

# H<sub>2</sub>O Activity in Albite Melts at Deep Crustal *P*-*T* Conditions Derived from Melting Experiments in the Systems NaAlSi<sub>3</sub>O<sub>8</sub>-H<sub>2</sub>O-CO<sub>2</sub> and NaAlSi<sub>3</sub>O<sub>8</sub>-H<sub>2</sub>O-NaCl<sup>1</sup>

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**Abstract**—The system NaAlSi<sub>3</sub>O<sub>8</sub> (albite, Ab)-H<sub>2</sub>O offers a simple and tractable model to study the thermodynamics of the volatile constituent H<sub>2</sub>O in felsic magmas. Although it has been studied in this context for nearly 100 years, developing a comprehensive model that adequately describes the activity of H<sub>2</sub>O ( $a_{\text{H}_2\text{O}}$ ) in hydrous albite liquids and vapors has proven challenging. There are several problems. First,  $a_{\text{H}_2\text{O}}$  in hydrous liquids relies on melting experiments in the presence of mixed fluids with reduced H<sub>2</sub>O activity (H<sub>2</sub>O-CO<sub>2</sub> and H<sub>2</sub>O-NaCl), but models of  $a_{\text{H}_2\text{O}}$  in these coexisting fluids have lacked sufficient accuracy. Second, the role of the solubility of albite in H<sub>2</sub>O has been assumed to be negligible; however, it is important to take solubility into account at pressure (*P*) above 0.5 GPa because it becomes sufficiently high that H<sub>2</sub>O activity at the wet solidus is significantly less than 1. Third, the dry melting temperatures and wet solidus temperatures are inconsistent between the datasets. We address these issues by combining previous experimental work on *T*-*X*<sub>H<sub>2</sub>O</sub> liquidus relations at 0.5–1.5 GPa with accurate activity formulations for H<sub>2</sub>O in mixed fluids (Aranovich and Newton, 1996, 1999). This yields isobaric *T*- $a_{\text{H}_2\text{O}}$  sections at 0.5, 0.7, 1.0 and 1.5 GPa. Data at each isobar were fit to cubic equations, which were used to derive the following equation for liquidus *T* as a function of  $a_{\text{H}_2\text{O}}$  and *P*:

$$T(a_{\text{H}_2\text{O}}, P) = m_0 + m_1 a_{\text{H}_2\text{O}} + m_2 a_{\text{H}_2\text{O}}^2 + m_3 a_{\text{H}_2\text{O}}^3 \text{ } ^\circ\text{C},$$

where *T* is °C,  $m_0 = 1119.6 + 112.3P$ ,  $m_1 = -856.5 - 578.9P$ ,  $m_2 = 1004.1 + 952.9P$ , and  $m_3 = -477.1 - 618.0P$ . The equation is valid at  $0.5 < P < 1.5$  GPa and  $T_{\text{solidus}} < T < T_{\text{dry melting}}$ . The nonzero solubility of albite in pure H<sub>2</sub>O is incorporated into the model to give the correct liquidus H<sub>2</sub>O activity when truncating the model equation in the limiting case where  $T \rightarrow T_{\text{solidus}}$  at a given pressure. This model equation reproduces both the liquidus-H<sub>2</sub>O contents and activities from the solubility measurements of Makhlu<sup>f</sup> et al. (2016) in the binary system Ab-H<sub>2</sub>O at 1.0 GPa. The model equation also accurately reproduces the liquidus H<sub>2</sub>O activities from Eggler and Kadik (1979) and Bohlen et al. (1982) when the Aranovich and Newton (1999) activity formulation for CO<sub>2</sub>-H<sub>2</sub>O mixed fluids is applied to their datasets.

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## INTRODUCTION

### *Importance of the Activity Concept*

Lewis and Randall's (1923) definition of chemical activity (*a*) has been an extremely useful concept in the field of geochemistry. The activity measures the degree of departure of the Gibbs free energy of a component *i* of a solution from the ideal mixing law of statistical physics:

$$\ln a_i = \ln X_i + \ln \gamma_i \quad (1)$$

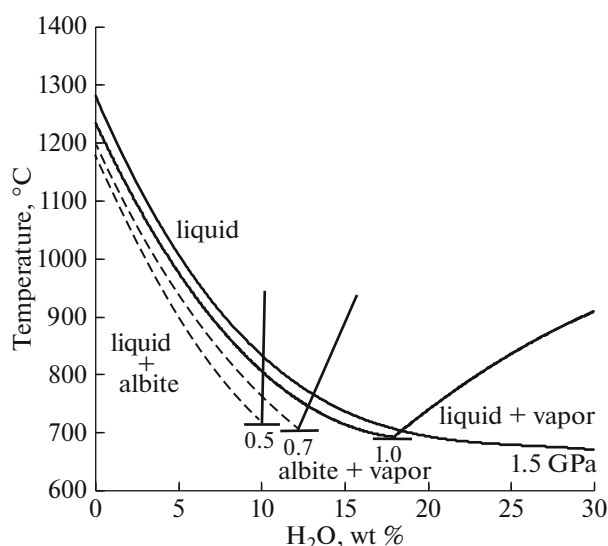
at constant temperature and pressure, where  $X_i$  is the mole fraction of component *i* in a homogeneous mix-

ture and the activity coefficient  $\gamma_i$  measures the non-ideality. The activity of H<sub>2</sub>O assumes a major role in formulation of the thermodynamics of natural fluids and melts (Khorzhinskii, 1959), as illustrated by the numerous discussions of model igneous systems, notably NaAlSi<sub>3</sub>O<sub>8</sub>-H<sub>2</sub>O (Wasserburg, 1957; Burnham, 1975; 1979; Stolper, 1982; Silver and Stolper, 1985; Blencoe, 1992; Paillat et al., 1992; Zeng and Nekvasil, 1996; Zhang, 1999; Stalder et al., 2000; Holland and Powell, 2001; Makhlu<sup>f</sup> et al., 2016).

### *Systems of Volatile and Non-Volatile Components*

G.W. Morey (1917) showed experimentally that some refractory silicates, such as K<sub>2</sub>SiO<sub>3</sub> and K<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>,

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**Fig. 1.** Phase relations in the water-rich part of the  $\text{NaAlSi}_3\text{O}_8\text{-H}_2\text{O}$  binary, showing experimentally constrained liquidus  $\text{H}_2\text{O}$  content and solidus temperatures in the range 0.5–1.5 GPa. Constructed using constraints from Boyd and England (1963; dry melting temperatures), Bohlen et al. (1982; solidus temperatures at 0.5 and 0.7 GPa), Paillat et al. (1992; dotted lines), MakhluF (2015; solid curve at 1.5 GPa), MakhluF et al. (2016; solid curve at 1.0 GPa).

become very soluble in their interaction with  $\text{H}_2\text{O}$  at elevated  $T$  and  $P$ , to the point where continuous solutions may form over large compositional ranges between the volatile and non-volatile components. The important consequence of the solution of  $\text{H}_2\text{O}$  into silicate melts is great lowering of the melting points of silicate minerals. Bowen (1928) applied Morey's (1917) work to discussion of granitic magmas, thus highlighting the importance of  $\text{H}_2\text{O}$  in igneous petrogenesis. D. S. Khorzhinskii (1959) drew attention to the mobile (quasi-volatile) nature of the alkali components at deep-crustal conditions where metasomatic and anatexis phenomena impinge on each other, blurring the distinction between their effects in granitic systems.

Following on the inspiration of Korzhinskii, L.Y. Aranovich and his coworkers have defined, observed and predicted petrological effects of the volatile components  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ , alkalis and halogens, in a series of experimental and theoretical contributions: Aranovich, 2013; Aranovich et al. (1987), Aranovich and Newton (1996–1999), Aranovich et al. (2010; 2013; 2014).

#### *Albite- $\text{H}_2\text{O}$ Models*

The hydrous melting of albite,  $\text{NaAlSi}_3\text{O}_8$ , is a simple but instructive model for the role of  $\text{H}_2\text{O}$  in granitic melts. Alkali feldspar is the dominant mineral constit-

uent of granite; its melting behavior at elevated  $\text{H}_2\text{O}$  pressures illustrates the essential principles of rock melting under deep-crustal  $P$  and  $T$  conditions. Goranson (1938) discovered that  $\text{H}_2\text{O}$  pressure up to 0.4 GPa, corresponding to ~15 km depth in the earth, lowers the melting point of albite from above 1100°C to below 800°C, a temperature range thought to prevail in high and ultra-high grade metamorphism. Thus, a link between metamorphic and igneous processes was established as a quantitative guide to petrogenesis in crustal evolution (Brown and Fyfe, 1970). Subsequent experimental study has provided a great deal of insight into the phase relations and thermodynamic properties, including  $P$ - $V$ - $T$  measurements (Lange and Carmichael, 1990), thermophysical properties (Stebbins et al., 1984) and volumetric measurements of  $\text{NaAlSi}_3\text{O}_8\text{-H}_2\text{O}$  melts (Burnham and Davis, 1971; 1974). Additional experimental studies of melting in the system  $\text{NaAlSi}_3\text{O}_8\text{-H}_2\text{O}$ , extended Goranson's (1938) measurements to higher pressure (Burnham and Jahns, 1962; Eggler and Kadik, 1979; Bohlen et al., 1982; Paillat et al., 1992; Stalder et al., 2000; MakhluF, 2015). Several theoretical models of the role of  $\text{H}_2\text{O}$  in aluminosilicate melts have been attempted to rationalize and extend the experimental measurements (Wasserburg, 1957; Stolper, 1982; Silver and Stolper, 1985; Blencoe, 1992; Zeng and Nekvasil, 1996). However, the modeling has chiefly focused on low pressures and the  $\text{NaAlSi}_3\text{O}_8$ -rich part of the binary. Modeling of the system at the higher pressures corresponding to the source region for most granites remains relatively unexplored, and requires experimental constraints across the entire binary.

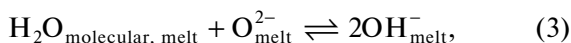
The importance of this issue can be seen in Fig. 1, which shows the liquidus curves in the  $\text{NaAlSi}_3\text{O}_8\text{-H}_2\text{O}$  system at 0.5, 0.7, 1.0 and 1.5 GPa, as constructed from experimental data of Burnham and Jahns (1962), Paillat et al. (1992), MakhluF (2015) and MakhluF et al. (2016). The figure illustrates the large effect of  $\text{H}_2\text{O}$  on phase relations: with increasing pressure,  $\text{H}_2\text{O}$  saturated conditions cause a dramatic decrease in melting temperature and a dramatic increase in  $\text{H}_2\text{O}$  solubility in the saturated liquid. These relations also require an increase in the size of the albite + liquid phase field (Fig. 1). As pressure increases, the slope of the L + V phase boundary changes from negative to positive due to the change from retrograde to prograde solubility of the  $\text{H}_2\text{O}$ -rich vapor into the silicate-rich liquid (Paillat et al., 1992). These facts all point to the onset of critical phenomena where the liquid and vapor phases are completely miscible and a critical endpoint (a.k.a. a second critical point) pressure where a miscibility gap ceases to exist. Any thermodynamic modeling of the albite- $\text{H}_2\text{O}$  system must account for the high-pressure critical mixing behavior between  $\text{NaAlSi}_3\text{O}_8$  liquid and  $\text{H}_2\text{O}$ , which requires consideration of the speciation of  $\text{H}_2\text{O}$  in the mixture and constraints on

the *P-T* trace of the critical curve marking the closure of the solvus between NaAlSi<sub>3</sub>O<sub>8</sub> liquid and vapor.

The role of water speciation in silicate melts as H<sub>2</sub>O vs. OH<sup>-</sup> has received wide attention. Burnham and Davis (1974) and Burnham (1975; 1979) interpreted their volumetric measurements on H<sub>2</sub>O-undersaturated albitic melts as evidence for ideal double dissociation of H<sub>2</sub>O in low-H<sub>2</sub>O melts, following Henry's Law:

$$a_{\text{H}_2\text{O}} = k' X_{\text{H}_2\text{O}}^2, \quad (2)$$

where  $X_{\text{H}_2\text{O}}$  is the mole fraction of H<sub>2</sub>O in the melt with NaAlSi<sub>3</sub>O<sub>8</sub> and  $k'$  is the Henry's Law constant. The activity of H<sub>2</sub>O becomes positively non-ideal, increasing exponentially with  $X_{\text{H}_2\text{O}}$ , when the latter quantity becomes greater than 0.50 on the *eight*-oxygen scale for albite. Stolper (1982) and Silver and Stolper (1985) recommended that the mole fractions of H<sub>2</sub>O and albite be placed on the *one*-oxygen scale for each component. This gives rise to the formula weight of 1/8 of a mole of albite (Na<sub>1/8</sub>Al<sub>1/8</sub>Si<sub>3/8</sub>O) equal to 32.78 g/mol, a convenient formulation which we adhere to in the present paper. They added the concept of a dissociation/equilibrium constant  $K_2$  controlling interaction of molecular H<sub>2</sub>O in the melt with a silicate framework oxygen (O<sub>melt</sub><sup>2-</sup>) to produce two hydroxyls in the melt via the following reaction



for which

$$K_3 = \frac{(a_{\text{OH}^{-}}^m)^2}{(a_{\text{O}^{2-}}^m)(a_{\text{H}_2\text{O, mol}}^m)}. \quad (4)$$

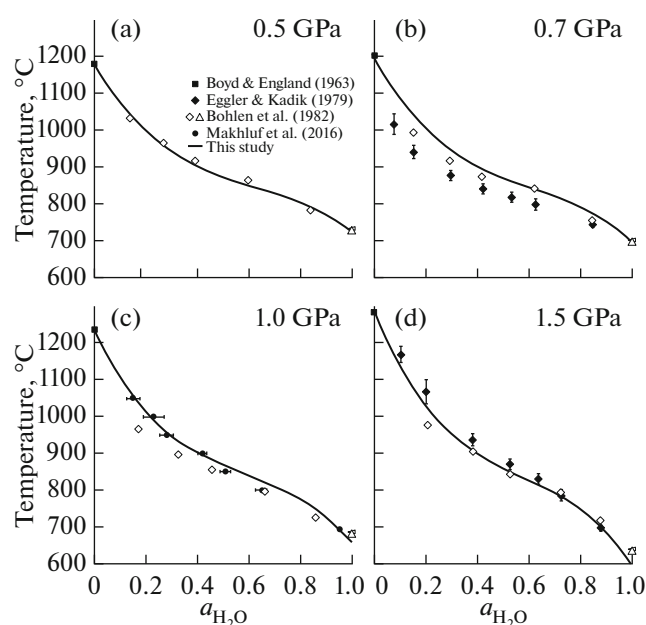
If the mixing is ideal, the activities may be replaced by their concentrations. The equilibrium constant  $K_2$  should depend on  $T$  and  $P$ , but not on  $X_{\text{H}_2\text{O}}$ . The degree of dissociation of H<sub>2</sub>O remains a key issue in discussions of hydrous silicate magmas.

Similarly, the trace of the critical curve has been constrained using multiple approaches. Shen and Keppler (1997) first showed, by optical observation of albite melting in a diamond-anvil pressure cell, that coexisting silicate-rich liquid and H<sub>2</sub>O-rich aqueous vapor converge in composition at pressures above 0.9–1.7 GPa and corresponding temperatures of 1000–700°C, to a single supercritical mixture. The direct observation of critical behavior in the NaAlSi<sub>3</sub>O<sub>8</sub>-H<sub>2</sub>O system was predicted by Paillat et al. (1992). These authors found, in contrast to previous studies, that above 0.4 GPa the solubility of H<sub>2</sub>O in NaAlSi<sub>3</sub>O<sub>8</sub> melts increases with increasing temperature, and they noted that this results in critical mixing between silicate melt and aqueous fluid at some higher temperatures, depending on pressure. They estimated a critical temperature of 1250°C at 1.0 GPa. Subsequent studies used different techniques to estimate *P-T* points along

the critical mixing curve. Stalder et al. (2000) used the diamond trap method to estimate the critical end point, or second critical point, at 1.5 GPa and 700°C. Hayden and Manning (2011) used rutile solubility in NaAlSi<sub>3</sub>O<sub>8</sub>-H<sub>2</sub>O melts to estimate a critical pressure of 0.9–1.0 GPa at 900°C. Makhluף et al. (2016) found an intermediate temperature for critical mixing at 1100°C and 1.0 GPa from albite solubility and H<sub>2</sub>O-saturated melt determinations in the binary system.

Critical mixing on the join NaAlSi<sub>3</sub>O<sub>8</sub>-H<sub>2</sub>O greatly complicates discussions of H<sub>2</sub>O activity and speciation. It must be shown that the first and second derivatives of H<sub>2</sub>O activity with respect to H<sub>2</sub>O mole fraction approach zero as the critical temperature is approached. It is clear that any thermodynamic account of melting in the system NaAlSi<sub>3</sub>O<sub>8</sub>-H<sub>2</sub>O at high pressures must involve H<sub>2</sub>O activity measurements as functions of  $T$ ,  $P$  and  $X_{\text{H}_2\text{O}}$ .

Recently, Makhluף et al. (2016) built on previous studies of H<sub>2</sub>O activity-concentration relations in albitic melts at high pressure (Eggler and Kaddik, 1979; Bohlen et al., 1982) by equilibrating liquidus melts (in equilibrium with crystalline albite) with aqueous NaCl solutions of known H<sub>2</sub>O activity. This activity estimate is made possible by the fact that Cl is very insoluble in the liquidus melts, as determined by electron microprobe analysis of quenched melts (glasses), and that the silicate components are, as Makhluף et al. (2016) also showed, very insoluble in NaCl-H<sub>2</sub>O solutions. These conditions allow the assumptions that the brines in equilibrium with albite and melt along the liquidus are, to a good approximation, binary H<sub>2</sub>O-NaCl mixtures, and that the coexisting melts are effectively binary NaAlSi<sub>3</sub>O<sub>8</sub>-H<sub>2</sub>O mixtures. Therefore, the H<sub>2</sub>O activity measurements of Aranovich and Newton (1996) in the binary system at high temperatures and pressures immediately yield H<sub>2</sub>O activity in coexisting albitic melts. Furthermore, Makhluף et al. (2016) measured the solubility of albite at the vapor-saturated solidus. They found substantial solubility of albite (8.8 ± 0.6 wt %) in the NaCl-free system and showed that this results in critical mixing between silicate melt and aqueous fluid at some higher temperature. Previous thermodynamic treatments typically ignored the solubility of albite (exceptions are Blencoe, 1992, and Zeng and Nekvasil, 1996), assuming that fluids in equilibrium with H<sub>2</sub>O-saturated melts can be considered pure H<sub>2</sub>O. Makhluף et al. (2016) showed that this assumption is inconsistent with critical mixing at any finite temperature. A subregular solution model applied to solidus NaAlSi<sub>3</sub>O<sub>8</sub>-H<sub>2</sub>O melts and aqueous vapors at 1.0 GPa yielded a critical temperature of 1100°C, quite consistent with the results of Shen and Keppler (1997), Hayden and Manning (2011) and as anticipated by melt compositions at lower pressures measured by Paillat et al. (1992).



**Fig. 2.** Liquidus  $H_2O$  activity as a function of temperature at 0.5 GPa (a), 0.7 GPa (b), 1.0 GPa (c) and 1.5 GPa (d). Data from Egger and Kadik (1979) and Bohlen et al. (1982) are measurements in  $NaAlSi_3O_8$ - $CO_2$ - $H_2O$ , converted to  $H_2O$  activities with the  $CO_2$ - $H_2O$  mixing data of Aranovich and Newton (1999). Data from MakhluF et al. (2016) at 1.0 GPa are for compositions in the system  $NaAlSi_3O_8$ - $NaCl$ - $H_2O$  with  $H_2O$  activity calculated using the  $H_2O$ - $NaCl$  mixing properties of Aranovich and Newton (1996).  $CO_2$ -free data from Bohlen et al. (1982) are plotted at  $a_{H_2O} = 1.0$  with a triangle to indicate that, due to albite solubility in  $H_2O$ , the  $a_{H_2O}$  value is a maximum but not realized due to the finite solubility of albite in pure  $H_2O$ . Error bars reflect bracket widths in temperature and where not shown are smaller than the symbol size. The solid curves plotted on each of the graphs was calculated using Eqs. (5) and (6) with parameters from Table 1 (see next page).

#### Scope of the Present Work

The present work extends the method of MakhluF et al. (2016) to pressures covering the deep-crustal range by making use of experimental determinations of fluid compositions in equilibrium with albite-saturated melts in the system  $NaAlSi_3O_8$ - $H_2O$ - $CO_2$ . Two comprehensive data sets exist on albite melting in the presence of  $H_2O$ - $CO_2$  fluids over large pressure ranges (0.5–2.0 GPa; Egger and Kadik, 1979; Bohlen et al., 1982). The former study showed that  $CO_2$  is dissolved quite sparingly in the hydrous albite melts. Other studies have shown that silicate minerals are quite insoluble in  $CO_2$ -rich fluids (Newton and Manning, 2009; Shmulovich and Graham, 2001). MakhluF et al. (2016) used these features to convert the Bohlen et al. (1982)  $CO_2$ - $H_2O$  albite melting data at 1.0 GPa to supplement their  $H_2O$  activity measurements from albite melting in  $NaCl$ - $H_2O$  fluids. A similar approach was used here

at 0.5, 0.7, and 1.5 GPa. Derivation of the  $H_2O$  activity at these conditions makes use of the measurements of Aranovich and Newton (1999) for  $H_2O$ - $CO_2$  mixing. This study was based on the CORK formulation of  $H_2O$  and  $CO_2$   $P$ - $V$ - $T$  relations of Holland and Powell (1991) and the Holland and Powell (1998) data set. This formulation is adhered to in the present study.

#### RESULTS OF CALCULATIONS

Temperatures of albite melting under various  $H_2O$  concentrations in  $H_2O$ - $CO_2$  solutions were compiled from Egger and Kadik (1979) and Bohlen et al. (1982), and then fluid compositions were used to derive  $H_2O$  activity. Following Stolper (1982) and Silver and Stolper (1985), the mixing units used to obtain  $H_2O$  activity were taken on a one-oxygen basis ( $H_2O$  and  $Na_{1/8}Al_{1/8}Si_{3/8}O$ ). The 2.0 GPa data from Egger and Kadik (1979) and Bohlen et al. (1982) are not included because the Aranovich and Newton (1999) activity-concentration formulation is limited to the range 0.6–1.4 GPa; it is however assumed here that their  $H_2O$  activity trends may be extrapolated safely by 0.1 GPa in both pressure directions.

Figures 2a–2d show the liquidus  $H_2O$  activity-temperature relations at 0.5, 0.7, 1.0 and 1.5 GPa as derived from the two data sets. The  $H_2O$  activity values resulting from the experimental data are quite consistent, except in the very  $CO_2$ -rich range. This is because of the substantially lower melting temperature of dry albite adopted by Bohlen et al. (1982: 1190°C at 1.0 GPa). We find that using these low temperatures results in reduced fitting quality (see below). We therefore adopted nominally dry melting temperatures of pure albite of Boyd and England (1963), consistent with conclusions of Holland and Powell (2001). The 1.0 GPa data (Fig. 2c) also includes derivations from experimental melting of albite in the presence of  $NaCl$ - $H_2O$  solutions (MakhluF et al., 2016).

The experimental constraints (Fig. 2) can be used to determine liquidus  $T$ - $a_{H_2O}$  relations over a range of pressures. Figure 2 shows that the 0.5, 1.0 and 1.5 GPa data are generally consistent. In contrast, at 0.7 GPa, the derived Egger and Kadik (1979) constraints are substantially displaced to lower  $H_2O$  activities and temperatures relative to the Bohlen et al. (1982) data (Fig. 2b). Accordingly, the 0.5, 1.0, and 1.5 GPa data were used impartially in regressions to determine  $H_2O$  activity curves, while the 0.7 GPa data were omitted. Derivation of an equation describing  $T$ - $a_{H_2O}$  relations as a function of pressure proceeded by first performing least squares fits to cubic equations at each pressure. Bohlen et al. (1982) reported  $H_2O$ -saturated melting temperatures, but they did not report fluid composition. As noted by Clark (1966), Manning et al. (2010), and MakhluF et al. (2016), the solubility of albite (and hydrous albite liquid) at  $H_2O$ -saturated melting may

be significant and increases strongly with pressure; i.e.,  $a_{\text{H}_2\text{O}}$  is not strictly 1.0. This is indicated in Fig. 2 by plotting pure H<sub>2</sub>O data from Bohlen et al. (1982) as triangles, to indicate that the constrained  $a_{\text{H}_2\text{O}}$  is strictly a maximum. For the purposes of deriving a  $T$ – $a_{\text{H}_2\text{O}}$  model, we assumed that  $a_{\text{H}_2\text{O}}$  was approximately 1.0 at wet melting at 0.5 GPa, and we included this “datum” in the fits. At 1.0 GPa, we used the solubility data from Makhluף et al. (2016). We omitted the pure-H<sub>2</sub>O results of Bohlen et al. (1982) at 1.0 and 1.5 GPa since the solubility of albite at these pressures has recently been determined to be nonzero (Makhluף, 2015; Makhluף et al., 2016).

Fits to cubic equations at 0.5, 1.0, and 1.5 GPa yielded fit parameters at each pressure which varied approximately linearly with pressure. This was used to derive an empirical expression for the variation in liquidus temperature with  $a_{\text{H}_2\text{O}}$ :

$$T = m_0 + m_1 a_{\text{H}_2\text{O}} + m_2 a_{\text{H}_2\text{O}}^2 + m_3 a_{\text{H}_2\text{O}}^3, \quad (5)$$

where  $T$  is in °C and

$$m_i = n_0 + n_1 P, \quad (6)$$

where  $P$  is in GPa. Parameters  $m_i$  are listed in Table 1. Equations (5) and (6) are applicable at  $0.5 < P < 1.5$  GPa and  $T_{\text{solidus}} < T < T_{\text{dry melting}}$ . We adopted  $T_{\text{dry melting}}$  from Boyd and England (1963), and took  $T_{\text{solidus}}$  to be 729°C at 0.5 GPa (Bohlen et al., 1982), 705°C at 0.7 GPa (Bohlen et al., 1982), 695°C at 1.0 GPa (Makhluף et al., 2016), 665°C at 1.5 GPa (Makhluף, 2015). Intermediate values for  $T_{\text{solidus}}$  can be interpolated.

The liquidus surfaces derived from Eqs. (5) and (6) are compared to the data in Fig. 2. Results indicate that the derived model accurately reproduces experimental data for H<sub>2</sub>O activity in albitic liquids, independent of whether  $a_{\text{H}_2\text{O}}$  reduction as achieved in the H<sub>2</sub>O–CO<sub>2</sub> or the H<sub>2</sub>O–NaCl systems. In contrast and as expected, results at 0.7 GPa indicate discrepancies (Fig. 2b). Relative to the model, Bohlen et al. (1982) data generally yield slightly lower  $a_{\text{H}_2\text{O}}$  at a given  $T$ ; however, the Eggler and Kadik (1979) differ more so. Uncertainties are large in the latter data set (see their Fig. 5).

Figure 3 shows  $T$ – $a_{\text{H}_2\text{O}}$  relations at 0.2 GPa increments, as derived using Eqs. (5) and (6). The curves show that H<sub>2</sub>O activity only varies significantly in pressure as  $a_{\text{H}_2\text{O}}$  approaches 0 and 1, but are quite similar for intermediate values of  $a_{\text{H}_2\text{O}}$ . H<sub>2</sub>O concentration is the predominant control for temperatures 100°C or more above the solidus. The predicted solubility of albite (and hydrous albite liquid) at the pure-H<sub>2</sub>O solidus is seen to increase with pressure, consistent with expectation (e.g., Anderson and Burnham, 1983; Stalder et al., 2000; Makhluף et al., 2016).

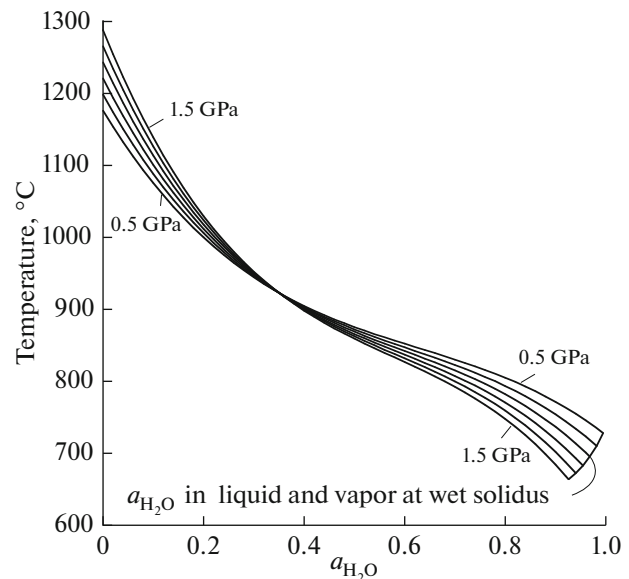
**Table 1.** Fit parameters for use in Equation (5)

$m_i$	$n_0$	$n_1$
$m_0$	1119.6	112.3
$m_1$	–856.5	–578.9
$m_2$	1004.1	952.9
$m_3$	–477.1	–618.0

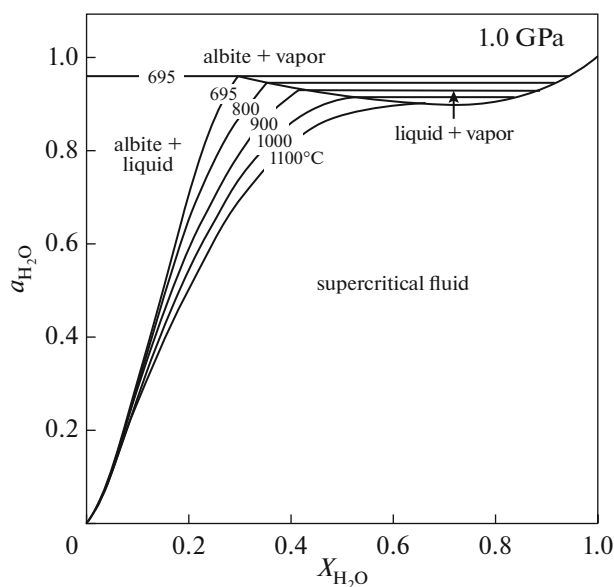
## DISCUSSION

### *Thermodynamic Interpretations*

Results on liquidus  $T$ – $a_{\text{H}_2\text{O}}$  relations can be combined with an NaAlSi<sub>3</sub>O<sub>8</sub>–H<sub>2</sub>O mixing model at a given  $P$  and  $T$  to portray, the quantitative relationships between  $a_{\text{H}_2\text{O}}$  and  $X_{\text{H}_2\text{O}}$  across the full  $Ab$ –H<sub>2</sub>O binary. Figure 4 shows these relations at 1.0 GPa, the pressure with the most constraints. In Fig. 4, the liquidus compositions and activities are derived from our model and agree closely with independent measurements of the liquidus compositions in the binary system  $Ab$ –H<sub>2</sub>O. The solvus between coexisting silicate melt (“liquid”) and aqueous fluid (“vapor”) is from Makhluף et al. (2016), as are the  $a_{\text{H}_2\text{O}}$ – $X_{\text{H}_2\text{O}}$  isotherms in the liquid/supercritical fluid phase field.



**Fig. 3.** Comparison of the isobaric H<sub>2</sub>O activity liquidus curves in the system NaAlSi<sub>3</sub>O<sub>8</sub>–H<sub>2</sub>O derived from temperature-composition melting data of albite with CO<sub>2</sub>–H<sub>2</sub>O and NaCl–H<sub>2</sub>O fluids (Fig. 2) at 0.2 GPa intervals. The plot reveals that the overwhelming determinant of liquidus temperature is the H<sub>2</sub>O activity; the effect of pressure is secondary except in the limits of  $a_{\text{H}_2\text{O}}$  approaching 0 or 1.



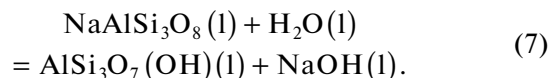
**Fig. 4.**  $H_2O$ -activity–concentration diagram for the system  $NaAlSi_3O_8$ - $H_2O$  at 1.0 GPa. The liquidus (Ab + liq = liq) is calculated using results of the present study. Other phase boundaries and  $a_{H_2O}$ - $X_{H_2O}$  isotherms in the liquid/supercritical fluid field are from MakhluF et al. (2016). The figure illustrates the remarkably high  $H_2O$  activity at the  $H_2O$  saturated solidus, as well as in the vapor phase even up to the closure of the solvus where  $NaAlSi_3O_8$  concentration is ~45 wt % and  $T_{critical} = 1100^\circ C$ . Note that  $X_{H_2O}$  represents the mole fraction of  $H_2O$  on a 1-oxygen basis (i.e. mixing with  $Na_{1/8}Al_{1/8}Si_{3/8}O$ ).

An important conclusion that can be drawn from Fig. 4 is that  $H_2O$  activity in the vapor coexisting with melt is very high and nearly constant over a broad range of bulk composition and temperature: the total variation from the solidus at  $695^\circ C$  ( $a_{H_2O} = 0.96$ ) to the critical point at  $1100^\circ C$  is only 0.06. At this point the supercritical fluid has close to 45 wt % silicate component. The critical activity-composition curve satisfies the necessary condition of zero slope at the critical temperature of  $1100^\circ C$ . The high  $H_2O$  activity shows that the majority of the hydrous component is molecular  $H_2O$  rather than hydroxyl. This conclusion was reached by MakhluF et al. (2016) by applying Silver and Stolper's (1985) modeling approach (Eq. (3)) to the 1.0 GPa  $NaCl$ - $H_2O$  melting data.

Another significant feature of the activity-concentration relations at 1.0 GPa (Fig. 4) is that all of the activity-concentration isotherms condense to a tight spindle as they approach  $X_{H_2O} = 0$ . This is, in effect, equivalent to Burnham's (1979) limiting law (Eq. 2) with  $k'$  (on an 8-O basis) nearly independent of temperature. The limiting  $k'$  value from Fig. 4 is 1.40, close to Burnham's (1979) recommended value of about 1.68 at 1.0 GPa in the range  $800$ – $1100^\circ C$ . Silver and

Stolper (1985) also note that  $a_{H_2O}$  is nearly proportional to the square of  $X_{H_2O}$  if their  $K_2$  is in the range 0.1–0.2. This condition is realized over much of the dilute concentration range of  $H_2O$  in albite melts, which is consistent with the model for  $H_2O$  speciation (Stolper, 1982), but not at higher  $H_2O$  contents.

Burnham (1975; 1979) interpreted the action of  $Na^+$  as a “dissociable” cation which expedites dissociation of  $H_2O$  in the silicate melt. His discussion included protons as a mixing unit, which makes for an awkward formulation. However, the dissociation reaction in  $NaAlSi_3O_8$ - $H_2O$  melts could be reinterpreted as a combination of the Burnham (1975) and Silver and Stolper (1985) concepts:



$NaOH$  could exist as an independently mixing component of the melt such that  $H_2O$  going into solution behaves as a doubly-dissociating solute, giving rise to  $X_{H_2O}$  dependence of the  $H_2O$  activity. The very high alkalinity ( $pH \geq 12$ ) found by MakhluF et al. (2016) in quenched fluids from  $H_2O$ -rich melting experiments as well as the dramatic decreases in solubility with increasing  $NaCl$  content of the fluid phase suggest that such a dissociation mechanism could be operative. Burnham's (1979) explanation for the departure of  $a_{H_2O}$  from  $X_{H_2O}^2$  dependence at high  $H_2O$  concentration is exhaustion of the limited supply of  $Na^+$  at high  $H_2O$ ; he did not consider possible partitioning of solute  $H_2O$  between molecular  $H_2O$  and hydroxyl. Burnham's (1979) model also suffers from the approximation that the fluid coexisting with saturated albite melts is, thermodynamically speaking, pure  $H_2O$ . This assumption allows immediate application of the  $H_2O$  equation of state, as determined accurately by the volumetric measurements of Burnham et al. (1969), but fails drastically at  $P \geq 0.2$ – $0.3$  GPa, where albite becomes very soluble in  $H_2O$ . It is easily shown that the assumption of a pure  $H_2O$  fluid coexisting with a  $H_2O$ -saturated albitic liquid can never lead to critical mixing of the melt and fluid. Similarly, the recognition by Silver and Stolper (1985) of  $H_2O$  partitioning can explain the very high  $H_2O$  activity found for  $H_2O$ -rich albitic melts at high pressures, but the range of values they derived for  $K_2$  likewise prohibits its recognition of critical mixing.

#### Petrological Interpretations

D. S. Khorzhinskii (1959) recognized the conspicuously independent action of the alkali elements in his classification of immobile and perfectly mobile components. This concept revived the subject of alkali metasomatism, which had languished for many years

perhaps because of the great attention paid to experimental melting diagrams in hydrous systems (Putnis and Austrheim, 2010). The physical chemistry of the system NaAlSi<sub>3</sub>O<sub>8</sub>-H<sub>2</sub>O, with elucidation of the dissociation of H<sub>2</sub>O in the melts (Burnham, 1975), the partitioning of dissolved H<sub>2</sub>O between molecular H<sub>2</sub>O and hydroxyl (Stolper, 1982), and the high solubility of albite in H<sub>2</sub>O at deep crustal *T* and *P* leading to critical mixing of melts and fluids (Paillat et al., 1992; Shen and Keppler, 1997), have all played important roles in an approach to understanding of the evolution of granitic melts in the deeper parts of the crust.

The very mobile nature of the alkalis in high-grade metamorphism and metasomatism, recognized by D.S. Khorzhinskii and documented by L.Y. Aranovich and his co-workers, may be largely the result of intergranular migration of concentrated chloride solutions. Because of the high solubility of carbonates, sulfates, and, to a lesser extent, phosphates, in aqueous chloride solutions (summarized by Manning and Aranovich, 2014), these components behave differently from the silicate constituents under deep-crust metamorphic conditions. Besides profound lowering of the H<sub>2</sub>O activity (Aranovich and Newton, 1997), concentrated interstitial brines have low contact angles with silicate minerals, thus greater intergranular mobility (Holness, 1992; Gibert et al., 1998).

CO<sub>2</sub> as an interstitial fluid has effects opposite to those of brines; it has high surface tension relative to silicate mineral grains; accordingly, it tends to accumulate and become trapped as fluid inclusions at triple-juncture grain boundaries (Johnson, 1991). The presence of CO<sub>2</sub> increases the H<sub>2</sub>O activity substantially, leading to immiscibility of CO<sub>2</sub>-rich and brine-rich aqueous fluids. This behavior is demonstrated by experimental studies of quartz recrystallization in the presence of H<sub>2</sub>O-NaCl-CO<sub>2</sub> fluids at high *P* and *T* (Gibert et al., 1998), by observation of apparently coeval carbonic and saline fluid inclusions in minerals of high grade metamorphic rocks (Touret, 1985; Newton et al., 2014), and by thermodynamic modeling of phase relations in the ternary system H<sub>2</sub>O-CO<sub>2</sub>-NaCl (Aranovich et al., 2010). The general effect of the saline and carbonic components in aqueous fluids is to elevate the solidus temperature in quartzofeldspathic rocks and thus provide for potent high-grade mineralizing fluids in the solid crust.

The foregoing discussion has shown how the simple system albite-H<sub>2</sub>O-CO<sub>2</sub>-NaCl can serve as a basis for discussion of the interaction of natural fluids and silicate melts under deep-crustal metamorphic conditions. Extension of the simple system to higher pressures becomes more difficult because of the high solubilities of silicate constituents, at conditions approaching critical mixing in the subsystem NaAlSi<sub>3</sub>O<sub>8</sub>-H<sub>2</sub>O, but is an important area for further research to elucidate the

nature of fluids and melts at very deep levels, as in subduction zones (Manning, 2004).

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