Contr. Mineral. and Petrol. 33, 1–20 (1971)

Silica Activity and P_{total} in Igneous Rocks

J. Nicholls
Dept. of Geology, University of Calgary, Alberta, Canada
I. S. E. Carmichael
Dept. of Geology and Geophysics, University of California, Berkeley, Calif. 94720
J. C. Stormer, Jr.
Dept. of Geology, University of Georgia, Athens, Georgia 30601

Received July 16, 1971

Abstract. The variation of silica activity with temperature and pressure for a variety of silica buffers (mineral pairs) allows P_{total} to be calculated for a wide range of igneous rocks. The method also depends on evaluating $(\partial \log a_{\text{SiO}_2}/\partial P)_T$ and $(\Delta \log a_{\text{SiO}_2}/\Delta T)_P$; the former is equivalent to the partial molar volume of silica in silicate liquids, while the latter is estimated from published experiments on natural melts. Results for calc-alkaline rhyolites with phenocrysts of quartz, olivine or orthopyroxene, and iron-titanium oxides, range from 3.45 to 9.58 kilobars; a pantellerite is intermediate at 7.53 kilobars. At 1327° C, the silicate inclusions in diamond equilibrated at 63.5 kilobars, and the kimberlite crystallisation path intersected the baddeleyite-zircon reaction at 55.7 kilobars. Two trachybasalts would equilibrate with their lherzolite xenoliths at 17.0 and 21.0 kilobars at surface quenching temperatures. Potassic lavas such as orendites and ugandites at 1300° C would be in equilibrium with mantle olivine-orthropyroxene at 35.1 and 69.0 kilobars respectively. Basalts and basaltic-andesites could equilibrate (at 1100° C) with quartz at between 24.9 and 26.8 kilobars; quartz can therefore be considered a possible high pressure "xenocryst" in lavas with low Sr^{87}/Sr^{86} ratios. Andesites will equilibrate at 1300° C with the mantle at a depth of 75 kilometres; at greater depths andesite will have a basaltic precursor. In general, lavas with low silica activity will equilibrate at greater depths in the mantle than those with higher silica activities.

The Apollo 11 basalts contain minerals which suggest equilibration at 37 kilobars; the calculated quenching temperature is 1009° C, from which $\log f_{O_2}$ can be derived (−15.2) which in turn indicates approximately 0.10% Fe_2O_3 in these lavas.

Introduction

In another paper on silica activity (a_{SiO_2}) in igneous rocks (Carmichael *et al.*, 1970) we examined the variation of a_{SiO_2} with temperature for a variety of mineral pairs, each of which would buffer or define silica activity in any magma in which they occur. However, despite a vast amount of work on experimental silicate equilibria, there is no generally applicable method of extracting estimates of total pressure (P_{total}) from igneous mineral assemblages. It now seems possible, within the limitations of the thermodynamic data, to use a_{SiO_2} to estimate P_{total} for a wide variety of igneous rocks; the procedure depends on only a few, and reasonable, assumptions.

As there has been an influx of new thermochemical data in the last two or three years, we have been able to add to the reactions which define a_{SiO_2} in igneous rocks, and, as a prelude to the discussion of the effect of P_{total} on a_{SiO_2}, we first summarise the effect of temperature.

If for example, crystals of pure fayalite and ferrosilite coexist in equilibrium with a silicate liquid, then the activity of silica in that liquid is only a function of temperature at constant pressure. The variation of $a_{\mathrm{SiO_2}}$ can be calculated from the reaction:

$$\underset{\text{fayalite}}{\mathrm{Fe_2SiO_4}} + \underset{\text{glass}}{\mathrm{SiO_2}} = \underset{\text{ferrosilite}}{\mathrm{2\,FeSiO_3}} \tag{1}$$

which at equilibrium ($\Delta\,\mathrm{G} = 0$) gives

$$\log a^{\text{liquid}}_{\mathrm{SiO_2}} = \Delta\,\mathrm{G^0/2.303\,RT} + 2\log a^{\text{pyroxene}}_{\mathrm{FeSiO_3}} - \log a^{\text{olivine}}_{\mathrm{Fe_2SiO_4}}. \tag{1a}$$

For the components in their standard states (pure solids of unit activity and silica glass) at the temperature of interest and a pressure of 1 bar, the variation of $\log a^{\text{liquid}}_{\mathrm{SiO_2}}$ with temperature can be represented by an equation of the form $A/T + B$. The two constants A and B, derived by least-squares analysis, are given in Table 1 for Eq. (1) and for the other reactions listed below. However as both fayalite and ferrosilite form solid solutions in nature, the reduced activity of the two components $\mathrm{Fe_2SiO_4}$ and $\mathrm{FeSiO_3}$ (subscripts) in their respective solid solutions (superscripts) is accounted for by the logarithm terms in Eq. (1a).

Other reactions which we will use in this paper are:

$$\underset{\text{glass}}{\mathrm{SiO_2}} = \underset{\text{quartz}}{\mathrm{SiO_2}} \tag{2}$$

and

$$\log a^{\text{liquid}}_{\mathrm{SiO_2}} = \Delta\,\mathrm{G^0/2.303\,RT}.$$

$$\underset{\text{forsterite}}{\mathrm{Mg_2SiO_4}} + \underset{\text{glass}}{\mathrm{SiO_2}} = \underset{\text{clinoenstatite}}{\mathrm{2\,MgSiO_3}} \tag{3}$$

and

$$\log a^{\text{liquid}}_{\mathrm{SiO_2}} = \Delta\,\mathrm{G^0/2.303\,RT} + 2\log a^{\text{pyroxene}}_{\mathrm{MgSiO_3}} - \log a^{\text{olivine}}_{\mathrm{Mg_2SiO_4}}. \tag{3a}$$

$$\underset{\text{baddeleyite}}{\mathrm{ZrO_2}} + \underset{\text{glass}}{\mathrm{SiO_2}} = \underset{\text{zircon}}{\mathrm{ZrSiO_4}} \tag{4}$$

and

$$\log a^{\text{liquid}}_{\mathrm{SiO_2}} = \Delta\,\mathrm{G^0/2.303\,RT} + \log a^{\text{zircon}}_{\mathrm{ZrSiO_4}} - \log a^{\text{baddeleyite}}_{\mathrm{ZrO_2}}. \tag{4a}$$

$$\underset{\beta\text{-nepheline}}{\tfrac{1}{2}\,\mathrm{NaAlSiO_4}} + \underset{\text{glass}}{\mathrm{SiO_2}} = \underset{\text{high-albite}}{\tfrac{1}{2}\,\mathrm{NaAlSi_3O_8}} \text{ for } T < 907^\circ\mathrm{C}, \tag{5}$$

at

$$T > 907^\circ\mathrm{C}$$

$$\underset{\gamma\text{-nepheline}}{\tfrac{1}{2}\,\mathrm{NaAlSiO_4}} + \underset{\text{glass}}{\mathrm{SiO_2}} = \underset{\text{high-albite}}{\tfrac{1}{2}\,\mathrm{NaAlSi_3O_8}} \tag{6}$$

and

$$\log a^{\text{liquid}}_{\mathrm{SiO_2}} = \Delta\,\mathrm{G^0/2.303\,RT} + \tfrac{1}{2}\log a^{\text{feldspar}}_{\mathrm{NaAlSi_3O_8}} - \tfrac{1}{2}\log a^{\text{nepheline}}_{\mathrm{NaAlSiO_4}}. \tag{6a}$$

$$\underset{\text{leucite}}{\mathrm{KAlSi_2O_6}} + \underset{\text{glass}}{\mathrm{SiO_2}} = \underset{\text{sanidine}}{\mathrm{KAlSi_3O_8}} \tag{7}$$

and

$$\log a_{\mathrm{SiO_2}}^{\mathrm{liquid}} = \Delta G^0/2.303\ \mathrm{RT} + \log a_{\mathrm{KAlSi_3O_8}}^{\mathrm{feldspar}} - \log a_{\mathrm{KAlSi_2O_6}}^{\mathrm{leucite}}. \tag{7a}$$

$$\underset{\alpha\text{-perovskite}}{\mathrm{CaTiO_3}} + \underset{\text{glass}}{\mathrm{SiO_2}} = \underset{\text{sphene}}{\mathrm{CaTiSiO_5}} \tag{8}$$

and

$$\log a_{\mathrm{SiO_2}}^{\mathrm{liquid}} = \Delta G^0/2.303\ \mathrm{RT} + \log a_{\mathrm{CaTiSiO_5}}^{\mathrm{sphene}} - \log a_{\mathrm{CaTiO_3}}^{\mathrm{perovskite}}. \tag{8a}$$

$$\underset{\text{kaliophilite}}{\mathrm{KAlSiO_4}} + \underset{\text{glass}}{\mathrm{SiO_2}} = \underset{\text{leucite}}{\mathrm{KAlSi_2O_6}} \tag{9}$$

and

$$\log a_{\mathrm{SiO_2}}^{\mathrm{liquid}} = \Delta G^0/2.303\ \mathrm{RT} + \log a_{\mathrm{KAlSi_2O_6}}^{\mathrm{leucite}} - \log a_{\mathrm{KAlSiO_4}}^{\mathrm{kaliophilite}}. \tag{9a}$$

$$\tfrac{2}{3}\ \underset{\text{magnetite}}{\mathrm{Fe_3O_4}} + \underset{\text{glass}}{\mathrm{SiO_2}} = \underset{\text{fayalite}}{\mathrm{Fe_2SiO_4}} + \tfrac{1}{3}\ \mathrm{O_2} \tag{10}$$

and

$$\log a_{\mathrm{SiO_2}}^{\mathrm{liquid}} = \Delta G^0/2.303\ \mathrm{RT} + \log a_{\mathrm{Fe_2SiO_4}}^{\mathrm{olivine}} + \tfrac{1}{3} \log f_{\mathrm{O_2}} - \tfrac{2}{3} \log a_{\mathrm{Fe_3O_4}}^{\mathrm{magnetite}}. \tag{10a}$$

$$\tfrac{1}{3}\ \underset{\text{magnetite}}{\mathrm{Fe_3O_4}} + \underset{\text{glass}}{\mathrm{SiO_2}} = \underset{\text{ferrosilite}}{\mathrm{FeSiO_3}} + \tfrac{1}{6}\ \mathrm{O_2} \tag{11}$$

and

$$\log a_{\mathrm{SiO_2}}^{\mathrm{liquid}} = \Delta G^0/2.303\ \mathrm{RT} + \log a_{\mathrm{FeSiO_3}}^{\mathrm{pyroxene}} + \tfrac{1}{6} \log f_{\mathrm{O_2}} - \tfrac{1}{3} \log a_{\mathrm{Fe_3O_4}}^{\mathrm{magnetite}}. \tag{11a}$$

The sources of the thermodynamic data used to calculate the A and B constants for each of the above reactions are given in Table 1. Data taken from Wones and Gilbert (1969) and Williams (1971) have been changed so that the standard state of silica is silica glass rather than quartz.

The variation of $\log a_{\mathrm{SiO_2}}^{\mathrm{liquid}}$ with temperature at 1 bar for the above reactions is plotted in Fig. 1, and updates the curves given previously by Carmichael *et al.* (1970). None of the conclusions suggested by them need to be modified in the light of the new data for kaliophilite, leucite and zircon. However, Williams (1970) has stated that the free energy of formation (ΔG_f^0) of enstatite should be decreased by about a kilocalorie. If this was applied equally over the temperature range shown in Fig. 1, it would depress the Fo–En curve so that it would intersect the Ab-Ne curve at about 770° C. As olivine, rather than orthopyroxene, is found with nepheline in trachytes and phonolites, it would appear that the data for nepheline are in error if William's enstatite measurements are correct.

The Effect of Pressure on $a_{\mathrm{SiO_2}}$

The effect of pressure on a silica buffer can be obtained by differentiating Eqs. (1) to (9) at constant temperature and assuming for the present that the solids have unit activity. Thus

$$\left(\frac{\partial \log a_{\mathrm{SiO_2}}^{\mathrm{liquid}}}{\partial P}\right)_T = \frac{1}{2.303\ \mathrm{RT}} \left(\frac{\partial \Delta G^0}{\partial P}\right)_T = \frac{\Delta V^0}{2.303\ \mathrm{RT}}, \tag{12}$$

where ΔV^0 is the volume change of the reaction for the components in their standard states. It will be assumed that the molar volume, ΔV^0, is independent

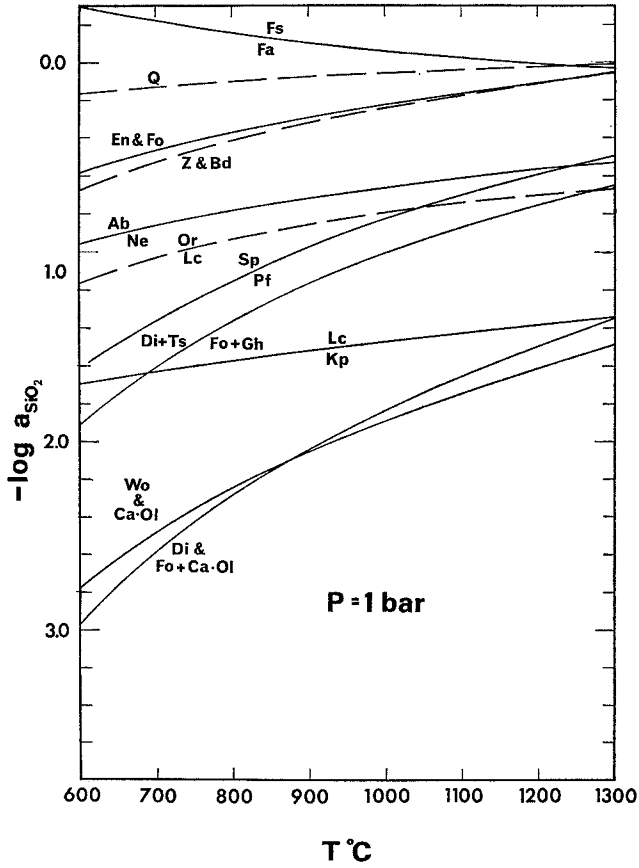

Fig. 1. Variation of $\log a_{\text{SiO}_2}$ with temperature at 1 bar for silica buffer reactions. In each case the desilicated mineral is stable at lower values of $\log a_{\text{SiO}_2}$. All reactions are explained in the text except for Fo + Gh + SiO$_2$ = Di + Ts which corresponds to $Mg_2SiO_4 + Ca_2Al_2SiO_7 + SiO_2 = CaMgSi_2O_6 + CaAl_2SiO_6$

of pressure; this is reasonable as the effect of temperature (800–1300° C) on increasing ΔV^0_{298} will be offset by the effect of pressure contracting ΔV^0, at least up to 10 kilobars. Thus (Eq. (12) can be integrated to give

$$(\log a^{\text{liquid}}_{\text{SiO}_2})^{P=P\text{ bars}} = (\log a^{\text{liquid}}_{\text{SiO}_2})^{P=1\text{ bar}} + \frac{\Delta V^0}{2.303\,\text{RT}}(P-1) \qquad (13)$$

where P is the pressure in bars. As $\frac{\Delta V^0}{2.303\,\text{R}}$ is a constant, values of $C = \frac{\Delta V^0}{2.303\,\text{R}}$ are given in Table 1 for each of the reactions listed above. The variation of $\log a_{\text{SiO}_2}$ with pressure at 1000° C (1273° K) for each of the reactions is plotted in Fig. 2. Note that with the exception of the kaliophilite-leucite reaction, all the slopes are negative, so that for all but the most silica-poor igneous rocks, an increase of pressure at constant T and composition promotes the presence of the more siliceous mineral of each buffer pair.

Table 1. *Coefficients A, B and C for the equation* $\log a_{\text{SiO}_2} = \Delta G^0/2.303\,RT = A/T + B + C\,(P-1)/T$ *for the listed reactions*

Eq. No.	Reaction	A	B	C	Source of Data
(1)	$Fe_2SiO_4 + SiO_2(gl) = 2FeSiO_3$	663	−0.46	−0.0406	Williams (1971), Robie and Waldbaum (1968), Kelley (1960)
(2)	$SiO_2(gl) = SiO_2(\beta - Q)$	−309	+0.183	−0.0239	Robie and Waldbaum (1968)
(3)	$Mg_2SiO_4 + SiO_2(gl) = MgSiO_3$	−1034	+0.597	−0.0424	Robie and Waldbaum (1968), Kelley (1960)
(4)	$ZrO_2 + SiO_2(gl) = ZrSiO_4$	−1228	+0.730	−0.0478	Kelley (1960), Robie and Waldbaum (1968), JANAF Tables
(5)	$\frac{1}{2}NaAlSiO_4(\beta) + SiO_2(gl) = \frac{1}{2}NaAlSi_3O_8$ ($T < 907°$ C)	−871	+0.031	−0.0216	Kelley (1960), Robie and Waldbaum (1968)
(6)	$\frac{1}{2}NaAlSiO_4(\gamma) + SiO_2(gl) = \frac{1}{2}NaAlSi_3O_8$ ($T > 907°$ C)	−855	+0.012	−0.0216	Robie and Waldbaum (1968), Kelley (1960)
(7)	$KAlSi_2O_6 + SiO_2(gl) = KAlSi_3O_8$	−972	−0.039	−0.0345	Robie and Waldbaum (1968); for leucite: ΔH_f^0—Kelley (1962) and Cp, Pankratz (1968)
(8)	$\alpha CaTiO_3 + SiO_2(gl) = CaTiSiO_5$	−2203	+0.905	−0.0274	Robie and Waldbaum (1968), Kelley (1960)
(9)	$KAlSiO_4(Kp) + SiO_2(gl) = KAlSi_2O_6$	−685	−0.928	+0.0064	Robie and Waldbaum (1968), and Cp—Pankratz (1968)
(10)	$^2/_3Fe_3O_4 + SiO_2(gl) = Fe_2SiO_4 + {}^1/_3O_2$	8270	−2.81	−0.0552	Wones and Gilbert (1969), Robie and Waldbaum (1968)
(11)	$^1/_3Fe_3O_4 + SiO_2(gl) = FeSiO_3 + {}^1/_6O_2$	4467	−1.63	−0.0479	Williams (1971), Robie and Waldbaum (1968)

A and B were obtained by a linear least squares analysis of calculated 1 bar data for $(\Delta G^0)/2.303$ RT.

It is also assumed that in all the solid solutions represented in Eqs. (1a) to (10a) by the logarithmic terms, the partial molar volume of each component is independent of composition, or in other words, so far as volume is concerned, the solid solutions are considered to be ideal. Thus the logarithmic activity terms in Eqs. (1a) to (10a) are assumed to be independent of pressure.

In any silicate liquid, the chemical potential of silica, is given by

$$\mu_{\text{SiO}_2}^{\text{liquid}} = \mu_{\text{SiO}_2}^{0} + \text{RT} \ln a_{\text{SiO}_2}^{\text{liquid}} \tag{14}$$

where $\mu_{\text{SiO}_2}^{0}$ is the chemical potential of silica in the standard state, namely silica glass. If Eq. (14) is differentiated at constant temperature, re-arranged and the appropriate substitutions made, then we obtain:

$$\left(\frac{\partial \log a_{\text{SiO}_2}^{\text{liquid}}}{\partial P}\right)_T = \frac{\overline{V}_{\text{SiO}_2} - V_{\text{SiO}_2}^{0}}{2.303\,\text{RT}} \tag{15}$$

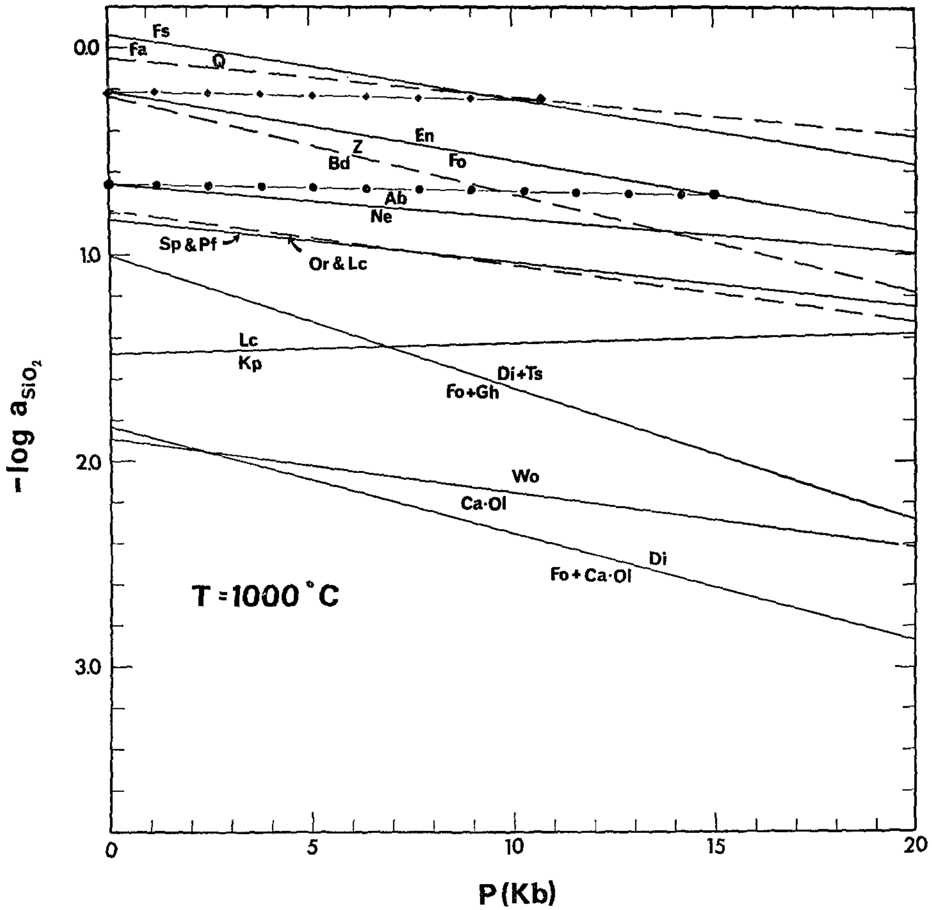

Fig. 2. The variation of log a_{SiO_2} with pressure at 1000° C for the mineral buffer reactions shown in Fig. 1. Note that all have negative slopes except for the Kp-Lc curve. The two dotted curves refer to the variation of log a_{SiO_2} as a function of pressure $(\bar{V}_{SiO_2} - V^0_{SiO_2})(P-1)/2.303\,RT$ in the absence of a silica buffer

where V^0 is the molar volume of pure silica glass, and $\bar{V}$ is the partial molar volume of SiO_2 in the silicate liquid or magma. Again we assume that the volumes are independent of pressure, so that Eq. (15) can be integrated at constant temperature to give:

$$(\log a^{\text{liquid}}_{SiO_2})^{P=P\text{ bars}} = (\log a^{\text{liquid}}_{SiO_2})^{P=1\text{ bar}} + \frac{\bar{V}_{SiO_2} - V^0_{SiO_2}}{2.303\,RT}(P-1). \qquad (16)$$

Bottinga and Weill (1970) have evaluated the partial molar volumes, $\bar{V}$, of many oxide components in liquid silicate systems for a large range of composition and temperature. Least-squares analysis of their data for $\bar{V}_{SiO_2}$ over the temperature range 1250°–1600° C gives:

$$\bar{V}_{SiO_2} = 2.573 \times 10^{-4}\,T\,(°\text{K}) + 26.37 \text{ c.c. mole}^{-1}$$

which with change of units (to cal. bar^{-1}) and substitution of $V^0_{\text{SiO}_2}$ gives:

$$\frac{\overline{V}-V^0}{2.303\,\text{RT}} = 1.34\times10^{-6} - \frac{0.0047}{T}\,. \tag{17}$$

By substitution of Eq. (17) into Eq. (16), we obtain:

$$(\log a^{\text{liquid}}_{\text{SiO}_2})^{P=P\text{ bar}} = (\log a^{\text{liquid}}_{\text{SiO}_2})^{P=1\text{ bar}} + \left[1.34\times10^{-6} - \frac{0.0047}{T}\right](P-1)\,. \tag{18}$$

Two hypothetical examples of the determination of P_{total} are shown in Fig. 2. Let us suppose that a basaltic lava has a glassy groundmass which was quenched at 1000° C and 1 bar, and $\log a^{\text{liquid}}_{\text{SiO}_2}$ is -0.219 (Fig. 2). The effect of pressure on $\log a^{\text{liquid}}_{\text{SiO}_2}$ at 1000° C using Eq. (18) is shown by the upper dotted curve in Fig. 2 assuming that a silica buffer is not present. This curve intersects the Quartz curve at 10.8 kilobars, so that the hypothetical basaltic liquid, at constant temperature and constant composition, would be saturated with quartz at pressures in excess of 10.8 kilobars. As another example, assume that a phonolitic lava is quenched at 1000° C on the surface to an assemblage of glass with microlites of nepheline and albite; then $\log a^{\text{liquid}}_{\text{SiO}_2}$ would be equal to -0.629 (Fig. 2). In the absence of a silica buffer, i.e., either nepheline or albite (or both) disappears, then $\log a^{\text{liquid}}_{\text{SiO}_2}$ will vary with pressure (Eq. 18) as shown by the lower dotted line in Fig. 2. A phonolitic liquid at 1000° C would therefore be in equilibrium with forsterite and enstatite at a pressure of 15 kilobars.

Before applying these equations to actual examples with measured mineral compositions, it is necessary to digress into the relationship between the activity, *a*, of a component in a solid solution, and the mole fraction, *X*, of that component. Williams (1971) has given the following equations relating activity to composition for olivines and the calcium-poor pyroxenes.

$$\log a_{\text{FeSiO}_3} = 0.22\,(1 - X_{\text{FeSiO}_3})^2 + \log X_{\text{FeSiO}_3}\,,$$
$$\log a_{\text{MgSiO}_3} = 0.22\,(1 - X_{\text{MgSiO}_3})^2 + \log X_{\text{MgSiO}_3}\,,$$
$$\log a_{\text{FeSi}_{0.5}\text{O}_2} = 0.16\,(1 - X_{\text{Fe}_2\text{SiO}_4})^2 + \log X_{\text{Fe}_2\text{SiO}_4}\,,$$
$$\log a_{\text{MgSi}_{0.5}\text{O}_2} = 0.16\,(1 - X_{\text{Mg}_2\text{SiO}_4})^2 + \log X_{\text{Mg}_2\text{SiO}_4}\,.$$

He indicates that these equations apply in the temperature range 900–1400° C and for pressures up to 10 kilobars. These equations contrast to the ideal mixing relationship ($\Delta H_{\text{mix}} = 0$) which for calcium-poor pyroxenes would be $X_{\text{FeSiO}_3} = a_{\text{FeSiO}_3}$ and for olivines, $a_{\text{Mg}_2\text{SiO}_4} = X^2_{\text{Mg}_2\text{SiO}_4}$, the squared term arising from an assumed random entropy of mixing on two lattice sites.

As an example of the application of William's equations, and their contrast to the ideal mixing relationship for olivine, we will use the mineral data obtained by Brown (1971) on a ugandite lava (U.111). The groundmass contains kalsilite (0.95 Kp), leucite (0.99 Lc), olivine (0.13 Fa), ilmenite and titanomagnetite (0.346 Mt). Using Buddington and Lindsley's (1964) curves, the co-existing iron-titanium oxides give an equilibration temperature of 990° C and $\log f_{\text{O}_2}$ of -11.2. Substitution of the kaliophilite-leucite data into Eq. (9a) gives a value for $\log a^{\text{liquid}}_{\text{SiO}_2}$ of -1.457 at 990° C. Substitution of the relevant mole fractions and f_{O_2} into Eq. (10a) at the same temperature gives a value of $\log a_{\text{SiO}_2}$ of -1.457

Table 2. *Values of P_{total} for quartz bearing acid lavas*

Locality and sample No.	$X_{Fe_2SiO_4}$	X_{FeSiO_3}	$T°$ C	$\log f_{O_2}$	$X_{Fe_3O_4}$	P_{total} (a = Williams) kilobars	P_{total} ($a = X$ or X^2) kilobars	P_{H_2O} [a] bars
Arran, Scotland (AC.7)	0.879	—	900	−12.9	0.442	5.62	5.44	—
Pantelleria (3112)	0.862	—	1025	−11.2	0.236	7.53	7.28	—
Mono Craters, California								
Cam. 73	0.893	—	810	−14.7	0.564	3.45	3.33	—
Cam. 99	0.893	—	790	−15.1	0.588	3.62	3.50	—
Cam. 86	—	0.629	940	−11.1	0.577	9.25	7.71	—
Cam. 93	—	0.630	960	−10.9	0.573	7.45	6.19	—
Cam. 95	—	0.664	850	−13.2	0.590	7.64	6.48	—
Lassen Peak, California								
Cal. 19	—	0.293	865	−10.9	0.844	7.83	2.61	265
Talasea, New Britain								
196	—	0.35	920	−10.5	0.768	4.94	0.30	—
279B	—	0.30	860	−11.5	0.802	3.82	−1.29	—
Taupo Region, New Zealand								
P30411	—	0.45	745	−14.6	0.783	9.58	6.77	1800
P30407	—	0.45	740	−14.6	0.783	9.58	6.77	1650
P28360	—	0.45	735	−15.2	0.752	6.12	3.32	1500
P27574	—	0.45	780	−13.6	0.755	8.91	5.99	—
P27575	—	0.447	755	−14.6	0.744	6.99	4.11	—
P27576	—	0.412	760	−14.1	0.758	8.24	4.97	—
P27580	—	0.408	755	−14.4	0.752	6.49	3.19	—
P27573	—	0.45	770	−14.0	0.752	8.55	5.66	—
P27579	—	0.45	750	−15.0	0.729	4.68	1.84	—
Average of calc-alkaline rhyolites						6.82	4.27	—

[a] P_{H_2O} has been calculated from f_{H_2O} using the tables of Burnham *et al.* (1969); f_{H_2O} was not corrected for P_{total}, which is equal to $P \Delta V_{\text{solids}}$ and is small.

for the ideal mixing assumption for olivine, and of −1.215 if the William's formulation is used. This descrepancy does not of necessity require that the William's equations are in error, but rather that the assumed ideal mixing of the titanomagnetite taken together with the ideal mixing assumption of olivine is a better way of approximating the mixing relationships of these two solid solutions; in other words the errors involved in the assumption for olivine are balanced by those for titanomagnetite. Hereafter we use the ideal mixing relationship for all solids unless the William's equations are specified for the olivine and calcium-poor pyroxene components.

The other assumptions used in the later part of the paper are as follows:

(i) The partial molar volume of any component in it's respective solid solution series is independent of composition.

(ii) A magma quenched on the surface ($P = 1$ bar) can exist as a liquid of identical composition at some depth in the crust or mantle.

(iii) The chemical potential of silica, μ_{SiO_2} is fixed at any temperature and pressure by the presence of a silica-buffer. Although the concept of the chemical potential does not require a liquid phase, we have to assume that a liquid was present in order to estimate the change of μ_{SiO_2} with pressure, Eq. (18).

(iv) Most temperatures have been estimated by using the equilibration temperatures of the coexisting iron-titanium oxides (Buddington and Lindsley, 1964); in several cases, inspired guesses have been made.

In the next two examples of calculating P_{total}, we do not have to take into account the effect of temperature on silica activity in a magma. This effect will be considered later.

Acid Lavas with Quartz Phenocrysts

Many acid lavas, particularly obsidians, contain phenocrysts of quartz together with a fayalitic olivine or an orthopyroxene, ilmenite and titanomagnetite. It is reasonable to assume that these phenocrysts crystallised at the same time, especially as they are often present in only small amounts, so that the values of temperature and oxygen fugacity (f_{O_2}) derived from the composition of the iron-titanium oxides can be assumed to apply to the whole phenocryst assemblage. By substituting $\log f_{\text{O}_2}$ and the relevant mineral data into either Eqs. (10a) or (11a), we obtain a value for $\log a_{\text{SiO}_2}^{\text{liquid}}$ at the iron-titanium oxide equilibration temperature and at P bars total pressure. This must be equal to $\log a_{\text{SiO}_2}^{\text{liquid}}$ given by Eq. (2) (Table 1) as quartz and the other phenocrysts are in equilibrium; the equations are illustrated below for a fayalite-pitchstone from Scotland (AC. 7) using William's equations (p. 7) for the olivine. The mineral compositions are taken from Table 2.

$$\left(\log a_{\text{SiO}_2}^{\text{liquid}}\right)^{\text{P bars, 1173° K}}$$

$$= \underbrace{\frac{8270}{1173} - 2.81 - \frac{0.0552}{1173}(P-1) + \log a_{\text{Fe}_2\text{SiO}_4}^{\text{olivine}} + \frac{1}{3}\log f_{\text{O}_2} - \frac{2}{3}\log a_{\text{Fe}_3\text{O}_4}}_{\text{Eq. (10a), Table 1.}} \tag{19}$$

$$= +0.0695 - \frac{0.0552}{1173}(P-1) = \underbrace{-\frac{309}{1173} + 0.183 - \frac{0.0239}{1173}(P-1)}_{\text{Eq. (2), Table 1.}}$$

$$P_{\text{total}} = 5.62 \text{ kilobars.}$$

We have tabulated in Table 2 the calculated values of P_{total} for a variety of acid lavas, the mineral data having been taken from Carmichael (1967a); Ewart *et al.* (1971) and Lowder (1970). We have given two values for P_{total} for each rock, one calculated on the ideal mixing assumption, and the other using William's equations (p. 7).

The values for P_{total} are systematically lower if the ideal mixing expression for activities is used in Eqs. (10a) and (11a), but the writers have no way of evaluating which set of data are more correct; we tend to believe the William's set here but we have no check in the rocks themselves on his activity expressions as we did in the ugandite lava (p. 7).

The data show that all the rhyolites equilibrated at less than 30 kilometres, with the one peralkaline rhyolite, a pantellerite, having an intermediate value of P_{total}. In four cases, values of P_{H_2O} are known, derived either from the occurrence of biotite or in the case of the three New Zealand rhyolites from the phenocryst assemblage of orthopyroxene, cummingtonite, and quartz (Ewart *et al.*, 1971). In all cases, P_{H_2O} is much lower than P_{total}, as has been suspected by petrologists for many years.

It is obvious from the Quartz curve in Fig. 2 that a typical acid magma precipitating quartz at a depth equivalent to an average of about 6 kilobars, will become unsaturated with quartz at lower pressure at constant temperature. Presumably this explains the resorbed or embayed quartz phenocrysts so common in acid lavas.

Many rhyolites do not contain phenocrysts of quartz, so that values of P_{total} derived from Eqs. (10a) and (11a) in conjunction with Eq. (2) will give minimum values of P_{total}. Two Icelandic rhyolites from Thingmuli have an average P_{total} of 4.19 kilobars, while a mildly peralkaline obsidian from another locality (Oraefi) indicates a minimum value of 7.58 kilobars.

Kimberlites

Nixon *et al.* (1963) have given a splendid account of the mineralogy of the Basutoland kimberlites which we use to estimate P_{total} for these rocks. A typical kimberlite contains olivine, diopside, perovskite, and ilmenite with substantial amounts of $MgTiO_3$ (giekielite). In addition, Nixon *et al.* report zircon with an outer rim of baddeleyite (ZrO_2) so that the crystallisation path must have cut the Bd-Z curve (Fig. 2) at some pressure and temperature; we have assumed a temperature of 1327°C (1600°K).

The major mineral components of a kimberlite can be represented by the following reaction

$$\underset{\beta\text{-perovskite}}{CaTiO_3} + \underset{\text{fayalite}}{\tfrac{1}{4}Fe_2SiO_4} + \underset{\text{forsterite}}{\tfrac{3}{4}Mg_2SiO_4} + \underset{\text{glass}}{SiO_2} = \underset{\text{ilmenite}}{\tfrac{1}{2}FeTiO_3} + \underset{\text{giekielite}}{\tfrac{1}{2}MgTiO_3} + \underset{\text{diopside}}{CaMgSi_2O_6}{}^{*}$$

which can be recast to:

$$\begin{aligned}(\log a_{SiO_2}^{\text{liquid}})^{P\text{ bars}} &= \Delta G^0/2.303\,RT \\ &+ \frac{\Delta V^0}{2.303\,RT}(P-1) + \log \frac{(a_{CaMgSi_2O_6}^{\text{pyroxene}})\cdot(a_{FeTiO_3}^{\text{ilmenite}})^{\frac{1}{2}}\cdot(a_{MgTiO_3}^{\text{ilmenite}})}{(a_{\beta\text{-}CaTiO_3}^{\text{perovskite}})\cdot(a_{Fe_2SiO_4}^{\text{olivine}})^{\frac{1}{4}}\cdot(a_{Mg_2SiO_4}^{\text{olivine}})^{\frac{3}{4}}}\,.\end{aligned} \tag{20}$$

Obviously the value of $\log a_{SiO_2}$ derived from Eq. (20) must be equal to that of Eq. (4a) for that point in the kimberlite crystallisation path where zircon was replaced by baddeleyite. Representative mineral data taken from Nixon *et al.* (1963) are olivine = 0.92 Fo ilmenite = 0.58 $FeTiO_3$; giekielite = 0.30 $MgTiO_3$; diopside = 0.60 $CaMgSiO_6$ and the value taken for perovskite (0.87) is the average analysis given by Smith (1970). Using the free-energy and molar volume data of Robie and Waldbaum (1968), Eq. (20), with substitution of the relevant mineral data, becomes:

$$(\log a_{SiO_2}^{\text{liquid}})^{P=P\text{ bars}} = -0.5253 - \frac{0.0338}{1600}(P-1)\,. \tag{21}$$

---

* Note that this equation involves cubic β-perovskite with a molar volume of 0.79766 cal.-bar^{-1} and fayalite whose ΔG_f^0 of the solid was extrapolated to 1600°K.

Eq. (21) is set equal to Eq. (4) (assuming unit activity for both zircon and baddeleyite), the value of which (Table 1) is given below in Eq. (22).

$$\underbrace{(\log a^{\text{liquid}}_{\text{SiO}_2})^{P=P\text{ bars}}}_{\text{Eq. (21)}} = -0.0375 - \frac{0.0478}{1600}(P-1). \qquad (22)$$

Solution for P gives a value of 55.7 kilobars for the pressure at which baddeleyite replaces zircon at 1327° C in a kimberlite. It is now assumed that either perovskite or ilmenite disappeared at higher pressure and that the liquid at 1327° C and 55.7 kilobars was present at the stage of diamond formation (Kennedy and Nordlie, 1970); then by using the analyses of Meyer and Boyd (1969, 1970) for the olivine (0.92 Fo) and orthopyroxene (0.94 En) inclusions in diamond, a value for P_{total} can be calculated. We can state that

$$\begin{aligned}&(\log a^{\text{liquid}}_{\text{SiO}_2})^{P=\text{diamond}}\\ &\quad= (\log a^{\text{liquid}}_{\text{SiO}_2})^{P=\text{Bd-Z eqlm.}} + \left[1.34\times10^{-6} - \frac{0.0047}{T}\right](P - P^{\text{Bd-Z}}). \qquad (23)\end{aligned}$$

where the right hand side is obtained from Eq. (18); the value of $(\log a^{\text{liquid}}_{\text{SiO}_2})^{P=\text{Bd-Z eqlm.}}$ is taken from either Eq. (21) or (22) at 55.7 kilobars and equals -1.7015. Thus the right hand term of Eq. (23) becomes

$$(\log a^{\text{liquid}}_{\text{SiO}_2})^{P=\text{diamond}} = -1.7015 + \left[1.34\times10^{-6} - \frac{0.0047}{1600}\right](P - 55700). \qquad (24)$$

The left-hand side of Eq. (23) is obtained from Eq. (3a) (Table 1) and if the values for the olivine and enstatite inclusions are inserted gives

$$(\log a^{\text{liquid}}_{\text{SiO}_2})^{P=\text{diamond}} = -0.0306 - \frac{0.0424}{1600}(P-1). \qquad (25)$$

At equilibrium, with Eq. (24) set equal to Eq. (25), we obtain a value of 63.5 kilobars for the pressure at the stage of diamond formation. For pressures of this magnitude, mineral compressibilities, or the variation of ΔV with pressure, should be taken into account, if the information were available. Despite this, these values of P_{total} are in accord with the various speculations on kimberlite which have recently been summarised by MacGregor (1970).

The Effect of Temperature on a_{SiO_2}

One of the principal applications of the method for determining P_{total} is to lavas quenched on the earth's surface. If a silica buffer assemblage is present in the groundmass, then $\log a^{\text{liquid}}_{\text{SiO}_2}$ can be determined at the quenching temperature. However it is unlikely that a lava was ever in equilibrium with mantle material at the quenching temperature, so that knowing $\log a^{\text{liquid}}_{\text{SiO}_2}$ at one temperature, it is necessary to calculate it at some higher temperature, and then calculate the effect of pressure using Eq. (18).

The appropriate thermodynamic relationship analogous to Eq. (15) is

$$\left(\frac{\partial \log a_{\text{SiO}_2}}{\partial T}\right)_P = \frac{-\bar{H}_{\text{SiO}_2} + H^0_{\text{SiO}_2}}{2.303\,\text{RT}^2} \qquad (26)$$

where $\bar{H}_{\text{SiO}_2}$ is the partial molar enthalpy of silica in the silicate liquid, and $H^0_{\text{SiO}_2}$ is the molar enthalpy of silica in the standard state (glass).

However there is no data, at least available to writers, on $\bar{H}_{\mathrm{SiO_2}}$ in silicate liquids. So we have attempted to estimate the effect of temperature on $a_{\mathrm{SiO_2}}$ by using two sets of experimental results on lavas.

For an andesite, Green and Ringwood (1968) report that quartz appears on the liquidus at 1240°C (1513°K) and 18 kilobars, and in the same composition at 1330°C (1603°K) and 27 kilobars. If it is assumed that the co-precipitation of the other minerals with quartz changed the liquid composition by the same amount in each case, then by using Eq. (2) we can calculate $\log a_{\mathrm{SiO_2}}^{\mathrm{liquid}}$ at each temperature and pressure. Thus

$$(\log a_{\mathrm{SiO_2}}^{\mathrm{liquid}})^{1513^\circ,\ 18000\ \mathrm{bars}} = \frac{-309}{1513} + 0.183 - \frac{0.0239}{1513}(18000) = -0.3055 \qquad (27)$$

and

$$(\log a_{\mathrm{SiO_2}}^{\mathrm{liquid}})^{1603^\circ,\ 27000\ \mathrm{bars}} = \frac{-309}{1603} + 0.183 - \frac{0.0239}{1603}(27000) = -0.4122. \qquad (28)$$

If these values are corrected back to 1 bar using Eq. (18), in this way;

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

we obtain -0.2738 and -0.3692 respectively. The difference between the two values, 0.0954, is taken to result from a temperature rise of 90°.

Therefore $$\frac{\Delta \log a_{\mathrm{SiO_2}}^{\mathrm{liquid}}}{\Delta T} = \frac{-0.0954}{90} = -10.60 \times 10^{-4}\, T^{-1}.$$

Similar reasoning for an olivine-tholeiite (Green and Ringwood, 1967) with a similar temperature range (110°C) gives a value of $\frac{\Delta \log a_{\mathrm{SiO_2}}^{\mathrm{liquid}}}{\Delta T} = -15.18 \times 10^{-4}\, T^{-1}$.

We follow a time honoured principle, and take the average of the two results, so that

$$(\log a_{\mathrm{SiO_2}}^{\mathrm{liquid}})_P^{T_2} = (\log a_{\mathrm{SiO_2}}^{\mathrm{liquid}})_P^{T_1} - 0.001289\,(T_2 - T_1). \qquad (30)$$

We are now in a position to calculate P_{total} for any lava if we know $\log a_{\mathrm{SiO_2}}^{\mathrm{liquid}}$ at 1 bar and any temperature.

Trachybasalts of Southern California

In the eastern Mojave desert, there are a series of Recent lavas of trachybasalt which contain phenocrysts of olivine and pyroxene, together with a residual glass with substantial amounts of normative nepheline (Smith and Carmichael, 1969). In two of these lavas 253 and 256, olivine, titanomagnetite and ilmenite are also found as groundmass constituents; the iron-titanium oxide equilibration temperatures are given below together with the appropriate mineral data.

Sample	$X_{\mathrm{Fe_2SiO_4}}$	T°C	$\log f_{\mathrm{O_2}}$	$X_{\mathrm{Fe_3O_4}}$	$\log a_{\mathrm{SiO_2}}^{\mathrm{liquid}}$ at 1 bar
253	0.320	980	−11.7	0.323	−0.7724
256	0.275	995	−11.4	0.320	−0.8794

Substitution of the relevant mineral compositions into Eq. (10a) gives values for $\log a_{\text{SiO}_2}$ at 1 bar for the two lavas at their respective temperatures.

In the Dish Hill cinder cone of this volcanic field there are abundant lherzolite nodules whose constituent minerals have been analysed by White (1966). Let us assume that these lavas could have been at a temperature of 1300°C, and then calculate the P_{total} at which they could have been in equilibrium with these nodules.

Using Eq. (30), we first calculate $\log a_{\text{SiO}_2}^{\text{liquid}}$ at 1300°C and 1 bar. For lava No. 253, a value of -1.1849 is obtained. Then at 1300°C, the variation of $\log a_{\text{SiO}_2}^{\text{liquid}}$ with pressure will be given by Eq. (18) (Table 1). Thus

$$(\log a_{\text{SiO}_2}^{\text{liquid}})_{1573}^{P=P\text{ bars}} = -1.1849 + \left[1.34 \times 10^{-6} \frac{-0.0047}{1573}\right](P-1). \tag{31}$$

In the lherzolite nodules, $\log a_{\text{SiO}_2}^{\text{liquid}}$ is defined by the assemblage of olivine and orthopyroxene. Typical values for the composition of these minerals are 0.899 Fo and, for the orthopyroxene, 0.889 En; $\log a_{\text{SiO}_2}^{\text{liquid}}$ for the lherzolite can be calculated from Eq. (3a). Thus

$$\begin{aligned}(\log a_{\text{SiO}_2}^{\text{liquid}})^{P=P\text{ bars}} &= (\log a_{\text{SiO}_2}^{\text{liquid}})^{P=1\text{ bar}} \\ &+ \frac{\Delta V^0}{2.303\,RT}(P-1) + \log a_{\text{Fo}} - 2\log a_{\text{En}}\end{aligned} \tag{32}$$

which from Table 1, and substituting the mineral data becomes

$$= \frac{-1034}{T} + 0.597 - \frac{0.0424}{T}(P-1) - 0.0098. \tag{33}$$

If Eq. (33) is set equal to Eq. (31), it can be solved for P. Below we have given the values of P_{total} for each of the two lavas, firstly calculated at 1300°C, and secondly at the quenching temperature, thus assuming that the lavas have not cooled since equilibrating with the lherzolite nodules.

	1300°C	Quenching T°C
253	44.0 kilobars	17.0 kilobars
256	47.5 kilobars	21.0 kilobars

These calculated results are not far from those obtained by Green and Hibberson (1970) who found that the near-liquidus orthopyroxenes of an alkali olivine-basalt (no normative nepheline) at 1200°C and 14 to 16 kilobars was similar in composition to it's orthopyroxene "xenocrysts".

Ugandite Lavas

These are potassic lavas from the African rift valley, whose mineral compositions (Brown, 1971) have already been noted on page 7. Log $a_{\text{SiO}_2}^{\text{liquid}}$ at 990°C and 1 bar was calculated to be -1.457 irrespective of whether Eq. (9a) or (Eq. (10a) was used. The lavas contain nodules of biotite-olivine-pyroxenite, or dunite with small amounts of biotite (Combe and Holmes, 1945). As yet orthopyroxene has not been found either in the nodules or as xenocrysts in the lavas. However we will assume that these lavas were in equilibrium at some pressure with a generalised mantle assemblage of olivine (0.90 Fo) and orthopyroxene (0.85 En). Presumably the absence of orthopyroxene indicates that these estimates of P_{total} will be maximal, for at all lower pressures orthopyroxene of En_{85} composition will be unstable.

If Eq. (3a) is taken in conjunction with Eq. (18), then P_{total} can be obtained assuming a constant temperature of 990° C. If on the other hand the lava is considered to have cooled since leaving the mantle, then using Eq. (30) we can calculate another value for P_{total}. The results for U. 111 are: 38.0 kilobars at 990°; 69.0 kilobars at 1300° C. The latter P_{total} value is not dissimilar to that calculated for kimberlite at the same temperature, which is not unsuspected, as many petrologists believe the two rock-types to be genetically connected.

Leucite Hills, Wyoming

Orendite lavas contain leucite and sanidine in the groundmass and may contain phenocrysts of olivine (ca. 0.90 Fo) or olivine with a reaction rim of phlogopite (Carmichael, 1967b). As co-existing iron-titanium oxides are absent in this suite of lavas, it is not possible to derive a temperature at which they were quenched on the surface. However as their solidus temperatures are close to, or above 1050° C, and as they often contain only small amounts of phenocrysts, it has been arbitrarily assumed that the groundmass was quenched at 1100° C. Sl is a jumillite lava from Spain, and of allied composition. Substitution of the leucite-sanidine mineral data, tabulated below, into Eq. (7a) gives log $a_{\text{SiO}_2}^{\text{liquid}}$ at 1100° C and 1 bar, which is then substituted into Eq. (18). Although orthopyroxene phenocrysts have not been found to accompany olivine phenocrysts in the Leucite Hills lavas, we have assumed that if they did occur they would have the composition 0.85 En. Substitution of the olivine and orthopyroxene data into Eq. (3a), and its equality to the appropriate data in Eq. (18), will allow P_{total} to be calculated. A parallel calculation gives P_{total} if the lavas are assumed to have equilibrated at 1300° C with an olivine-orthopyroxene assemblage. The results are shown below.

Table 3

Sample	X_{Leucite}	X_{Sandine}	$T°$ C	$(\log a_{\text{SiO}_2}^{\text{liquid}})^{1\text{ bar}}$	P_{total} at 1100° C	P_{total} at 1300° C
Sl	1.000	0.903	1100	−0.7912	20.3 kilobars	37.1 kilobars
LH3-13	0.965	0.980	1100	−0.7396	18.5 kilobars	35.1 kilobars
LH-10	0.965	0.979	1100	−0.7406	18.6 kilobars	35.1 kilobars
LH-11	0.965	0.983	1100	−0.7388	18.5 kilobars	35.0 kilobars
LH-15	0.965	0.981	1100	−0.7407	18.6 kilobars	35.1 kilobars

Phonolitic Trachytes

Two kenytes from Antarctica described by Carmichael (1964) contain phenocrysts of anorthoclase enclosed by a glass with infrequent crystals of nepheline. The composition of the nepheline (0.593 Ne) suggests a temperature of about

800° C (Hamilton, 1961) and the alkali feldspar microlites have a composition of 0.464 Ab. Substitution of this mineral data into Eq. (6a) (Table 1) gives a value for log $a_{\mathrm{SiO_2}}^{\mathrm{liquid}}$ at 800° C and 1 bar of −0.8340. The problem is to calculate P_{total} at which the anorthoclase phenocrysts (0.646 Ab) were in equilibrium with nepheline of groundmass composition. As nepheline did not in fact co-precipitate with the anorthoclase phenocrysts, the calculated P_{total} will be a minimum estimate, and at all higher pressures nepheline of that particular composition will be unstable. Solution of Eqs. (18) and (6a) for a kenyte (1910 — 199) gives a P_{total} value of 4.20 kilobars; the parallel calculation for 1000° C gives a value of P_{total} of 31.3 kilobars. The rather large difference between these two results for a temperature rise of 200° C, reflects the rather shallow slope of the Ab–Ne curve in Fig. 2 in comparison to the Fo–En curve.

Basic Lavas with Quartz "Xenocrysts"

Many of the basalts or basaltic-andesites associated with volcanism along the continental margins contain resorbed crystals of quartz with coronae of pyroxene grains. Examples are found in the 1851 and pre-1851 eruptions of Lassen Peak, California (Smith and Carmichael, 1968) and in Talasea, New Britain, lavas (Lowder and Carmichael, 1970), but in neither case do the Sr^{87}/Sr^{86} ratios give any indication of the incorporation of silicic material (Peterman *et al.*, 1970a, b). As the groundmass mineral compositions of these lavas are known, and assuming a quenching temperature of 1000° C, the pressure at which these lavas would be saturated with quartz can be calculated. Eq. (3a) gives a value for log $a_{\mathrm{SiO_2}}^{\mathrm{liquid}}$ at 1 bar, which is inserted into Eq. (18) which in turn is equated to Eq. (2) and solved for P. The Lassen basalt gives a value of 14.3 kilobars, and the Talasea basaltic-andesite a value of 16.0 kilobars.

If a temperature of 1100° C is assumed to be the temperature at which these basalts equilibrated at depth, then the calculated values of P_{total} are 24.9 kilobars and 26.8 kilobars respectively. The so-called quartz "xenocrysts" may in fact be stable at elevated pressures, and cognate in the same way as more widely recognised high-pressure pyroxene phenocrysts in lavas (e.g., Binns *et al.*, 1970).

Basaltic Liquids and the Mantle

Many basalts show evidence either in their xenoliths or their phenocrysts of having come from the mantle, or having been in a higher pressure environment. Thus it is interesting to calculate P_{total} for these lava suites, assuming, as before, that they equilibrated with a mantle made up of olivine (0.90 Fo) and orthopyroxene (0.85 En). One example is the iron-rich tholeiitic series of Thingmuli in eastern Iceland (Carmichael, 1964). These lavas commonly have liquidus temperatures near 1100° C (Carmichael, 1967) and we shall assume, as before, that if they did equilibrate with the mantle they did so at a temperature of 1300° C. The calculations indicate that a basaltic-andesite and an olivine-tholeiite would equilibrate at 11.1 and 15.6 kilobars respectively. At their liquidus temperatures, this suite of basic lavas would become saturated with quartz over a range of 5.95 to 13.4 kilobars, and must therefore have acquired their 1 bar silica activity, or composition, at depths corresponding to lower pressures.

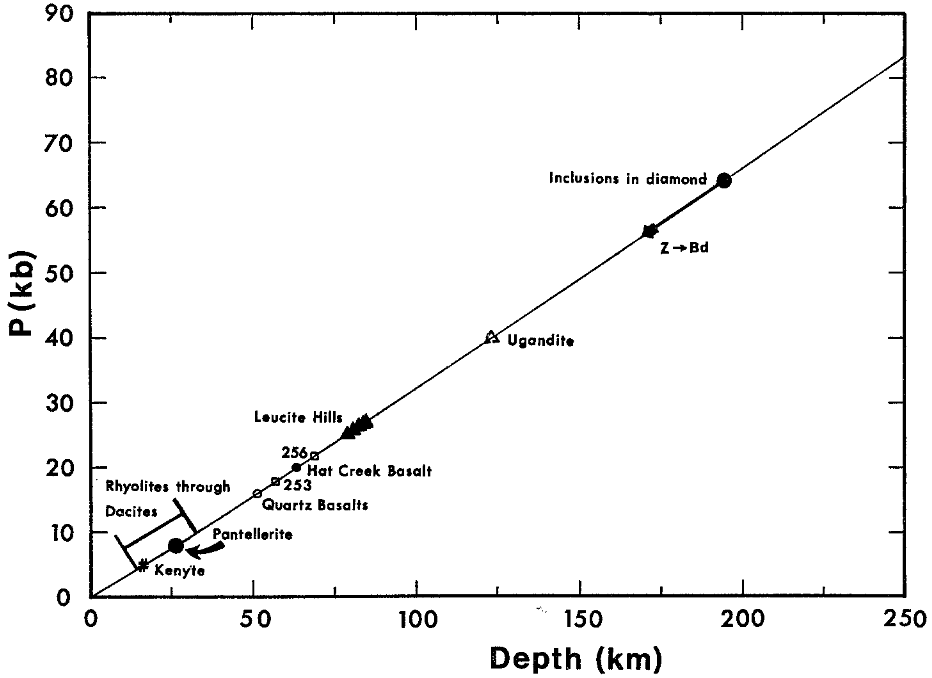

Fig. 3. The calculated values of P_{total} plotted against depth for the rock types described in the text at their quenching temperatures. 253 and 256 refer to two trachybasalts from southern California; Quartz-Basalts represents one sample from Lassen, California, and one from Talasea, New Britain; P_{total} (at 1327° C) for inclusions in diamond and Z-Bd (zircon-baddeleyite) refer to kimberlite

An olivine-bearing high-alumina basalt from the Lassen region, California, (Hat Creek) (Smith and Carmichael, 1968) would become saturated with quartz at 47.6 kilobars at it's liquidus temperature (1050° C) and at 1300° C would be in equilibrium with our generalised mantle composition at 40.2 kilobars.

In Fig. 3 we have plotted the calculated P_{total} for all the rocks described above, which can be equated to depths using Birch's (1964) depth-pressure curve. All the plotted points are derived from the actual quenching temperatures, rather than the assumed temperature of 1300° C which we have used to calculate the total pressure for equilibration with a generalised mantle composition. The general trend is for liquids of low-silica activity to equilibrate with a particular limiting reaction at greater depths than those lavas with high silica activities. We may note in passing that the calcium-content of olivine becomes diminished with increasing pressure at constant temperature (Fig. 2, lowest curve), so that as more plentiful and accurate data becomes available (e.g., Simpkin and Smith, 1966), the calcium content of olivine could be used as an indication of P_{total} in a wide variety of rocks.

Andesites and the Benioff Zone

Dickinson (1968) and Hatherton and Dickinson (1969) have shown that a correlation exists between the potassium content of andesites and basaltic-andesites and the depth to the underlying Benioff zone. This correlation has become so widely accepted that maps are now being made of the configuration of the Benioff zone, one example being the Great Basin of western north America (Lipman *et al.*, 1971). The low velocity zone of the upper mantle lies approximately between 90 and 180 kilometres, and Hatherton and Dickinson (1969, Fig. 1) envisage this region, or it's intersection with the Benioff zone, to be the source of andesite magma or it's precursor. It is obviously informative to calculate P_{total} for an andesite lava in equilibrium with a generalised mantle composition of olivine (0.90 Fo) and orthopyroxene (0.85 En). Presumably an andesite lava (ca. 60% SiO_2) will have a value of $\log a_{SiO_2}^{\text{liquid}}$ between that defined by the Fo–En and Quartz curves in Fig. 1; we will take a value of -0.200 at 1000°C, a plausible quenching temperature for this type of lava. By using Eq. (30), we can calculate $\log a_{SiO_2}^{\text{liquid}}$ at 1300°C or 1400°C, again a reasonable estimate of the temperature at which an andesite magma could be in equilibrium with the mantle composition. The calculated values are 18.8 kilobars (1300°C) and 27.0 kilobars (1400°C) using Eq. (3a) (Table 1). Allowing for a small variation in mantle mineralogy and uncertainty of the precise value of $\log a_{SiO_2}^{\text{liquid}}$ in an andesite, an upper limit of perhaps 25 kilobars at 1300°C is reasonable. Andesites therefore equilibrate with mantle material at depths of 75 kilometres or less (Fig. 3) and at all greater depths, the andesite liquid must change in composition, or lower it's silica activity, to remain in equilibrium with the mantle.

Magmas generated at greater depths will tend to be more basaltic than andesitic, and the continued equilibration of an andesite precursor at depths between perhaps 200 kilometres and 75 kilometres may generate, by fractionation of crystalline phases which reject K_2O, the requisite increase in K_2O shown by Hatherton and Dickinson (1969) if indeed the Benioff zone is the source of the parent magma of andesite.

If magma of *andesite* composition is generated at depths greater than 75 kilometres (Green and Ringwood, 1968) then in order to maintain it's composition it will have to be segregated from the surrounding mantle. At pressures above 42.3 kilobars (1300°C) or 55.7 kilobars (1400°C), this andesite magma will become saturated with quartz. It is apparent from the density data of Bottinga and Weill (1970), that there may sufficient density contrast for quartz to sink in an andesite magma. The distribution of quartz "xenocrysts" in island arc volcanic suites with low Sr^{87}/Sr^{86} ratios could be a productive study of magma history at depth.

Lunar Basalts (Apollo 11)

Brown (1970) has provided a concise summary of the mineralogy of the lunar basalts collected by Apollo 11 and also a few preliminary comments on the Apollo 12 basalts. There are, in the Apollo 11 basalts, striking mineral incompatibilities, one for example, being the occurrence of perovskite and plagioclase, which has never been found to coexist in terrestrial lavas (Carmichael *et al.*, 1970). Other examples are the occurrence of cristobalite, perovskite and baddeleyite which are unstable at all pressures and temperatures (Figs. 1 and 2); baddeleyite and perovskite are only stable above 37 kilobars at 1000°C (Fig. 2). It seems not unlikely that these basalts are partly a mechanical mix of incompatible phases, so that it is facile to accept the vast amount of chemical data on these basalts as indicative of a magma with the same composition as the lavas.

However silica activity can be used to give estimates of T, f_{O_2} and the rather thorny problem of the existence of an Fe_2O_3 component in these basalts. We start with the occurrence of fayalite (1.00 Fa) and pyroxferroite (0.85 Fs) in the groundmass of a lunar basalt (Brown, 1970, p. 6487). Substitution of this data into Eq. (1) at 1 bar (Table 1) gives a value for $\log a_{SiO_2}^{\text{liquid}}$ which must be equal (at 1 bar) to that defined by Eq. (2) (cristobalite has been substituted for quartz as the solid phase); the solution for T gives a value of 1009°C.

The value of $\log a_{SiO_2}$ obtained from either Eq. (1) or Eq. (2) at 1009°C is substituted in the following reaction

$$\underset{\text{iron}}{2\,Fe} + O_2 + \underset{\text{glass}}{SiO_2} = \underset{\text{fayalite}}{Fe_2SiO_4} \tag{34}$$

which re-arranged gives

$$\log f_{O_2} = \Delta G^0/2.303\,RT + \log a_{Fe_2SiO_4}^{\text{olivine}} - \log a_{SiO_2}^{\text{liquid}} - 2\log a_{Fe}^{\text{iron}}. \tag{35}$$

By using a value of $\Delta G^0/2.303\,RT$ at 1009°C (1282°K) taken from Eugster and Wones (1962), corrected for silica glass, and substituting $\log a_{SiO_2} = -0.0840$, $a_{Fa} = 1$, and $a_{Fe} = 1$, gives $\log f_{O_2} = -15.18$.

If a_{SiO_2}, f_{O_2}, and a_{Fa} are now substituted in the following reaction

$$Fe_3O_4 + \tfrac{3}{2}\,SiO_2 = \tfrac{3}{2}\,Fe_2SiO_4 + \tfrac{1}{2}\,O_2 \tag{36}$$

or

$$\log a_{Fe_3O_4}^{\text{magnetite}} = \Delta G^0/2.303\,RT + \tfrac{3}{2}\log a_{Fe_2SiO_4}^{\text{olivine}} + \tfrac{1}{2}\log f_{O_2} - \tfrac{3}{2}\log a_{SiO_2} \tag{36a}$$

a value of $a_{Fe_3O_4}$ is obtained. The value calculated is 0.0099, which is equivalent to 0.99% Fe_3O_4 in the spinel phase if ideal mixing is assumed. This in turn gives approximately 0.68% Fe_2O_3 in the spinel phase, or if the basalt contained 15% of this iron-titanium oxide, approximately 0.10% Fe_2O_3 in the rock. Most analytical chemists would shy away from reporting such small quantities of Fe_2O_3 in the presence of so much FeO ($\sim$19%), particularly with metallic iron as a component.

Conclusion

In all the calculations of P_{total} we have assumed that the composition of the lava or magma remains constant. To what extent this is true of the major components is unknown, but certainly many lavas are likely to lose water as they approach the surface and crystallise on it. It is at least possible that a magma at depth may only differ substantially from one at the surface by an increased amount of water. Experimental work on silicate systems, particularly the granite system (Tuttle and Bowen, 1958) indicates that increasing the water content of a silicate liquid increases a_{SiO_2}; in other words liquid compositions which crystallise feldspar as the initial phase when dry, crystallise quartz as the initial phase when the liquid contains water. Thus the calculated values of P_{total} for rhyolites will be *decreased* if their water component increases with depth. For basaltic magmas, increasing the water content may have the opposite effect. The data on the system diopside-forsterite-silica (Kushiro, 1969) shows that water ($P_{H_2O} = 20$ kilobars) causes the migration of the Fo–En boundary curve to higher silica contents compared to the same boundary with dry liquids at 20 kilobars. Although the effect of water on silica activity is difficult, if not impossible, to evaluate, in principle it appears that one way a basaltic liquid of otherwise constant composition could remain in equilibrium with the mantle over a range of pressures is to increase it's water content as it migrates towards the surface.

Acknowledgements. The authors are indebted to NSF (GA-11735), NASA (NGR05-003-414) and NRC of Canada A-7372, for material support. The computation of the heat capacity data (Table 1) was enormously helped by the use of one of Professor Helgeson's programs. The last author also acknowledges the support of an NSF graduate fellowship.

References

Binns, R. A., Duggan, M. B., Wilkinson, J. F. G.: High-pressure megacrysts in alkaline lavas for north-eastern New South Wales. Am. J. Sci. **269**, 132–168 (1970).
Birch, F.: Density and composition of mantle and core. J. Geophys. Res. **69**, 4377–4388 (1964).
Bottinga, Y., Weill, D. F.: Densities of liquid silicate systems calculated from partial molar volumes of oxide components. Amer. J. Sci. **269**, 169–182 (1970).
Brown, F. H.: Volcanic petrology of Recent volcanic rocks in the Lake Rudolf region, Kenya. Unpublished Ph. D. thesis, University of California, Berkeley (1971).
Brown, G. M.: Petrology, mineralogy and genesis of lunar crystalline igneous rocks. J. Geophys. Res. **75**, 6480–6496 (1970).
Buddington, A. F., Lindsley, D. H.: Iron-titanium oxide minerals and synthetic equivalents. J. Petrol. **5**, 310–357 (1963).
Burnham, C. W., Holloway, J. R., Davis, N. F.: Thermodynamic properties of water to 1000° C and 10,000 bars. Geol. Soc. Am. Spec. Paper **132** (1969).
Carmichael, I. S. E.: Natural liquids and the phonolitic minimum. Geol. J. **4**, 55–60 (1964a).
— The petrology of Thingmuli, a Tertiary volcano in eastern Iceland. J. Petrol. **5**, 435–460 (1964b).
— The iron-titanium oxides of salic volcanic rocks and their associated ferromagnesian silicates. Contr. Mineral. and Petrol. **14**, 36–64 (1967a).
— The mineralogy and petrology of the volcanic rocks from the Leucite Hills, Wyoming. Contr. Mineral. and Petrol. **15**, 24–66 (1967b).
— The mineralogy of Thingmuli, a Tertiary volcano in eastern Iceland. Am. Mineralogist **52**, 1815–1841 (1967c).
— Nicholls, J., Smith, A. L.: Silica activity in igneous rocks. Am. Mineralogist **55**, 246–263 (1970).
Combe, A. P., Holmes, A.: The kalsilite-bearing lavas of Kabirenge and Lyakauli, southwest Uganda. Trans. Roy. Soc. Edinburgh **41**, 359–379 (1945).
Dickinson, W. R.: Circum-Pacific andesite types. J. Geophys. Res. **73**, 2261–2270 (1968).
Eugster, H. P., Wones, D. R.: Stability relations of the ferruginous biotite, annite. J. Petrol. **3**, 82–125 (1962).
Ewart, A., Carmichael, I. S. E., Brown, F. H., Green, D. C.: Voluminous low temperature rhyolitic magmas in New Zealand. Contr. Mineral. and Petrol. (in press).
Green, D. H., Hibberson, W.: Experimental duplication of conditions of precipitation of high-pressure phenocrysts in a basaltic magma. Phys. Earth Planet. Interiors **3**, 247–254 (1970).
— Ringwood, A. E.: The genesis of basaltic magmas. Contr. Mineral. and Petrol. **15**, 103–190 (1967).
Green, T. H., Ringwood, A. E.: Genesis of the calc-alkaline igneous rock suite. Contr. Mineral. and Petrol. **18**, 105–162 (1968).
Hamilton, D. L.: Nephelines as crystallization temperature indicators. J. Geol. **69**, 321–329 (1961).
Hatherton, T., Dickinson, W. R.: The relationship between andesitic volcanism and seismicity in Indonesia, the Lesser Antilles and other island arcs. J. Geophys. Res. **74**, 5301–5310 (1969).

Kelley, K. K.: High-temperature heat-content, heat-capacity, and entropy data for the elements and inorganic compounds. U. S. Bur. Mines Bull. **584** (1960).

— Heats and free-energies of formation of anhydrous silicates. U. S. Bur. Mines Rept. Invest. **5901** (1962).

Kennedy, G. C., Nordlie, B. E.: The genesis of diamond deposits. Econ. Geol. **63**, 495–503 (1968).

Kushiro, I.: The system forsterite-diopside-silica with and without water at high pressures. Am. J. Sci. **267**-A, (Schairer) 269–294 (1969).

Lipman, P. W., Prostka, H. J., Christiansen, R. L.: Cenozoic volcanism and plate-tectonic evolution of the western United States. Part I: Early and Middle Cenozoic. Trans. Roy. Soc. (London) (in press).

Lowder, G. G.: The volcanoes and caldera of Talasea, New Britain: Mineralogy. Contr. Mineral. and Petrol. **26**, 324–340 (1970).

— Carmichael, I. S. E.: The volcanoes and caldera of Talasea, New Britain: Geology and petrology. Bull. Geol. Soc. Am. **81**, 17–38 (1970).

MacGregor, I. D.: An hypothesis for the origin of kimberlite. Mineral. Soc. Amer. Spec. Pap. **3**, 51–62 (1970).

Meyer, H. O. A.: Inclusions in diamonds. Ann. Rept. Carnegie Inst. Washington Yr. Book **68**, 315–320 (1970).

— Boyd, F. R.: Mineral inclusions in diamonds. Ann. Rept. Carnegie Inst. Wash. Yr. Book **67**, 130–135 (1969).

Nixon, P. H., Knorring, O. von, Rooke, J. M.: Kimberlites and associated inclusions of Basutoland: a mineralogical and geochemical study. Am. Mineralogist **48**, 1090–1132 (1963).

Pankratz, L.: High temperature heat contents and entropies of dehydrated analcite, kaliophilite and leucite. U. S. Bur. Mines, Rept. Invest. **7201** (1968).

Peterman, Z. E., Carmichael, I. S. E., Smith, A. L.: Sr^{87}/Sr^{86} ratios of Quaternary lavas of the Cascade range, northern California. Bull. Geol. Soc. Am. **81**, 311–318 (1970a).

— Lowder, G. G., Carmichael, I. S. E.: Sr^{87}/Sr^{86} ratios of the Talasea series, New Britain, Territory of New Guinea. Bull. Geol. Soc. Amer. **81**, 39–40 (1970b).

Robie, R. A., Waldbaum, D. R.: Thermodynamic properties of minerals and related substances at 298.15° K (25.0° C) and one atmosphere (1.013 bars) pressure and higher temperatures. U. S. Geol. Surv. Bull. **1259** (1968).

Simpkin, T., Smith, J. V.: Minor element distribution in olivine. Geol. Soc. Am. Spec. Paper **203** (1966).

Smith, A. L.: Sphene, perovskite and co-existing Fe-Ti oxide minerals. Am. Mineralogist **55**, 264–269 (1970).

— Carmichael, I. S. E.: Quaternary lavas from the Southern Cascades, western U.S.A. Contr. Mineral. and Petrol. **19**, 212–238 (1968).

— — Quaternary trachybasalts from southern California. Am. Mineralogist **54**, 909–923 (1969).

Tuttle, O. F., Bowen, N. L.: Origin of granite in the light of experimental studies in the system $NaAlSi_3O_8$–$KAlSi_3O_8$–SiO_2–H_2O. Geol. Soc. Am. Mem. **74** (1958).

White, R. W.: Ultramafic inclusions in basaltic rocks from Hawaii. Contr. Mineral. and Petrol. **12**, 245–314 (1966).

Williams, R. J.: Reaction constants in the system FeO–MgO–SiO_2–O_2 at 1 atm. between 900° and 1300° C: Experimental results. Am. J. Sci. **270**, 334–360 (1971a).

— Equilibrium temperatures, pressures, and oxygen fugacities of the equilibrated chondrites. Geochim. et Cosmochim. Acta **35**, 407–411 (1971b).

Wones, D. R., Gilbert, M. C.: The fayalite-magnetite-quartz assemblage between 600° C and 800° C. Am. J. Sci. **267**-A, 480–488 (1969).

Professor Dr. I. S. E. Carmichael
Department of Geology and Geophysics
University of California
Berkely, California 94720, U.S.A.