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SILICA ACTIVITY IN IGNEOUS ROCKS

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Abstract

In igneous rocks the occurrence of such mineral pairs as leucite and sanidine, or nepheline and albite indicates that silica activity may be buffered over a range of temperatures. Using published thermodynamic data, the variation of silica activity with temperature for these and other reactions has been calculated. Two bounding reactions are $Mg_2SiO_4+SiO_2=2MgSiO_3$ and $CaTiO_3+SiO_2=CaTiSiO_5$; the former separates the tholeiitic magma series from alkali olivine-basalt and all its derivatives, whereas the latter separates the feldspar-present from the feldspar-free assemblages, and thus the nephelinites (*sensu lato*) from the alkali olivine-basalt series. The lower limit of silica activity in silicate rocks is probably defined by the reaction $KAlSiO_4+SiO_2=KAlSi_2O_6$. Throughout the whole range (T, X) of igneous rocks, silica activity varies by slightly more than two orders of magnitude; surprisingly, in the tholeiitic series (olivine tholeiite to quartz-rhyolite) silica activity may only increase from $10^{-0.15}$ to $10^{-0.10}$ over the range 1150 to 850°C.

The calculated melilite reactions fall in the feldspar-free region, and suggest that the feldspar-melilite antipathy in volcanic rocks is influenced by silica activity. In calcium-rich pyroxenes Al_2O_3 increases with decreasing a_{SiO_2} until plagioclase ceases to precipitate, and in association with melilite, Al_2O_3 in pyroxene declines. The sequence of a_{SiO_2} curves correspond above 1050°C with the desilication steps of the CIPW norm; however two alternatives to these steps are proposed. The desilication of orthoclase should precede that of albite and the desilication of leucite should precede that of diopside.

Introduction

Any geologist who has taken more than a cursory glance at analyses of igneous rocks will surely agree that silica percentages are only indicative of their mineralogy, and hence of their type, in a gross way. Thus rocks rich in silica invariably contain quartz, but those poor in silica may contain nepheline, leucite, melilite, perovskite, or olivine. In lavas, particularly those which are partially glassy, it is convenient to recalculate the rock analyses into a series of standard minerals, such as those of the CIPW procedure, and then to use these normative assemblages as the basis of comparison. While it will become only too clear that considerable discrepancies can exist between that which is calculated and that which is found, particularly in the silica-poor lavas, these discrepancies will be neglected until later. For the present discussion, it is assumed that the calculated normative (CIPW) mineral assemblage corresponds closely with what is found.

In Table I, we have set down two pairs of analyses of comparable silica

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Table 1. Two Pairs of Rock Analyses with Comparable Silica Percentages. CIPW Norms Also Presented

	1	2	3	4		1	2	3	4
SiO_2	55.80	56.00	43.07	43.56	Q	4.79	—	—	—
TiO_2	1.28	1.22	0.25	2.31	or	10.52	25.29	0.89	1.67
Al_2O_3	16.51	19.74	4.20	7.85	ab	32.83	39.43	3.22	—
Fe_2O_3	2.20	1.37	2.19	5.57	an	22.38	6.23	9.31	—
FeO	5.12	3.30	9.40	0.85	ne	—	14.37	—	0.17
MnO	0.13	0.20	0.26	0.15	lc	—	—	—	32.00
MgO	4.75	1.12	36.43	11.03	ac	—	—	—	2.17
CaO	7.38	3.26	2.98	11.89	di	8.56	85.55	4.07	36.73
Na_2O	3.88	7.97	0.38	0.74	hy	13.40	—	13.55	—
K_2O	1.78	4.28	0.15	7.19	ol	—	2.45	64.56	7.32
P_2O_5	0.56	0.50	0.05	1.50	mt	3.19	1.99	3.18	—
Others	0.74	0.95	0.64	6.87	il	2.43	2.32	0.47	2.06
Total	100.13	99.91	100.00	99.51	ap	1.33	1.18	0.12	3.56
					pf	—	—	—	2.08
					Rest		1.10	—	11.19

1. Basaltic-andesite, Modoc Lava Beds, California (Smith and Carmichael, 1968)
2. Kenyte, Antarctica (Carmichael, 1964).
3. Pyroxene peridotite (Nockolds, 1954).
4. Madupite, Wyoming (Carmichael, 1967a).

contents which show that silica percentage, considered alone, need not be a diagnostic characteristic. The first pair, a Cascade basaltic-andesite and a kenyte (phonolitic-trachyte) contain respectively 4.8 percent normative quartz and 14.5 percent normative nepheline, a striking, but not unsuspected, example that it is silica content taken in *conjunction* with the other constituents which may be determinate. However, neither the silica content nor the presence in the norm of such minerals as nepheline or leucite give any indication of the degree of silica undersaturation. For example, which is the more silica undersaturated, a pyroxene peridotite (Table 1, No. 3) which contains 65 percent normative olivine, or a madupite which contains 32 percent normative leucite (Table 1, No. 4)? If silica either alone or in combination with the other constituents (*e.g.*, according to the CIPW procedure), does not indicate the degree of silica saturation or undersaturation, is there some other way in which this can be shown more unambiguously or precisely.

In the reaction

$$\underset{\text{Forsterite}}{Mg_2SiO_4} + \underset{\text{liquid}}{SiO_2} = \underset{\text{Clinoenstatite}}{2MgSiO_3} \tag{1}$$

and in the absence of crystals of quartz, the effective concentration of silica in the liquid, or its activity, will be fixed at any given T(and P) by the equilibrium assemblage forsterite-clinoenstatite. Although in the two-component system Mg_2SiO_4-SiO_2, liquid, forsterite and clinoenstatite coexist at only one temperature (at a given P), in such systems as $KAlSi_2O_6$-Mg_2SiO_4-SiO_2 (Schairer, 1954) and $NaAlSiO_4$-Mg_2SiO_4-SiO_2 (Schairer and Yoder, 1961), liquids on the boundary curves separating the fields of forsterite and clinoenstatite have their silica activity buffered by the coexistence (in equilibrium) of the two solid phases over a range of temperature. In nature, the coexistence of olivine and a calcium-poor pyroxene over a range of temperature (*e.g.*, in the Skaergaard: Wager and Brown, 1968) will also restrict the variation of silica activity, but because of the progressive substitution of Fe for Mg in the two solids, the *natural* curve of silica activity with temperature will not coincide with that of the synthetic iron-free systems. In what follows, the progressive substitution of Fe for Mg in many of the solids which could buffer silica activity in natural assemblages has been ignored.

As almost all of the naturally occurring crystalline phases considered in this paper are solid solutions, a certain amount of leeway is inevitable in attempting to characterise various igneous suites by silica activities calculated from thermodynamic data on pure end members. For the purposes of this paper, consideration of the end-members only is generally sufficient, although the equations are modified to take into account solid solutions if these are either ideal, or if nonideal activity coefficients then their known. In the usual case, little is known of the activity coefficients of the mineral in question, so we will have to be content with the assumption of ideality, and use mole fractions.

The variation with temperature of silica activity ($a_{SiO_2}^{\text{liquid}}$) can be calculated for reaction 1 from the relationship

$$\Delta G_r = \Delta G_r^\circ - RT \ln a_{SiO_2}^{\text{liquid}} = 0$$

or

$$\log a_{SiO_2}^{\text{liquid}} = \Delta G_r^\circ / 2.303\, RT.$$

As the standard state of silica we have used silica glass rather than quartz, because a natural silicate liquid can be considered as a mixture of silica with the other oxides[1]. Thus $RT \ln a_{SiO_2} = \mu_{SiO_2}^{\text{liquid}} - \mu^\circ{}_{SiO_2}$ where $\mu_{SiO_2}^{\text{liquid}}$ is the chemical potential of silica in the liquid and $\mu^\circ{}_{SiO_2}$ is the chemical potential in the standard state. This energy difference ($\mu - \mu^\circ$) will arise from mixing. If quartz or tridymite had been chosen as the

[1] We are concerned with components here, not species.

standard state, then the mixing process would have included the disruption of the bonds of the crystal lattice, followed by mixing of the liquefied silica with the other components.

SILICA ACTIVITY BUFFER ASSEMBLAGES

Using the data of Robie and Waldbaum (1968) and Kelley (1962), we have calculated the variation of silica activity over a range of temperatue for a series of reactions that represent assemblages found in a wide range of igneous rocks. The calculated curves of silica activity have been plotted in Figure 1, and have been extended beyond the temperatures over which natural silicate liquids are generally considered to exist, but this is of no consequence to the calculated curves. For each curve, the equivalent natural assemblages are treated in more detail below. Reactions for which thermodynamic data are not available are also discussed, since data exist on the natural assemblages that may illustrate the influence of silica activity. However, these reactions can be considered only in a general way in setting limits of silica activity in the whole spectrum of igneous, and particularly volcanic, rocks. Thus the common progressive substitution of Fe for Mg in natural olivines and pyroxenes, or as another example, K for Na in nepheline or alkali feldspar, will not be considered. Each rock-type or magma-series can just as easily be distinguished or characterized by the presence or absence of the magnesian end-member or a feldspathoid rather than by their composition.

a) SiO_2 (glass) $=$ SiO_2 (quartz)

Because we have chosen silica glass as the standard state of silica, the activity of silica in equilibrium with quartz is not unity. The variation of silica activity for this reaction is shown as the top curve in Figure 1. Tridymite is the stable silica mineral over the crystallization temperature range of most volcanic rocks, but as the curve of the reaction silica-glass—tridymite virtually coincides with the silica-glass-quartz curve (Fig. 1), it has been neglected as quartz is the predominant silica mineral in acid volcanics.

b) $Mg_2SiO_4 + SiO_2 = 2MgSiO_3$

Tilley (1950) has suggested that the essence of the tholeiitic series is a reaction relationship of olivine to liquid, represented mineralogically by the occurrence of a calcium-poor pyroxene, either pigeonite or hypersthene. This reaction was later made the basis of a CIPW normative classification of basalts by Yoder and Tilley (1962), whose "critical plane of silica under-saturation" corresponds to the absence of normative hypersthene (any effect on the norm due to subsequent oxidation of the iron-titanium oxides can be disregarded here). Thus the presence of a

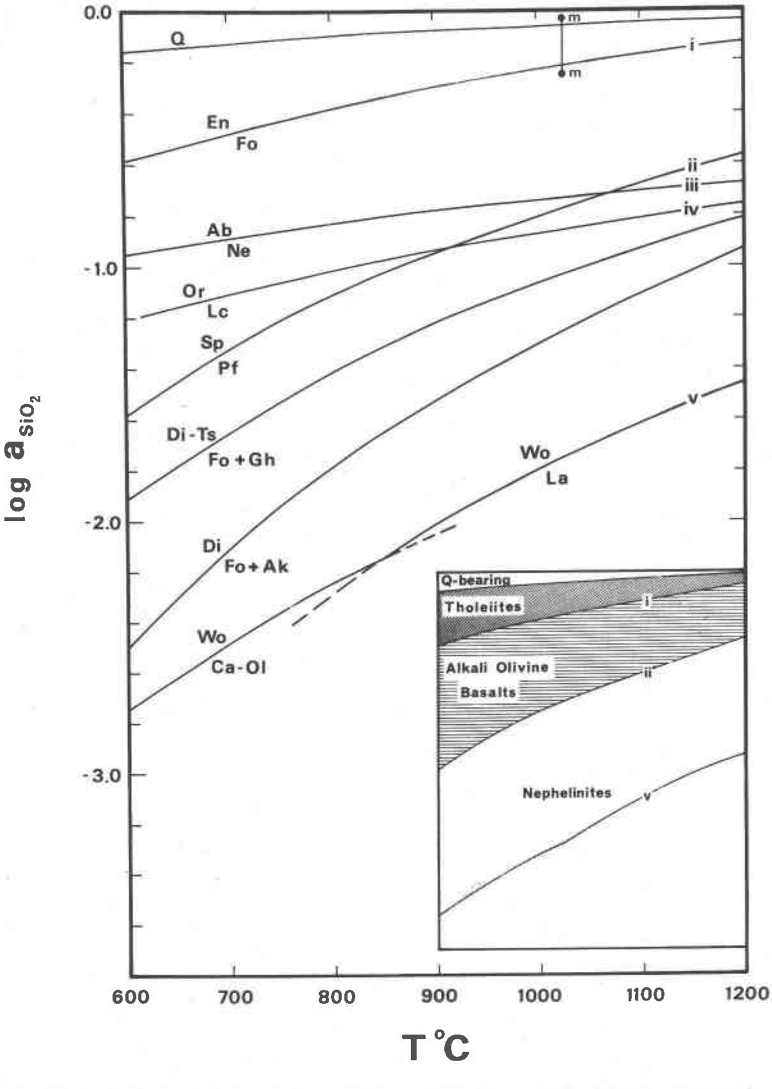

FIG. 1. Plot of calculated variation of silica activity (log units) with temperature for the labelled reactions each, of which, is treated in the text. Line labelled **m-m** corresponds to the calculated a_{SiO_2} of the Makaopuhi lava lake at 1027°C. Roman numerals refer to the order of desilication steps in the CIPW norm. Inset diagram shows the a_{SiO_2} regions in which tholeiites and their derivatives, alkali olivine-basalts and their derivatives crystallise. The lower limit of the nephelinite suite is not known precisely.

calcium-poor pyroxene stamps a basalt as tholeiitic and we may take the above reaction to represent this class of basaltic liquids.

The low-pressure fractionated products of a tholeiitic parent, namely basaltic-andesite, andesite (icelandite), dacite and rhyolite contain increasing amounts of normative quartz, which in their holocrystalline equivalents is present modally. These derivatives, lying on the tholeiitic liquid line of descent and constituting thereby the tholeiitic magma series, will, with respect to silica activity, lie between the two bounding reactions:

$$SiO_2 \text{ (glass)} = SiO_2 \text{ (quartz)}$$

and

$$Mg_2SiO_4 + SiO_2 = 2MgSiO_3$$

This area has been stippled in the inset diagram of Figure 1. It is of more than casual interest to note that in the passage from a basaltic parent at 1150°C to a quartz-bearing rhyolitic derivative at 850°C, the activity of silica changes from approximately $10^{-0.15}$ at 1150°C to $10^{-0.10}$ at 850°C (Fig. 1). This small increase in activity corresponds to an increase from about 48 to 75 weight percent SiO_2, a decisive illustration of nonideality.

In the early residual liquids of the Skaergaard intrusion, the increase in iron is accompanied by a small decrease in silica weight percentage (Wager, 1960); this decrease in no way requires that silica *activity* should also decrease any more (or less) than in any other liquids of comparable mineralogy.

As an example of the calculation of silica activity in a specific basaltic liquid, we have used the reaction:

$$2Fe_3O_4 + 3SiO_2 = 3Fe_2SiO_4 + O_2$$

which is often used an an indicator of oxygen fugacity (f_{O_2}) in natural assemblages, and as an oxygen buffer in synthetic systems (Wones and Gilbert, 1969). However, if direct determinations of f_{O_2} are available, and with data on the composition of coexisting olivine and titanomagnetite, then by substituting the appropriate mole fractions (ideality assumed) in the following equation

$$\begin{aligned} 3 \log a^{\text{liquid}}_{SiO_2} &= \Delta G^{\circ}_{r}/2.303\,RT + 3 \log a^{\text{olivine}}_{Fe_2SiO_4} + \log f_{O_2} \\ &\quad - 2 \log a^{\text{titanomagnetite}}_{Fe_3O_4} \end{aligned}$$

we may calculate the silica activity (subscript component in the superscript phase). As the example, we have used Sato and Wright's (1966) data on oxygen fugacity in the Makaopuhi (Hawaii) tholeiitic lava lake (at 1027°C, $10^{-9.2}$ and $10^{-10.2}$ atmospheres) in combination with the mineral data given by Wright and Weiblen (1968). The two values plotted in Figure 1 correspond to different solutions using the two different f_{O_2} determinations combined with a mole fraction of Fe_2SiO_4 of 0.45 and a mole fraction of Fe_3O_4 of 0.37. The calculated values of silica activity were modified by subtracting $3(\Delta G_r^\circ/2.303\ RT$ at 1027°C) for the SiO_2 glass-quartz reaction, as the standard state of SiO_2 in the reaction evaluated by Wones and Gilbert (1969) is quartz and not silica-glass.

c) $\frac{1}{2}NaAlSiO_4+SiO_2=\frac{1}{2}NaAlSiO_3O_8$

In the sodic part of the system $NaAlSiO_4$-$KAlSiO_4$-SiO_2-H_2O, Hamilton and MacKenzie (1964) showed that liquid, nepheline and alkali feldspar coexist over a range of temperature at constant water pressure. In this system, both feldspar and nepheline change in composition, the latter in a rather more complex way as the substitution of K for Na is also accompanied by a progressive decrease in the SiO_2 content as temperature falls. We have represented this complex relationship by the simple reaction above, and the calculated variation of silica activity with temperature for this has been plotted in Figure 1.

In natural assemblages, the occurrence of anorthoclase and nepheline together with liquid (*e.g.*, Carmichael, 1964) would buffer the activity of silica in the liquid, although the variation of this with temperature is unlikely to correspond with the calculated curve of the above reaction. Using activity coefficients computed from Thompson and Waldbaum (1968) and Waldbaum and Thompson's data (1968) on feldspar, and the K-Na mixing model for nepheline (Perchuk and Ryabchikov, 1967), Nash *et al.* (1969) have calculated the silica activity in mildly peralkaline phonolites; this was in turn used to calculate the range of f_{O_2} for the coexisting olivine-titanomagnetite assemblage.

d) $KAlSi_2O_6+SiO_2=KAlSi_3O_8$

The calculated variation of silica activity with temperature for this reaction is plotted in Figure 1, but rather surprisingly, this curve falls below that for the silication of nepheline. Potash feldspar melts incongruently to leucite plus a siliceous liquid, and furthermore leucite is the primary phase in binary liquids that are as siliceous as 26 percent silica (Schairer and Bowen, 1955). Therefore we would have expected the curve to plot above the nepheline curve (Fig. 1). Possibly the thermodynamic data for leucite are bad, for Robie and Waldbaum (1968) do not tabulate them[1]; moreover the curves in Figure 1 indicate that perov-

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[1] The data we used to calculate the change in free-energy in reaction (d) was the estimated value given for leucite by Kelley (1962).

skite and sanidine could exist at geologically reasonable temperatures, but this association is rare or unknown in nature (see below). Thus there seems to be some reason to suspect that the leucite-sanidine silica activity curve should plot above the nepheline-albite curve in Figure 1.

Natural examples of the reaction relationship of leucite to liquid do not abound in the literature, nor have the writers seen any petrographic evidence of this. Natural liquids which may have their silica activity buffered by the coexistence of leucite and sanidine include orendites and jumillites (Carmichael, 1967a) and the leucite-phonolites of the Italian volcanic province (Savelli, 1967).

e) $CaTiO_3 + SiO_2 = CaTiSiO_5$

In the etindite (leucite-nepheline-titanaugite) lavas of Mt. Etinde, Cameroon (Tilley, 1953), the occurrence of sphene and perovskite suggested that silica activity was buffered for the cooling interval in which they and the liquid were in equilibrium, and it was this paragenesis that led to this study of silica activity. It was also initially assumed that in these lavas sphene and perovskite would have compositions close to their written formulas, but as the analyses of these two minerals show extensive substitution (Smith 1970), the activity of the two written formlua components cannot be unity. The calculated variation of silica activity for the perovskite-sphene reaction above is plotted in Figure 1.

Although these lavas, or this reaction, may seem rather esoteric, its relevance lies in the petrographic observation that perovskite is rarely, if ever, found with feldspar in igneous assemblages. This reaction therefore sets a lower limit of silica activity in feldspar-bearing assemblages. Accordingly, alkali-olivine basalts, basanites, tephrites and their assumed derivatives, phonolites, leucite-phonolites and equivalent trachytes all crystallise in the area of silica activity between the sphene-perovskite curve and the forsterite-clinoenstatite curve as an upper limit. This area has been shaded in the inset diagram of Figure 1 and labelled alkali-olivine-basalts.

Below the sphene-perovskite curve are the great diversity of feldspar-free igneous assemblages: the nephelinites, etindites, leucitites, ugandites, mafurites, katungites, and madupites to name a volcanic contribution to the exhausting plethora of petrographic types and titles. This feldspar-free field has been labelled nephelinite in Figure 1.

f) Melilite reactions:

$$\tfrac{2}{3}Ca_2Al_2SiO_7 + \tfrac{1}{3}Mg_2SiO_4 + SiO_2 = \underbrace{\tfrac{2}{3}CaMgSi_2O_6 + \tfrac{2}{3}CaAl_2SiO_6}_{\text{Diopside solid solution}}$$

$$\tfrac{2}{3}Ca_2MgSi_2O_7 + \tfrac{1}{3}Mg_2SiO_4 + SiO_2 = \tfrac{4}{3}CaMgSi_2O_6$$

Common associates of melilite in volcanic rocks are magnesian olivine and diopsidic augite so that the two equations above, one for gehlenite and the other for akermanite, are plausible representations of natural assemblages. The two calculated curves of silica activity are plotted in Fig. 1 and fall below the limiting perovskite-sphene curve in the feldspar-free region. As there seems to be universal agreement that feldspar in nature is antipathetic to melilite (Tilley, 1952; Yoder and Schairer, 1969), this suggests that silica activity could be one reason for the "melilite-plagioclase incompatibility dilemma in igneous rocks" (Yoder and Schairer, 1969).

In the calculation of silica activity (over a range of temperature) for a natural melilite-diopside-olivine assemblage, both equations should give the same result provided that the solid solutions are either ideal or their activity coefficients are known.

g) $KAlSiO_4+SiO_2=KAlSi_2O_6$

No high-temperature thermodynamic data are available for this reaction. In the potassic ultramafic lavas of Uganda (Combe and Holmes, 1945; Carmichael, 1969), kalsilite and leucite coexist with diopsidic augite and a magnesian olivine. Presumably therefore the curve of silica activity for this reaction would fall above the wollastonite-larnite curve discussed below; this conclusion is at variance with the authors of the CIPW norm and it is discussed in more detail below.

h) $Ca_2SiO_4+SiO_2=2CaSiO_3$

The reaction which sets the lower limit of silica activity in silica-poor igneous rocks is not known to the writers, but the rarity or absence of either rankinite ($Ca_3Si_2O_7$) or larnite (Ca_2SiO_4) in igneous parageneses (Tilley and Harwood, 1931; Tilley, 1952) suggests that the above reaction could represent the lower limit (Fig. 1). Due to the polymorphism of Ca_2SiO_4 there are two curves of silica activity which intersect at 847°C (Fig. 1), the temperature above which calcium-olivine inverts to larnite. No thermodynamic data on rankinite are given by Robie and Waldbaum (1968).

In Heinrich's (1966) survey of the mineralogy of carbonatites, wollastonite is reported as being "moderately common," but neither rankinite nor larnite are listed. Certainly throughout that account, and in the various papers in Tuttle and Gittin's (1966) volume on carbonatites, there is no sign of any calcium orthosilicate. As potassium feldspar, nepheline, perovskite, sphene and quartz have all been found in various carbonatite associations, the range of silica activity in these rocks must be considerable, but apparently it never falls below the curve defined by the larnite-wollastonite reaction (Fig. 1).

SILICA ACTIVITY AND ALUMINA IN PYROXENES

Kushiro (1960) and LeBas (1962) have shown that aluminum increases systematically in calcium-rich pyroxenes in relation to decreasing silica concentration (or silica activity) of the host magma. This conclusion is supported by Verhoogen (1962), who suggested that silica activity would directly influence the titanium (and hence aluminum) content of a diopsidic augite. The following reaction may be taken as a simple representation of the role of Al_2O_3 in calcium-rich pyroxenes:

$$\underset{\text{Ca-Tschermak's pyroxene}}{CaAl_2SiO_6} + SiO_2 = CaAl_2Si_2O_8$$

When recast to:

$$\frac{\overset{\text{plagioclase}}{a_{CaAl_2Si_2O_8}}}{\overset{\text{pyroxene}}{a_{CaAl_2SiO_6}} \cdot \overset{\text{liquid}}{a_{SiO_2}}} = K_{(T,P)}$$

it illustrates that a decrease in silica activity requires a corresponding increase in the Ca-Tschermak's component in the calcium-rich pyroxene for a given plagioclase composition. Examples of this in nature can be seen in the augitic pyroxenes of basanites (Brown and Carmichael, 1969) which become progressively enriched in Al_2O_3 from core to margin as silica activity declines in the residual liquid (attested to by the presence of interstitial nepheline and leucite). This trend, also noted by LeBas (1962) and well represented in the contaminated dolerite of Scawt Hill (Tilley and Harwood, 1931), is quite the opposite of the calcium-rich pyroxenes of tholeiitic series (LeBas, 1962) which at Thingmuli, Iceland become progressively poorer in Al_2O_3 (Carmichael, 1967b).

This equation also indicates that in the sequence tholeiite, alkali olivine-basalt, basanitoid and basanite or tephrite (decreasing silica activity), all of which could conceivably have CIPW normative feldspars [An/(An+Ab)] of the same composition, there could be a progressive decrease in the anorthite component of the early crystallising plagioclase. The writers have insufficient data on this at the moment.

If silica activity is reduced so that plagioclase is replaced by melilite, then the diopsidic augite may no longer be enriched in Al_2O_3 as the reaction below illustrates:

$$\tfrac{2}{3}Ca_2Al_2SiO_7 + \tfrac{1}{3}Mg_2SiO_4 + SiO_2 = \underset{\text{diopside solid solution}}{\tfrac{2}{3}CaMgSi_2O_6 + \tfrac{2}{3}CaAl_2SiO_6}$$

Decreasing silica activity would tend to drive the reaction towards the left, and diminish the Al_2O_3 content of the pyroxene. Data on the Al_2O_3

content of calcium-rich pyroxenes associated with melilite (Sahama, 1962; White, 1966, and Carmichael, 1969) indicate a range of 1 to 4 percent Al_2O_3 in contradistinction to the 7–9 percent Al_2O_3 in comparable pyroxenes in basanites (Brown and Carmichael, 1969). Thus the role of Al_2O_3 in calcium-rich pyroxenes in response to decreasing silica activity is first to increase, and then, when the place of plagioclase is taken by melilite, to decrease.

One further aspect of silica activity and the ferromagnesian minerals is illustrated by the reaction:

$$MgAl_2O_4 + SiO_2 = MgAl_2SiO_6 \text{ (Mg-Tschermak's molecule)}$$

so that titanomagnetites in alkali-olivine basalts or basanites may be expected to be richer in MgO and Al_2O_3 than their counterparts in tholeiitic lavas. This is supported by the analytical data on one-phase titanomagnetites which in trachybasalts (Smith and Carmichael, 1969) and in basanites (Brown and Carmichael, 1969) have between 1.1 and 5.0 percent MgO and 1.1 and 4.4 percent Al_2O_3 in contrast to the average titanomagnetite in the Thingmuli, Iceland, tholeiitic lavas (Carmichael, 1967b) which have 0.3 percent MgO and 1.3 percent Al_2O_3.

MINERALS WHICH COULD DEFINE SILICA ACTIVITY

Eugster (1959), in a discussion of redox reactions in metamorphic rocks, distinguished between a buffered system, or one in which both members of the redox mineral pair were present, and an unbuffered system, in which a silicate or an oxide mineral responded to the prevailing oxygen fugacity (or defined it at given T). Up to this point, our discussion has been concerned with silica buffers, for in many igneous assemblages both members of a silica buffer pair are present. But in the absence of a buffer assemblage, certain minerals may define (at given T) the activity of a given component; two common examples are $Fe_{1-x}O$ (wustite) for f_{O_2} (Muan, 1958) and $Fe_{1-x}S$ (pyrrhotite) for f_{S_2} (Toulmin and Barton, 1964).

Two minerals whose compostion could vary systematically with silica activity are leucite and alkali feldspar. Fudali (1963) has synthesised leucite with excess SiO_2 at 1000 bars H_2O pressure; so presumably, the silica content of leucite could be used to define silica activity. Carman and Tuttle (1967) have shown that the alkali feldspars (sanidines) from rhyolites contain excess silica which can be exsolved at high pressure, whereas those from phonolites show no such excess. Although the variation in silica content of alkali feldspar appears to be an insenstitive indicator of silca activity, with calibration and precise analysis, it could become a "silica definer" of great value in view of its widespread occurrence.

DESILICATION STEPS IN THE CIPW NORM

In the calculation of the CIPW norm of a silica-poor igneous rock, there is a sequence of desilication steps of the normative minerals which was presumably based on the petrographic experience of the authors of the norm. The order of these steps is shown in small Roman numerals in Figure 1—with the exception of the last step (*vi*) (desilication of leucite), for which high-temperature free-energy data are lacking. At temperatures above 1050°C, the order of CIPW desilication steps corresponds to decreasing silica activity, surely a striking tribute to Cross, Iddings, Pirsson and Washington.

On the basis of our study, we offer two modifications to the sequence of desilication steps. Firstly, the curve leucite-sanidine will probably plot above the nepheline-albite curve in Figure 1 when the thermodynamic data for leucite are re-determined. Thus the desilication of normative orthoclase to leucite should precede the desilication of normative albite to nepheline, a suggestion also made by Baker *et al.* (1964) with reference to the Tristan da Cunha leucite-bearing lavas.

The second modification is concerned with those rocks which contain kalsilite; the CIPW procedure (Johannsen, 1939) is to desilicate normative diopside to forsterite and larnite (Fig. 1, *v*) before desilicating leucite to kalsilite. Put another way, the following reaction should run to the right according to CIPW;

$$2CaMgSi_2O_6 + 2KAlSiO_4 = Ca_2SiO_4 + Mg_2SiO_4 + 2KAlSi_2O_6$$

but at 298°C, the ΔG of this reaction is positive (+22.7kcal). Thus (at 298°C) diopside and kalsilite are the stable assemblage, which is in accord with the observed paragenesis of kalsilite, leucite, diopside and a magnesian olivine with only normal (*ca.* 0.3%) amounts of CaO. Thus the desilication of leucite to kalsilite should precede the desilication of diopside in the normative calculation.

In natural silicate liquids the lower limit of silica activity is suggested to be that defined by the assemblage leucite-kalsilite. We have no knowledge of (iron-free) wollastonite precipitating in silica-poor liquids uncontaminated by limestone, and certainly there is no evidence of either larnite or rankite. Thus the kalsilite-leucite curve should plot above the wollastonite-larnite curve (Fig. 1).

CONCLUSIONS

It has been shown that certain mineral assemblages could act as silica buffers, and in terms of these and hence of silica activity, we may distinguish three broad groups of magma series: the tholeiitic, the alkali olivine-basalts, and although really not a series, the feldspar-free rocks.

But it is difficult to answer the unspoken comment: what value, apart from classification, is there in the concept of silica activity, or what use can be made of the calculated values? Surely not just to decide which of two rocks is the most silica undersaturated (Table 1, No. 4). In many olivine-bearing lavas, particularly the alkali olivine-basalts, basanites and the silica-poor potassic ultramafics, titanomagnetite is the only iron-titanium oxide present, so that, in the absence of discrete ilmenite, no use can be made of the iron-titanium oxide geothermometer and geobarometer (Buddington and Lindsley, 1964). In order to get some idea of the range of f_{O_2} of these various lava types, we may have to calculate it from a relationship such as

$$3Fe_2SiO_4 + O_2 = 2Fe_3O_4 + 3SiO_2 \quad \text{(Wones and Gilbert, 1969)}$$

or

$$\log f_{O_2} = \frac{\Delta G_r^\circ}{2.303\ RT} + 2 \log a_{Fe_3O_4} + 3 \log a_{SiO_2} - 3 \log a_{Fe_2SiO}.$$

The curves in Figure 1 indicate that at 1100°C, silica activity varies from $10^{-0.2}$ for basic liquids which contain clinoenstatite to $10^{-1.6}$ for those which are feldspar free; this range will affect a calculated f_{O_2} by more than four orders of magnitude.

It the whole spectrum of silicate igneous rocks is acknowledged to range from 38 to 77 percent SiO_2, then over the magmatic temperature range of 1100 to 800°C, the corresponding range of silica activity is slightly more than two orders of magnitude. Surprisingly, the tholeiitic series of basalt to rhyolite may show only a very small increase in a_{SiO_2} ($10^{0.05}$) throughout its temperature range.

Lindsley and Munoz (1969) have suggested that the limit of the two-pyroxene field in the large tholeiitic layered intrusions (*e.g.*, Skaergaard and Bushveld) is influenced by the silica activity of the liquid. At this limit, the calcium-poor pyroxene (pigeonite) ceases to crystallize and its place is taken by olivine (Wager and Brown, 1968). In the Skaergaard intrusion the pyroxenes are less iron-rich when pigeonite ceases to crystallize than those of the Bushveld (Lindsley and Munoz, 1969, Fig. 7), and the effect of silica activity on the position of this limit, in terms of Fe/Mg ratios of the pyroxenes, is represented by them in the following reaction:

$$\underset{\text{in pyroxene}}{(Fe_2Si_2O_6)_{ss}} = \underset{\text{olivine}}{(Fe_2SiO_4)_{ss}} + \underset{\text{in melt}}{SiO_2}$$

or

$$K_{3_{[T,P]}} = \frac{a_{Fe_2SiO_4} \cdot a_{SiO_2}}{a_{Fe_2Si_2O_6}}$$

Obviously, a decrease in silica activity will increase the iron content of the olivine at the expense of the pyroxene, which becomes correspondingly magnesian. It was this equation which formed the basis of Lindsley and Munoz' suggestion that "the different Fe/Mg ratios of the last Ca-poor pyroxenes in each body reflect—at least in part—a slightly higher value of a_{SiO_2} during the intermediate stages of crystallization in the Bushveld intrusion than during the equivalent stages of the Skaergaard intrusion."

Using published data (Atkins, 1969; Brown, 1957; Brown and Vincent, 1963; Wager and Brown, 1968) on the composition of coexisting pigeonite and olivine (*i.e.*, at the limit of the two-pyroxene field) it is possible to calculate silica activity over a range of temperatures for both the Bushveld and Skaergaard intrusions. In both intrusions there was a small cooling interval during which both olivine and pigeonite accumulated together, so that the onset of the recurrent precipitation of olivine did not coincide exactly with the disappearance of pigeonite. Tabulated below are the compositions (mole fractions) of coexisting olivine ($X^{olivine}_{Mg_2SiO_4}$) and pigeonite ($X^{pigeonite}_{mgSiO_3}$) at these two stages in both the Bushveld and Skaergaard intrusions

	$X^{olivine}_{Mg_2SiO_4}$	$X^{pigeonite}_{MgSiO_3}$	Sum of log terms
Bushveld			
Olivine re-enters	0.49	0.40	−0.176
Pigeonite leaves	0.30	0.36	+0.158
Skaergaard			
Olivine re-enters	0.40	0.46	+0.121
Pigeonite leaves	0.35	0.42	+0.158

If ideality in the solids is assumed, and if the reaction $Mg_2SiO_4 + SiO_2 = 2MgSiO_3$ is modified to take account of solid solution, then

$$\log a_{SiO_2} = \frac{\Delta G_r^{\circ}}{2.303\,RT} + 2 \log a^{pigeonite}_{MgSiO_3} - \log a^{olivine}_{Mg_2SiO_4}$$

Then by substitution of the relevant mole fractions[1], the sum of the logarithmic terms which are to be added to $\Delta G_r^{\circ}/2.303\,RT$ (Fig. 1) have been obtained, and are tabulated above. The evidence of the logarithmic terms is not decisive in indicating which intrusion had the greater silica activity. This is because the limit of the two-pyroxene field is taken to be at

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[1] $\log a^{olivine}_{Mg_2SiO_4} = 2 \log X^{olivine}_{Mg_2SiO_4}$ (ideality assumed) (Darken and Schwerdtfeger, 1966).

the same temperature in both intrusions; however if the Bushveld temperature was lower, than its silica activity would also be lower than the Skaergaard (Fig. 1). Certainly Lindsley and Munoz' (1969) suggestion that silica activity was slightly higher in the Bushveld, is not clearly supported, but also really not denied by the mineralogical evidence.

One of the contrasts between these two layered intrusions is the relative stage in their cooling history where titanomagnetite became a primary precipitate; in the Skaergaard intrusion it happened when olivine ceased to crystallize at the base of the middle gabbros (Vincent, 1960), but in the Bushveld, it more closely coincided with the recurrent precipitation of olivine (Atkins, 1969). The effect of the onset of precipitation of titanomagnetite on the composition of the later crystallizing ferromagnesian silicates has been considered elsewhere (Carmichael, 1963, 1967c), where it was shown that the more extensive the titanomagnetite precipitate, the more magnesian are the later ferromagnesian silicates. Perhaps a similar affect is present in the Bushveld, for when olivine re-appears, it is 9 percent more magnesian than the corresponding Skaergaard olivine, despite the fact that the coexisting pyroxenes are more iron-rich than those of the Skaergaard. It is worth noting that if iron was not withdrawn from potential olivine in the Bushveld, and if this had a composition of about Fo_{30} (instead of Fo_{49}), not only would the pigeonite-olivine tie-line be parallel that of the Skaergaard, but the calculated silica activity would be greater than the Skaergaard (as suggested by Lindsley and Munoz, 1969). The point we wish to make is that a_{SiO_2}, f_{O_2}, the composition (and amounts) of the various primary precipitate minerals, and the liquid, seem so interdependent that at this stage to choose one variable rather than any other requires some degree of certainty that this chicken came before that egg.

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