# THE EQUILIBRATION TEMPERATURE AND PRESSURE OF VARIOUS LAVA TYPES WITH SPINEL- AND GARNET-PERIDOTITE

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## Abstract

Using groundmass mineral compositions of basic lavas, $\log a_{SiO_2}$ and $\log a_{Al_2O_3}$ can be calculated at 1 bar and at the quenching temperature of the lava. In the absence of mineral buffers, the variation of $\log a_{SiO_2}$ and $\log a_{Al_2O_3}$ in a silicate liquid with temperature and pressure can be calculated, and set equal to the activities of both components defined by the mineral assemblages of spinel- or garnet-peridotites. The simultaneous equations provide unique solutions for temperature and $P_{total}$. Representative values for the equilibration of various lava compositions with the two peridotite types are:

| | Spinel-peridotite | | Garnet-peridotite | |
| --- | --- | --- | --- | --- |
| | T°C | $P_{total}$ | T°C | $P_{total}$ |
| Trachybasalt | 1396 | 24.2 kbar | 1321 | 22.7 kbar |
| High-alumina basalt | 1648 | 31.2 | 1588 | 30.0 |
| Olivine-tholeiite | 1074 | 1.8 | 750 | −5.1 |
| Basaltic-andesite | 1065 | 2.2 | 767 | −3.6 |
| Ugandite | 1340 | 45.2 | 1658 | 51.6 |

Andesite magma (55–60 percent $SiO_2$) cannot have equilibrated with either peridotite composition type at any $P_{total}$, so that andesite either has a basaltic precursor, or alternatively liquids of andesite composition generated at depth (probably less than 120 kms) must remain segregated from mantle peridotite. In general silica-poor lavas (*i.e.*, low $\log a_{SiO_2}$) equilibrate at higher pressures than high silica-activity lavas. The precipitation of corundum or andalusite in salic metaluminous magmas requires extreme pressures (25–50 kilobars) so that compositional changes in these magmas are likely to be responsible for their very rare occurrence.

High-temperature thermodynamic data for $Al_2O_{3(corundum)}$ and $Al_2O_{3(liquid)}$ have been calculated from Zen's (1972) suggested value for corundum.

## Introduction

In another paper on silica activity (Nicholls *et al.*, 1971) we were able to calculate the pressure ($P_{total}$) at which the phenocrysts of rhyolites equilibrated, and, for basic lavas, the pressures at which they would be in equilibrium with olivine and orthopyroxene, equivalent to a probable mantle assemblage. However, this method involved making an intelligent guess of the temperature at which basic magma could have been in equilibrium with the mantle.

In this paper we show that if both the activities of silica ($a_{SiO_2}$) and of alumina ($a_{Al_2O_3}$) are known at any pressure and temperature, then it is possible to calculate a unique value of temperature and pressure at which a particular magma could have equilibrated with either a spinel-peridotite or a garnet-peridotite. It is convenient to calculate both $a_{SiO_2}$ and $a_{Al_2O_3}$ for a lava, whose groundmass was presumably quenched at 1 bar, and at a temperature which can be obtained from the composition of the co-existing iron-titanium oxides (Buddington and Lindsley, 1964). In what follows, we make the assumption, as we did in the last paper, that any lava can exist as a liquid of identical composition at depth in the earth.

In the same way that certain pairs of minerals can act as silica buffers, so can certain mineral assemblages buffer $a_{Al_2O_3}$, and at equilibrium the variation of $a_{Al_2O_3}$ in the presence of such a buffer is only a function of temperature at constant pressure. One example of an alumina buffer assemblage is given below:

$$\underset{\text{diopside}}{CaMgSi_2O_6} + \underset{\text{glass}}{SiO_2} + \underset{\text{liquid}}{Al_2O_3} = \underset{\text{anorthite}}{CaAl_2Si_2O_8} + \underset{\text{enstatite}}{MgSiO_3} \tag{1}$$
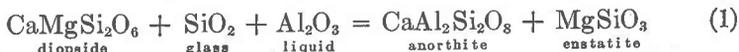
With all the components in their standard states (pure glass and liquid for $SiO_2$ and $Al_2O_3$ respectively), namely pure solids of unit activity, the variation of $a_{Al_2O_3}$ with temperature is given by

$$\log a_{Al_2O_3}^{liquid} = \Delta G^\circ / 2.303\,RT - \log a_{SiO_2}^{liquid} \tag{1a}$$

As the solid components form solid solutions, we can take account of the reduced activity of these components by keeping the logarithmic terms; thus

$$\log a_{Al_2O_3}^{liquid} = \Delta G^\circ / 2.303\,RT - \log a_{SiO_2}^{liquid} + \log a_{CaAl_2Si_2O_8}^{plagioclase}$$
$$+ \log a_{MgSiO_3}^{orthopyroxene} - \log a_{CaMgSi_2O_6}^{pyroxene} \tag{1b}$$

where the subscripts refer to components and the superscripts to phases.

The effect of pressure on $\log a_{Al_2O_3}$ is obtained by differentiating Equation 1a at constant temperature, and assuming, for the moment, that all the components have unit activity. Thus

$$\left( \frac{\partial \log a_{Al_2O_3}}{\partial P} \right)_T = \frac{1}{2.303\,RT} \left( \frac{\partial \Delta G^\circ}{\partial P} \right)_T = \frac{\Delta V^\circ}{2.303\,RT} \tag{1c}$$

where $\Delta V^\circ$ is the difference between the molar volumes of the products and reactants in their standard states. It will be assumed that $\Delta V^\circ$ is independent of pressure, so that Equation 1c can be integrated to give

$$(\log a_{\text{Al}_2\text{O}_3}^{\text{liquid}})_T^{P=P \text{ bars}} = (\log a_{\text{Al}_2\text{O}_3}^{\text{liquid}})_T^{P=1 \text{ bar}} + \frac{\Delta V^\circ (P-1)}{2.303 \, RT} \tag{1d}$$

$$= \Delta G^\circ / 2.303 \, RT + \frac{\Delta V^\circ (P-1)}{2.303 \, RT} \tag{1e}$$

$\Delta G^\circ / 2.303 \, RT$ can be represented by an equation of the form $A/T+B$, but because of the large effect of temperature on the molar volume of liquid $\text{Al}_2\text{O}_3$ (Kirshenbaum and Cahill, 1960), $\Delta V^\circ / 2.303 \, R$ cannot be assumed to be independent of temperature. This point will be taken up again below, and it is sufficient to emphasise here that with $\text{Al}_2\text{O}_{3(\text{liquid})}$ as a component in contrast to $\text{SiO}_{2(\text{glass})}$ (Nicholls *et al.*, 1971), the temperature dependence of the molar volume of a reaction $\Delta V^\circ / 2.303 \, R$ cannot be disregarded, although, as compressibility data for $\text{Al}_2\text{O}_3$ liquid are not known, any pressure dependence of $\Delta V^\circ / 2.303 \, R$ cannot be treated. If we let $\Delta V^\circ / 2.303 \, R = C$, then Equation 1e becomes

$$(\log a_{\text{Al}_2\text{O}_3})^{P=P \text{ bars}} = \frac{A}{T} + B + \frac{C(P-1)}{T} \tag{1f}$$

where $T$ is in $^\circ$K. We have given values of $A$, $B$, and $C$, derived by least-squares analysis, in Table 1. The sources of the thermodynamic data are also given there, with the exception of the data for $\text{Al}_2\text{O}_{3(\text{crystals})}$ and $\text{Al}_2\text{O}_{3(\text{glass})}$. Zen (1972) has suggested that the free energy of formation $(\Delta G^\circ{}_f)$ at $298^\circ$ of corundum should be decreased by 7 kilocals. We have accordingly recalculated $\Delta G^\circ{}_f$ for both $\text{Al}_2\text{O}_{3(\text{crystals})}$ and $\text{Al}_2\text{O}_{3(\text{liquid})}$ using this revision, and the values are given in Table 2. Values for $A$, $B$, and $C$ for all the reactions used in the sequel are given in Table 1. We have also assumed, as in the last paper, that the partial molar volumes of the solid components are independent of composition, or in other words, that so far as volume is concerned, the solid solutions are taken to be ideal. The logarithmic terms for the *solid* components in Equation 1b are therefore assumed to be independent of pressure.

Many mineral assemblages may define $a_{\text{Al}_2\text{O}_3}$, or act as $a_{\text{Al}_2\text{O}_3}$ buffers, and the reactions we will use are listed below.

$$\underset{\text{liquid}}{\text{Al}_2\text{O}_3} = \underset{\text{corundum}}{\text{Al}_2\text{O}_3} \tag{2}$$

and

$$\log a_{\text{Al}_2\text{O}_3}^{\text{liquid}} = \Delta G^\circ / 2.303 \, RT \tag{2a}$$

$$\underset{\text{glass}}{\text{SiO}_2} + \underset{\text{liquid}}{\text{Al}_2\text{O}_3} = \underset{\text{andalusite}}{\text{Al}_2\text{SiO}_5} \tag{3}$$
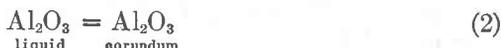
Table 1.  Values of $\Delta G°/2.303\ RT = A/T + B + C(P - 1)/T$

| Equation No. | | A | B | C | Source of Data |
|---|---|---|---|---|---|
| 1 | $CaMgSi_2O_6 + SiO_2 + Al_2O_3 = CaAl_2Si_2O_8 + MgSiO_3$ | -6662 | +1.156 | $\frac{0.1945}{T} - 0.72339 \times 10^{-4}$ | Roble and Waldbaum (1968) Table 2 |
| 2 | $Al_2O_3 \text{(liquid)} = Al_2O_3 \text{(corundum)}$ | -5846 | +2,476 | $\frac{0.1249}{T} - 0.72339 \times 10^{-4}$ | Zen (1971; JANAF tables; Table 2 |
| 3 | $Al_2O_3 + SiO_2 = Al_2SiO_5$ | -6548 | +2,800 | $\frac{0.1180}{T} - 0.72339 \times 10^{-4}$ | Roble and Waldbaum (1968) |
| 4 | $CaMgSi_2O_6 + \frac{1}{2}SiO_2 + Al_2O_3 = CaAl_2Si_2O_8 + \frac{1}{2}Mg_2SiO_4$ | -6145 | +0.858 | $\frac{0.2157}{T} - 0.72339 \times 10^{-4}$ | Roble and Waldbaum (1968) Table 2 |
| 5 | $CaMgSi_2O_6 + Al_2O_3 = CaAl_2SiO_6 + \frac{1}{2}SiO_2 + \frac{1}{2}Mg_2SiO_4$ | -4735 | +1,393 | $\frac{0.1634}{T} - 0.72339 \times 10^{-4}$ | Roble and Waldbaum (1968) Table 2 |
| 6 | $Mg_2SiO_4 + Al_2O_3 = MgSiO_3 + MgAl_2O_4$ | -8131 | +2,632 | $\frac{0.1344}{T} - 0.72339 \times 10^{-4}$ | Roble and Waldbaum (1968) Table 2 |
| 7 | $Mg_2SiO_4 + MgSiO_3 + SiO_2 + Al_2O_3 = Mg_3Al_2Si_3O_{12}^{*}$ | -9709 | +4,556 | $\frac{0.0475}{T} - 0.72339 \times 10^{-4}$ | Roble and Waldbaum (1968) MacGregor (1964); Table |
| 8 | $Mg_2SiO_4 + SiO_2 = 2MgSiO_3$ | -1034 | +0.597 | $\frac{-0.0424}{T}$ | Nicholls, Carmichael and Stormer (1971) |

\* See note on page

and

$$\log a_{Al_2O_3}^{liquid} = \Delta G°/2.303\ RT - \log a_{SiO_2}^{liquid} \tag{3a}$$

$$\underset{\text{diopside}}{CaMgSi_2O_6} + \underset{\text{glass}}{\tfrac{1}{2}SiO_2} + \underset{\text{liquid}}{Al_2O_3} = \underset{\text{anorthite}}{CaAl_2Si_2O_8} + \underset{\text{forsterite}}{\tfrac{1}{2}Mg_2SiO_4} \tag{4}$$

and
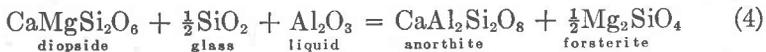
$$\log a_{Al_2O_3}^{liquid} = \Delta G°/2.303\ RT + \log\left[\frac{(a_{CaAl_2Si_2O_8}^{plagioclase}) \cdot (a_{Mg_2SiO_4}^{olivine})^{1/2}}{(a_{CaMgSi_2O_6}^{pyroxene})}\right]$$
$$- \tfrac{1}{2}\log a_{SiO_2}^{liquid} \tag{4a}$$

$$\underset{\text{diopside}}{CaMgSi_2O_6} + \underset{\text{liquid}}{Al_2O_3} = \underset{\substack{\text{Ca-Tschermaks}\\\text{pyroxene}}}{CaAl_2SiO_6} + \underset{\text{glass}}{\tfrac{1}{2}SiO_2} + \underset{\text{forsterite}}{\tfrac{1}{2}Mg_2SiO_4} \tag{5}$$

and

$$\log a_{Al_2O_3}^{liquid} = \Delta G°/2.303\ RT + \log\left[\frac{(a_{CaAl_2SiO_6}^{pyroxene}) \cdot (a_{Mg_2SiO_4}^{olivine})^{1/2}}{(a_{CaMgSi_2O_6}^{pyroxene})}\right]$$
$$- \tfrac{1}{2}\log a_{SiO_2}^{liquid} \tag{5a}$$

and for the two generalized mantle assemblages:

$$\underset{\text{forsterite}}{Mg_2SiO_4} + \underset{\text{liquid}}{Al_2O_3} = \underset{\text{enstatite}}{MgSiO_3} + \underset{\text{pleonaste}}{MgAl_2O_4} \tag{6}$$

and

$$\log a_{Al_2O_3}^{liquid} = \Delta G°/2.303\ RT$$
$$+ \log a_{MgSiO_3}^{pyroxene} + \log a_{MgAl_2O_4}^{spinel} - \log a_{Mg_2SiO_4}^{olivine} \tag{6a}$$

Table 2. $\Delta G_f^\circ/2.303 \ RT$ for $Al_2O_3$ (corundum) and $Al_2O_3$ (liquid) on the basis of $(\Delta G_f^\circ)_{298}$ for corundum of 371 kcals (Zen, 1971).

| T°K | $Al_2O_3$ (corundum) | $Al_2O_3$ (liquid) |
|---|---|---|
| 500 | −155.524 | −146.227 |
| 600 | −126.871 | −119.544 |
| 700 | −106.414 | −100.494 |
| 800 | − 91.080 | − 86.216 |
| 900 | − 79.163 | − 75.116 |
| 1000 | − 69.546 | − 66.160 |
| 1100 | − 61.653 | − 58.754 |
| 1200 | − 55.082 | − 52.680 |
| 1300 | − 49.527 | − 47.505 |
| 1400 | − 44.770 | − 43.072 |
| 1500 | − 40.650 | − 39.236 |
| 1600 | − 37.052 | − 35.882 |

$$\underset{\text{forsterite}}{Mg_2SiO_4} + \underset{\text{enstatite}}{MgSiO_3} + \underset{\text{glass}}{SiO_2} + \underset{\text{liquid}}{Al_2O_3} = \underset{\text{pyrope}}{Mg_3Al_2Si_3O_{12}} \tag{7}$$

and
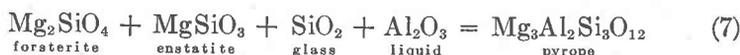
$$\log a_{Al_2O_3}^{liquid} = \Delta G^\circ/2.303 \ RT + \log a_{pyrope}^{garnet} - \log a_{Mg_2SiO_4}^{olivine} - \log a_{MgSiO_3}^{pyroxene}$$
$$- \log a_{SiO_2}^{liquid} \tag{7a}$$

but as $\Delta G^\circ_f$ for pyrope is not known, we have calculated it, as noted later, using MacGregor's (1964) experimental results. We also require a mineral assemblage which defines $\log a_{SiO_2}$ in our generalized peridotite composition; the following reaction is used:

$$\underset{\text{forsterite}}{Mg_2SiO_4} + \underset{\text{glass}}{SiO_2} = \underset{\text{enstatite}}{2MgSiO_3} \tag{8}$$

and

$$\log a_{SiO_2} = \Delta G^\circ/2.303 \ RT + 2 \log a_{MgSiO_3}^{pyroxene} - \log a_{Mg_2SiO_4}^{olivine} \tag{8a}$$

### THE VARIATION OF $a_{Al_2O_3}$ WITH PRESSURE

In the absence of an alumina buffer, the variation of $a_{Al_2O_3}$, in a silicate liquid or magma, with pressure can be obtained by differentiating

the following equation at constant temperature.

$$\mu_{Al_2O_3}^{liquid} = \mu_{Al_2O_3}^{\circ} + RT \ln a_{Al_2O_3}^{liquid} \tag{9}$$

where $\mu_{Al_2O_3}^{\circ}$ is the chemical potential of $Al_2O_3$ in the standard state, namely $Al_2O_3$ liquid. With the appropriate substitutions and re-arrangement we obtain

$$\left(\frac{\partial \log a_{Al_2O_3}}{\partial P}\right)_T = \frac{\bar{V}_{Al_2O_3} - V_{Al_2O_3}^{\circ}}{2.303\,RT} \tag{10}$$

where $V_{Al_2O_3}^{\circ}$ is the molar volume of pure $Al_2O_3$ liquid and $\bar{V}_{Al_2O_3}$ is the partial molar volume of $Al_2O_3$ in the silicate liquid or magma. If we make the assumption that $\bar{V}_{Al_2O_3} - V_{Al_2O_3}^{\circ}$ is independent of pressure, then Equation 10 can be integrated to give

$$(\log a_{Al_2O_3}^{liquid})_T^{P\ bars} = (\log a_{Al_2O_3}^{liquid})_T^{P=1\ bar} + \frac{\bar{V}_{Al_2O_3} - V_{Al_2O_3}^{\circ}}{2.303\,RT}(P-1) \tag{11}$$

Bottinga and Weill (1970) have calculated the partial molar volumes of many oxide components in liquid silicate systems for a range of temperature and composition. Least-squares analysis of their data for $\bar{V}_{Al_2O_3}$ over the temperature range 1573–1873°K gives

$$\bar{V}_{Al_2O_3} = 1.0195 \times 10^{-3}T(°K) + 36.25\ cc\ mole^{-1} \tag{12}$$

or

$$\bar{V}_{Al_2O_3} = .0243666 \times 10^{-3}T(°K) + .866396\ cal\ bar^{-1} \tag{12a}$$

The density of liquid $Al_2O_3$ is a linear function of temperature over the range 2300–2600°K (Kirshenbaum and Cahill, 1960), and least-squares analysis of their density data, recalculated in terms of molar volumes (cal bar$^{-1}$) yields

$$V_{Al_2O_3}^{\circ} = 0.331002 \times 10^{-3}T(°K) + .0398282\ cal\ bar^{-1} \tag{13}$$

Combining Equations 12a and 13 gives

$$\frac{\bar{V}_{Al_2O_3} - V_{Al_2O_3}^{\circ}}{2.303\,RT} = \frac{0.18061}{T} - 0.67002 \times 10^{-4} \tag{14}$$

By substituting Equation 14 into Equation 11, we get

$$(\log a_{Al_2O_3}^{liquid})_T^{P\ bar} = (\log a_{Al_2O_3})_T^{P=1\ bar}$$

$$+ \left[\frac{0.18061}{T} - 0.67002 \times 10^{-4}\right](P-1) \tag{11a}$$

Before applying Equation 11a to a natural example, it is appropriate

to consider the anhydrous aluminous minerals that occur in igneous rocks.

### Aluminous Minerals in Igneous Rocks

Anhydrous aluminous minerals in igneous, or igneous-looking, rocks are very rare and one of the most familiar examples is corundum in the nepheline-syenites of Blue Mountain, Ontario. Andalusite has been reported in granitic pegmatites (Deer, Howie, and Zussman, 1962), but the occurrence of any alumino-silicate (mullite, kyanite, sillimanite, or andalusite) is usually considered to be evidence for, or the result of, contamination of the magma.

In Figure 1 we have plotted log $a_{Al_2O_3}$ as a function of temperature for Equation 2 and Equation 3. As the andalusite curve falls below the corundum curve, cooling magmas with high silica activities will precipitate andalusite rather than corundum, but nepheline-syenites with lower silica-activities (Equation 3) will precipitate corundum, as
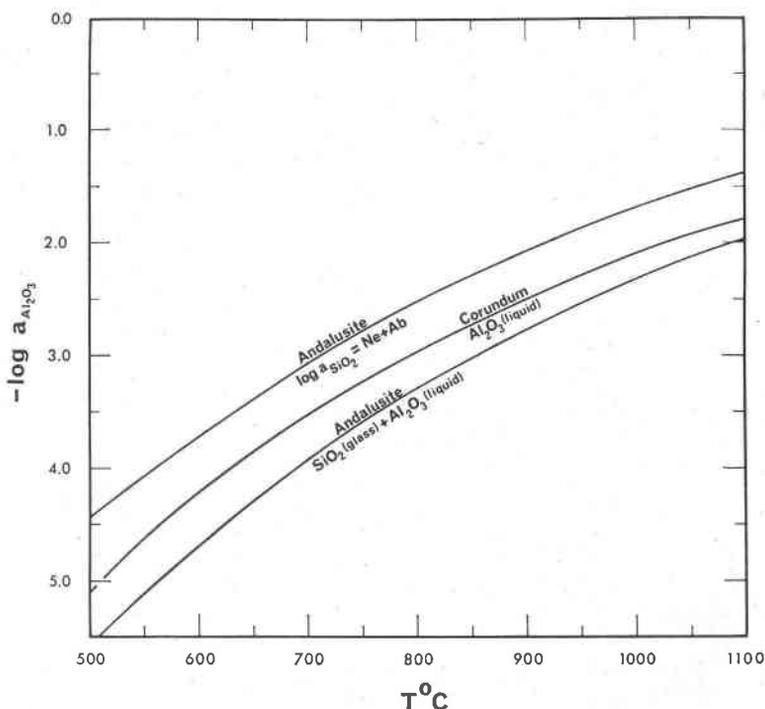


Fig. 1. The variation with temperature of log $a_{Al_2O_3}$ for the labelled reactions (Equation 2 and 3 in text). The upper curve corresponds to the lower curve except that log $a_{SiO_2}$ is defined by the reaction $\frac{1}{2}NaAlSiO_4 + SiO_2 = \frac{1}{2}NaAlSi_3O_8$.

the reduced activity of silica displaces the andalusite curve above the corundum curve (Fig. 1).

As an example of the calculation of the pressure at which a nepheline-trachyte (kenyte) magma could become saturated with corundum, we will use Equation 5 to estimate $\log a_{Al_2O_3}$ at 1 bar and at the quenching temperature, which we will arbitrarily take to be 900°C. Thus from Table 1 we get for Equation 4

$$(\log a_{Al_2O_3}^{liquid})^{P=1\ bar,1173} = -\frac{6145}{1173} + 0.858$$
$$+ \log \left[ \frac{(a_{Mg_2SiO_4}^{olivine})^{1/2} \cdot (a_{CaAl_2Si_2O_8}^{feldspar})}{(a_{CaMgSi_2O_6}^{pyroxene}) \cdot (a_{SiO_2}^{liquid})^{1/2}} \right] \quad (15)$$

In the paper on silica activity (Nicholls et al., 1971), we discussed the relationship between the activity, $a$, of a component in a solid solution and the mole fraction, $X$, of that component. It is sufficient to state here that the ideal mixing assumption ($\Delta H_{mix} = 0$) does not exclude an entropy term arising from the random mixing of atoms on different lattice sites, so that for the magnesian olivines, $a_{Mg_2SiO_4}^{olivine}$ can be taken to equal $X_{Mg_2SiO_4}^2$. (Nicholls et al., 1971). In all the other mineral components we have assumed $a = X$, unless noted otherwise. For the kenyte in question the mole fractions are: pyroxene 0.540 $CaMgSi_2O_6$; olivine 0.570 Fo; feldspar 0.191 An; and $\log a_{SiO_2}$ at 900°C is approximately $-0.6636$. Substitution of the relevant mineral data into the logarithmic terms of Equation 15 gives $\log a_{Al_2O_3}$ at 1 bar and 1173°K of $-4.7444$. If it is now assumed that the temperature of the kenyte lava is raised by a very small increment, so that the alumina and silica buffers dissolve, then $\log a_{Al_2O_3}$ will change in the liquid, due to increasing pressure, according to Equation 11a. Thus

$(\log a_{Al_2O_3}^{liquid})^{P=P\ bars}$

$$= (\log a_{Al_2O_3}^{liquid})^{P=1\ bar} + \left[ \frac{0.18061}{T} - 0.67002 \times 10^{-4} \right](P-1)$$

$$= -4.7444 + \left[ \frac{0.18061}{1173} - 0.67002 \times 10^{-4} \right](P-1) \quad (16)$$

If this kenyte liquid is to precipitate corundum at 900°C and some pressure, then $(\log a_{Al_2O_3})^{P=P\ bars}$ of Equation 16 must equal Equation 2 (Table 1) and hence we can solve for $P$. We obtain

$$-4.7444 + \left[ \frac{0.18061}{1173} - 0.67002 \times 10^{-4} \right](P-1)$$

$$= -\frac{5846}{1173} + 2.746 + \left[ \frac{0.1249}{1173} - 0.72339 \times 10^{-4} \right](P-1) \quad (17)$$

$$P = 47.4 \text{ kilobars.}$$

Similar calculations for metaluminous rhyolites ($Al < Na + K + Ca$) indicate that acid magmas at $850°C$ would not be saturated with either andalusite or corundum below 25–45 kbar; obviously for corundum or an alumino-silicate to precipitate in metaluminous magma requires extreme, and unlikely pressures, and the occurrence of these phases is more likely to be due either to contamination of the magma, or to a change in its composition, perhaps by loss of alkali (Luth *et al.*, 1964).

## THE EFFECT OF TEMPERATURE ON $a_{Al_2O_3}$

It is not geologically realistic to assume that a lava at depth was at the same temperature as that at which it was quenched on the earth's surface. We therefore have to take account of the influence of increasing temperature on $\log a_{Al_2O_3}$ in the absence of an alumina buffer assemblage. Thermodynamically the effect of temperature can be obtained by differentiating $\log a_{Al_2O_3}$ at constant pressure. If the appropriate substitutions are made, we obtain

$$\left(\frac{\partial \log a_{Al_2O_3}}{\partial T}\right)_P = -\frac{\bar{H}_{Al_2O_3} + H^\circ_{Al_2O_3}}{2.303\, RT^2} \tag{18}$$

where $\bar{H}_{Al_2O_3}$ is the partial molar enthalpy of $Al_2O_3$ in the magma or silicate liquid, and $H^\circ_{Al_2O_3}$ is the molar enthalpy of $Al_2O_3$ in pure $Al_2O_3$ liquid (the standard state). However, there are no data available to us on $\bar{H}_{Al_2O_3}$, so we are unable to use this approach.

Kudo and Weill (1970) have shown that silicate liquids can be treated as regular solutions, or, in other words, the activity coefficient $\gamma_i$ is a function of composition, $\phi_i$, which is itself independent of temperature. We can therefore write

$$\log \gamma_{Al_2O_3} = \log a_{Al_2O_3} - \log X_{Al_2O_3} = \frac{\phi_{Al_2O_3}}{T} \tag{19}$$

and in the appendix we provide data on the system $Na_2O$-$Al_2O_3$-$SiO_2$ to illustrate an example of our assumption of regular solution behavior. Any basic lava with a groundmass composed of plagioclase, pyroxene, and olivine, together with the iron-titanium oxides for a quenching temperature, can be used to give a value of $(\log a_{Al_2O_3})^{P=1\ bar}$ at the quenching temperature if the appropriate mineral compositions are substituted in Equation 1 or Equation 4. For basic lavas without a feldspar, such as a nephelinite or a ugandite, Equation 5 should be used, but this poses a problem of the random entropy of mixing term for $CaAl_2SiO_6$ in $CaMgSi_2O_6$; Verhoogen (1962) calculates that $a_{CaAl_2SiO_6} = X^2(2 - X)/4$ where $X$ is the mole fraction of $CaAl_2SiO_6$, which itself cannot be unambiguously calculated.[1]

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[1] In the only lava, a ugandite (Table 3), for which this component was used to calculate $\log a_{Al_2O_3}$, we assumed that the standard state of $CaAl_2SiO_6$ was disordered, and thus used $X^2(2 - X)$ to obtain the activity of $CaAl_2SiO_6$.

For any lava, $\log a_{Al_2O_3}$ at the quenching temperature can be calculated, and substituted into Equation 19, together with the mole fraction of $Al_2O_3$, $X_{Al_2O_3}$, which allows $\log \gamma_{Al_2O_3}$ or $\phi_{Al_2O_3}/T$ to be calculated for that particular lava. $\phi_i$ is dependent upon composition, but in what follows we assume that a particular lava can exist as a liquid of identical composition at elevated pressure and temperature. We are now in a position to calculate $\log a_{Al_2O_3}$ at any pressure (Equation 11a) or temperature (Equation 19) if it is known at 1 bar and the quenching temperature of the lava.

## Basic Lavas and Spinel-Peridotites

For a basic liquid to be in equilibrium with a spinel-peridotite, the chemical potentials or the activities of the various components in the liquid have to be identical to those defined by the solid assemblage. The mineral assemblage of a generalized spinel-peridotite can be plausibly represented by Equation 6 and from a perusal of the literature (O'Hara and Mercy, 1963; Green, 1964), typical compositions are 0.90 Fo, 0.85 En, and 0.75 $MgAl_2O_4$ for the spinel phase. Substitution of the mineral compositions into Equation 6 gives

$$(\log a_{Al_2O_3}^{peridotite})^{P,T} = -\frac{8131}{T} + 2.632 + \left[ \frac{0.1344}{T} - 0.72339 \times 10^{-4} \right]$$
$$\cdot (P - 1) - .104. \qquad (20)$$

Note that $\log a_{SiO_2}$ is also fixed by the presence of olivine and enstatite (Equation 8) and the value of this with the mineral compositions substituted is given by (Table 1)

$$(\log a_{SiO_2}^{peridotite})^{P,T} = -\frac{1034}{T} + 0.597 - \frac{0.0424}{T}(P - 1) - 0.050 \qquad (21)$$

For a liquid of basaltic composition, the variation of $\log a_{Al_2O_3}$ with pressure and temperature is given by either Equation 1 or Equation 4; for the example taken in detail here, we use the mineral data on a Recent trachybasalt (253) from southern California (Smith and Carmichael, 1969), and therefore Equation 4a is appropriate to obtain $\log a_{Al_2O_3}$ at 1 bar and 1253°K, the quenching temperature; this can be equated thus

$$(\log a_{Al_2O_3}^{liquid})^{P=1 \ bar, 1253} = \log X_{Al_2O_3} + \log \gamma_{Al_2O_3} \qquad (22)$$

$$= \log X_{Al_2O_3} + \frac{\phi_{Al_2O_3}}{1253} \qquad (23)$$

Substitution of the groundmass mineral compositions into Equation

Table 3. Calculated temperatures and pressures of equilibration of basic lavas with spinel- and garnet-peridotites

| Rock Type | Quenching Temperature T°C | 1 bar log $a_{SiO_2}$ | 1 bar log $a_{Al_2O_3}$ | $X_{SiO_2}$ | $X_{Al_2O_3}$ | $\phi_{SiO_2}$ | $\phi_{Al_2O_3}$ | Spinel-Peridotite T°C | Spinel-Peridotite P(kb) | Garnet-Peridotite T°C | Garnet-Peridotite P(kb) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 253 Trachybasalt S. California | 980 | -0.7724 | -3.8519 | 0.520 | 0.100 | -612.0 | -3573.4 | 1396 | 24.2 | 1321 | 22.7 |
| 256 Trachybasalt S. California | 995 | -0.8794 | -3.7077 | 0.516 | 0.101 | -750.6 | -3438.8 | 1546 | 30.8 | 1524 | 30.3 |
| U111 Ugandite Africa | 990 | -1.457 | -4.8369 | 0.477 | 0.063 | -1434.1 | -4592.5 | 1340 | 45.2 | 1658 | 51.6 |
| Hat Creek, High Alumina Basalt, California | 1050 | -0.8057 | -3.3689 | 0.512 | 0.108 | -681.3 | -3178.2 | 1648 | 31.2 | 1588 | 30.0 |
| Pre-1851 Quartz Basalt (basaltic-andesite), Lassen Park, California | 1000 | -0.2948 | -3.7722 | 0.597 | 0.101 | -90.1 | -3534.5 | 1065 | 2.2 | 767 | -3.6 |
| 339 Basaltic Andesite, Talasea, New Britain | 1000 | -0.3232 | -3.9604 | 0.592 | 0.100 | -121.6 | -3657.3 | 1033 | 2.5 | 752 | -3.0 |
| H-128 Olivine Tholeiite, Thingmuli, Iceland | 1100 | -0.2748 | -3.5315 | 0.511 | 0.095 | + 23.1 | -3445.1 | 1074 | 1.8 | 750 | -5.1 |

Data from Smith and Charmichael (1968, 1969), Brown (1971), Lowder (1970), Lowder and Carmichael (1970), Nicholls, Carmichael and Stormer (1971).

4a allows the left-hand side of Equation 22 to be calculated; the value is $-3.8519$. Substitution of the mole fraction ($X_{Al_2O_3} = 0.100$) allows $\phi_{Al_2O_3}$ to be obtained ($-3573.4$; Table 3). An exactly parallel procedure gives

$$(\log a_{SiO_2}^{liquid})^{P=1 \ bar, 1253} = \log X_{SiO_2} + \log \gamma_{SiO_2} \tag{24}$$

$$= \log X_{SiO_2} + \frac{\phi_{SiO_2}}{1253} \tag{25}$$

where $(\log a_{SiO_2}^{liquid})$ at 1 bar and 1253°K is taken from Nicholls *et al.* (1971; Table 3). The value of $\phi_{SiO_2}$ is $-612.0$ (Table 3).

The value of $\log a_{Al_2O_3}$ in the liquid at any elevated pressure and temperature is given by combining Equation 11a and Equation 23, and is given below

$$(\log a_{Al_2O_3}^{liquid})^{P, T}$$

$$= (\log a_{Al_2O_3}^{liquid})^{P=1 \ bar, \ T} + \left[\frac{0.18061}{T} - 0.67002 \times 01^{-4}\right](P - 1) \tag{26}$$

$$= \log X_{Al_2O_3} + \frac{\phi_{Al_2O_3}}{T} + \left[\frac{0.18061}{T} - 0.67002 \times 10^{-4}\right](P - 1) \tag{27}$$

$$= -1.0000 - \frac{3573.4}{T} + \left[\frac{0.18061}{T} - 0.67002 \times 10^{-4}\right](P - 1) \tag{28}$$

In an analogous way (Nicholls *et al.*, 1971)

$$(\log a_{SiO_2}^{liquid})^{P, T}$$

$$= (\log a_{SiO_2}^{liquid})^{P=1 \ bar, T} + \left[1.34 \times 10^{-6} - \frac{0.0047}{T}\right](P - 1) \tag{29}$$

$$= \log X_{SiO_2} + \frac{\phi_{SiO_2}}{T} + \left[1.34 \times 10^{-6} - \frac{0.0047}{T}\right](P - 1) \tag{30}$$

$$= -.2840 - \frac{612.0}{T} + \left[1.34 \times 10^{-6} - \frac{0.0047}{T}\right](P - 1) \tag{31}$$

Equations 20, 21, 28, and 31 are combined and re-arranged as a quadratic equation for $T$. Although there are two possible values for $T$, one is physically unreasonable, and a value of $P_{total}$ corresponding to the plausible temperature can be extracted for the equilibration of the trachybasalt 253 with a spinel-peridotite whose mineral compositions have been stated above. The calculated values for 253 are $T = 1396$°C and $P = 24.2$ kbar. In Table 3 we show the calculated temperatures and pressures which various lava-types could equilibrate with a spinel-peridotite; none of these results seems too discordant with the various speculations found in the literature. It is obvious that lavas with low silica-activities equilibrate at greater pressures with spinel-peridotite

than those with high-silica activities. As we have used a different expression for the effect of temperature on $a_{SiO_2}$ in the liquid than that used before (Nicholls *et al.*, 1971), the results in Table 3 are not exactly comparable to our previous estimates of $P_{total}$, which depended on estimating a temperature for each lava at depth.

## BASIC LAVAS AND GARNET-PERIDOTITES

Another possible mineral assemblage with which a basic magma could equilibrate at depths in the earth is garnet-peridotite, and Equation 7 represents a typical assemblage. However, free-energy data for pyrope are unknown, so the variation of log $a_{Al_2O_3}$ with temperature for Equation 7a cannot be calculated. So we have attempted to calculate $\Delta G°_f$ for pyrope using MacGregor's (1964) experimental results on the reaction

$$\underset{\text{enstatite}}{4MgSiO_3} + \underset{\text{pleonaste}}{MgAl_2O_4} = \underset{\text{forsterite}}{Mg_2SiO_4} + \underset{\text{pyrope}}{Mg_3Al_2Si_3O_{12}} \qquad (32)$$

He gave the following equation for the equilibrium curve:

$$T°C = 0.0546P - 173$$

where $P$ is the pressure in bars. Substituting $T°C = T°K - 273$ gives

$$T°K = 0.0546P + 100 \qquad (33)$$

The slope of the equilibrium curve is given by

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V} = \frac{1}{0.0546} \qquad (34)$$

from which we obtain

$$\Delta S = \frac{\Delta V}{0.0546} = -\frac{0.2037}{0.0546} = -3.731 \text{ e.u.}$$

using the molar volume data of Robie *et al.* (1967).

The temperature derivative of the Gibbs free energy of the reaction at constant pressure is given by

$$\left(\frac{\partial \Delta G}{\partial T}\right)_P = -\Delta S \qquad (35)$$

Integrating at constant pressure gives

$$\Delta G_{T_2} = \Delta G_{T_1} - T_2 \Delta S + T_1 \Delta S \qquad (36)$$

if we choose $T_1$ such that $\Delta G_{T_1}$ is zero (*i.e.*, $T = 0.0546P + 100$), and substitute into Equation 36, we get

$$\Delta G_{T_2} = -T_2 \Delta S + 0.0546P \Delta S + 100 \Delta S \qquad (37)$$

and

$$\Delta G_{T_2} = 3.731T + 0.2037P - 373.1$$

and dividing by 2.303 $RT$ gives

$$\frac{\Delta G}{2.303\,RT} = -\frac{81.5}{T} + 0.815 - \frac{0.0445}{T}\,P \qquad (38)$$

If pure enstatite is to be the standard state in Equation 32, some account must be taken of the extensive amounts of $Al_2O_3$ which dissolve in enstatite in equilibrium with pyrope, and Equation 37 can be re-written to include the reduced activity of the enstatite component

$$\frac{\Delta G}{2.303\,RT} = -\frac{81.5}{T} + 0.815 - \frac{0.0445}{T}\,P - 4\,\log a_{MgSiO_3}^{pyroxene} \qquad (39)$$

The solubility of $Al_2O_3$ in enstatite along the equilibrium curve (Boyd and MacGregor, 1964) with garnet, olivine, and spinel can be represented to a high degree of precision for $MgSiO_3 < 0.99$ by the equation

$$\log X_{MgSiO_3}^{pyroxene\ s.s.} = \frac{115.5}{T} - 0.1281 \qquad (40)$$

If it can be assumed that $a_{MgSiO_3} = X_{MgSiO_3}$, then Equation 39 becomes, by utilizing Equation 40,

$$\frac{\Delta G}{2.303\,RT} = -\frac{544}{T} + 1.327 - \frac{0.0445}{T}\,P \qquad (41)$$

If values of $\Delta G°_f$ for pleonaste, forsterite, and enstatite[1] (Robie and Waldbaum, 1968) are substituted into Equation 41, a value of $\Delta G°_f/$ 2.303 $RT$ for pyrope can be extracted, which, however, is subject to a rather large uncertainty because of the unknown mixing properties of $Al_2O_3$ in the enstatite solid solutions.

Using this estimate of the free energy of formation ($\Delta G°_f$) of pyrope from Equation 41, we can calculate $\Delta G°/2.303\,RT$ for Equation 7, our model mantle assemblage; the result of least-squares analysis is given in Table 1.

After that digression on estimating the thermodynamic data for pyrope, we return to estimating the temperature and pressure at which a basic lava would equilibrate with an assemblage represented by Equation 7 shown below:

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[1] The values given are for clinoenstatite, which will be only a few hundred calories different from enstatite.

$$Mg_2SiO_4 + MgSiO_3 + SiO_2 + Al_2O_3 = Mg_3Al_2Si_3O_{12} \quad (7)$$

forsterite    enstatite    glass    liquid    pyrope
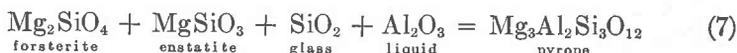
and

$$(\log a_{Al_2O_3}^{peridotite})^{P=1\ bar,\ T} = \Delta G^\circ / 2.303\ RT + \log a_{Mg_3Al_2Si_3O_{12}}^{garnet}$$
$$- \log a_{Mg_2SiO_4}^{olivine} - \log a_{MgSiO_3}^{pyroxene} - \log a_{SiO_2}^{liquid} \quad (7a)$$

we have taken as typical garnet-peridotite mineral compositions, olivine: 0.90 Fo; pyroxene: 0.85 En; and garnet: 0.65 pyrope, so that by substitution of these mineral compositions into the logarithmic terms[1] of Equation 7a, a value of $\log a_{Al_2O_3}$ can be obtained if $\log a_{SiO_2}$ is known. As olivine and enstatite coexist in Equation 7, $\log a_{SiO_2}$ is defined, and with the substitution of the relevant mineral compositions, $\log a_{SiO_2}$ can be obtained (Equation 8a). By subtracting Equation 7a from Equation 8a (Table 1), we obtain

$$(\log a_{Al_2O_3}^{peridotite})^{P,T} = -\frac{8675}{T} + 3.959 + \left[\frac{0.0899}{T} - 0.72339 \times 10^{-4}\right]$$
$$\cdot (P - 1) - 0.349 \quad (42)$$

where 0.349 is the sum of the activity terms.

At equilibrium, a basic liquid will have $\log a_{Al_2O_3}$ and $\log a_{SiO_2}$ equal to that defined by the mineral assemblage of the garnet-peridotite, and we now have to solve the equations in order to find the unique pressure and temperature at which this could occur. Again we take as an example the trachybasalt (253) from southern California, whose variation of $\log a_{Al_2O_3}$ and $\log a_{SiO_2}$ with pressure and temperature is given by Equation 28 and Equation 31, respectively. Combination of Equation 27, Equation 30, Equation 42, and Equation 8 with re-arrangement gives a quadratic equation for $T$, and the physically plausible value of $T$ is substituted to obtain $P$. For the trachybasalt 253 (Table 3) we obtain 1321°C and 22.7 kilobars as the temperature and pressure at which a liquid of identical composition to this lava would equilibrate with a garnet-peridotite of the assumed mineral composition. As may be seen from the data set down in Table 3, the pressures of equilibration do not differ greatly from those calculated for equilibration with spinel-peridotite. However, lavas such as the Icelandic olivine-tholeiite and the basaltic-andesites from New Britain and western U.S.A. equilibrate at low or negative pressures and at temperatures often lower than their 1 bar quenching temperatures. This strongly suggests that the origin of these particular lavas does not involve either spinel- or garnet-peridotite. They are either derivatives of a more basic parental liquid, and have

[1] Note that $a_{Mg_3Al_2Si_3O_{12}} = X^3_{Mg_3Al_2Si_3O_{12}}$ and $a_{Mg_2SiO_4} = X^2_{Mg_2SiO4}$.

fractionated at low pressure, or they have been generated by fusion of transformed oceanic crust (eclogite), and have remained segregated from mantle material containing spinel or garnet. In contrast, the equilibration temperatures and pressures for the ugandite lava (Table 3) indicate a region close to the diamond stability field (Clark, 1966). Perhaps the sporadic occurrence of diamonds in this part of the Uganda rift valley (Reece, 1961) is related to nearby explosion craters of this lava-type, which many petrologists believe to be related to kimberlite in accord with the pressure calculations.

One of the most characteristic lavas of the island arc volcanic suites are andesites with perhaps 55-60 percent $SiO_2$. The composition of andesite lavas, particularly $K_2O$, has been correlated to the depth of the underlying Benioff zone (Hatherton and Dickinson, 1969), and it is either in this zone, or in its intersection with the low-velocity zone (90-180 kilometres) that many geologists believe that andesite magma is generated.

A typical andesite lava is unlikely to have log $a_{SiO_2}$ lower than $-0.200$ at 1 bar and 1000°C, a reasonable quenching temperature. If we take the compositions of the groundmass minerals of a Shasta andesite (Smith and Carmichael, 1968), we can calculate the temperatures and pressures at which a magma of identical composition could equilibrate with either a spinel- or a garnet-peridotite. The results are shown below:

|  | $T°C$ | $P_{total}$ kilobars |
|---|---|---|
| Spinel-peridotite | 905 | $-3.9$ |
| Garnet-peridotite | 584 | $-9.9$ |

and suggest that andesite never equilibrated with a mantle of the assumed mineral compositions. Either andesite has a basaltic precursor, and is therefore the result of some fractionation process despite the relatively small volumes of associated basaltic lava, or andesite liquids are directly generated by the partial fusion of transformed oceanic crust (Green and Ringwood, 1968). If the latter hypothesis is correct, then this andesite magma must be completely segregated from mantle material in order to preserve its composition. This raises the possibility of the fractionation of quartz, with which the andesite liquid will become saturated at 42.3 kilobars and 1300°C (Nicholls et al., 1971); for andesite magma with higher silica activities than $-0.200$, which is itself a low estimate, the pressure at which quartz would precipitate would be lower. If the geological evidence was available to indicate that quartz never precipitated at depth in an andesitic magma, then the magma source region would be at a depth of less than 120 kilometers.

Although the calculations in this paper are precise within the limitations of the mineral and thermodynamic data, there is also considerable uncertainty in the composition of spinel and garnet in peridotites, compositions which themselves are likely to change with pressure and temperature. Until more is known of this variation, the calculated values will remain rather general; but with more data on mantle assemblages, and particularly on lavas of all types, precise values of $T$ and $P_{total}$ are possible. We have also assumed in this paper that any lava can exist as a liquid of identical composition at elevated temperatures and pressures, but it seems likely that the water content may increase with depth. Unfortunately, we have no way at present to evaluate the effect of increasing water content on log $a_{SiO_2}$ and log $a_{Al_2O_3}$ in the absence of a mineral buffer assemblage; possibly the effect could substantially modify the calculated values of temperature and $P_{total}$ shown in Table 3.

### APPENDIX

In the system $Na_2O$-$Al_2O_3$-$SiO_2$, alumina activities for liquids in equilibrium with corundum at one bar will be given by Equation 2:

$$\log a_{Al_2O_3}^{liquid} = -\frac{5486}{T°K} + 2.476 \text{ (Table 1)} \tag{A-1}$$

The logarithm of the activity coefficient of $Al_2O_3$ will be given by:

$$\log \gamma_{Al_2O_3}^{liquid} = \log a_{Al_2O_3}^{liquid} - \log X_{Al_2O_3}^{liquid} \tag{A-2}$$

This we assume to have the form:

$$\log \gamma_{Al_2O_3}^{liquid} = \frac{\phi}{T} \tag{A-3}$$

where $\phi$ is a function of composition only. In a three-component system there are only two independent compositional variables, which we choose to be $X_{SiO_2}^{liquid}$ and $X_{Na_2O}^{liquid}$. A second-degree equation for a symmetric ternary solution (Thompson, 1967) in these two variables is:

$$\phi = T[\log a_{Al_2O_3}^{liquid} - \log X_{Al_2O_3}^{liquid}] = a_1 X_{SiO_2}^2 + a_2 X_{Na_2O}^2 + a_3 X_{SiO_2} X_{Na_2O} \tag{A-4}$$

where $a_1$, $a_2$, and $a_3$ are constants solely related to this power series.

Using the data plotted and tabulated by Schairer and Bowen (1956), values of $\phi$ were calculated for various liquids in equilibrium with corundum at known temperatures by combining equations (A-1) and (A-2):

$$\phi = T - \frac{5486}{T} + 2.476 - \log X_{Al_2O_3}^{liquid}. \tag{A-5}$$

A least-squares analysis of the resulting data for $\phi$ and composition gave the following values for the constants in equation (A-4) :

$$a_1 = -2297.7$$

$$a_2 = 2538.5$$

$$a_3 = -1879.4$$

A comparison of $\log a_{Al_2O_3}^{liquid}$ values calculated from equation (A-1) and from:

$$\log a_{Al_2O_3}^{liquid} = \log X_{Al_2O_3}^{liquid} + \frac{a_1}{T}X_{SiO_2} + \frac{a_2}{T}X_{Na_2O} + \frac{a_3}{T}X_{Na_2O}X_{SiO_2} \tag{A-6}$$

can be made as follows for a range of temperatures.

| Eq. (A-1) | Eq. (A-6) |
|---|---|
| − .8684 | − .8766 |
| −1.0183 | −1.0166 |
| −1.2405 | −1.2638 |
| −1.8997 | −1.7411 |
| −1.3127 | −1.3410 |
| −1.4928 | −1.5069 |
| −1.7818 | −1.7010 |
| −1.7818 | −1.8083 |
| −1.7572 | −1.8880 |

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