Calorimetric evidence for ideal mixing of silicon and germanium in glasses and crystals of sodium feldspar composition

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Abstract

High temperature oxide melt solution calorimetric data have been obtained for glasses and crystals of sodium feldspar composition, NaAl $(Si, Ge)_3O_8$, with varying degrees of substitution of Ge for Si. A linear dependence on composition for the enthalpies of solution implies ideal mixing behavior for both crystalline and glassy phases. The results are discussed in light of the rather different reported viscosities for end-member melts. The thermodynamic data collected allow calculation of a simple phase diagram for this two-component system. The calculated value of $K_D = (X^c_{Ge}/X^c_{Si})/X^l_{Ge}/X^l_{Si})$ is 0.87 ± 0.05.

Introduction

The study of albite melts and glasses has a long history in experimental petrology. As a major component in "petrogeny's residua system," albite is of particular significance to granite petrogenesis. To model a generalized silicate melt, water solubility measurements on this composition set the experimental foundation for understanding the interactions of volatiles with magmas, (Burnham, 1979). In addition, a sharp decrease in viscosity of albite melts reported from high pressure measurements has been cited as contributing evidence for pressure induced coordination changes in magmas (Kushiro, 1978), or for other structural changes (Sharma *et al.*, 1978).

In the present study, this celebrated sodium aluminosilicate was chosen for investigation of the thermodynamic mixing behavior of Ge and Si. Solution calorimetric measurements were made on glasses and on crystals in the high albite solid solution between Ge-albite ($NaAlGe_3O_8$) and Si-albite ($NaAlSi_3O_8$). Because the geochemistry of Ge^{4+} is usually described in terms of its substitution for Si^{4+} in silicate systems, it is of interest to discover whether this substitution in a highly siliceous phase like albite involves appreciable departures from ideal thermodynamic behavior. The utility of the germanates as analogues to silicate systems has been exploited in the past to predict high pressure silicate phase transitions. Many of the extrapolations from germanate to silicate phase

transitions are based on the assumption of ideal mixing between Si and Ge (Ringwood, 1975, p 360). This study tests the validity of that assumption and comments on the significance of homovalent substitutions into melt framework sites. The data collected also enable prediction of feldspar/melt trace element partition coefficients for germanium.

Experimental methods

Sample preparation

Glass samples used for calorimetry were prepared from reagent SiO_2, GeO_2, Al_2O_3 and Na_2CO_3 dried at 400° C (oxides) and 100° C (carbonate). Carbonated stoichoimetric end-member compositions were mixed in an agate mortar under acetone for at least 30 minutes. Mixes were decarbonated and fused at 1300° C in 95% Pt–5% Au crucibles until measured weight loss agreed with that calculated. These glasses were subjected to at least three cycles of grinding under acetone for 30 minutes followed by fusion. Varying proportions of Ge to Si in the albite glasses were obtained from intimate mixtures of powdered endmember glasses. Intermediate compositions were held at 1300° C for an initial fusion of 30 minutes. Quenched glasses were ground again (at least 30 minutes) and remelted at 1300° C for 2 hours. The viscosity of the Ge-bearing melts was noted to be much less than that of the very Si-rich compositions because the Ge-rich compositions formed clear and bubble-free glasses. Glasses were analyzed by electron microprobe and

Table 1. Glass densities of Ge, Si albite

mol % $NaAlGe_3O_8$	ρ *(gm/cm^3)
0†	2.382
23.6	2.625
49.2	2.896
76.0	3.143
100.0††	3.368

*Estimated error ± 0.002.
†Robie et al. (1979).
††Riebling (1966).

found to be homogeneous in composition and to correspond to nominal compositions within 0.7%. Sodium volatilization during melting did not appear to be a problem in these glasses with equal molar concentrations of aluminum and sodium. Glasses were crushed and sieved prior to calorimetry to obtain grains between 35 and 100 mesh.

Densities of small bubble-free chunks of glass approximately 2 mm in diameter were measured for several compositions. Methylene iodide–chloride solutions were prepared in which the glass samples neither floated nor sank but remained suspended within the liquid. Two milliliters of the isopycnic liquid were drawn off with a calibrated pipette and accurately weighed to calculate glass densities, see Table 1; from replicate analyses the precision is estimated as ~ ±0.002 gm/cm^3.

Crystalline solid solutions were prepared by devitrification of glasses at 1000° C for up to 1 week. Because of the high viscosity of pure Si-albite melts, crystalline material suitable for calorimetry

could not be prepared by this technique. No traces of glass could be detected microscopically in devitrified samples and X-ray powder patterns exhibited only high albite diffraction peaks. Between 18 and 21 peaks were used for least squares refinement of lattice parameters. Potassium bromate was used as an internal reference standard ($a = 6.0160\pm0.0015$ Å, $c = 8.1558\pm0.0021$Å) which was previously refined using N.B.S. Si (supplied by Dr. B. Wechsler) as an internal standard. Refined lattice parameters for crystals used in calorimetry are given in Table 2. Molar volumes for crystals were calculated from these values. Refined peak positions for $2\theta_{131}-2\theta_{1\bar{3}1}$ were found to increase smoothly from Si-rich albites to Ge-albite confirming the high structural state. Crystals were analysed by electron microprobe and found to be homogeneous with respect to Ge and Si and correspond to nominal compositions within 0.7%. No apparent fractionation of these elements occurred during devitrification. Powdered unsieved samples were used for calorimetry.

Calorimetry

Oxide melt solution calorimetry has been described by Kleppa (1972) and Navrotsky (1977). The general technique, calibration and preparation of the $2PbO\cdot B_2O_3$ solvent were all as previously described. Modifications described by Navrotsky et al. (1980) for glass samples were also employed. The Ge-rich glasses were prone to devitrification within the calorimeter (708° C) before dissolution. The lower viscosity of these glasses apparently enhanced the kinetics for the transition from the metastable glass to the stable crystalline state. Shortening the length of time required to achieve

Table 2. Unit cell parameters for Ge, Si albite crystals

Mol % $NaAlGe_3SiO_8$	a_o	b_o	c_o	α	β	γ
99.5	8.417(3)*	13.290(3)	7.343(2)	94.35(2)	116.24(2)	90.93(2)
74.0	8.341(7)	13.169(7)	7.278(5)	94.37(7)	116.26(5)	90.60(5)
47.4	8.282(5)	13.128(19)	7.215(6)	93.93(15)	116.21(5)	90.73(8)
23	8.209(1)	12.942(1)	7.145(1)	93.67(3)	116.16(2)	90.21(2)
0 ✶	8.149	12.880	7.106	93.37	116.30	90.28

*Number in parentheses is standard error of last digit, a_o, b_o, c_o in Å, α, β, γ in degrees ✶pure albite parameters from Borg and Smith (1969).

Table 3. Enthalpies of solution of Ge,Si albite crystals and glasses in $2PbO \cdot B_2O_3$ at 708° C

mol% $NaAlGe_3O_8$	ΔH_{sol} kcal/mol*
Glasses	
99.5†	-8.497 ± 0.995(4)
84.1	-6.293 ± 0.360(5)
66.2	-3.888 ± 0.262(4)
48.2	-1.538 ± 0.342(4)
30.4	1.596 ± 0.382(5)
19.8	3.249 ± 0.488(4)
10.0	4.289 ± 0.286(3)
0.0	5.418 ± 0.110(4)
Crystals	
99.5†	4.229 ± 0.206(5)
74.0	7.433 ± 0.158(5)
47.4	11.006 ± 0.340(4)
23.6	14.548 ± 0.156(4)

*Error is two standard deviations of the mean, in parentheses is number of successful runs.
†Silica comprises remainder.

thermal equilibrium before calorimetry mostly circumvented this problem. Careful sample loading procedures which reduced the initial thermal imbalance allowed equilibration time to be reduced to 1.5 to 2 hours instead of the typical 3 hour period. This procedure prevented devitrification of most of the high germanium content glasses, as checked by optical examination of "dummy runs," in which the glass samples were thermally equilibrated in the calorimeter but not dissolved. However, for the fully substituted germanium albite glass, a small amount of devitrification may be responsible for the great scatter in the heat of solution. However, the amount of crystal detectable under the microscope
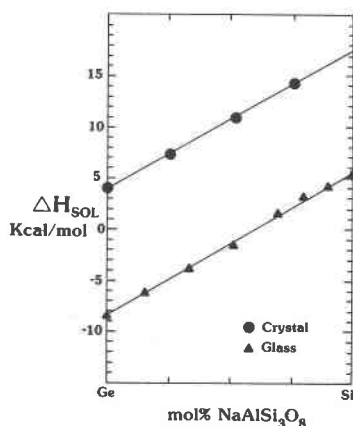
was <1%, so no correction was made to the heat of solution. A similar problem had been seen for GeO_2 glass (Navrotsky, 1971).

Results and discussion

Calorimetric data are presented in Table 3 and Figure 1 for both crystals and glasses in the system $NaAlGe_3O_8$–$NaAlSi_3O_8$.[1] Within experimental error, the heat of solution of glasses varies linearly with mol fraction, implying a zero heat of mixing. We note however, that the heat of solution of the Si-albite glass is ~ 650 cal/mol higher than the previously reported value of 4778 cal/mol (Navrotsky *et al.*, 1980). This difference seems to be a systematic one which is also found in the extrapolated heat of solution for crystalline high albite. The cause of this difference may be related to slight variations in the composition of the calorimetric solvent and a slightly different operating temperature (708° C instead of 713° C). Such variations have been seen previously, (*e.g.* Navrotsky and Coons, 1976; Charlu *et al.*, 1975). This difference does not alter the straightforward interpretation of the data in terms of heats of mixing and of vitrification. The enthalpy of vitrification obtained for albite (12.181 kcal/mol) is within the experimental error of the previously reported values, (12.402 kcal/mol, Navrotsky *et al.* 1980) and exemplifies the fact that it is the magnitude of the difference between heats of solution which provide thermodynamic information.

An important but perhaps not unexpected conclu-

[1] 1 cal = 4.184 joule.

Fig. 1. Enthalpies of solution of crystals and glasses on the join $NaAlGe_3O_8$–$NaAlSi_3O_8$ at 981 K. *Solid lines*—ideal mixing of end-members.
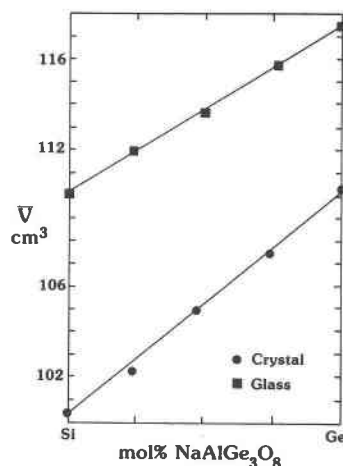

Fig. 2. Molar volumes of crystals and glasses calculated from X-ray powder diffraction unit cell refinement and heavy liquid density measurements, respectively. *Solid lines*—ideal mixing of end-members. Pure albite from Borg and Smith (1969).

sion of this study is that Ge and Si do, in fact, mix without any enthalpy of mixing in both glassy and crystalline phases as examination of Figure 1 reveals, (fitting the data to a regular solution model results in an interaction parameter smaller than experimental error). The volumetric data (Fig. 2) also exhibit approximately ideal behavior. However, there may be a suggestion of nonideality for the crystalline albites; the 23.6% Ge-albite point falls off the line. This may be similar to the behavior described by Newton and Wood (1980) as "equivalent site substitution." Nevertheless, the main trend is indeed linear; additional synthesis will be required to confirm possible non-ideal volume behavior near the end member.

The absence of a heat of mixing suggests that end-member glasses along with the intermediate compositions are similar in structure, at least on a distance scale which determines major energetic interactions. Supporting evidence for this is provided by the constant value for the enthalpy of vitrification. If the major structural organization of the germanate glass were different from the silicate one might expect the enthalpy change on transformation to the isostructural crystalline feldspar to change with composition.

Riebling (1965) reported viscosity data for Ge-albite liquid over a limited range of temperature ($\log_{10}\eta = -5.3053 + 12002/T$ (K); (1240–1460° C)). If we compare the viscosities of the two end-member melts at the melting points of their crystalline phases ($T^\circ_{m,Ge}$ = 1068° C (Goldsmith, 1950); $T^\circ_{m,Si}$ = 1100° C (Boettcher et al., 1982) we find a difference of four orders of magnitude ($\log_{10}\eta$ (Ge-albite, 1068° C) = 3.64, (Riebling, 1965) $\log_{10}\eta$ (Si-albite, 1100° C) = 8.1, (Crammer and Uhlmann, 1981). From this it is evident that large changes in viscosity, by themselves, do not necessarily imply either pronounced changes in thermodynamic properties or substantial rearrangement of structural units on a nearest neighbor coordination scale.

The mechanisms involved in viscous flow of silicate melts may differ substantially when the overall structure changes, but, for a given structural class, it seems reasonable that similar flow mechanisms will apply. Cranmer and Uhlmann (1981) compared viscosity data for the classic random tetrahedral networks GeO_2 and SiO_2 with data for Si-albite over a large temperature interval (measuring 9 orders of magnitude in η). When they chose the glass transition temperatures (T_g) as a corresponding states parameter and plotted the data in log η vs. T_g/T, the linear trends were coincident (Fig. 3). Ge-albite also plots in coincidence with the other network materials over the restricted temperature range for which η is available. Furthermore, the trend in activation energies for viscous flow for network germanates and silicates parallel each other. For SiO_2 the activation energy is between 120 and 130 kcal/mol while for Si-albite it is 95 kcal/mol, (Cranmer and Uhlmann, 1981); a 25% decrease accompanies the addition of sodium aluminate tetrahedra in 1:3 proportion to silicate tetrahedra. Riebling (1965) reports an activation energy for Ge-albite of ~ 55 kcal/mol which, when compared with 70 kcal/mole for GeO_2 (Fontana and Plummer, 1966), is seen also to be a 25% decrease.

For fully polymerized melts the mechanism for flow must involve the breaking and reforming of T–O–T bonds (T = Si, Al or Ge) in some manner. Yet the energy required to break Si–O and Ge–O bonds is comparable (106 kcal/mol, 108 kcal/mol respectively, Kingery, et al. 1976). In fact, our calorimetric data support the idea that neither tetravalent cation is capable of polarizing the oxygen to which it is bound more strongly than the other; otherwise non-zero enthalpies of mixing should be manifest, as are seen along the SiO_2–$Ca_{0.5}AlO_2$ join, (Navrotsky et al., 1982). Radial distribution functions calculated from X-ray data on vitreous SiO_2 and GeO_2 have revealed that the randomness of the
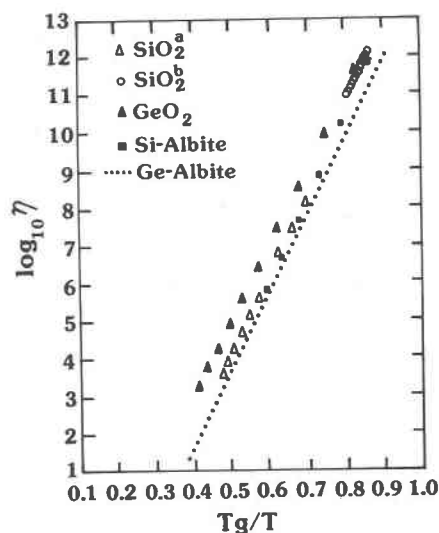

Fig. 3. Viscosity of network materials as a logarithmic function of a reduced temperature parameter. Tg is glass transition temperature for each material. Data for SiO_2 (a and b), GeO_2, Si-albite are from Cranmer and Uhlmann (1981); for Ge-albite are from Riebling (1965).

network for SiO_2 results from a wide distribution of the T–O–T angles whereas for GeO_2 the T–O–T bond angle distribution is rather sharp and the randomness arises mainly from a distribution of tetrahedral rotation angles (Kingery, et al. 1976). The viscosity decrease from the silicates to the germanates may be related to such structural details. Perhaps the activation energy is decreased if the T–O–T angle is fairly constant by optimizing the average geometry in which a species transfers momentum or in which a T–O bond breaks, compared to the case where the T–O–T angle takes on a wide range of values. It is also worth noting that, for equal bond strengths (force constants) for Ge–O and Si–O bonds, the vibrational frequency for Ge–O stretching is significantly less than for Si–O simply because of the difference in mass.

Geochemical implications and conclusions

Germanium and silicon mix ideally in terms of heats of mixing in albite glasses and crystals. Thus they probably also mix close to ideally in terms of activities (for one mol of Ge plus Si) in isostructural crystals and in melts. This confirms the expected behavior of these elements and should be useful in interpreting the geochemistry of germanium. In a previous study (Capobianco and Watson, 1982) concerning the trace element partitioning behavior of Ge between olivine and melts in the Di–An–Fo ternary, it was concluded that Ge and Si would not be fractionated significantly at low pressures, but at pressures near 20 kbar some enrichment of Ge with

respect to Si in the melt would be expected. Based on the thermodynamic data collected in this study we predict close but not exact geochemical coherence for Ge and Si in highly siliceous systems like albite at low pressure. If Ge and Si mix ideally in both crystals and melts, then the distribution of these elements, and therefore the crystal–liquid binary loop, is governed by the following equations (Mueller and Saxena, 1977, p. 30):

$$X_{Ge}^c/X_{Ge}^l = \exp[\Delta H_{f,Ge}/R(1/T - 1/T_{m,Ge}^\circ)] \quad (4)$$

$$X_{Si}^c/X_{Si}^l = \exp[\Delta H_{f,Si}/R(1/T - 1/T_{m,Si}^\circ)] \quad (5)$$

where X_i^c, X_i^l $T_{m,i}^\circ$ $\Delta H_{f,i}$, respectively represent mole fractions of subscripted components in crystal and liquid and the melting points and heats of fusion of pure end–member phases. In general, because the heat capacity of the liquid is greater than that of the crystal, the heat of fusion will depend on temperature and be substantially larger than the heat of vitrification (Navrotsky et al., 1980). Detailed heat capacity data allow the calculation of the heat of fusion for albite (Navrotsky et al, 1980). For Ge-albite no such heat capacity data are available, but the enthalpy of transformation of $NaAlGe_3O_8$ from the crystalline to the amorphous state has been measured in the present work. This amorphous state, because of its low viscosity (Riebling, 1965), is in fact a super-cooled liquid at the calorimetric temperature, 708° C. As a first approximation we have assumed that the difference in heat capacity between liquid and crystal (ΔC_p) is the same for albite and for germanium albite and used the temperature dependence of the heat of fusion of albite given by Navrotsky et al. (1980) to calculate the heat of fusion of Ge-albite at its melting point. This gives, for $NaAlGe_3O_8$ at 1068° C, $\Delta H_f = 15.820$ kcal/mol, while for $NaAlSi_3O_8$ at 1100° C, $\Delta H_f = 15.700$ kcal/mol, for use in equations (4) and (5). Because of the near equivalence of ΔH_f for both phases and the small temperature interval of the melting loop (1068–1100° C), we can ignore the temperature dependence of the heats of fusion in that range. The resulting liquidus loop, calculated using equations (4) and (5) is shown in Figure 4. It is remarkably narrow and quite similar to that for the Al, Ga plagioclases (Goldsmith, 1950) in which no detectable difference was found between the liquidus and solidus. An estimate of K_D for Ge/Si partitioning may be determined by combining equations (4) and (5), with $\Delta H_{f,Ge} \approx \Delta H_{f,Si} = 15.76$ kcal/ mol.

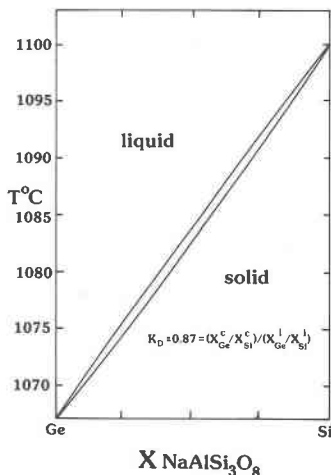Fig. 4. Calculated 1 atm phase diagram of two-component system $NaAlGe_3O_8$–$NaAlSi_3O_8$ (see text).

$$K_D = (X_{Ge}^c / X_{Si}^c) / (X_{Ge}^l / X_{Si}^l) =$$

$$\exp \left(\Delta H_f / R (1/T_{m,Si}^\circ - 1/T_{m,Ge}^\circ) \right) \quad (6)$$

Equation 6 is independent of temperature (Ge/Si ratio in coexisting melt and crystal is *not* a geothermometer) and yields a value of 0.87 for K_D. This value may be a slight overestimate of K_D since it appears likely that ΔC_p may be larger for Ge-albite than for albite both because of the lower viscosity and lower T–O stretching vibrational frequencies of the former. However, assuming that ΔC_p is 50% greater for Ge-albite than for albite lowers K_D by only 0.01. We conclude that a value of K_D of 0.87 ± 0.05 for albite-melt equilibria is a reasonable estimate when one takes into account other sources of error (assuming ideal entropy of mixing in melts and crystals, errors in calorimetric data, *etc.*)

This value of K_D should apply to albite-melt equilibria in melts of complex composition provided the addition of other components affects Ge and Si in a similar manner. We note also that because the volume change on melting for Ge-albite is less than that of Si-albite (Fig. 2), pressure will decrease K_D provided there is ideal volume behavior in the feldspar at natural concentration levels of Ge. This effect is similar to the olivine/melt K_D for Ge and Si which was experimentally observed to decrease with increasing pressure (Capobianco and Watson, 1982). Melts generated at high pressure should therefore exhibit higher Ge/Si ratios than those formed at low pressure. This behavior could be modified if Ge entered 6 fold coordination at high pressure, however such a situation is considered unlikely in view of the spectroscopic data of Mammone and Sharma (1979) who found no evidence for octahedral Ge in GeO_2 glasses even up to 78 kbar.

The difference in molar volumes between the end-member components seems to have virtually no effect on the energetics of mixing in the highly polymerized glassy and crystalline systems studied. This is consistent with the view that the oxygen polyhedra surrounding the network-forming cations comprise the locus of energetic interaction. Other ions may interact non-ideally with the framework but the energetics of linking the oxygen polyhedra appear insensitive to homovalent substitutions within the framework of tetrahedral ions having similar T–O bond strengths. However, immiscibility has been reported for GeO_2–SiO_2 glasses (Pye *et al.*, 1978) suggesting that the "simple" binary system may have more stringent energetic constraints than the more complex alkali aluminosilicate and aluminogermanate or than the even more complex melts of geological importance.

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