

The partial molar volume of Fe_2O_3 in multicomponent silicate liquids and the pressure dependence of oxygen fugacity in magmas

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ABSTRACT. Density measurements of eight silicate liquids containing substantial amounts of Fe_2O_3 have been made over a range of 250 °C. These have been combined with published density measurements on multicomponent silicate liquids to yield (by multiple regression) partial molar volumes of SiO_2 , TiO_2 , Al_2O_3 , Fe_2O_3 , FeO , MgO , CaO , Na_2O , and K_2O . The data on Fe_2O_3 -liquids are neither precise nor abundant enough to show a compositional dependence of $\bar{V}_{\text{Fe}_2\text{O}_3}^{\text{liq}}$. In a liquid of constant composition and temperature, the pressure dependence of the oxygen fugacity is given by

$$RT \int_1^P d \ln f_{\text{O}_2} = \int_1^P (2\bar{V}_{\text{Fe}_2\text{O}_3}^{\text{liq}} - 4\bar{V}_{\text{FeO}}^{\text{liq}}) dP$$

which, if ΔV is independent of pressure, necessitates an increase in f_{O_2} with increasing pressure of about 1 log₁₀ unit for 10 kbars.

Combining an equation relating oxygen fugacity to composition, T , and Fe_2O_3 at 1 bar (Sack *et al.*, 1980) with the results for partial molar volumes, the oxygen fugacity of any magma can be calculated as a function of P and T . If basic magmas have their $\text{Fe}_2\text{O}_3/\text{FeO}$ set in the source regions, and ascend isochemically, then the calculated oxygen fugacities in the mantle increase as pressure increases and silica activity decreases. A P - T grid has been constructed to show the calculated oxygen fugacities in a source region which has equilibrated with some common lava types, based on their FeO and Fe_2O_3 contents.

DENSITY measurements of a variety of silicate liquids were used by Bottinga and Weill (1970) to derive partial molar volumes of oxide components and their temperature dependence. Since then ternary and multicomponent silicate liquids containing TiO_2 have been measured and estimates of the partial molar volumes of the components SiO_2 , TiO_2 , Al_2O_3 , FeO , MgO , CaO , Na_2O , and K_2O were given by Nelson and Carmichael (1979). Although many of the density measurements of

FeO -containing systems report small amounts of Fe_2O_3 (e.g. Henderson, 1964; Shiraishi *et al.*, 1978) the concentrations were so small that Bottinga and Weill constrained its volume in silicate liquids by analogy to that of crystalline Fe_2O_3 (hematite).

This paper reports on the density measurements of Fe_2O_3 -containing liquids, and gives estimates of the partial molar volumes of the nine oxide components most abundant in natural silicate liquids. The effect of pressure on oxygen fugacity in an isochemical silicate liquid can be calculated by making simple assumptions about the partial molar oxide compressibilities, and is used to illustrate the conditions of equilibration of various basic magmas with a mineral assemblage in the mantle.

Experimental techniques. The apparatus used for the density determination is similar to that described by Bockris *et al.* (1956). It consists of a Pt/Rh-wound resistance furnace and temperature controller that operates in the range of 500 to 1600 °C. The furnace is mounted on a hydraulic jack so that it can be raised and lowered, with the distance measured on a micrometer dial gauge. A concrete platform mounted above the furnace supports an electronic balance that has a precision of ± 0.001 g. The silicate liquid sample, in a platinum crucible, is placed in the furnace whose temperature is measured with a Pt/Pt 10%Rh thermocouple calibrated periodically at the melting points of Au and Pd. A platinum bob, the volume of which is known at room temperature, is suspended from the balance in the furnace atmosphere. The furnace and crucible containing the silicate liquid are raised until the tip of the bob makes contact with the surface of the liquid. The contact causes a deflection on the balance and the point at which this occurs on the micrometer gauge is noted. Then the crucible and liquid are raised a constant distance (2.0 cm) to submerge the Pt bob, and the weight of the bob is read on the balance. The thermal gradient is less than 3° in the region of the furnace occupied by the crucible. Measurements were made in air every 50° on both heating and cooling, and each composition was allowed to equilibrate for half an

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hour at each temperature before measurement. The effect of surface tension on the emergent stem of the bob was eliminated by making runs on each liquid composition using two bobs with different volumes but with the same stem diameter. Density was then determined by first fitting a least squares line to the buoyancy-temperature data on the large bob and then solving for density at the measured temperature of the small bob. The procedure was then inverted, first fitting a least squares line to the small bob buoyancy as a function of temperature and then solving for density at the measured temperature of the large bob.

The formula from which we calculated the density is:

$$\rho = \frac{B_2(T) - B_1(T)}{V_2(T) - V_1(T)}$$

where ρ = density of the liquid at the measured temperature (T),

$B_2(T)$ = the measured buoyancy of one bob at temperature T ,

$B_1(T)$ = the buoyancy of the other bob calculated from its equation at temperature T ,

$V_2(T), V_1(T)$ = the known submerged volume of bob nos. 1 and 2, respectively, at the temperature of measurement.

The value of $V(T)$ is given by:

$$V(T) = v \cdot W$$

where

W is the weight of the submerged Pt bob measured at room temperature by weighing in air, correcting to vacuum, and subtracting the weight of the non-submerged stem of the bob.

v is the specific volume of Pt,

$v = 4.64056 \times 10^{-2} + 6.0757 \times 10^{-7} T(\text{K}) + 4.675 \times 10^{-10} T^2(\text{K}) \text{cm}^3/\text{g}$, where the thermal expansion of pure Pt is taken from Waseda *et al.* (1975) and Edwards *et al.* (1951).

The effect of bubbles in the liquid or adhering to the Pt bob could be detected by deviations from a smooth plot of buoyancy against temperature.

The samples were prepared either from ground Hawaiian basalt, or by mixing reagent grade SiO_2 , Al_2O_3 , Fe_2O_3 , MgO , CaCO_3 , Na_2CO_3 , K_2CO_3 , and $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$. The powders were weighed in the proportions required and then mixed in glass jars. For all synthetic compositions the mixed powders were then fused in a large Pt crucible at 1450–1600°C in a glass-making furnace for 7–8 hours until a bubble-free liquid was obtained. It was then quenched to a glass and ground into powder. The same procedures were repeated twice to get homogeneous glass powder. The glass powder was then placed in the smaller Pt crucibles and heated in the furnace until all bubbles had disappeared. After determining the density of each liquid by the method described above, the liquids were poured onto a graphite slab, and later analysed by wet chemical methods. Rapid cooling and the slow rate of diffusion of oxygen prevented reaction between the liquid and graphite during quench.

The submerged stem of one bob was analysed by electron microprobe and was found to contain less than 0.2% Fe. This contamination has a negligible effect on the bob density.

Results. Wet chemical analyses of the investigated liquids are given in Table I. All but sample 009 readily quenched to a glass in air, and each was crushed for analysis after completion of the density measurements. (Sample 009 contained abundant hematite formed during quench.) To avoid possible oxidation of the powdered glass during sample preparation, small chips of the glasses were used for replicate determinations of FeO using the colorimetric technique described by Wilson (1960). The Fe_2O_3 and FeO concentrations reported in Table I are taken to represent equilibration in air at the temperature of the quench. That this is reasonable can be seen by comparing the analysed $\text{Fe}_2\text{O}_3/\text{FeO}$ (Table I) with the values predicted using Sack *et al.* (1980)'s equation 9. These are shown in Table I, together with the temperature predicted from the analysed $\text{Fe}_2\text{O}_3/\text{FeO}$ and the known f_{O_2} (air). Generally the agreement between the calculated temperatures, or $\text{Fe}_2\text{O}_3/\text{FeO}$, and those measured is good. Strangely basalt 004 has $\text{Fe}_2\text{O}_3/\text{FeO}$ which departs significantly from that predicted, for which there is no obvious explanation. The equilibration of a basaltic liquid in air reported by Kennedy (1948) was the only source of data at high oxygen fugacities used by Sack *et al.* (1980); the results on 004 are clearly inconsistent with those at 1709 K. Composition 002 was made up as $\text{NaFe}^{3+}\text{Si}_2\text{O}_6$ but after equilibration in air at 1724 K contains significant amounts of FeO, which is at odds with the Mossbauer spectra of Mysen *et al.* (1980) for liquids of similar composition.

Given the values of $\text{Fe}_2\text{O}_3/\text{FeO}$ for the glasses at the known quench temperature (only 009 is uncertain in this respect), then the value of this ratio in equilibrium with air ($f_{\text{O}_2} = 0.21$) at any other temperature can be calculated using the temperature dependence relationship of Sack *et al.* (1980)'s equation 9; the ratios for each composition were calculated at 1523, 1573, 1673, 1773, and 1873 K, the temperatures at which the values of the partial molar volumes were regressed. There are also liquids reported which contain small amounts of Fe_2O_3 (usually less than 2 mole %) but no attempt was made to calculate its variation with temperature, for in general neither the temperature of the quench nor the oxygen fugacity were known. The published concentration of Fe_2O_3 , after correction to FeO for the small amount of Fe that occurred in the cooled silicate composition, was therefore taken as constant.

TABLE I. Analyses of liquid compositions (wt. %)

	002	003	003b	004	005	006	009	010	FS-2†
SiO ₂	52.26	32.84	29.05	49.61	44.77	40.08	41.51	32.41	36.50
TiO ₂	—	0.64	nil	3.26	2.97	2.68	0.11	nil	—
Al ₂ O ₃	—	2.69	—	13.40	12.20	10.77	2.44	—	0.67
Fe ₂ O ₃	27.45	28.78	34.40	8.62	15.67	20.96	23.72	28.46	2.51
FeO	6.62	4.23	4.14	5.05	6.64	9.01	9.09	3.22	60.02
MnO	—	0.05	—	0.19	0.17	0.15	0.04	—	—
MgO	—	1.00	—	5.94	5.36	4.75	17.81	—	—
CaO	—	28.43	31.63	9.93	8.90	8.06	0.27	35.27	—
Na ₂ O	13.46	0.42	—	2.63	2.25	2.03	4.60	—	—
K ₂ O	0.02	0.09	—	0.67	0.61	0.55	0.01	—	—
P ₂ O ₅	—	0.04	—	0.32	0.29	0.26	0.06	—	—
Total	99.81	99.21	99.22	99.62	99.83	99.30	99.66	99.36	99.70
Quench									
T, K	1724	1615	1573	1709	1692	1673	1795	1577	1494
Predicted from Fe ₂ O ₃ /FeO (Sack <i>et al.</i> , 1980)									
T	1764	1621	1600	1798	1687	1664	—	1632	—
<u>X_{Fe₂O₃}</u>									
X _{FeO}	1.87	3.06	3.74	0.77	1.06	1.05	1.17*	3.98	0.019
Predicted from T of quench (Sack <i>et al.</i> , 1980)									
X _{Fe₂O₃}	2.22	3.10	4.32	1.13	1.04	1.00	—	5.27	—
X _{FeO}	±0.13	±0.15	±0.26	±0.07	±0.07	±0.06	—	±0.32	—

The FeO content was determined in the glassy material after quenching in air at the indicated temperatures.

* Did not quench to a glass.

† Run in Fe crucible at low, but unmeasured *f*_{O₂}. Log₁₀ *f*_{O₂} predicted from composition and quench T = -9.50. Al₂O₃ content is due to contamination after density was measured.

Wet chemical analyses by I. S. E. Carmichael and J. Hampel.

Equations of specific volume as a function of temperature for each of our compositions are presented in Table II, and the density data for each

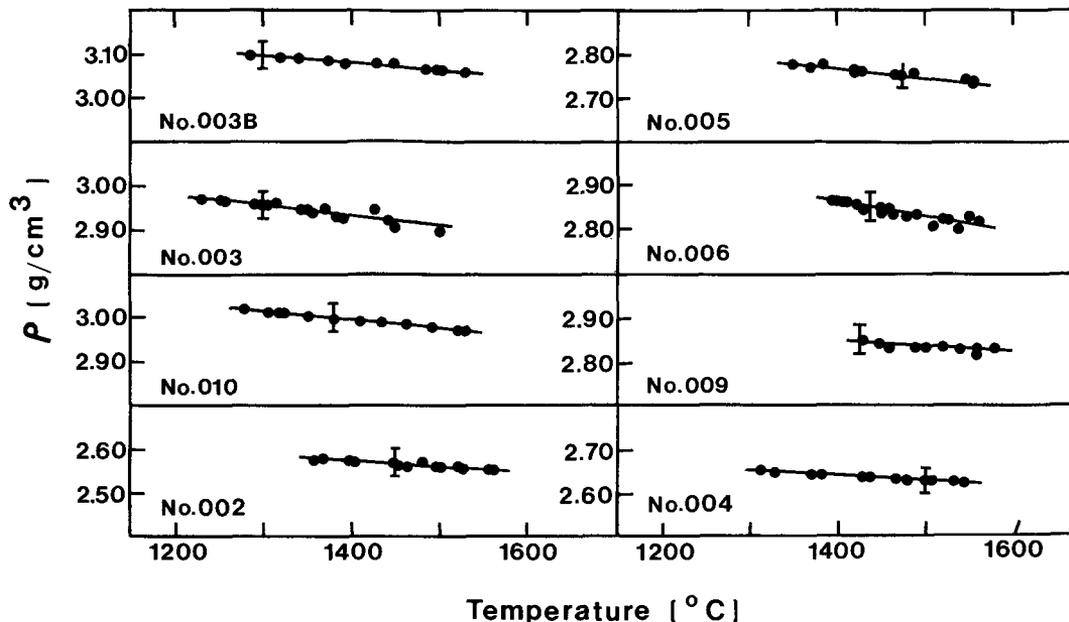
TABLE II. Specific volumes of compositions studied

$$V = a + bT(\text{K})$$

Comp.	a cc/g	b × 10 ⁵ cc/gK	Temp. range (°C)
002	0.3563	1.9255	1360-1565
003	0.2985	2.5508	1230-1500
003B	0.2987	1.5526	1285-1530
004	0.3553	1.4090	1310-1550
005	0.3184	2.6066	1350-1560
006	0.3021	2.8490	1395-1560
009	0.3307	1.2392	1430-1580
010	0.2942	2.3664	1275-1530
FS-2	0.2455	2.4812	1221-1409

are shown in fig. 1. Several compositions were re-determined after an interval of several weeks, and in all cases the greatest deviation between successive results is 0.5%, with an average reproducibility of 0.3%. Generally the less viscous liquids are those with the most precise density measurements, as is well illustrated by Nelson and Carmichael (1979).

There seems to be a general consensus among investigators reporting liquid densities that individual experimental reproducibility is of the order of 0.5%, or better, although replicate experiments by Tomlinson *et al.* (1958) at 1700°C on liquid 0.525 CaO-0.475 SiO₂ are just within 1.1%. A cursory perusal of density measurements shows that the disagreement between investigators measuring the same composition may be much larger. For example Nelson and Carmichael (1979)'s density for 0.5 Na₂O-0.5 SiO₂ is 1.6% larger at 1400°C than Bockris *et al.*'s (1956). The agreement is even worse for liquid Fe₂SiO₄ as the measurements of Shiraishi *et al.* (1978) differ by more than 3% at 1300°C and



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FIG. 1. Density determinations as a function of temperature for the eight liquids. Error brackets represent $\pm 1\%$.

1400°C from those of Lee and Gaskell (1974). As there is no a priori reason to accept one set of results for FeO-rich liquids in preference to another, we have measured the density of a liquid with 60% FeO (FS-2, Table II) over the range 1494–1682 K. Our results are given in Table II and are in close agreement with those of Shiraishi *et al.* (1978); accordingly we have ignored the data of Lee and Gaskell (1974) in our subsequent treatment.

As Askay and Pask (1979) have demonstrated that liquid volumes in the $\text{Al}_2\text{O}_3\text{-SiO}_2$ system are not linear functions of composition, then multi-component liquids must strictly also show a non-linear relationship between volume and composition. However, the capacity to demonstrate this will depend on highly precise measurements if the compositional dependence is small. Although the variation between investigators may be as large as 3%, it is typically in the 1–2% range. Clearly if the compositional dependence of volume in multi-component liquids is such that it contributes 1–2% of the whole, then it will become obscured by the experimental uncertainty.

We have chosen to take the measurements of density on a variety of liquids, some 2-component, but mainly 3- or more, to test whether or not the volume of each can be represented as a linear function of composition within an overall precision for the whole data set of about 1–2%.

The partial molar volumes of the oxide components in these silicate liquids have been calculated from the relationship

$$V = \sum_{i=1} \bar{V}_i X_i$$

where V is the volume of a gram formula weight of the silicate liquid. For our samples, V was obtained by multiplying the specific volumes (Table II) by the respective gram formula weight, which changes slightly as $\text{Fe}_2\text{O}_3/\text{FeO}$ changes with temperature in equilibrium with air. \bar{V}_i is the partial volume of component i , and X_i is the mole fraction of i . By combining the data of Tables I and II* at five different temperatures with published data (Barrett and Thomas, 1959; Bockris *et al.*, 1956; Henderson, 1964; Nelson and Carmichael, 1979; Riebling, 1964; 1966; Shartsis *et al.*, 1952; Shiraishi *et al.*, 1978) at the same temperatures, values of \bar{V}_i for nine oxide components were calculated at each temperature using the Statistical Package for the Social Sciences multiple linear regression program. The regressed values of \bar{V}_i , together with the respective standard errors, are given in Table III at these temperatures. At 1573 K there are 129 sets

* The volume of FS-2 was not included in the regression, and is within 0.25% of the volume predicted using the values given in Table III. Its density was measured with Pt and Fe bobs which gave identical results.

TABLE III. Partial molar volumes of oxide components in silicate liquids (cc/mole)

	1523 K	1573 K	1673 K	1773 K	1873 K
SiO ₂	27.07(0.14)	27.04(0.14)	27.01(0.14)	26.99(0.18)	27.01(0.23)
TiO ₂	21.67(0.83)	22.00(0.79)	22.64(0.83)	23.23(1.02)	23.79(1.29)
Al ₂ O ₃	35.81(0.35)	36.09(0.33)	36.64(0.35)	37.18(0.43)	37.70(0.55)
Fe ₂ O ₃	42.86(1.07)	43.16(1.06)	43.89(1.23)	44.37(1.70)	44.68(2.52)
FeO	13.28(0.20)	13.44(0.19)	13.73(0.20)	14.27(0.27)	14.81(0.36)
MgO	11.25(0.33)	11.32(0.31)	11.46(0.32)	11.57(0.40)	11.62(0.51)
CaO	15.38(0.21)	15.70(0.20)	16.32(0.21)	16.96(0.27)	17.57(0.34)
Na ₂ O	27.74(0.24)	28.10(0.23)	28.80(0.24)	29.48(0.29)	30.10(0.37)
K ₂ O	44.18(0.52)	44.79(0.50)	45.97(0.52)	47.12(0.64)	48.18(0.82)

Numbers in parentheses represent 1 standard error.

of data, with a standard deviation of 0.349 about the regression surface, equivalent to a coefficient of variability of 1.4% ($r^2 = 0.9998$), but at 1873 K, the 124 data points are less precisely fitted ($r^2 = 0.9995$) with a standard deviation of 0.574, or a coefficient of variability of 2.2%.

The magnitude of the standard errors in Table III is frequently larger than one would like, although this may in part be due to the small number of liquids which contain a particular component. There are, for example, only eight liquids which contain TiO₂, and only a few more with Fe₂O₃ out of the 120 or so in the data set, so that these few liquids tend to accumulate the uncertainties of the whole data set, which is then ascribed to either Fe₂O₃ or TiO₂ in the regression. Another possibility is that there is a volume difference between Fe³⁺ in fourfold coordination and Fe³⁺ in sixfold coordination with oxygen and both may occur in these liquids. This can be evaluated as Mysen *et al.* (1980) have shown that Fe³⁺ in glassy NaFe³⁺Si₂O₆ is in tetrahedral coordination, whereas in alkali-free glasses such as Ca(Mg,Fe)Si₂O₆ it is in octahedral coordination. Our composition 002 is essentially acmite whereas 003b and 010 are both alkali-free and less silica-rich than metasilicate, and according to Mysen *et al.* (1980)'s results, are likely to have Fe³⁺ in sixfold coordination. Any difference in volume due to Fe³⁺ being in different coordination should be shown by

$$(\text{Volume/g.f.w.} - \sum_i X_i \bar{V}_i) / X_{\text{Fe}_2\text{O}_3} = \bar{V}_{\text{Fe}_2\text{O}_3}^*$$

where $i \neq \text{Fe}_2\text{O}_3$. The calculated values of $\bar{V}_{\text{Fe}_2\text{O}_3}^*$ for each liquid are plotted in fig. 2, using the data given in Tables I, II, and III. These results assume that there are no errors in the other partial molar volumes (Table III), and that the error limits of

$\pm 0.8\%$, which are just twice the experimental reproducibility, are assigned completely to the volume of Fe₂O₃. The calculated volumes of Fe₂O₃ in the three ternary liquids 002, 003b, and 010 plotted in fig. 2 show that any difference in volume arising from a difference in coordination cannot be detected within the resolution of these measurements at either temperature. The data in fig. 2 illustrate the difficulty in determining precise values for the partial molar quantities. As the concentration of Fe₂O₃ decreases, the volume attributable to it is a small difference between two big numbers divided by a small number; it is for this reason that the data become less precise at 1873 K, for the concentration of Fe₂O₃ falls with increasing temperature. Although there may be a compositional dependence of the volume of Fe₂O₃ in multicomponent silicate liquids, the data we have are neither precise nor abundant enough to demonstrate this.

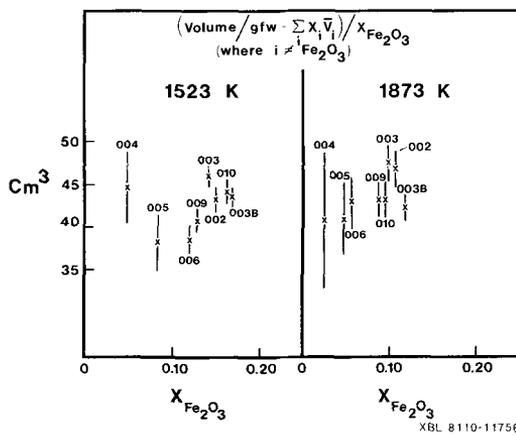


FIG. 2. The calculated molar volumes of Fe₂O₃ in each liquid plotted against mole fraction of Fe₂O₃. Error bars are $\pm 0.8\%$ in volume/gfw.

In general it would appear that the variation of volume over the range of temperature and composition of this set of data can be represented reasonably well as a linear function of composition, but one would be ill-advised to depend on this conclusion, or the data in Table III, to represent the volume of liquids in binary systems, such as Al_2O_3 - SiO_2 . That the volume of these multi-component systems can be represented as a linear function of composition may be a consequence of insufficient experimental resolution and precision, coupled of course with their restricted range of composition.

In Table IV equations are given for the variation of each oxide partial molar volume with temperature, and it is with these that our example of a petrological application can be illustrated.

TABLE IV. Partial molar volumes of oxide components in silicate liquids

$$\bar{V} = a' + b'T(\text{K})$$

Oxide component	a' cc/mole	$b' \times 10^3$ cc/mole K
SiO_2	27.33	-0.1793
TiO_2	12.46	6.0634
Al_2O_3	27.59	5.4061
Fe_2O_3	34.79	5.3463
FeO	6.56	4.3622
MgO	9.61	1.0890
CaO	5.84	6.2646
Na_2O	17.46	6.7659
K_2O	26.76	11.4590

Petrological applications. Although we are unable to distinguish any contribution to the volume of Fe_2O_3 arising from a change in the coordination of Fe^{3+} within this range of silicate liquids, it is intriguing to compare the liquid partial molar volumes with molar volumes of the crystalline oxides, which are given in Table V.

Most striking is the correspondence between the volume of SiO_2 glass and \bar{V}_{SiO_2} , and most puzzling is that the volumes of both crystalline MgO and CaO at 1673 K are greater than the respective liquid values, in contrast to all other components. Both Al_2O_3 and Fe_2O_3 show a large increase compared to corundum and hematite, in which both Al and Fe are in sixfold coordination. But the ratio of the volumes of Al_2O_3 : Fe_2O_3 for the crystalline state is 0.845 at 298 K, 0.807 at 1673 K, and in the liquids is virtually constant at 0.838 over a range of 350 K. It would seem unlikely that this

TABLE V. Volumes of crystalline oxides at 298 K and 1673 K (cc/mol)

Oxide	at 298 K*	at 1673 K†	liquid/solid at 1673 K
SiO_2 (cristobalite)	25.74	27.14	0.99
SiO_2 (glass)	27.27	27.32	0.99
TiO_2 (anatase)	20.52	21.30	1.06
Al_2O_3	25.58	26.46	1.38
Fe_2O_3	30.27	32.76	1.34
FeO	12.00	12.79	1.07
MgO	11.25	11.95	0.96
CaO	16.76	17.70	0.92
Na_2O	25.88	—	—
K_2O	40.38	—	—

* The volumes are from Robie *et al.* (1978).

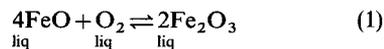
† The data of thermal expansion of solid oxides are from Touloukian (1967) except that of SiO_2 glass which is from Gray (1972).

ratio would be preserved so closely unless the same fraction of Al and Fe were in fourfold coordination in the liquids.

The presence of Al^{VI} in silicate liquids induced by pressure has yet to be unambiguously demonstrated (Sharma *et al.*, 1979), so that the pressure dependence of $\bar{V}_{\text{Al}_2\text{O}_3}^{\text{liq}}$ is unlikely to be unusually large. By analogy, we will assume that $\bar{V}_{\text{Fe}_2\text{O}_3}^{\text{liq}}$ is also not unusually pressure dependent, for in what follows this could have a strong effect on the ascent path of basic magma.

If during ascent basic magmas remain constant in composition (including constant Fe:O ratio), then we may use the fugacity of oxygen in the various types of basic magmas to deduce mineralogical assemblages in their respective source regions. Values of oxygen fugacity for any natural silicate liquid may be calculated at 1 bar for any temperature (Sack *et al.*, 1980), and if the effect of pressure can be estimated, then the oxygen fugacity in the source regions can be found.

The essential reaction is:



and given the constraint of constant composition we have at equilibrium

$$d\Delta G = \Delta V dP - \Delta S dT$$

which leads at constant temperature to

$$0 = (2\bar{V}_{\text{Fe}_2\text{O}_3} - 4\bar{V}_{\text{FeO}} - \bar{V}_{\text{O}_2}) dP$$

and from the properties of a gas (Denbigh, 1971, pp. 122-6) we have under the same constraints

$$RT d \ln f_i = \bar{V}_i dP$$

which after substitution gives

$$\int_1^P d \ln f_{O_2} = \frac{1}{RT} \int_1^P (2\bar{V}_{Fe_2O_3} - 4\bar{V}_{FeO}) dP$$

and if ΔV is assumed to be independent of pressure, then the equation may be integrated to give

$$\ln f_{O_2}^{P \text{ bar}} = \ln f_{O_2}^{1 \text{ bar}} + \frac{1}{RT} (2\bar{V}_{Fe_2O_3} - 4\bar{V}_{FeO})(P-1) \quad (2)$$

and with substitution of the appropriate values in Table IV we obtain

$$\ln f_{O_2}^{P \text{ bar}} = \ln f_{O_2}^{1 \text{ bar}} + \left(\frac{0.52126}{T} - 8.126 \times 10^{-5} \right) (P-1) \quad (3)$$

indicating that oxygen fugacity will increase strongly with pressure in liquids of constant Fe:O. At 1 bar the oxygen fugacity of any silicate lava is related to Fe₂O₃/FeO by

$$\ln(X_{Fe_2O_3}/X_{FeO}) = a \ln f_{O_2} + \frac{b}{T} + c + \sum_i d_i X_i \quad (4)$$

where $\sum_i d_i X_i$ reflects the compositional dependence of Fe₂O₃/FeO (Sack *et al.*, 1980).

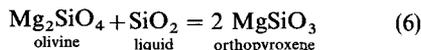
By combination of Eqn. 3 and 4 we obtain

$$\ln f_{O_2}^{P \text{ bar}} = \left\{ \ln(X_{Fe_2O_3}/X_{FeO}) - \frac{b}{T} - c - \sum_i d_i X_i + \left(\frac{0.52126}{T} - 8.126 \times 10^{-5} \right) (P-1) \right\} \frac{1}{a} \quad (5)$$

which gives the variation of $\ln f_{O_2}$ for any lava of constant composition as a function of P and T ; the constants a , b , c , and d are given by Sack *et al.* (1980).

This result can be combined with calculations of solid-liquid equilibria to examine the oxygen fugacities in the source regions of basic magmas.

Most basic magmas could be in equilibrium with both orthopyroxene and olivine at their sources in the mantle. We may then write the reaction:



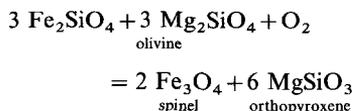
and at equilibrium,

$$\ln a_{SiO_2} = \frac{\Delta G^0}{RT} + \int_1^P \left(\frac{\Delta V}{RT} \right) dP + 2 \ln a_{MgSiO_3}^{\text{opx}} - \ln a_{Mg_2SiO_4}^{\text{olivine}} \quad (7)$$

We have used data from the appendix of Ghiorso and Carmichael (1980), from Robie *et al.* (1978), and expansivities and compressibilities from Clark

(1966). With $a_{Mg_2SiO_4}^{\text{olivine}} = 0.81$ and $a_{MgSiO_3}^{\text{opx}} = 0.80$, contours of silica activity as a function of P and T have been calculated and are plotted in fig. 3 (sub-horizontal curves). With an effective solution model for multicomponent silicate liquids, the silica activity of any lava can be calculated as a function of pressure and temperature (Ghiorso and Carmichael, 1980). At equilibrium this must equal a_{SiO_2} defined by equation 7. At a given temperature, the pressure at which a lava is in equilibrium with the mantle can thus be calculated, and from equation 5 the oxygen fugacity can then be derived. Contours of $\log_{10} f_{O_2}$, with uncertainties of about ± 1 log unit, have been drawn from data for typical natural liquids of various magma types and are shown in fig. 3 (near-vertical curves). Because examples of the tholeiitic lava type have $\log_{10} a_{SiO_2}$ values greater than -0.5 , the area between this limit and 0.0 has been labelled accordingly. Also shown in fig. 3 are silica activity regions typical of alkali olivine basalt, basanite, and nephelinite lava types, and, for the first two, contours of $\log_{10} f_{O_2}$ derived from equation 5. The oxygen fugacity curves are discontinuous from one lava type to another, and values for nephelinites are so variable that they have not been contoured. These results are in accord with the general observation that the more alkali-rich and silica-poor lavas are more oxidized (Carmichael *et al.*, 1974).

The oxygen fugacity of magmas at their sources is presumably determined by the solid assemblage of olivine, orthopyroxene, and spinel through the reaction:



At equilibrium at P and T :

$$\ln f_{O_2}^{P,T} = \frac{\Delta G^0}{RT} + \int_1^P \left(\frac{\Delta V_{\text{solid}}}{RT} \right) dP + 2 \ln a_{Fe_3O_4}^{\text{spinel}} + 6 \ln a_{MgSiO_3}^{\text{opx}} - 3 \ln a_{Fe_2SiO_4}^{\text{olivine}} - 3 \ln a_{Mg_2SiO_4}^{\text{olivine}} \quad (8)$$

By equating reactions (5) and (8), and choosing solid compositions, a curve in P - T space for a given lava can be calculated independent of the derivation based on silica activity. The initial estimate used data from the sources given above, along with Hewitt's (1976) data on the equilibrium between fayalite, magnetite, and β -quartz, and $a_{Fe_2SiO_4}^{\text{olivine}} = 0.01$. The activity of the magnetite component in spinel was based on the mixing model of Sack (1982) coupled with analytical results on ilmenite spinels given by Brown *et al.* (1980).

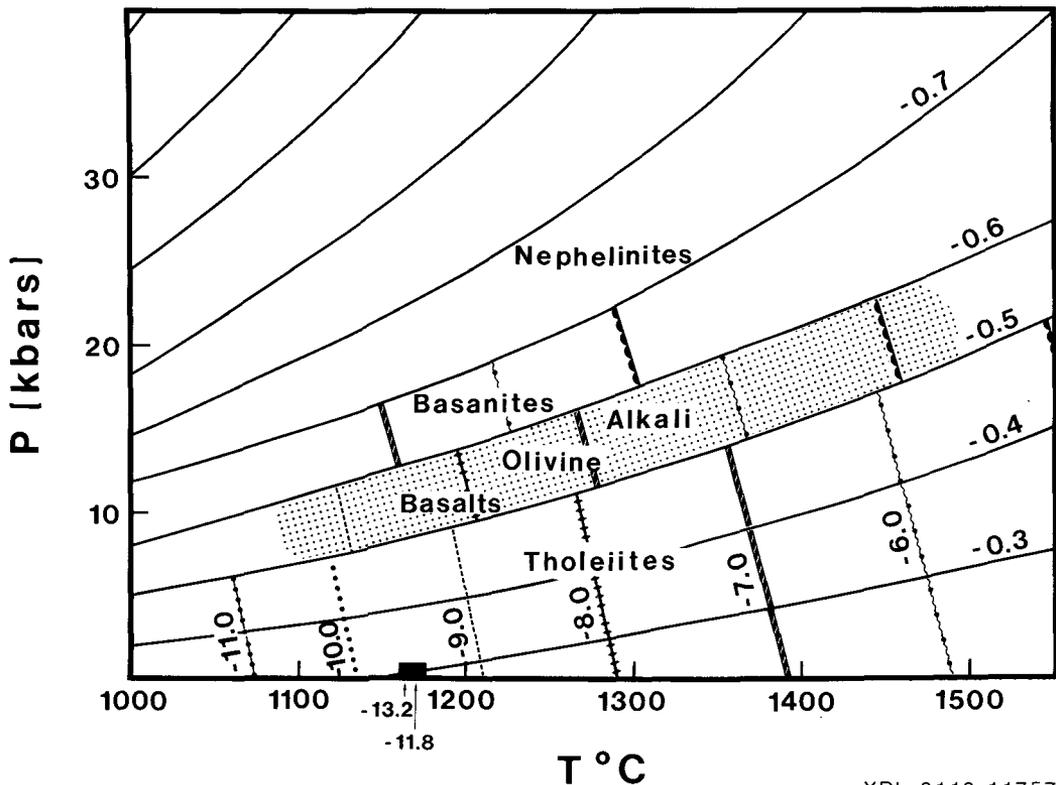
This led to an average value of $a_{\text{Fe}_3\text{O}_4}^{\text{spinel}}$ of 6.5×10^{-4} at 1250°C .

Comparison of the results of this calculation with those based on equation (5) made it clear that if $\text{Fe}_2\text{O}_3/\text{FeO}$ in lavas ranging from mid-ocean ridge basalts through alkali olivine basalts to basanites and nephelinites was pristine, then virtually every sample equilibrated with a different spinel. Put another way, there must be a considerable range in $a_{\text{Fe}_3\text{O}_4}$ in spinel in the mantle if it influences f_{O_2} and thence $\text{Fe}_2\text{O}_3/\text{FeO}$ in basic magmas. The results imply that the spinels in the source regions of lavas with increasing alkali content and decreasing silica activity have increasingly higher activities of the magnetite component.

As an indication of how sensitive the content of Fe_2O_3 in a spinel is to oxygen fugacity, we may compare the intrinsic oxygen fugacity measurements of Arculus and Delano (1981). Two spinels

varying only by 2.6% Fe_2O_3 were 1.4 \log_{10} units of oxygen fugacity different at 1443 K. Values of f_{O_2} for both of these lherzolitic spinels were far too low to be in equilibrium with a tholeiitic magma (fig. 3).

There remains a major inconsistency arising from the measurements of intrinsic oxygen fugacity (Sato, 1978; Arculus and Delano, 1981) on minerals such as olivine and spinel that could have equilibrated with basic magma in a mantle source region. These data essentially require an oxygen fugacity close to the Fe-FeO(I-W) buffer, or about 4 \log_{10} units lower than fayalite-magnetite-quartz (F.M.Q.). Sato (1978) has argued therefore that the ascent of terrestrial basic magmas is accompanied by loss of H_2 , in order that they reach the surface with their observed oxidized state. Arculus and Delano (1981), while accepting this contention in general, are puzzled by the absence of lavas on the



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FIG. 3. Effect of pressure on oxygen fugacity of magmas. Sub-horizontal curves show \log_{10} of silica activity of liquids in equilibrium with mantle olivine and orthopyroxene. Near-vertical curves are contours of \log_{10} of oxygen fugacity defined by $\text{Fe}_2\text{O}_3/\text{FeO}$ in typical magmas, with the assumption that their composition remains constant during ascent. Note that the f_{O_2} curves are not continuous across lava type boundaries, since alkali-rich, silica-poor lavas are generally more oxidized. The measured intrinsic oxygen fugacities of two lherzolitic spinels are also plotted (Arculus and Delano, 1981). See text for details.

surface with oxygen fugacities between I-W and F-M-Q, as might be expected by the vagaries of H₂ loss on ascent. For example, lavas such as basanites which often contain ultrabasic nodules might be expected to be the most reduced, as their ascent was relatively fast, and yet they are among the more oxidized of basaltic magmas.

The discrepancy, however, cannot be resolved simply by appealing to the conditions of ascent of basic magma. For the oxygen fugacity given by equation 8 to correspond at 1573 K with that measured intrinsically for a spinel with 2.1 % Fe₂O₃ (Arculus and Delano, 1981, no. 271), the activity of Fe₃O₄ in spinel, for any reasonable olivine composition, would have to lie between 1.5×10^{-5} and 3.4×10^{-6} , which seems far too small (Sack, 1982) for the analysed spinel composition. The inconsistency between the thermodynamic data will not be resolved by postulates about conditions during ascent of basic magma; that is a subordinate and independent question which cannot be used to reconcile inconsistent data. In those magmas whose ascent is isochemical, then unless ΔV of equation 3 becomes negative with pressure, the oxygen fugacity will increase with increasing pressure, and therefore the oxygen fugacity in the source regions of basic magmas must be greater than on the surface.

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REFERENCES

Aksay, I. A., and Pask, J. A. (1979) *J. Am. Ceram. Soc.* **62**, 332-6.
 Arculus, R. J., and Delano, J. W. (1981) *Geochim. Cosmochim. Acta*, **45**, 899-913.
 Barrett, L. R., and Thomas, A. G. (1959) *Soc. Glass Tech. J.* **43**, 179-90T.
 Bockris, J. O'M., Tomlinson, J. W., and White, J. L. (1956) *Faraday Soc. Trans.* **52**, 299-310.

Bottinga, Y., and Weill, D. F. (1970) *Am. J. Sci.* **269**, 169-82.
 Brown, G. M., Pinsent, R. H., and Coisy, P. (1980) *Ibid.* **280A**, 471-88.
 Carmichael, I. S. E., Turner, F. J., and Verhoogen, J. (1974) *Igneous petrology*. McGraw-Hill. 739 pp.
 Clark, S. P., Jr. (1966) *Handbook of physical constants*. Geol. Soc. Am. Mem. 97, 587 pp.
 Denbigh, K. (1971) *The principles of chemical equilibrium* (3rd edn.). Cambridge Univ. Press. 494 pp.
 Edwards, J. W., Speiser, R., and Johnston, L. (1951) *J. Appl. Phys.* **22**, 424-8.
 Henderson, J. (1964) *Am. Inst. Min. Engr., Metall. Soc. Trans.* **20**, 501-4.
 Hewitt, D. A. (1976) *Trans. Am. Geophys. Un.* **57**, 1020.
 Ghiorso, M. S., and Carmichael, I. S. E. (1980) *Contrib. Mineral. Petrol.* **71**, 323-42.
 Gray, D. E. (1972) *Americal Institute of physics handbook*. McGraw-Hill. 2351 pp.
 Kennedy, G. C. (1948) *Am. J. Sci.* **246**, 529-49.
 Lee, Y. E., and Gaskell, D. R. (1974) *Met. Trans.* **5**, 853-60.
 Mysen, B. O., Seifert, F., and Virgo, D. (1980) *Am. Mineral.* **65**, 867-84.
 Nelson, S. A., and Carmichael, I. S. E. (1979) *Contrib. Mineral. Petrol.* **71**, 117-24.
 Riebling, E. F. (1964) *Can. J. Chem.* **42**, 2811-21.
 — (1966) *J. Chem. Phys.* **44**, 2857-65.
 Robie, R. A., Hemingway, B. S., and Fisher, J. R. (1978) *U.S.G.S. Bull.* 1452, 456 pp.
 Sack, R. O. (1982) Spinel as petrogenetic indicators. Activity-composition relations at low pressure. (In press.)
 — Carmichael, I. S. E., Rivers, M., and Ghiorso, M. S. (1980) *Contrib. Mineral. Petrol.* **75**, 369-76.
 Sato, M. (1978) *Geophys. Res. Lett.* **5**, 447-9.
 Sharma, S. K., Virgo, D., and Mysen, B. O. (1979) *Am. Mineral.* **64**, 779-87.
 Shartsis, L., Spinners, S., and Capps, W. (1952) *Am. Ceram. Soc. Bull.* **35**, 155-60.
 Shiraishi, Y., Ikeda, K., Tamura, A., and Saito, T. (1978) *Trans. Jap. Inst. Metal.* **19**, 264-74.
 Tomlinson, J. W., Heines, M. S. R., and Bockris, J. O'M. (1958) *Faraday Soc. Trans.* **54**, 1822-33.
 Touloukian, Y. S. (1967) *Thermophysical properties of high temperature solid materials* (Vol. 4). The Macmillan Comp., N.Y. 1877 pp.
 Waseda, Y., Hirata, K., and Ohtahni, M. (1975) *High Temp. High Press.* **7**, 211-26.
 Wilson, A. D. (1960) *Analyst*, **85**, 923-7.