

FLUORINE LOSS FROM SILICATES ON IGNITION

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ABSTRACT

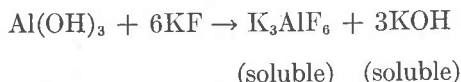
Fluorine loss from hectorite (2.3% F in the $<2 \mu\text{m}$ fraction) upon heating for 24 hours at temperatures of 110° and 300°C was negligible, and at 540°C was less than 3%; however, upon ignition at 950°C for 6 hours, the fluorine loss was 100%. Addition of $\text{Mg}(\text{OAc})_2$ failed to prevent ignition loss of fluorine from hectorite at 950°C while the addition of $\text{Ca}(\text{OAc})_2$ or CaCO_3 decreased it from 100% to 55%. Fluorine losses from NaF (Control) ranged from 7% at 110°C without SiO_2 to 100% at 950° with SiO_2 (ground quartz) addition. X-ray diffractograms showed that CaF_2 had been formed by the heating at 950°C of calcium salts with NaF. The F/Si atomic ratios in the evolved gas averaged 6.3 from NaF/ SiO_2 samples which contained initial F/Si ratios of 1.2 to 2.6, but averaged 3.6 from samples having initial F/Si ratios of 0.3 to 0.7. Hence, besides SiF_4 gas loss, other chemical forms of fluorine are lost upon ignition, such as NaF or M_2SiF_6 , in which M is H, Na, or other cation.

INTRODUCTION

Fluorine occurs as a constituent of many minerals and rocks (Correns, 1956) as well as in soils (Robinson and Edgington, 1946). Phosphorites and fluorite (CaF_2) occur in marine deposits (Degens, 1965) and apatite is found in neutral and alkali soils (Lindsay and Moreno, 1960). In metamorphic rocks fluorine is mainly found in fluorite and topaz (Correns, 1956). Some amphiboles and micas contain F proxying for OH. Some micas contain as much as 2 to 4 percent fluorine (Robinson and Edgington, 1946). The chemical analysis of California hectorite (A.P.I. 34A), a magnesium aluminosilicate clay, as reported (Bowden and Gruner, 1950, p. 55), did not include a fluorine determination. The fluorine content of this unfractionated sample was 1.7 percent, while that of the $<2\mu\text{m}$ fraction of this hectorite was 2.3 percent (Huang and Jackson, 1967), based on the Willard and Winter MClO_4 distillation combined a colorimetric determination of the fluorine in minerals and rocks. Use of H_2SO_4 or H_3PO_4 distillation and titration of the F has been employed (Ingamells, 1962).

Synthetic fluorosilicates have been prepared under specified environmental and ionic conditions (Van Valkenburg and Pike, 1952; Van Valkenburg, 1955; Johnson and Shell, 1963) for industrial requirements. The synthesized fluorosilicates did not undergo direct exchange of F for OH in water or aqueous NaOH solutions (Johnson

and Shell, 1963). Unlike earlier reports of F exchange for OH on edges of clays (Weiss, 1959; Hofmann *et al.*, 1961), OH from aluminosilicate clays did not exchange for F from aqueous neutral KF solutions (Huang and Jackson, 1965); rather the release of hydroxyl ions from minerals in such solutions was accompanied by an equivalent dissolution of structural aluminum and iron. These trivalent ions formed soluble fluorocomplexes in the KF solution, as illustrated by the type equation:



Ignition loss of fluorine from hectorite was surmised to be the cause of a 5.4 percent deficit in a system of mineralogical analysis which involved thermal gravimetric analysis (TGA) of hydroxyl loss (Alexiades and Jackson, 1966). Although the behavior of F of silicates on thermal treatment is an important consideration for both theoretical mineralogy and quantitative clay mineralogical analysis, the reaction mechanism for fluorine loss on heating is not given in standard analytical texts.

The purpose of the present study was to establish the effect of both ignition temperature and added materials on fluorine volatilization from hectorite, as compared to controls (NaF with and without ground quartz as a source of Si) and to determine the chemical form, such as SiF_4 , HF, *etc.*, in which fluorine is evolved during the ignition of fluorosilicates.

MATERIALS AND METHODS

Samples of California hectorite (A.P.I. sample 34a, 0.1 g of $< 2\mu\text{m}$ size fraction) and reagent grade NaF (Control) were ignited at 110°, 300°, and 540°C for 24 hours and at 950°C for 6 hours to determine the total fluorine volatilized. The effects on F loss caused by 0.1 g additions of Mg(OAc)_2 , MgCO_3 , Ca(OAc)_2 , CaCO_3 , and SiO_2 (finely ground quartz) added to separate 0.1 g samples of hectorite or NaF prior to ignition were determined.

After ignition, the samples were fused in platinum crucibles with a flux mixture of 2.5 g of Na_2CO_3 and 0.5 ZnO (Huang and Jackson, 1967). The residue was digested with distilled water on a steamplate at 85°C for one hour and quantitatively transferred to a flask for steam distillation. Fluorosilicic acid was distilled from the residue in the presence of HClO_4 at a temperature of 135 to 140°C. Aliquots from 250 ml of distillate were used for fluorine determination by the zirconium eriochrome cyanine R method (Haung and Jackson, 1967).

Additional samples of NaF and SiO_2 were fused with ZnO and Na_2CO_3 , and treated with HClO_4 in preparation for the extraction and the determination of silicon in the residue, in order to establish (by difference) the amount of Si lost. The treated residue was boiled in 5 ml of distilled water for 10 minutes, the

soluble material was removed by washing with 0.2 *N* HCl, and the silica remaining was transferred to a nickel beaker and dissolved by boiling in 0.5 *N* NaOH for 2.5 minutes (Jackson, 1956). The silicon in solution was then determined by the heteropoly blue molybdosilicate method (Boltz and Mellon, 1947).

RESULTS AND DISCUSSION

The fluorine volatilized from separate samples of hectorite did not exceed 3 percent of the original fluorine present upon heating at 110°C, 300°C, and 540°C for 24 hours (Fig. 1) After ignition at 950°C for 6 hours, however, hectorite lost all of its initial fluorine. The addition of $\text{Ca}(\text{OAc})_2$ to hectorite decreased F loss to 55 percent, but addition of $\text{Mg}(\text{OAc})_2$ did not decrease loss of F (Fig. 1).

Analytical grade NaF (Control) heated at 950°C gave a loss of 54 percent of its initial fluorine content; however, the fluorine loss decreased to 4 to 12 percent when $\text{Mg}(\text{OAc})_2$, MgCO_3 , $\text{Ca}(\text{OAc})_2$, or CaCO_3 was added to the NaF crystals previous to ignition. The in-

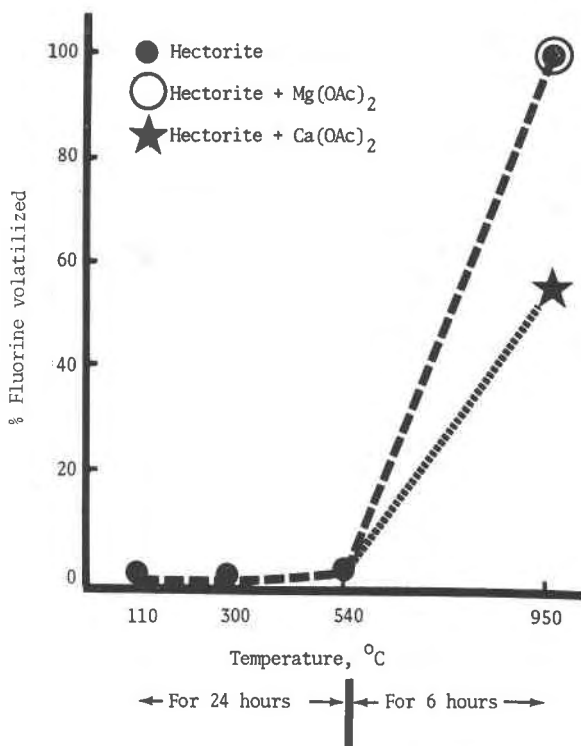


FIG. 1. Fluorine loss on ignition of hectorite, hectorite + $\text{Mg}(\text{OAc})_2$, or hectorite + $\text{Ca}(\text{OAc})_2$.

creased recovery of fluorine from the treated NaF samples suggested the formation upon ignition of an alkaline earth fluoride (CaF_2 or MgF_2) in the absence of silicon (Fig. 2). Little difference occurred between the use of the acetate or carbonate salts. When the Na_2CO_3 -ZnO flux mixture was used to fuse the NaF for the analyses (Huang and Jackson, 1967) none of the fluorine was lost.

The addition of SiO_2 to the NaF before heating at 950°C increased the fluoride loss to between 75 and 79 percent, thus providing evidence that fluorine evolution is enhanced by the presence of silica, analogous to the results on heating hectorite (Fig. 1). The fluorine could be evolved as SiF_4 according to the equation:



or from a hydroxy silicate system as HF according to the equation:



giving different TGA results. In further tests in the presence of SiO_2 , the fluorine loss from NaF ranged from 76 to 82 percent in the presence of $\text{Mg}(\text{OAc})_2$ or MgCO_3 , and decreased only to 42 to 53 percent in the presence of $\text{Ca}(\text{OAc})_2$ or CaCO_3 . In the presence of Si and Ca or Mg, the fluorine is partly held by the divalent ions and partly volatilized. Further study showed that the F/Si ratio lost depended on the initial NaF/ SiO_2 ratio taken (Table 1). The F/Si atomic ratios of constituents volatilized ranged from 10 to 3.3, averaging 6.3 (Table 1) when the initial F/Si ratio was high (1.2 to 2.6). The results suggested that fluorine was lost both as SiF_4 and NaF from samples having a F/Si atomic ratio in excess of 1. This was true even though the stoichiometric ratio of SiF_4 involves a F/Si ratio of 4 (equation 2). With an initial F/Si molar ratios of 0.3 to 0.7, the ratios of F/Si in the evolved gas averaged 3.6 (Table 1), suggesting that fluorine was evolved from NaF in the presence of excess SiO_2 approximately stoichiometrically as SiF_4 , according to equation (2).

For the thermal synthesis of fluoromicas, an excess of F above stoichiometry was required (Van Valkenburg and Pike, 1952; Johnson and Shell, 1963), possibly to make up for F volatilization during the synthesis through fusion. Also in that experiment, moisture and CO_2 had to be excluded to prevent fluorine volatilization from melts containing Al_2O_3 , MgO, SiO_2 , and K_2SiF_6 (Van Valkenburg and Pike, 1952). These results like ours, indicate the ease with which F can be volatilized at high temperatures from charges containing both Si and F. In the presence of a great excess of Na_2CO_3 -ZnO, as used for

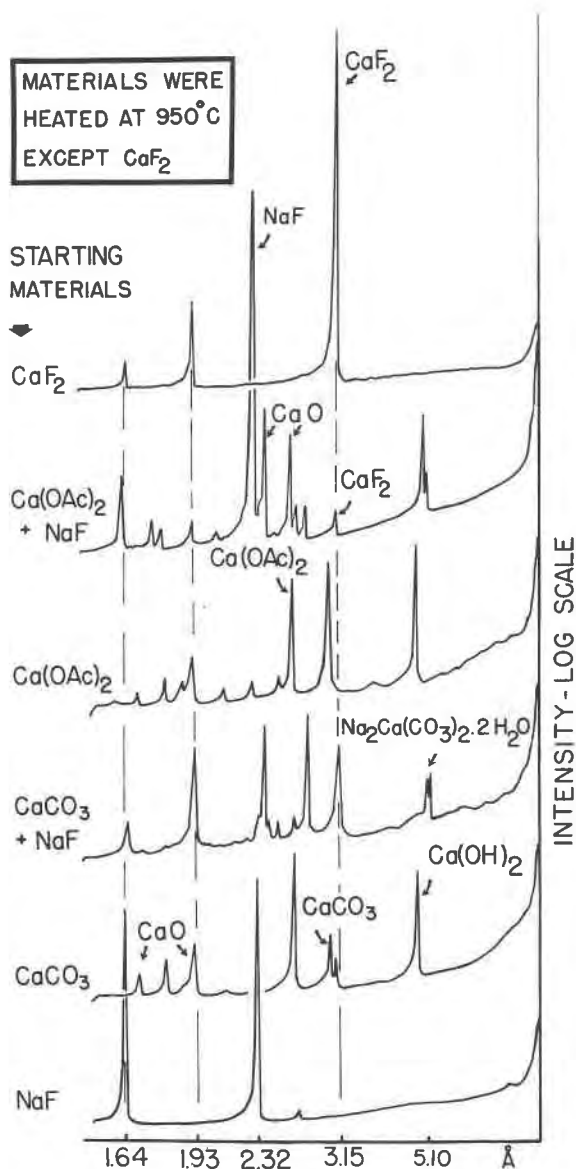


FIG. 2. X-ray diffractograms of materials after ignition at 950°C for 6 hours and CaF₂ (control).

TABLE 1. F AND Si VOLATILIZED UPON IGNITION OF MIXTURES OF NaF AND SiO₂ AT 950°C FOR 6 HOURS.

Sample Taken (mg)		Total* (mg)		Residual (mg)		Volatilized				Molar Ratio		
NaF	SiO ₂	F	Si	F	Si	(mg)		F Si		Taken F/Si	Volatilized F/Si	
						F	Si	F	Si			
<i>First Series -- with high F/Si</i>												
138.9	73.7	60.8	34.3	12.5	nd	48.3	7.2	79.4	nd	2.6	9.9	
90.8	69.1	39.7	32.2	8.1	nd	31.6	6.7	79.5	nd	1.8	6.9	
81.4	72.5	35.6	33.5	nd	26.9	28.4	6.6	nd	19.8	1.6	6.3	
104.3	100.0	45.6	46.6	10.0	nd	35.6	8.8	78.1	nd	1.5	6.0	
100.5	101.3	43.9	47.2	6.3	nd	37.7	8.9	85.8	nd	1.4	6.2	
104.0	103.0	45.5	48.0	nd	40.0	37.3	8.0	nd	16.6	1.4	6.8	
100.2	101.1	43.8	47.1	nd	40.0	35.9	7.1	nd	15.1	1.4	7.4	
99.8	100.8	43.7	47.0	nd	36.6	35.8	10.3	nd	22.0	1.4	5.1	
98.7	100.2	43.2	46.7	nd	36.6	35.4	10.1	nd	21.6	1.4	5.2	
132.9	144.2	58.1	67.2	7.5	nd	50.6	14.0	87.1	nd	1.3	5.3	
77.3	86.0	33.8	40.0	nd	31.3	27.0	8.8	nd	21.9	1.2	4.6	
									Av.	82.0	19.5	Av. 6.3
<i>Second Series -- with low F/Si</i>												
53.8	104.0	23.5	48.4	0	nd	23.5	nd	100	nd	0.7	4.0	
40.3	109.6	17.6	51.2	0	nd	17.6	nd	100	nd	0.5	2.9	
49.6	98.9	21.2	46.2	0	nd	21.2	nd	100	nd	0.7	3.8	
51.4	108.9	21.9	50.8	nd	41.7	nd	9.2	nd	18.0	0.6	3.5	
52.7	107.4	22.9	50.1	nd	41.3	nd	8.8	nd	17.6	0.7	3.9	
									Av.	17.8		
28.1	106.2	12.3	49.3	nd	44.4	nd	4.9	nd	9.9	0.4	3.7	
28.7	113.5	12.6	52.9	nd	47.8	nd	5.2	nd	9.8	0.4	3.6	
25.8	109.2	11.3	51.0	0	nd	11.3	nd	100	nd	0.3	3.3	
									Av.	100	9.9	Av. 3.6

*Values calculated on the basis that the NaF contained 43.75% F, as determined analytically, and the SiO₂ contained 46.6% Si, theoretically.

nd = not determined because only F or Si could be determined on a given ignited sample.

example in the standard method of analysis for fluorine, no F is lost during fusion.

CONCLUSIONS

1. Loss of fluorine from the magnesian aluminosilicate, hectorite, was complete upon ignition of sample at 950°C for six hours.
2. In the absence of Si, either calcium or magnesium salts decreased the ignition loss of fluorine from NaF (control) from 54 to less than 7 percent.
3. In the presence of SiO₂ with NaF or in hectorite samples, calcium salts were more effective than magnesium salts in decreasing fluorine loss, because of the formation of CaF₂ (fluorite). Even with calcium present fluorine loss was still 42 to 53 percent of the total F present.
4. On ignition of variable amounts of NaF with SiO₂, the F/Si atomic ratio in the evolved gas approached 4 when SiO₂ was in excess of NaF but increased to 10 when NaF was in excess of SiO₂, indicating gaseous loss of not only SiF₄ but also of NaF.

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