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THE FREE ENERGY OF SODALITE AND THE BEHAVIOR OF CHLORIDE, FLUORIDE AND SULFATE IN SILICATE MAGMAS

J. C. STORMER, JR. AND I. S. E. CARMICHAEL, *University of California, Berkeley, California 94720*

ABSTRACT

The Gibbs free energy of formation for sodalite, $Na_4Al_3Si_3O_{12}Cl$, calculated from published data on its decomposition to nepheline and NaCl is:

T (deg. K)	1000	1100	1200	1300	1400
ΔG_f (K cal/gfw)	-1305.8	-1273.5	-1239.6	-1199.9	-1160.2

Sodalite stability is strongly controlled by silica activity. At high temperatures it will be found only in magmas whose silica activities are near or below the nepheline-albite equilibrium. At lower temperatures its stability field expands and it will be stable at higher silica activities, and will therefore precede nepheline in the crystallization sequence of phonolitic trachytes. If f_{Cl_2} is not more than 10^8 greater than f_{F_2}, villiaumite (NaF) or fluorite and nepheline will take the place of sodalite. ΔG°_f for nosean ($Na_8Al_6Si_6O_{24}[SO_4]$) has also been estimated, and it similarly can precede nepheline in the crystallization order of phonolitic trachytes. The ratio of f_{SO_2}/f_{Cl_2} of nosean coexisting with sodalite has been calculated for various temperatures and f_{O_2}. The stability of sulphate (nosean) rather than sulphide minerals is controlled not only by f_{O_2}, but also by silica activity and peralkalinity.

Values of f_{Cl_2} calculated from the sodalite-bearing trachytes of Mt. Suswa, Kenya, vary from $10^{-13.4}$ at 1400°K to $10^{-23.5}$ at 1000°K, and the upper limits of f_{F_2} vary from 10^{-23} to 10^{-35} atmospheres. Estimated fugacities of HCl and SO_2 are several orders of magnitude lower than the partial pressures of the same components in fumarolic gases of a hypersthene-dacite, as is to be expected. Siliceous magmas rich in Cl will generate a fluid phase rich in Cl which is expelled as crystallization proceeds. Magmas of lower silica activities (trachytes, leucite-basanites) will retain their Cl or SO_2, as sodalite or nosean are stable.

INTRODUCTION

With the exception of volcanic gases, the fugitive components in silicate magmas are not conveniently studied, and only analyses of quenched natural liquids provide any approach to their distribution and concentration. However, if during the crystallization of a silicate magma, the presence of a halogen induces a particular mineral to precipitate, then with the necessary thermodynamic data on that mineral, we can calculate a parameter (an intensive variable) which can characterize the behavior of the particular fugitive component. For example, the occurrence of sodalite in lavas can be used as a clue to the behavior of Cl, or nosean or hauyne can be used for SO_3.

As the data for sodalite are more reliable, in this paper we consider Cl and its contrasting behavior with F in silicate magmas. As an indication of the concentration of Cl in various igneous rock types, several average values are given in Table 1. Granite and basalt, comprising the vast

TABLE 1. CHLORIDE ABUNDANCES IN SOME IGNEOUS ROCKS

Rock Description	Percent Cl
Average Igenous Rocks	
Granite (Taylor, 1964)	0.02
Basalt (Taylor, 1964)	0.006
Phonolite (Nockolds, 1954)	0.23
Pantellerites	
Pantelleria (Carmichael, 1962)	
glassy (av. of 6)	0.56
microcrystalline	0.04
Comendites	
New Zealand (Nicholls and Carmichael, 1968)	
glassy (av. of 5)	0.24
microcrystalline (av. of 2)	0.02
Phonolites	
Mt. Suswa, Kenya (Nash *et al.*, 1969)	
glassy (av. of 2)	0.17
crystalline (av. of 7)	0.21
Leucite Tephrites and Basanites	
Vesuvius	
Savelli, 1967 (av. of 21)	0.48
Carmichael, 1971 (av. of 4)	0.46

majority of crustal igneous rocks, have less than 0.02 percent Cl; however one variety of acid lava, the peralkaline glassy pantellerites and comendites contain more than ten times as much Cl (Table I), but the low Cl contents of their crystalline counterparts show that Cl is expelled during crystallization. However, in peralkaline sodic trachytes the precipitation of sodalite retains Cl, so that the glassy and crystalline varieties of these lavas contain comparable amounts (Table I). In the holocrystalline and potassic leucite-basanites of Vesuvius, the occurrence of sodalite in the groundmass similarly retains a high concentration of Cl (Table I). It seems clear that the key to the retention of Cl in a crystalline lava lies in the stability or precipitation of sodalite, and in its absence, Cl will be expelled as part of the fluid phase.

This fluid phase, particularly in magmas with a high silica activity (Carmichael *et al.*, 1970) is rich in NaCl (Roedder and Coombs, 1967), a common component of volcanic sublimates (White and Waring, 1963). The work of Roedder and Coombs (1967) coupled with the experiments of Van Groos and Wyllie (1969) have indicated that a Cl-rich fluid phase is immiscible with silicate liquids. Thus the generation of a Cl-rich fluid is the alternative in magmas with high silica activities to the crystallization of sodalite in magmas with lower silica activities; both may initially contain comparable amounts of Cl (Table I).

THE FREE ENERGY (ΔG°_f) OF SODALITE

The data published by Wellman (1969) on the vapor pressure of NaCl over decomposing sodalite, provides a basis for the calculation of the free energy of sodalite. These data were obtained by determining the temperature of precipitation of halite from the gas evolved by decomposing sodalite to nepheline and NaCl vapor in an evacuated quartz tube placed in a gradient furnace. Two slightly different methods of calculation can be used to determine a value for the free energy of sodalite.

One may assume the equilibrium of sodalite, nepheline and gas at the temperature of the sodalite. The equilibrium of the two predominant sodium chloride polymers, NaCl and Na_2Cl_2, in the gas can be calculated, and the free energies of nepheline and the gas summed to obtain the sodalite free energy.

$$NaCl_{(gas)} + \underset{(nepheline)}{3NaAlSiO_4} = \underset{(sodalite)}{Na_4Al_3Si_3O_{12}Cl} \qquad \Delta G = 0 \qquad (1)$$

$$\Delta G^\circ_{(NaCl\ gas)} + 3\Delta G^\circ_{(nepheline)} - RT \ln f_{NaCl} = \Delta G^\circ_{(sodalite)}$$

$$\text{(where } f = \text{fugacity of NaCl species)} \qquad (1a)$$

Alternatively one may assume that the sodalite and the nepheline at a higher temperature (T_1) are in equilibrium with pure halite at a lower temperature (T_2) through the medium of the gas:

$$NaCl_{(halite,T_2)} + 3NaAlSiO_{4(nepheline,T_1)} = Na_4Al_3Si_3O_{12}Cl_{(sodalite,T_1)} \qquad (2)$$

$$\Delta G^\circ_{(halite,T_2)} + 3\Delta G^\circ_{(nepheline,T_1)} = \Delta G^\circ_{(sodalite,T_1)} \qquad (2a)$$

The calculated values of free energy are shown in Figure 1. The agreement between both sets of calculations is quite good.

In the discussion which follows, we have assumed that all liquids and solids mix ideally, so that $a_{(activity)} = X_{(mol.\ fraction)}$. We are also concerned with components in a liquid rather than species.

SODALITE STABILITY AND SILICA ACTIVITY

As sodalite is found only in silica-undersaturated rocks, and never in quartz-bearing assemblages, its stability is obviously strongly influenced by silica activity (Carmichael *et al.*, 1970). Using the reaction (3) below, the effect of varying silica activity on the stability of sodalite can be calculated. At the same time the effect of varying the activity of NaCl in

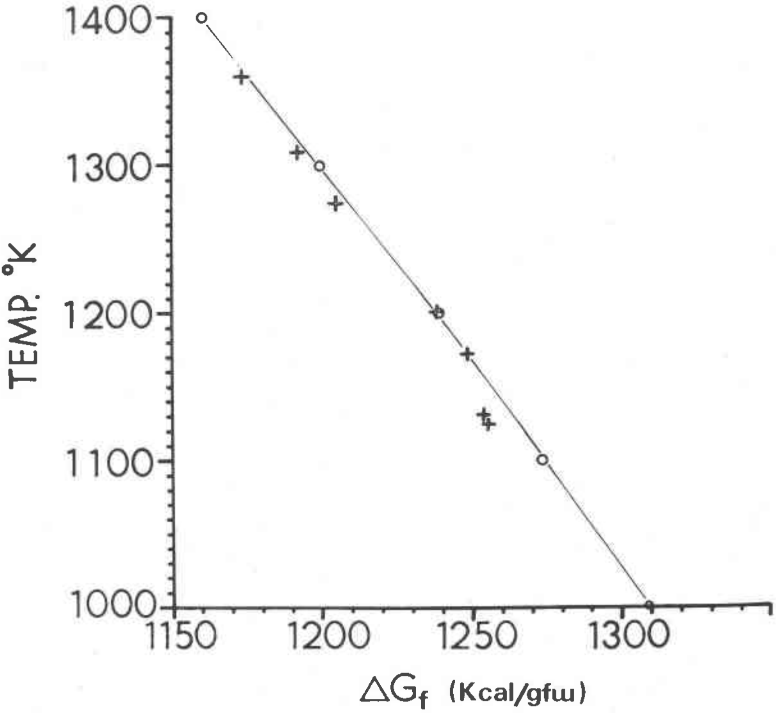

FIG. 1. The free energy of formation of sodalite ($Na_4Al_3Si_3O_{12}Cl$) calculated from measurements of the vapor pressure of NaCl over decomposing sodalite (Wellman, 1969). Calculations using reaction 1 shown as circles, reaction 2 as crosses.

the liquid, a_{NaCl}^{liquid}, which can be taken as a measure of Cl concentration, together with the effect of changing the composition of the coexisting feldspar, can be shown (assuming sodalite remains stoichiometric or nearly so).

$$\underset{\text{sodalite}}{Na_4Al_3Si_3O_{12}Cl} + \underset{\text{liquid}}{6SiO_2} = \underset{\text{liquid}}{NaCl} + \underset{\text{albite}}{3NaAlSi_3O_8} \tag{3}$$

$$\log a_{SiO_2}^{\text{liquid}} = \frac{1}{6}\left[\frac{\Delta G^\circ}{2.303\ RT} + \log a_{NaCl}^{\text{liquid}} + 3 \log a_{NaAlSi_3O_8}^{\text{feldspar}}\right] \tag{3a}$$

In Figure 2, the limit of the stability field of sodalite is shown at two temperatures. If the coexisting feldspar is pure albite ($a_{NaAlSi_3O_8}^{\text{feldspar}} = 1$), then sodalite is stable at higher silica activities than those defined by the reaction

$$NaAlSiO_4 + 2SiO_2 = NaAlSi_3O_8 \tag{4}$$

in a typical phonolite assemblage (Carmichael *et al.*, 1970). The curves in

Figure 2 indicate that sodalite will co-precipitate with feldspar in trachytic liquids *before* they become sufficiently poor in silica to precipitate nepheline; this sequence of crystallization is particularly well displayed in the Mt. Suswa phonolitic trachytes (Nash *et al.*, 1969). However if the coexisting feldspar is not pure albite, then the precipitation of sodalite will be delayed at both temperatures (Fig. 2), until silica activity is lower than under the corresponding conditions of pure feldspar. The calculated data shown in Figure 2 may be emphasised in a different way; the lower the crystallization temperature, the more likely sodalite is to precede nepheline in the order of crystallization of a trachytic magma whose residual liquid is changing in composition so as to eventually crystallize nepheline. The greater the activity of NaCl or concentration of Cl in the trachyte magnia, the greater will this precedence of sodalite be in comparison to nepheline (Fig. 2).

In a paper on silica activity in igneous rocks, Carmichael *et al.* (1970) suggested that the thermodynamic data for leucite are likely to be wrong, and that the variation in a_{SiO_2} with temperature defined by the reaction

$$\underset{\text{leucite}}{KAlSi_2O_6} + \underset{\text{liquid}}{SiO_2} = \underset{\text{feldspar}}{KAlSi_3O_8} \tag{5}$$

should be at higher values of a_{SiO_2} than the corresponding curve for the nepheline-albite assemblage. This conclusion is not invalidated by the occurrence of sodalite in the crystalline groundmass of the Vesuvius leucite-basanites (Carmichael, unpublished work). In these, leucite, plagioclase (An_{56}), sodalite and phlogopite coexist, an assemblage which in view of the calculated stability of sodalite (Fig. 2) could well have a higher silica activity than the analogous nepheline-albite assemblage.

In magmas with high silica activities, namely rhyolites and siliceous trachytes, the Cl component, represented as NaCl (Fig. 2) will presumably form an immiscible fluid phase if the results of Van Groos and Wyllie (1969) in the immiscibility of liquid NaCl in $NaAlSi_3O_8$ liquid are applicable to siliceous magmas.

SODALITE STABILITY AND FLUORINE FUGACITY

One of the intriguing contrasts between chlorine and fluorine in igneous rocks is seen in the absence of a fluoride analogue of sodalite. Villiaumite (NaF) and nepheline are the stable equivalent association, and although very rare in nature, they do occur (Stormer and Carmichael, 1970). Another example of the separation of these two halides is found in the groundmass assemblage of the Vesuvius leucite-basanites (Carmichael, 1971a) there, as noted above, sodalite is associated with chloride-poor fluorphlogopite.

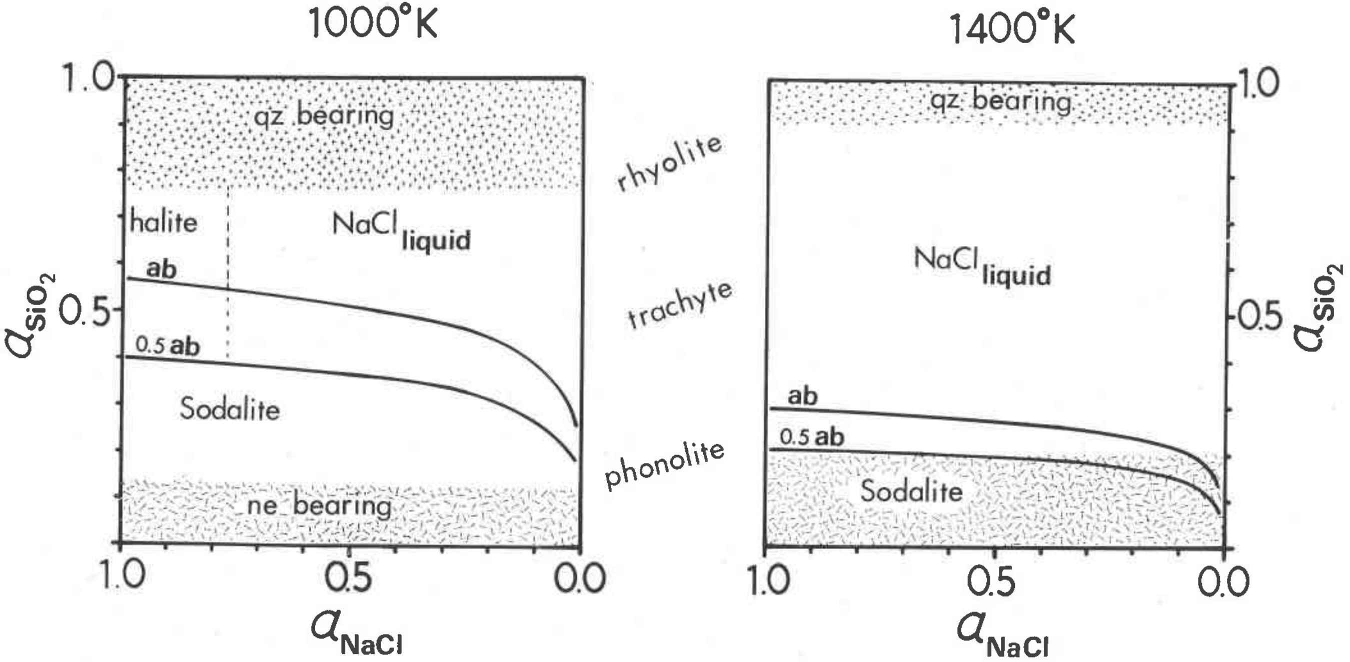

FIG. 2. The stability field of sodalite at 1000°K (727°C) and 1400°K (1127°C) as calculated by reaction 3. Sodalite will be stable at silica and NaCl activities below the curves: the upper curve is for pure albite, the lower for an activity of 9.5 albite in coexisting feldspar. The standard state for SiO_2 has been taken as silica glass (cf. Carmichael *et al.*, 1970). The lower boundary of the shaded area labeled "quartz bearing" is defined by the activity of silica glass in equilibrium with crystalline quartz. Below this line quartz will not be stable. Rhyolitic magmas will have silica activities near this boundary. The upper boundary of the shaded area labeled "ne bearing" is defined by the activity of silica in equilibrium with nepheline and albite. Above this line nepheline will not be stable; below it an albite-rich feldspar will not be stable. Phonolitic magmas will have silica activities near this value. Trachytic magmas will have intermediate values of silica activity. Liquid NaCl was similarly chosen as the standard state for sodium chloride. Therefore at temperatures below the melting temperature of halite, crystalline halite will be in equilibrium with NaCl liquid at activities less than one. The activity of liquid NaCl in equilibrium with halite is shown at 1000°K (727°C) by the dashed boundary. Magmas having activities of liquid NaCl on this boundary, and silica activities above the sodalite stability field would contain crystalline halite. No natural example of such a magma has been reported.

It is possible to calculate limits of the ratio of the fugacities of F to Cl (f_{F_2}/f_{Cl_2}) for rocks which contain sodalite. In the following reaction

$$2Na_4Al_3Si_3O_{12}Cl + F_2 = 2NaF + 6NaAlSiO_4 + Cl_2 \qquad (6)$$

$$\log f_{F_2}/f_{Cl_2} = \frac{\Delta G^\circ}{2.303\ RT} + 6 \log \overset{\text{nepheline}}{a_{NaAlSiO_4}} \qquad (6a)$$

the ratio f_{F_2}/f_{Cl_2} is approximately $10^{-8.4}$ over the temperature range 1000°–1400°K for the equilibrium assemblage sodalite, nepheline and villiaumite. If water is present as a component in reaction (6) then HF and HCl will be the predominant halide species, and, as hydrolysis of fluorine is the more complete, the corresponding fugacity ratios f_{HF}/f_{HCl} vary between $10^{4.8}$ and $10^{2.4}$ over the same temperature range (1000–1400°K). It is therefore possible to calculate the *upper* limit of the two fugacity ratios f_{F_2}/f_{Cl_2} and f_{HF}/f_{HCl} for natural assemblages of sodalite and nepheline. The calculated fugacity ratios are not greatly changed if reaction (6) is modified to include albite (7), provided that the silica activity is appropriately low:

$$\underset{\text{sodalite}}{2Na_4Al_3Si_3O_{12}Cl} + \underset{\text{liquid}}{12SiO_2} + F_2 = \underset{\text{villiaumite}}{2NaF} + \underset{\text{albite}}{6NaAlSi_3O_8} + Cl_2 \qquad (7)$$

Stormer and Carmichael (1970) have shown that villiaumite in reaction (7) will be replaced by fluorite if the anorthite component of the feldspar exceeds about 10 mole percent. Fluorite and nepheline will then take the place of sodalite at the expense of anorthite as indicated in the reaction below

$$\underset{\text{sodalite}}{2Na_4Al_3Si_3O_{12}Cl} + \underset{\text{anorthite}}{CaAl_2Si_2O_8} + F_2 = \underset{\text{fluorite}}{CaF_2} + \underset{\text{nepheline}}{8NaAlSiO_4} + Cl_2 \qquad (8)$$

and

$$\log f_{F_2}/f_{Cl_2} = \frac{\Delta G^\circ}{2.303\ RT} + 8 \log \overset{\text{nepheline}}{a_{NaAlSiO_4}} - \log \overset{\text{feldspar}}{a_{CaAl_2SiO_8}} \qquad (8a)$$

In Figure 3, we have plotted the results for the two reactions (6) and (8) at 1200°K. Using the data on the Vesuvius leucite-basanites where sodalite coexists with An_{56} in the groundmass, the calculated stability curve of sodalite in Figure 3 indicates a *maximum* value of f_{F_2}/f_{Cl_2} of about 10^{-9} at 927°C for these lavas. Savelli (1967) has given an average value of 2700 ppm F and 4800 ppm Cl for the Vesuvius lavas, which correspond to a concentration ratio of 0.56 or $10^{-0.25}$.

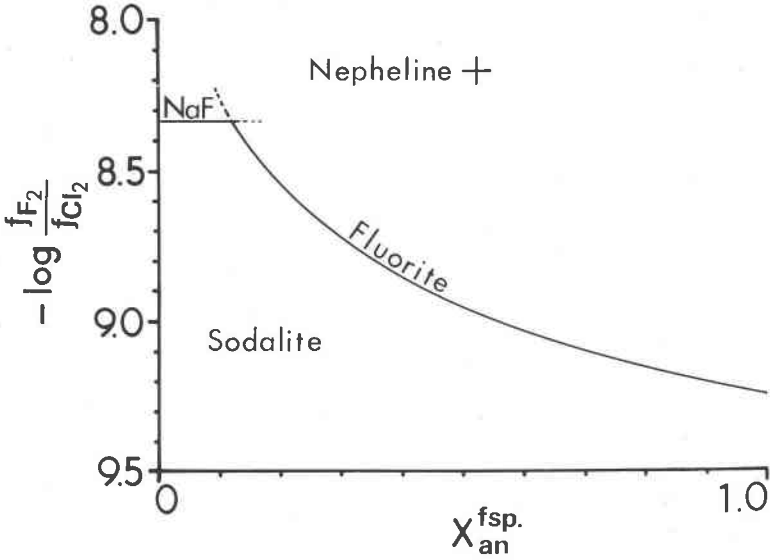

FIG. 3. The stability field of sodalite as limited by high ratios of fluorine to chlorine at 1200°K (927°C); see reactions 7 and 8 in text. If a feldspar containing more than 10 mole percent anorthite coexists with sodalite, fluorite plus nepheline will take the place of sodalite, the ratio of fluorine to chlorine falling with increasing anorthite. If a feldspar with more than 10 mole percent anorthite is not present villiaumite and nepheline will take the place of sodalite. These relationships remain essentially the same over the temperature range 1000°K (727°C)–1400°K (1127°C).

NOSEAN AND SULPHATE ACTIVITY

In order to estimate the free energy of nosean ($\Delta G°_f$), we can assume that over the temperature range of interest, the sum of the free energies of nepheline and thenardite (Na_2SO_4) are equal to that of nosean in an analogous way to the discussion of sodalite. In other words, it can be assumed that ΔG of the following reaction is zero

$$\underset{\text{thenardite}}{Na_2SO_4} + \underset{\text{sodalite}}{2Na_4AlSi_3O_{12}Cl} = \underset{\text{halite}}{2NaCl} + \underset{\text{nosean}}{Na_8Al_6Si_6O_{24}(SO_4)} \quad (9)$$

Then

$$\Delta G°_{f\,(\text{nosean})} = 2\Delta G°_{f\,(\text{sodalite})} + \Delta G°_{f\,(\text{thenardite})} - 2\Delta G°_{f\,(\text{halite})} \quad (9a)$$

Since nosean can be produced from sodalite, and sodalite from nosean, in a flux of the appropriate sodium salt (Pauling, 1930), this assumption may not be far wrong.

Using the estimated values of $\Delta G°_f$ for nosean, it is possible to calculate the stability of nosean at various temperatures as a function of silica activity and Na_2SO_4 activity using the reaction:

$$\underset{\text{nosean}}{Na_8Al_6Si_6O_{24}(SO_4)} + \underset{\text{liquid}}{12SiO_2} = \underset{\text{liquid}}{Na_2SO_4} + \underset{\text{albite}}{6NaAlSi_3O_8} \qquad (10)$$

The calculated curves are almost identical[1] to those for sodalite plotted in Figure 2, and indicate that nosean can precede nepheline in the order of crystallization of a trachytic magma whose residual liquid will eventually precipitate nepheline. Both the experimental results of Taylor (1967) on the system nosean-albite-orthoclase, and observations on the Wolf Rock nosean phonolite (Tilley, 1959) indicate that nosean may precede nepheline in magmas crystallizing feldspar.

Peteghem and Burley (1963) and Tomisaka and Eugster (1968) have investigated the sodalite-nosean join. There is a large miscibility gap, and both solids show limited solid solution. However there is substantial disagreement between the two sets of results on the extent of solid solution in the two phases. Analyses of natural sodalite and nosean (Deer *et al.*, 1963; Taylor, 1967) suggest that there is considerably more solid solution of the chloride component in nosean than of the sulphate component in sodalite. If the extent of the mutual solid solution in the nosean-sodalite series is assumed to be minimal at magmatic temperatures, then the following reaction can be used to calculate the limiting fugacity ratio f_{SO_2}/f_{Cl_2} for nosean or sodalite. It is also assumed that SO_2 is the predominant sulphur-oxygen species at magmatic temperatures (Heald *et al.*, 1963).

$$\underset{\text{sodalite}}{2Na_4Al_3Si_3O_{12}Cl} + SO_2 + O_2 = \underset{\text{nosean}}{Na_8Al_6Si_6O_{24}(SO_4)} + Cl_2 \qquad (11)$$

$$\log f_{SO_2}/f_{Cl_2} = \frac{\Delta G^\circ}{2.303\ RT} - \log f_{O_2} - 2\log a^{\text{sodalite}}_{Na_4Al_3Si_3O_{12}Cl} + \log a^{\text{nosean}}_{Na_8Al_6Si_6O_{24}(SO_4)} \qquad (11a)$$

The variations of the fugacity ratio f_{SO_2}/f_{Cl_2} with temperature and f_{O_2} has been plotted in Figure 4 assuming unit activity of nosean and sodalite. Each curve represents the f_{SO_2}/f_{Cl_2} ratio for the coexistence of nosean and

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[1] It may appear that the stability fields of nosean and sodalite in terms of the activities of silica, albite and sodium salt (reactions (3) and (10) Fig. 2) are necessarily identical because of the assumptions used to estimate the free energy of nosean. However, the standard state of the sodium salt in equation (3) was the pure liquid, whereas that used to estimate the free energy of nosean was the crystalline solid. As a result the stability field of nosean in terms of these variables will differ from that of sodalite by an amount determined by the difference in the solid-liquid transition energies of Na_2SO_4 and NaCl. This difference is in fact negligibly small; at 1000°K it would be represented by an increase of about 0.01 in the silica activity.

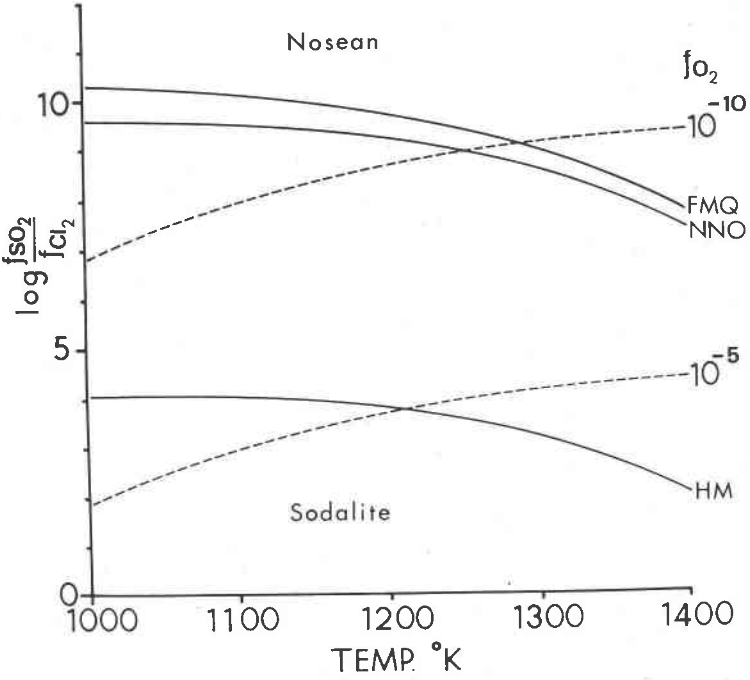

FIG. 4. Reaction 11, equilibrium between nosean and sodalite, plotted in terms of the ratio of SO_2 to Cl_2 and temperature for several oxygen fugacities. Dashed curves for constant oxygen fugacities. Solid curves for oxygen fugacities buffered by the following assemblages: FMQ, fayalite-magnetite-quartz; NNO, nickel-nickel oxide; HM, hematite-magnetite.

sodalite for particular oxygen-fugacity conditions. Thus nosean in equilibrium with hematite and magnetite would have a minimum value of f_{SO_2}/f_{Cl_2} of 10^2 to 10^4 over the temperature range of Figure 4.

NOSEAN AND OXYGEN FUGACITY

The presence of sulphate sulphur in a magma rather than sulphide sulphur is often thought to require an unusually high f_{O_2}, or at least values higher than those normally associated with sulphide minerals (Skinner and Peck, 1969, 319). But the association of nosean with olivine and titaniferous magnetite in alkali olivine-basalt bombs in Quaternary cinder cones of northeastern New Mexico (Baldwin and Muehlberger, 1958; Stormer, 1970) shows that unless either of the ferromagnesian minerals have extreme composition, the oxygen fugacity will not differ greatly from any other olivine-basalt, or from that in equilibrium with the synthetic fayalite-magnetite-quartz assemblage (Carmichael and Nicholls, 1967). The more common paragenesis of nosean, or perhaps of hauyne, a calcium-bearing sulphate variety, is in olivine-free lavas, for example, the etindites of West Africa (Tilley, 1953; Carmichael, unpublished work), where noseanhauyne solid solutions occur with titan-augite, titaniferous magnetite and perovskite. In some salic lavas, nosean or hauyne may occur with melanite, augite titaniferous magnetite and leucite. In both parageneses, the absence of olivine could be suggestive of a higher f_{O_2}.

Perhaps the problem of the occurrence of sulphate rather than sulphide can be illustrated by the following reaction, a plausible representation of a nosean paragenesis

$$\underset{\text{nosean}}{Na_8Al_6Si_6O_{24}(SO_4)} + \underset{\text{magnetite}}{Fe_3O_4} + \underset{\text{liquid}}{16SiO_2}$$
$$= \underset{\text{pyrrhotite}}{FeS} + \underset{\text{acmite}}{2NaFeSi_2O_6} + \underset{\text{albite}}{6NaAlSi_3O_8} + 2O_2 \qquad (12)$$

A cursory inspection shows that if silica activity falls, the reaction will run to the left, despite f_{O_2} remaining constant. This reaction illustrates an essential point: the occurrence of sulphate rather than sulphide need not require an unusually high f_{O_2}, because it is also controlled by the overall composition of the silicate magma. In this example, low silica activity and a large component of acmite in the coexisting pyroxene would promote the crystallization of nosean. Sulphate minerals are therefore to low silica activity peralkaline magmas what sulphide minerals are to high silica activity magmas; even though f_{O_2} may be constant (at comparable T), witness the occurrence of olivine and titaniferous magnetite.

Calculation of Fugitive Fugacities in Igneous Assemblages

The volatile constituents of a magma as we have seen are often lost in the later stages of crystallization. However, thermodynamic data can be used to recalculate the activities or fugacities from analyses of the mineral phases whose presence and composition was controlled by, or controlled, them.

The sodalite-bearing trachytic lavas of Mt. Suswa, Kenya, have been studied by Nash *et al.* (1969) and analyses of the mineral phases are available. The fugacity of chlorine in one lava (W158) can be calculated using the following reaction:

$$2NaFeSi_2O_6 + 6NaAlSiO_4 + Cl_2$$
$$= 2Na_4Al_3Si_3O_{12}Cl + 4SiO_2 + \tfrac{2}{3}Fe_3O_4 + \tfrac{2}{3}O_2 \qquad (13)$$

$$\log f_{Cl_2} = \frac{\Delta G^\circ}{2.303\ RT} + 2\log \overset{\text{sodalite}}{a_{Na_4Al_3Si_3O_{12}Cl}} + 4\log a_{SiO_2} + \tfrac{2}{3}\log \overset{\text{magnetite}}{a_{Fe_3O_4}}$$
$$+ \tfrac{2}{3}\log f_{O_2} - 2\log \overset{\text{pyroxene}}{a_{NaFeSi_2O_6}} - 6\log \overset{\text{nepheline}}{a_{NaAlSiO_4}} \qquad (13a)$$

The activity of silica is calculated from the data for nepheline and feldspar (Carmichael, *et al.*, 1970; Nash *et al.*, 1969). Activity coefficients for nepheline obtained from the data of Perchuck and Ryabchikov (1968) were used although they do not take the excess silica component into account. In the absence of any better information the activities of the other components were assumed to be equal to their mole fractions in the respective mineral phases.

The fugacity of chlorine has been calculated and plotted in Figure 5 as a function of temperature, assuming that all the phases in reaction (9) coexist at a given temperature. In all probability they coexist only for a limited range of temperature, which unfortunately is not known. As neither villiaumite nor nosean are present, only the *upper* limits of the fugacities of F_2 and SO_2 for the observed mineral assemblage can be calculated using reactions (8a) and (11a), and they are plotted in Figure 5. In order to facilitate comparison with analysed volcanic gases, it was assumed that the fugacity of water in the lava was 1 atm and the approximate fugacity of HCl calculated. Also shown in Figure 5 are the partial pressures of HCl and SO_2 derived from analyses of fumarolic gases associated with the extrusion of a hypersthene dacite dome at Showa-Shinzan, Japan (White and Waring, 1963). The Showa-Shinzan data was selected because of the completeness of the analyses and the appropriateness of the temperature range. HCl and SO_2 in these analyses are not unusually high when compared with other data. A hypersthene dacite such as this will, of course, have a much higher silica activity than the phonolites with which it is being compared, and will no doubt generate and expel a fluid phase rich in Cl as crystallization proceeds. It is not surprising therefore that the fugacity of HCl, and also SO_2, is so much higher at Showa-Shinzan than the values calculated for Mt. Suswa lavas. The most striking feature of Figure 5 is the very low volatile pressure (equal to fugacity at 1 atm H_2O) required to stabilize sodalite in trachyte lavas (*cf.* Nash *et al.*, 1969). It is obvious that sodalite may be unstable only in a very thin zone of the flow crust (Nash *et al.*, 1969). It is also apparent that high activities of chlorine are not necessarily characteristic of sodalite-bearing undersaturated magmas in spite of the high chloride contents of such rocks. Other chemical parameters, particularly silica activity, are the controlling factors in the behavior of chloride in magmas and its distribution in rocks. Relatively silicic magmas may be expected to show a rising activity of chlorine and higher fugacities of HCl upon crystallization, even though the chloride content of the resulting rock is very low. Conversely, silica-undersaturated peralkaline magmas will precipitate sodalite and retain their chloride in the rock. The occurrence of sodalite or any other halide or sulfate mineral in a rock is not necessarily indicative of unusual activity of that component in the parent magma.

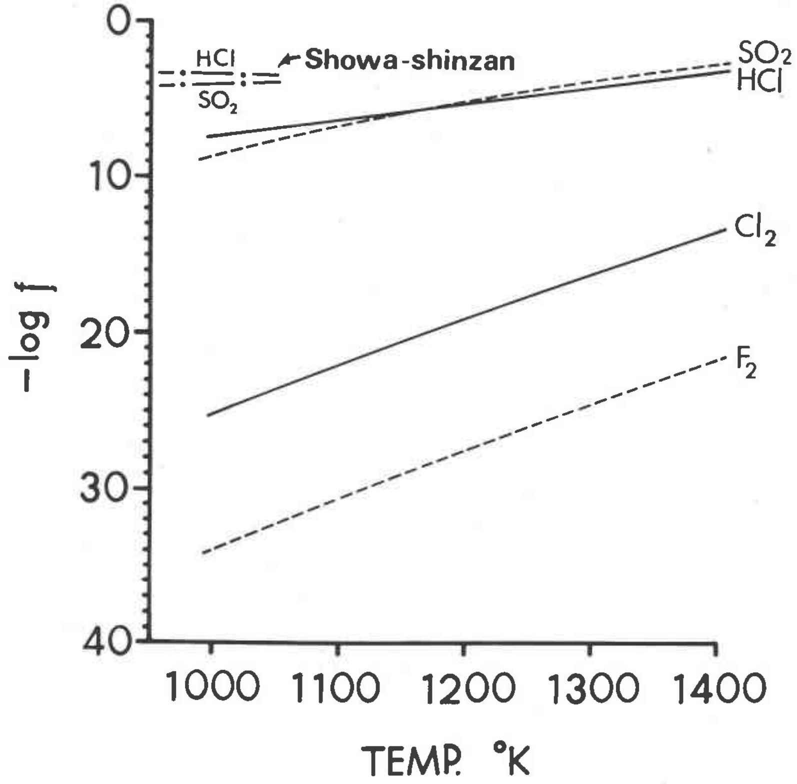

FIG. 5. Fugacities of certain volatile components calculated for one lava of Mt. Suswa, Kenya between 727°C (1000°K) and 1127°C (1400°K). The fugacities of Cl_2 and HCl calculated by reaction 13 (see text). Upper limits of the fugacities of F_2 and SO_2 were determined by reactions 8a and 11a. Partial pressures of HCl and SO_2 in analysed fumarolic gases from a hypersthene dacite at Showa-Shinzan, Japan are also shown.

Quantitative definition of the role halogens and other fugitive components play in the genesis and differentiation of magmas require this type of thermodynamic investigation, which will indicate more clearly than has previously been possible the behavior of volatiles in magmatic liquids.

THERMODYNAMIC DATA

Sodalite ($Na_4Al_3Si_3O_{12}Cl$)—calculated from Wellman's (1969) data.

$T°$ (°K)	1000	1100	1200	1300	1400	
ΔG_f (Kcal/gfw)	−1305.8	−1273.5	−1239.6	−1199.9	−1160.2	all ±3.0

Nosean ($Na_8Al_6Si_6O_{24}(SO_4)$)—estimated this paper.

T (°K)	1000	1100	1200	1300	1400

ΔG_f (Kcal/gfw)	-2695.0	-2624.2	-2550.5	-2468.3	-2386.0	all ±3.0 (numerical errors)

Acmite ($NaFeSi_2O_6$)—estimated by Nicholls and Carmichael (1969)

NaCl and HF (liquid and gaseous)—JANAF Thermochemical Tables

All other data—Robie and Waldbaum (1968)

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