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Publication Date

1979-11-01

Published in Contributions to Mineralogy
and Petrology, 71, pp. 323-342 (1980)

LBL-9755 c.2
Preprint

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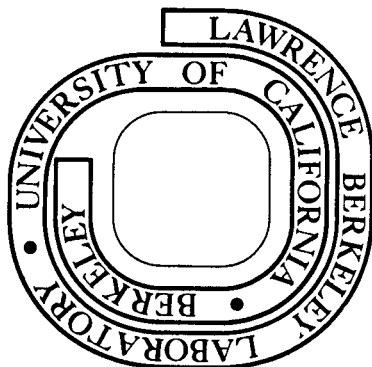
November 1979

Prepared for the U.S. Department of Energy
under Contract W-7405-ENG-48

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A Regular Solution Model for Met-Aluminous Silicate Liquids: Applications to Geothermometry, Immiscibility, and the Source Regions of Basic Magmas

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Abstract. Adopting a set of multioxide components and using published compositional data on olivine- and plagioclase-liquid equilibria we have developed a 17 component regular solution model for met-aluminous silicate liquids. The partial molar excess free energies predicted from this model can be used together with phenocryst compositions as an effective geothermometer, with an approximate error of 20°C (30°C for olivine, 12°C for plagioclase). The regular solution formulation is also successful in predicting liquid immiscibility at (1) high mole fractions of silica commonly observed in phase diagrams, and at (2) lower temperatures in lunar basalts and intermediate lavas. The model yields activities of silica which are consistent with those obtained from solid-liquid silica buffers in rocks which contain olivine and enstatite or quartz. From predicted activities of KAlSi_3O_8 in liquids coexisting with plagioclase a value is obtained for the limiting Henry's law activity coefficient of KAlSi_3O_8 in the solid. This coefficient agrees well with that inferred from plagioclase-sanidine equilibrium phenocryst assemblages in rhyolites. The activities of silica obtained from this model are used to place constraints on the pressure-temperature regions where various types of basic magmas are generated. In conjunction with plagioclase geothermometry an application is given where the pressure, temperature, and water content of an olivine andesite is predicted from the activity of silica.

Introduction

There is now a considerable body of experimental data on the compositions of minerals in equilibrium with anhydrous silicate liquids at high temperatures. These experiments, generally made at 1 bar total pressure, are represented by the work of Roeder

(1974) on olivine-liquid, Drake (1972) on plagioclase-liquid and more recently Walker et al. (1979) and Bender et al. (1978) on the composition of coexisting olivine, plagioclase, and pyroxene in basaltic liquids, at pressures up to 12 kbars, as a function of temperature. Mainly arising from this type of study are a number of postulated geothermometers often expressed in the form:

$$\ln X = \frac{A}{T} + B \quad (1)$$

where X represents some function, usually a ratio, of the concentration of elements or oxides in the solid to those in the coexisting liquid, T is the absolute temperature, and A and B are fit parameters. This type of formulation will generally only apply to liquids of almost identical composition to those experimentally investigated. For example, Longhi et al. (1978) offer a plethora of values of the constants A and B for olivine-liquid equilibrium depending on the composition of the liquid, so that the choice of equation, and often the inconsistency of the calculated temperatures derived from the known compositions of olivine and liquid, may bewilder the petrologist anxious to estimate a temperature for a particular phenocryst-liquid assemblage.

It can be said in general, however, that the results of these liquid-solid equilibrium studies have been underutilized. The approach of this paper is to express the compositional-temperature dependence of solid-liquid equilibrium using a generalized silicate liquid solution model, calibrated on existing experimental data. This will allow the prediction of solution properties over a wide compositional range and provide for adequately precise solid-liquid geothermometers and methods for calculating a variety of derived properties of relevance to the cooling history of igneous rocks. The heart of the problem is

to find an expression for the Gibbs free energy of the solution (G^{soln}), given formally by:

$$G^{\text{soln}} = G^0 + G^{\text{ideal}} + G^{\text{xs}} \quad (2)$$

where G^0 is the free energy of the liquid in the standard state, which we will define as unit activity of the pure component at any temperature and pressure, G^{ideal} the free energy associated with the ideal entropy of mixing, and G^{xs} the excess free energy of mixing. Hence, the excess partial molar free energy of component i , μ_i^{xs} , is:

$$(\partial G^{\text{xs}}/\partial n_i)_{T,P,n_j} = \mu_i^{\text{xs}} = RT \ln \gamma_i \quad (3)$$

with n_i being the number of moles of component i , R the universal gas constant, and γ_i the activity coefficient of component i . The subscript n_j denotes the number of moles of each component except $j=i$. Clearly:

$$(\partial \mu_i^{\text{xs}}/\partial P)_{T,n_j} = RT(\partial \ln \gamma_i/\partial P)_{T,n_j} = \bar{v}_i^{\text{xs}} \quad (4)$$

and

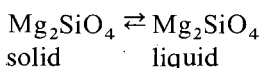
$$(\partial \mu_i^{\text{xs}}/\partial T)_{P,n_j} = (\partial RT \ln \gamma_i/\partial T)_{P,n_j} = -\bar{s}_i^{\text{xs}} \quad (5)$$

and

$$(\partial \bar{s}_i^{\text{xs}}/\partial T)_{P,n_j} = \bar{C}_p^{\text{xs}}/T \quad (6)$$

where \bar{v}_i^{xs} and \bar{s}_i^{xs} are the partial molar excess volume and entropy of the i -th component.

It follows that the energy terms involved in the equilibrium between a solid solution, such as olivine or plagioclase, and a silicate liquid may be represented by two parts: a pure component (G^0 , solid and liquid terms) and a mixing (G^{ideal} , G^{xs} , solid and liquid terms) contribution. It is the past failure to separate out the one from the other that has largely made geothermometers (Eq. 1) based on mineral-solution equilibria so compositionally restricted. In a more rigorous thermodynamic treatment solid-liquid equilibria may be represented, using Mg_2SiO_4 as a possible component, by:



so that at equilibrium at any P and T

$$\begin{aligned} 0 = & \Delta H_{Tr}^0 + \int_{Tr}^T (Cp_{\text{liq}}^0 - Cp_{\text{sol}}^0) dT \\ & - T \left(\Delta S_{Tr}^0 + \int_{Tr}^T \left(\frac{Cp_{\text{liq}}^0 - Cp_{\text{sol}}^0}{T} \right) dT \right) \\ & + \int_1^P \Delta V^0(T) dP + RT \ln X_{\text{Mg}_2\text{SiO}_4}^{\text{liq}} \\ & + RT \ln \gamma_{\text{Mg}_2\text{SiO}_4}^{\text{liq}} - RT \ln a_{\text{Mg}_2\text{SiO}_4}^{\text{sol}} \end{aligned} \quad (7)$$

where ΔH_{Tr}^0 and ΔS_{Tr}^0 are the molar enthalpy and entropy of the reaction at the reference temperature Tr , which we take for convenience as the 1 bar fusion temperature (2,163 K for Mg_2SiO_4); Cp_{liq}^0 and Cp_{sol}^0 are the molar heat capacities (at constant pressure) of the liquid and solid respectively and $\Delta V^0(T)$ is the molar volume of the liquid minus the volume of the solid as a function of pressure at the temperature T . The mole fraction of Mg_2SiO_4 dissolved in the liquid is represented by X , $RT \ln \gamma_{\text{Mg}_2\text{SiO}_4}^{\text{liq}}$ is the excess partial molar free energy of Mg_2SiO_4 dissolved in the liquid, and $a_{\text{Mg}_2\text{SiO}_4}^{\text{sol}}$ is the activity (relative to pure Mg_2SiO_4 crystals at any P and T) of Mg_2SiO_4 in the olivine crystals. This equation, in its general form, will be used to calculate partial molar excess free energies from experimental solid-liquid equilibria in silicate systems, which in turn will be employed in the calibration of the liquid solution model to be postulated below. We shall first comment upon the nature of the standard state thermodynamic properties and relevant compositional relations in the solids, necessary for the evaluation of Eq. (7), before addressing the problems of modelling the free energy of the liquid.

Sources of Thermodynamic Data

Thermodynamic data for pure liquid and solid Mg_2SiO_4 , Fe_2SiO_4 , $\text{CaMgSi}_2\text{O}_6$, MgSiO_3 , SiO_2 , $\text{CaAl}_2\text{Si}_2\text{O}_8$, and $\text{NaAlSi}_3\text{O}_8$ are given in the Appendix, and are derived in part from experimental pressure-temperature fusion curves. Typically only the liquid compressibility, or $(\partial V^{\text{liq}}/\partial P)$, and the one bar heat of fusion are unknown. The latter can be calculated from the initial slope of the fusion curve using the Clapeyron relationship:

$$(dP/dT)_{Tr, 1 \text{ bar}} = \frac{\Delta H_{Tr}^0}{Tr \Delta V_{Tr}^0}$$

whereas $(\partial V^{\text{liq}}/\partial P)$ can be obtained from the experimentally determined slope at elevated pressures. In reality the calculated values of $(\partial V^{\text{liq}}/\partial P)$ are really fit parameters for they include the uncertainties in the extrapolation of Cp_{sol}^0 above Tr , which is normally close to the upper limit of the heat capacity data; they also tend to compensate any uncertainty in the heat of fusion, and any pressure dependence of the thermal expansion of the liquid. All the standard state properties are internally consistent with each of the experimental fusion curves of the chosen components, but there is very little evidence to demonstrate their mutual consistency.

Activity-Composition Relations: Solid Solutions

Throughout this paper it has been assumed that Mg and Fe mix ideally on octahedral sites in olivine and the components $\text{NaAlSi}_3\text{O}_8$ and $\text{CaAl}_2\text{Si}_2\text{O}_8$ observe ideal mixing in plagioclase. These assumptions are consistent with the relatively high temperature range of the data (1,000–1,700 K). As a consequence the activity

of either olivine component is $X_{\text{Mg or Fe}}^{2\text{olivine}}$, to take account of the two energetically identical lattice sites, and the activities of the albite and anorthite components in plagioclase are given by their respective mole fractions (Kerrick and Darken, 1975).

In pyroxenes however, there are two non-equivalent octahedral lattice site, an *M2* sites and a smaller *M1* site. By analogy with the treatment of diopside by Wood (1976) and Newton (1976), we have approximated the activity of MgSiO_3 in orthopyroxene as:

$$a_{\text{MgSiO}_3}^{\text{opx}} = [(X_{\text{Mg}} \gamma_{\text{Mg}})^{M2} \cdot (X_{\text{Mg}} \gamma_{\text{Mg}})^{M1}]^{\frac{1}{2}}$$

where X and γ represent site mole fractions and activity coefficients, and $(\gamma_{\text{Mg}}^{M2} \gamma_{\text{Mg}}^{M1})^{\frac{1}{2}}$ is assumed to be unity. However, the assignment of atoms in a pyroxene analysis is not unambiguous, so they have been distributed as follows:

M2 contains Ca, Mn, Na, Mg^1 , Fe^1

M1 contains Cr, Ti, Al/2, Mg^1 , Fe^1

where Mg^1 and Fe^1 represent the amounts of assigned Mg and Fe in proportion to the ratio $\text{Mg}/(\text{Mg} + \text{Fe})$ in the pyroxene analysis, and allocated so that the total number of atoms in *M1* and *M2* are identical. Thus:

$$X_{\text{Ca}}^{M2} = y_{\text{Ca}} / (y_{\text{Ca}} + y_{\text{Mn}} + y_{\text{Na}} + y_{\text{Mg}^1} + y_{\text{Fe}^1})$$

and

$$X_{\text{Mg}}^{M1} = y_{\text{Mg}} / (y_{\text{Cr}} + y_{\text{Al}} + y_{\text{Ti}} + y_{\text{Mg}^1} + y_{\text{Fe}^1})$$

where y represents the number of atoms in each lattice site. As the amount of Al assigned to the tetrahedral sites depends conventionally upon the amount of Si in the analysis, and as this is known only to $\pm 1\%$ at best, we have arbitrarily assumed that half the amount of Al present is octahedrally coordinated.

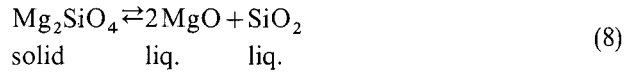
Any departure of the modelled activity from the actual activity of each crystalline component will affect (through the assumption of solid-liquid equilibrium) the calculated excess partial molar free energies in the liquid.

Activity-Composition Relations: Liquids

a) Components

The choice of components used to describe the composition of silicate liquids is arbitrarily determined by convenience and simplicity. Generally mole fractions of a component are computed in terms of the simple

oxides. For our purposes however, this formulation has severe disadvantages. Consider for example the equilibria:



In order to evaluate the standard state thermodynamic properties of this reaction we require the volumes and heat capacities as functions of P and T as well as the enthalpies and temperatures of fusion for forsterite, MgO , and SiO_2 . The state functions for many oxides are poorly known, so that to compute thermodynamic excess properties for the liquid oxide components from olivine-liquid equilibria would necessitate simultaneous regression of the standard state thermodynamic properties of the oxides. The situation is further complicated by considering liquids saturated with other phases containing MgO and SiO_2 (i.e., enstatite) for which the same standard state properties must hold, and the derived liquid excess functions must conform to those of Mg_2SiO_4 -liquid equilibria within the constraints of the adopted solution model. It is clear that agreement between all solid-liquid equilibria in silicate liquids using oxide liquid components would involve the evaluation (through regression) of a large number of constants most of which, we believe, would be poorly constrained in composition, temperature and pressure space by the paucity of experimental data.

Carmichael et al. (1977) made an attempt to avoid this difficulty and still evaluate equilibria of the form of Eq.(8) by postulating a quantity \hat{X} - the ideal contribution to the activity - which for Mg_2SiO_4 would be written:

$$\hat{X}_{\text{Mg}_2\text{SiO}_4}^{\text{liq}} = (X_{\text{MgO}}^{\text{liq}})^2 \cdot (X_{\text{SiO}_2}^{\text{liq}}) \cdot \lambda^*$$

where λ^* is a constant defined such that for a pure Mg_2SiO_4 liquid, $\hat{X}_{\text{Mg}_2\text{SiO}_4}^{\text{liq}} = 1$ (i.e., $\lambda^* = 6.75$). Similarly for MgSiO_3 one would write:

$$\hat{X}_{\text{MgSiO}_3}^{\text{liq}} = X_{\text{MgO}}^{\text{liq}} \cdot X_{\text{SiO}_2}^{\text{liq}} \cdot 4.0$$

It can be readily shown that the definition of \hat{X} results from equivalent expressions of the total Gibbs free energy of the liquid, in terms of a simple set of oxide components in one case and a more complex set, including the multi-oxide compounds (like Mg_2SiO_4 or MgSiO_3), in the other. Thus for the Mg_2SiO_4 component we can write (making the substitution for $\mu_{\text{Mg}_2\text{SiO}_4}^0$ by initially evaluating the expression at $X_{\text{MgO}} = 2/3$ and $X_{\text{SiO}_2} = 1/3$, i.e., pure Fo liquid):

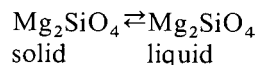
$$\ln a_{\text{Mg}_2\text{SiO}_4} = \ln \left[\left(\frac{27}{4} \right) X_{\text{MgO}}^2 X_{\text{SiO}_2} \right] +$$

$$2 \ln(\gamma_{\text{MgO}} / \gamma_{\text{MgO}=2/3}^{\text{(pure Foliq)}}) \\ + \ln(\gamma_{\text{SiO}_2} / \gamma_{\text{SiO}_2=1/3}^{\text{(pure Foliq)}})$$

where $(\frac{27}{4}) X_{\text{MgO}}^2 X_{\text{SiO}_2}$ is simply $\hat{X}_{\text{Mg}_2\text{SiO}_4}$ and

$\gamma_{\text{MgO}=2/3}^{\text{(pure Foliq)}}$ is the activity coefficient of MgO in the solution at $X_{\text{MgO}}=2/3$; similarly for SiO_2 at $X=1/3$. Although the activity of Mg_2SiO_4 in the liquid is constrained by this relation its mole fraction, $X_{\text{Mg}_2\text{SiO}_4}$, depends on the choice of the compounds in the complex component set used to describe the composition of the liquid. X is not equal to \hat{X} . Nevertheless we could evaluate solid-liquid equilibria, using the concept of \hat{X} , and obtain for each different mineral-solution pair expressions involving sums of the excess properties of oxide liquid components. A solution model could then be fitted to these sums of excess properties by regression. This procedure is identical to using the oxides as components directly through reactions of the form of (8), except that here we have eliminated the need to simultaneously evaluate the standard state properties of the oxides, but still cannot unambiguously define the individual excess properties of those oxides.

It would be far more convenient, and less cumbersome numerically, to be able to directly define a set of excess properties from the experimental solid-liquid equilibria; that is for instance to obtain $\gamma_{\text{Mg}_2\text{SiO}_4}$ from $a_{\text{Mg}_2\text{SiO}_4} = X_{\text{Mg}_2\text{SiO}_4} \gamma_{\text{Mg}_2\text{SiO}_4}$. This can be done by adopting a set of complex-oxide components which can uniquely define the composition of a silicate liquid and which have molecular configurations stoichiometrically identical to the solid phases (generally solid solution end members) in equilibrium with these liquids. To write down such a *unique* set of components for the whole compositional range of igneous rocks is impossible (without allowing for negative concentrations), as is evidenced by the complexity of the CIPW norm. Confining one's interests however to the met-aluminous group of rocks, to which the large proportion of experimental data applies, a comprehensive set of components can be postulated. We have adopted such a set, which is given along with a scheme describing a method for their calculation from the simple oxides in Table 1. With these we can now write reactions of the form:



for olivine and plagioclase liquid equilibria (for which standard state properties can be derived directly from fusion curves). Pyroxene end members diopside and enstatite were not used as components because they severely restricted the compositional range of the silicate liquids that could be treated.

Table 1. Adopted components

| | | | |
|---------------------------|--------------------------------------|--------------------------------------|------------------------------|
| SiO_2 | Co_2SiO_4 | $\text{NaAlSi}_3\text{O}_8$ | Fe_3O_4 |
| Mg_2SiO_4 | Mn_2SiO_4 | KAlSi_3O_8 | FeTiO_3 |
| Fe_2SiO_4 | Ca_2SiO_4 | $\text{SrAl}_2\text{Si}_2\text{O}_8$ | FeCr_2O_4 |
| Ni_2SiO_4 | $\text{CaAl}_2\text{Si}_2\text{O}_8$ | $\text{BaAl}_2\text{Si}_2\text{O}_8$ | $\text{Ca}_3(\text{PO}_4)_2$ |
| H_2O | | | |

If moles of the simple oxides are first computed, they can be transformed to moles of the new components in the following manner:

$$n_{\text{SiO}_2}^{\text{new}} = n_{\text{SiO}_2} + 0.5 n_{\text{TiO}_2} - 1.5 n_{\text{Al}_2\text{O}_3} + 0.5 n_{\text{Fe}_2\text{O}_3} \\ + 0.5 n_{\text{Cr}_2\text{O}_3} - 0.5 n_{\text{FeO}} - 0.5 n_{\text{MnO}} - 0.5 n_{\text{MgO}} \\ - 0.5 n_{\text{NiO}} - 0.5 n_{\text{CoO}} - 0.5 n_{\text{CaO}} - 4.5 n_{\text{Na}_2\text{O}} \\ - 4.5 n_{\text{K}_2\text{O}} + 1.5 n_{\text{P}_2\text{O}_5} - 0.5 n_{\text{SrO}} - 0.5 n_{\text{BaO}}$$

$$n_{\text{Mg}_2\text{SiO}_4} = 0.5 n_{\text{MgO}}$$

$$n_{\text{Fe}_2\text{SiO}_4} = -0.5 n_{\text{TiO}_2} - 0.5 n_{\text{Fe}_2\text{O}_3} - 0.5 n_{\text{Cr}_2\text{O}_3} + 0.5 n_{\text{FeO}}$$

$$n_{\text{Ni}_2\text{SiO}_4} = 0.5 n_{\text{NiO}}$$

$$n_{\text{Co}_2\text{SiO}_4} = 0.5 n_{\text{CoO}}$$

$$n_{\text{Mn}_2\text{SiO}_4} = 0.5 n_{\text{MnO}}$$

$$n_{\text{Ca}_2\text{SiO}_4} = -0.5 n_{\text{Al}_2\text{O}_3} + 0.5 n_{\text{CaO}} + 0.5 n_{\text{Na}_2\text{O}} + 0.5 n_{\text{K}_2\text{O}} \\ - 1.5 n_{\text{P}_2\text{O}_5} + 0.5 n_{\text{SrO}} + 0.5 n_{\text{BaO}}$$

$$n_{\text{CaAl}_2\text{Si}_2\text{O}_8} = n_{\text{Al}_2\text{O}_3} - n_{\text{Na}_2\text{O}} - n_{\text{K}_2\text{O}} - n_{\text{SrO}} - n_{\text{BaO}}$$

$$n_{\text{NaAlSi}_3\text{O}_8} = 2 n_{\text{Na}_2\text{O}}$$

$$n_{\text{KAlSi}_3\text{O}_8} = 2 n_{\text{K}_2\text{O}}$$

$$n_{\text{SrAl}_2\text{Si}_2\text{O}_8} = n_{\text{SrO}}$$

$$n_{\text{BaAl}_2\text{Si}_2\text{O}_8} = n_{\text{BaO}}$$

$$n_{\text{Fe}_3\text{O}_4} = n_{\text{Fe}_2\text{O}_3}$$

$$n_{\text{FeTiO}_3} = n_{\text{TiO}_2}$$

$$n_{\text{FeCr}_2\text{O}_4} = n_{\text{Cr}_2\text{O}_3}$$

$$n_{\text{Ca}_3(\text{PO}_4)_2} = n_{\text{P}_2\text{O}_5}$$

$$n_{\text{H}_2\text{O}}^{\text{new}} = n_{\text{H}_2\text{O}}$$

The compositional restrictions imposed by our choice of components will now be discussed in detail. Examination of Table 1 shows that the requirement of positive mole numbers (n_i) of Ca_2SiO_4 and $\text{CaAl}_2\text{Si}_2\text{O}_8$ (ignoring for the moment the generally minor contributions of SrO , BaO , and P_2O_5 to the liquid composition) implies the met-aluminous condition:

$$n_{\text{CaO}} + n_{\text{Na}_2\text{O}} + n_{\text{K}_2\text{O}} > n_{\text{Al}_2\text{O}_3} > n_{\text{Na}_2\text{O}} + n_{\text{K}_2\text{O}}$$

It is not clear, however, that the stipulation of positive $n_{\text{SiO}_2}^{\text{new}}$ is synonymous with this inequality. Let m be the sum of moles calculated in terms of the new components. m is positive. Then it can be easily shown that, consequently:

$$n_{\text{SiO}_2} + n_{\text{TiO}_2} + n_{\text{Fe}_2\text{O}_3} + n_{\text{P}_2\text{O}_5} + n_{\text{Cr}_2\text{O}_3} \\ > n_{\text{Al}_2\text{O}_3} + 3 n_{\text{Na}_2\text{O}} + 3 n_{\text{K}_2\text{O}}$$

Consider a rock with normative larnite (x moles), anorthite (y), nepheline (z), and kalsilite (p) (an exam-

ple is given by Carmichael et al., 1974, p. 499, Table 10-2, an ijolite from Uganda). In terms of oxide components we have:

$$n_{\text{SiO}_2} = x + 2y + z + p$$

$$n_{\text{Al}_2\text{O}_3} = y + \frac{1}{2}z + \frac{1}{2}p$$

$$n_{\text{CaO}} = 2x + y$$

$$n_{\text{Na}_2\text{O}} = \frac{1}{2}z$$

$$n_{\text{K}_2\text{O}} = \frac{1}{2}p.$$

Such rocks are clearly met-aluminous for all values of x , y , z , and p :

$$2x + y + \frac{1}{2}z + \frac{1}{2}p > y + \frac{1}{2}z + \frac{1}{2}p > \frac{1}{2}z + \frac{1}{2}p.$$

Substitution into the other inequality derived above however, yields:

$$x + n_{\text{TiO}_2} + n_{\text{Fe}_2\text{O}_3} + n_{\text{P}_2\text{O}_5} + n_{\text{Cr}_2\text{O}_3} > z + p - y.$$

Granted the assumptions made by only considering Si, Al, Ca, Na, and K (i.e., by ignoring silica associated with the other metals), this inequality could be violated if z , p , or $z + p$ are sufficiently large. That is, the transformation from oxide mole numbers to those of the new components will result in negative mole fractions of silica for some met-aluminous rocks with substantial amounts of nepheline or kalsilite in the norm.

There is no fundamental thermodynamic objection to a negative mole number, resulting in a negative mole fraction of a particular component. In such a circumstance the ideal entropy contribution can be shown to be $-R|X_i|\ln|X_i|^1$, and the total free energy of solution, being independent of the component set chosen, implies the existence of a real G^{excess} (activity coefficient). Thus $\ln a_i$ will be a real number despite the fact that $X_i < 0$. It remains however a matter of conjecture whether the calculations pursued below (where in the data base all n_i were required to be > 0) will ever be useful for rocks removed from the compositional space bounded by positive mole fractions of the adopted set of components. Preliminary results, on slightly per-aluminous rhyolites (with negative mole fractions of larnite) indicate that such extensions may be applicable.

b) Calculation and Regression of Excess Partial Molar Free Energies

On the basis of the thermodynamic data given in the Appendix, and using the activity formulations of the

various components in the solid phases as described above, together with the mole fractions of the adopted components (Table 1) in the liquid, values of $RT \ln \gamma_i^{\text{liq}}$ can be calculated for the appropriate component using compositions of both solid and liquid in equilibrium at any known temperature and pressure. Of the data available to the writers, 235 cases are experimental points, and 20 represent silicic lavas where the intensive parameters and compositions of both liquid (now glass) and phenocrysts are known. These data were obtained from the experimental results of Bender et al. (1978), Green et al. (1979), Leeman (1974), Longhi et al. (1978), Mysen and Kushiro (1977), Roeder (1974), Takahashi (1978), Thompson (1974; 1975), Walker et al. (1979), Drake (1972), Egger (1972), and Helz (1973; 1976). Data on natural silicic lavas were taken from Carmichael (1960; 1962; 1967), and Hildreth (1977). It is appropriate now to show how the values of $RT \ln \gamma_i^{\text{liq}}$, the excess partial molar free energies, derived from the 255 cases were treated in forming a consistent solution model.

Carmichael et al. (1977) and Nelson and Carmichael (1979) have demonstrated that within experimental uncertainty (about 2%) anhydrous silicate liquids of the range in composition found in nature, expressed in terms of simple oxide components, have no excess volume of mixing and no partial molar excess heat capacity. It follows at once that any other set of components (Table 1) that can be related by a linear mapping to the simple oxides will also show an absence of excess volume and heat capacity. This conclusion is of critical importance and can be seen from the following proof.

Consider a set of components, indexed on i , and represented by the vector \mathbf{N} (moles), for which some physical property Q (say volume or C_p) exhibits ideal mixing. Thus:

$$Q = \sum_{i=1}^n Q_i^0 N_i \quad (9)$$

where N_i are the number of moles of each component comprising the vector \mathbf{N} , and Q_i^0 is the property in question of the pure component i . Given another set of components, indexed on j , and represented by the vector \mathbf{M} (moles) we define a linear mapping:

$$\mathbf{M} = \mathbf{C}\mathbf{N}$$

or

$$M_j = \sum_i C_{ij} N_i \quad (10)$$

where \mathbf{C} is a square matrix of rank n . We can now write (at constant P and T):

¹ Where $|X|$ denotes the absolute value of X here and subsequently

$$dQ = \sum_{i=1}^n Q_i^0 dN_i$$

and

$$dM_j = \sum_{i=1}^n C_{ij} dN_i$$

from which, holding M_k constant, yields:

$$\left(\frac{\partial Q}{\partial M_j} \right)_{M_k} = \left(\frac{\sum_{i=1}^n Q_i^0 dN_i}{\sum_{i=1}^n C_{ij} dN_i} \right)_{M_k} \quad (k \neq j). \quad (11)$$

We must now show this derivative is independent of composition. From Eq.(10) we may write:

$$\mathbf{N} = \mathbf{C}^{-1} \mathbf{M}$$

or

$$N_i = \sum_{j=1}^n C_{ij}^{-1} M_j$$

from which

$$dN_i = \sum_{j=1}^n C_{ij}^{-1} dM_j. \quad (12)$$

It follows at once from the requirements of (11), namely constant M_k , $k \neq j$, and Eq.(12) that:

$$dN_i = C_{ij}^{-1} dM_j$$

Substitution into (11) with simplification yields:

$$\left(\frac{\partial Q}{\partial M_j} \right)_{M_k} = \sum_i Q_i^0 C_{ij}^{-1}.$$

The right hand side is independent of the components of the vector \mathbf{M} , and the proof is complete.

In light of the discussion above we have chosen to represent the excess properties derived from the experimental solid-liquid equilibria, calculated using the components of Table 1, by a regular solution formulation. This choice warrants further clarification. The experimental data of Carmichael et al. (1977) and Nelson and Carmichael (1979) is not inconsistent with an ideal solution treatment but the prevalent immiscibility repeatedly found in silicate liquid systems is. A regular solution model allows for immiscibility and is comparatively easy to apply to systems of large (~ 17) numbers of components. The justification for regular solution behavior, however, has not been established for hydrous silicate liquids and clearly can only be an approximation, since as $X_{\text{H}_2\text{O}} \rightarrow 1$ hydrous silicate liquids become electrolytes

which demonstrably cannot be described in terms of regular or ideal solutions. The treatment of water, then, as a regular or ideal solution component in a silicate liquid can only be successful at very small $X_{\text{H}_2\text{O}}$ (see below).

The total Gibbs free energy of mixing, G^{mix} , can be written:

$$G^{\text{mix}} = G^{\text{ideal}} + G^{\text{excess}} \quad (13)$$

where

$$G^{\text{ideal}} = RT \sum_{i=1}^n n_i \ln X_i. \quad (14)$$

for an n component system, with n_i being the number of moles of the i th component and X_i its mole fraction. For a simple regular solution G^{excess} is defined to be:

$$G^{\text{excess}} = \sum_{i=2}^n \sum_{j=1}^{i-1} W_{ij} n_i X_j \quad (15)$$

where W_{ij} are constants independent of temperature, pressure and composition. The W 's represent binary interaction coefficients and could in principle be derived from liquid-solid equilibria within all possible binary subsystems of the n component system. In a more complex regular solution model one could postulate ternary and higher order interactions; however, we have chosen not to do so and have adopted Eq.(15) as the functional form of the excess free energy surface.

Differentiation of (15) with respect to n_k yields the partial molar excess free energy of the k -th component:

$$\begin{aligned} \left(\frac{\partial G^{\text{excess}}}{\partial n_k} \right)_{n_j} &= RT \ln \gamma_k \\ &= \sum_{i=1}^n \left(X_i^2 + X_i \sum_{\substack{j=1 \\ i \neq j}}^n X_j \right) W_{ik} - \sum_{i=2}^n \sum_{j=1}^{i-1} W_{ij} X_i X_j \\ & \quad i, j \neq k. \end{aligned} \quad (16)$$

Eq.(16) can be rearranged into the more familiar form:

$$\begin{aligned} RT \ln \gamma_k &= \sum_{i=1}^n W_{ik} X_i^2 \\ &+ \sum_{i=2}^n X_i \sum_{j=1}^{i-1} (W_{ik} + W_{kj} - W_{ij}) X_j \quad i, j \neq k. \end{aligned} \quad (17)$$

The excess partial molar free energies obtained, as described above, from experimental solid-liquid equilibria can now be used along with their corresponding liquid compositions to derive a consistent set of

Table 2. Binary interaction parameters. (all those not listed are zero)

| Interaction | W (cals) | Std. error of W |
|---|------------|-------------------|
| Fe ₂ SiO ₄ , Mg ₂ SiO ₄ | -24,135.6 | 752.5 |
| Ca ₂ Al ₂ Si ₂ O ₈ , Mg ₂ SiO ₄ | -11,069.9 | 805.6 |
| SiO ₂ , Mg ₂ SiO ₄ | -6,801.71 | 552.26 |
| SiO ₂ , NaAlSi ₃ O ₈ | 6,460.71 | 330.15 |
| H ₂ O, KAlSi ₃ O ₈ | 309,321 | 48,608 |
| Ca ₂ SiO ₄ , Mn ₂ SiO ₄ | 268,388 | 90,076 |
| SiO ₂ , Fe ₂ SiO ₄ | 4,838.84 | 601.58 |
| CaAl ₂ Si ₂ O ₈ , Fe ₂ SiO ₄ | -5,948.71 | 1,052.30 |
| NaAlSi ₃ O ₈ , Mg ₂ SiO ₄ | -8,836.45 | 883.98 |
| Ca ₂ SiO ₄ , Fe ₂ SiO ₄ | -35,688.8 | 2,842.4 |
| FeTiO ₃ , Fe ₂ SiO ₄ | 12,506.2 | 1,870.2 |
| KAlSi ₃ O ₈ , Fe ₂ SiO ₄ | 9,681.68 | 3,143.29 |
| Ca ₃ (PO ₄) ₂ , Fe ₂ SiO ₄ | -130,674 | 21,765 |
| SiO ₂ , H ₂ O | -29,219.0 | 8,862.5 |
| CaAl ₂ Si ₂ O ₈ , Mn ₂ SiO ₄ | -140,218 | 52,653 |
| Mn ₂ SiO ₄ , Mg ₂ SiO ₄ | -35,128.3 | 14,774.9 |
| FeTiO ₃ , Mg ₂ SiO ₄ | -5,535.20 | 1,783.53 |
| NaAlSi ₃ O ₈ , Fe ₂ SiO ₄ | 3,914.24 | 1,169.44 |
| Ca ₂ SiO ₄ , Mg ₂ SiO ₄ | -9,719.72 | 2,603.07 |
| NaAlSi ₃ O ₈ , CaAl ₂ Si ₂ O ₈ | 1,608.89 | 477.05 |
| FeTiO ₃ , CaAl ₂ Si ₂ O ₈ | -12,099.8 | 4,696.3 |

binary interaction parameters, W , which will lead to a quantitative description of the excess free energy surface of the solution. In the 17 component regular solution formulation given by Eq. (15) there are 136 W 's. The majority of these were initially set to zero (all interactions involving Co₂SiO₄, Ni₂SiO₄, SrAl₂Si₂O₈, BaAl₂Si₂O₈, Fe₃O₄, and FeCr₂O₄) because we judged that the compositional variation of these components was insufficient to resolve their binary interaction parameters which must necessarily span the whole compositional spectrum. The remaining 55 W 's were evaluated as coefficients preceding the compositional variables in the right hand side of Eq. (16), and regressed against the values of $RT \ln \gamma_k$ for Mg₂SiO₄, Fe₂SiO₄, NaAlSi₃O₈, and CaAl₂Si₂O₈. The 255 experimental equilibria resulted in 530 statements of Eq. (16)² from which were extracted 21 binary interaction parameters that were significant, as regression coefficients, above the 5% level (determined by F -test criteria). This was done in order to avoid the numerical instability of having 55 regression coefficients being determined from 478 sets of data. Those W 's not selected as statistically significant were set to zero. The resulting interactions, which through Eq. (15) describe the excess free energy surface of met-aluminous silicate liquids, are tabulated in Table 2.

One of the intriguing thermodynamic consequences of this solution model is the ability to

² 52 had to be rejected due to their drastic inconsistency with respect to the majority of the data - see later

predict from the thermodynamic properties of the components of Table 1 and the W 's of Table 2, the standard state properties, as functions of P and T , of the molten oxides. If m_j refers to the number of moles of the j -th component of Table 1, and n_i the number of moles of the i -th simple oxide, then clearly we can define:

$$m_j = \sum_{i=1}^n c_{ij} n_i$$

and furthermore

$$p = \sum_{i=1}^n n_i$$

$$m = \sum_{j=1}^n m_j = \sum_{j=1}^n \sum_{i=1}^n c_{ij} n_i.$$

The total free energy of the solution is thus:

$$G = \sum_{i=1}^n \mu_i^0 n_i + \sum_{i=1}^n n_i RT \ln \left(\frac{n_i}{n} \right) + \sum_{i=1}^n RT n_i \ln \gamma_i$$

or

$$G = \sum_{j=1}^n \mu_j^0 m_j + \sum_{j=1}^n |m_j| RT \ln \left| \frac{m_j}{m} \right| + \sum_{j=1}^n RT m_j \ln \gamma_j$$

where the primed quantities correspond to the components labeled by m_j . Setting these two equations equal to each other, expressing $RT \ln \gamma_j$ in terms of the regular solution formulation Eq. (16) and evaluating the result at all $n_i = 0$, except for $i = \hat{i}$, we obtain an expression for the standard state chemical potential of the \hat{i} -th molten oxide:

$$\begin{aligned} \mu_{\hat{i}}^0 = & \sum_{j=1}^n c_{\hat{i}j} \mu_j^0 + RT \sum_{j=1}^n |c_{\hat{i}j}| \ln \left| \frac{c_{\hat{i}j}}{c} \right| \\ & + \sum_{j=1}^n c_{\hat{i}j} \left[\sum_{k=1}^n \left(c_{ik}^2 / c^2 + \frac{c_{ik}}{c} \sum_{i=1, i \neq k}^n \frac{c_{ij}}{c} \right) W_{kj} \right. \\ & \left. - \sum_{k=2}^n \sum_{i=1}^{k-1} W_{ki} \frac{c_{ik} c_{ii}}{c^2} \right] \quad i, k \neq j, \end{aligned}$$

$$\text{where } c \equiv \sum_{j=1}^n c_{\hat{i}j}.$$

Appropriate derivatives yield the volume, entropy and heat capacity of the pure component \hat{i} .

The usefulness of this expression is tempered somewhat by the uncertainties in the W 's (to be discussed below) and the large errors in, or complete absence of data for, some of the μ_j^0 's as functions of T

and P (see Appendix). For these reasons we have not pursued the calculations quantitatively. Instead we present this result to suggest that an acceptable and potentially experimentally preferable way of determining the pure molten oxide properties may be to predict them using relationships of this type and precise solution models of compounds of those oxides.

Significance of the Interaction Parameters

The values of the binary interaction parameters given in Table 2 must be considered in terms of the restricted compositional variation in the experimental data. The volume which encloses the data set in our 17 dimensional component space is but a small fraction of the total volume of this space. It is inappropriate, therefore, to assume that the W 's derived by regression of these data will yield interaction parameters that conform strictly to the corresponding binary phase equilibria. This can be inferred from the interaction parameter for the system Fo—Fa, reported in Table 2. The magnitude of this term (probably a consequence of the necessity of assuming all iron in the liquids to be in the ferrous state; see below) does not predict the solid-liquid relationships known from the experimental binary phase diagram. However, it should at this point be stated that using the thermodynamic data in the appendix for Fo and Fa and treating both the liquid and solid as ideal does not result in a liquidus-solidus loop matching the experimental binary system³. There exists a fundamental experimental inconsistency between olivine fusion curve data (used by us to extract thermodynamic constants – see Appendix) and the experimentally determined phase diagram Mg_2SiO_4 — Fe_2SiO_4 . This fact must also lead to the large and unexpected magnitude of $W_{\text{Mg}_2\text{SiO}_4, \text{Fe}_2\text{SiO}_4}$. In a similar manner objections might be raised to the rather large W 's associated with binaries that have not been experimentally determined (like $\text{CaAl}_2\text{Si}_3\text{O}_8$, Mn_2SiO_4). It should be emphasized that the derivatives of the excess free energy surface depend on combinations of the W 's and by mutual cancellation of errors may not show the drastic inconsistency evidenced by the Fo—Fa system. The success of the model (see below) in application as a geothermometer, and in predicting (1) the activity of silica in the liquid, (2) immiscibility, and (3) activity coefficients in coexisting solids, in part substantiates this assumption.

³ Strictly speaking this is not a binary as Fe_2SiO_4 melts incongruently to Fe and liquid, which will also contain small amounts of Fe_2O_3

Geothermometry

Some measure of the validity of the regression procedure utilized above can be seen by substituting Eq. (16) into Eq. (7) and, for any of the experimental solid-liquid equilibria, solving for an equilibration temperature. Predicted temperatures obtained in this manner are compared to their corresponding experimental temperatures for the whole data set in Table 3. We consider the average temperature recovery for olivine- and plagioclase-liquid equilibria to be within acceptable error and cite it to justify in part the adequacy of the proposed modelling of these excess properties. It follows that Eq. (7) and Eq. (16) along with the W 's of Table 2 can be used as a geothermometer for all but the most silica-poor met-aluminous silicate liquids that contain olivine or plagioclase.

The larger errors associated with temperature prediction of olivine-liquid equilibria deserves some comment. Equilibration temperatures predicted from the forsterite component of olivines found in silicic lavas (Carmichael, 1960; 1962; 1967) are poor, presumably because of the evident difficulty of determining small amounts of MgO in fayalitic olivines and particularly in the residual glasses of these lavas. Large inconsistencies also exist between some predicted fayalite and forsterite equilibration temperatures. This must in part be due to the necessity of assuming that all iron in the crystals and residual glasses was in the ferrous state.

As the microprobe is invariably used to analyse the experimental liquid-solid assemblage, only total Fe is determined (usually reported as FeO), which for a solid phase such as olivine is appropriate. However Fe_2O_3 will also be present in the liquid, and at present there is no way to calculate its concentration as a function of either temperature or composition. Since the vast majority of the experimental conditions reflected equilibrium with metallic iron, or were constrained to an oxygen fugacity defined by the fayalite-magnetite-quartz (FMQ) buffer, as a first approximation all Fe was assumed to exist as FeO, despite the widespread evidence that Fe_2O_3 will be present. Another way of looking at this approximation is that it assumes that an olivine in equilibrium with a silicate liquid does not change composition significantly at constant temperature if the oxygen fugacity is increased from that defined by metallic iron to that of the FMQ buffer.

The excess properties for the olivine components in 24 of the experiments (see Table 2) generated residuals that were greater than two standard deviations about the regression surface and were statistically segregated from the data set used to obtain

Table 3. Average errors of recovered temperatures for experimental data and rhyolitic phenocryst assemblages

| | Temp. range K | Pressure | Olivine | | | Plagioclase | | | Plagioclase- olivine | |
|----------------------------------|------------------|-------------------------------------|--------------------|-------------------|-----------------|--------------------|-------------------|-----------------|-------------------------|-------------------|
| | | | Av. error °C | No. of samples | No. rejected | Av. error °C | No. of samples | No. rejected | Av. error °C | No. of samples |
| Bender et al. (1978) | 1,478-1,563 | to 10 kb | 15 | 18 | 0 | 14 | 7 | 0 | 8 | 7 |
| Drake (1972) | 1,368-1,570 | 1 bar | - | - | - | 12 | 63 | 0 | - | - |
| Eggler (1972) | 1,303 | 1 kb | 3 | 1 | 0 | - | - | - | - | - |
| Helz (1973; 1976) | 973-1,273 | 5 kb (4.3 wt % H ₂ O) | 1 | 11 ^b | 0 | - | - | - | - | - |
| Green (1979) mix E | 1,873 | 20 kb | 13 | 1 | 0 | - | - | - | - | - |
| Leeman (1974) | 1,344-1,673 | 1 bar | 19 | 66 | 15 | 6 | 8 | 0 | 14 | 8 |
| Longhi et al. (1978) | 1,397-1,648 | to 12.5 kb | 38 | 18 | 1 | - | - | - | - | - |
| Mysen and Kushiro (1977) | 1,636-1,973 | 20 kb | 117 | 10 | 4 | - | - | - | - | - |
| Roeder (1974) | 1,427-1,579 | 1 bar | 47 | 18 | 1 | - | - | - | - | - |
| Takahashi (1978) | 1,473-1,673 | 1 bar | 29 | 10 | 3 | - | - | - | - | - |
| Thompson (1974; 1975) | 1,398-1,498 | to 10 kb | 28 | 7 | 0 | - | - | - | - | - |
| Walker et al. (1979) | 1,379-1,472 | 1 bar | 31 | 8 | 0 | 16 | 14 | 0 | 12 | 8 |
| <i>Rhyolites</i> | | | | | | | | | | |
| Carmichael (1960; 1963; 1967) | 1,000-1,300 | - | a | - | - | 13.4 | 6 | 2 | - | - |
| Hildreth (1977) | | | | | | | | | | |
| Average | | | 30.2 | 157 | 24 | 12.4 | 98 | 2 | 11.4 | 23 |

^a Water concentration unknown in fayalite-rhyolites

^b All but one of these are peraluminous, and could not be used in the regression

the final *W* values (Table 2). We believe that the source of their inconsistency lies primarily in the problem regarding the oxidation state of iron.

For the hydrous silicate liquids that comprise part of the data set (the natural samples, and the experimental results of Helz and Eggler) the temperature recovery is also good. If these liquids are dehydrated (by calculation) and new equilibration temperatures recovered, a reasonable inverse relationship between temperature and the mole fraction of water is inferred.

Liquid-Solid Geothermometry: A Caveat

In general it seems doubtful whether experimental results presently available will allow temperatures to be calibrated from silicate liquid-solid equilibria which are meaningful to better than 15°C. Although single sets of experiments, performed in one laboratory, may be able to detect a significant change in the composition of both liquid and solid in much less than a 15°C interval, there is insufficient precision for this to be sustained when comparing analytical results from one laboratory to another. At the heart of the problem is the lack of interlaboratory

standardisation on microprobe analytical techniques, an all too familiar problem of analysis which has haunted geologists since the days of *G*-1 and *W*-1 in the mid-fifties (Fairbairn et al., 1951). With a sustained effort to improve interlaboratory standardisation, geothermometers based on solid-liquid equilibria could improve their resolution to 10°C or better. For experiments at high pressures, which are woefully small in number, there is evidently severe technical difficulty (e.g., Mysen and Kushiro, 1977) in analysing the glass phase due to Na loss.

In using the excess free energy surface as a geothermometer, the reader should be aware that it is based essentially on basaltic liquids of a rather restricted compositional range, together with a few silicic lavas. The further an unknown phenocryst-liquid assemblage departs from the experimental compositional range, the larger the temperature uncertainty will be. Thus it becomes a matter of some importance to experiment on liquids other than tholeiitic basalts, particularly andesites, basanites, and feldspar-free basic lavas. Only in this way will a geothermometer of general applicability come into being, for compositional effects dominate liquid solid activity relations.

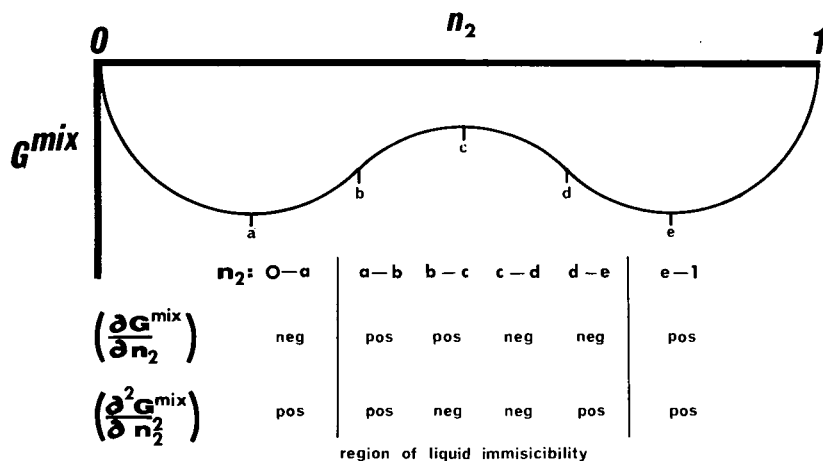


Fig. 1. Idealized free energy of mixing (G^{mix}) for the hypothetical binary 1–2, showing a region of immiscibility a – e

Applications to Igneous Petrology

a) Immiscibility

If the excess free energy of mixing is significantly positive then the total free energy of mixing will take on a shape similar to that of the binary system displayed in Fig. 1. An immiscible region lies between the points a and e . In a multicomponent system immiscibility in the direction of a particular component can best be studied by examining the first and second derivatives of G^{mix} (with respect to that component) whose behavior, as can be seen in two dimensions from Fig. 1, is diagnostic. For a multicomponent regular solution we can obtain, by repeated differentiation of Equations (13–15):

$$\begin{aligned} \left(\frac{\partial G^{\text{mix}}}{\partial n_k}\right)_{n_j} &= RT \ln X_k + RT \ln \gamma_k \\ &= RT \ln X_k + \sum_{i=1}^n \left(X_i^2 + X_i \sum_{\substack{j=1 \\ i \neq j}}^n X_j \right) W_{ik} \\ &\quad - \sum_{i=2}^n \sum_{j=1}^{i-1} W_{ij} X_i X_j \quad i, j \neq k \end{aligned} \quad (18)$$

and

$$\begin{aligned} \left(\frac{\partial^2 G^{\text{mix}}}{\partial n_k^2}\right)_{n_j} &= \frac{RT}{n_k} (1 - X_k) - 2 \frac{RT}{n_k} \ln \gamma_k \\ &= \frac{RT}{n_k} (1 - X_k) - \frac{2}{n_k} \left[\sum_{i=1}^n \left(X_i^2 + X_i \sum_{\substack{j=1 \\ i \neq j}}^n X_j \right) W_{ik} \right. \\ &\quad \left. - \sum_{i=2}^n \sum_{j=1}^{i-1} W_{ij} X_i X_j \right] \quad i, j \neq k \end{aligned} \quad (19)$$

which can be restated in terms of mole fraction derivatives thus:

$$\begin{aligned} \left(\frac{\partial G^{\text{mix}}}{\partial X_k}\right)_{n_j} &= \frac{n}{(1 - X_k)} [RT \ln X_k + RT \ln \gamma_k] \\ &= \frac{n}{(1 - X_k)} \left[RT \ln X_k + \sum_{i=1}^n \left(X_i^2 + X_i \sum_{\substack{j=1 \\ i \neq j}}^n X_j \right) W_{ik} \right. \\ &\quad \left. - \sum_{i=2}^n \sum_{j=1}^{i-1} W_{ij} X_i X_j \right] \quad i, j \neq k \end{aligned} \quad (20)$$

and

$$\begin{aligned} \left(\frac{\partial^2 G^{\text{mix}}}{\partial X_k^2}\right)_{n_j} &= -\frac{nRT}{2X_k} + \frac{nRT \ln \gamma_k}{(1 - X_k)} \\ &= -\frac{nRT}{2X_k} + \frac{n}{(1 - X_k)} \left[\sum_{i=1}^n \left(X_i^2 + X_i \sum_{\substack{j=1 \\ i \neq j}}^n X_j \right) W_{ik} \right. \\ &\quad \left. - \sum_{i=2}^n \sum_{j=1}^{i-1} W_{ij} X_i X_j \right] \quad i, j \neq k \end{aligned} \quad (21)$$

We present derivatives corresponding to Eq. (18) and Eq. (19) for the component silica evaluated using the liquid compositions from the data set and the W 's of Table 2 in Figs. 3 and 4. The molar excess free energy of mixing calculated in a similar manner is plotted against X_{SiO_2} in Fig. 2.

It is clear from Fig. 4 that those samples with higher mole fractions of silica tend to have positive excess free energies of mixing which can become as large as two kcal/mole. The magnitude of the ideal free energy of mixing however ranges from zero for a pure component to a minimum of $RT \ln(1/17)$ at the compositional midpoint of the system. The struggle between the ideal and excess contributions is dramatically shown in Figs. 3 and 4, where with the shape of the general G^{mix} curve of Fig. 1 in mind, we have extrapolated the derivatives to the pure silica axis. Both derivatives imply unmixing of the liquid at

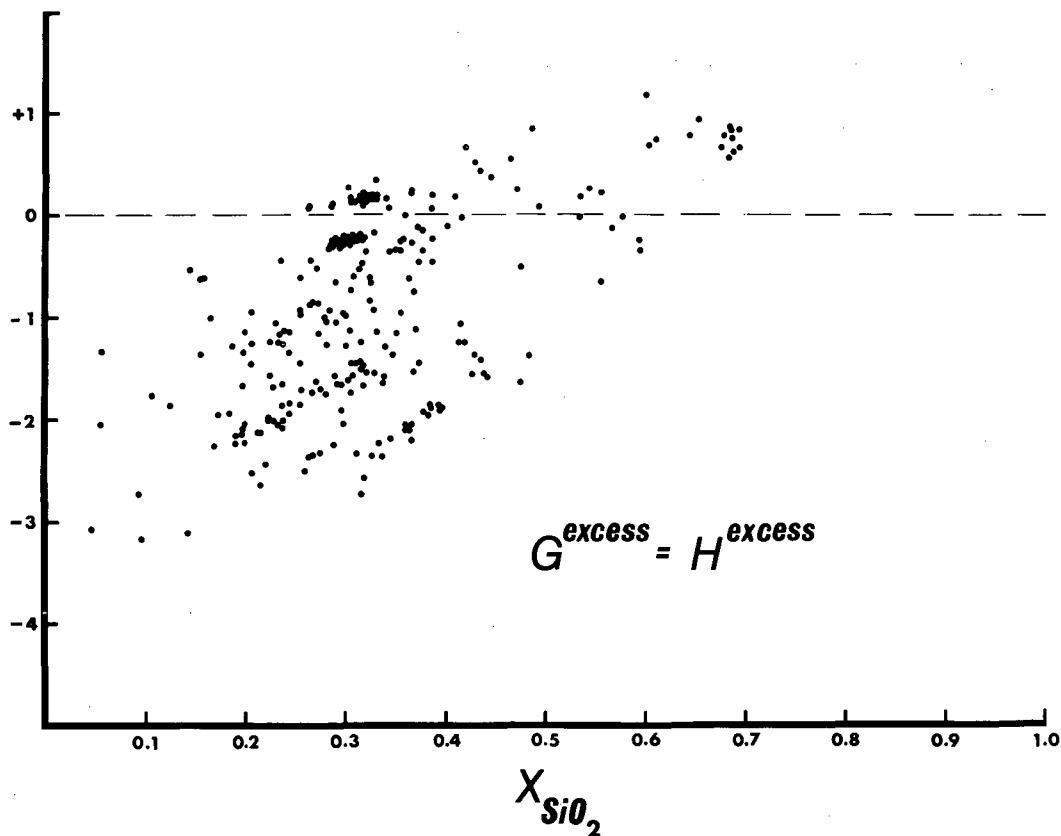


Fig. 2. Molar excess free energy of mixing predicted for all the samples used in the regression of the interaction parameters of Table 2, as a function of the mole fraction of silica. Note that the abscissa represents a projection of the variation of 17 independent variables onto 1 axis. The units of G^{excess} are kcal/mole

high mole fractions of silica; a conclusion not unwarranted by liquid behavior in the silica-rich portions of experimentally determined three component systems (e.g., Bowen, 1928). In addition the positive H^{xs} term (Fig. 2) for many liquids of intermediate silica content demonstrates an incipient immiscibility at low temperatures. For example, a liquid of olivine-andesite composition (Col. 11, to be discussed in detail below), would unmix between 1,000 K and 1,300 K, which is in good agreement with the experimental results and observations of Philpotts (1979) on the residual liquids of tholeiitic basalts. Immiscibility is also indicated (by the stars in Fig. 4) for the lunar basaltic liquids of Longhi et al. (1978) and commences between 1,300 K and 1,000 K. Petrographic evidence for unmixing in these lavas has recently been summarised by Roedder (1978). The ability to correctly predict immiscibility in highly siliceous liquids shows the power of a thermodynamic approach, for this solution model was calibrated from plagioclase-olivine-liquid equilibria in predominantly basaltic systems.

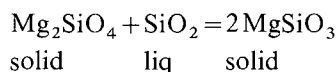
b) Activity of Silica

Since:

$$RT \ln a_k = \left(\frac{\partial G^{\text{mix}}}{\partial n_k} \right)_{n_i}$$

then through Eq. (18) we can predict the activity of any of the components given in Table 1 in any met-aluminous silicate liquid. The most interesting of these activities is perhaps that of silica. The silica activity in a magma on the liquidus can be readily calculated if a suitable buffer reaction between phenocrysts can be written (see Nicholls et al., 1971, Carmichael et al., 1970; 1974, and DePaolo, 1979).

From the experiments of Green (1979) and Mysen and Kushiro (1977) involving liquids in equilibrium with both olivine and orthopyroxene, it is possible to calculate the activity of SiO_2 in these liquids defined by the reaction:



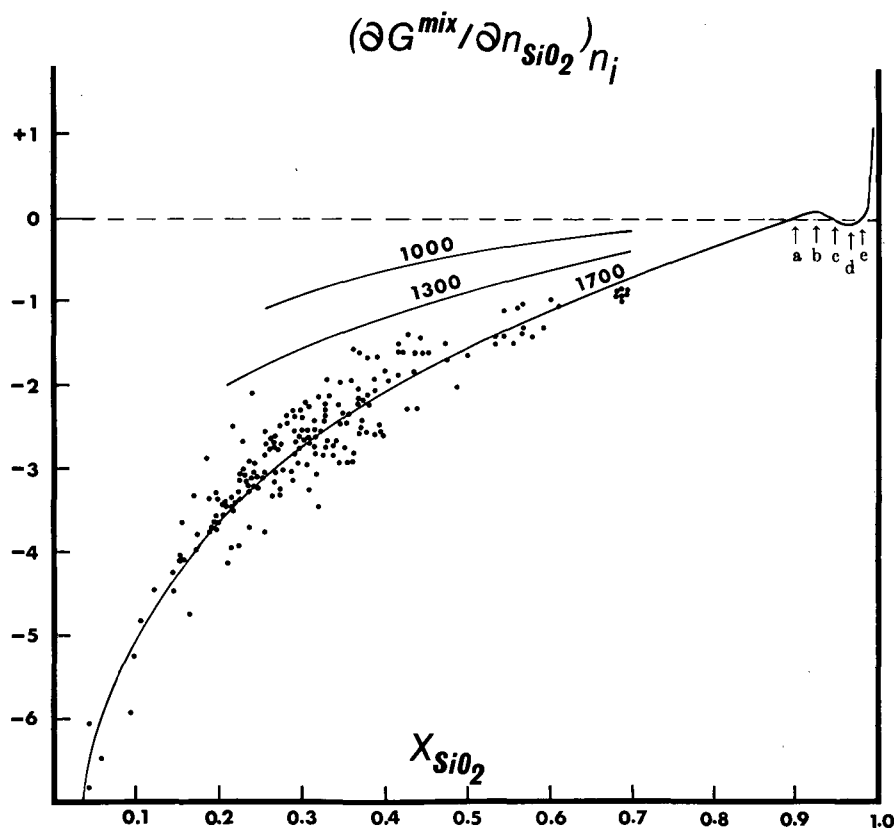


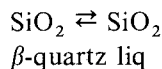
Fig. 3. The first derivative of the free energy of mixing with respect to silica (identical to $RT \ln a_{\text{SiO}_2}$) for the same data set as Fig. 2 as a function of X_{SiO_2} . The unit is kcal/mole. The data are plotted at 1,700 K with trends at 1,300 K and 1,000 K indicated. The temperature dependence arises solely through the ideal contribution [Eq. (18)]. Comparison with Fig. 1 allows extrapolation to and prediction of an immiscible region (a–e) at high mole fractions of silica. The asymmetry of the immiscible region in this figure and the next is undoubtedly due to the fact that we are projecting a 17 component system into two dimensions

so that at equilibrium at P and T :

$$0 = \Delta G^0 + \int_1^P \Delta V^0(T) dP + 2RT \ln a_{\text{MgSiO}_3}^{\text{pyroxene}} - RT \ln a_{\text{Mg}_2\text{SiO}_4}^{\text{olivine}} - RT \ln a_{\text{SiO}_2}$$

The standard state thermodynamic properties ($\Delta G(T)$, $\Delta V(T, P)$) are given in the appendix. Values of $RT \ln a_{\text{SiO}_2}^{\text{liq}}$, calculated from the compositions of the solids and this equilibria are reported in Table 4. Also shown in Table 4 are the predicted silica activities, obtained from the W 's of Table 2 and the compositions of the liquids, evaluated using Eq. (18). The agreement between the two calculations is good, being on average equal, in cal, to the standard error of the G^{xs} regression surface. With this error in mind it should be noted that Mysen and Kushiro had difficulty analysing their glasses, quenched from 20 kbars, and they estimate that their reported values, for Na, may be 50% too low. This will undoubtedly affect the calculated temperatures and silica activities,

and is the reason that a number of their experimental results were rejected from the data set in deriving the W 's of Table 2, and accordingly are not reported in Table 4. To further evaluate the predictive ability of this solution model we have calculated the silica activity in 3 rhyolites saturated with quartz on the liquidus (Table 4). The agreement between the silica activity calculated from Eq. (18) and that obtained from the buffer:



is very good (in light of the uncertainty of the equilibration pressure of the natural samples) if the liquid is considered to be anhydrous. This point brings to light the instability that water induces in the free energy surface calculations. Only two sets of experimental results (Eggler, 1972; Helz, 1973; 1976) are available which report both the composition of liquid and crystals, and for which the concentration of

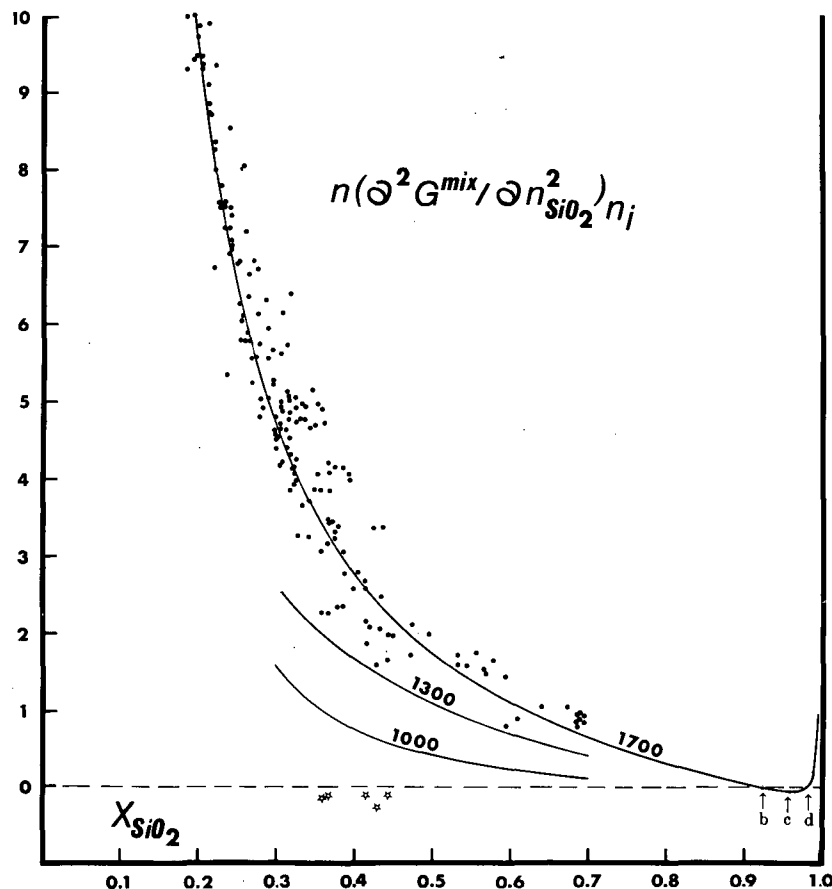


Fig. 4. The second derivative of the free energy of mixing with respect to silica for the same data set as figs. 2 and 3 as a function of X_{SiO_2} . The unit is kcals-mole. The data are plotted at 1,700 K with trends at 1,300 K and 1,000 K indicated. The temperature dependence arises solely through the ideal contribution [Eq. (19)]. The extrapolated region, at high mole fractions of silica should be compared to figs. 1 and 3. The starred symbols are calculated second derivatives at 1,000 K for lunar basalts, clearly indicating liquid immiscibility

Table 4. Partial molar free energies of $SiO_2(RT \ln \gamma_{SiO_2}^{liq} \cdot X_{SiO_2}^{liq})$ in cal/mole

| | T K | Calculated from liq. composition Eq. (8) | Calculated from solid assemblage | Δ | |
|----------------------------------|------------|--|----------------------------------|----------|--------|
| <i>β-quartz</i> | | | | | |
| Bishop Tuff (Hildreth, 1977) | 1,063 | -521 | -423 (3kb); -579 (5kb) | - | |
| | 1,036 | -506 | -408 (3kb); -562 (5kb) | - | |
| | 1,029 | -467 | -408 (3kb); -562 (5kb) | - | |
| <i>Olivine-opx</i> | | | | | |
| Mysen and Kushiro (20kb) | No. 1611 | 1,723 | -5,358 | -4,131 | -1,227 |
| | | 1,748 | -4,646 | -3,986 | -660 |
| | | 1,773 | -3,099 | -3,960 | +861 |
| | | 1,798 | -3,504 | -3,680 | +176 |
| | No. 66SAL1 | 1,648 | -3,631 | -4,980 | +1,349 |
| | 1,673 | -3,887 | -4,698 | +811 | |
| Eggler (1kb) | 1,303 | -1,331 | -1,776 | +445 | |
| Green (20kb) mix E | 1,698 | -4,106 | -4,349 | +243 | |

water in the liquid is small, known, or can be calculated. In addition, the concentration of water may be calculated for siliceous magmas using phenocryst assemblages which define its fugacity (e.g., Hildreth, 1977). As there is so little data on liquids containing

water (10 compositions out of 255), it is not surprising that the regressed surface is dominated by the anhydrous data. The partial molar free energies of Mg_2SiO_4 , Fe_2SiO_4 , $NaAlSi_3O_8$, and $CaAl_2Si_2O_8$ are constrained by the regression, so that the re-

covered temperatures for hydrous liquids are good Table 2). However the predicted activities of silica, calculated for these *hydrous* liquids are unreasonable. The large mole-fractions of water (about 10 mole% for each wt. % in the liquid) dominate the compositional terms preceding the predominantly anhydrous binary interaction W 's of Eq. (18), creating this inconsistency. The same instability can be seen in the components KAlSi_3O_8 , and Ca_2SiO_4 . We have therefore elected to calculate all mixing properties on an anhydrous basis, and where appropriate apply these properties to temperatures calculated for solid-liquid assemblages containing water (see below).

c) Activity of KAlSi_3O_8 in Plagioclase

From Eq. (18), it is possible to calculate the activity of KAlSi_3O_8 in a silicate liquid at any temperature of interest. When these calculations are applied to the plagioclase-liquid experiments cited above they invariably yield liquid activities of KAlSi_3O_8 larger than those calculated from the composition of the plagioclase crystals, assuming ideal dilution by KAlSi_3O_8 . This discrepancy may be resolved if an activity coefficient is associated with KAlSi_3O_8 dissolved in the plagioclase solid solution series. The form of this activity-composition relation is required by exactness criteria to be a function only of the number of moles of KAlSi_3O_8 in the plagioclase, since the components $\text{NaAlSi}_3\text{O}_8$ and $\text{CaAl}_2\text{Si}_2\text{O}_8$ were considered to mix ideally. Plots of predicted $\gamma_{\text{KAlSi}_3\text{O}_8}^{\text{plag}}$ vs $X_{\text{KAlSi}_3\text{O}_8}^{\text{plag}}$ are very scattered, especially at low $X_{\text{KAlSi}_3\text{O}_8}^{\text{plag}}$, due presumably to the difficulty of analysing for K at very low concentrations (<0.5 wt. %) in plagioclases and coexisting glasses. In light of this we have elected to ignore all data with $X_{\text{KAlSi}_3\text{O}_8}^{\text{plag}} < 0.03$ and have obtained a Henry's law coefficient (γ) such that:

$$a_{\text{KAlSi}_3\text{O}_8}^{\text{plag}} = \gamma X_{\text{KAlSi}_3\text{O}_8}^{\text{plag}}, \quad \gamma = 9.47.$$

Within the plagioclase-liquid equilibria considered no temperature or pressure dependence of γ can be found but note that we are dealing with variations of only a few kbars and 2-3 hundred degrees.

On the basis of this relation, the activity of KAlSi_3O_8 in plagioclase coexisting with sanidine may be calculated and compared to the activity of KAlSi_3O_8 in the sanidine after extrapolating the alkali-feldspar activity-composition relations of Thompson and Waldbaum (1968) to the crystallization temperature. Four results for rhyolites are given in Table 5, and show satisfactory correspondence, particularly when the error in γ is taken into account ($\sigma = 2.44$).

Table 5. Predicted compositions of alkali feldspar (mole%)

| Rhyolite | Temp. | Calculated ^a | Observed |
|----------|---------|-------------------------|---|
| Cam 73 | 1,073 K | Or _{72.2} | Or _{67.6} - Or ₆₄ |
| B.T. 107 | 1,029 | Or _{72.2} | Or _{67.4} - Or _{63.5} |
| B.T. 72 | 1,036 | Or _{70.9} | Or _{68.9} - Or _{60.0} |
| B.T. 77 | 1,063 | Or _{61.3} | Or _{66.1} - Or _{59.0} |

^a Calculated from average Henry's law constant $\gamma_{\text{KAlSi}_3\text{O}_8}^{\text{plag}} = 9.47$ ($\sigma = 2.44$)

One reason for the lack of closer agreement possibly lies in the unknown composition of the residual glass in some of the crystal-rich rhyolites, for which the whole rock was taken as an approximation.

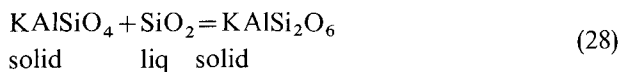
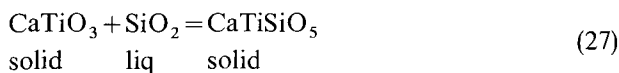
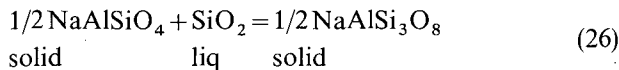
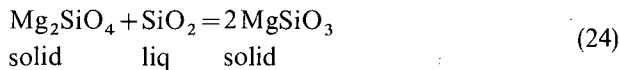
d) Source Regions of Basic Magmas

We turn now to a consideration of the source regions of basic magmas. In particular we will concentrate on magmas which yield plagioclase and are basaltic. The solution model proposed above provides a general framework to demonstrate the $P-T$ conditions of generation of these magmas. To simplify the discussion and the calculations, we shall assume that subsequent to their generation in the mantle, and during their ascent to the surface, silicate liquids (magmas) behave as isochemical systems. This assumption is not intended to deny that mass transfer may take place during ascent through the upper mantle or crust, but rather to acknowledge that its effects are difficult to quantify especially with regard to the major elements, and may in fact be small (e.g., Carmichael et al., 1977). Additionally, the role of crystal fractionation in the liquid en route to the surface will be ignored for the reason that it is hard to make any general statement concerning compositional changes caused by this process for all basic magmas. Thus, as a first approximation, we take the composition of lavas at the surface as being representative of magmas generated at depth in the mantle.

From the solution model and our choice of standard state it follows that the activity of silica in the liquid is independent of pressure. A magma having left a source region where $a_{\text{SiO}_2}^{\text{liq}}$ was buffered by some solid assemblage would maintain that $a_{\text{SiO}_2}^{\text{liq}}$ if it ascended isothermally. Thus for any silicate liquid in a closed system the activity of silica can only change with temperature, and the magnitude of this change depends on the value of $RT \ln \gamma_{\text{SiO}_2}^{\text{liq}}$.

The relevance of this discussion can best be shown in relation to a number of solid-liquid equilibria plotted as functions of $\log a_{\text{SiO}_2}^{\text{liq}}$ and T in Fig. 5.

Thermodynamic data were obtained from Robie et al. (1978) and from the appendix for the following reactions:



Reaction (27) is particularly significant in that perovskite has never been found with either plagioclase or sanidine in nature (Carmichael et al., 1971) so that this reaction represents the lower stability bound, in terms of silica activity, for feldspar. It effectively separates the general basic lava type nephelinite from the various types of basalts, which by definition contain feldspar. Reaction (24) is shown in Fig. 5 at several different pressures.

All reactions are plotted assuming unit activities of the solids. Considering reaction (24), a typical composition of mantle olivine is Fo₉₀, so that the activity of Mg₂SiO₄ = 0.81; this is very close to the square (stoichiometric coefficient is 2 in reaction 24) of the activity of MgSiO₃ in the coexisting orthopyroxene (e.g., Mysen and Kushiro, 1977) unless it has substantial amounts of Al₂O₃ in octahedral sites. Thus allowing for the reduced activity of the magnesian components in olivine and orthopyroxene, typical of a mantle assemblage, hardly displaces the standard state curves.

If it is granted that in the source regions of basic magmas olivine and orthopyroxene coexist in equilibrium with liquid, then the activity of silica in that liquid is given at any pressure and temperature by the curves labelled Fo—En in Fig. 5. To investigate the consequences of this consideration we have plotted the variation of silica activity with T [calculated from Eq.(18)] for six general lava types, an olivine- and an amphibole-andesite, a Hawaiian tholeiite, an alkali-olivine-basalt and a basanite, both from Hawaii, and an olivine nephelinite. Aside from the two andesites, which will be discussed in more detail below, we have assumed that the liquidus temperature is 1,400 K. If the intersection of these silica

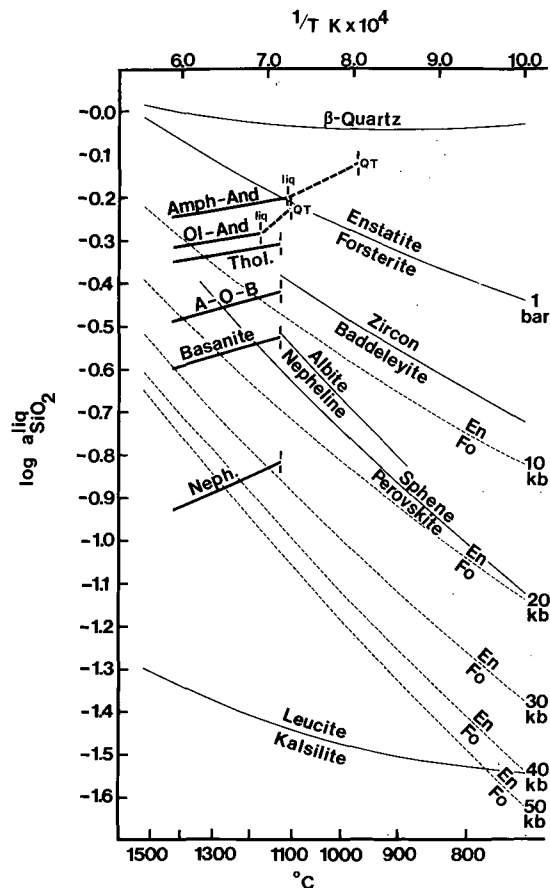


Fig. 5. Predicted temperature variations of the $\log a_{\text{SiO}_2}^{\text{liq}}$ in typical lavas of various compositions compared to that obtained from mineral buffers as a function of temperature and pressure. Bold dotted lines represent crystallization paths of an olivine and amphibole andesite (see text)

activity curves with an olivine-orthopyroxene assemblage at 20 kbars is considered, then the basanite is in equilibrium at a lower temperature than the alkali-olivine-basalt which in turn is lower than that of the tholeiite.

Alternatively at constant temperature (e.g., 1,400 K) the tholeiite equilibrates with opx and olivine at the lowest pressure and the nephelinite at the highest. Isothermal or isobaric equilibration represents a limiting constraint to what must actually happen in nature where temperature is generally considered to increase monotonically with pressure. Thus it appears that tholeiites must be generated at lower temperatures and pressures than basanites. For lavas with very low silica activities, such as ugandites which precipitate leucite and kalsilite, the trends in Fig. 5 suggest that they were either generated from a source region without orthopyroxene, or they came from extreme depths (high P and T).

The effects of water can be readily deduced from Fig. 5. Consider, a hydrous mantle assemblage,

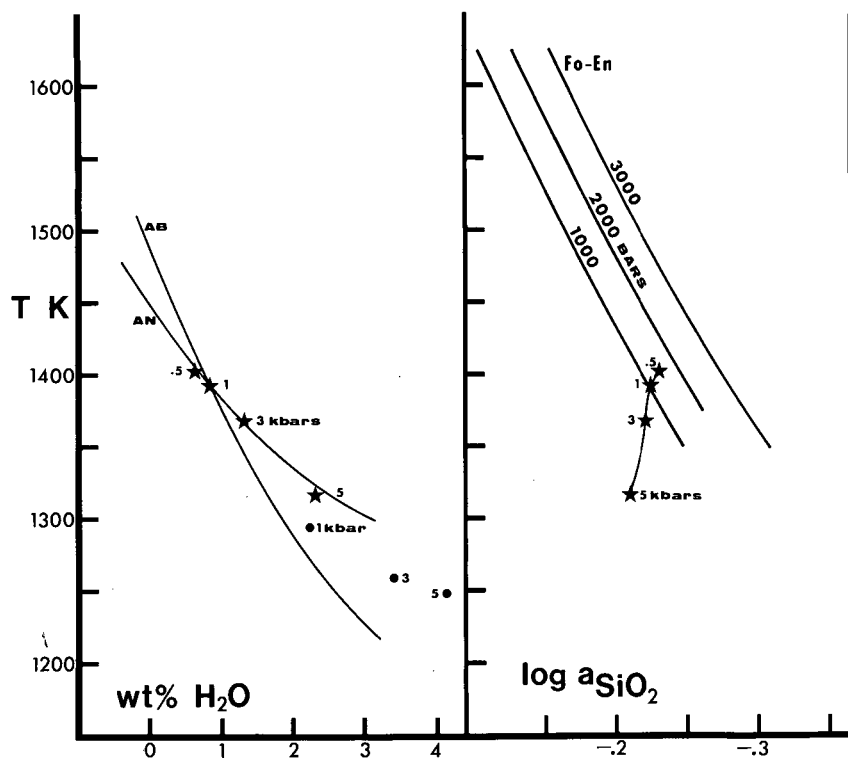


Fig. 6. Correlation plots of predicted temperatures and $\log a_{\text{SiO}_2}^{\text{liq}}$ as a function of pressure and wt. % H_2O for an olivine andesite (stars) from Volcán Colima, Mexico. Equilibration temperature and concentration of water in an amphibole andesite (dots) as a function of pressure. See text

which melts at a lower temperature than an anhydrous one (Mysen and Boettcher, 1975), at constant pressure, the drop in temperature caused by the addition of water will lower the activity of silica in the liquid (imagine sliding down the relevant isobar in Fig. 5). This diagram also indicates that in terms of silica activity, a dry mantle source will produce a more tholeiitic (siliceous) liquid than one containing water at the same pressure.

The liquid-solid equilibria displayed in Fig. 5 form a petrologic grid of the P - T conditions of basic magma generation given that olivine and orthopyroxene are universally present in the mantle source regions. Although the isochemical assumptions made above seem an obvious simplification for the whole dynamic process of magma generation, which for large bodies of magma may involve a range of pressures and temperatures, following a complex ascent path, by using the geothermometers proposed in the earlier part of this paper temperatures can be calculated for the equilibration of any met-aluminous lava type with a mantle of any stipulated composition utilizing the techniques exemplified in Fig. 5. Such calculations have been done elsewhere (Carmichael et al., 1977) and need not be repeated here.

The influence of water may be demonstrated in more detail using the example of an olivine and an amphibole-andesite from Volcán Colima, Mexico (Luhr and Carmichael, 1979). In Fig. 6 the calculated

equilibration temperatures of the $\text{CaAl}_2\text{Si}_2\text{O}_8$ and $\text{NaAlSi}_3\text{O}_8$ components in the plagioclase phenocrysts with the groundmass (treated as the coexisting liquid) are plotted as a function of weight percent H_2O in the liquid at various total pressures. The Ab and the An curves intersect to give an equilibration temperature as a function of water concentration at each total pressure. These intersections are shown at 0.5, 1.0, 3.0, and 5.0 kbars, yielding unique values of temperature and water concentration. At each temperature the $\log a_{\text{SiO}_2}^{\text{liq}}$ can be calculated from the liquid composition and these values are also plotted in Fig. 6. A curve drawn through these points will intersect the paths of $\log a_{\text{SiO}_2}^{\text{liq}}$ defined by the buffer reaction between coexisting phenocrysts of olivine and orthopyroxene at a particular pressure (Fig. 6), so that in the example of this andesite which contains phenocrysts of olivine, orthopyroxene and plagioclase, the calculated conditions of phenocryst equilibration with the liquid are:

$$t = 1,393 \pm 20 \text{ K}; \quad P \approx 1,000 \text{ bars};$$

$$\text{H}_2\text{O} \approx 0.82 \text{ wt. \%}$$

which is in general agreement with the experimental results of Eggler (1972) and Eggler and Burnham (1973). For the amphibole-andesite, which does not contain olivine phenocrysts, only a track of equilibration temperatures at various concentrations of wa-

ter at selected total pressures (probably 1–2 kbars) can be obtained (dots in Fig. 6).

The equilibration conditions of the phenocryst-liquid assemblages of these two andesites are plotted in Fig. 5, and in addition, the activity of silica of each is indicated at the calculated liquidus-temperature (obtained by equilibrating the whole rock composition, considered to be the parent liquid, with phenocryst cores), so that the cooling path from the liquidus to 40%–50% phenocrysts is depicted in terms of temperature and silica activity. Above the liquidus, the variation of silica activity with temperature is also shown, and intersects the 10 kbar Fo–En curve at high temperatures. The results indicate that it may be reasonably doubted if the mantle at shallower depths in andesite terrains is the source of these andesitic lavas.

Summary and Conclusions

Based on standard state thermodynamic data consistent with P – T fusion curves, the free energy surface of met-aluminous silicate liquids has been calculated and fitted to a regular solution model. The surface was calibrated by 255 sets of experiments recording the composition of olivine and/or plagioclase in equilibrium with liquid over the range 1,000 K–1,973 K and from 0.001 to 20 kbars. Only 10 sets of data were available for liquids containing less than 8% water and for which compositions of both liquid and coexisting solids are given. Regression of this equilibrium data provides values for 21 W 's which are interaction parameters between unlike pairs of the 17 components in the liquids.

Recovery of temperature using the solution model as a geothermometer is good, being on average within 30° for olivine, and 12° for plagioclase. The solution model predicts immiscibility within a SiO_2 -rich melt at high mole fractions of SiO_2 , but for certain lunar and andesitic lavas immiscibility is found at much lower mole fractions of SiO_2 . Both of these predictions are substantiated by phase equilibria and observations on the rocks themselves.

There is also good agreement between the activity of silica calculated from the appropriate W 's [Eq. (18)] and that inferred either from the occurrence of quartz phenocrysts, or from the coexistence of olivine and orthopyroxene in equilibrium with the liquid. This is a testament to the predictive power of the model, for no statements on quartz or orthopyroxene saturation of various liquids were included in the regression of the excess free energy surface.

As another example, the limiting (Henry's Law) activity coefficient of KAlSi_3O_8 dissolved in plagioclase

can be estimated, and leads to a satisfying correspondence with the concentration of KAlSi_3O_8 in sanidines coexisting with plagioclase in rhyolites.

A petrogenetic grid can be constructed (Fig. 5) that shows P – T equilibration conditions for any basic lava with a mantle composed of olivine and orthopyroxene using the activity of silica (as a function of T) calculated from the composition of the lava. The broad trends indicate that the more siliceous the lava (or higher the activity of silica) the higher the temperature and the lower the pressure that it would equilibrate with the mantle. The effect of water is to lower the temperature, and thus the silica activity of the liquid in equilibrium with olivine and orthopyroxene at constant pressure. Tholeiitic magmas would therefore be drier than basanitic magmas if both were generated at the same depth. All these broad implications are in accord with current experimental work, although there may be inconsistency in detail.

Lastly, it is possible to plot the temperature of equilibration of the $\text{CaAl}_2\text{Si}_2\text{O}_8$ and $\text{NaAlSi}_3\text{O}_8$ components of plagioclase phenocrysts with a liquid as a function of both water concentration and total pressure. These surfaces will intersect to indicate unique values of both temperature and water concentration as a function of pressure, so that with olivine and orthopyroxene phenocrysts also present (defining the activity of silica), it is possible to estimate temperature, pressure and water concentration of a phenocryst-liquid assemblage (Fig. 6). This has been done for an olivine-andesite and leads to entirely plausible results.

In order to improve solution models based on solid-liquid equilibria for the whole range of liquid compositions found in nature, there is a great need for data on the compositions of olivine, augite or feldspar in equilibrium with basanitic, andesitic, or any of the varieties of nephelinitic liquids, as a function of both temperature and pressure. Certainly the evident experimental difficulties of analysing liquids quenched from high pressures makes most of the published results uncertain. The petrological conclusions based on these experiments may be generally valid (e.g., Mysen and Kushiro, 1977) but the lack of their thermodynamic consistency should generate some scepticism.

A program (written in Fortran IV) is available for calculating solution properties and equilibration temperatures from the proposed model and a copy will be provided to anyone upon request.

Acknowledgements. We would like to thank Professor J. Nicholls for his thorough and illuminating review. This paper profited much from his comments. The second author is greatly indebted to

Dr. David Walker of Harvard University for his counterperspectives on the petrologic significance of phase equilibria, and particularly for his familiarity with solid-liquid equilibria in basaltic systems. This work was supported in part by the Department of Energy under contract W-7405-ENG-48, and in part by NSF (EAR 78-03642). The first author wishes to express and acknowledge an appropriate comment, admittedly not originally made in recognition of the present work: "Though this be madness, yet there is method in 't".

Appendix

Thermodynamic data for six multioxide liquid components and SiO_2 are given below. As neither the precision nor accuracy of these data are known, the number of decimal places is given only to avoid significant roundoff errors. The units for heat capacity at constant pressure (C_p) are cal mole⁻¹ K⁻¹, for heats of fusion, cal mol⁻¹; for entropies of fusion, cal mole⁻¹ K⁻¹, for volumes, cal bar⁻¹ mole⁻¹; and all temperatures (T) are absolute (K). Pressure, P , is in bars.

Mg_2SiO_4 :

$$C_{p_{\text{liq}}} = 64.03 \quad (\text{Carmichael et al., 1977})$$

$$C_{p_{\text{sol}}} = 35.81 + 6.54 \times 10^{-3} T - 8.52 \times 10^5 T^{-2} \quad (\text{Kelley, 1960})$$

$$T_{\text{fusion}} = 2,163 \text{ K}; \Delta H_{\text{fusion}} = 40,677; \Delta S_{\text{fusion}} = 18.806$$

$$V_{\text{liq}} = 1.0912 + 8.157 \times 10^{-5} T - 5.899 \times 10^{-6} P + 4.28 \times 10^{-11} P^2$$

$$V_{\text{sol}} = [1.0381 + 2.490 \times 10^{-5} T + 1.061 \times 10^{-8} T^2] (1 - 0.77 \times 10^{-6} P) \quad (\text{Skinner, 1966; Birch, 1966}).$$

As the heat of fusion estimated from phase equilibria (summarised by Bottinga and Richet, 1978) is much lower than that estimated from the slope of the fusion curve (Davis and England, 1964) the number chosen is obtained by taking the smallest value consistent with the initial slope of the fusion curve. The volume of the liquid is taken from Nelson and Carmichael (1979) and by fitting the fusion curve.

Fe_2SiO_4 :

$$C_{p_{\text{liq}}} = 57.30 \quad (\text{Orr, 1953})$$

$$C_{p_{\text{sol}}} = 36.51 + 9.36 \times 10^{-3} T - 6.70 \times 10^5 T^{-2} \quad (\text{Kelley, 1960})$$

$$T_{\text{fusion}} = 1,490 \text{ K}; \Delta H_{\text{fusion}} = 22,030 \quad (\text{Orr, 1953});$$

$$\Delta S_{\text{fusion}} = 14.785$$

$$V_{\text{liq}} = 1.0558 + 1.187 \times 10^{-4} T - 2.603 \times 10^{-6} P + 7.515 \times 10^{-12} P^2$$

$$V_{\text{sol}} = [1.0969 + 4.013 \times 10^{-5} T - 5.748 \times 10^{-9} T^2] (1 - 0.91 \times 10^{-6} P) \quad (\text{Skinner, 1966; Birch, 1966}).$$

The volume of the liquid is taken from Nelson and Carmichael (1979) and by fitting the fayalite fusion curve (Lindsley, 1967). Using the initial slope of the fusion curve and the volume data, the calculated heat of fusion is 21,264 cal, in good agreement with that measured.

$\text{CaAl}_2\text{Si}_2\text{O}_8$:

$$C_{p_{\text{liq}}} = 101.8 \quad (\text{Ferrier, 1969})$$

$$C_{p_{\text{sol}}} = 64.42 + 13.70 \times 10^{-3} T - 16.89 \times 10^5 T^{-2} \quad (\text{Kelley, 1960})$$

$$T_{\text{fusion}} = 1,823 \text{ K}; \Delta H_{\text{fusion}} = 32,000 \quad (\text{Weill et al., 1979});$$

$$\Delta S_{\text{fusion}} = 17.553$$

$$V_{\text{liq}} = 2.1072 + 2.662 \times 10^{-4} T - 1.577 \times 10^{-5} P$$

$$V_{\text{sol}} = [2.4007 + 2.944 \times 10^{-5} T + 3.186 \times 10^{-9} T^2] (1 - 1.5 \times 10^{-6} P) \quad (\text{Skinner, 1966; Birch, 1966}).$$

There is great uncertainty in the thermodynamic properties of the liquid. Weill et al. (1979) have estimated the heat of fusion as being between 32,098 and 39,900 cal whereas Robie et al. (1978) give 19,360 cal. We have chosen 32,000 cal; the volume of the liquid is taken from Nelson and Carmichael (1979) and from Lindsley (1968) on the assumption that $\text{CaAl}_2\text{Si}_2\text{O}_8$ is stable to 8 kbars at 1,853 K (cf., Goldsmith, 1979).

$\text{NaAlSi}_3\text{O}_8$:

$$C_{p_{\text{liq}}} = 85.69 \quad (\text{Carmichael et al., 1977})$$

$$C_{p_{\text{sol}}} = 61.70 + 13.90 \times 10^{-3} T - 15.01 \times 10^5 T^{-2} \quad (\text{Kelley, 1960})$$

$$T_{\text{fusion}} = 1,391 \text{ K}; \Delta H_{\text{fusion}} = 15,620 \quad (\text{Weill et al., 1979})$$

$$\Delta S_{\text{fusion}} = 11.229$$

$$V_{\text{liq}} = 2.5224 + 1.210 \times 10^{-4} T - 2.505 \times 10^{-5} P + 2.506 \times 10^{-10} P^2$$

$$V_{\text{sol}} = [2.3877 + 3.566 \times 10^{-5} T + 2.065 \times 10^{-8} T^2] (1 - 1.48 \times 10^{-6} P) \quad (\text{Skinner, 1966; Birch, 1966}).$$

The volume of the liquid was obtained from Nelson and Carmichael (1979) and by fitting the fusion curve of Boyd and England (1963). However, Windom and Boettcher (1977) have suggested quite a different pressure dependence of the fusion curve. These data are therefore uncertain.

$\text{CaMgSi}_2\text{O}_6$:

$$C_{p_{\text{liq}}} = 82.52 \quad (\text{Carmichael et al., 1977})$$

$$C_{p_{\text{sol}}} = 52.87 + 7.84 \times 10^{-3} T - 15.74 \times 10^5 T^{-2} \quad (\text{Kelley, 1960})$$

$$T_{\text{fusion}} = 1,664.5 \text{ K}; \Delta H_{\text{fusion}} = 34,435; \Delta S_{\text{fusion}} = 20.688$$

$$V_{\text{liq}} = 1.6726 + 1.808 \times 10^{-4} T - 1.172 \times 10^{-5} P + 3.408 \times 10^{-11} P^2$$

$$V_{\text{sol}} = [1.5698 + 2.490 \times 10^{-5} T + 1.082 \times 10^{-8} T^2] (1 - 1.07 \times 10^{-6} P) \quad (\text{Skinner, 1966; Birch, 1966}).$$

The heat of fusion is calculated from the initial slope of the fusion curve (Rosenhauer and Eggler, 1975) which compares well with 34,085 cal given by Weill et al. (1979). The volume of the liquid is taken from Nelson and Carmichael (1979) and from the fusion curve of Rosenhauer and Eggler (op.cit.) combined with that of Boyd and England (1963).

MgSiO_3 :

$$C_{p_{\text{liq}}} = 42.41 \quad (\text{Carmichael et al., 1977})$$

$$C_{p_{\text{sol}}} = 24.55 + 4.74 \times 10^{-3} T - 6.28 \times 10^5 T^{-2} \quad (\text{Kelley, 1960})$$

$$T_{\text{fusion}} = 1,832 \text{ K}; \Delta H_{\text{fusion}} = 19,576; \Delta S_{\text{fusion}} = 10.686$$

$$V_{\text{liq}} = 0.8786 + 3.602 \times 10^{-5} T - 5.658 \times 10^{-6} P + 2.370 \times 10^{-11} P^2$$

$$V_{\text{sol}} = [0.7453 + 1.962 \times 10^{-5} T + 2.186 \times 10^{-9} T^2] (1 - 1.01 \times 10^{-6} P) \quad (\text{Skinner, 1966; Birch, 1966}).$$

The heat of fusion has been taken from the initial slope of the fusion curve, which was redrawn to include the results of Chen and Presnall (1975) below 25 kbars in preference to those of Boyd et al. (1964) which are accepted above 25 kbars. The volume of the liquid was obtained from Nelson and Carmichael (1979) and from fitting the fusion curve (above).

SiO_2 :

$$C_{p_{\text{liq}}} = 20.79 \quad (\text{Carmichael et al., 1977})$$

$$(\Delta H_f^0)_{298.15} = -222,258; S_{298}^0 = 1.591$$

$$V_{\text{liq}} = 0.6660 - 9.532 \times 10^{-6} T - 4.204 \times 10^{-6} P$$

The liquid properties have been calculated at 298.15, for although SiO_2 liquid would transform to a glass at high temperatures, these are above the temperatures at which multicomponent silicate liquids are stable. $(\Delta H_f^0)_{298}$, the heat of formation from the elements at 298.15 K is the average of the cristobalite data of Helgeson et al. (1978) and of Robie et al. (1978) taken to the fusion temperature, combined with the heat of fusion of 1950 cal (Robie et al., 1978) and brought back down to 298.15 K with the heat capacity of SiO_2 liquid. The quantity $(\Delta H_f^0)_{T_f}$ is very close to the enthalpy of formation of silica glass at the fusion temperature (Robie et al. 1978) with an error of 170 cal. The volume at 1 bar is taken from Nelson and Carmichael (1979) and the pressure dependence is an average derived from the adiabatic compressibility measurements in binary silicate liquids (Bockris and Kojonen, 1960; Baidov and Kunin, 1968) extrapolated to pure SiO_2 liquid.

The thermodynamic data used in Fig. 4 are taken from Robie et al. (1978) except that the following values have been used for the molar heats of formation at 298.15 and entropies at 298.15:

Mg_2SiO_4 (sol): $(\Delta H_f^0)_{298} = -520,000$ cal; $S_{298}^0 = 22.75$

MgSiO_3 (sol): $(\Delta H_f^0)_{298} = -370,200$ cal; $S_{298}^0 = 16.2$

modified from Helgeson et al. (1978) and Robie et al. (1978) so as to conform with the observed incongruent melting of MgSiO_3 at 1,832 K. The values of the heat capacities for these two solids are given above.

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Received August 27, 1979; Accepted October 30, 1979

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

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