FELDSPAR-LIQUID TEMPERATURE-COMPOSITION
RELATIONSHIPS

A DISSERTATION SUBMITTED TO THE GRADUATE DIVISION OF THE
UNIVERSITY OF HAWAII IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

IN GEOLOGY AND GEOPHYSICS

DECEMBER 1982

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ACKNOWLEDGEMENTS

The completion of this project is due in great part to the guidance, support, and constant encouragement of John A. Philpotts. Innumerable discussions between us were invaluable. The advice, criticisms, and suggestions of Shiv K. Sharma and John M. Sinton are also gratefully acknowledged.
ABSTRACT

The variation of the compositions of coexisting feldspars and liquids as a function of their one atmosphere equilibration temperatures was studied, and an expression that quantitatively relates these parameters was derived. This expression may be used as a magmatic geothermometer. As such it is a superior predictor of equilibration temperatures compared to previously proposed feldspar-liquid geothermometers. It is also applicable to feldspars of any composition, not just plagioclase. It can also be used to calculate the melting points of some other aluminates. This expression is also a structural and thermodynamic probe into the nature of feldspar-liquid equilibria.

The derived expression is interpreted in terms of crystal-liquid equilibria at the feldspar-liquid interface. It is proposed that feldspar in equilibrium with liquid is surrounded by a surface melt of the feldspar's composition. The structure of this surface melt may be similar to that of high pressure feldspar melts of the same composition. The surface melt may, therefore, be saturated with crystalline corundum. The expression is interpreted in terms of equilibrium among corundum, the feldspar surface melt, and the surfaces of the liquid and feldspar.
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CHAPTER 1
INTRODUCTION

The solid surfaces of the Earth, Moon, Mars, Venus, and Mercury, as well as many meteorites, are predominantly igneous. The solid rock of which they are composed was once molten. The minerals and glass which make up these frozen magmas are a coded record of their magmatic history. Feldspars are the most common minerals in igneous rocks (Deer et al, 1966). The purpose of my dissertation research is to break the code that relates the composition of coexisting feldspars and liquids to their one atmosphere equilibration temperatures.

Geology is the study of the Earth. Knowledge of the temperature at which an igneous rock formed can be a crucial piece of information in a geologic study. For instance, in the late eighteenth and early nineteenth centuries Werner and the Neptunists argued that basalts were formed as precipitates from a primordial ocean (Eicher, 1968, chapter 1). Hutton and the Uniformitarianists argued, however, that basalts were the products of volcanic eruptions (Eicher, 1968, chapter 1). Knowledge of the temperature at which basalts form would have proven Hutton correct, as these temperatures are greatly in excess of the boiling point of water.

The importance of using experimental data to deduce the thermal history of igneous rocks was first pointed out by Bowen (1912) in his first experimental paper which was on the system
anorthite-carnegieite. In this study Bowen determined that nepheline inverted to its high temperature polymorph, carnegieite, at 1521(K). Since carnegieite has never been observed in natural rocks Bowen surmised that natural nepheline bearing igneous rocks all form below 1521(K).

Like Bowen, I chose to try to say something about magmatic temperatures with the aid of results of high temperature phase equilibria studies. However, it was my desire to derive a quantitative relationship between the compositions of coexisting feldspars and liquids and their equilibration temperatures. I attacked this problem by compiling a data bank of the compositions of coexisting feldspars and liquids equilibrated experimentally at known temperatures at one atmosphere pressure. I maintained only one rigid rule during this study: experimental observations must be held to be valid above any theoretical, statistical, or empirical manipulations.

I tried to interpret and refine the composition-temperature variations I observed in light of current hypotheses on the structures of feldspars and liquids as functions of composition and temperature; on the occurrence, composition, and morphology of feldspars and glasses in natural rocks; on the thermodynamics of phase equilibria; as well as on current theories of crystallization and fusion.

I attempted to break the feldspar-liquid temperature-composition code as I would a jigsaw puzzle. After
collecting the pieces to the puzzle, i.e. the data, I first searched for large scale patterns. My initial data set consisted of experiments in which the compositions of coexisting plagioclase and liquid had been determined with the electron microprobe. These data are restricted almost entirely to experiments on terrestrial and lunar basalts and the system An-Ab-Di. My data set continually grew in size as new or unpublished experimental studies came to my attention. It seemed that every time I successfully derived a quantitative plagioclase-liquid temperature-composition relationship I would discover a new data set that involved compositional variations I had not yet considered.

The form of the plagioclase-liquid geothermometer I empirically derived from the basaltic data and the system An-Ab-Di was the cryoscopic equation for corundum-liquid equilibria. The constants of this equation were the experimentally determined heat of fusion and melting point of corundum. The form of the three factors which comprised this expression appeared to be related to the structural state of aluminum in plagioclase and liquid. The expression I derived also accurately calculated the range of melting points of the alkaline earth feldspars, and the melting points of carnegieite and sodium-aluminate. The combined knowledge that this expression accurately calculated plagioclase-liquid equilibration temperatures, that the constants of this expression were experimentally determined thermodynamic properties of corundum, that the form of the three factors that comprise this equation appeared
to be related to the structural state of Al in both phases, and the fact that this expression accurately calculated the melting points of other aluminates convinced me that the study of this expression should be pursued further.

At this point in my research I did what any good jigsaw puzzler does towards the end of the puzzle. I looked for the missing pieces. And, as with all things that are hard to find, I found them in the most obvious place. The missing pieces to this puzzle consisted of the anorthite and alkali-feldspar liquidi determinations that had been made in the experimental studies of simple systems since the turn of the century. What I found in studying the simple systems is that the compositional variations considered by these are much greater than those of the natural systems that have been experimentally studied. The consideration of those systems allowed me to refine one of my factors, that is based on the binomial distribution and the concentration of Al in the melt, into a form that appears to be theoretically significant.

Besides greatly expanding the compositional variation of my data set the consideration of simple systems has increased my data set by about an order of magnitude, almost doubled the temperature range of my data, and demonstrated that the expression I derived could be applied to feldspars of any composition, not just plagioclase. The temperature-composition variations in the simple systems are easily related to those in the natural systems. The expression generated in this study can be used as an accurate and precise
magmatic geothermometer. The expression may also be used as a thermodynamic and structural probe into the nature of crystal-liquid equilibria.

The structure of this dissertation is as follows: First, I present the relationship I derived that relates the composition of coexisting feldspars and liquids to their one atmosphere equilibration temperatures. Second, I discuss the nature of the terms that comprise the expression. Third, I present a model that may account for this temperature-composition relationship. Fourth, I demonstrate that this approach may be extended to other aluminates. Finally, I compare my thermometer with other feldspar-melt thermometers that have been proposed and show them to be both inferior predictors of temperature, and restricted to a much smaller compositional range of feldspars and liquids.

I believe this dissertation to be an important and original contribution to the study of the Earth. I hope that the reader will find something of value and much of interest herein.
CHAPTER 2
RESULTS

One atmosphere feldspar-liquid equilibration temperatures for the data cited in Table 1 can be calculated as follows:

\[
T(K) = \frac{1}{((1/T_{cor})- (R/\Delta H_{cor}) \ln(w))} \quad \text{eq. (1)}
\]

where:

\[
w = \frac{(4AF+AN+2ANAF(AN-AF))(12A_1^3x(1-A_1x))(12(b/z)^3(1-(b/z)))}{12Al_1^3(1-Alx)(12(b/z))(1-(b/z))}
\]

\(T(K)\) is the temperature of interest in Kelvin

\(T_{cor}^{fus}\) is corundum's melting point = 2333(K)

\(R\) is the universal gas constant = 8.314 joules/(mol(K))

\(\Delta H_{cor}^{fus}\) is corundum's enthalpy of fusion = 107315 joules/mol

\(AN = \frac{(3A_1x-Si_x)}{(A_1x+Si_x)}\)

\(AF = 1-AN\)

\(b = (A_1-f/3)(1-P_1-2(A_1)(Ti_1)-i/5)\)

\(f = (Ne-Ac/6)\) or 0, whichever is greater

\(i = 2Ab\) or Or, whichever is less

\(z = y-v\)

\(y = (3A_1/2+Si_1+P_1/2+Ak/5+u+x+k)\) or 1, whichever is less

\(u = 5(Na_1+K_1)\) or \(A_1/2\), whichever is less

\(x = (Il+Mgt+Hem+a)\) or \(A_1\), whichever is less

\(a = (2Fo/3+2Fa/3+En/4+Fs/4-p)\) or 0, whichever is greater

\(p = (Di/8+Hd/8+Ak/10-3(Ab+Or)/2)\) or 0, whichever is greater

\(k = (Sd/2-e)\) or 0, whichever is greater

\(e = Ac\) or \(4Qz\), whichever is less
## TABLE 1

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</tr>
<tr>
<td>(only those liquids with Si&gt;Fe)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Schairer(1950)</td>
<td>Or-Mg-Fe</td>
<td>37</td>
<td>1</td>
<td>7</td>
</tr>
<tr>
<td>Schairer &amp; Bowen(1947)</td>
<td>An-Lc-Fe</td>
<td>38</td>
<td>-2</td>
<td>11</td>
</tr>
<tr>
<td>Schairer &amp; Bowen(1955)</td>
<td>Or-Kd-Fe</td>
<td>52</td>
<td>-7</td>
<td>14</td>
</tr>
<tr>
<td>Schairer &amp; Bowen(1956)</td>
<td>Ne-Fe-Sc</td>
<td>47</td>
<td>3</td>
<td>13</td>
</tr>
<tr>
<td>Schairer &amp; Toder(1967)</td>
<td>Ab-Fa</td>
<td>1</td>
<td>20</td>
<td>0</td>
</tr>
<tr>
<td>Stolper(1977)</td>
<td>meteorite</td>
<td>1</td>
<td>-7</td>
<td>0</td>
</tr>
<tr>
<td>Walker et al(1977)</td>
<td>lunar</td>
<td>8</td>
<td>-9</td>
<td>13</td>
</tr>
<tr>
<td>Walker et al(1979)</td>
<td>terrestrial</td>
<td>14</td>
<td>-13</td>
<td>7</td>
</tr>
<tr>
<td>Weill &amp; Mackay(1975)</td>
<td>lunar</td>
<td>4</td>
<td>14</td>
<td>8</td>
</tr>
<tr>
<td>Yang et ai(1972)</td>
<td>An-AK-Fa</td>
<td>17</td>
<td>-3</td>
<td>8</td>
</tr>
</tbody>
</table>

*note: number of data points
mean = mean ± T (calculated - experimental)
s.d. = standard deviation from mean
\[ v = \frac{d}{n} + \frac{q}{5} + \frac{2f}{3} \]

\[ d = \frac{(Qz - m - 10g - 3f/5)}{2} \text{ or } 0, \text{ whichever is greater} \]

\[ m = \frac{(Fs/2 + En/2 - 6(Ab + Or))}{2} \text{ or } 0, \text{ whichever is greater} \]

\[ g = c \text{ or } An, \text{ whichever is less} \]

\[ c = \frac{(Fs - j)}{2} \text{ or } 0, \text{ whichever is greater} \]

\[ j = \frac{(An - 3.25Ab)}{2} \text{ or } 0, \text{ whichever is greater} \]

\[ n = \frac{(1.5 + 10(1 - Qz - An - Ab - Or))}{2} \text{ or } 2, \text{ whichever is less} \]

\[ q = \frac{(Or - 2Ab - 5h)}{2} \text{ or } 0, \text{ whichever is greater} \]

\[ h = \frac{(Fe_{1} - Mg_{1})}{2} \text{ or } 0, \text{ whichever is greater}. \]

Element concentrations are in cation mole fractions. The subscript \( x \) refers to the feldspar, \( 1 \) to the liquid. Mole fraction CIPW norms in which the cation sum of each component equals one are used to calculate b. Normative components are listed in Table 2. I use the norm calculation in Holmes (1921). In peralkaline systems the CIPW norm is modified to calculate sodium disilicate and potassium disilicate instead of sodium metasilicate and potassium metasilicate; also potassium disilicate must be converted to potassium tetrasilicate prior to the calculation of normative quartz. These modifications are consistent with the phase relations in the alkali-alumina-silica systems (Schairer and Bowen, 1955, 1956).

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Name</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Qz</td>
<td>quartz</td>
<td>SiO₂</td>
</tr>
<tr>
<td>Ab</td>
<td>albite</td>
<td>Na₁/₅Al₁/₅Si₃/₅O₈/₅</td>
</tr>
<tr>
<td>Or</td>
<td>orthoclase</td>
<td>K₁/₅Al₁/₅Si₃/₅O₈/₅</td>
</tr>
<tr>
<td>An</td>
<td>anorthite</td>
<td>Ca₁/₅Al₂/₅Si₂/₅O₈/₅</td>
</tr>
<tr>
<td>Lct</td>
<td>leucite</td>
<td>K₁/₄Al₁/₄Si₁/₂O₃/₂</td>
</tr>
<tr>
<td>Ne</td>
<td>nepheline</td>
<td>Na₁/₃Al₁/₃Si₁/₃O₄/₃</td>
</tr>
<tr>
<td>Di</td>
<td>diopside</td>
<td>Ca₁/₄Mg₁/₄Si₁/₂O₃/₂</td>
</tr>
<tr>
<td>Hd</td>
<td>hedenbergite</td>
<td>Ca₁/₄Fe₁/₄Si₁/₂O₃/₂</td>
</tr>
<tr>
<td>En</td>
<td>enstatite</td>
<td>Mg₁/₂Si₁/₂O₃/₂</td>
</tr>
<tr>
<td>Fs</td>
<td>ferrosilite</td>
<td>Fe₁/₂Si₁/₂O₃/₂</td>
</tr>
<tr>
<td>Wo</td>
<td>wollastonite</td>
<td>Ca₁/₂Si₁/₂O₃/₂</td>
</tr>
<tr>
<td>Ac</td>
<td>acmite</td>
<td>Na₁/₄Fe₁/₄Si₁/₂O₃/₂</td>
</tr>
<tr>
<td>Ak</td>
<td>akermanite</td>
<td>Ca₁/₃Mg₂/₅Si₂/₅O₇/₅</td>
</tr>
<tr>
<td>Fo</td>
<td>forsterite</td>
<td>Mg₂/₃Si₁/₃O₄/₃</td>
</tr>
<tr>
<td>Fa</td>
<td>fayalite</td>
<td>Fe₂/₅Si₁/₃O₄/₃</td>
</tr>
<tr>
<td>Sd</td>
<td>sodium disilicate</td>
<td>Na₁/₂Si₁/₂O₅/₄</td>
</tr>
<tr>
<td>Kd</td>
<td>potassium disilicate</td>
<td>K₁/₂Si₁/₂O₅/₄</td>
</tr>
<tr>
<td>Kt</td>
<td>potassium tetrasilicate</td>
<td>K₁/₃Si₂/₃O₃/₂</td>
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<tr>
<td>Sp</td>
<td>sphene</td>
<td>Ca₁/₃Ti₁/₃Si₁/₃O₅/₃</td>
</tr>
<tr>
<td>Il</td>
<td>ilmenite</td>
<td>Fe₁/₂Ti₁/₂O₃/₂</td>
</tr>
<tr>
<td>Wu</td>
<td>wustite</td>
<td>FeO</td>
</tr>
<tr>
<td>Mgt</td>
<td>magnetite</td>
<td>FeO₄/₃</td>
</tr>
<tr>
<td>Hem</td>
<td>hematite</td>
<td>FeO₃/₂</td>
</tr>
<tr>
<td>Wh</td>
<td>whitlockite</td>
<td>Ca₃/₅P₂/₅O₈/₅</td>
</tr>
</tbody>
</table>

Note: The cation sum of each component equals one.
Sack et al (1980). Ferrous/ferric ratios for Roeder and Osborn (1966) are extrapolated from their determinations of this ratio in super-liquidus runs. Ferrous/ferric ratios of 0.5, 2.75, 3.5, and 4.45 are assumed for Roeder and Osborn's (1966) experiments with oxygen fugacities of $10^{-0.7}$, $10^{-7}$, $10^{-9}$, $10^{-11}$, respectively. All iron in the peralkaline experiments of Bailey and Schairer (1966) is treated as ferric. The remaining experiments on iron-bearing systems are all at oxygen fugacities near that of the iron-wustite buffer, and all iron in these is treated as ferrous. Calculated versus experimental equilibration temperatures for the data cited in Table 1 are plotted in Figure 1.

Equation (1) is an empirical fit to the data. However, it is written in the form of the cryoscopic equation for freezing point depression for corundum liquid equilibria, i.e.:

$$T(K) = \frac{1}{\left(\frac{1}{T_{\text{cor}}^{\text{fus}}}-\frac{R}{H_{\text{cor}}^{\text{fus}}}\ln\left(\frac{a_{\text{cor}}^{\text{liq}}}{a_{\text{cor}}^{\text{xtl}}}\right)\right)}$$

where $a_{\text{cor}}^{\text{liq}}$ is the activity of liquid corundum at $T(K)$ and $a_{\text{cor}}^{\text{xtl}}$ is the activity of crystalline corundum at $T(K)$ if:

$$w = \frac{a_{\text{cor}}^{\text{liq}}}{a_{\text{cor}}^{\text{xtl}}}$$

and $\Delta H_{\text{fus}}^{\text{cor}}$ is not a function of temperature. If this is the case then the terms of equation (1) are amenable to thermodynamic interpretation. Each of the three factors in the above statement is discussed below from this point of view. In the third factor the concentration of Al in the melt is modified by a number of terms. These are not regression coefficients, but modifiers necessary to
Figure 1: T experimental vs calculated; all data.
calculate feldspar-liquid equilibration temperatures in simple systems.

\[ \Delta H_{\text{fus}} \] was determined by drop calorimetry by Shpil'rain et al (1972). \( T_{\text{cor}} \) used in eq. (1), 2333(K), is between that reported by Shpilrain et al (1972), 2323(K), and that reported by Robie et al (1979), 2345(K), and within the brackets reported by Fomichev et al (1973), 2327-2333 (K).

Assuming ideality Kelley (1936) cryoscopically calculated \( \Delta H_{\text{fus}} \) to be 108789 joules/mol from the corundum liquidus on binary phase diagrams. This determination is within 2% of that of Shpil'rain et al (1972). The extraordinary agreement between the calculated and experimentally determined heat of fusion of corundum supports the assumption that \( \Delta H_{\text{fus}} \) is not a function of temperature.
CHAPTER 3
DISCUSSION OF THE TERM "4AF+AN+2ANAF(AN-AF)"

The best explanation of the expression \((4AF+AN+2ANAF(AN-AF))\) is that it equals the number of sites available for Al occupancy per Al atom in feldspar.

The distribution of Si and Al atoms among the tetrahedral sites of crystalline albite at temperatures approaching its one atmosphere melting point is believed to be completely random. Helgeson et al (1978) state that crystalline albite is completely disordered at temperatures greater than its triclinic to monoclinic inversion. A range of temperatures for this inversion has been reported. Reported inversion temperatures are: greater than 1378 (K) (Prewitt et al, 1976); 1203 (K) (Okamura and Ghose, 1975); between 1253 and 1381 (K), depending on annealing times and temperatures (Winter et al, 1979); and about 1238 (K) (Thompson et al, 1974). Winter et al (1979) state that the distribution of Si and Al among the tetrahedral sites of albite obtains monoclinic topochemoical symmetry, i.e. the distribution is random, at a lower temperature than the crystallographic symmetry inversion.

Therefore there are four sites available for Al occupancy per Al atom for crystalline albite at high temperature. The distribution of Si and Al atoms among the tetrahedral sites of sanidine is believed to be completely random above 1173(K) (Ribbe, 1975). Albite-liquid and sanidine-liquid equilibration temperatures
as low as 1000 (K) are accurately calculated with eq. (1). This suggests that the distribution of Si and Al among the tetrahedral sites of these phases is random at these temperatures.

The X-ray crystallographic analysis of anorthite by Kempster et al (1962) and Megaw et al (1962) indicate complete order in the distribution of Al and Si among the tetrahedral sites of anorthite at room temperature. The high temperature crystallographic studies on anorthite of Czank (1973) are consistent with a completely ordered distribution of Si and Al atoms among the tetrahedral sites of anorthite up to 1703 (K), the highest temperature studied. Therefore, within the experimental errors of these studies, anorthite has one site available for Al occupancy per Al atom. On the basis of the variation of unit cell parameters as a function of the temperature and duration of annealing, Smith (1972) suggested that anorthite is slightly disordered at its one atmosphere melting point.

The success of eq. (1) in calculating alkali feldspar-liquid equilibration temperatures suggests that the distribution of Si and Al among the tetrahedral sites of all alkali feldspars is completely random above 1000 (K), and that the effect of the Or component on the distribution of Si and Al atoms among the tetrahedral sites in intermediate feldspars is the same as that of Ab. The entire alkali feldspar component is treated as AF in the following discussion.

If the distribution of Si and Al atoms among the tetrahedral sites of An is completely ordered at its melting point, then it is
impossible for this distribution to become more ordered with decreasing temperature. Similarly if the distribution of Si and Al atoms among the tetrahedral sites of high albite and high sanidine is completely disordered then it is impossible for this distribution to become more disordered with increasing temperature. Intermediate plagioclases therefore represent the remarkable situation of a solid solution formed by the mixing of a completely ordered high temperature end member, AN, with a completely disordered low temperature end member, AF. If mixing of the AN and AF components have no affect on the order/disorder relationship of Si and Al then the number of sites available for Al occupancy per Al atom in feldspar is equal to \((4AF+AN)\).

Mixing, however, may have two possible effects. Mixing may induce partial ordering of the AF component, and it may induce partial disordering of the An component. The data are better fit to eq. (1) with \(4AF+AN+2ANAF(AN-AF)\) than with \(4AF+AN\). The term \(2ANAF(AN-AF)\) may equal the increase in the number of sites available for Al occupancy per Al atom due to the partial disordering of the AN component minus the decrease in the number of sites available for Al occupancy per Al atom due to the partial ordering of the AF component in intermediate feldspar.

The mixing term \(2ANAF(AN-AF)\) was empirically derived. It is an easy task to derive a number of other algorithms which would also adequately serve as the mixing term. It is not theoretically obvious which of these is the "correct" formulation. It is
important, therefore, not to place too much physical emphasis on the form of this term.

This treatment does not rely on the Al avoidance principle of Lowenstein (1954), which states that no two Al tetrahedra will share the same oxygen in feldspar, and in fact eq. (1) requires some Al-O-Al bridging in all feldspars, with the exception of pure anorthite. As pointed out by Kerrick and Darken (1975) Al-O-Al bridging will occur in albite if it is completely disordered. Any degree of disorder in anorthite will also require some Al-O-Al bridging. Iishi et al (1971) assign a band in the infrared spectrum of crystalline anorthite to an Si-O-Si vibration. This indicates that a certain degree of disorder and Al-O-Al bridging does occur in anorthite. Sharma (personal communication, 1982) has also observed an Si-O-Si band in the Raman spectra of crystalline anorthite. As noted above Smith (1972) has suggested that anorthite may be slightly disordered at its one atmosphere melting point.

The calculated anorthite melting point with Eq. (1) is 1823(K), 3 degrees below that determined experimentally by Schairer (1957a). Solving for the number of sites available for Al occupancy per Al using Schairer's (1957a) melting point, 1826(K), results in a value of 1.02. This apparent discrepancy may indicate that anorthite is 2% disordered at its one atmosphere melting point, which is consistent with the observations of Smith (1972), Iishi et al (1971), and Sharma (personal communication, 1982). Assuming that the anorthite melting point is known only to with five degrees,
eq. (1) predicts that the degree of disorder in anorthite at its melting point is between 0 and 5 percent. Since this discrepancy results in an insignificant error in calculated temperatures, and since the distribution of Al and Si in anorthite eventually becomes completely ordered at lower temperature, I assume that the number of sites available for Al occupancy per Al atom is one for An in eq. (1).

The small amount of disorder present in anorthite at one atmosphere should decrease with increasing pressure. Goldsmith (1980) has shown that corundum exsolves from crystalline anorthite below its melting point at pressures in excess of 9 kilobars. As pressure increases the distribution of Si and Al atoms among the tetrahedral sites of anorthite becomes more ordered until it is completely ordered. The number of sites available for Al occupancy per four tetrahedra can be further reduced only through the loss of Al atoms via the exsolution of an aluminous phase, such as corundum. This suggests that, after attaining a completely ordered distribution of Si and Al atoms, increased pressure drives anorthite towards a distribution of tetrahedral cations similar to that found in low albite, which has only one specific Al site for every four tetrahedral sites.

A tendency towards the distribution of cations in tetrahedral sites similar to that in low albite with increasing pressure would explain why stoichiometric anorthite is unstable at pressures greater than nine kilobars. The increase of albite content of
liquidus plagioclase with increasing pressure in a quartz diorite, as demonstrated by Green (1968), may be due to the same effect.

It may also be mentioned that non-stoichiometric An, with a composition $\text{An}_{x}\text{Qz}_{1-x}$, cannot be formed simply by the exsolution of corundum from stoichiometric anorthite. If this were possible then the following exchange reaction would be valid:

$$(1.5)\text{CaAl}_2\text{Si}_2\text{O}_8 \rightleftharpoons \text{Al}_2\text{O}_3 + \text{Ca}_{1/2}\text{AlSi}_3\text{O}_8.$$ 

This reaction is, however, unbalanced in terms of Ca and O. In order to balance this equation a third phase must be added to the right hand side to account for the missing CaO. In other words it is impossible to form nonstoichiometric anorthite of the formula $\text{An}_{x}\text{Qz}_{1-x}$ simply by the removal of corundum, as suggested by Goldsmith (1980).

The composition of the non-stoichiometric anorthite reported by Goldsmith (1980) for his subsolidus run number An17 is also of interest. The weight percent analyses may be rewritten in molecular proportions as:

$$\text{Ca}_{0.23}\text{Al}_{0.37}\text{Si}_{0.40}O_{1.585}.$$ 

This formula indicates not only an excess of Si over Al, but also an excess of Ca over both Al/2 and Si/2, apparently indicating solid solution between anorthite and CaO. The solid solution of CaO into
anorthite requires the introduction of non-bridging oxygens into the three dimensional framework structure of crystalline feldspar, a situation that is highly unfavorable energetically. The composition reported by Goldsmith (1980) for run number An17 is probably an integrated analyses of two phases, non-stoichiometric An and a CaO-rich phase, and not the analyses of non-stoichiometric anorthite alone. Crystallographic arguments aside, the removal of corundum alone from stoichiometric anorthite should result in a feldspar that has a Si/Ca ratio of 2.0, as in stoichiometric anorthite, and therefore cannot produce the feldspar composition reported by Goldsmith (1980) for his run number An17. The analyses of the feldspar from Goldsmith's super-solidus run number An16a is indeed that of a non-stoichiometric anorthite of the formula An\(_{x}\)Qz\(_{1-x}\)

Goldsmith (1980) also observed that corundum exsolved from An95 at high pressure. Sturt (1970) has described the exsolution of corundum from intermediate plagioclase in a nepheline syenite, and from a perthitic intergrowth in a nepheline-free syenite. Lindsley (1968) has shown that crystalline plagioclases from about An10 to An100 melt incongruently to plagioclase plus corundum plus liquid at high pressures. Sturt (1970) suggests that prior to exsolution a single phase that was a solid solution of plagioclase and corundum existed. This hypothesis suffers from the same problem as does the solid solution of anorthite and CaO: solid solution between plagioclase and corundum requires the introduction of non-bridging oxygens into the feldspar structure, which seems impossible on the
basis of crystal-chemical arguments. Ito (1976) noted that, although he was able to grow siliceous non-stoichiometric anorthite from high temperature solutions, he was unable to grow anorthite with excess alumina. Ito (1976) also stated that the presence of corundum along with anorthite in his runs was a good indication that the anorthite was stoichiometric.

The model proposed by Sturt (1970) for the exsolution of corundum from a solid solution of corundum and plagioclase may be tested with a Roozeboom type five binary phase diagram, as shown in Figure 2. The maximum amount of solid solution of component B in A occurs at the eutectic temperature, and the amount of component B dissolved in the A-rich crystalline solution must be less than that of the eutectic liquid.

The Ab-Cor and An-Cor eutectics occur at 1.5 and 4.0 weight percent corundum respectively. One atmosphere liquidus regions in the system An-Ab-Cor, inferred from the limiting binary systems, are shown in Figure 3. Also shown in Figures 4, 5, and 6 are the liquidus fields of this system at 10, 20, and 30 kilobars, inferred from the high pressure studies of Lindsley (1968) along the plagioclase join. The migration of the plagioclase corundum cotectic towards the plagioclase join, and the actual occurrence of corundum on the liquidus of more than ninety percent of that join at high pressure, indicates a decrease of maximum thermodynamically possible corundum solubility in plagioclase to zero with increasing pressure.
Figure 2: Roozeboom type 5 binary phase diagram.
Figure 3: Liquidus fields in the system An-Ab-Cor: 1 atm.
corundum

1 atm

Ab

plagioclase

An

Cor
Figure 4: Liquidus fields in the system An-Ab-Cor: 10 kb.
Cor

Corundum

10 kbars

Ab

plagioclase

An
Figure 5: Liquidus fields in the system An-Ab-Cor: 20 kb.
Figure 6: Liquidus fields in the system An-Ab-Cor: 30 kb.
Cor

corundum

Ab plagioclase

30 kbar

An
The volume of corundum exsolved from the plagioclase estimated from Figure 7, taken from Sturt (1970), is 9 percent. Using a density of corundum of 4.0 gm/cc (Robie et al, 1966), and of intermediate plagioclase of 2.7 gm/cc (Day and Allen, 1905), the weight percent of corundum in this corundum-plagioclase intergrowth is about 13 percent. Therefore, the plagioclase-corundum intergrowth described by Sturt (1970) cannot be the product of exsolution of corundum from a plagioclase-corundum solid solution.

However, the petrographic evidence reported by Sturt (1970) indicate that corundum has exsolved from the host plagioclase. As discussed above Goldsmith (1980) has demonstrated that corundum exsolves from An100 and An95 at high pressure. The exsolution of corundum from plagioclase, however, requires the simultaneous exsolution of another phase to remove those octahedral cations that charge balanced the exsolved Al into the three dimensional tetrahedral plagioclase framework prior to exsolution. Silica may also be removed during exsolution, or may remain in the form of siliceous non-stoichiometric plagioclase. The nature, composition, and present location of the phase containing the exsolved octahedral cations is unknown.

It was suggested above that the saturation of anorthite with corundum observed by Goldsmith (1980) occurred when anorthite attained complete tetrahedral order at high pressure. Lindsley's (1968) observations indicate that for over ninety percent of the An-Ab join crystalline plagioclase will become saturated with
Figure 7: Plagioclase-corundum intergrowth in Ne-syenite.
corundum at high pressure. This may also be due to increased
tetrahedral order in plagioclase with increased pressure. It is
well known that plagioclase feldspars become increasingly ordered
with decreasing temperatures at one atmosphere. Increased pressure
should also favor increased order in plagioclase.

Plagioclase may become saturated with corundum at those
pressures at which it attains complete tetrahedral order. The
observations of Lindsley (1968), which indicate that the pressure at
which plagioclase breaks down to corundum plus liquid increases with
increasing albite content are consistent with the fact that the
degree of tetrahedral disorder increases with increasing albite
content at one atmosphere pressure and high temperatures. The
observations of Sturt (1970) in light of those of Lindsley (1968)
suggests that the expansion of Goldsmith’s (1980) experiments to
investigate the subsolidus behavior of albitic plagioclase should
demonstrate the exsolution of corundum from these as well as from
anorthite.

What are the effects of non-stoichiometry on eq.(1)? Longhi
and Hays (1979) redetermined the liquidus and determined the solidus
of the join An-Qz, demonstrating extensive solid solution of silica
in An along this join. The equilibration temperatures that they
determined can be calculated with eq. (1) by substituting one for
the term (4AF+AN+2ANAF(AN-AF)). This indicates that there is only
one site available for Al occupancy per Al in non-stoichiometric
anorthite, i.e. the distribution of Al and Si atoms among the
tetrahedral sites of non-stoichiometric anorthite is completely ordered.

There are two hypotheses that account for the structural state of excess silica in non-stoichiometric plagioclase. The first, proposed by Ito (1976), Longhi and Hays (1979), and Beatty and Albee (1980), is solid solution of anorthite with the coesite polymorph of silica. Zoltai and Buerger (1959) and Megaw (1970) have shown that coesite has the feldspar structure. The second hypothesis, originally proposed by Schwantke (1909), is solid solution between anorthite and Schwantke's component, $\text{Ca}_{1/2}\text{AlSi}_{3}\text{O}_{8}$. The present analyses indicates that there is complete tetrahedral order in non-stoichiometric anorthites which contain no Na, K, Fe, or Mg.

A completely ordered distribution of Al and Si in non-stoichiometric anorthite is consistent with either of the above hypothesis. For instance, if excess silica dissolves in anorthite as a coesite molecule then there is no reason for the anorthite component to become disordered. Alternatively, if excess silica forms Schwantke's component then this component may have a completely ordered distribution of tetrahedral cations, such as is observed in low albite.

The gamma angle of non-stoichiometric anorthites determined by Bruno and Fachinelli (1974b) are indistinguishable from those of low structural state intermediate plagioclase with the same Si to Al ratios. The gamma angles of non-stoichiometric anorthites determined by Ito (1976) and by Longhi (1976) are in good agreement.
with those determined by Bruno and Fachinelli (1974b). On the basis of this crystallographic similarity Bruno and Fachinelli (1974a) suggested that the distribution of Si and Al among the tetrahedral sites of non-stoichiometric anorthites is the same as that in low intermediate plagioclase with the same Si to Al ratio.

Of specific interest in this regard is the fact that the albite and sanidine liquidus temperatures in the systems Ab-Qz, Ab-Or-Qz, Ab-Sd-Qz, and Or-Kt-Qz are very accurately calculated by assuming that the alkali feldspar is stoichiometric. This implies that there is no solid solution between silica and alkali feldspar. This is an indication that excess silica in plagioclase is present as Schwantke’s component and not as a coesite component. If excess silica in feldspars was present in a coesite molecule, it would affect the calculation of alkali feldspar temperatures in quartz normative systems.

This discussion permits a good demonstration of the effects of analytical errors on temperatures calculated with eq. (1). The Al/Ca ratio of the anorthites analyzed by Longhi and Hays (1979) is 2.0. The Al/Ca ratio in the starting compositions of all their experiments along the join An-Qz is 2.0. Therefore the Al/Ca ratio of all residual liquids produced along the An-Qz join also should be 2.0, as they are for their runs 4/1-4, 1758(K), and 3/2-3, 1695(K). However, the residual liquid composition reported for run 55B-3, 1647(K), has an Al/Ca ratio of 1.8, clearly indicating either an analytical error or a typographical misprint.
The calculated temperature using the reported composition is 1598(K), 49 degrees below the experimental temperature. However, recalculating this analysis by setting Al equal to 2Ca, and normalizing so that the cation sum is again one results in a composition in very good agreement with the liquidus composition determined by Schairer and Bowen (1947) for this temperature. An equilibration temperature of 1642 (K), only five degrees below the experimental temperature, is calculated using this composition. In general, it is impossible to note or correct such errors in more complex systems.

AF and AN are calculated solely on the basis of the Si to Al ratio in the feldspar. Tetrahedral and octahedral substitutions of Fe, Mg, Ti vacancies, and others do not enter the calculation. Calculated temperatures will be incorrect if an inappropriate method is used to calculate AN and AF.
CHAPTER 4
DISCUSSION OF THE EXPRESSION "12(X^3)(1-X)"

In eq. (1) there are two factors of the form 12(X^3)(1-X). This expression can be rewritten as (3)(4)(X^3)(1-X). The term 4(X^3)(1-X) is the binomial distribution for calculating the probability of succeeding in 3 out of 4 attempts if the probability of succeeding in a single attempt is X.

The binomial distribution is only valid when applied to a random ensemble. I assume that the populations of cations to which the binomial distribution is applied in eq. (1) are random ensembles in oxygen frameworks. This assumption is discussed below. Further I assume that Al_x and (b/z) represent the probability of an Al cation, that has the potential of forming a corundum melt species, occupying any cation site in the respective population. Subsequently 4(Al_x^3)(1-Al_x) and 4((b/z)^3)(1-(b/z)) equal the probabilities that any 3 out of 4 sites will be simultaneously occupied by these Al atoms in each population. The additional factor of 3 equals the number of Al atoms present in each 3 out of 4 arrangement. Therefore, the terms 12(Al_x^3)(1-Al_x) and \(12((b/z)^3)(1-(b/z))\) equal the number of Al atoms in these arrangements, if each arrangement is counted separately. Those Al atoms that are simultaneously in multiple 3 out of 4 arrangements are, therefore, counted more than once.
The oxygen atoms in crystalline corundum define a slightly distorted hexagonal close pack arrangement at room temperature (Pauling and Hendricks, 1925), which becomes more regular at higher temperatures (Ishizawa et al, 1980). Al atoms occupy two-thirds of the octahedral voids that occur between the oxygen atoms in crystalline corundum (Lindsley, 1976). On the basis of the X-radial diffraction pattern of molten corundum at 2373 (K) Nukui et al (1976) inferred that Al is octahedrally coordinated in molten corundum, and that the short range structure of molten corundum is similar to that of crystalline corundum.

Figure 8 is an idealized sketch of the cation and vacancy arrangement in the (0001) plane of crystalline corundum. In the figure this arrangement has been subdivided into parallelepipeds, in which 3 out of 4 vertices are occupied by Al atoms, and rows of vacancies. This figure is presented to suggest that 3 Al atoms in 4 adjacent sites is a physically significant arrangement in crystalline corundum. The significance of this arrangement in eq. (1) may be that these are the units which attach or detach as corundum crystallizes or melts.
Figure 8: Cation and vacancy arrangement in corundum (0001) plane.
CORUNDUM
(0001) plane

▪ Al
▪ vacancy
CHAPTER 5
DISCUSSION OF THE TERM "12(Al\textsuperscript{3}_{x})(1-Al_{x})" 

It was assumed above that the term 12(Al\textsuperscript{3}_{x})(1-Al_{x}) applies to some random ensemble of cations in an oxygen framework, in which the probability of an Al atom occupying any given cation site equals the Al cation mole fraction. The phase whose composition is used in calculating this term is the crystalline feldspar. Crystalline feldspar is not a random collection of cations dispersed in an oxygen framework. There may, however, exist a volume within systems saturated with both feldspar and liquid that has the composition of the equilibrium feldspar, but that lacks long range order.

Anomalies in the measured thermodynamic and physical properties of crystalline solids at temperatures approaching their melting points have been interpreted as indicating disordering, and possibly melting, of the crystalline surface at temperatures below its melting point (Ubbelohde, 1978). Ubbelohde (1978) calls this phenomena "homophase premelting" in order to distinguish it from simple freezing point depression due to the presence of impurities, i.e. "heterophase premelting". Of particular interest are the proton magnetic resonance measurements of Bell et al (1971) which indicate the existence of a "liquid-like" component on the surface of poly-crystalline ice twelve degrees below its freezing point. Bell et al (1971) demonstrated that the concentration of impurities in their ice was too low for this to be heterophase premelting.
Similarly, the Gibbs-Volmer theories of crystallization, summarized in Mullin (1972), call for an absorbed layer around a growing crystal in which "units of the crystallising substance are not immediately integrated into the lattice, but merely lose one degree of freedom and are free to migrate over the crystal surface (surface diffusion). There will therefore be a loosely absorbed layer of integrating units at the interface, and a dynamic equilibria is established between this layer and the bulk solution." (Mullin, 1972, p.154). The crystallization theory of Burton, Cabrera, and Frank (1951) hypothesizes the disordering of the surface of crystals via the process of "surface melting" at temperatures as low as half the bulk melting point. The calculation of the change in free energy of the surface of a growing crystal in the treatment of Jackson (1967) involves the summation of four terms, one of which is the increase of entropy of the crystal due to the positional disorder of the atoms added to the surface of a growing crystal.

Recent theoretical and experimental advances, summarized in Brinkman et al (1982), indicate that two-dimensional solids melt via an intermediate phase, termed the "hexatic phase". Brinkman et al (1982) note that the structure of the surfaces of three-dimensional crystals are significantly different from the bulk of the crystal, and that crystal surfaces are, in fact, two-dimensional solids. Unlike the melting of three-dimensional solids, which is a first order transition in which thermodynamic properties vary
discontinuously, melting of a two-dimensional solid is a higher order
transition in which thermodynamic properties vary continuously from
one phase to another. The observation of continuous anomalies in
thermodynamic and physical properties of crystals prior to melting
(Ubbelohde, 1978) and the hypothesis that the surface of solids may
melt at temperature as low as one half of their absolute melting
temperatures (Burton, Cabrera, and Frank, 1951), in light of the
discussion of Brinkman et al (1982), is consistent with the
suggestion that the surfaces of three-dimensional solids may be
two-dimensional solids that melt continuously via an intermediate
phase. Along somewhat different, but possibly related lines
nucleation and crystallization in many ceramic systems is aided by
the formation of metastable immiscible liquids (Roeder, 1979).

The thermodynamic model of the interface between two phases of
Guggenheim (1940) postulates the existence of an "interphase" of
definite volume. The thermodynamic and physical properties of this
interphase vary continuously in going from one phase to the other,
but are constant in the direction that parallels the surfaces of the
two phases.

These observations and hypotheses suggest that melting and
crystallization occur via the formation of a disordered volume of
the crystal's composition. This volume may be similar to the
absorbed layer in the Gibbs-Volmer hypothesis which Mullin (1972)
refers to as the "third phase". Since crystal liquid equilibria is
a dynamic state in which the rates of crystallization and fusion are
equal, it is reasonable to extrapolate the above kinetic ideas to equilibrium conditions. The form of the term $12(Al_x^3)(1-Al_x)$ suggests that a disordered volume of crystalline feldspar composition exists at the surface of the crystalline feldspar. 

Raman spectroscopic (Sharma et al, 1982) and X-radial diffraction (Taylor and Brown, 1979a) investigations of the structures of feldspar glass indicate that the tetrahedral cations are arranged in four and higher member rings in An glass and in six and higher member rings in Ab glass. Sharma et al (1982) have shown that the proportion of six to four member rings increases continuously with Ab content in intermediate feldspar glass. The basic "building block" of feldspars is the four member tetrahedral ring (Ribbe, 1975). In this regard the structure of An glass is similar to that of An crystal. However, the structures of Ab glass and crystal are not similar. If the structure of Ab liquid is similar to that of Ab glass then a structural rearrangement from six to four member rings is required for Ab to crystallize congruently. This structural rearrangement may occur in the surface melt of feldspar composition at the feldspar liquid interface. This idea will be discussed further below.

Feldspar crystallization may be preceded by the segregation of a "melt" of feldspar composition from the bulk liquid. Similarly, the fusion of feldspar may be preceded by the formation of a disordered surface "melt" surrounding the crystal. Finally feldspar in equilibrium with a liquid may be surrounded by a surface "melt"
of the equilibrium feldspar's composition. The structure of this feldspar surface "melt" may be significantly different from the structure of bulk feldspar liquid of the same composition at one atmosphere.
CHAPTER 6

DISCUSSION OF THE TERM "12((b/z)³)(1-(b/z))"

The factor $12((b/z)^3)(1-(b/z))$ is calculated from the composition of the bulk liquid. The term $b$ is the mole fraction of Al structurally capable of entering a corundum melt species. The term $z$ appears to equal the sum of the network associated cations in the melt, as will be discussed below, and may represent the composition of the bulk liquid at the feldspar-liquid interface.

The expression $12((b/z)^3)(1-(b/z))$ is only valid when applied to a melt in which the probability of an Al cation occupying a given site is $(b/z)$. Our present understanding of the structure of silicate melts indicates that they are not random ensembles of cations in oxygen frameworks. Spectroscopic, physical, and thermodynamic studies indicate a significant degree of short range order, including alumina-alkali complexing, in silicate melts (Hess, 1980, Bottinga et al, 1981). The term $12((b/z)^3)(1-(b/z))$, therefore, is not obviously applicable to the bulk melt.
CHAPTER 7
DISCUSSION OF THE TERMS "b" AND "z"

The variation of the terms b and z in simple systems is examined in this chapter. Interpretations of the physical significance of the expressions used to calculate b and z are based on the physical properties of these simple systems. Expressions derived from simple systems are used to calculate b and z in complex systems. Figures comparing calculated versus experimentally determined equilibration temperatures are included for each system discussed.

Normative quantities are used in igneous petrology to determine the hypothetical mineral assemblage of the coarse-grained equivalent of a volcanic rock (Holmes, 1921). In this study, however, normative quantities are used to delineate the compositional end members of feldspar saturated liquids. As such, normative calculations are useful both in mapping out temperature composition relationships, and in relating complex systems to simpler ones. Some of the terms used to calculate b and z appear to be modifiers of the normative calculation that introduce liquid components that have no crystalline counterparts. Other terms allow for the compositional variation of existing normative components. As discussed above, mole fraction normative components are used in this study, with the cation sum of each end member component set to unity.
An-Ab and An-Lct

In the systems An-Ab and An-Lct:

\[ b = Al_1 \]
\[ z = 1. \]

The term \( z \) is the sum of all the cations in the liquid, i.e. \( z \) equals one, these include network formers, i.e. Si and Al, and Al charge balancers, i.e. Ca, Na, and K.

An-Di-Wo

In the system An-Di-Wo:

\[ b = Al_1 \]
\[ z = 3Al_1/2 + Si_1. \]

The term \( z \) is the sum of the network forming cations, \( Al_1 + Si_1 \), and the divalent cations which charge balance Al into the alumino-silicate network, \( Al_1/2 \). In the An-Ab, An-Lct, and An-Di-Wo systems \( z \) is the sum of all the network associated cations, both the network formers and the Al charge balancers.
Figure 9: T experimental vs calculated; system An-Ab.
The graph shows a linear relationship between T(K) Experimental and T(K) Calculated for the an·ab phase. The data points align closely with the straight line, indicating a strong correlation between the two measurements.
Figure 10: T experimental vs calculated; system An-Lct.
Figure 11: T experimental vs calculated; system An-Di-Wo.
An-Mgt

In the system An-Mgt:

\[ b = 3Al_1 \]
\[ z = 3Al_1/2 + Si_1 + Mg_1 = 1.0. \]

In this system \( z \) is the sum of all the cations in the liquid. In
the system An-Ab, An-Lct, and An-Di-Wo \( z \) is the sum of all the
network associated cations. This suggests that the Mgt melt
component is also associated with the melt network. \( \text{Fe}^{3+} \) tetrahedra
are linked with Si into infinite networks in iron-leucite and
iron-orthoclase (Faust, 1936) and acmite glass (Mysen et al, 1980).
In these three substances \( \text{Fe}^{3+} \) tetrahedra are charge balanced into
the network by alkali cations. Dickenson and Hess (1981)
experimentally demonstrated that \( \text{Fe}^{2+} \) can also charge balance \( \text{Fe}^{2+} \) into the melt network. The addition of Mgt to \( z \) suggests that each
\( \text{Fe}^{2+} \) cation charge balances two \( \text{Fe}^{3+} \) cations into the melt network
in this system.

An-Ak-Di

In the system An-Ak-Di:

\[ b = 3Al_1 \]
\[ z = 3Al_1/2 + Si_1 + Ak_5. \]

In crystalline akermanite Mg tetrahedra link Si dimers into infinite
Figure 12: T experimental vs calculated; system An-Mgt.
Figure 13: T experimental vs calculated; system An-Ak-Di.
has shown, however, that Mg is not charge balanced into the crystalline akermanite network. Therefore, although Mg is topologically associated with the Si network in crystalline akermanite, the Mg-O-Si bonds are non-bridging in nature, i.e. they are more ionic than covalent. The number of network associated cations in crystalline akermanite is, therefore, Si+Mg. The mole fraction of Mg in akermanite is one-fifth. The addition of Ak/5 to z indicates that the Mg cations of the akermanite component are topologically associated with the melt network, as they are in the crystal. Sharma and Yoder (1979) studied the structure of akermanite glass with Raman spectroscopy and concluded that the marked similarity between the crystal and glass spectrums indicates that most of the glass has a structure similar to the crystal.

An-Fo-En-Wu-Fs and Ab-Fa

In the systems An-Fo-En-Wu-Fs and Ab-Fa:

\[ b = \text{Al}_1 \]

\[ z = \frac{3}{2} \text{Al}_1 + \frac{1}{2} \text{Si}_1 + \frac{1}{2} \text{Na}_1 + x \]

\[ x = (\text{Wu} + \frac{2}{3} \text{Fa} + \frac{2}{3} \text{Fo} + \frac{4}{3} \text{En} + \frac{4}{3} \text{Fs}) \text{ or } \text{Al}_1, \text{ whichever is less.} \]

The quantity \( \left( \frac{3}{2} \text{Al}_1 + \frac{1}{2} \text{Si}_1 + \frac{1}{2} \text{Na}_1 \right) \) is the sum of the network forming cations and Al charge balancers in this system.

Since the Si in the normative olivine and orthopyroxene components is added to z independently of the term x, the term x must equal a quantity of Fe and Mg cations. The terms Wu, 2Fo/3,
Figure 14: T experimental vs calculated; system An-Fo-En-Wu-Fs.
Figure 15: T experimental vs calculated; system Ab-Fa.
and $2\text{Fe}/3$ equal all the Fe and Mg in the normative wustite and olivine components. The terms $\text{En}/4$ and $\text{Fs}/4$ equal half of the Fe and Mg in the normative orthopyroxene components.

In the An-Ab, An-Lct, An-Di-Wo, An-Mgt, and An-Ak-Di systems $z$ is the sum of all the network associated cations. This suggests that the Mg and Fe added to $z$, in terms of fractions of the normative oxide, olivine, and orthopyroxene components, are also associated with the melt network.

Mg and Fe$^{2+}$ associate with crystalline alumino-silicate networks in two ways. As discussed above, Mg tetrahedra are topologically associated with, but not charge balanced into, the crystalline akermanite network. Mg and Fe$^{2+}$ are, however, charge balanced into the network as tetrahedral cations in feldspars of the formula $\text{CaMgSi}_3\text{O}_8$ and $\text{CaFeSi}_3\text{O}_8$, synthesized by Sclar and Stead (1981) and Sclar and Kastelic (1979), respectively. Bryan (1974), Longhi et al (1976), and Murphy (1977) demonstrated appreciable solid solution of these components in plagioclase.

The presence of the spinel field on the liquidus of the An-Fo-En-Wu-Fs system suggests that Mg and Fe topologically associate with the network as non-charge balanced species, and, as in akermanite, introduce non-bridging oxygens into the alumino-silicate network. The introduction of non-bridging oxygens into the melt network should promote the nucleation and crystallization of spinel. The Fe$^{2+}$ and Mg addition to $z$ cannot exceed $\text{Al}_1$. This suggests that these cations occupy sites that are
specifically associated with Al. The specific association of Fe and Mg with Al should also promote spinel nucleation and crystallization in this system. The specific association with Al makes this Mg and Fe network association distinctly different from that in akermanite.

If Mg and Fe enter the network as charge balanced species in this system, then half of the network associated Mg and Fe must charge balance the other half into the network. For instance, a melt species such as MgMgSi$_3$O$_9$ may be produced. This would mean that there would be no non-bridging oxygens in liquids in the system An-Fo-Fa, with Al greater than Fe plus Mg, a situation that seems hardly likely to stabilize spinel on the An-Fo liquidus.

In the systems An-Fo-En-Wu-Fs and Ab-Fa, z is best explained as the sum of all the network formers, plus all the Al charge balancers, plus all the Mg and Fe$^{2+}$ that is topologically associated with, but not charge balanced into, the alumino-silicate network.

An-Di-Fo-En and An-Ak-Fo

In the systems An-Di-Fo-En and An-Ak-Fo:

$$b=\text{Al}$$
$$z=3\text{Al}+2\text{Si}+x$$
$$x=a \text{ or } \text{Al}, \text{ whichever is less}$$
$$a=(2\text{Fo}/3+\text{En}/4-\text{Di}/8-\text{Ak}/10) \text{ or } 0, \text{ whichever is greater.}$$

The quantities Di/8 and Ak/10 equal half of the Mg in excess of the Fo and En components. The reduction of the Mg addition observed in
Figure 16: T experimental vs calculated; system An-Di-Fo-En.
Figure 17: T experimental vs calculated; system An-Ak-Fo.
the system An-Fo-En suggests the formation of a melt species that blocks the topologic association of Mg with the melt network.

Volcanic augites invariably have Ca less than Mg plus Fe (Carmichael et al, 1974). The same is true of diopsides crystallized in the system An-Ab-Di by Kushiro (1973), Murphy (1977), and Lindstrom (1976). Biggar and O'Hara (1969) and Kushiro (1973) experimentally demonstrated that diopside melts incongruently to a Di-En solid solution and a liquid on the join Wo-Di. Biggar and O'Hara (1969) found that stoichiometric Di is unstable at temperatures above 1623 (K), and possibly lower. The Di liquidus occurs at 1665 (K). Pure Di therefore has a melting interval of at least 42 degrees. Similarly, Biggar and O'Hara (1969) demonstrated that akermanite melts incongruently to a Mg rich melilite and a Ca rich liquid.

The subtraction of Di/8 and Ak/10 from (2Fo/3+En/4) may be a modification of the normative calculation that reflects the formation of sub-calcic augite and melilite melt species.

Ab-Sd

In the system Ab-Sd:

\[ b = A_{1} \]
\[ z = 2A_{1} + Si_{1} + Sd/2 = 1.0. \]

The quantity \((2A_{1} + Si_{1})\) is the sum of the network formers plus Al charge balancers in this system.
Figure 18: T experimental vs calculated; system Ab-Sd.
The Si in the Sd component is added to z independently of the Sd/2 addition. The Sd/2 addition therefore represents the addition of the Na in the Sd component to z. Crystalline sodium disilicate is a sheet silicate in which silica tetrahedra form six member rings that are joined to form infinite sheets. The sheets are linked via ionic bonds with Na atoms that occupy sites between the sheets (Brawer and White, 1975). The Na cations in sodium disilicate, therefore, play a structurally similar role to Mg in akermanite.

Brawer and White (1975) studied the structure of sodium disilicate crystal and glass with Raman spectroscopy. They state "that the similarity of the disilicate crystal and glass spectra is consistent with a preponderance of disordered Si$_2$O$_5$ vibrating units with one non-bridging oxygen per silicon." (Brawer and White, 1975, page 2426), and further that: "The disilicate (glass), since each tetrahedra has only one non-bridging oxygen, is probably constructed in the form of convoluted sheets, i.e structures which are topologically similar to sheets but which may be greatly distorted." (Brawer and White, 1975, page 2427). Sharma et al (1978) studied the structure of both sodium disilicate glass and liquid with Raman spectroscopy, and concluded that the structure of the sodium disilicate glass and liquid are similar. Therefore the structure of sodium disilicate melt is similar to that of sodium disilicate crystal. The main structural difference between the crystal and liquid phases appears to be the random orientation and distortion of the Si$_2$O$_5$ sheets in the liquid.
The Sd/2 addition to z suggests that the Na in the Sd component associates with the melt network. It is likely that this addition reflects the formation of Na-Si complexes that link the contorted Si$_2$O$_5$ sheets in the melt. The Sd/2 addition to z differs from that of (Wu+2Fo/3+2Fa/3+En/4+Fs/4) in that it can exceed Al$_1$. In fact, at the Sd-Ab eutectic Sd/2 equals 0.32 while Al$_1$ only equals 0.073. This indicates that the Na in the Sd component does not form Na-Al complexes or associations.

In the system An-Wh:

\[
b = (\text{Al}_1 - (\text{Al}_1)(\text{P}_1))
\]
\[
z = (3\text{Al}_1/2 + \text{Si}_1 + \text{P}_1/2).
\]

Phosphorus is believed to be a network former in alumino-silicate liquids (Hess, 1979, Ryerson and Hess, 1980, Mysen et al 1981). This behavior is consistent with the role of P in crystalline berline, AlPO$_4$, which has the quartz structure (Berry and Mason, 1959), and alumino-phosphate variants of feldspar synthesized by Simpson (1977). As in berline, quintavalent P may enter the network in melts by charge balancing an equal number of trivalent Al. P then plays both the role of a network former and an Al charge balancer. The addition of P/2 to z is equivalent to the addition of P to z, along with the subtraction of P/2 divalent Al charge balancers, that are no longer required to charge balance Al.
Figure 19:  T experimental vs calculated; system An-Wh.
The subtraction of \((\text{Al}_1)(\text{P}_1)\) from \(\text{Al}_1\) in \(b\) suggests that a berlinite-like species is formed through the following reaction:

\[
\text{AlO}_{1.5} + \text{PO}_{2.5} = \text{AlPO}_4.
\]

The equilibrium constant for this reaction is:

\[
K = \frac{[\text{AlPO}_4]}{[\text{AlO}_{1.5}][\text{PO}_{2.5}]}.
\]

The quantity \((\text{Al}_1)(\text{P}_1)\) may, therefore, be the berlinite activity in the melt.

An-Sp-Wo

In the systems An-Sp-Wo:

\[
b = \text{Al}_1 - 2(\text{Al}_1)(\text{Ti}_1)
\]

\[
z = 3\text{Al}_1/2 + \text{Si}_1.
\]

The subtraction of \(2(\text{Al}_1)(\text{Ti}_1)\) from \(\text{Al}_1\) in \(b\) is similar in form to the subtraction of \((\text{Al}_1)(\text{P}_1)\) in the An-Wh system. The subtraction suggests the formation of a tialite, \(\text{Al}_2\text{TiO}_5\), melt species through the following reaction:

\[
2\text{AlO}_{1.5} + \text{TiO}_2 = \text{Al}_2\text{TiO}_5
\]

The equilibrium constant for this reaction is:

\[
K = \frac{[\text{Al}_2\text{TiO}_5]}{[\text{AlO}_{1.5}][\text{TiO}_2]}.
\]

The term \((\text{Al}_1)(\text{Ti}_1)\) may, therefore, represent the activity of tialite in the melt. Two times this quantity equals the Al in this melt species. This suggests that Al in the form of a tialite melt species is unable to be part of a corundum melt species.
Figure 20: T experimental vs calculated; system An-Sp-Wo.
An-Il-Di

In the systems An-Il and An-Il-Di:

\[
b = \text{Al}_1 - 2(\text{Al}_1^2)(\text{Ti}_1)
\]

\[
z = \frac{3\text{Al}_1}{2} + \text{Si}_1 + x
\]

\[
x = \text{Il}_1 \text{ or } \text{Al}_1, \text{ whichever is less.}
\]

The same subtraction from b observed in the system An-Sp-Wo is observed in the system An-Il-Di, again suggesting the formation of a tiallite melt species. In these systems, however, the Fe and Ti of the Il component, up to the limit of Al$_1$, are added to z. The fact that this addition cannot exceed Al$_1$ indicates that it is similar to the \((\text{Wu}+2\text{Fo}/3+2\text{Fa}/3+\text{En}/4+\text{Fs}/4)\) addition. This suggests that the physical processes responsible for both additions to z are the same.

According to arguments presented above, therefore, the addition of Il to z is best explained as the topological association of the Il component with the melt network.

A major difference between the Il addition and the \((2\text{Fo}/3+\text{En}/4)\) addition is the insensitivity of the former to the addition of a Di component. The addition of Di to the system An-Il does not result in the diminution of the Il addition to z. This suggests that the association of Fe and Ti in an Il component is favored over the formation of a sub-calcic augite melt species.
Figure 21: T experimental vs calculated; system An-Il-Di.
An-Qz and Ab-Qz

In the systems An-Qz and Ab-Qz:

\[ b = Al_1 \]
\[ z = 1 - 2Qz/3. \]

The subtraction of two thirds of the normative quartz component from \( z \) suggests nascent immiscibility in liquids with normative quartz. In other words, a portion of the liquid, equal to \( 2Qz/3 \), may form a silicate network which totally excludes Al.

There is a significant amount of independent evidence that indicates the existence of sub-phase partitioning of Si between Si rich and Si poor melt species. Greig (1927) determined the extent of the high temperature liquid immiscibility fields in the systems MO-SiO\(_2\), where M is Mg, Ca, and Sr. Kracek (1930) suggested that flat S-shaped curves in the systems BaO-SiO\(_2\), and R\(_2\)O-SiO\(_2\), where R is Li, or Na, indicate metastable immiscibility in these systems. This has subsequently been demonstrated by glass annealing studies (Haller et al, 1974, Charles, 1973, Seward et al, 1968).

Roedder (1951) demonstrated that a low temperature immiscibility field exists in the system Or-Fa-Qz. Naslund (1976, 1977) extended these observations, demonstrating low temperature immiscibility in simple systems containing Na and Ca as well as K for a large range of oxygen fugacities. Several other studies, summarized in Roedder (1979), have demonstrated stable low temperature immiscibility in natural systems. Holgate (1954) noted
Figure 22: T experimental vs calculated; system An-Qz.
The diagram shows a linear relationship between \( T(K) \) calculated and \( T(K) \) experimental. The data points are marked with squares. The labels 'an' and 'qz' are included in the graph.
Figure 23: T experimental vs calculated; system Ab-Qz.
that liquidi in the systems Ab-Fa-Qz and Di-Or-Qz were very flat and
proposed that this was indicative of metastable immiscibility in
these systems. Irvine (1975a) suggested that the high temperature
immiscible fields between silica and mafic phases are reflected in
the orientation of the plagioclase-mafic phase cotectics in ternary
and more complicated systems noting that these cotectics curve away
from the fields of immiscibility between SiO₂ and the mafic phase.
Irvine (1975a) calls this the "silica immiscibility effect". Irvine
(1976) experimentally determined the extent of metastable liquid
immiscibility in the system Fo-Fa-An-Or-Qz.

The effects of sub-phase separation are also apparent on the
binary join SiO₂-Al₂O₃. MacDowell and Beall (1969) experimentally
demonstrated a metastable miscibility gap from 7 to 55 mole percent
Al₂O₃ in glasses along this join. Thermodynamic calculations of
Risbud and Pask (1977) indicate that the extremely flat liquidus
segment on the join SiO₂-Al₂O₃ (Bowen and Greig 1924, Aramki and Roy
1962) is due to metastable liquid immiscibility which extends from
11 to 49 mole percent Al₂O₃ at 1373 K. The results of the X-radial
diffraction study of Morikawa et al (1982) on the structure of
glasses along this join indicates the segregation of Si into Si rich
and Al rich species.

In the Ab-Qz and An-Qz systems z equals all the network
formers, plus the Al charge balancers minus the Si in Al excluding
melt species.
In the system Ab-Ne-Sd:

\[ b = \left( \frac{Al_1}{3} - \frac{Ne}{3} \right) \]

\[ z = 2Al_1 + Si_1 + Sd / 2 - 2Ne / 3 = 1 - 2Ne / 3. \]

In the previous section the reduction of \( z \) by \( 2Qz / 3 \) was accounted for by the segregation of \( Si \) into \( Al \) excluding melt species. The subtraction of \( Ne / 3 \) from \( Al_1 \) in \( b \), and the subtraction of \( 2Ne / 3 \) from \( z \), can similarly be explained as the result of the formation of a NaAlO\(_2\) melt network in Ne normative melts. Barth (1935) demonstrated that crystalline NaAlO\(_2\) is a structural derivative of cristobalite. Similar behavior between NaAlO\(_2\) and SiO\(_2\) melt components is consistent with the structural similarity of their crystalline polymorphs. The subtraction of \( Ne / 3 \) from \( Al_1 \) in the term \( b \) suggests that all the \( Al \) in the Ne component is contained in a NaAlO\(_2\) species. The same conclusion can be reached from the subtraction of \( 2Ne / 3 \) from \( z \). That subtraction indicates that only the \( Si \) in the Ne component is associating with the alumino-silicate network, and that the Na and Al in the Ne component form an independent sodium-aluminate network. The proposed existence of a NaAlO\(_2\) melt species in Ne normative melts is consistent with the continuous increase in liquidus temperatures along the SiO\(_2\) -NaAlO\(_2\) join from the Ab-Ne eutectic to NaAlO\(_2\) (Schairer and Bowen, 1956).
Figure 24: T experimental vs calculated; system Ab-Ne-Sd.
Ab-Ac-Sd

In the system Ab-Ac-Sd:

\[ b = Al_1 \]
\[ z = 2Al_1 + Si_1 + Sd/2. \]

In this system the Si from the Ac component is added to \( z \), but its Na and Fe\(^{3+} \) are not. This can be interpreted in two ways. First, this may be similar to the system An-Di, where the Si in the Di component is added to \( z \), but the non-network associated divalent cations are not. Second, this may be similar to the system Ab-Ne-Sd, where the Si in the Ne component is added to \( z \), but the Na and Al in the Ne component, which form an independent melt network, are not. The structure of acmite glass determined by Mysen et al (1980) indicates that the Na and Fe\(^{3+} \) cations are part of a three dimensional network. This suggests that the Na and Fe\(^{3+} \) not added to \( z \) in this system may form an independent NaFeO\(_2\) melt network.

Ab-Ne-Ac-Sd

In the system Ab-Ne-Ac-Sd:

\[ b = (Al_1 - f/3) \]
\[ f = (Ne-Ac/6) \) or 0, whichever is greater \]
\[ z = 2Al_1 + Si_1 + Sd/2 - 2f/3 \]

In this system the Ne/3 subtraction from \( Al_1 \), and the 2Ne/3 subtraction from \( z \), are reduced or eliminated by Ac/6. In a manner
Figure 25: T experimental vs calculated; system Ab-Ac-Sd.
Figure 26: T experimental vs calculated; system Ab-Ne-Ac-Sd.
similar to that proposed above for Ne, the Ac melt component may be divided into $\text{NaFeO}_2$ and $\text{SiO}_2$ components. The excess Si supplied to the alumino-silicate network by the Ac component may promote the reincorporation of the $\text{NaAlO}_2$ species into the alumino-silicate network.

"An-Ab-Di"

Murphy (1977), Kushiro (1973), Lindstrom (1976), and Drake (1972) (the last two added minor amounts of trace elements) have reported microprobe determinations of crystal and liquid composition for samples with bulk compositions in the system An-Ab-Di. Besides the formation of peralkaline liquids due to the crystallization of intermediate plagioclase along the Ab-Di join, the system is significantly non-ternary, and in fact many of the residual liquids are Ne normative. The production of Ne normative liquids in this system is the result of the solid solution of the $\text{CaMgSi}_3\text{O}_8$ component in plagioclase. For the system "An-Ab-Di":

\[
\begin{align*}
\text{b} &= (\text{Al}_1 - \text{Ne}/3) \\
\text{z} &= y - 2\text{Ne}/3 \\
y &= (3\text{Al}_1/2 + \text{Si}_1 + u) \text{ or } 1, \text{ whichever is less} \\
u &= \text{Al}_1/2 \text{ or } 5\text{Na}_1, \text{ whichever is less}
\end{align*}
\]

The major change in calculating $z$ is the term $u$. Since in the system An-Ab:

\[
z = 3\text{Al}_1/2 + \text{Si}_1 + \text{Na}_1/2
\]
Figure 27: T experimental vs calculated; system "An-Ab-Di".
The diagram shows a comparison between calculated temperatures (T(K) Calculated) and experimental temperatures (T(K) Experimental) across a range from 1400 K to 1800 K. The data points are plotted as a scatter plot, indicating a strong correlation between the calculated and experimental values.
and in the system An-Di:

\[ z = \frac{3}{2}Al_1 + Si_1 \]

we might expect that in the system An-Ab-Di that

\[ z = \frac{3}{2}Al_1 + Si_1 + \frac{1}{2}Na_1 \]

but this is not the case.

The term \( z \) in this system increases to the limit of \( (2Al_1 + Si_1) \). This suggests that in the presence of sufficient Na each Al atom is individually charge balanced, i.e. the number of charge balancing cations equals the number of Al cations, even though Al is in excess of Na. When \( z \) equals \( 2Al_1 + Si_1 \) each divalent charge balancing cation uses half of its charge to stabilize a single Al cation into the network. Comparison with the system An-Di-Wo demonstrates that this is a Na related phenomena. Many of the liquids in that system have Ca greater than Al, but \( z \) always equals \( (3Al_1 / 2 + Si_1) \).

The term \( u \) equals either \( 5Na_1 \) or \( Al_1 / 2 \), whichever is less. The magnitude of this addition suggests that each Na cation can induce 4.5 non-associated divalent cations to become network associated charge balancers. The term \( (3Al_1 / 2 + Si_1 + u) \) is limited to be less than or equal to one. When equal to one all the cations in the liquid are associated with the network.
An-Di-Qz and Ab-Sd-Qz

In the systems An-Di-Qz and Ab-Sd-Qz:

\[ b = Al_1 \]
\[ z = 3Al_1/2 + (Al_1 - 2Ca_1)/2 + Si_1 + Sd/2 - Qz/n \]
\[ n = (1.5 + 10(Di + Sd)) \text{ or } 2 \text{ whichever is less.} \]

The term \( 3Al_1/2 + (Al_1 - 2Ca_1)/2 \) equals the number of Al cations and Al charge balancers in the network.

With the addition of Di, or Sd, to the system An-Qz, or Ab-Qz, the silica subtraction drops from two thirds to one half of the normative Qz. The diminution of the Qz subtraction corresponds with the introduction of non-bridging oxygens into the melt. This suggests that the introduction of non-bridging oxygens into the melt decreases the magnitude of the sub-phase segregation of Si into Al excluding species.

Ab-Sd-Ac-Qz

In the system Ab-Sd-Ac-Qz:

\[ b = Al_1 \]
\[ z = 2Al_1 + Si_1 - Qz/n + k \]
\[ n = (1.5 + 10Sd) \text{ or } 2, \text{ whichever is less} \]
\[ k = (Sd/2 - e) \text{ or } 0, \text{ whichever is greater} \]
\[ e = Ac \text{ or } 4Qz, \text{ whichever is less.} \]
Figure 28: T experimental vs calculated; system An-Di-Qz.
\[ T(K) \text{ Experimental} \]

\[ T(K) \text{ Calculated} \]

\text{an·di·qz}
Figure 29: T experimental vs calculated; system Ab-Sd-Qz.
Figure 30: T experimental vs calculated; system Ab-Sd-Ac-Qz.
The Sd/2 addition to z is reduced by the subtraction of either Ac or 4Qz, whichever is less. This reduction of the Sd/2 addition indicates that a ternary reaction occurs in the melts between the Sd, Ac, and Qz components. This reduction is not observed in the systems Ab-Sd-Qz or Ab-Sd-Ac. It was proposed above that the Sd/2 addition represents the addition of the Na in the Sd component to z, and that Na forms Na-Si complexes that link distorted Si₂O₅ sheets in the melt. For some reason, which remains enigmatic, the Sd sheet structure appears to be destroyed in this system.

Or-Kt-Kd and An-Or-Lct

In the systems Or-Kt-Kd and An-Or-Lct:

\[ b = \text{Al} \]
\[ z = \frac{3\text{Al}}{2} + \frac{\text{Al} - 2\text{Ca}}{2} + \frac{3\text{Si}}{5} - \text{Or}/5. \]

The term \( (1.5\text{Al} + \frac{\text{Al} - 2\text{Ca}}{2} + 3\text{Si}) \) equals the sum of the network formers plus the Al charge balancers in the liquid.

The Or/5 subtraction from z is similar to the Qz/1.5 subtraction from z in the systems Ab-Qz and An-Qz, and the Ne/1.5 subtraction from z in the Ab-Ne system. Those subtractions appear to indicate sub-phase segregation of a portion of the melt network. The quantity Or/5 equals the Si in the Or component in excess of the Lct formula. The Or/5 subtraction suggests that the network structure of the Or liquid component is divided into two populations. One population may have a structure and composition
Figure 31: T experimental vs calculated; system Or-Kt-Kd.
Experimental vs. Calculated Temperatures

T(K) Experimental vs. T(K) Calculated

980 1100 1220
980 1100 1220

or·kt·kd
Figure 32: $T$ experimental vs calculated; system An-Or-Lct.
similar to that of pure Lct liquid. The other population may
contain the Si in excess of the Lct formula and have a tridimite or
cristobalite-like structure. This model is consistent with the
incongruent melting of Or to Lct plus liquid. There is a melting
interval of 375 degrees between the liquidus and solidus for the Or
composition. It is also consistent with the interpretation of the
Raman spectra of Or and Lct glasses (Matson et al, 1982) that the
structures of both Lct and Or glasses are similar to that of
crystalline Lct.

Although both Ab and Or glasses have short range structure
based on six member rings (Taylor and Brown, 1979a, Sharma et al,
1982, Matson et al, 1982) the calculation of z in systems with
normative Ab does not involve an Ab/5 subtraction. The incongruent
melting of sanidine to leucite plus liquid versus the congruent
melting of albite suggests that there is a structural distinction
between Ab and Or liquids. Jantzen (1980) observed spinodal
decomposition in glass of the composition Or_{39.7}Ab_{59.2}An_{1.1} that was
quenched in water from 1473 (K). A modulated spinodal structure
with an average spacing of fifty to seventy angstroms was observed
with transmission electron microscopy. Jantzen (1980) suggests that
the observed spinodal decomposition is a quench product due to the
existence of a metastable two liquid field, as in the system SiO\textsubscript{2}-
Al\textsubscript{2}O\textsubscript{3}. The observed spinodal decomposition of the alkali feldspar
glass indicates that there is a tendency towards immiscibility in
the system Ab-Or, and this, in turn, indicates that there must be a
structural distinction between Ab liquid and Or liquid. The Or/5 subtraction is observed in both the An-Or-Lct and Or-Kt-Kd systems, even though the liquidus feldspar in the system An-Or-Lct is anorthite, and that in the system Or-Kt-Kd is sanidine.

An-Or-Qz and Or-Qz-Kt

In the systems An-Or-Qz and Or-Qz-Kt:

\[ b = Al_1 \]
\[ z = (2Al_1 + Si_1 - v/n - Or/5) \]
\[ v = (Qz - 3f/5) \text{ or } 0, \text{ whichever is greater} \]
\[ f = (Or - 4An) \text{ or } 0, \text{ whichever is greater} \]
\[ n = (1.5 + 10Kt) \text{ or } 2, \text{ whichever is less} \]

The Qz/n subtraction from z is diminished or eliminated by the term f. The term f is greater than zero only in melts in which the Or to An ratio is greater than four. This term is important in the low temperature, potassic, An-saturated liquids in the system An-Or-Qz. The subtraction of 3f/5 completely eliminates the Qz in all but one of the experiments in the system Or-Kt-Qz. This indicates that Or and Qz liquids mix ideally, i.e. there is no metastable immiscibility between Or and Qz.
Figure 33: T experimental vs calculated; system An-Or-Qz.
Figure 34: T experimental vs calculated; system Or-Qz-Kt.
Ab-Or-Qz

In the system Ab-Or-Qz:

\[ b = Al_1 - Al_1 \left( \frac{1}{5} \right) \]

\[ i = 20r \text{ or } Ab, \text{ whichever is less} \]

\[ z = l - v / 1.5 - q / 5 \]

\[ v = (Qz - 3f / 5) \]

\[ f = (Or - 4Ab) \text{ or } 0, \text{ whichever is greater} \]

\[ q = (Or - 2Ab) \text{ or } 0, \text{ whichever is greater} \]

There are three points to be made with reference to this system. The first is about the term \( i \). The subtraction of \( Al_1(i/5) \) from \( Al_1 \) in \( b \) is similar to the subtractions of \( Al_1P_1 \) and \( 2Al_1Ti_1 \) discussed above. All three are the products of \( Al_1 \) with another compositional term. This suggests that the term \( Al_1(i/5) \) represents a quantity of \( Al \) that is not capable of being incorporated into a corundum melt species. The fact that \( i \) is zero in systems in which either \( Ab \) or \( Or \) is zero suggests that this term reflects the formation of a mixed-alkali complex. These complexes may have a one to one \( Na \) to \( K \) ratio. The number of alkali cations in these complexes between \( Ab \) and \( Ab_2Or_1 \) is \( 20r / 5 \). From \( Ab_2Or_1 \) to \( Or \) the number of complexed alkali cations is \( Ab / 5 \). This suggests that the ratio of complexed to non-complexed \( Na \) cations can not exceed one. The \( Al \) cations in the melt species that results from the reaction of these complexes...
Figure 35: T experimental vs calculated; system Ab-Or-Qz.
T(K) Calculated vs. T(K) Experimental for ab·or·qz
with Al is not capable of being simultaneously incorporated into a corundum melt species.

The second point is about the term \( f \). The subtraction of \( 4\text{Ab} \) from \( \text{Or} \) in the term \( f \) is similar to the subtraction of \( 4\text{An} \) from \( \text{Or} \) in \( f \) in the system \( \text{An-Or-Qz} \). Both subtractions indicate that the sub-pase segregation of the liquid into \( \text{Qz} \) and feldspar rich components occurs with even minor concentrations of the plagioclase feldspar components.

The third point is about the term \( q \). In \( q \) the \( \text{Or}/5 \) subtraction from \( z \) is diminished and eliminated by \( 2\text{Ab} \). The term \( q \) is zero in melts with \( \text{Or} \) to \( \text{Ab} \) ratios less than two. This subtraction may reflect the reorganization of the feldspar melt structure from \( \text{Or-like} \) to \( \text{Ab-like} \). In this regards it is interesting to note that the alkali feldspar join is binary from \( \text{Ab}_{51}\text{Or}_{49} \) to \( \text{Ab} \) (Schairer, 1950).

\[ \text{Ab-Or-Ne} \]

In the system \( \text{Ab-Or-Ne} \):

\[ b = (\text{Al}_1 - \text{Ne}/3)(1-i/5) \]

\[ i = 2\text{Or} \text{ or } \text{Ab}, \text{ whichever is less} \]

\[ z = 1-2\text{Ne}/3-q/5 \]

\[ q = (\text{Or}-2\text{Ab}) \text{ or } 0, \text{ whichever is greater} \]

The \( i/5 \) subtraction from \( b \) involves only that \( \text{Al} \) that is not part of the \( \text{NaAlO}_2 \) melt species. The rest of the terms are discussed above.
Figure 36: T experimental vs calculated; system Ab-Or-Ne.
An-En-Di-Qz and An-En-Fs-Qz

In the systems An-En-Di-Qz and An-En-Fs-Qz:

\[ b = \text{Al}_1 \]

\[ z = y - \frac{d}{2} \]

\[ y = \left( \frac{3\text{Al}_1}{2} + \text{Si}_1 + x \right) \text{ or } 1, \text{ whichever is less} \]

\[ d = (\text{Qz-En}/2 - \text{Fs}/2) \text{ or } 0, \text{ whichever is greater} \]

\[ n = (1.5 + 10(\text{En} + \text{Fs} + \text{Di})) \text{ or } 2, \text{ whichever is less} \]

\[ x = (\text{En}/4 + \text{Fs}/4 - \text{Di}/8) \text{ or } 0, \text{ whichever is greater}. \]

The reduction of the Qz subtraction in term \( d \) by \((\text{En}/2 + \text{Fs}/2)\) appears to indicate a reduction in the number of Si atoms in Al excluding melt species, possibly through the formation of a sheet like melt species of the formula \( \text{MSi}_2\text{O}_5 \), where M equals Mg or Fe. This is suggested by the magnitude of the subtraction which reduces the normative Qz to what it would be if normative \( \text{MgSi}_2\text{O}_5 \) and \( \text{FeSi}_2\text{O}_5 \) were calculated. Although there is no crystalline \((\text{Mg,Fe})\text{Si}_2\text{O}_5\) polymorphs Ubbelohde (1978) states that liquids that readily form glasses often form melt clusters that have no crystalline analogue.

The formation of a melt species of the formula \( \text{MSi}_2\text{O}_5 \), where M equals Mg or Fe, may also be inferred from the extent of the two liquid fields in the systems \( \text{MgO-SiO}_2 \) and \( \text{FeO-SiO}_2 \). In both systems the mafic immiscible liquid at the two-liquid plus cristobalite monotectic has the composition 40\% \( \text{MgO} \), 60\% \( \text{SiO}_2 \). This composition is only six percent more mafic than the composition \( \text{MSi}_2\text{O}_5 \).

Additional evidence that supports the existence of melt species of
Figure 37: T experimental vs calculated; system An-En-Di-Qz.
Figure 38: T experimental vs calculated; system An-En-Fs-Qz.
\[ T(K) \text{ Calculated} \]

\[ T(K) \text{ Experimental} \]
the formula MSi$_2$O$_5$ comes from the experimental and thermodynamic study of the metastable two liquid solvus in the join BaO-SiO$_2$.

Haller et al. (1974) demonstrated that the metastable solvus in this system determined by Seward et al. (1968) extended from SiO$_2$ to BaSi$_2$O$_5$. Haller et al. (1974) were able to calculate the metastable solvus with mixing equations by assuming that the cations in the melt were distributed between SiO$_2$ and BaSi$_2$O$_5$ melt species.

An-Qz-Or-En and Ab-Qz-Fs

In the An-Qz-Or-En and Ab-Qz-Fs systems:

- $b = A_{11}$
- $z = \frac{y - d}{n - Or}/5$
- $y = (3A_{11}/2 + Si_{1} + x + u)$ or 1, whichever is less
- $x = (En/4 + Fs/4)$ or $A_{11}$, whichever is less
- $u = 5(Na_{1} + K_{1})$ or $A_{11}/2$, whichever is less
- $d = (Qz - m - 3f/5)$ or 0, whichever is greater
- $m = (Fs/2 + En/2 - 6(Ab + Or))$ or 0, whichever is greater
- $f = (Or - 4An)$ or 0, whichever is greater
- $n = (1.5 + 10(En + Fs))$ or 2, whichever is less.

The (Fs/2 + En/2) subtraction from Qz in the term d is reduced or eliminated by the alkali feldspar component. This suggests that (Fe, Mg)Si$_2$O$_5$ melt species are unstable in alkaline melts.
Figure 39: T experimental vs calculated; system An-Qz-Or-En.
Figure 40: T experimental vs calculated; system Ab-Qz-Fs.
In the system An-Or-Fa-Fo-Qz:

\[ b = Al_1 \]
\[ z = y - d/n - q/5 \]
\[ y = (3Al_1/2 + Si_1 + x + u) \text{ or } 1, \text{ whichever is less} \]
\[ x = (2Fo/3 + 2Fa/3 + En/4 + Fs/4) \text{ or } Al_1, \text{ whichever is less} \]
\[ u = Al_1/2 \text{ or } 5K_1, \text{ whichever is less} \]
\[ q = (Or - 5h) \text{ or } 0, \text{ whichever is greater} \]
\[ h = (Fe_1 - Mg_1) \text{ or } 0, \text{ whichever is greater} \]
\[ d = (Qz - m - 10g - 3f/5) \text{ or } 0, \text{ whichever is greater} \]
\[ m = (Fs/2 + En/2 - 60r) \text{ or } 0, \text{ whichever is greater} \]
\[ g = (Fs - An) \text{ or } 0, \text{ whichever is greater} \]
\[ f = (Or - 4An) \text{ or } 0, \text{ whichever is greater} \]
\[ n = (1.5 + 10(Fs + En)) \text{ or } 2, \text{ whichever is less} \]

In this system the Or/5 subtraction from \( z \) is diminished and eliminated by the Fe in excess of Mg in the liquid. Similarly, the Qz/n subtraction from \( z \) is diminished and eliminated by the Fs in excess of An. Both of these modifications are probably related to the depolymerized nature of Fe-rich silicate melts. The viscosities of Fe-rich lunar basalts, to which these terms also apply, are orders of magnitude less than that of terrestrial basalts (Murase and Mc Birney, 1970).
Figure 41: T experimental vs calculated; system Or-An-Fa-Fo-Qz.
Natural and Simple Systems

For all the systems considered in this study:

\[ b = (Al_1 - f/3)(1-P_1 -2(Al_1)(Ti_1)-i/5) \]
\[ f = (Ne-Ac/6) \text{ or } 0, \text{ whichever is greater} \]
\[ i = 2Ab \text{ or } Or, \text{ whichever is less} \]
\[ z = y - v \]
\[ y = (3Al_1/2+Si_1+P_1/2+Ak/5+u+x+k) \text{ or } 1, \text{ whichever is less} \]
\[ u = 5(Na_1+K_1) \text{ or } Al_1/2, \text{ whichever is less} \]
\[ x = Il+Wu+Mgt+Hem+a \text{ or } Al_1, \text{ whichever is less} \]
\[ a = (2Fo/3+2Fa/3+En/4+Fs/4-p) \text{ or } 0, \text{ whichever is greater} \]
\[ p = (Di/8+Hd/8+Ak/10-3(Ab+Or)/2) \text{ or } 0, \text{ whichever is greater} \]
\[ k = (Sd/2-e) \text{ or } 0, \text{ whichever is greater} \]
\[ e = Ac \text{ or } 4Qz, \text{ whichever is less} \]
\[ v = d/n+q/5+2f/3 \]
\[ d = (Qz-m-10g-3f/5) \text{ or } 0, \text{ whichever is greater} \]
\[ m = (Fs/2+En/2-6(Ab+Or)) \text{ or } 0, \text{ whichever is greater} \]
\[ g = c \text{ or } An, \text{ whichever is less} \]
\[ c = (Fs-j) \text{ or } 0, \text{ whichever is greater} \]
\[ j = (An-3.25Ab) \text{ or } 0, \text{ whichever is greater} \]
\[ n = (1.5+10(1-Qz-An-Ab-Or)) \text{ or } 2, \text{ whichever is less} \]
\[ q = ((Or-2Ab-5h) \text{ or } 0, \text{ whichever is greater} \]
\[ h = (Fe_1-Mg_1) \text{ or } 0, \text{ whichever is greater} \]

For the most part the calculation of \( b \) and \( z \) in natural systems is simply the summation of terms derived in the simple systems.
Figure 42: T experimental vs calculated; all data.


T(K) Experimental

T(K) Calculated

feldspar · liquid

1190 1510 1830

1190 1510 1830
There are, however, modifications of two existing terms that reflect compositional variations in the natural systems not observed in the simpler ones.

First, Hd/8 is added to the (Di/8+Ak/10) from the normative olivine and orthopyroxene addition in the term x. Second, the subtraction of An from Fs in the term c is diminished or eliminated by 3.25Ab.

Summary

The evolution of the terms b and z as functions of their variations in simple systems has been examined. The term b is the mole fraction of Al capable of forming a corundum melt species. The term z is the sum of the cations that are associated with the alumino-silicate network. The term z may represent the composition of the bulk liquid at the feldspar-liquid interface. The ratio (b/z) is the probability of a cation site in the population z being occupied by an Al cation that is capable of forming a corundum melt species.

The calculations of b and z appear to be a reflection of melt structural organization. If an Al cation is in a melt species that is incompatible with a corundum melt species then it is subtracted from b. Likewise if an Al cation is part of a melt network that does not associate with the alumino-silicate network then it is subtracted from b. The term z is the sum of all the network forming
cations, plus Al charge balancers, plus cations that are
topologically associated with, but not charge balanced into, the
melt network, minus those cations that form separate melt networks.
CHAPTER 8
DISCUSSION OF THE TERM "w"

It was suggested above that feldspar in equilibrium with liquid is surrounded by a surface melt of the feldspar's composition. The one atmosphere Ab-Cor (Schairer and Bowen, 1956) and An-Cor (Rankin and Wright, 1915) joins are shown in Figures 43 and 44. Corundum is the liquidus phase over 98.5 and 96 weight per cents of these two systems, respectively. At one atmosphere melts of nearly plagioclase composition are saturated with corundum. Melting relations of the An-Ab join determined experimentally at 10 and 20 kilobars and proposed for 30 kilobars by Lindsley (1968) are shown in Figure 45. At 30 kilobars corundum is the liquidus phase from An10 to An100. At slightly higher pressures more Ab rich melts may also have corundum on the liquidus, however, corundum is never on the liquidus at Ab100 due to the breakdown of Ab to jadeite plus liquid at 32 kilobars. The plagioclase-corundum cotectic in the system An-Ab-Cor is extremely close to the join An-Ab at one atmosphere. With increasing pressure corundum becomes the liquidus phase over more than 90% of the plagioclase join. If the one atmosphere plagioclase surface melt is structurally similar to high pressure plagioclase melts, then these surface melts may be saturated with corundum.

The problem of crystallizing albite, which has a crystalline structure based on four member tetrahedral rings, from albite
Figure 43: The system Ab-Cor at one atmosphere.
Figure 44: The system An-Cor at one atmosphere.
Figure 45: The System An–Ab at 10, 20, and 30 kbars.
liquid, which from analogy with albite glass has a structure based on six and higher member tetrahedral rings was discussed above. A structural rearrangement from six to four member rings is necessary for albite to crystallize congruently. This rearrangement may take place in the plagioclase surface melt.

Kushiro (1980) demonstrated that the viscosity of albite liquid decreases rapidly between 10 and 15 kilobars at 1673 (K), and that the density of albite liquid increases rapidly between 15 and 20 kilobars at 1523 (K). Kushiro (1980) suggested that these changes were due to a change in coordination of alumina from tetrahedral to octahedral with increasing pressure. However, Sharma et al (1979b) demonstrated with Raman spectroscopy that there is no aluminum coordination shift in glasses of jadeite composition quenched at different pressures. Jadeite melts have density and viscosity relationships similar to albite (Kushiro, 1980). Therefore it is unlikely that the increase in density and decrease in viscosity in albite liquid at high pressure is due to a coordination shift in alumina. Sharma et al (1979b) studied the structure of jadeite glasses quenched at one atmosphere to 20 kilobars with Raman spectroscopy. Their findings indicate a structural rearrangement in jadeite melt from predominantly six to predominantly four member tetrahedral rings, i.e. from a "cristobalite" like to a "coesite" like structure, with increasing pressure. Sharma et al (1978a) demonstrated that the one atmosphere structures of jadeite and albite glasses are very similar. A similar structural shift from
six to four member rings may therefore occur in albite liquid at high pressures. If a structural shift occurs in albite liquid from six to four member rings with increasing pressure, then the structure of high pressure albite liquid may be similar to the structural arrangement that was proposed above for the albite surface melt at the crystal liquid interface. The surface melt may therefore be saturated with crystalline corundum.

Some support for these ideas is gained from the high pressure results of Lindsley (1968) (Figure 45) in light of the structures of one atmosphere plagioclase melts determined by Sharma et al (1982). The plagioclase melt that is saturated with corundum at the lowest pressure is pure An liquid at about 9 kilobars (Goldsmith, 1980). With increasing pressure corundum becomes the liquidus phase for more and more Ab rich melts. At 30 kilobars all plagioclase liquids from An10 to An100 have corundum on the liquidus. The Raman spectroscopic results of Sharma et al (1982) indicate that An liquid is composed primarily of four member tetrahedral rings, and that the proportion of six to four member tetrahedral rings increases continually from An to Ab. Therefore, if higher member rings are converted to four member rings in plagioclase liquid with increasing pressure, then the conversion should occur most rapidly in An liquid, which has the highest proportion of four to six member rings of all the plagioclase liquids at one atmosphere. Structural conversion for more albitic liquids will occur at increasingly higher pressures. This is exactly the sequence in which corundum
becomes the liquidus phase in plagioclase melts, i.e. from An to increasingly more Ab rich liquids.

The melting relationships of Or from one atmosphere to forty kilobars determined by Lindsley (1966) are shown in Figure 46. With increased pressure the field of leucite plus liquid shrinks until sanidine becomes a congruently melting phase. It can be seen from Figure 46 that corundum is not a liquidus phase in liquids of Or composition from one atmosphere to forty kilobars. It is unknown if corundum will be a liquidus phase in liquids of Or composition at pressures higher than this. However, if sanidine is surrounded by a surface melt of Or composition then it may be inferred from the incongruent melting of sanidine to leucite plus liquid at low pressures that this surface melt must be structurally similar to high pressure Or melts. Otherwise the surface melt would not be saturated with sanidine.

Writing about the boundary layers of liquids at solid surfaces Derjaguin and Churaev (1981) state: "The fact that the structure of liquid layers close to a solid substrate does change is in itself beyond doubt." (page 70). Derjaguin and Churaev (1981) go on to state: "wetting liquids form boundary layers of an increased density, while non-wetting liquids form boundary layers of a decreased density when compared to that of the bulk liquid phase." (page 73). A wetting liquid is one that spreads out and covers the surfaces of the crystals with which it is in contact, a non-wetting liquid is one that balls-up and runs off the surface of the crystal
Figure 46: Or P-T diagram.
(Adamson, 1976). The experiments of Mehnert et al (1973) demonstrate that a thin film of liquid surrounds all the grains in gneisses and granulites at small degrees of partial melting. Similarly Day and Allen (1905) described the progressive stages of melting of natural albite. They note that the first melts form on the surface of the feldspar and along the cleavage plains within the feldspar. As the percentage of melt increases "islands" of albite were observed within channels of melt that were centered along the original cleavage plains. Also the formation of fusiform bombs by the covering of gabbroic and dunitic xenoliths with basaltic liquid is commonly observed. These observations indicate that silicate melts wet their crystals.

The above ideas on the boundary layers of liquids suggest that the structure of albite liquid is different at the crystal liquid interface then in the bulk liquid, and that the liquid at the interface is denser than the bulk liquid. If the albite melt at the surface of the crystal is chiefly composed of four member tetrahedral rings then it will be denser than the bulk albite liquid composed of six and higher member rings.

It follows from equation (1) that in systems with feldspar and liquid in equilibrium:

\[
\frac{a_\text{cor}}{a_\text{cor}} = \left( \frac{4AF+AN+2ANAF(AN-AF))}{12A_l^3(1-A_l)} \right) \left( \frac{12(b/z)}{(1-(b/z))} \right) \]

To which crystal and which liquid does this equation apply?
The equation works for any feldspar, therefore it should be applicable to systems with two feldspars in equilibrium with a liquid, such as along the anorthite-sanidine cotectic in the system An-Lct-Qz. If the crystal of interest in equation (1) is feldspar it follows that:

\[ a_{\text{san an}} = a_{\text{cor}} \]

since for two feldspars in equilibrium in which corundum is an actual component:

\[ \mu_{\text{san an}} = \mu_{\text{cor}} \]

and:

\[ xt_{\text{a cor}} = e^{(\mu_{\text{cor}} - \mu_{\text{cor}})/RT} a_{\text{cor}} \]

therefore:

\[ a_{\text{cor}} \neq 1/(4AF+AN+2ANAF(AN-AF)) \]

and

\[ a_{\text{cor}} \neq 1/(4AF+AN+2ANAF(AN-AF)) \]

since otherwise:

\[ a_{\text{cor}} \neq a_{\text{cor}}. \]

The product

\[ (4AF+AN+2ANAF(AN-AF))(12Al^3_x(1-Al_x)) \]

is equal for both feldspars. However, if:

\[ xt_{\text{a cor}} = 1/(4AF+AN+2ANAF(AN-AF))(12Al^3_x(1-Al_x)) \]

then:

\[ a_{\text{corr}} > 1, \]

and it would follow that all feldspar bearing systems would be supersaturated with corundum. This is obviously not true.
Further:
\[
x_{\text{cor}} = \frac{1}{(4A\text{F}+AN+2AN\text{A}(AN-A\text{F}))(12A_{1-x}(1-A_{1-x}))(12(b/z)^3(1-(b/z)))}
\]
because it would follow that:
\[
x_{\text{cor}} > 1
\]
and:
\[
\text{liq}_{\text{cor}} = 1,
\]
which would mean that the system was both oversaturated with

crystalline corundum and saturated with corundum liquid.

Another possibility is:
\[
x_{\text{cor}} = 1
\]
\[
\text{liq}_{\text{cor}} = 1
\]
(4A\text{F}+AN+2AN\text{A}(AN-A\text{F}))(12A_{1-x}(1-A_{1-x}))(12(b/z)^3(1-(b/z))).

This possibility can be tested by considering phase relations in the

system An-Cor-Cr\text{O}_3 (eskolaite). The liquidus fields in the ternary

system inferred from the limiting binaries are shown in Figure 47.

If corundum is an actual component in anorthite then:

\[
\Delta_{\text{cor}} (\text{cor-esk}) \mu_{\text{cor}} = \mu_{\text{cor}}
\]

and:

\[
a_{\text{an}} (\text{cor-esk}) = a_{\text{cor}}
\]

Since \(a_{\text{cor}}^{(\text{cor-esk})}\) varies from one in pure corundum to zero in

eskolaite it is obvious that the activity of corundum in the

feldspar is not always one in this system.
Figure 47: Liquidus fields in the system An-Cor-Esk.
The same conclusion is reached by considering the system $K_2O$-$Al_2O_3-SiO_2$ in Figure 48. Sanidine and corundum do not stably coexist with a liquid in this system. However, sanidine does coexist with mullite. If corundum is an actual component in both sanidine and mullite then it is necessary that:

$$a_{\text{san}} \cdot mull = a_{\text{cor}}$$

at equilibrium. The composition of mullite is variable, becoming more siliceous sympathetically with its equilibrium liquid. Therefore, the activity of corundum in mullite is less than one in this system except along the mullite-corundum cotectic. Therefore, if corundum is an actual component in sanidine it follows that:

$$a_{\text{san}} < 1$$

everywhere in this system. Similar arguments can be made with respect to the An-mullite and Ab-mullite cotectics in the systems $CaO-Al_2O_3-SiO_2$ and $Na_2O-Al_2O_3-SiO_2$.

The activity of corundum in feldspar is not always one. None of the terms in equation (1) is the activity of corundum in feldspar. Hence, whatever crystal equation (1) is concerned with, it is not the equilibrium feldspar. However, many of the systems considered in this work contain only two macroscopic phases, crystalline feldspar and liquid.

The activity of corundum in crystalline corundum is one. The activity of corundum in the surface feldspar melt may be:

$$12(Al_x^3)(1-Al_x).$$
Figure 43: The System $\text{K}_2\text{O-}\text{Al}_2\text{O}_3-\text{SiO}_2$. 
As stated above the term:
\[ 12\left(\frac{b}{z}\right)^3\left(1-\frac{b}{z}\right) \]
cannot be applied directly to the bulk melt due to the presence of significant short range order in silicate melts. The term:
\[ \frac{1}{(AN+4AF+2ANAF(AN-AF))} \]
cannot equal the activity of corundum in the feldspar because this would require two feldspars in equilibrium with the same liquid to have different chemical potentials of corundum. However, the term:
\[ 12\left(\frac{b}{z}\right)^3\left(1-\frac{b}{z}\right) \]
must apply to some liquid of the same composition as the bulk liquid, but with less order. The term:
\[ \frac{1}{(4AF+AN+2ANAF(AN-AF))} \]
is related to the order disorder distribution of Al in the tetrahedral sites of the crystalline feldspar.

An answer to this problem may be found in the energetics of the feldspar-liquid interface. Figure 49 is a proposed energy-distance diagram across a feldspar liquid interface. The energy of both bulk phases in equilibrium is equal. The energy of the surface is, however, higher than this. Where do the crystal and liquid phases end on this diagram? There are two possibilities. The first is that the interface between both phases is infinitely thin, and therefore both phases terminate at the maxima. This, however, is inconsistent with the existence of an "interphase" of definite volume at the surface, as proposed by Guggenheim (1940).
Figure 49: Energy vs distance from feldspar to liquid.
Crystal

Liquid

DISTANCE

ENERGY→
The second likely place to put the surfaces of the solid and liquid phases is at the inflection points on the energy-distance curve. These may be points at which one process involved in crystallization (fusion) has terminated and another begins.

In Figure 50 the energy-distance curve is divided into segments that may relate to the various processes involved in crystallization (fusion). I have drawn this as a four step process:

1) loss of liquid short range liquid order
2) compositional segregation
3) attainment of crystal short range order
4) attainment of crystal long range order.

Fusion may occur in the reverse order.

The activity of corundum at the liquid's surface may be:

\[ 12((b/z)^3)(1-(b/z)) \]

and that the activity of corundum at the crystal's surface may be:

\[ \frac{1}{(4AF+AN+2ANAF(AN-AF))}. \]

The term \( w \), which equals:

\[ (12(Al_{3x})(1-Al_{x}))(12((b/z)^3)(1-(b/z)))(4AF+AN+2ANAF(AN-AF)), \]

may therefore be the equilibrium constant for the following reaction:

\[ \text{cor}_{xsur} + \text{cor}_{lsur} \rightarrow \text{cor}_{sur} + \text{cor}_{fdv} \]

where: \( xsur \) is the crystal surface

\( \text{cor} \) is crystalline corundum in the surface melt

\( lsur \) is the liquid surface

\( fdv \) is the feldspar surface melt.
Figure 50: Annotated energy-distance diagram.
Crystal

- loss of long range order

- loss of short range order

- compositional segregation

- loss of short range order

Liquid
CHAPTER 9
THE CALCULATION OF THE MELTING POINTS OF
SOME OTHER ALUMINATES

It is possible to calculate the melting points of some other
aluminates with equation (1). Congruent melting points of
alkaline-earth feldspar and hexacelsian are given in Table 3. The
experimentally determined melting temperature of these compounds
melt range from 1826 to 2013 (K). The number of sites available for
Al occupancy per Al atom in this group of compounds can vary from 1
to 2, reflecting the variation in the number of sites available for
Al occupancy per Al atom as the distribution of Si and Al among the
tetrahedral sites of these compounds varies from completely ordered
to completely random. The range of melting temperatures calculated
with equation one for these compounds is from 1823 to 2020 (K). The
temperature 1823 (K) is calculated for the completely ordered state,
and 2020 (K) is the temperature calculated for a completely
disordered compound. The excellent agreement between the observed
and calculated melting intervals suggests that equation (1) may be
used as an indicator of the structural state of a compound at its
melting point.

Evidence that indicates that anorthite is almost completely
ordered at its melting point was discussed above. The melting point
of BaAl₂Si₂O₈ may be accurately calculated by assuming the
distribution of Si and Al among its tetrahedral sites is completely
<table>
<thead>
<tr>
<th>Compound</th>
<th>T(K)</th>
<th>nsapa</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaAl$_2$Si$_2$O$_8$</td>
<td>1826</td>
<td>1</td>
</tr>
<tr>
<td>SrAl$_2$Si$_2$O$_8$</td>
<td>1983</td>
<td>1.75</td>
</tr>
<tr>
<td>BaAl$_2$Si$_2$O$_8$</td>
<td>2013</td>
<td>2</td>
</tr>
</tbody>
</table>
random. Lin and Foster (1968) demonstrated that the stable polymorph of BaAl$_2$Si$_2$O$_8$ above 1863 (K) is hexacelsian. Takeuchi (1958) determined the structure of hexacelsian and noted that the distance between the tetrahedral cations and oxygens in hexacelsian varies from 1.65 to 1.67 angstroms. In studying the structure of anorthite Megaw et al (1962) noted that the distances between tetrahedral cations and oxygens could be divided into two groups, one group with a mean distance of 1.614 angstroms, and the other group with a mean distance of 1.749 angstroms. Megaw et al (1962) state that the sites with the larger distances are occupied by Al cations, while those with smaller T-O distances are occupied by Si cations, reflecting the highly ordered nature of anorthite. The fact that the T-O distances determined by Takeuchi in hexacelsian are nearly constant suggests, in turn, that the distribution of Si and Al atoms among the tetrahedral sites in hexacelsian is highly disordered. Takeuchi's measurements were made at room temperature. No high temperature study of the structure of hexacelsian has been reported. On the basis of equation (1), however, it appears that the distribution of Si and Al atoms among the tetrahedral sites of hexacelsian is completely random at its melting point.

From the melting point of SrAl$_2$Si$_2$O$_8$ I have calculated that there are 1.75 sites available for Al occupancy per Al atom in this compound. This indicates the distribution of Si and Al atoms among the tetrahedral sites of SrAl$_2$Si$_2$O$_8$ is partially ordered at its melting point. The X-ray crystallographic study of Chiari et al
(1975) on synthetic stoichiometric Sr-feldspar demonstrated that this phase is partially disordered at room temperature. It is reasonable to assume that Sr-feldspar may become more disordered at elevated temperatures. However, equation (1) suggests that Sr-feldspar is still partially ordered at its melting point.

The melting points of albite, carnegieite, and sodium-aluminate are given in Table 4. Experimental temperatures are plotted against ones calculated with equation (1), assuming the Si/Al distribution is completely random in both of the silicate phases, in Figure 51. The high temperature structural state of albite is believed to be completely random, as discussed above. Therefore, albite has four sites available for Al occupancy per Al atom. Sodium-aluminate has a cristobalite-like structure with Al atoms tetrahedrally coordinated in a three dimensional framework, with Na atoms occupying interstitial octahedral sites. There is only one site available for Al occupancy per Al atom in NaAlO₂. Structural information as to the distribution of Si and Al among the tetrahedral sites in carnegieite is lacking. However the agreement between the calculated and experimental temperatures suggest that it is completely disordered at its melting point. Barth and Posnjak (1932) demonstrated that the structure of high temperature alpha carnegieite is cubic. A regular alternation of Si and Al atoms in alpha carnegieite would result in the loss of the cubic center of
TABLE 4
SODIUM ALUMINATE MELTING POINTS

<table>
<thead>
<tr>
<th>Compound</th>
<th>T(K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaAlO$_2$</td>
<td>2133</td>
</tr>
<tr>
<td>NaAlSiO$_4$</td>
<td>1799</td>
</tr>
<tr>
<td>NaAlSi$_3$O$_8$</td>
<td>1391</td>
</tr>
</tbody>
</table>
Figure 51: T experimental vs calculated; Na-aluminates.
\[ T(K) \text{ Calculated} \]

\[ T(K) \text{ Experimental} \]

- Sodium aluminate
- Carnegieite
- Albite
symmetry. Therefore, the cubic symmetry of alpha carnegieite indicates that the distribution of Si and Al atoms among the tetrahedral sites of this phase is highly disordered.

Goldsmith (1950) has demonstrated that alkali feldspars of the formula NaAlGe$_3$O$_8$ and KA1Ge$_3$O$_8$ melt congruently at 1340 and 1395 (K) respectively. The melting point of KA1Ge$_3$O$_8$ is, within experimental error, indistinguishable from that of albite, 1391 (K). The melting point of KA1Ge$_3$O$_8$ can therefore be calculated with equation (1) by assuming that the distribution of Al and Ge atoms among its tetrahedral sites is completely random, i.e. that there are four sites available for Al occupancy per Al atom in this phase.

Similarly, the melting point of NaAlGe$_3$O$_8$ may be used to infer that there are 2.75 sites available for Al occupancy per Al atom in this phase.

Although this approach gives consistent results for the above examples, it is not a panacea for the calculation of all aluminate melting points. There are, however, other predictions of aluminate melting points that may be simply fortuitous. These are in regards to the melting points of leucite, KA1Si$_2$O$_6$, and spinel, MgAl$_2$O$_4$. Experimentally determined melting points of these compounds are 2022 and 2408 (K) respectively. Melting points of 2018 and 2406 (K), respectively, may be calculated with the following equation:

\[ T(K) = \frac{1}{1/T_{fus}^{\text{cor}}} - \frac{R}{\Delta H_{fus}^{\text{cor}}} \ln((12\text{Al}_1^3(1-\text{Al}_1))(\text{nsapa})). \]

\[ \text{nsapa} = \text{number of sites available for Al occupancy per Al atom in the crystal.} \]
The above equation was solved for leucite and spinel by assuming that there are three sites in leucite and one site in spinel available for Al occupancy per Al atom. This equation differs from equation (1) in that the term $12(A_{x}^{3})(1-A_{x})$ is absent. The fact that the calculated melting points agree so well with the experimental ones for these two phases suggests that the form of the calculation may be valid. The melting points of these two compounds may be above the liquidus temperature of corundum in their surface melts. Spinel, in fact, melts at higher temperatures than corundum. The highest temperature that can be calculated for a compound of leucites formula with equation (1) is 1544 (K). The above equation may therefore be the equilibrium constant for the reaction:

$$cor_{x,sur} = cor_{1,lsur}$$

where:

- $cor_{x,sur}$ is the activity of corundum in the crystal's surface
- $cor_{1,lsur}$ is the activity of corundum in the liquid's surface.

A final point of interest is the relation of equation (1) to corundum itself. Since the cation mole fraction of Al in corundum is 1.0 the expression:

$$12(A_{1}^{3})(1-A_{1})$$

equals zero for pure corundum liquid. Vacancies, however, may play a role in the calculation of the Al mole fraction in molten corundum. The structure of crystalline corundum is based on the hexagonal close packing of oxygen atoms, with Al atoms occupying two thirds of the octahedral voids. Therefore in crystalline corundum
there is one octahedral vacancy for every two Al atoms. If the number of vacancies in the liquid is equal to the crystal then the effective mole fraction of Al in molten corundum may be $2/3$. However, the expression:

$$12\left(\frac{2}{3}\right)^3(1-\frac{2}{3})$$

is greater than one. Solving the equation:

$$12(Al^1_1)(1-Al^1_1)=1$$

results in a value of $Al^1_1$ of $(1/1.706)$. If this result is meaningful it may indicate that there are 1.412 vacancies for every two Al atoms in molten corundum, an increase of 0.412 vacancies for every two Al atoms over that in crystalline corundum. At present there is no way of knowing if this result is correct. What can be said, however, is that it is perfectly reasonable to expect the number of vacancies in liquid corundum to be greater than that in crystalline corundum, that vacancies play a major role in the structure of crystalline corundum, and that the increase of vacancies predicted above for the fusion of corundum does not appear to be excessive.
CHAPTER 10
OTHER FELDSPAR-LIQUID GEOTHERMOMETERS

There have been several previous attempts to formulate an igneous feldspar-liquid geothermometer. All of these deal exclusively with plagioclase feldspar. The expression I have presented above is applicable to any feldspar. These thermometers may be broken into two groups, those that are supposedly based upon theoretical criteria, and those that are simply statistical manipulations of the data. It is curious that all of the theoretical attempts have sprung from the United States, while all the statistical attempts have been generated in Great Britain and Canada. In this section I am chiefly interested in the ability of these thermometers to reproduce experimentally determined plagioclase-liquid equilibration temperatures. Each thermometer is tested against only those systems for which they are designed. All the thermometers are tested against a set of experiments on analogues of terrestrial magmas. Those thermometers which are in part based on data from simpler systems are also tested against experimental data from the system anorthite-albite-diopside.

The first of the theoretical thermometers is that of Kudo and Weill (1970). This thermometer is a modified equilibrium constant for the reaction:

$$\text{albite}_{\text{liq}} + \text{anorthite}_{\text{xtl}} = \text{albite}_{\text{xtl}} + \text{anorthite}_{\text{liq}}$$

This equation is based on data from various simple systems,
including the Ab-An binary. There must be finite amounts of both albite and anorthite present to use this thermometer. Therefore, even if it worked it would be of little use on alkali poor rocks from meteorites and the moon. Temperatures calculated with this thermometer, versus those experimentally determined, for experiments on terrestrial analogues and in the system anorthite-albite-diopside are presented in Figure 52. Errors on the order of 100 degrees are common. Therefore the Kudo-Weill equation is of little use as a quantitative geothermometer.

Mathez (1973) presented a revision of the Kudo-Weill geothermometer. Mathez was prompted to do this by noting that basaltic temperatures calculated with the Kudo-Weill thermometer are invariably too high. Mathez believed this is due to non-ideality in the crystalline plagioclase at magmatic temperatures. Mathez used the Kudo-Weill relationship to derive activity-composition relationships for plagioclase. He used these relationships to revise the constants in the Kudo-Weill expression. His equation is different from that of Kudo-Weill both in having different constants, and in using what Mathez believed was the ratio of the activity of anorthite to albite, versus simply the ratio of their mole fractions. Temperatures calculated with the Mathez thermometer are plotted versus experimentally determined temperatures in Figure 53. Again the very large errors associated with this equation make it of little petrogenetic use.
Figure 52: T experimental vs calculated; Kudo-Weill.
Kudo, Weill

\[ T(K) \text{ Calculated} \]

\[ T(K) \text{ Experimental} \]

100°
Figure 53: T experimental vs calculated; Mathez-Kudo-Weill.
Drake (1976) presented yet another revision of the Kudo-Weill thermometer. This revision was based on experiments Drake performed for his Ph.D. thesis (Drake, 1972). The revision of Drake was simply a recalibration of the constants of the Kudo-Weill equation with the additional data of Drake (1972). Temperatures calculated with the Drake revision of the Kudo-Weill thermometer are plotted versus experimental temperatures, for the same data in the last two figures, in Figure 54. Again the very large errors associated with this equation make it of no use in quantitative petrologic work.

The potential danger in using this equation can be demonstrated with a recent example from the literature. Echeverria (1979) calculated a plagioclase-liquid equilibration temperature for the Gorgona komatiite of 1475°C, using the above equation. The plagioclase she used in her calculation has a composition of An83. Figure 55 is the plagioclase binary phase diagram determined by Bowen (1913). The solidus temperature for An83 in the binary system is 1460°C, fifteen degrees below the temperature Echeverria calculated for her sample with the Drake-Kudo-Weill equation. It is altogether inconceivable that the An83 in the Gorogona komatiite grew at a temperature greater than that of the solidus of this composition on the plagioclase binary. On the basis of this incorrect calculated temperature Echeverria stated that the eruption temperature of the komatiite was between 1450 and 1500°C. Therefore an erroneous petrologic conclusion may have been made on the basis of this equation.
Figure 54: T experimental vs calculated Drake-Kudo-Weill.
Figure 55: The system An-Ab at one atmosphere.
Drake (1976) also presented a series of equations which related the log of the ratio of various compositional parameters to temperature. The equilibrium constant $K_8$ was cited by Drake as the best of these. $K_8$ may be rewritten as:

$$\frac{NaAlSi_3O_8x}{(NaAlO_{2\text{liq}})(SiO_{2\text{liq}})}$$

where:

$$NaAlO_{2\text{liq}} = Na_1/(Si_1+Na_1/2+K_1/2+Al_1/2)$$

$$SiO_{2\text{liq}} = Si_1/(Si_1+Na_1/2+K_1/2+Al_1/2)$$

$$NaAlSi_3O_8x = Na_x/(Na_x+Ca_x).$$

According to Drake:

$$T(K)=6100/(\ln(K_8)+2.29).$$

Calculated versus experimental temperatures using the above equation are shown in Figure 56 for the same data used in the above figures. Again the very large errors associated with this equation make it of no use in quantitative petrologic work.

Ghiorso and Carmichael (1980) published a regular solution model for silicate melts which may be used as both an anorthite-liquid and an albite-liquid geothermometer. Ghiorso and Carmichael (1980) assumed that phase equilibria could be modeled with freezing point depression equations which accounted for the change in the heat of fusion with temperature and the excess free energy of mixing the various components. Assuming that plagioclase is an ideal solid solution of albite and anorthite, and using published standard state thermodynamic quantities, these authors solved for the excess free energy of mixing values for a number of
Figure 56: T experimental vs calculated; Drake, K₈.
components, which they specified. Their original equation could then be used as a geothermometer once these values were known.

Figures 57 and 58 are calculated versus experimental temperatures using their albite and anorthite equations, respectively, on only that data they cite in their paper. Errors in excess of 100 degrees are common with the albite equation. Errors in excess of 30 degrees and up to 60 degrees are common in the anorthite equation. These results are unusual in that Ghiorso and Carmichael state an average error of 12 degrees for their plagioclase equation. Figure 59 is a plot of temperatures calculated with their albite equation versus temperatures calculated with their anorthite equation, using the same data. Again errors up to and in excess of 100 degrees are common.

The remaining geothermometers are all based on the statistical fitting of the composition of plagioclase saturated liquids versus their equilibration temperature. They all require a knowledge of the ferrous/ferric ratio of the liquid. For experiments performed at known temperatures and oxygen fugacity the ferrous/ferric ratio may be calculated with the equation of Nathan and Van Kirk (1979). Calculated versus experimental temperatures for the equations of French (1970), French and Cameron (1981), and Nathan and Van Kirk (1980) are shown in figures 60, 61, and 62. The data used for Nathan and Van Kirk (1980), who used simple systems in their data set, consists of experiments on terrestrial analogues and data from the system.
Figure 57: T experimental vs calculated; Ghiorso and Carmichael. Ab-liquid.
Figure 58: T experimental vs calculated; Ghiorso and Carmichael, An-liquid.
Figure 59: T calculated Ab vs T calculated An; Ghiorso and Carmichael.
GHIORSO, CARMICHAEL
Ab vs An

T[K] calculated Ab

T[K] calculated An

1330 1450 1570

1330 1450 1570

100°
Figure 60: T experimental vs calculated; French.
French

T(K) Calculated vs T(K) Experimental

1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0

1700
1540
1380
1380
1540
1700

100°
Figure 61: T experimental vs calculated; French and Cameron.
French, Cameron

\[ T(K) \text{ Calculated} \]

\[ T(K) \text{ Experimental} \]

1300 1460 1620

1300 1460 1620

\[ 100^\circ \]
Figure 62: T experimental vs calculated; Nathan and Van Kirk.
Nathan, Van Kirk

T(K) Calculated

T(K) Experimental

100°
anorthite-albite-diopside. Data from the system anorthite-albite-diopside was not used for French (1980) and French and Cameron (1981), who considered only terrestrial analogues. Again large errors are associated with each of these equations. A very good feldspar-liquid geothermometer, however, might be generated with a sophisticated enough statistical model and a sufficiently large data set. Such an equation could be a useful tool for the igneous petrologist, and may provide some clues into the physical nature of feldspar saturation.

Figure 63 shows experimental temperatures versus those calculated with my equation (1) for all the above data. The fit is better than that of all the above thermometers. Equation (1) may also be applied to a much wider range of liquid and feldspar compositions than any of the other geothermometers discussed above.
Figure 63: T experimental vs calculated; this study.
this study

T(K) Calculated

T(K) Experimental

100°
An expression that relates the composition of coexisting feldspar and liquid to their one atmosphere equilibrium temperature has been derived and presented. This expression is written in the form of a freezing point depression equation for corundum-liquid equilibria. Thermodynamic and structural considerations indicate that the expression cannot be physically related to equilibrium among the bulk phases in these systems. Consequently a model that relates this expression to equilibrium at the crystal-liquid interface has been developed.

The expression consists of the product of three factors. The first factor equals the number of sites available for Al occupancy per Al atom in the crystal. The second and third factors are based on the binomial distribution for calculating the probability of succeeding in three out of four attempts given that the probability of a single success is a function of the Al mole fraction in each population. The second factor uses the cation mole fraction of Al in the crystal. The second factor may apply to a volume of melt of the equilibrium feldspar's composition that may exist at the crystal-liquid interface. The third factor uses a portion of the cation mole fraction of Al in the liquid with respect to part of the total cation population of the liquid. The portion of the cation mole fraction of Al used in the equation appears to equal the amount.
of Al structurally capable of forming a corundum melt species. The population of cations in the melt represented by the term $z$ appears to equal all the cations associated with the melt network as network formers, charge balancers, topologically associate non-charge balanced cations, minus those cations in separate melt networks. The third factor may represent the activity of corundum in the liquid adjacent to the feldspar-liquid interface.

The expression developed in this study has been compared to other feldspar-liquid geothermometers and has been shown to be a superior predictor of equilibrium temperatures. The expression presented herein is also applicable to a much wider range of feldspar and liquid compositions than other feldspar-liquid geothermometers. It can also be used to calculate the melting points of some other aluminates.

Although much has been discovered since the turn of the century, our knowledge of the structures of crystals, liquids, and their interfaces is very rudimentary. Much work, some of which will require yet-to-be discovered techniques, will be needed to address some of the questions raised in this study.
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