GENERAL GEOCHEMISTRY OF FLUORINE

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Fluorine (F) is the most electronegative and reactive of elements. It reacts with practically all of the organic and inorganic substances. It never occurs in the elemental state in nature because it’s high reactivity. The average fluorine concentrations in the Earth’s crust are estimated at 0.05-0.1% or 500-1000mg/kg and ranks 13th among the elements (Turekian & Wedepohl, 1961; Adriano, 1986; Wedepohl, 1995). Fluorine may occur in limestones associated with tremolite-, actinolite pyroxene- or with mica-chlorite-skarn formation where F concentrations may reach the level of 0.4-1.2%. Part of fluorine may be present in clay material admixed with weathered limestones. It can also be combined with phosphate minerals (Lahermo & Backman, 2000).

The most important fluorous minerals are fluorite (CaF$_2$), fluor-apatite Ca$_5$ (PO$_4$)$_3$F and apatite Ca (PO$_4$)$_3$(F/OH/Cl). They are characteristic accessory minerals in many types of rocks. Since fluorite may contain nearly half of fluorine by weight, it contributes substantially to F concentrations in rock and water even though the mineral is present in small quantity (Correns, 1956). Pure fluor-apatite (Ca$_5$(PO$_4$)$_3$F) could contain up to 3.8% fluorine.

Fluorine may occur also in the composition of clay minerals, micas and pyroxenes. Soils dominated by clay minerals have high sorption capacity and frequently serve as natural geochemical barriers preventing pollutants from reaching groundwater. Fluorides are adsorbed on clay minerals; where ionic exchange takes place- fluoride ions party replace hydroxyl groups (Hubner, 1969; Fluhler, et al., 1982). More than 90 of natural fluoride in soils are bound to clay particles (Lahermo & Backman, 2000).

The role of micas and amphiboles in the occurrence and mobility of fluoride in soils is enhanced by their relative readiness to disintegrate in weathering processes. Fluorides in micas are likely to be released soon after the
onset of weathering. According to Koritnig (1972) in clay fractions 80-90 % of fluorides are contained in muscovite, illite and related minerals of the mica group.

Apart from natural sources, a considerable amount of fluoride may be contributed due to anthropogenic activities. Remarkable amounts of fluorides are transferred into agricultural soils by phosphate fertilizers. Phosphorites may contain up to 4 % of fluorine depending on its origin and contents of fluorapatite (Fleischer et al., 1974). The use of fluorocarbons insecticides and weak killers may also contribute to local fluoride concentrations in soils. In addition to agriculture part of the fluorides are derived from industrial emissions and waste waters. The steel, aluminium, glass, brick and ceramic industries use fluoride in their production process that occurs with the encounter of fluoride containing aerosols, dust and wastewater into the surrounding environment (Arnesen, 1998; Haidouti, 1995).

In groundwater fluorine occurs as fluoride ions and forms soluble complexes with many kinds of inorganic and organic ligands. Fluorides are released into aqueous solution during weathering process of rocks and minerals and through anthropogenic pollution. Solubility of fluoride from F-bearing minerals is relatively low under normal conditions, but the slow kinetics often enhances leaching and fluoride enrichment in groundwater (Hem, 1989). Part of fluorides may occur in groundwater as a result of mineral fluorite (CaF2) dissolution. The solubility product for fluorite (Kfluor) can be determined according to the following dissociation formula (Helgeson, 1969):

\[
\text{CaF}_2 \leftrightarrow \text{Ca}^{+2} + 2\text{F}^-
\]

\[K_{\text{fluor}} = [a_{\text{Ca}^{+2}}] * [a_{\text{F}^-}]^{10^{-9.04}} \text{ at 25° C}
\]

Where \([a_{\text{Ca}^{+2}}]\) and \([a_{\text{F}^-}]\) are the activities of the concerned ions.

Both Smyshlyaev and Edeleva (1962) and Handa (1975) have reported for Kfluor the values of 10-10.75. Due to the relatively low solubility of fluoride the occurrence of aqueous \(\text{F}^-\) is predominantly controlled by the availability of free \(\text{Ca}^{+2}\) water (Jacks, 1973).
The dissolution constant of calcium carbonate (CaCO$_3$) is much larger than that of fluorite:

$$\text{CaCO}_3(s) + \text{H}^+ \leftrightarrow \text{Ca}^{+2} + \text{HCO}_3^-$$

$$K_{\text{cal}} = a\text{Ca}^{+2} \cdot a\text{HCO}_3^- / a\text{H}^+ = 0.97 \times 10^2$$

Since the solubility product for fluorite is constant, the activity of fluoride is directly proportional to HCO$_3^-$, if the pH is constant. When computing the thermodynamic equilibrium in the groundwater system in contact with calcite and fluorite, a combined equation is derived (Handa, 1975):

$$\text{CaCO}_3(s) + \text{H}^+ + 2\text{F}^- \rightarrow \text{CaF}_2 + \text{HCO}_3^-$$

$$K_{\text{Cal-fluor}} = a\text{HCO}_3^- / a\text{H}^+ \cdot [\text{F}^-] = 1.06 \times 10^{-11}$$

The above values are taken from Helgeson (1969). The corresponding value by Smyshlyaev and Edeleva (1962) is $K_{\text{Cal-fluor}} = 3.6 \times 10^{-12}$. From the last equation can be concluded that the aqueous F$^-$ concentrations are proportional to HCO$_3^-$ concentration and pH values. Consequently, highly fluorous waters are usually HCO$_3^-$ dominating waters what favour the dissociation of fluoride from soils. Therefore water with high concentrations of fluorides can form in the areas where alkaline carbonate-containing waters are in contact with fluorine-bearing rocks.

Fluoride concentrations are relatively independent of the other watersoluble components, but noteworthy correlation exists between fluoride and pH values. The fluoride solubility in soils is lowest in the pH range of 5.0-6.5 (Adriano, 1986). At higher pH values ionic exchange occur between fluoride and hydroxyl ions (illites, chlorites, micas and amphiboles) that leads to fluoride increase in groundwater. In acid environment (pH < 6) both F$^-$ and Al$^{+3}$ steep into water and formation of [AlF]$^{+2}$ and [AlF2]$^+$ complexes mainly takes place in solution (Hem, 1989; Haidouti, 1995; Neal, 1995). Hitchon (1995) has observed that the formation of [MgF]$^+$ complexes on the account of fluoride ions intensifies while the saltiness of groundwater calcium content and temperature increases.

During the volcanic eruptions a lot of volcanic gas arid ash falls into atmosphere and to ground from there. Plumes of ash and dust, which may cover
hundreds of kilometers, may carry a variety of adsorbed chemicals. After the ash settles to the ground, these toxins may be dissolved and thus leach into the environment. The dominant chemicals that may adsorb to tephra and thus act as leachates are: chlorine, sulphur compounds, sodium, calcium potassium, magnesium and fluorine (Weinstein & Cook, 2005). Other elements are present in smaller quantities. Various studies of volcanic emission have shown that volcanic gases and ash are rich in fluorine (Barclay et al., 1996; Cronin et al., 2003), thus clay-rich volcanic ash beds provide adsorption and ion exchange sites for F- ions. Fluorine occurs mainly in the form of HF, H₂F₂ or F₂ as well as SiF₄ and H₂SiF₆ (Fleischer et al., 1974).