Hydrofluoride decomposition of natural materials including zirconium–containing minerals

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Abstract. Recently, interest in ammonium hydrogen difluoride (NH₄HF₂) as a versatile fluorinating agent for the decomposition of natural materials resumed. It is considered to be a new and more efficient than hydrofluoric acid (HF) reagent in analytical chemistry. Thermodynamically possible fluorination reactions with NH₄HF₂ are exothermic and proceed even at room temperature with the entropy reserve. The fluorination products are of high symmetry phases (tetragonal or cubic) with partial substitution of fluoride ion for oxide (or hydroxide). The fluorination of refractory silicate zircon (ZrSiO₄) is kinetically hindered, and its complete decomposition requires the use of a Teflon autoclave at 200°C. The fluorination products are cubic (NH₄)₃Zr(OH)ₓF₇₋ₓ (x ≤ 0.3) and tetragonal double salt (NH₄)₃SiF₇, which can be separated due to incongruent sublimation of (NH₄)₂SiF₆. The mechanism of the latter process is proposed.

1. Introduction

It is known that geological samples are not easy to dissolve, due to the presence of resistant minerals, such as garnets, spinel, and zircon. Usually, geological sample dissolution of refractory silicates requires hydrofluoric acid and a mixture of oxidizing acids, such as nitric and perchloric, in the case of open acid digestion. Then, the choice of decomposition method depends on the mineralogical composition of the rock [1]. In recent years, a simple, effective, and comparatively safe dissolution method with the use of ammonium fluorides (NH₄HF₂ or NH₄F) shows great potential for the digestion of geological samples. NH₄HF₂ was used in innovative method for preparation of mullite-based refractories from aluminosilicate quartz-topaz ores [2] or for the synthesis of mullite from kaolin [3]. A new technique of decomposing beryl ore [4] or a treatment of gold-containing graphite-bearing ores with NH₄HF₂ to concentrate gold [5] was recently suggested. Tantalite dissolution using NH₄HF₂ as alternative to HF [6] or processing of tantalite ore from Mozambique with molten NH₄HF₂ [7] were also described. For decomposition of refractory zircon, an autoclave breakdown with ammonium fluorides [8] or microwave digestion with NH₄HF₂ were studied [9, 10]. Today, the NH₄HF₂ acid digestion is recognized as a new method in analytical chemistry which is practical and effective and has lower toxicity and cost, compared with traditional hydrofluoric acid digestion [11–13]. However, we suggested this method earlier for analysis of silicon-containing materials [14, 15].
2. Fluorination reactions with NH₄HF₂

Ammonium hydrogen difluoride is a solid, so it is more convenient in handling than HF. It melts at 126°C and sublimes incongruently at 239°C. During its decomposition, adducts of HF with NH₃ are formed [16]:

\[ \text{NH}_4\text{HF}_2(s) \rightarrow \text{H}_3\text{N}--\text{HF}(g) + \text{HF}(g); 2\text{NH}_4\text{HF}_2(s) \rightarrow \text{H}_3\text{N}--\text{HF}(g) + \text{HF}(g) + \text{H}_2\text{N}--\text{HF}--\text{HF}(g) \]  

(1)

Table 1 represents fluorination reactions of silicon-containing minerals of different compositions and structure with NH₄HF₂. All thermodynamically possible reactions with the formation of silicon double salt (NH₄)₂SiF₇ = (NH₄)₂SiF₇·NH₄F are exothermic.

Table 1. Thermodynamic function changes of fluorination reactions of silicon-bearing minerals with NH₄HF₂

| Mineral      | Fluorination reaction                                                                                | -ΔH°₂⁹⁸ kJ | -ΔG°₂⁹⁸ kJ |
|--------------|------------------------------------------------------------------------------------------------------|------------|------------|
| quartz       | SiO₂ + 3.5NH₄HF₂ = (NH₄)₂SiF₇ + 0.5NH₃ + 2H₂O                                                       | 21.3       | 65.0       |
| wollastonite | CaSiO₃ + 4.5NH₄HF₂ = CaF₂ + (NH₄)₂SiF₇ + 1.5NH₃ + 3H₂O                                              | 44.9       | 140.8      |
| larnite      | Ca₃SiO₄ + 5.5NH₄HF₂ = 2CaF₂ + (NH₄)₂SiF₇ + 2.5NH₃ + 4H₂O                                           | 112.9      | 61.5       |
| zircon       | ZrSiO₄ + 7NH₄HF₂ = (NH₄)₂ZrF₇ + (NH₄)₂SiF₇ + NH₃ + 4H₂O                                            | 53.0       | 134.5      |
| kaolinite    | Al₂Si₂O₅·2H₂O + 13NH₄HF₂ = 2(NH₄)₃AlF₆ + 2(NH₄)₂SiF₇ + NH₃ + 9H₂O                                   | 488.0      | 605.8      |
| topaz        | Al₂SiO₄(OH)₂ + 9.5NH₄HF₂ = 2(NH₄)₃AlF₆ + (NH₄)₂SiF₇ + 0.5NH₃ + 6H₂O                                 | 467.0      | 583.3      |
| chlorite     | Mg₆Si₄O₁₀(OH)₈ + 20NH₄HF₂ = 6MgF₂ + 4(NH₄)₂SiF₇ + 8NH₃ + 18H₂O                                      | 39.0       | 580.3      |
| diopside     | CaMgSi₂O₆ + 9NH₄HF₂ = CaF₂ + MgF₂ + 2(NH₄)₂SiF₇ + 3NH₃ + 6H₂O                                     | 56.9       | 249.9      |
| forsterite   | Mg₃SiO₄ + 5.5NH₄HF₂ = 2MgF₂ + (NH₄)₂SiF₇ + 2.5NH₃ + 4H₂O                                          | 58.1       | 204.1      |
| sphene       | CaTiSiO₄ + 8NH₄HF₂ = CaF₂ + (NH₄)₂TiF₇ + (NH₄)₂SiF₇ + 2NH₃ + 5H₂O                                  | 28.7       | 164.9      |
| anortite     | CaAl₂SiO₆ + 14NH₄HF₂ = CaF₂ + 2(NH₄)₃AlF₆ + 2(NH₄)₂SiF₇ + 2NH₃ + 8H₂O                           | 539.9      | 680.3      |

Indeed, a well pronounced exoeffect can be observed on DTA curves of a framework-structure quartz (figure 1), ribbon amphibole (figure 2), chain chrome diopside (figure3) with NH₄HF₂. The layered minerals such as chlorite (figure 4) or vermiculite (figure 5) are fluorinated easier. In the latter case, the exoeffect does not appear because of complete fluorination of vermiculite during the grinding of initial components at room temperature. The same concerns the natural mineral scheelite. Elemental silicon just inflames under grinding with NH₄HF₂.

The corresponding reactions can be expressed as follows:

\[ \text{SiO}_2 + 3.5\text{NH}_4\text{HF}_2 = (\text{NH}_4)_2\text{SiF}_7 + 0.5\text{NH}_3 + 2\text{H}_2\text{O} \]  

(2)

\[ \text{Ca}_2\text{Mg}_3\text{Fe}^{2+}_2\text{Fe}^{3+}_{0.7}\text{Al}_2\text{Si}_6\text{O}_{22}\text{(OH)}_2 + 37.1\text{NH}_4\text{HF}_2 = 2\text{CaF}_2 + 3\text{MgF}_2 + 2\text{NH}_4\text{FeF}_3 + 0.7(\text{NH}_4)_3\text{FeF}_6 + 2(\text{NH}_4)_3\text{AlF}_6 + 6(\text{NH}_4)_2\text{SiF}_7 + 9\text{NH}_3 + 24\text{H}_2\text{O} \]  

(3)

\[ \text{CaMgSi}_2\text{O}_6 + 9\text{NH}_4\text{HF}_2 = \text{CaF}_2 + \text{MgF}_2 + 2(\text{NH}_4)_3\text{SiF}_7 + 3\text{NH}_3 + 6\text{H}_2\text{O} \]  

(4)
\[ \text{Mg}_2\text{Al}_3\text{Si}_3\text{O}_{10}(\text{OH})_8 + 24.5\text{NH}_4\text{HF}_2 = 2\text{MgF}_2 + 4(\text{NH}_4)_2\text{AlF}_6 + 3(\text{NH}_4)_3\text{SiF}_7 + 3.5\text{NH}_3 + 18\text{H}_2\text{O} \]  

(5)

**Figure 1.** Thermal curves of the mixture of quartz with \( \text{NH}_4\text{HF}_2 \) in molar ratio of 1 : 3.5.

**Figure 2.** Thermal curves of amphibole with \( \text{NH}_4\text{HF}_2 \).

**Figure 3.** Thermal curves of chrom diopside with \( \text{NH}_4\text{HF}_2 \).
CaMg₄FeAl₅Si₅O₂₀(OH)₄·8H₂O + 35.5NH₄HF₂ = CaF₂ + 5MgF₂ + (NH₄)₃FeF₆ + 3(NH₄)₂AlF₆
+ 5(NH₄)₃SiF₇ + 8.5NH₃ + 32H₂O

2CaWO₄ + 7NH₄HF₂ = 2CaF₂ + (NH₄)₂WO₃F₂ + (NH₄)₃WO₃F₃ + 2NH₄HF₂ + HF + 2H₂O

→ 2CaF₂ + 2(NH₄)₂WO₃F₅ + NH₃ + 4H₂O \[17\]

Si + 3.5NH₄HF₂ = (NH₄)₂SiF₇ + 2H₂ + 0.5NH₃ \[18\]

We presented here stoichiometric formulae of the fluorination reaction products. In fact, they were nonstoichiometric due to the water molecules isolated during the reagent interactions, as we clearly demonstrated in the case of ilmenite fluorination with NH₄HF₂ \[18, 19\]:

0.8FeTiO₃·0.1Fe₂O₃ + 4.4NH₄HF₂ = 0.8(NH₄)₂Ti(OH)₀.₄F₆.₆ + 0.2(NH₄)₂.₈Fe(OH)₀.₂F₅.₆

+ 0.8NH₄H₀.₄FeO₀.₂F₃ + 0.64NH₃ + 2.18H₂O \[19\]

Ammonium fluoro- or oxofluorometallates (the fluorination products) are the phases of high symmetry: tetragonal double salts of silicon, germanium, tin, titanium and cubic fluoroperovskites or elpasolites characterized by strong dynamic orientational disorder \[20, 21\]. On cooling, these compounds undergo phase transitions (PT) of order-disorder type with a rather large value of entropy change. This means that fluorination reactions with NH₄HF₂ occur spontaneously with a reserve of entropy.

3. Fluorination of zircon-containing natural materials

It should be noted that natural mineral zircon (ZrSiO₄) with island structure is the most difficult to complete recovery with NH₄HF₂. Melnichenko et al. \[22\] mentioned that it was not decomposed even
during 48 h at 200°C. Since its interaction with NH₄HF₂ is thermodynamically possible (see table 1), it is evident that the reaction is kinetically hindered. We managed to overcome this barrier using Teflon autoclave at 200°C (Teflon inner vessel and an outer stainless steel pressure jacket were used). For two hours, the samples were decomposed completely. Zircon was presented by the Brazil sample of Pocos de Caldas deposit. On the other hand, fine dispersive and amorphous sample of gel zircon of Algoma deposit (Khabarovsk region, Russia) interacts with NH₄HF₂ with a strong heating (exoeffect) under simple mixing of reagents. The main fluorination products are stoichiometric double salt (NH₄)₃SiF₇ and nonstoichiometric seven-coordinated (NH₄)₃Zr(OH)ₓF₇₋ₓ (x ≤ 0.3). We refined the elpasolite-like crystal structure of the latter [23] to avoid abnormally short F–F distances in pentagonal bipyramid previously determined by Hurst and Taylor [24]. The structure is highly disordered (figure 6) with six independent orientations of [ZrF₇]₃⁻ and eight orientations of one ammonium group.

![Figure 6. Dynamically disordered crystal structure of (NH₄)₃ZrF₇: sp. gr. F23, a = 9.4185(3) Å, Z = 4.](image)

The former complex (NH₄)₃SiF₇ decomposes above 200°C with the formation of (NH₄)₂SiF₆ which is a rather unique compound. It does not hydrolyze and pyrohydrolyze, corresponds fully to its stoichiometry. The solubility in water is 18.75 %. It can be obtained in a highly pure form by incongruent sublimation and/or recrystallization. The history of compound numbers more than 200 years but its thermal properties are still under discussion.

**4. Sublimation of (NH₄)₂SiF₆**

Davy was the first who described thermal properties of (NH₄)₂SiF₆ [25]. He mentioned that the compound “just perceptibly redens litmus paper and appears to sublime unaltered when heated”. Marignac described cubic (cuboocahedra) and hexagonal (thin plate or large flat crystal) [26] forms of (NH₄)₂SiF₆. “Heated up to 100°C, the latter became white and volatilized without melting, while cuboocahedra cracked and volatilized without albication”. Mel’nichenko et al. suppose that (NH₄)₂SiF₆ sublimes mainly as a hole molecule and decomposes only partly through NH₄SiF₅, which is moisture-sensitive and hydrolyzes with the formation of volatile ammonium oxofluorosilicates [27]. However, the more accepted statement is that it decomposes with the formation of five gas molecules [28, 29]:

\[
\text{(NH}_4\text{)}_2\text{SiF}_6(s) \rightarrow \text{SiF}_4(g) + 2\text{NH}_3(g) + 2\text{HF}(g) \quad (10)
\]

Our tensimetric investigation of thermal behavior of cubic (NH₄)₂SiF₆ (cryptohalite) showed that, in fact, it decomposes with the formation of four gas molecules. Since the (NH₄)₂SiF₆ vapours have an
acid reaction, it is logically to suppose that HF isolates and adduct of silicon fluoride with ammonia is formed. We tried to scavenge HF by elemental silicon, and in the mass-spectrum of the reaction product detected the fragment with the mass of 223 that corresponded to dinuclear silicon fluoride complex \( \text{Si}_2\text{F}_7\text{NH}_2\text{NH}_3 \), so we suppose that the process of incongruent sublimation of \((\text{NH}_4)_2\text{SiF}_6\) can be expressed as follows:

\[
\begin{align*}
(\text{NH}_4)_2\text{SiF}_6 &= \text{Si}(\text{NH}_3)_2\text{F}_4 + 2\text{HF} \\
\text{Si}(\text{NH}_3)_2\text{F}_4 &= \text{SiF}_4 + 2\text{NH}_3 \\
\text{Si}(\text{NH}_3)_2\text{F}_4 + \text{SiF}_4 &= \text{Si}_2\text{F}_7\text{NH}_2\text{NH}_3 + \text{HF}
\end{align*}
\] (11) (12) (13)

The overall reaction is following:

\[
2(\text{NH}_4)_2\text{SiF}_6 = \text{Si}_2\text{F}_7\text{NH}_2\text{NH}_3 + 5\text{HF} + 2\text{NH}_3
\] (14)

Our preliminary quantum chemical calculations of dinuclear complex give the only viable structural model consisting of silicon octahedron and tetrahedron joined by the bridging \text{NH}_2 group (figure 7).

![Figure 7](image_url)

**Figure 7.** Structure of dinuclear silicon complex \( \text{Si}_2\text{F}_7\text{NH}_2\text{NH}_3 \) with bridging \text{NH}_2 group.

Sublimation properties of \((\text{NH}_4)_2\text{SiF}_6\) were used for separation of zirconium and silicon from Tugan zircon deposit of Tomsk region (Russia) [8]. We performed the trace elements analysis of precious opals of deposit Raduzhnoe (Primorsky region, Russia) with respect to the problem of their coloring using sublimation of \((\text{NH}_4)_2\text{SiF}_6\) [15]. Using \(\text{NH}_4\text{HF}_2\) we could obtain the balanced results during the analysis of zircon raw material of Pocos de Caldas deposit (Brazil), when classical decomposition methods were very tedious and did not lead to balanced results.

5. Conclusions
The ease of use \(\text{NH}_4\text{HF}_2\) digestion method suggests that it will become the method of choice in the future. This simple, effective, and comparatively safe dissolution method shows great potential for the decomposition of natural raw materials. Complete dissolution of Indian coal sample has been just achieved for the quantitative determination of major to ultra-trace elements using \(\text{NH}_4\text{HF}_2\) instead of highly toxic HF [30].

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