. (1976). This difference in volume is likely

caused by incomplete disorder of the high albite specimen of Prewitt et al. (1976). Winter et al. (1979) also reported a unit-cell volume for heat-treated, disordered albite at 25 °C, but there is a misprint in their paper. For the unit-cell parameters that they report ($a = 8.161 \text{ \AA}$, $b = 12.875 \text{ \AA}$, $c = 7.110 \text{ \AA}$, $\alpha = 93.53^\circ$, $\beta = 116.46^\circ$, $\gamma = 90.24^\circ$), the calculated unit-cell volume is 667.12 \AA^3 ($100.45 \text{ cm}^3/\text{mol}$) and not 669.8 \AA^3 ($100.85 \text{ cm}^3/\text{mol}$) as given in their Table 2. Anovitz and Blencoe (1999) noted the discrepancy between the reported results of Prewitt et al. (1976) and Winter et al. (1979) for high albite at 25 °C and chose to use the larger volume reported Winter et al. (1979) under the assumption that it was likely for fully disordered albite. According to the data of Wruck et al. (1991), the unit-cell volume of 667.12 \AA^3 from the data of Winter et al. (1979) reflects an albite crystal that is $\sim 80\%$ disordered ($Q_{\text{od}} = \sim 0.2$).

The difference in volume between the triclinic and monoclinic forms of albite was measured by Winter et al. (1979) at 980 and 1060 °C. The average difference is $0.23 \pm 0.07 \text{ cm}^3/\text{mol}$. Therefore, the volume at 298 K and 1 bar used in this study is that for fully disordered albite ($100.57 \pm 0.03 \text{ cm}^3$) to which $0.23 \pm 0.07 \text{ cm}^3$ is added at high temperature for the triclinic-monoclinic transition. The combined 2σ uncertainty ($\pm 0.16 \text{ cm}^3$) in the volume of crystalline albite, independent of the errors in the thermal expansion coefficient and the bulk modulus of crystalline albite (discussed below), leads to an uncertainty in the temperature of the calculated fusion curve of $\pm 1 \text{ }^\circ\text{C}$ at 3 kbar and $\pm 3 \text{ }^\circ\text{C}$ at 10 kbar.

The thermal expansion of crystalline albite

The thermal expansion coefficient for crystalline albite used in this study is that for high albite given by Fei (1995):

$$\alpha(T) = 0.2455 \cdot 10^{-6} + 0.7621 \cdot 10^{-8} (T - 298 \text{ K}) K^{-1} \quad (4)$$

which is based on the data of Prewitt et al. (1976) and Winter et al. (1979). As noted by Anovitz and Blencoe (1999), there is good agreement between those two studies for the thermal expansion of high albite. It is unlikely that the difference between the measured thermal expansion coefficient for disordered, triclinic albite and the unmeasured thermal expansion coefficient for disordered, monoclinic albite is $>20\%$ (the difference in α between low and high albite; Fei 1995). An uncertainty of $\pm 20\%$ on the thermal expansion coefficient for crystalline albite leads to a negligible effect on calculated temperatures of the fusion curve at pressures ≤ 10 kbar.

The compressibility of crystalline albite

All published data on the compressibility of albite have been for low albite (Yoder and Weir 1951; Angel et al. 1988; Downs et al. 1994). Anovitz and Blencoe (1999) used the compressibility equation given in Yoder and Weir (1951), which is based on macroscopic measurements of the change in volume of albite to 1 GPa in a Bridgman apparatus. Using in-situ X-ray diffraction in a diamond-cell, Angel et al. (1988) obtained the comparative compressibilities of anorthite, low albite, and high sanidine to 5 GPa; they reported a bulk modulus for low albite of $57.6 \pm 2.0 \text{ GPa}$. Downs et al. (1994) presented both the structure and compressibility of low albite from unit-cell parameter

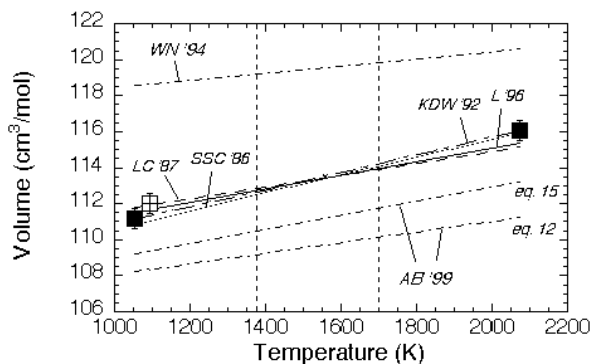


FIGURE 1. The volume of liquid $\text{NaAlSi}_3\text{O}_8$ as a function of temperature at one bar. The dashed-dot line labeled WN '94 is calculated from the equation used by Wen and Nekvasil (1994), the solid line labeled L '96 is from the equation of Lange (1996), the dashed line labeled KDW '92 is from the linear equation of Knoche et al. (1992), the dotted line labeled SSC '86 is from the equation of Stein et al. (1986), the dashed line labeled LC '87 is from the equation of Lange and Carmichael (1987), and the dashed-dot lines labeled AB '99 are calculated from equations 12 and 15 in Anovitz and Blencoe (1999). The solid squares are the measured volumes from Knoche et al. (1992), whereas the square with a cross inside is the measured volume from Lange (1996). The vertical dashed lines bracket the temperature interval of the albite fusion curve between 1 bar and 33 kbar.

measurements to 4 GPa; they obtained a bulk modulus (K) of $54 \pm 1 \text{ GPa}$ and a K' of 6 ± 1 from a fit of their volume data with pressure to a third-order Birch-Murnaghan equation.

Unfortunately, the compressibility of high albite has not yet been measured and may differ from that of low albite. For example, compressibility measurements on sanidine and microcline indicate that Al/Si disorder affects the bulk modulus. Values of 52.3 ± 0.9 and $57.2 \pm 1.0 \text{ GPa}$ were obtained for two sanidine samples that bracket the composition of a microcline sample with a bulk modulus of $63.3 \pm 2.2 \text{ GPa}$ (Angel et al. 1988; Hackwell 1993). The results for K-feldspar suggest that the bulk modulus of high albite may be $\sim 15\%$ lower (more compressible) than that determined for low albite. Conversely, it is also possible that the bulk modulus may be somewhat higher in disordered albite owing to the effect of putting two Si atoms around the oxygen site that is not bonded to Na in albite (R. Downs, personal communication). As a consequence, the unknown effect of disorder is estimated to give rise to an uncertainty on the bulk modulus of albite used in this study (54 GPa , from Downs et al. 1994) that may be as large as $\pm 15\%$. This error in K for crystalline albite leads to an uncertainty in the temperature of the calculated fusion curve that is negligible at 3 kbar and $\pm 2 \text{ }^\circ\text{C}$ at 10 kbar. As for the liquid, the effect of the solid K' on the fusion curve is unimportant below 10 kbar.

The volume of liquid $\text{NaAlSi}_3\text{O}_8$ at one bar as a function of temperature

Most of the problems with published calculations of the albite fusion curve are related to the volume of liquid $\text{NaAlSi}_3\text{O}_8$ at one bar (e.g., Anovitz and Blencoe 1999; Wen and Nekvasil

1994). This is surprising because direct volume measurements on $\text{NaAlSi}_3\text{O}_8$ liquid (Knoche et al. 1992; Lange 1996) are in good agreement with model equations in the literature (e.g., Stein et al. 1986; Lange and Carmichael 1987), which have been used to calculate the volume of liquid $\text{NaAlSi}_3\text{O}_8$ at one bar. Direct volume measurements were made at high temperature (1800 °C) using the Ir double-bob method by Knoche et al. (1992) and in the supercooled liquid region at 780 °C by Knoche et al. (1992) and at 819 °C by Lange (1996), with reported experimental errors that are $\leq 0.4\%$. The linear fit of Knoche et al. (1992) to their two data points falls within 0.4% (between 1373 and 1700 K; Fig. 1) of the volumes calculated for $\text{NaAlSi}_3\text{O}_8$ liquid from the models of Stein et al. (1986), Lange and Carmichael (1987), and Lange (1996).

In the present study, the model equation of Lange (1996) has been used to calculate the volume of liquid $\text{NaAlSi}_3\text{O}_8$ with temperature at one bar:

$$V^{\text{NaAlSi}_3\text{O}_8}(T) = 112.72 + 0.00382(T - 1373 \text{ K}) \text{ cm}^3/\text{mol} \quad (5)$$

A 2σ error in volume of $\pm 0.4\%$ over the temperature interval of the albite fusion curve leads to an uncertainty in the temperature of the calculated fusion curve of ± 3 °C at 3 kbar and ± 9 °C at 10 kbar. A 2σ uncertainty of $\pm 26\%$ in the thermal expansivity of the liquid leads to a negligible uncertainty in the temperature of the fusion curve below 10 kbar.

By neglecting these direct measurements, Anovitz and Blencoe (1999) erroneously concluded that the volume and thermal expansivity of liquid $\text{NaAlSi}_3\text{O}_8$ at one bar are not well known. This led them to present two new equations (their Equations 12 and 15) for the volume of liquid $\text{NaAlSi}_3\text{O}_8$ with temperature. These equations were derived by adjusting the model equation for liquid $\text{NaAlSi}_3\text{O}_8$ given by Stein et al. (1986):

$$V(T) = 105.5 (\pm 0.7) + 5.00 (\pm 2.5) \times 10^{-3} T \text{ (cm}^3/\text{mol)} \quad (6)$$

However, the adjustments of Anovitz and Blencoe to Equation 6, within the errors given for this equation, caused their two new volume equations to fall outside the errors on the measured volumes of Knoche et al. (1992) and Lange (1996), as illustrated here in Figure 1. Their adjusted equations are also outside the errors on the more general equation of Stein et al. (1986), from which Equation 6 was derived:

$$V(T) = \sum X_i [\bar{V}_{i,1673 \text{ K}} + \partial \bar{V}_i / \partial T (T - 1673)] \quad (7)$$

The form of this equation is designed to restrict its application to temperatures close to those of the experiments (1373–1873 K). The problem lies with the form of the equation given by Stein et al. (1986) for liquid $\text{NaAlSi}_3\text{O}_8$ in Equation 6 above. This led Anovitz and Blencoe (1999) to lower the value of the slope intercept in Equation 6 (i.e., the hypothetical volume of liquid $\text{NaAlSi}_3\text{O}_8$ at 0 K) by 0.4% and the slope (i.e., the thermal expansivity) by 41% for their Equation 12 (and 22% for their Equation 15). By applying these corrections at 0 K, and then integrating up to temperatures ≥ 1373 K, the resultant volume-temperature trend for their Equation 12 (and 15) plots outside the errors of Stein et al. (1986) for Equation 7 (Fig. 2)

and outside the errors of the measured volumes (Fig. 1). As a consequence, application of Equation 12 from Anovitz and Blencoe (1999) leads to a calculated fusion temperature for albite that is ~ 21 °C too low at 3 kbar and ~ 70 °C too low at 10 kbar (Fig. 3).

Wen and Nekvasil (1994), in contrast, used an hypothetical volume equation for $\text{NaAlSi}_3\text{O}_8$ liquid at one bar (chosen to obtain an optimal free energy function for the standard state of their hypothetical disproportionation reaction in the liquid; H. Nekvasil, personal communication), although they mistakenly cited Lange and Carmichael (1987) as their source for this equation. The volume equation given in their Table 1, $V(T) = 2.80 \times \exp[1.65 \times 10^{-3}(T - 298 \text{ K})]$ cal/bar, leads to liquid volumes between 1373 and 1773 K that are $\sim 5.7\%$ higher than those given by the model equation of Lange and Carmichael (1987), as shown here in Figure 2. In this case, application of their volume equation leads to a calculated temperature for the albite fusion curve that is ~ 42 °C too high at 3 kbar and ~ 115 °C too high at 10 kbar (Fig. 3). It is the location of their fusion curve at much higher temperatures than those indicated by available phase-equilibrium data that led Wen and Nekvasil (1994) to invoke a reduction in the activity of $\text{NaAlSi}_3\text{O}_8$ in pure $\text{NaAlSi}_3\text{O}_8$ liquid with pressure. However, because this substantial deviation in temperature is caused by their use of an hypothetical volume equation for liquid $\text{NaAlSi}_3\text{O}_8$ at one bar, which is well above the range of the measured volumes, postulates of melt disproportionation are not necessary to explain the position of the fusion curve.

Anovitz and Blencoe (1999) noted the large discrepancy between the location of their calculated fusion curve and that of Wen and Nekvasil (1994), and they assumed that this difference reflected the errors in the various thermodynamic property measurements used to calculate the fusion curve. Fortunately, this is not the case. The large discrepancy in the location of the respective fusion curves of these two studies

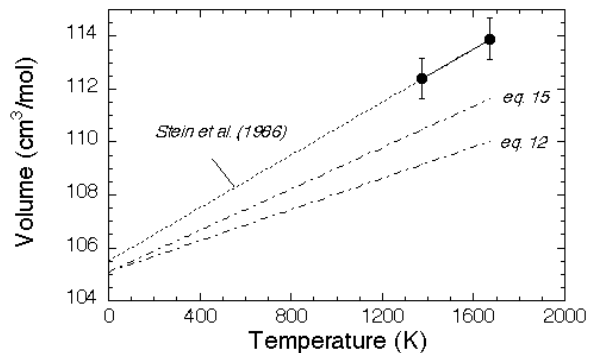


FIGURE 2. The volume of liquid $\text{NaAlSi}_3\text{O}_8$ as a function of temperature at one bar. The solid circles and two-sigma error bars, as well as the solid line that connects them, are calculated at 1373 and 1673 K, respectively, from the general equation of Stein et al. (1986), (Eq. 7 in this paper). The dashed line, labeled Stein et al. (1986), is the volume equation for albite liquid (Eq. 6 of this paper). The dashed-dot lines [equations 12 and 15 in Anovitz and Blencoe (1999)] are adjusted volume-temperature trends for liquid $\text{NaAlSi}_3\text{O}_8$. See text for details.

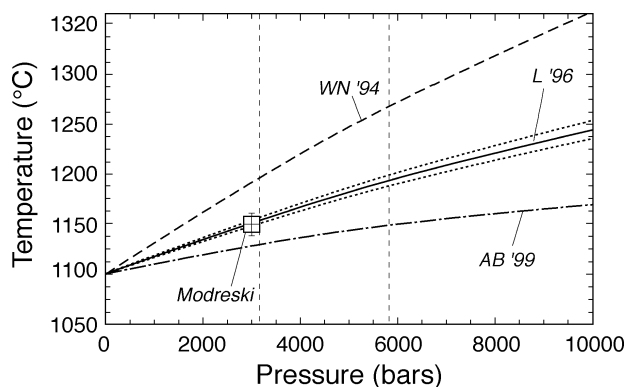


FIGURE 3. The calculated temperature of the albite melting reaction as a function of pressure to 10 kbar. The solid line (labeled L '96) is based on the volume of liquid $\text{NaAlSi}_3\text{O}_8$ given by Lange (1996), and the dotted lines show the variation in the calculated curve for a $\pm 0.4\%$ uncertainty in liquid volume. The dashed line (labeled W '94) is based on the volume of liquid $\text{NaAlSi}_3\text{O}_8$ used by Wen and Nekvasil (1994), whereas the dashed-dot line (labeled AB '99) is based on the volume of liquid $\text{NaAlSi}_3\text{O}_8$ given by equation 12 in Anovitz and Blencoe (1999). Also shown (cross enclosed in a square) is the phase-equilibrium experiment of Modreski (Boettcher et al. 1982) performed in a gas vessel with Ar as the pressure medium. This data point provides the maximum temperature (1150 ± 5 °C) of the melting reaction at 3 kbar.

(~ 180 °C difference at 10 kbar) is caused primarily by the difference between the *hypothetical* volume equation for liquid $\text{NaAlSi}_3\text{O}_8$ used by Wen and Nekvasil (1994) and the *adjusted* volume equations used by Anovitz and Blencoe (1999), both of which deviate from the measured volumes.

The one-bar compressibility of liquid albite

The final property measurement required for calculation of the albite fusion curve to 10 kbar is the compressibility of liquid $\text{NaAlSi}_3\text{O}_8$ at one bar. The isothermal compressibility of liquids may be obtained from relaxed (frequency-independent), sound speed measurements, if the volume, thermal expansion, and heat capacity are also known. Kress et al. (1988) measured relaxed sound speeds in a variety of $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ liquids between 1185 and 1620 °C, for which the requisite thermodynamic data are available. Although the sound speed of $\text{NaAlSi}_3\text{O}_8$ liquid was not measured directly, it was measured for a liquid very close in composition to albite (sample B from Kress et al. 1988; $\text{SiO}_2 = 74.89$ mol%, $\text{Al}_2\text{O}_3 = 7.71$ mol% and $\text{Na}_2\text{O} = 17.40$ mol%). Therefore, the extrapolation of the sound speed data to $\text{NaAlSi}_3\text{O}_8$ composition is a very small one. The experimental errors in β_T are $\leq 2\%$ for liquids for which both sound speed and volume measurements were made in the $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system.

The data of Kress et al. (1988) allow derivation of a model equation for the isothermal compressibility of liquids in the $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system at one bar:

$$\beta(T) = \sum X_i \left[\beta_{i,1773 \text{ K}} + \partial\beta_i/\partial T (T - 1773) \right] \quad (8)$$

where X_i is the mole fraction of each oxide component, and β_i

and $\partial\beta_i/\partial T$ are the compressibility and the temperature dependence of the compressibility of each oxide component, respectively. The fitted parameters for this equation and their one-sigma errors are given in Table 7 of Kress et al. (1988) and allow the compressibility of $\text{NaAlSi}_3\text{O}_8$ liquid to be obtained:

$$\beta_T^{\text{NaAlSi}_3\text{O}_8} = 5.78(\pm 0.11) + 0.00026(\pm 0.00032)(T - 1773) 10^{-6} \text{ bar}^{-1} (9)$$

The 2σ errors given in Equation 9 are based on a propagation of the fitted errors given for Equation 8 in Table 7 of Kress et al. (1988) (doubled to be at the two-sigma level). These errors lead to an uncertainty in $\beta_T^{\text{NaAlSi}_3\text{O}_8}$ of $\sim 2\%$, similar to the experimental error on individual liquids. This uncertainty contributes a negligible uncertainty to the calculation of the albite fusion curve at pressures ≤ 10 kbar.

The fusion curve to 10 kbar and assessment of errors

The location of the calculated fusion curve at pressures ≤ 10 kbar, on the basis of the thermodynamic data listed above, is shown in Figure 3. Propagation of the 2σ errors from all the various thermodynamic data leads to an uncertainty in the temperature of the fusion curve of ± 7 °C at 3 kbar and ± 24 °C at 10 kbar. Therefore, at the 95% confidence level, the maximum error envelope for the albite fusion curve at 10 kbar is 48 °C, which is considerably smaller than those reported in earlier studies (~ 200 °C, Anovitz and Blencoe 1999; ~ 120 °C, Wen and Nekvasil 1994). The temperature of the calculated fusion curve at 3 kbar is thus constrained to be 1152 ± 3.5 (1 σ) °C, which is fully consistent with the phase-equilibrium experiment of Modreski (Boettcher et al. 1982) at 3 kbar.

In the Modreski experiment, crystalline albite (replicated with natural and synthetic albite, both disordered) was held at $1150 (\pm 5)$ °C for 23 hours. The run product was a mixture of glass + crystals. This result is a half-reversal because a reaction took place (i.e., melting of crystals), but it was not reversed (i.e., crystallization from liquid). Therefore, only the maximum temperature for the melting reaction at 3 kbar is constrained, because complete melting may have been inhibited by sluggish kinetics. That the calculated temperature (1152 ± 3.5 °C) for the fusion curve at 3 kbar is within error of the experimental temperature (1150 ± 5 °C) suggests that the P - T condition chosen by Modreski is quite close to that of the melting reaction. Of significance is the fact that the Modreski result confirms the 1bar melting temperature given by Boettcher et al. (1982) of 1100 °C. In contrast, the 1118 °C value of Schairer and Bowen (1956) leads to a calculated fusion temperature at 3 kbar that is ~ 20 °C higher than (and outside the error of) the maximum given by Modreski. The key point is that the initial slope of the calculated albite fusion curve is fully consistent with the best available phase-equilibrium data below 10 kbar.

PHASE-EQUILIBRIUM EXPERIMENTS AT PRESSURES ≥ 10 KBAR

There have been four phase-equilibrium studies on the melting reaction of crystalline albite at pressures ≥ 10 kbar. This reaction is limited to pressures ≤ 33 kbar by the albite = jadeite + quartz reaction (e.g., Holland 1980). The earliest experiments

were those of Birch and LeComte (1960) conducted between 10 and 23 kbar in an internally heated, gas-pressure vessel (Fig. 4a). Soon after, Boyd and England (1963) conducted similar experiments between 10.8 and 32.3 kbar in a solid-medium, piston-cylinder apparatus and obtained broadly similar results (Fig. 4b). Two decades later, Boettcher et al. (1982) conducted a third study between 10 and 30 kbar (Fig. 4c), which at the time was perceived to be the most accurate. Whereas the previous two studies only provided half-reversals, the experiments of Boettcher et al. (1982) were fully reversed, of longer duration (3–24 hours), well characterized (e.g., the starting material included both natural and synthetic varieties of high albite), and specifically designed to be as dry (free of water) as possible. The most recent phase-equilibrium study was performed at 11.3 kbar by Nekvasil and Carroll (1996). These piston-cylinder experiments were also fully reversed, of long duration (1–5 days), well characterized, and also designed to be as dry as possible. However, because this experiment was performed at a relatively low pressure, close to 10 kbar, it does not place as tight a constraint on the value of K' for liquid $\text{NaAlSi}_3\text{O}_8$ as those performed in 20–30 kbar range.

The experiments of Boettcher et al. (1982)

The results of Boettcher et al. (1982) place the albite fusion curve at temperatures that are ~50–70 °C lower than those of both Birch and LeComte (1960) and Boyd and England (1963), and ~25 °C lower than that of Nekvasil and Carroll (1996). Most confusing at the time of publication, however, was that these apparently definitive results were inconsistent with calculations of the fusion curve based on measured thermodynamic data. This discrepancy between the best-available phase-equilibrium experiments and thermodynamic property measurements spawned a wide debate in the literature on the possibility of dramatic changes in the structure and/or speciation of $\text{NaAlSi}_3\text{O}_8$ liquid with pressure as an explanation (e.g., Boettcher et al., 1982; Navrotsky et al. 1982; Bottinga 1985; Wen and Nekvasil 1994; Zheng and Nekvasil 1996).

It is more likely, however, that the run products from the high-pressure experiments of Boettcher et al. (1982) were contaminated by water, despite the experimental efforts to avoid it. Fine and Stolper (1985) measured 0.20 and 0.49 wt% H_2O in two albite glass samples provided by Professor A. Boettcher. These two samples were held at 1450 °C and 20 kbar in a piston-cylinder apparatus for 1 and 3 hours, respectively, using the exact same drying techniques and NaCl/silica glass pressure medium as that used by Boettcher et al. (1982). It is plausible that water concentrations ≥ 0.5 wt% may have been present in the high-pressure melting experiments of Boettcher et al. (1982), which were equilibrated for 3 to 24 hours. This inference is especially likely given the additional results of Fine and Stolper (1985), wherein several $\text{NaAlSi}_3\text{O}_8$ liquid samples, held at 1450 °C between 15 and 33 kbar for 60 min in a pressure medium identical to that of Boettcher et al. (1982), quenched to glasses with 0.14 to 0.89 wt% H_2O .

It is notable that most of the liquids from the high-pressure experiments of Boettcher et al. (1982) did *not* quench to glass, unlike the case for Birch and LeComte (1960), Boyd and England (1963), and Nekvasil and Carroll (1996). Instead

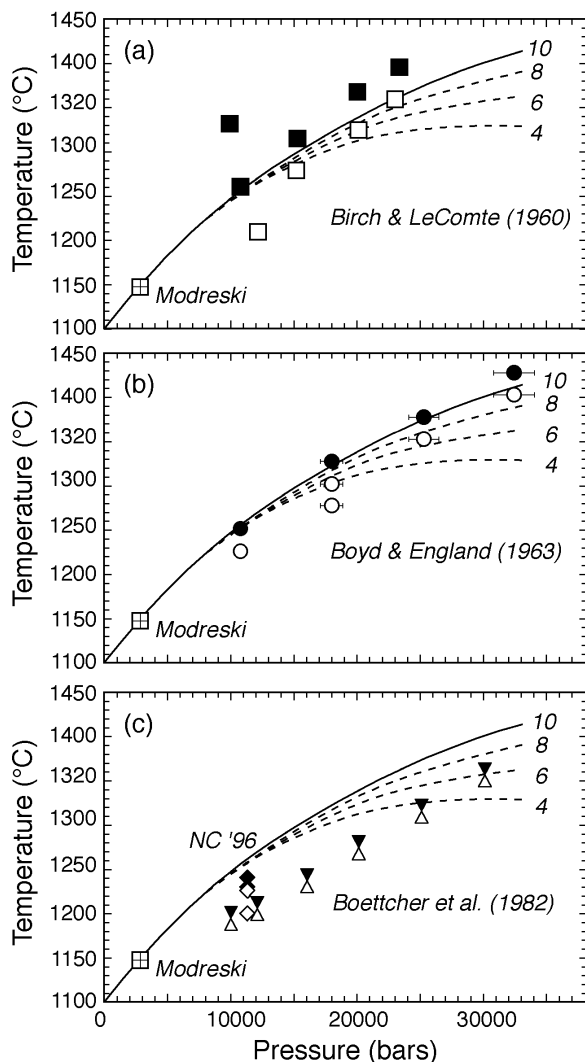


FIGURE 4. The calculated temperature of the albite melting reaction as a function of pressure to 33 kbar. These calculations use the Birch-Murnaghan relation to calculate the volume of liquid $\text{NaAlSi}_3\text{O}_8$ at high pressure. The solid line is for a K' value of 10, whereas the three dashed lines are for K' values of 8, 6, and 4, respectively. The phase-equilibrium data point of Modreski (Boettcher et al. 1982) is shown for comparison. (a) The open squares define the minimum-temperature, stability field of crystalline albite based on the experiments of Birch and LeComte (1960) in a gas vessel with Ar as the pressure medium. The solid squares show the $\text{NaAlSi}_3\text{O}_8$ liquid field (see text for details). The errors in temperature and pressure for the experimental data points are smaller than the symbols. (b) The open circles define the minimum-temperature, stability field of crystalline albite based on the experiments of Boyd and England (1963) in a piston-cylinder apparatus. The solid circles show the $\text{NaAlSi}_3\text{O}_8$ liquid field (see text for details). The errors in temperature and pressure for the experimental data points are shown or are smaller than the symbols. (c) The open triangles define the minimum-temperature, stability field of crystalline albite based on the experiments of Boettcher et al. (1982) in a piston-cylinder apparatus, whereas the solid triangles show the liquid field (see text for details). The open diamonds shown the stability field of crystalline albite based on the experiments of Nekvasil and Carroll (1996), whereas the solid diamonds show the liquid field. The errors in temperature and pressure for the experimental data points are smaller than the symbols.

Boettcher et al. (1982) used the distinct texture of albite crystals in sheaves or radial aggregates to identify the quench from the liquid. Such diagnostic quench crystals were described by Boyd and England (1963) in their experiments on diopside, but not on albite; instead, they commented on the tendency for $\text{NaAlSi}_3\text{O}_8$ liquid to quench to a glass. Similarly, Birch and LeComte (1960) also remarked on the ease with which $\text{NaAlSi}_3\text{O}_8$ liquid quenched to a glass in their high-pressure experiments. It is well established that dissolved water dramatically reduces the viscosity of polymerized liquids like $\text{NaAlSi}_3\text{O}_8$ (Dingwell 1987), which in turn affects the ease at which nucleation occurs. The pervasive formation of quench crystals in the run products of Boettcher et al. (1982) may be a further indication of higher water concentrations in their runs compared with other studies in which $\text{NaAlSi}_3\text{O}_8$ liquid quenched to a clear glass (e.g., Birch and LeComte 1980; Boyd and England 1964; Fine and Stolper 1985; Nekvasil and Carroll 1996). Note that the experiments of Boettcher et al. (1982) at one bar are not subject to these potential problems of water contamination.

An examination of the water-saturated fusion curve of albite at 0.5, 1, and 2 kbar from Tuttle and Bowen (1958), combined with measurements of the solubility of H_2O in albite liquid at these pressures and temperatures (Behrens et al. 2001), allow a quantitative assessment of the effect of dissolved water on the depression of the albite melting temperature. As demonstrated by Tuttle and Bowen (1958), the melting temperature of albite under water-saturated conditions is 955 ± 5 °C at 0.5 kbar, 910 ± 10 °C at 1 kbar, and 845 ± 5 °C at 2 kbar. These results indicate a lowering of the melting temperature, ΔT , by approximately 154 ± 5 , 208 ± 10 , and 291 ± 6 °C at 0.5, 1, and 2 kbar, respectively. These ΔT values are based on anhydrous melting temperatures for albite of 1109 ± 1 , 1118 ± 2 and 1136 ± 3 °C at 0.5, 1, and 2 kbar, respectively, which are calculated from the thermodynamic data. The water concentrations in the melt along the water-saturated albite fusion curve are obtained from the measurements of Behrens et al. (2001). The solubility of water in $\text{NaAlSi}_3\text{O}_8$ liquid is ~ 2.85 wt% at 955 °C and 0.5 kbar, ~ 4.48 wt% at 910 °C and 1 kbar, and ~ 7.00 wt% at 845 °C and 2 kbar. These water concentrations are plotted against the drop in the melting temperature of albite (ΔT) in Figure 5. A polynomial through the data gives the following equation:

$$\text{wt\% H}_2\text{O} = -6.45 \cdot 10^{-3} + 1.03 \cdot 10^{-2}(\Delta T) + 6.76 \cdot 10^{-5}(\Delta T)^2. \quad (10)$$

For ΔT values of 50 and 70 degrees, the amount of water required in the melt is ~ 0.75 and ~ 1.11 wt%, respectively. As discussed above, these water concentrations are not unreasonable for equilibration durations in the piston-cylinder experiments of Boettcher et al. (1982) of 3 to 24 hours. It is thus not unexpected that the Boettcher et al. (1982) fusion curve temperatures are 50–70 °C below the *minimum* temperatures constrained by the gas-vessel experiments of Birch and LeComte (1960).

The experiments of Birch and LeComte (1960)

The experiments of Birch and LeComte (1960) had the advantage that H_2O and/or H_2 contamination was precluded by

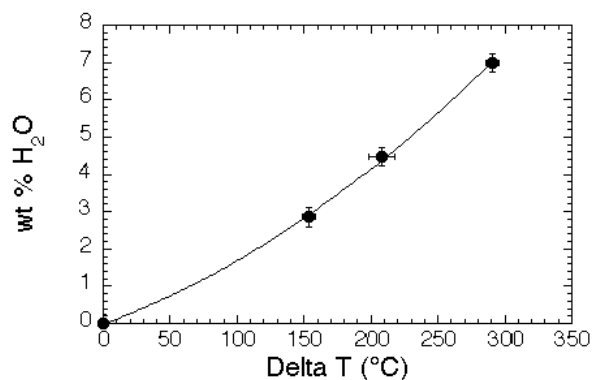


FIGURE 5. A plot of wt% H_2O dissolved in $\text{NaAlSi}_3\text{O}_8$ liquid as a function of the drop in the melting temperature of albite (ΔT) compared to anhydrous conditions. The data shown are derived from the water-saturated fusion curve for albite of Tuttle and Bowen (1958) and the water solubility measurements on $\text{NaAlSi}_3\text{O}_8$ liquid of Behrens et al. (2001). The line through the points is a fitted polynomial (Eq. 10 in the text).

the use of Ar gas as the pressure medium. Nonetheless, of the nine experiments conducted by Birch and LeComte (1960), only two provide unequivocal, half-reversal constraints on the *minimum* temperature of the fusion curve. All others are ambiguous because they are either “no-reaction” results, which are difficult to interpret because of sluggish kinetics, or the ordering state of the crystalline albite, used as starting material, is unknown. As pointed out by Anovitz and Blencoe (1999), low albite will melt metastably at lower temperatures than high albite. As a result, only those experiments of Birch and LeComte (1960) in which crystallization occurred (from a starting material of glass) can be used. These two half-reversal, experiments provide minimum temperatures of the melting reaction at 12.2 kbar (≥ 1210 °C) and 15.1 kbar (≥ 1279 °C), respectively.

Anovitz and Blencoe (1999) rejected the crystallization experiments of Birch and LeComte (1960), as well as those of Boyd and England (1964) (discussed below), on the grounds that crystallization may have occurred metastably during run up to the P - T condition, as found by Boyd and England (1964) in their experiments of 5 and 10 min durations, or by quench crystallization, as found by Boettcher et al. (1982) in nearly all their runs quenched from liquids. However, Boyd and England (1964) found that these metastable crystals grew during the first 5–10 minutes of a run and disappeared after ≥ 40 minutes; the experiments in question by Birch and LeComte (1960) were 4 and 2 hours long, respectively. The question of whether quench crystals were a pervasive problem in the Birch and LeComte (1960) experiments was tested by three other experiments in that study in which melting occurred (starting material was crystalline) and the run products were glass. Unlike the case for Boettcher et al. (1982), there was no problem in producing glass upon quench from the liquid in the experiments of Birch and LeComte (1960).

Both Anovitz and Blencoe (1999) and Boettcher et al. (1982) argue that the phase-equilibrium experiment of Birch and LeComte (1960), performed at 15.1 kbar and 1279 °C, is ambiguous in its interpretation. Here it is shown that this experi-

ment provides a robust constraint on the minimum temperature of the fusion curve ($\geq 1279 \pm 10$ °C) at 15.1 kbar. Birch and LeComte (1960) equilibrated two capsules (one began with crystalline albite, the other with $\text{NaAlSi}_3\text{O}_8$ glass) at this P - T condition for two hours. The run products revealed that the crystalline albite melted and quenched to a glass, whereas the glass crystallized. There are thus two interpretations of these data as reported. First, there may have been a temperature gradient across the two capsules, such that one capsule was at a temperature above the melting temperature of albite and the other capsule was at a temperature below it. In this case, the temperature of the fusion curve at 15.1 kbar must lie close to 1279 °C (within the magnitude of the temperature gradient; $\pm 10^\circ$), and therefore well above that determined in the Boettcher et al. (1982) experiments. A second interpretation is that the crystalline starting material was low albite (ordered) and melted metastably without sufficient time during the experiment to recrystallize, whereas the glassy starting material had the full two hours of the experiment to crystallize. In this interpretation, the temperature of the fusion curve is constrained to be at a temperature above 1279 °C. There is no reasonable interpretation of these experimental results that would place the fusion temperature well below 1279 °C at 15.1 kbar, except to invoke quench crystallization. However, the arguments against this interpretation are given in the previous paragraph.

In summary, the two half-reversal, crystallization experiments of Birch and LeComte (1960) provide minimum temperatures of the melting reaction at 12.2 kbar (≥ 1210 °C) and 15.1 kbar (≥ 1279 °C), respectively. Two additional, "no-reaction" experiments by Birch and LeComte (1960) may also be useful. In these experiments, crystalline albite was held at 1323 °C for 2.5 hours and 1358 °C for 4 hours at 20 and 24 kbar, respectively. In neither case did melting occur. Although "no-reaction" experiments are often difficult to interpret because kinetics may have prevented reaction, melting of crystalline albite readily occurred at lower temperatures (1210 and 1279 °C) within four and two hours, respectively, in two other experiments of Birch and LeComte (1960). These results demonstrate that the kinetics of melting albite are not prohibitive within 2–4 hours at temperatures > 1300 °C, and these "no-reaction" results thus give reasonable estimates of the minimum temperature of the melting reaction at 20 and 23 kbar, respectively.

The experiments of Boyd and England (1963)

The Boyd and England (1963) study also provides half-reversal constraints on the *minimum* temperature of the fusion curve, but at higher pressures (to 32 kbar). These experiments were conducted in a piston-cylinder apparatus with talc as the pressure medium. Thus, diffusion of hydrogen into the sample capsules may have occurred, lowering the melting temperature of albite. As a consequence, only the crystallization experiments can be used, which constrain the *minimum* temperatures (≥ 1300 , 1350, and 1400 °C, respectively) of the albite fusion curve (at 18, 25, and 32 kbar, respectively). These temperatures are considerably higher than those given by Boettcher et al. (1982), possibly because of the shorter run durations (0.3 to 1 hour) in the three highest pressure experiments of Boyd and England (1963), limiting the effect of hydrogen diffusion.

Again, the crystallization observed in these experiments cannot be dismissed as caused by quench effects because at temperatures only 25 degrees higher, at the same three pressures, the run products of Boyd and England (1963) quenched to glasses. Moreover, the textural difference between quench crystals and equilibrium crystals is quite marked, and the two types are easily distinguished. Certainly Boyd and England (1963) were alert to the difference, as they describe the texture of quench crystals in their description of their diopside runs.

The experiments of Nekvasil and Carroll (1996)

The final experiments to examine are those of Nekvasil and Carroll (1996) where four runs were performed at 11.3 kbar. In all four cases, crystalline albite was first held at 1400 °C for 24 hours (shown by these authors to cause melting) and then dropped to a final equilibration temperature, where the sample was held for four days. For experiments with final equilibration temperatures of 1240 and 1230 °C, the run products were 100% glass, whereas for those held at 1225 and 1200 °C, the run products were crystalline (Table 1 in Nekvasil and Carroll 1996). These results indicate a fusion temperature at 11.3 kbar that is ~ 25 °C higher than indicated by the results of Boettcher et al. (1982), as seen here in Figure 4c. This temperature is also ~ 30 °C lower than the calculated fusion curve; the discrepancy is just outside the 2σ error on the calculation at 11 kbar of ± 25 °C. However, as with the piston-cylinder experiments of Boyd and England (1963) and Boettcher et al. (1982), the ingress of small amounts of water into the experimental charges of Nekvasil and Carroll (1996) cannot be ruled out. From Equation 10, only 0.37 wt% H_2O is required to drop the melting temperature of albite by ~ 30 °C. Therefore, only the crystallization experiments of Nekvasil and Carroll (1996) can be used.

The combination of *all* the crystallization experiments discussed above define the minimum temperature of the albite fusion curve and are shown in Figure 4. These data allow derivation of the *minimum* value of K' for $\text{NaAlSi}_3\text{O}_8$ liquid. This is achieved by extending calculations of the fusion curve to 33 kbar, as detailed below.

CALCULATION OF THE FUSION CURVE TO 33 KBAR

To extend calculations of the albite fusion curve from 10 to 33 kbar, the volume of liquid $\text{NaAlSi}_3\text{O}_8$ must be known to these higher pressures. This calculation requires incorporation of the pressure dependence to the liquid compressibility into the liquid volume expression in Equation 1. The third-order, Birch-Murnaghan equation of state, a truncated series expansion derived from finite strain theory of solids (Birch 1978), models the volume of silicate liquids to high pressure (tens of GPa) remarkably well (e.g., Rigden et al. 1989; Stixrude and Bukowski 1990). The third-order form is:

$$P = \frac{3}{2} K_{T,0} (R^{7/3} - R^{5/3}) \left[1 - \frac{3}{4} (4 - K'_0) (R^{2/3} - 1) \right] \quad (11)$$

where $R = V_{T,0}/V_{T,P}$, $V_{T,0}$ is the volume at temperature and zero pressure (1 bar), $V_{T,P}$ is the volume at temperature and pressure, $K_{T,0}$ is the bulk modulus ($K_{T,0} = 1/\beta_{T,0}$, where $\beta_{T,0}$ is the isothermal compressibility) at zero pressure, and K'_0 is the pressure dependence of the bulk modulus ($\partial K_{T,0}/\partial P$) at zero pressure. In

the present study, the Birch-Murnaghan relation has been used to describe the volume of liquid $\text{NaAlSi}_3\text{O}_8$ up to 33 kbar for values of K'_0 between 4 and 10; the resultant volume vs. pressure curves are shown in Figure 6. Also shown is the volume of crystalline albite calculated from the K_0 and K'_0 values of Downs et al. (1994) and the 3rd order Birch-Murnaghan equation of state. The volumetric relations in Figure 6 demonstrate that if the pressure dependence of the liquid β_T is not considered, then a density cross-over between liquid and crystal is expected at ~ 21 kbar (the effect of neglecting the K' of the solid is negligible). Such an inversion will cause the slope (dT/dP) of the fusion curve to reach a maximum at ~ 21 kbar, which is not observed.

Incorporation of the Birch-Murnaghan relation (Equation 11) into Equation 1 requires an integration that is readily evaluated following a method suggested by Asimow (P. Asimow, personal communication). Its derivation is outlined in the appendix of Ghiorso et al. (2002), and only the resultant integral is shown here:

$$\int_1^P V_{T,P}^{\text{liq}} dP = PV_{T,P}^{\text{liq}} - V_{T,0}^{\text{liq}} + \frac{9}{8} K V_{T,0}^{\text{liq}} [R^{2/3} - 1]^2 \left\{ 1 + \frac{1}{2} (K' - 4) [R^{2/3} - 1] \right\} \quad (12)$$

Equation 12 allows the fusion curve to be calculated up to 33 kbar for various K' values. The resultant family of fusion curves, illustrated in Figure 4, indicates that a *minimum* K' value of ~ 10 satisfies all of the *crystallization* experiments of Birch and LeComte (1960), Boyd and England (1963), Boettcher et al. (1982), and Nekvasil and Carroll (1996) between 10 and 32 kbar, as well as the two additional, “no-reaction” results of Birch and LeComte (1960) at 20 and 23 kbar.

This K' value of ≥ 10 for liquid $\text{NaAlSi}_3\text{O}_8$ is considerably higher than those reported by Kress et al. (1988) and Anovitz and Blencoe (1999) of ≤ 6 and ~ 4.5 , respectively. However, these authors did not arrive at these K' values through the Birch-Murnaghan relation (Eq. 11), but from determinations of $\partial\beta_T/\partial P$

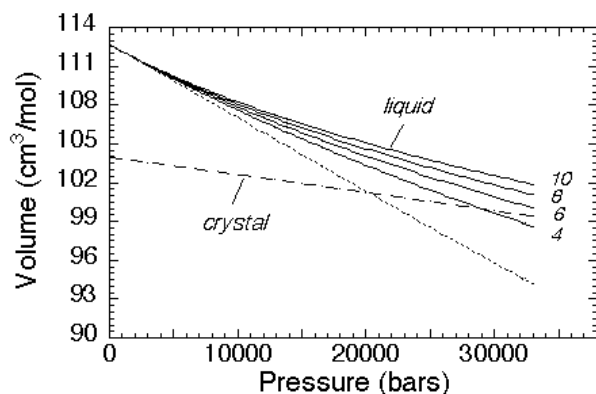


FIGURE 6. A comparison between the volume of liquid vs. crystalline $\text{NaAlSi}_3\text{O}_8$ as a function of pressure. The solid lines are the volume of liquid $\text{NaAlSi}_3\text{O}_8$ at temperatures along the fusion curve for various K' values. The dotted line is the volume of liquid $\text{NaAlSi}_3\text{O}_8$ for the case where β_T at one bar is applied over the entire pressure interval. The dashed line is the volume of crystalline albite. See the text for the sources of these data.

that best fit the experimentally determined fusion curve. Values for K' were then calculated from the relation,

$$K' = \frac{\partial K}{\partial P} = - \left(\frac{1}{\beta_T^2} \right) \left(\frac{\partial \beta_T}{\partial P} \right). \quad (13)$$

Kress et al. (1988) did not report the specific values of $\partial\beta_T/\partial P$ used to calculate their K' values, whereas Anovitz and Blencoe (1999) report a pressure-independent value of $-1.515 \times 10^{-10}/\text{bar}$. Because this value of $\partial\beta_T/\partial P$ is independent of pressure, Equation 13 shows that K' will be strongly pressure-dependent, as illustrated in Figure 7. K' increases from ~ 4.5 at one bar to ~ 317 at 33 kbar; the average K' is ~ 42 . In contrast, use of the Birch-Murnaghan relation leads to a gradual decrease in K' with pressure. In the case for $\text{NaAlSi}_3\text{O}_8$ liquid, a zero-pressure K' of 10 decreases to ~ 7 at 33 kbar (a full discussion is given below). This is not to say that use of Equation 13 is inherently wrong, but rather that K' values derived from it cannot be compared directly to those derived from the Birch-Murnaghan relation.

THE COMPRESSIBILITY OF LIQUID $\text{NaAlSi}_3\text{O}_8$ WITH PRESSURE

It is of interest to examine not only how the volume of liquid $\text{NaAlSi}_3\text{O}_8$ varies with pressure for different K' values (Fig. 6), but also how the compressibility changes. Its variation with pressure is calculated from the simple relation:

$$\beta_T(P) = \frac{1}{K_T(P)} = - \frac{1}{V_T} \left[\left(\frac{\partial P}{\partial V} \right)_T \right]^{-1} \quad (14)$$

where $(\partial P/\partial V)_T$ is the derivative of Equation 11 with volume:

$$\left(\frac{\partial P}{\partial V} \right)_T = \frac{3}{4} \frac{K_{T,0}}{V_{T,0}} (R^{7/3} - R^{5/3}) (4 - K') R^{5/3} + \frac{3}{2} \frac{K_{T,0}}{V_{T,0}} \left(\frac{5}{3} R^{8/3} - \frac{7}{3} R^{10/3} \right) \left(1 - \frac{3}{4} (4 - K') (R^{2/3} - 1) \right) \quad (15)$$

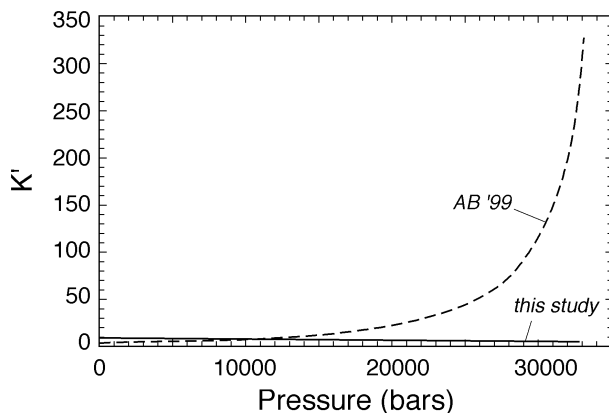


FIGURE 7. A plot of K' vs. pressure for the constant value of $\partial\beta_T/\partial P$ given by Anovitz and Blencoe (1999). Application of Equation 13 in the text shows that their pressure-independent value for $\partial\beta_T/\partial P$ leads to a strong pressure-dependence to calculated values of K' , which varies from ~ 4.5 at one bar to ~ 317 at 33 kbar. The value of K' derived in this study varies from ~ 10 at one bar to ~ 7 at 33 kbar.

The resultant β_T vs. P curves (Fig. 8) show that, for a K' value of 10, there is pronounced curvature with β_T decreasing rapidly at low pressure. In contrast, a K' value of 4 leads to a less steep decrease in β_T with pressure. The constant slope for $\partial\beta_T/\partial P$ given by Anovitz and Blencoe (1999) is also shown in Figure 8.

THE RELATIONSHIP BETWEEN K' AND THE COMPRESSIBILITY AT 1 BAR

Anovitz and Blencoe (1999) pointed out that a K' value of ~ 4 –5 is expected for liquid $\text{NaAlSi}_3\text{O}_8$, given K' values of 5.3 and 6.9 for liquid $\text{CaAl}_2\text{Si}_2\text{O}_8$ and $\text{CaMgSi}_2\text{O}_6$, respectively, derived from the shock-wave experiments of Rigden et al. (1989) to 35 GPa. On the basis of these data, Rigden et al. (1989) suggested that values of K' for multi-component silicate liquids vary inversely with the fraction of network-forming, tetrahedrally coordinated cations (e.g., Si^{4+} and Al^{3+}), and they estimated K' values of ~ 10 –11 for silica-poor liquids like Mg_2SiO_4 and Fe_2SiO_4 . This prediction is consistent with the K' value of ~ 10 for molten Fe_2SiO_4 obtained by Agee (1992) on the basis of sink/float experiments. Within this context, a K' value of ≥ 10 for a liquid like $\text{NaAlSi}_3\text{O}_8$ is perhaps surprising. However, there are now several lines of evidence to suggest that an inverse relationship between K' and the abundance of tetrahedrally coordinated cations may not be general.

For example, the best estimates of K' for molten komatiite (a Si- and Al-poor, Mg-rich liquid) are ~ 4.5 –4.9 on the basis of both shock-wave experiments (Miller et al. 1991) and sink/float experiments (Agee and Walker 1993). In contrast, the partial molar volume of the SiO_2 component (\bar{V}_{SiO_2}) in rhyolite liquid between 10 and 35 kbar, determined by Gaetani et al. (1998), is incompatible with a K' value of ~ 4 –5, as illustrated in Figure 9. Gaetani et al. (1998) measured the solubility of quartz in rhyolite melt as a function of pressure, from which values of \bar{V}_{SiO_2} between 10 and 35 kbar were derived. Their recommended values are shown in Figure 9, along with a family

of $\bar{V}_{\text{SiO}_2}(P)$ curves, for different values of K' , calculated from the third-order Birch-Murnaghan equation of state with the one-bar value of \bar{V}_{SiO_2} of 26.91 cm^3/mol from Lange (1997) and the one-bar value of $K_T = 137.2$ kbar from Kress et al. (1991) at 1350 °C. As illustrated in Figure 9, a K' value of ~ 8 –12 for the SiO_2 component is most consistent with the experimental results of Gaetani et al. (1998).

In Figure 10, K' is plotted as a function of $\beta_{T,0}$ for five liquids for which a combination of sound-speed measurements (Rivers 1987; Secco et al. 1991) and shock-wave or sink/float experiments provide the relevant data. These five liquids are $\text{CaAl}_2\text{Si}_2\text{O}_8$ and $\text{CaMgSi}_2\text{O}_6$ (Rigden et al. 1989), a model basalt (64 mol% $\text{CaMgSi}_2\text{O}_6$ –36 mol% $\text{CaAl}_2\text{Si}_2\text{O}_8$; Rigden et al. 1988), komatiite (Miller et al. 1991), and Fe_2SiO_4 (Agee 1992). The minimum K' value for liquid $\text{NaAlSi}_3\text{O}_8$ obtained in this study is also plotted in relation to its $\beta_{T,0}$ value in Figure 10. The data illustrate that, to first order, those liquids that are most compressible at one bar tend to have the highest K' values, with liquid $\text{CaAl}_2\text{Si}_2\text{O}_8$ an exception to this trend. A similar relationship has been found for several crystalline compounds (Duffy and Anderson 1989).

The consequences of this relationship to changes in β_T with pressure are illustrated for these six liquids (at 1600 °C) in Figure 11. These calculations are extended to 25 GPa, although the most important features are seen by 3.5 GPa (close to the upper pressure limit of the albite fusion curve). For example, liquid $\text{NaAlSi}_3\text{O}_8$ and Fe_2SiO_4 have the largest values of $\beta_{T,0}$, and because of their relatively high K' values, their respective $\beta_T(P)$ curves drop sharply at low pressure. By 3.2 and 3.5 GPa, respectively, the compressibility of molten $\text{NaAlSi}_3\text{O}_8$ and Fe_2SiO_4 drops to 40% of their one-bar values, and are less than or equal to those of the other four liquids (Fig. 11).

It is interesting to speculate why two such different liquids,

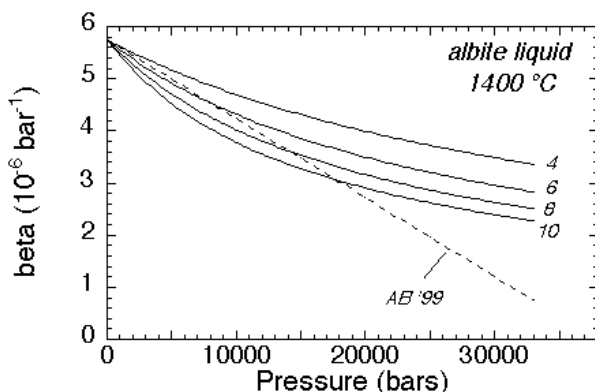


FIGURE 8. A plot of β_T for liquid $\text{NaAlSi}_3\text{O}_8$ as a function of pressure for various K' values. For K' value of 10, there is pronounced curvature in the β_T function with pressure, with a substantial drop in β_T at low pressure. In contrast, for a K' value of 4, β_T decreases more steadily and less sharply over the same pressure interval.

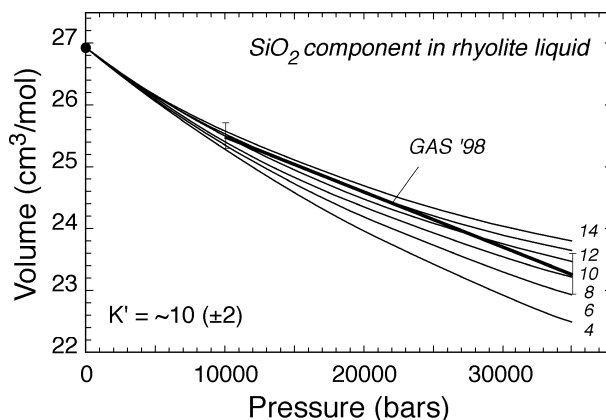


FIGURE 9. A plot of the partial molar volume of the SiO_2 component (\bar{V}_{SiO_2}) in rhyolite liquid as a function of pressure at 1350 °C. The solid lines are calculated values of $\bar{V}_{\text{SiO}_2}(P)$ based on the Birch-Murnaghan relation (Equation 11 in the text), with the one-bar \bar{V}_{SiO_2} from Lange (1997), the 1bar K_T from Kress et al. (1991), and K' values from 4 to 14. Superimposed on these curves are the recommended values of \bar{V}_{SiO_2} between 10 and 35 kbar from the quartz solubility measurements of Gaetani et al. (1998). Within the one-sigma error bars reported by Gaetani et al. (1998), their data are most consistent with a K' value of $\sim 10 \pm 2$.

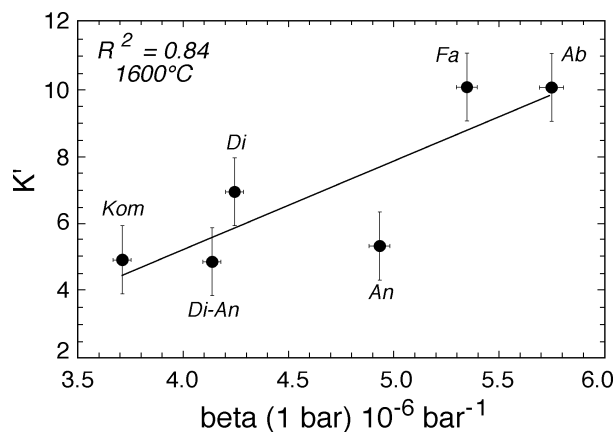


FIGURE 10. A plot of K' vs. $\beta_{T,0}$ for various liquids at 1600 °C for which both parameters have been measured independently (see text for details). These liquids are: (1) Kom (komatiite), (2) Di-An (64 mol% $\text{CaMgSi}_2\text{O}_6$ – 36 mol% $\text{CaAl}_2\text{Si}_2\text{O}_8$), (3) Di ($\text{CaMgSi}_2\text{O}_6$), (4) An ($\text{CaAl}_2\text{Si}_2\text{O}_8$), (5) Fa (Fe_2SiO_4), and (6) Ab ($\text{NaAlSi}_3\text{O}_8$). Error bars in K' are typically not reported and are arbitrarily given here as ± 1 (for scale). Errors in $\beta_{T,0}$ reported for the individual liquids by Rivers and Carmichael (1987) and Secco (1991) are $\leq 1\%$ (the error shown). The solid line is a linear fit to the data, which shows a strong, positive correlation ($R^2 = 0.84$) between K' and $\beta_{T,0}$. A similar correlation is observed for various crystalline minerals (Duffy and Anderson 1989).

$\text{NaAlSi}_3\text{O}_8$ and Fe_2SiO_4 , with dramatically different melt structures, have compressibility curves that are nearly identical. It is clear that modes of compression available to $\text{NaAlSi}_3\text{O}_8$ liquid at one bar (e.g., changes in T-O-T bond angles, increases in average ring size, the formation of triclusters, etc.), which are not available to Fe_2SiO_4 liquid, are rapidly lost within the first few GPa. Alternatively, the low-pressure compression of Fe_2SiO_4 liquid may involve electronic contributions (L. Stixrude, personal communication). The change-over to the high-pressure regime, where β_T decreases more slowly with pressure is likely caused by the onset of Al^{3+} and/or Si^{4+} coordination change.

In conclusion, the minimum K' value of ~ 10 for liquid $\text{NaAlSi}_3\text{O}_8$ is constrained robustly by the half-reversal, crystallization experiments of Boyd and England (1963) and Birch and LeComte (1960). This relatively high K' value for molten $\text{NaAlSi}_3\text{O}_8$ is consistent with the positive correlation between K' and $\beta_{T,0}$ observed for several liquids (and also several solids; Duffy and Anderson 1989) for which the requisite data are available. The correlation between K' and $\beta_{T,0}$ can be tested plausibly by in-situ sound speed measurements (e.g., in an internally heated, pressure vessel) for liquids with high values of $\beta_{T,0}$.

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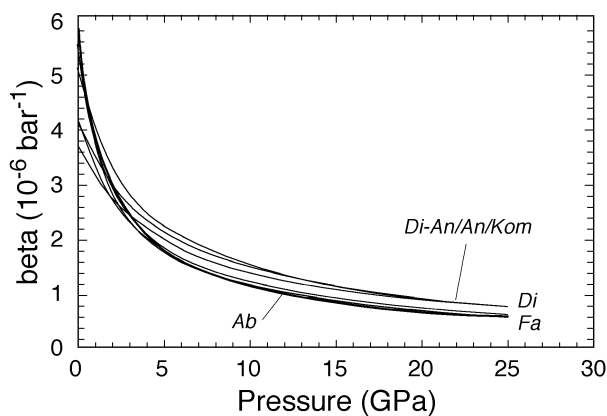


FIGURE 11. A plot of β_T as a function of pressure for six liquids (the same as those in Fig. 10) at 1600 °C. Note that those liquids with the highest compressibility at one bar have the lowest compressibility between 2.5 and 25 GPa, owing to their high K' values.

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