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VILLIAUMITE AND THE OCCURRENCE OF FLUORIDE MINERALS IN IGNEOUS ROCKS

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Abstract

The first occurrence of villiaumite (NaF) in the U.S.A. has been discovered in Colfax County, New Mexico, where it is found in a peralkaline phonolitic sill. Electron probe analysis of this specimen and specimens from Isles de Los, Guinea, and Lovozero, U.S.S.R., shows that only very limited substitution of Al exists; our data also suggest that published analyses showing substantial substitution of other elements (*e.g.*, K, Ca) in villiaumite are likely to be in error. The lattice constants of three villiaumites show a small variation around $a=4.630$ Å. Thermodynamic calculations show that fluorite is to be expected as the common fluoride mineral in both silica-saturated and undersaturated igneous rocks; in calcium-and silica-poor assemblages villiaumite is favored, but in calcium-poor quartz-bearing rocks, cryolite will prevail.

A new occurrence of villiaumite (NaF) has been found in Peck's Mesa, eastern Colfax County, New Mexico (R26E T26N). There, in an abandoned quarry on the southwestern edge of the mesa, villiaumite is found in the phonolitic sill which forms the mesa. The phonolite forms part of an extensive volcanic province described by Stobbe (1949) and Wood *et al.* (1953). The sill contains phenocrysts of aegirine, alkali feldspar, and almost completely replaced nepheline. The groundmass consists of alkali feldspar, analcite and accessory villiaumite, serandite, zeolites and eudialyte.

Villiaumite was first described by Lacroix (1908) from the nepheline syenites of Rouma, Isles de Los, Guinea, West Africa. It has since been reported from the Lovozero Massif, U.S.S.R. (Gerasimovsky, 1941) and the Ilimaussaq intrusion, Greenland (Bondam and Ferguson, 1962). It has also been found in saline lake deposits (Baker, 1958). Specimens from the first two of these localities were available for study.

The color of the villiaumite specimens ranges from a deep carmine red in the Rouma specimen to a slightly lighter shade in the Lovozero specimen and a variable lavender pink to light orange in the New Mexican specimen. Very slight pleochroism and a weak irregular birefringence can be observed in 0.1 to 0.2 mm thick grains of the Rouma villiaumite only. No evidence of anisotropy can be seen in a standard thin section. The color of all three specimens was permanently lost by heating to about 500°C for a few minutes. Barth and Lunde (1927) reported this bleaching at 300°C. We found the higher temperature necessary.

Electron microprobe analyses of villiaumite from New Mexico, Rouma and Lovozero were made for the following elements: Ca, K, Al, Fe, Mn, Mg, Si, Ti, Mo, Zr and Cl. All were found to be below the limit of detection (in all cases less than 0.02%) except for Al.

Levin *et al.* (1964) present phase diagrams for a number of binary systems with NaF; of the elements looked for (above), only Al (as AlF_3) forms a solid solution with NaF. In the villiaumite from New Mexico, up to 0.04 percent (equivalent to 0.06% AlF_3) was found. Our analytical results coupled with the experimental data (Levin *et al.*, 1964) suggest that the analyses of villiaumite tabulated by Bondam and Ferguson (1962) which report over 1 percent Ca and Zr and 0.32 percent K are likely to be in error.

A Jagodzinski-Guinier camera equipped with a quartz monochromator was used to take the X-ray powder photographs with Fe K-alpha radiation ($\lambda = 1.93728$ Å). Silicon ($a = 5.43054$ Å) was added as an internal standard to the powder prepared from samples of villiaumite handpicked from the crushed rock specimens. Photographs were also taken of identical material after annealing at about 600°C for three hours in an attempt to determine if any crystallographic change accompanied the bleaching phenomenon.

The lines of villiaumite both before and after annealing were consistently much more diffuse than those of the silicon standard, although the crystallite sizes are likely to have been similar. The villiaumite lines appeared to have a normal distribution of intensity about a single peak, rather than any splitting which would be expected if this diffuseness was due to slight tetragonality as suggested by Barth and Lunde (1927) for villiaumite from Rouma.

The powder data was refined by computer using a program by Burnham (1962). The results are as follows:

Specimen Locality	*Natural*	*Annealed* (colorless)
Rouma, Isles de Los	$a = 4.633$ Å	$a = 4.628$ Å
Lovozero, U.S.S.R.	$a = 4.632$	$a = 4.628$
New Mexico, U.S.A.	$a = 4.630$	$a = 4.628$

Standard deviations computed by the program varied from 0.0008 to 0.0024 Å. The precision of the observations is ±0.002 Å. The small variation of a is not considered to be significant.

RELATIVE STABILITY OF FLUORIDE MINERALS

There are three principal fluoride minerals in igneous rocks: villiaumite, cryolite (Na_3AlF_6), and fluorite (CaF_2) (Palache *et al.*, 1951). Villiaumite has only been found in peralkaline nepheline-syenites where it occurs in association with nepheline, analcite, alkali feldspar, aegirine or alkali amphibole, and thus never with quartz. Cryolite, however, is usually accompanied by quartz; otherwise the associated minerals are not unlike those found with villiaumite (Troger, 1967).

Fluorite is the most widespread fluoride mineral; it is, for example, a typical accessory of hypersolvus granites (Tuttle, personal communication, 1966). These granites are characteristically undersaturated in alumina, and often contain aegirine or an alkali amphibole (Luth *et al.*, 1964). Fluorite also occurs in nepheline-syenites, syenites and in large pervasive hydrothermal veins (Deer, *et al.*, 1962, p. 352).

In short, it appears that villiaumite and quartz are incompatible, whereas cryolite occurs only with quartz. Fluorite, however, is the typical fluoride accessory mineral in a wide range of silica saturated to undersaturated rocks.

Using the thermodynamic data of Robie and Waldbaum (1968) and the appropriate estimates for acmite by Nicholls and Carmichael (1969) it is possible to calculate the relative stability of these three fluoride minerals using reactions which correspond reasonably with their observed parageneses. The following reaction represents the typical occurrence of villiaumite in an assemblage of aegirine, nepheline, albite and an iron-oxide mineral.

$$\underset{\text{acmite}}{6NaFeSi_2O_6} + \underset{\text{nepheline}}{6NaAlSiO_4} + 3F_2 = 6NaF + \underset{\text{albite}}{6NaAlSi_3O_8} + \underset{\text{magnetite}}{2Fe_3O_4} + 2O_2 \qquad (1)$$

If all the minerals are assumed to be in their standard states, then the variation of the fugacity of fluorine with oxygen fugacity and temperature can be obtained from the following relationship:

$$3 \log f_{F_2} = \frac{\Delta G_r^0}{2.303\ RT} + 2 \log f_{O_2} \qquad (1a)$$

In Figure 1A contours of log f_{F_2} have been plotted as a function of log f_{O_2} and temperature. Oxygen fugacities defined by the two synthetic oxygen buffers, hematite-magnetite (Eugster and Wones, 1962), and fayalite-magnetite-quartz (Wones and Gilbert, 1969) are also shown. If a cooling nepheline-syenite or phonolite has the mineral assemblage represented by reaction (1) and an f_{O_2} close to that defined by the synthetic fayalite-magnetite-quartz buffer, then at 850°C villiaumite will form if the fugacity of fluorine is more than 10^{-30} atm. (This is approximately equivalent to one molecule of F_2 in nearly 10^6 cubic meters.) These very low fugacity values immediately suggest that fluorine will also be present as some other species; in the presence of H_2O, HF will predominate.

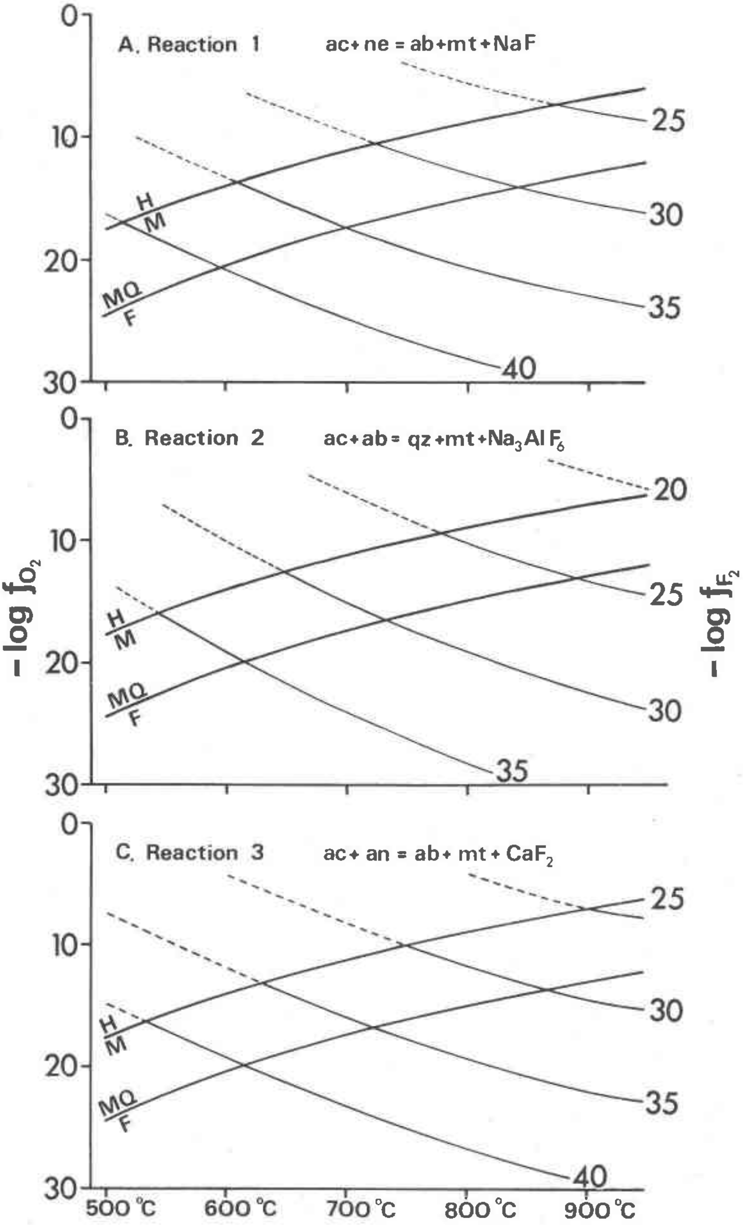

FIG. 1. (A) Contours of fluorine fugacity (f_{F_2}) for reaction (1) (see text) plotted against oxygen fugacity (in atmospheres) and temperature. The oxygen fugacity curves for the assemblage hematite-magnetite (HM) and fayalite-magnetite-quartz (FMQ) (Eugster and Wones, 1962; Wones and Gilbert, 1969) have also been plotted. (B and C) Contours of fluorine fugacity (f_{F_2}) for reactions (2) and (3) (see text) plotted as above.

Reaction (2) represents the mineral association found in cryolite occurrences.

$$\underset{\text{acmite}}{6NaFeSi_2O_6} + \underset{\text{albite}}{3NaAlSi_3O_8} + 9F_2 = 3Na_3AlF_6 + \underset{\text{quartz}}{21SiO_2} + \underset{\text{magnetite}}{2Fe_3O_4} + 5O_2 \quad (2)$$

Again with all mineral components in their standard states the equilibrium values of log f_{F_2} have been calculated and are plotted against log f_{O_2} and temperature in Figure 1B. At any given temperature and log f_{O_2}, fluorine fugacity is several orders of magnitude higher than that calculated for reaction (1). This suggests that cryolite could have a more restricted occurrence than villiaumite.

Reaction (3) represents the feldspar, pyroxene and iron-oxide components of typical fluorite assemblages without regard to silica saturation.

$$\underset{\text{acmite}}{6NaFeSi_2O_6} + 3F_2 + \underbrace{3CaAl_2Si_2O_8 = 6NaAlSi_3O_8}_{\text{plagioclase}} + 3CaF_2 + \underset{\text{magnetite}}{2Fe_3O_4} + 2O_2 \quad (3)$$

The calculated variaton of log f_{F_2} with log f_{O_2} and temperature is shown in Figure 1C. The fugacity of fluorine for this reaction is much lower than for reaction (2) suggesting that fluorite will be more widespread than cryolite. However, the fluorine fugacities calculated for reaction (1), with all mineral components in their standard states, are not sufficiently higher than those of reaction (3) to allow any prediction of the relative stabilities of villiaumite and fluorite.

The antipathy of villiaumite and quartz can be represented by the following reaction:

$$2NaF + 4SiO_2 + \underbrace{CaAl_2Si_2O_8 = 2NaAlSi_3O_8}_{\text{plagioclase}} + CaF_2 \quad (4)$$

It can be seen from this reaction that if silica activity and the anorthite component of the feldspar are low, then the reaction will proceed to the left and favor villiaumite. This is illustrated in Figure 2, where calculated curves for coexisting NaF and CaF_2 are plotted (at two different temperatures) in terms of silica activity and of the composition of the associated plagioclase. Silica activity in nepheline-syenites and phonolites (Carmichael I. S. E., J. Nicholls, and A. L. Smith, 1969) may be taken to approximate that defined by the reaction:

$$\underset{\text{nepheline}}{\tfrac{1}{2}NaAlSiO_4} + SiO_2 = \underset{\text{albite}}{\tfrac{1}{2}NaAlSi_3O_8} \qquad (5)$$

and calculated values at two different temperatures have also been plotted in Figure 2. It is therefore only in silica- and anorthite-poor rocks, such as phonolites, that villiaumite is to be expected.

Cryolite, in contrast to villiaumite, is typically found with quartz. The relative stability of cryolite to villiaumite may be calculated using the following reaction.

$$\underset{\text{acmite}}{12NaFeSi_2O_6} + 3Na_3AlF_6$$

$$= 18NaF + \underset{\text{magnetite}}{4Fe_3O_4} + \underset{\text{albite}}{3NaAlSi_3O_8} + \underset{\text{quartz}}{15SiO_2} + O_2 \qquad (6)$$

The absence of any data on the activity coefficients, particularly $NaFeSi_2O_4$ in pyroxene, limits any quantitative application of this reaction. However, some evaluation of the relative stability of villiaumite and cryolite can be made by drawing equilibrium curves for reaction (6)

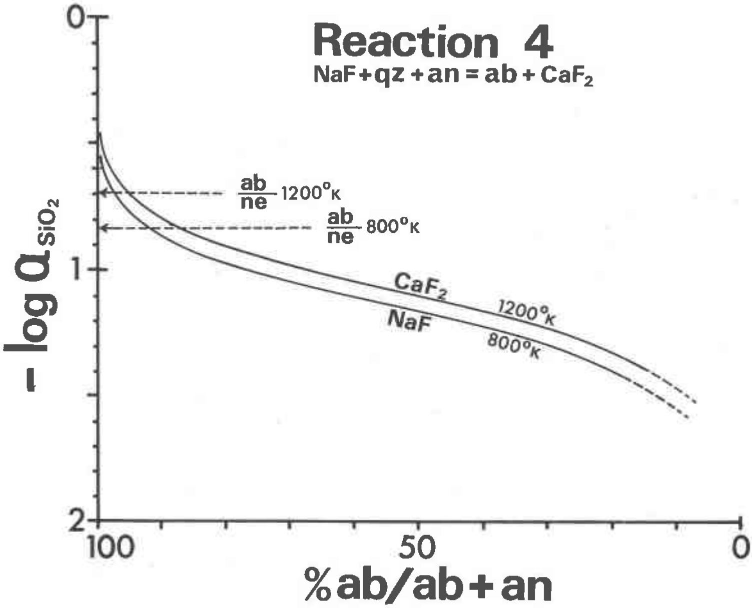

FIG. 2. Equilibrium curves ($\Delta G_r^0/2.303\ RT=0$) for reaction 4 at 800°K (527°C) and 1200°K (927°C) plotted against the logarithm of silica activity and plagioclase composition. Log $a_{SiO_2}=0.0$ for quartz-bearing assemblages, and values of a_{SiO_2} defined by the reaction $\frac{1}{2}Ne+SiO_2=\frac{1}{2}Ab$ are shown at two temperatures. Villiaumite is stable with respect to fluorite at lower activity of silica and mol. fraction anorthite.

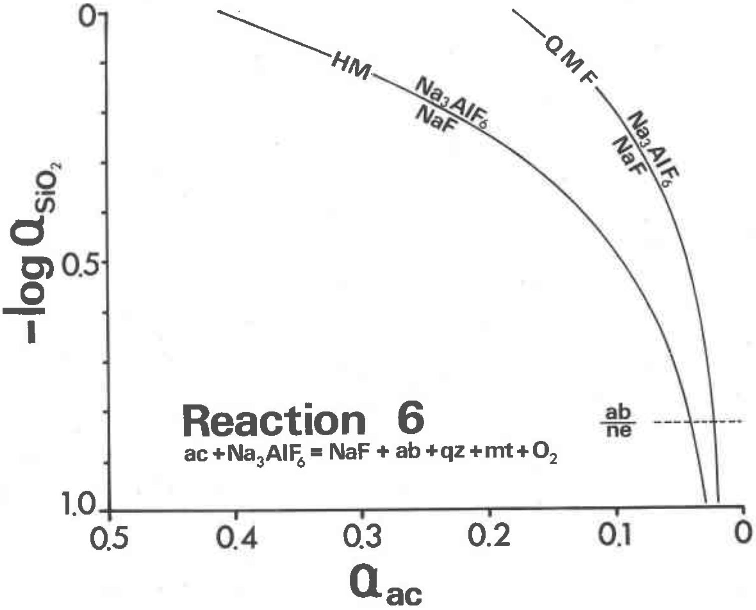

FIG. 3. Equilibrium curves ($\Delta G_r^0/2.303\ RT=0$) for reaction 5 at 800°K (527°C) plotted for oxygen fugacities corresponding to those of the fayalite-magnetite-quartz buffer (QMF) and the haematite-magnetite (HM) buffer, with respect to the activities of acmite and silica. Silica activity defined by the reaction $\frac{1}{2}$Ne+SiO$_2$= $\frac{1}{2}$Ab at 800°K is also shown. Relationships remain essentially similar at 1200°K.

in terms of the activities of silica and acmite at oxygen fugacities corresponding to the hematite-magnetite and fayalite-magnetite-quartz buffers as shown in Figure 3. For the purpose of illustration it has also been assumed that the activity of Fe_3O_4 in magnetite and of $NaAlSi_3O_8$ in feldspar is 0.7; small changes in these activities will not affect the picture greatly since their coefficients in reaction (6) are much lower than those of the other components. Obviously increasing the activity of silica or the fugacity of oxygen at a given activity of acmite will increase the stability of cryolite relative to that of villiaumite. Also reducing the activity of acmite, *i.e.*, reducing the proportion of $NaFeSi_2O_6$ in the pyroxene, will also favor the formation of cryolite. Kogarko (1966) has also concluded that cryolite would be thermodynamically unstable in undersaturated alkaline rocks.

Fluorite is by far the most common fluoride mineral in quartz-bearing rocks and the relative stability of cryolite to fluorite can be illustrated using the following reaction:

$$12\underset{\text{acmite}}{NaFeSi_2O_6} + 21SiO_2 + 3Na_3AlF_6$$

$$+ \underbrace{9CaAl_2Si_2O_8 = 21NaAlSi_3O_8}_{\text{plagioclase}} + 9CaF_2 + 4\underset{\text{magnetite}}{Fe_3O_4} + O_2$$

Obviously, if the activities of anorthite, acmite and silica are reduced, then cryolite formation will be favored. However, if silica activity is low, villiaumite will take the place of cryolite (equation (6); Fig. 3) so that it is only in anorthite-poor siliceous rocks that cryolite will form in preference to fluorite.

The occurrence of large quantities of siderite ($FeCO_3$) with cryolite at Ivigtut, Greenland (Pauly, 1960) suggests that CO_2 has played some role in the paragenesis of the fluoride minerals, perhaps as in the following reaction:

$$\underset{\text{albite}}{NaAlSi_3O_8} + 2\underset{\text{acmite}}{NaFeSi_2O_6} + 3F_2 + 2CO_2$$

$$= Na_3AlF_6 + 2\underset{\text{siderite}}{FeCO_3} + 7\underset{\text{quartz}}{SiO_2} + 2O_2 \qquad (8)$$

All other things being equal, higher fugacities of CO_2 in this reaction will enhance the formation of cryolite. The same will be true of other volatiles, particularly sulfur species (pyrite and sphalerite are present in the villiaumite-bearing phonolite from New Mexico). In any case, the presence of cabon or sulphur compounds should not alter the relative stability relationships between the three fluoride minerals.

To summarize: if reactions are written which correspond reasonably closely with the observed igneous parageneses of the three fluoride minerals NaF, Na_3AlF_6 and CaF_2, then their relative stabilities may be calculated. Thus villiaumite will be restricted to silica- and calcium-poor salic rocks, *e.g.*, peralkaline nepheline syenites and phonolites, cryolite will occur in silica-rich but calcium-poor salic rocks (*e.g.*, granites), and fluorite will be the prevalent fluoride mineral in all rocks, silica-saturated to undersaturated, which are not unusually poor in calcium.

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