

## Chapter 2

# Fluoride: A World Ubiquitous Compound, Its Chemistry, and Ways of Contamination

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**Abstract** Fluoride, an incompatible lithophile and the most electronegative element, forms a number of soluble, pH-dependent formation of complexes with polyvalent metal ions in water. The interaction between water and sedimentary carbonates ultimately causes fluoride concentration gradient as a sequel of hydrogeochemistry. The occurrence of fluoride in groundwater due to fluorapatite solubility and the other governing factors such as rock chemistry, residence time, well depth, preferential pathways for the upward movement of deep groundwater, hydrologic condition of the pathways, and geologic structure have also been discussed. In this chapter, in addition to the geochemistry of fluoride, the chemistry of fluoride in water and its association with the other physicochemical parametric factors such as total dissolved solids and dissolved ions such as sodium, calcium, magnesium, arsenic, boron, and hydrogen carbonate have been elaborated. As fluoride and arsenic ions participate together in their occurrence in soil and hence water, their co-contamination has been exemplified from the research reports. Fluoride solubility as a function of evaporation, evapotranspiration, temperature, and water softening has also been accounted. The leaching aspects of soil-based adsorption–desorption mechanism and its ultimate destiny on fluoride enrichment of groundwater have also been added in the chapter.

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## 2.1 Introduction

Fluorine holds the 13th rank among the elements (Adriano 1986; Krauskopf and Bird 1995) in its abundance in the earth. It is accounted as an incompatible lithophilic element (Faure 1991) and the most electronegative. Fluoride ion, as a strong ligand in water, forms a number of soluble complexes with polyvalent metal ions such as  $\text{Mg}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$ , and  $\text{Ca}^{2+}$  based on the pH of the medium (Nordstrom and Jenne 1977). It can also form hydroxide complexes with boron as  $[\text{BF}_n(\text{OH})_{4-n}]^-$ , silica complexes ( $\text{SiF}_4$  and  $\text{SiF}_6^{2-}$ ), and other strong complexes with beryllium, uranium, vanadium, and REEs (Serrano et al. 2000). In groundwater, a major part of fluoride is presumed to present either as a free anion or as aquo complexes. Due to low concentrations of aluminum and iron in neutral water, fluoride is unable to bind with these cations to any appreciable extent. This insignificant binding ability of fluoride in neutral water makes it in the form of a free fluoride ion along with minor amounts of major cation complexes and some minor and/or trace constituent complexes (Edmunds and Smedley 2005; Ozsvath 2009). Although the anthropogenic sources play a significant role in fluoride contamination of groundwater, the occurrence of fluoride is mainly pertinent to the geogenic processes which govern its concentration in groundwater.

## 2.2 Geochemistry of Fluoride

In the earth's crust, the average fluorine concentration was estimated to be about 0.05–0.1 % (500–1000 mg per kg). The fluorine concentration in igneous, sedimentary, and metamorphic rocks ranges from several hundreds to thousands of mg per kg of water as reported by Frencken (1992). As a result of the interaction with sedimentary carbonates, the chemical properties of groundwater, in particular the concentration of fluoride, are significantly affected (Marques et al. 2006).

High fluorine in clastic sediments is concentrated in micas and illites (clay fractions). Possible occurrence of fluoride (as fluorite) in carbonate type of sedimentary rocks and sedimentary phosphate beds of shark teeth and, volcanic layers as well was substantiated (Frencken 1992). He et al. (2013) conducted the fluoride analysis along the Yin Mountains at Hangjinhouqi, China. From their study, the average total fluorine concentration of the major rocks such as metamorphic, sedimentary, and igneous was found to contain 1503 mg per kg, 1175 mg per kg, and 1043 mg per kg, respectively, with the crust's fluoride average concentration of 660 mg per kg. The fluorine-enriched metamorphic rocks by metasomatic processes have fluorine concentration between 100 ppm for regional metamorphism and greater than or equal to 5000 ppm as a consequence of contact metamorphism. In addition, the analysis on the average total fluorine concentration in each rock type reported by He and his coworkers is in the decreasing order as follows:

*Killas (1873 mg per kg) > schist (1703 mg per kg) > gneiss (1563 mg per kg) > granite (1043 mg per kg) > sillexite (982 mg per kg) > conglomerate (963 mg per kg) > sandstone (903 mg per kg)*

The generation of fluorine-rich lavas in the (calc)alkaline volcanoes, typical of continental rift (East Africa), hot spot, and continental margin (Andes) or island arc (Japan), was reported by Rosi et al. (2003).

Researchers, in view of the hydrogeochemistry, identified certain minerals containing fluoride include apatite [ $\text{Ca}_5(\text{PO}_4)_3(\text{Cl}, \text{F}, \text{OH})$ ], topaz [ $\text{Al}_2\text{F}_2(\text{SiO}_4)$ ], cryolite ( $\text{Na}_3\text{AlF}_6$ ), villiaumite ( $\text{NaF}$ ), silicates such as the phyllosilicates of micas and clays, and the double-chain silicates of amphiboles (Chae et al. 2006; Subba Rao and Devadas 2003). Apatite, amphibole, and mica are ubiquitous in igneous and metamorphic rocks, while the occurrence of apatite is frequent as accessory minerals in sedimentary horizons (Kundu et al. 2001). Sepiolite and palygorskite are considered to be unstable minerals and reported to have a dominant control on the fluoride concentration in groundwater (Jacks et al. 2005). Fan et al. (2003) established that the sorption of fluoride over the entire calcite surfaces occurs rapidly by precipitating fluorite at step edge and kinks where surface  $\text{Ca}^{2+}$  concentration is high.

### 2.2.1 Fluoride and Magma

The ionic radius of F and OH is almost similar and as a consequence, the substitution of F in OH positions during magmatic differentiation takes place more readily. But its later stage participation into silicate minerals was studied because of the preferential partitioning as magmatic crystallization proceeds. This ultimately results in the formation of late stage pegmatite granites, hydrothermal vein deposits, and crystallized rocks from pristine magmas which often contain fluorite, fluorapatite, and fluoride-enriched micas and/or amphiboles (Nagadu et al. 2003; Scailliet and Macdonald 2004).

### 2.2.2 Fluoride and Granites

Naseem et al. (2010) studied the correspondence of fluoride from granite rocks to water sources through kaolin, soil, and sand as a consequence of the weathering process. Studies conducted by Shah and Danishwar (2003), Tirumalesh et al. (2007), and Fordyce et al. (2007) ascertained that granitic rocks especially in igneous terrains are the dominant and ejecting sources for groundwater with high fluoride content. Certain sensitive factors behind high fluoride concentration in groundwater include crystalline rocks especially granites of alkaline nature with calcium deficiency. Especially the peralkaline granites containing villiaumite ( $\text{NaF}$ ) dissolve more fluoride in groundwater during the interaction and corroborated to have high

solubility rate among the other minerals (Krainov et al. 1969). Cretaceous granitoids are also one among the contributors of fluoride and supported by experiments conducted by Chae et al. (2006). The study indicated that the biotite and Mesozoic granites (fluoride-bearing minerals) cause fluoride-rich groundwater in Korea and suggested that the fluoride concentration in bedrock groundwater serves as an indicator for the subsurface geology and the depth of circulation. Colombo et al. (2010) unveiled that micas in pegmatites and A-type carboniferous granites are proved to be fluoride rich in the northern Sierras Pampeanas region where the rivers and groundwater sources were studied with fluoride contamination due to constant interaction of water with the fluoride-rich rocks (García et al. 2012). According to Schwinn and Markl (2005), the negative cerium anomaly of granites indicates the presence of fluorite due to  $\text{Ce}^{4+}$  precipitation by  $\text{Ce}^{3+}$  oxidation along fractures in the granites during the mineralization process.

### 2.2.3 Fluoride and Calcretes

Other weathered materials which remain with much abundance and overlying under granitic rocks are calcretes. These calcrete materials are often referred to as the sink for fluoride. Calcretes and dolocretes are found to contain fluoride to a maximum of 1 % (Jacks et al. 1993). Chemical analyses of calcrete samples, conducted by Reddy et al. (2010), revealed the fluoride content in the range of 440–1160 mg  $\text{kg}^{-1}$  in Nalgonda District of India. Jacks and his coworkers (2005) investigated high contents of fluoride in 25 calcrete samples from arid areas of Indian granitic terrain in the range of 510–9000 mg  $\text{kg}^{-1}$ . These studies revealed that the concentration of fluoride was found to be the same as that of granitic rocks of the study area. The minerals with calcretes include silica (quartz chalcedony), and clay varieties of frequent references such as palygorskite, sepiolite, and smectite (Watts 1980; Rodas et al. 1994; Kadir and Eren 2008) function as potential sites for fluoride sorption. The fluoride concentration of limited range in fluorite under saturated (saturation index =  $-4.72$  to  $-1.22$ ) water sources may be associated with the buffering action by coprecipitation with calcrete or sorption onto calcrete (Carpenter 1969; Jacks et al. 2005).

## 2.3 Dynamics of Fluoride in Groundwater

The most obvious factors which affect the release of fluoride are mineralogical composition, the extent of alteration of sediments, and the geochemistry of water. The minerals which contribute fluoride in groundwater include Na-bearing feldspar (albite), biotite, hornblende, riebeckite, aegirine (Ozsvath 2006; Chae et al. 2006), and other sporadic accessory minerals, namely, sphene, epidote, muscovite, and apatite. A substantial amount of fluoride held in the structure of minerals is ejected

into the groundwater sources often encouraged and termed as geogenic in nature. The fluoride content of groundwater during mineral dissolution is governed by the solubility of  $\text{CaF}_2$ , whereas the solubility of calcite and fluorite controls the dissolution of  $\text{Ca}^{2+}$  in groundwater. The dissolution of calcite and fluoride is inversely proportional to each other (Kim et al. 2012; Rafique et al. 2009), and the activities of calcium, fluoride, and carbonate are interdependent in groundwater. Hence, the interaction of groundwater with aquifer sediments induces the variation of chemical signature with respect to  $\text{Na-HCO}_3$  compositions with enriched dissolution of fluoride.

The attribution of high fluoride concentrations in groundwater to apatite, mica, and amphibole group minerals in trachyandesite “melt rock” associated with the meteorite impact event was explored by Leybourne et al. (2008). The above minerals are much less soluble than fluorite and their dissolution is favored at low pH values.

Kim and Jeong (2005) inferred that  $\text{CaF}_2$  dissolution is not necessarily dependent on pH unless it is coupled with the precipitation of  $\text{CaCO}_3$  by common ion effect. The precipitation of  $\text{CaF}_2$  is made enhanced at high pH levels and thereby enabling further dissolution of fluorite in groundwater saturated with both  $\text{CaF}_2$  (fluorite) and  $\text{CaCO}_3$  (calcite) at the same time.

### ***2.3.1 Interaction Dynamics of Groundwater with Rocks and Minerals and Associated Fluoride Concentration***

The occurrence of fluoride in groundwater and its governing factors such as rock chemistry, residence time, well depth, preferential pathways for the upward movement of deep groundwater, hydrologic condition of the pathways, and geologic structure could be investigated with the help of natural tracers and the geochemical data of the location (Kim and Jeong 2005).

Weathering and circulation of water in rocks and soils leach out fluoride which then dissolves in groundwater. As a consequence, fluoride is enriched in the bedrock aquifers of alkali granites and metamorphic rocks (Ayenew 2008; Kundu et al. 2001; Mamatha and Rao 2010; Tekle-Haimanot et al. 2006; Tirumalesh et al. 2007) and sedimentary aquifers of granitic parent rocks (Chae et al. 2007; Guo et al. 2007; Wang et al. 2009).

In fluvial sediments, the release of fluoride in groundwater under acidic conditions is likely to be controlled by dissolution/alteration of fluorapatite and biotite minerals originated from fluoride-rich igneous and metamorphic rocks. Unlike fluvial sediments, the degree of mineral alteration in loess samples is comparatively higher, and these are able to generate  $\text{Na-HCO}_3$  ion pairs leading to pH alkaline levels ( $\text{pH} \geq 8$ ). In loess samples, the ejection of fluoride from detritic fluorapatite and biotite is less common in contrast to fluvial sediments, but it is made feasible under more acidic conditions developed locally by anthropogenic activities (García et al. 2007).

He et al. (2013) studied that the long-term water–rock interaction which facilitates the mobility of fluoride from the Yin Mountains leads to the ultimate accumulation in the groundwater of sand or clay aquifers in Hangjinhouqi area. The average soluble fluoride concentration of the three major rocks and rock types (as mentioned above) unveiled the easy dissolution of soluble fluorine into groundwater from these rocks through vertical infiltration from rainfall during the recharge process. This geochemical mechanism ultimately leads to the increase in the fluoride in groundwater. It is well documented that high fluoride concentration in groundwater is likely in those areas where fluoride-bearing minerals are abundant in the rocks (Frengstad et al. 2001; Carrillo-Rivera et al. 2002).

Shallow aquifers containing recent infiltration of rainwater have low fluoride content. Nevertheless, fluoride concentration of shallow aquifers increases as a consequence of temperature-enhanced fluorite solubility and hydrogen fluoride (HF) gas dissolution due to hydrothermal activation caused in active volcanic areas (Frencken 1992). The traditionally considered and the main source of fluoride in the groundwater of Chaco-Pampean plain (Nicolli et al. 2012) was volcanic glass grains with high surface-adsorbed fluorine. This usually exist as soluble sulfate and halide salts mixed with sparingly soluble fluorine compounds ( $\text{CaF}_2$ ,  $\text{AlF}_3$ , and  $\text{Ca}_5(\text{PO}_4)_3\text{F}$ ). Similarly, extensive investigations were conducted and reported world wide by various researchers (Ruggieri et al. 2010, 2011, 2012).

Due to the low rate of groundwater recharge and prolonged water–rock interaction, high fluoride concentration is registered in semiarid environments (Handa 1975). Groundwater with long residence time is usually associated with deep aquifer systems and a slow groundwater movement as well.

Fantong et al. (2010) reported that the provenance of fluoride from fluorapatite is likely and associated with the depletion of phosphate.

On account of hydro-geochemistry and prolonged period of interaction, the enrichment of fluoride in groundwater takes place. This enrichment continues even after the equilibrium between soluble fluoride and fluorite ( $\text{CaF}_2$ ) due to the depletion of Ca as calcite (Rafique et al. 2009) as depicted in Fig. 2.1.

### **2.3.2 Hydrogeologic and Hydro-Geochemical Conditions Favoring High Fluoride in Groundwater**

The geochemical environments, likely to cause endemic fluorosis, are (a) soda groundwater under arid and semiarid conditions, (b) Fe-rich soil under humid conditions, and (c) brackish groundwater with high total dissolved solids (Wen et al. 2013). This work attributed three significant factors which cause the geochemical fluoride in groundwater in addition to the dissolution of fluoride-rich minerals. They are represented as follows.

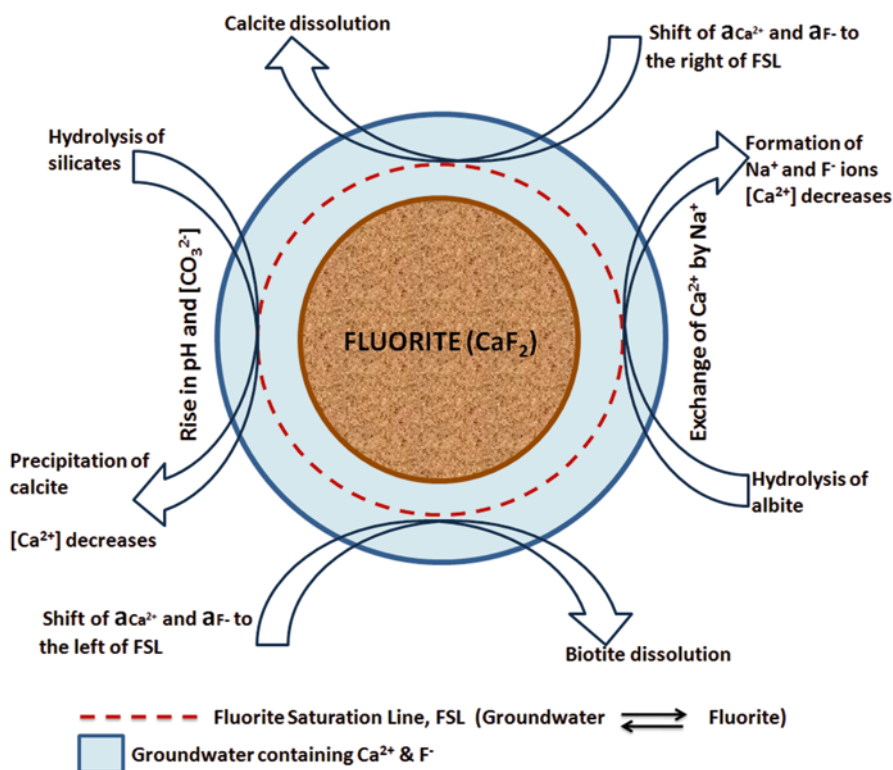


Fig. 2.1 Dynamics of fluoride in response to groundwater chemistry

### 2.3.2.1 Soda Groundwater

Groundwater of this kind is weakly alkaline and of  $Na-HCO_3$  (Cl) type which is a subgroup of soda water with  $Na/(Cl+SO_4)$  (in meq) greater than unity. The enrichment of fluoride takes place as a result of evapotranspiration in shallow groundwater sources (Xie et al. 2013), and hence, the fluoride of these sources was greater than that of deep groundwater sources. Fluoride-rich shallow groundwater is associated with the sources like phreatic water in Alashan Desert ( $F = 15.5 \text{ mg L}^{-1}$ ), and marine transgression sourcing fluoride to deep groundwater was reported in northern China (Wen et al. 2013). It is illustrated in Fig. 2.2 that anorthite and albite (aluminosilicates) due to incongruent dissolution produce kaolinite and other dissolved ions including  $Ca^{2+}$ . As  $Ca^{2+}$  precipitates into calcite under alkaline pH with abundant  $CO_2$ , the dissolution of fluorite is thus enhanced, leading to fluoride-enriched calcium-poor groundwater. Unlike  $Ca^{2+}$  and  $Mg^{2+}$ ,  $Na^+$  does not undergo mineral precipitation reactions, and hence, its appreciable dissolution makes it dominant in groundwater with perfect Na-TDS correlation.

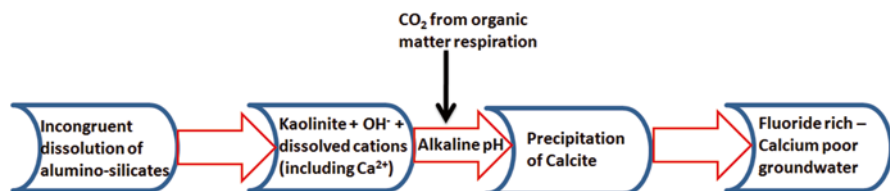


Fig. 2.2 Geochemical reactions accompanying soda water

### 2.3.2.2 The Influence of Marine Transgression on the Coastal Aquifers

Seawater contaminates the fresh groundwater aquifers because of marine transgressions. This causes groundwater with brackish nature containing high dissolved solids including high fluoride. It was already reported that transgression events are the significant factors which left the groundwater signature with the enrichment of Na-Cl and other minor components such as borate, fluoride, bromide, etc.

The third factor includes the occurrence of fluoride leaching and bioaccumulation under semi-humid conditions in iron-rich soils.

### 2.3.3 Fluoride Dynamics in Soils

Due to the agricultural practices, the substantial increase of soluble fluoride in acidic soils is mainly due to the dissolution of metal-fluoride complexes (Manoharan et al. 2007), whereas the soluble fluoride is retained under alkaline conditions in soils (Skjelkvåle 1994). Irrespective of the pH conditions, the labile fluoride in mineral phases can be readily released into groundwater. The plausible governing factors for the available labile fluorides in soils include the weathering conditions and the maturity of soils (Zhu et al. 2007).

#### 2.3.3.1 Leaching of Fluoride in Groundwater

The possibility of fluoride adsorption-leaching process in soil followed by the migration and exchange from soil to water is also one of the explored researches in spite of the other geochemical background and biological processes which are involved in the enrichment of fluoride in groundwater. The fluoride level in groundwater is governed by the presence of soluble and/or labile fluoride in soils. Naturally, the distribution of fluoride in the rocks shows a wide range due to an extensive diversity in the composition and types of rocks. Abdelgwad et al. (2009) reported the nonuniformity in the distribution of fluoride-rich minerals in granitic rock and the measured fluoride contents varied in the range of 200–1300 mg/kg at different depths in boreholes. The fluoride contents of alkaline rocks are in conformity with the findings of Wedepohl (1978).



Fluoride in its leaching rate is associated with its mobility from different soils. Wang et al. (2002) ranked the fluoride leaching ability of different soils as follows:

*Drab soil > sierozem > black soil > purplish soil > red earth > dark brown earth*

The leaching of fluoride was substantial from the alkaline soils such as drab soil and sierozem in temperate arid and semiarid areas. Conversely, an insubstantial leaching was effected from acidic soils which include red earth and purplish soil (in tropical humid areas) and dark brown earth and black soil in temperate semi-humid areas. Chae et al. (2006) studied the fluoride leaching behavior and demonstrated that the leaching of fluoride from mica is an irreversible process. This is primarily pertained with mineral weathering and the reluctant exchange between  $F^-$  and  $OH^-$  species at high pH which causes a minor increase in fluoride concentration in water.

### 2.3.3.2 Fluoride in Clay and Adsorption–Desorption Process

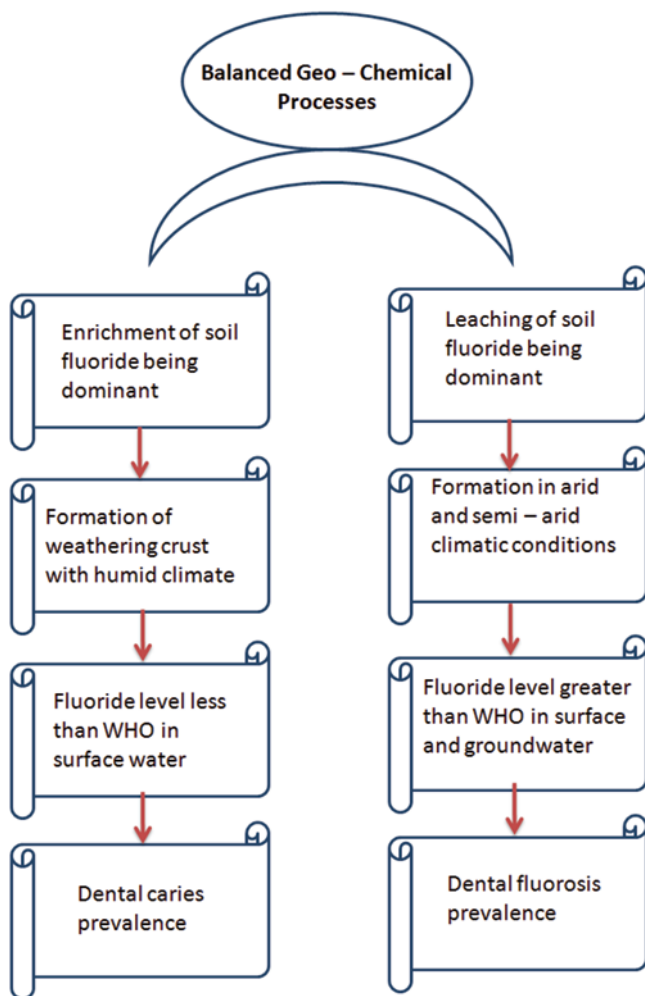
Fluoride in soil is operated by a dynamic balance of two geochemical processes such as enrichment and leaching as shown in Fig. 2.3. These two geochemical processes witness the adsorption and desorption behavior of clay minerals present in the soil.

High concentration of fluoride in mixed clay minerals can cause coal combustion-type fluorosis in China as reported by Dai et al. (2007) and Xiaoging and Binbin (2014). Under certain conditions, fluoride leaching takes place along with aluminum and ultimately changes the composition of clay minerals (Egli et al. 2001). It is reported that the retention of fluoride is proportional to the amount of clay minerals in the soil. Conversely, the fluoride desorption behavior of clay is also possible but it takes place at a faster rate as compared to that of the adsorption of fluoride onto clay minerals.

Clay in the soil functions as a natural barrier to protect groundwater from fluoride pollution due to its strong adsorption potential of fluoride by an exchange mechanism (exchange of F for OH). Due to the exchange the pH of the soil solution is improved (Zhang et al. 2007).

Sediments from shallow aquifers in the Hetao basin at Inner Mongolia were reported with high content of clay minerals which include smectite, illite, and kaolinite (Guo et al. 2012). The strong adsorption of fluoride at lower pH onto clay minerals and oxyhydroxides was also witnessed by Gao et al. (2009). Groundwater with pH values between 7.0 and 9.0 was studied to have point of zero charge (PZC) of most minerals with the nature from neutral to negative which lessens the adsorption of negatively charged fluoride onto the surface.

At elevated alkalinity, the presence of OH sites in biotite, mica, clay, and similar other minerals is most likely to be replaced with F, and their subsequent dissolution leads eventually to remarkable fluoride in water sources. The replacement of F for OH is feasible as the ionic radius of F (1.23–1.36 Å) is almost closer to OH (1.37–1.40 Å). Information on chemical composition of groundwater can be used as an (proxy) indicator of potential fluoride problems. Jayawardana et al. (2012)



**Fig. 2.3** Dynamic balance in the geochemical processes

highlighted that the basement rocks in Medirigiriya and Talawa Districts containing residual soils with unconsolidated sandy clays at neutral pH assist the progress of labile fluoride from the soil into the groundwater.

The factors which govern the adsorption–desorption process of fluoride in clay minerals include pH and grain size of the soil, initial fluoride concentration in clay minerals, and salinity. Based on these factors, the order of adsorption capacity of different clay minerals containing fluoride is as follows:

*Bentonite > halloysite > gibbsite, kaolinite ≫ soap alkaline soil, vermiculite, goethite; layered silicate mineral > various oxides*

The ease of fluoride sorption is multiplied to about ten times in acidic soils than in alkaline soils (Xu and Xing 1995). Soils which facilitate the precipitation of iron and aluminum (III) hydroxides are beneficial to anionic sorption especially fluoride. Contradictorily, the ability of fluoride sorption in soils containing free aluminum and iron (III) ions in the soil solution (Fung et al. 1999), amorphous iron, and aluminum oxide (Zhuang and Yu 2002) is affected based on the alteration of electrochemical properties of clay minerals. In addition, the amount of rainfall, intensified agricultural use, natural vegetation, and grazing are likely to affect the fluoride adsorption and desorption behavior of clay minerals.

### ***2.3.4 Correlation Significance of Other Parameters Associated with Fluoride in Groundwater***

Fluoride input in groundwater either through weathering or water–rock interaction can be well attributed through the dynamics of other parameters. The weathering of albite and other Na-bearing minerals is possible in the vicinity of fluoride-rich groundwater sources.

Fluoride from a silicate origin is well acknowledged from the positive correlation with the residence time of groundwater, pH, electrical conductivity (EC), and Na (Chae et al. 2006, 2007; Saxena and Ahmed 2003; Smedley et al. 2002). Conversely, the negative correlation of fluoride with calcium indicates that the dissolution of fluoride is suppressed by increasing the concentration of calcium above the limit of the solubility of fluorite (Boyle 1992). On the other hand, the precipitation of calcium as  $\text{CaCO}_3$  is likely due to the oversaturation of water with respect to  $\text{CaCO}_3$ . This type of geochemical process expedites the release the fluoride in the groundwater (Frengstad et al. 2001; Kim and Jeong 2005).

#### **2.3.4.1 Correlation Between Fluoride and TDS**

The correlation between fluoride and total dissolved solids (TDS) indicates the enhancement of ionic strength and increased fluoride solubility in groundwater (Sreedevi et al. 2006). Su et al. (2013) reported the aqueous geochemistry of high-fluoride groundwater and observed that weakly alkaline pH, moderate TDS, high hydrogen carbonate ( $\text{HCO}_3^-$ ) and sodium ( $\text{Na}^+$ ), and lower calcium ( $\text{Ca}^{2+}$ ) content are favorable parameters associated in enriching the fluoride content in groundwater. As a sequel of high  $\text{HCO}_3^-$  content in groundwater, fluorite dissolution takes place along with the exchange of  $\text{Ca}^{2+}$  for  $\text{Na}^+$  as shown in (2.1).



### 2.3.4.2 Correlation Between Fluoride and Na<sup>+</sup> and HCO<sub>3</sub><sup>-</sup> Ions

Groundwater with alkaline nature is associated with high HCO<sub>3</sub><sup>-</sup> and Na<sup>+</sup> contents. Hence, they ought to contain OH ions which are capable of exchanging replaceable F ions present in fluoride-bearing minerals. Thus, subsequent dissolution and the corresponding increase in groundwater fluoride take place spontaneously as a result of the reactions (2.2 and 2.3) as follows:



It is well discerned that the positive correlation of fluoride with Na/Na+Ca is associated with the replacement of Ca<sup>2+</sup> with Na<sup>+</sup> by cation exchange capacity (Kainosho et al. 2008) and leads to more dissolution of fluoride from the mineral phases into water (Satake et al. 2007). Martin et al. (1966) designated that type of process as preferential adsorption of Ca<sup>2+</sup> and Mg<sup>2+</sup> on abundant clay minerals such as montmorillonite, illite, and kaolinite. Naseem et al. (2010) indicated the presence of Na/Na+Cl ratio in groundwater as 0.45 which indicates the normative mineral composition of albite which is high in granitic rocks. Ozsvath (2006) unveiled a good relationship between albite and high-fluoride-contaminated groundwater. It is quite apparent that the existence of positive correlation of fluoride with Na<sup>+</sup> and (K<sup>+</sup>+Na<sup>+</sup>)/(K<sup>+</sup>+Na<sup>+</sup>+Ca<sup>2+</sup>+Mg<sup>2+</sup>) ratio unveils the influence on the mobility of fluoride by the water softening process.

### 2.3.4.3 Correlation Between Fluoride and Boron

In general, the groundwater sources containing rich Na<sup>+</sup> and Cl<sup>-</sup> ions are presumed to register the fluoride and boron concentrations higher than 1.5 mg L<sup>-1</sup> and 0.5 mg L<sup>-1</sup>, respectively, whereas sources assessed with HCO<sub>3</sub>-Ca-Mg type are analyzed less than 1.5 mg L<sup>-1</sup> (fluoride) and 0.5 mg L<sup>-1</sup> (boron). A strong correlation ( $R^2=0.905$ ) between fluoride and boron in groundwater sources associated with the Lake Saint Martin impact structure was studied by Desbarats (2009) at Manitoba, Canada. Karro and Uppin (2013) studied the Silurian and Ordovician aquifer systems especially with a focus on fluoride and boron concentrations at Central and Western Estonia. Fluoride and boron exhibited a mutual positive correlation of 0.85 and displayed a significant positive and negative correlation values, respectively, with Ca<sup>2+</sup> and Na<sup>+</sup> ions. The assumption was made on the basis of an increase in the hydrogeological profile with respect to depth due to longer residence time and slower water exchange. Additionally, the above concentrations and correlations were interpreted with respect to the local geology and construction type of wells which could also be suggestive facts for the groundwater chemistry.

### 2.3.4.4 Correlation Between Fluoride and Arsenic

An appreciable correlation between arsenic and fluoride in oxidizing aquifers (Bhattacharya et al. 2006; Gomez et al. 2009) becomes inappreciable because of precipitation by saturation with minerals as reported by Farooqi et al. (2007) in Pakistani groundwater. Groundwater can exhibit good correlation between arsenic and fluoride under neutral to alkaline oxidizing conditions as far as they are conserved. On the other hand, the feasibility of reductive dissolution of Fe (hydro) oxides not only increases the arsenic concentration but also the fluoride concentration especially in those aquifers with reducing environment. Any deviation from the perfect correlation of arsenic with fluoride may be accounted with the differences in geochemical behaviors of that area. The reductive dissolution of arsenic in alluvial aquifers in the presence of sulfate keeps the fluoride concentration remains intact with the reduction. The concentration of arsenic and fluoride as a function of depth although stands consistent up to a particular level becomes ambiguous on increasing the depth further (Kim et al. 2012).

## 2.4 Co-contamination of Fluoride and Arsenic in Water

The co-contamination by arsenic and fluoride in groundwater is made possible by the two most common processes desorption and reductive dissolution under oxidizing and reducing environments of aquifers. This type of contamination is conspicuous in arid or semiarid regions and reported in Arizona and California, the United States (Robertson 1989; Levy et al. 1999), Mexico (Mahlknecht et al. 2004), Argentina (Bhattacharya et al. 2006; Gomez et al. 2009), Yuncheng basin in China (Currell et al. 2011), and Pakistan (Farooqi et al. 2007). It was presumed that the consequence of desorption takes place from iron (hydro)oxides and these are the major sorption hosts (point of zero charge is between 8.5 and 9.3) for anions such as arsenate and fluoride in soils and sediments under alkaline pH (Bhattacharya et al. 2006; Currell et al. 2011; Appelo and Postma 2005). The anionic sorption capacity of Fe (hydr)oxides is inversely proportional to pH due to the development of negatively charged surfaces at higher pH, leading to the desorption of anions (Streat et al. 2008). Both the fluoride and arsenic anions are strongly held to the positive surfaces of the Fe (hydr)oxide matrix and get detached as free ions upon increasing the pH. Due to the similar desorption patterns of arsenic (as arsenate) and fluoride from Fe (hydr)oxides with respect to the pH increase, it is quite reasonable to infer the co-contamination of the above anions in the oxidizing aquifers (Bhattacharya et al. 2006; Farooqi et al. 2007; Currell et al. 2011). In supporting the above observation, Borgnino et al. (2013) ascertained the predominating dissolution mechanism of calcite at acidic pH which further enables the adsorption of  $\text{HCO}_3^-$  onto Fe (hydr)oxide surfaces. As a consequence, the fluoride–hydrogen carbonate ( $\text{HCO}_3^-$ ) competitive desorption facilitates the release of fluoride even under acidic pH conditions. The relationship of fluoride with other parameters resembles as that

of arsenic in groundwater. High fluoride concentration in the arsenic-contaminated groundwater under reducing environments may be associated as a result of the weathering of fluorapatite and/or fluorite. The strong dependence of fluoride on pH and the weak correlation between arsenic and fluoride were observed in aquifers with strong reducing environments unlike oxidizing aquifers (BGS and DPHE 2001; Smedley et al. 2003; Holm et al. 2004; Guo et al. 2008; He et al. 2009).

The geological co-occurrence of arsenic and fluoride is reported by many researchers (Castro 2006; Espinoza-Altamirano 2006; Lopez et al. 2012). Especially in the locations in Latin America which prevail under arid and semiarid conditions, high probability of arsenic–fluoride co-occurrence was investigated and characterized by a mixture of calcareous and volcano-clastic sediments and rocks (shale and sandstone) or alkaline groundwater sources of Na–HCO<sub>3</sub> type (Pauwels and Ahmed 2007). Alarcon-Herrera et al. (2013) explored the consequence of arsenic–fluoride co-contamination as a geological cause of igneous rocks together with the conglomerates and the derived quaternary alluvium materials in several aquifers. In addition, the other factors identified for the cause were aridity, poor monsoon, and groundwater exploitation in the aforementioned areas (Noyola-Medrano et al. 2009).

In Mexican regions, the main hydro-geological environments responsible for high arsenic and fluoride contaminations, established by Alarcon-Herrera and his colleagues (2013), are (1) geothermal activity, (2) mining activity, and (3) alluvial aquifers.

In pertinent to the geothermal activity, the causative factors for high arsenic and fluoride have been reported to include (1) wastewater injection into aquifers from a power plant and (2) intensive surface evaporation of these aquifers especially in arid areas in Los Azufres and Michoacan where the water temperature (89–93 °C) was close to its boiling point.

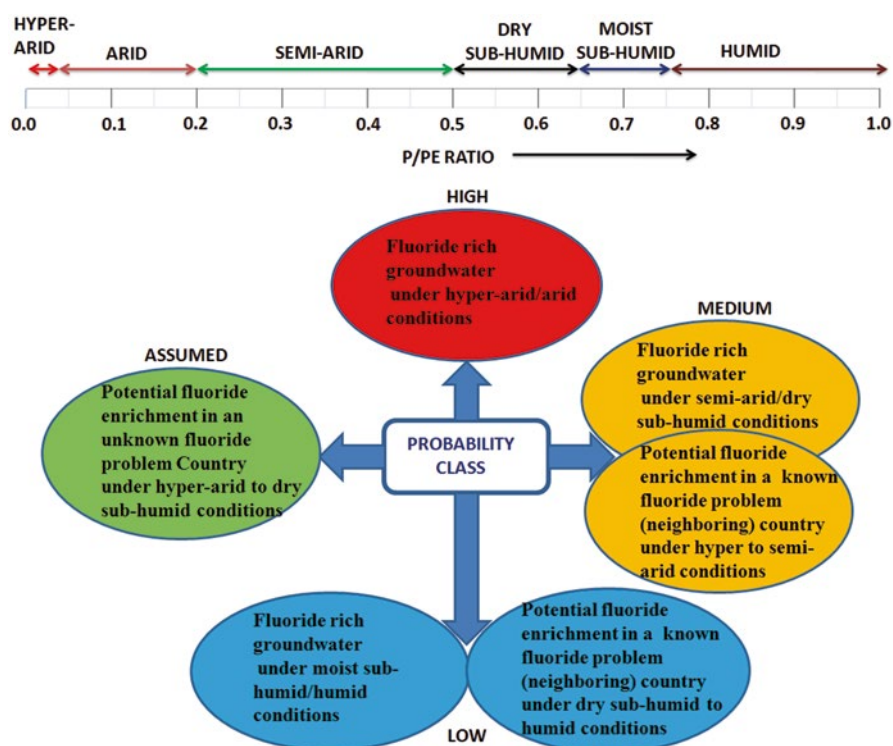
Based on the mining activities, the presence of high co-contamination of arsenic and fluoride in wells in North–Central Mexico was attributed with alluvium deposits. High concentrations of arsenic and fluoride in the Independence Basin of North–Central Mexico were reported to be associated with the dissolution of minerals present in the rhyolite–ignimbrite rocks of Na–HCO<sub>3</sub> type. In association with the alluvial aquifers, the existence of arsenic and fluoride in these aquifers is due to the exposed rocks mainly rhyolites which are composed of quartz, orthoclase, sanidine, illite, and volcanic glass. The possible detection of arsenic and fluoride contents of 540 mg/kg and 41 mg/kg, respectively, and the water temperature of about 32 °C were the substantiated facts for the co-occurrence of arsenic and fluoride in groundwater.

An aquifer (GTALH) at Chihuahua was reported to contain arsenic and fluoride and this co-occurrence was most likely attributed to geogenic origins with the presence of rhyolite (arsenic in its matrix) and shale (containing fluorapatite and arsenic-bearing minerals). Bundschuh et al. (2004) observed the correlation between arsenic and fluoride and noted the occurrence of As–F complexes in groundwater. Geographic distribution of sediments derived from loess and fluvial loess was demonstrated with the spatial variation of arsenic and fluoride in groundwater. The variability in the distribution of arsenic and fluoride in groundwater at endorheic lakes (or lagoons) at Southern Chaco-Pampean plain, reported by Alarcon-Herrera et al. (2013), was

quite acknowledged with the controlling factors such as geology, geomorphology, and local landform features. The influence of evaporation, cation exchange ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  versus  $\text{Na}^+$ ), adsorption of  $\text{K}^+$  on clay minerals (in the modification of water chemistry), and groundwater flow path were also addressed as the additional factors which enhanced the solubility of arsenic and fluoride (Bundschuh et al. 2004).

## 2.5 Probability on the Occurrence of Excessive Fluoride Concentration

It is always an apparent fact that the potential fluoride-rich environments are mainly associated with the Precambrian basement areas and areas affected by recent volcanism. Milich (1997) characterized the main climatic types based on Meig's classification with respect to precipitation/potential evaporation ratio (P/PE). The four probability classes to assess the excess fluoride occurrence in accordance with geologic and climatic conditions are illustrated in Fig. 2.4. The usefulness of the above probability classes in the preparation of continental maps is very much appreciated



**Fig. 2.4** The four probability classes to assess the excess fluoride occurrence in accordance with geologic and climatic conditions



to represent the occurrence of excess fluoride concentration. Apart from the depicted four probability classes, the fifth class was added and called as “not confirmed.” The fifth class is referred (by International Groundwater Resources Assessment Centre and/or United Nations Children’s Fund) to those countries with fluoride problem in groundwater, having no any specific information on fluoride sources and the distribution.

## **2.6 Influence of Evaporation and Evaporation–Transpiration in Fluoride Concentration in Groundwater**

Fluoride content in arid regions is high due to the slow flow rate of groundwater and the long reaction time with rocks. Due to the increase in evaporation and the established equilibrium of groundwater with calcite, the fluoride level ascends. The deposition of evaporative salts in arid zones is also evident to act as a significant source of fluoride. Conversely, in humid tropics, the fluoride increase is less prominent because of high rainfall leading to dilution of groundwater chemical composition (Frencken 1992).

Researchers acknowledged that the processes such as evaporation and/or evaporation–transpiration lead to the condensation of soluble components in arid and semiarid regions, resulting in fluoride-enriched groundwater (Guo et al. 2007; Jacks et al. 2005). Semiarid climate with low rainfall (225–400 mm per year), high rate of evaporation (>2000 mm per year), and low groundwater hydraulic conductivity are the facilitating factors in dissolving the fluoride-bearing minerals. The increase in fluoride concentration is also accountable with respect to high solubility of magnesium and sodium fluorides. Conversely, at a high rate of evaporation, the generation of fluoride ions from magnesium counterparts becomes less favored as magnesium fluoride begins to precipitate due to high concentration of  $Mg^{2+}$  ions. Thus, it is explicable that the fluoride contribution from magnesium counterpart is more accelerated during winter than summer as a consequence of evaporation. The genesis study on fluoride conducted in the Coimbatore District of Tamil Nadu revealed the formation of a sequence of concretions with high fluoride and  $Mg^{2+}$  contents downslope over a distance of about 1 km due to evaporation–transpiration (Jacks and Sharma 1995). Similar observation was reported by Reddy and Raj (1997) in the Nalgonda District of Andhra Pradesh, India.

## **2.7 Influence of Depth in the Fluoride Concentration of Groundwater**

Researchers correlated the fluoride concentration and well depth through the supporting natural factors such as temperature and residence time as these factors help in the perfect dissolution of fluoride (Nordstrom et al. 1989; Saxena and Ahmed



2003). Figure 2.5 depicts the vertical distribution of fluoride content on the basis of geology of aquifer sediments (Mondal et al. 2014). The interpretation of Mondal and his coworkers (2014) substantiated the presence of high fluoride content in groundwater due to the interaction dynamics of groundwater with clay/silty clay layers between the depth ranges of 24–27 m and 27–30 m. In general, granitic rocks contain relatively large proportion of fluoride-bearing minerals (Bailey 1977) between 500 and 1400 mg per kg (Koritnig 1978; Krauskopf and Bird 1995; Naseem et al. 2010) and considered to contain much higher amount of fluoride than any other rock type. Based on the direct relation between equilibrium constant and temperature, it is also evident that the fluoride dissolution increases with respect to the depth as there could be an increase in the geothermal gradient (Faure 1991). Thus, control in drilling to greater depths is rather encouraged (Apambire et al. 1997). Although the observation on the interdependency between borehole/well depth and fluoride concentration (Edmunds and Smedley 2005; Kim and Jeong 2005; Hudak and Sanmanee 2003) was positively correlated, its consistency is lost with respect to geographic locations. Karro and Uppin (2013) advocated that the length of the open intervals of boreholes and the concentrations of fluoride have an inverse relationship with each other. The lower fluoride concentrations in the drilled well with long open intervals (unlike the shorter open intervals) may be associated with the mixing of water with different chemical composition.

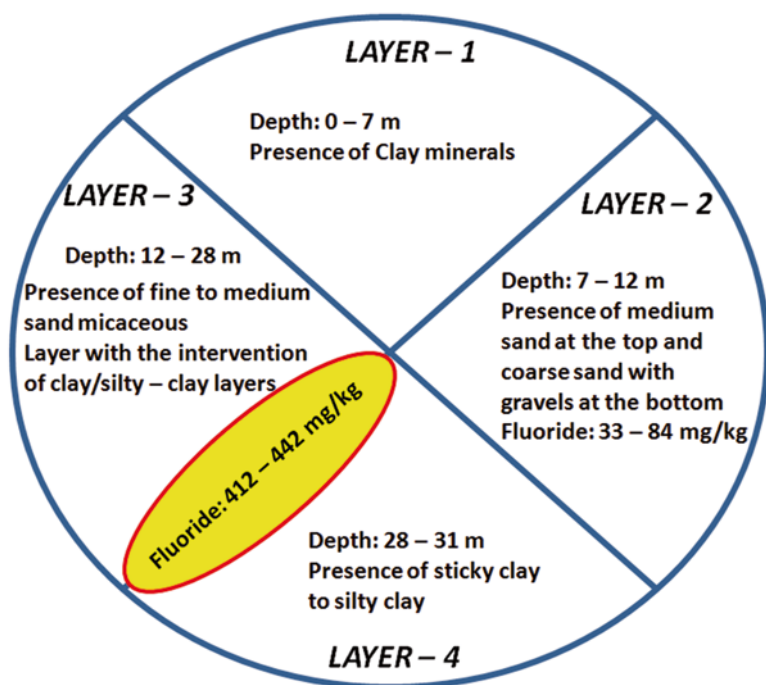


Fig. 2.5 Depth-wise distribution of fluoride in aquifer sediments

## 2.8 Fluoride Solubility and Chemistry

The hydrochemistry on fluoride dissolution from silicates is governed by certain prominent factors, viz., alkaline pH, anion exchange (OH for F) capacity of aquifer materials, cation exchange capacity (CEC), residence time of water (to enable water–rock interaction system), and climate (Boyle 1992; Saxena and Ahmed 2001; Ozsvath 2009). Reddy et al. (2010) reported the natural occurrence of fluorite as anhedral grains which disseminate in the gray and pink porphyritic gneiss. During the petrographic investigations, they explored the presence of fluorite (0–3.3 %), biotite (0.1–1.7 %), and hornblende (0.1–1.1 %). Zhang and his colleagues (2015) ascertained the significance of constant ionic strength in enhancing the dissolution of fluorite using Na<sub>2</sub>SO<sub>4</sub> and NaHCO<sub>3</sub> molal solutions. The dissolution was determined to be more than twofold and sevenfold, respectively, for Na<sub>2</sub>SO<sub>4</sub> and NaHCO<sub>3</sub> solutions as compared to that of pure water. The effect of calcite-bearing aquifers on fluoride concentration, studied by Zhang et al. (2015), unveiled that the solubility of fluorite in calcite-bearing NaCl and Na<sub>2</sub>SO<sub>4</sub> aquifers was lower than non-calcite-bearing aquifers. On the other hand, the fluorite solubility in calcite-bearing NaHCO<sub>3</sub> aqueous solution was equal to that in the non-calcite-bearing NaHCO<sub>3</sub> aqueous system, because HCO<sub>3</sub><sup>−</sup> dissociates into CO<sub>3</sub><sup>2−</sup> which combines with Ca<sup>2+</sup> and precipitates as CaCO<sub>3</sub>. Pertinent to the dissolution rate of fluorite, it was suggested that high groundwater fluoride is more likely to result from the dissolution of biotite in which the F<sup>−</sup> are occupied at the OH<sup>−</sup> sites of the octahedral sheet (Li et al. 2003; Chae et al. 2006).

The integral frequency values for the temperature and depths of groundwater samples were computed as sketched by Chebotarev (1951). The saturation of groundwater with respect to calcite and fluorite was calculated using equations as follows:



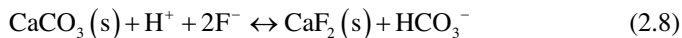
$$\mathbf{K}_1 = \left[ \text{Ca}^{2+} \right] \left[ \text{HCO}_3^- \right] / \left[ \text{H}^+ \right] = 0.97 \times 10^2 \text{ (Hem 1970)} \quad (2.5)$$



$$\mathbf{K}_2 = \left[ \text{Ca}^{2+} \right] \left[ \text{F}^- \right]^2 = 10^{-10.57} \text{ (Smyshlyaev and Edeleva 1962)} \quad (2.7)$$

where  $\mathbf{K}_1$  and  $\mathbf{K}_2$  are the equilibrium solubility products of calcite and fluorite dissolved in water, respectively. From (2.4–2.7) it would be apparent that a decrease in Ca<sup>2+</sup> increases the F<sup>−</sup> concentration. Hence, to account the thermodynamic equilibrium in groundwater with calcite and fluorite solid phases, the combined mass law equation was given in order to relate both the solute species.

Thus, the equation is



$$\begin{aligned} K_1 / K_2 = [\text{HCO}_3^-] / [\text{H}^+] [\text{F}^-]^2 &= 3.6 \times 10^{12} \text{ (Smyshlyaev and Edeleva 1962)} \\ &= 1.06 \times 10^{11} \text{ (Helgeson 1969)} \end{aligned}$$

From the above equation (2.8), it can be inferred that at a constant pH, the change in  $[\text{HCO}_3^-]$  will accompany the corresponding alteration in  $[\text{F}^-]$  as  $K_3$  is constant. Hence,  $[\text{HCO}_3^-]$  and  $K_3$  are positively correlated to each other.

The chemical composition of water is controlled naturally due to the solubility products of fluorite and calcite and associated with the independence among  $\text{Ca}^{2+}$ ,  $\text{F}^-$ , and  $\text{CO}_3^{2-}$  (Kundu et al. 2001). The calculated saturation index (SI) for fluorite in groundwater of Hangjinhouqi area reflected the unsaturated nature of the samples with respect to fluorite and suggested the dissolution of minerals which possibly eject fluoride in water (He et al. 2013).

### 2.8.1 Fluoride Solubility and Temperature

The possibility of fluorite ( $\text{CaF}_2$ ) as a dominant source of fluoride especially in granitic terrains was explored with slow solubility and dissolution rate in freshwater (Kim and Jeong 2005). The equilibrium constant of fluoride is proportional to temperature, and about 30 % of fluoride dissolution is ensured when the equilibrium constant increases from  $10^{-10.8}$  (at 10 °C) to  $10^{-10.57}$  (at 25 °C). Fluorite solubility is directly proportional to temperature and evidenced in substantiation to the study of Zhang et al. (2015) which investigated that the solubility of fluorite increases in multifold as the temperature rises from 273.15 to 373.15 K.

### 2.8.2 Fluoride Solubility and Water Softening

Fluoride contamination due to water–rock interaction has been a widely appreciated research and it is frequently studied across the world (Saxena and Ahmed 2003; Shah and Danishwar 2003; Kim and Jeong 2005; Ozsvath 2006; Chae et al. 2006). In a study conducted by Naseem et al. (2010), the spatial distribution pattern of fluoride with respect to different lithologies revealed that the water–rock interaction at the vicinity of rocks and kaolin recorded high fluoride content in groundwater. The highly recorded fluoride content was acknowledged with the presence of fluoride-bearing rocks and kaolin which leads to the replacement of  $\text{Ca}^{2+}$  by  $\text{Na}^+$  in the aquifer matrices to form soft water containing dissolved  $\text{NaHCO}_3$  (pH up to 8.5). Guo et al. (2007) discovered the limited cation exchange (between  $\text{Na}^+$  and  $\text{Ca}^{2+}$ ) in discharge areas composed of coarse-grained sediments.

On the contrary, an appreciable cation exchange in the discharge areas containing fine sediments of clay minerals was observed. The  $[\text{Na}^+]/[\text{Ca}^{2+}]$  ratio in the groundwater was comparatively lower as a result of restricted exchange but gets increased during the operation of appreciable exchange. The appreciable  $\text{Na}^+ - \text{Ca}^{2+}$  exchange between fine clay minerals and groundwater gained high value of  $[\text{Na}^+]/[\text{Ca}^{2+}]$  ratio leads to the fluoride-rich groundwater sources. At this condition, the formation of  $\text{CaF}_2$  precipitate becomes disabled, and thus, the free mobility of  $\text{F}^-$  into the solution at lower  $\text{Ca}^{2+}$  content becomes enabled.

The softened water is capable of holding high fluoride ions and enriches the fluoride content in groundwater (Edmunds and Smedley 2005; Fantong et al. 2010). In general, the plausible factors which govern the fluoride enrichment in groundwater include size and type of geological formations (through which groundwater permeates), geochemical and climatic conditions, flow velocity of groundwater, temperature (higher than  $50^\circ\text{C}$ ), pH (greater than 6), and the presence or absence of precipitating and/or complexing ions (Chae et al. 2007; Gizaw 1996; Gomez et al. 2009; Gosselin et al. 1999; Guo et al. 2007; Kim et al. 2012; Mamatha and Rao 2010; Meenakshi et al. 2004; Rafique et al. 2009; Wang et al. 2009). Due to the governance of these variables, fluoride concentration in groundwater ranges as  $1 \leq \text{F}^- \leq 35 \text{ mg L}^{-1}$  (WHO 1994). The occurrence of high fluoride concentrations restricted to groundwater with field  $\text{pH} > 6$  and temperature  $> 50^\circ\text{C}$  was studied in the Lower, Midway, Upper, and West Thumb Geyser Basins and parts of Bechler Canyon and Boundary Creek regions (Deng et al. 2011). From the experimental results on aqueous fluoride speciation by Deng et al. (2011), the free fluoride activity was directly proportional to pH between 6 and 8, whereas it was lowered in acidic water and becomes declined (nearly zero) when pH is less than 3. In supporting the observation made by Deng et al. (2011), the fluoride solubility was lowest in the pH range of 5–6.5 (Adriano 1986) and the occurrence of  $\text{F} - \text{OH}$  ion exchange increased at higher pH (Datta et al. 1996) were substantiated earlier. The occurrence of ion-exchange process between fluoride and hydroxyl ions was otherwise interpreted as though the sorption of fluoride onto clay takes place at acidic pH, whereas the reverse (as desorption of fluoride) takes place in an alkaline environment. The tendency of desorption supplements the dissolution of fluoride in groundwater (Singh et al. 2011, 2013; Gupta et al. 2012).

## 2.9 Fluoride Pollution by Other Sources

The other sources being considered as anthropogenic in fluoride pollution in the environment include coal, steel, aluminum, copper, and nickel smelting, glass, fertilizer, brick, and tile industries (Pickering 1985; Skjellkvåle 1994). Investigations on the crustal source-based atmospheric deposition leading to a considerable amount of fluoride in groundwater were done by several researchers (Das et al. 1981; Singh et al. 2001; Satsangi et al. 1998).

Fluoride derived from other sources such as local soil dust (Das et al. 1981; Singh et al. 2001; Satsangi et al. 1998) and crustal signature from wet and dry depositions (Jain et al. 2000; Chandrawanshi and Patel 1999; Satsangi et al. 2002) was also studied by many researchers in various Indian cities like Uttar Pradesh, Madhya Pradesh, Delhi, Agra, and Haryana. In a study conducted by Chandrawanshi and Patel (1999), the fluoride concentration range of 0.05–0.22 mg L<sup>-1</sup> was analyzed in rainwater. It was then corroborated that the higher concentration of fluoride was associated due to an industrial plant which extracts aluminum. The wet and dry deposits of aluminium were estimated about 200 kg per km<sup>2</sup> per annum based on the formula of Rangarajan and Athavale (2000). The estimated 200 kg per km<sup>2</sup> per annum in the recharge was presumed to raise the fluoride concentration up to 1 mg L<sup>-1</sup>.

The reported industrial sources to cause fluoride contamination in groundwater are fertilizer industry (Rao 1997), phosphate industry (Patra et al. 2000), brick industry (Datta et al. 1996), and textile dyeing industry (Sharma 1999). Kundu et al. (2009) ascertained the possible correlation between fluoride in groundwater and the quantity of the single superphosphate (from rock phosphates). In addition, he made an indication that the application of phosphatic fertilizers followed by leaching of fluoride into groundwater aquifers is rather possible under the well-drained and intensive agroecosystem.

The contribution of fertilizers to the elevated fluoride concentration in groundwater located in agricultural fields than the domestic wells was substantiated by Brindha and Elango (2013) in the area of Andhra Pradesh, Southern India.

## 2.10 Fluoride in Artesian Water

Some artesian waters of Nasipur-I Block were reported to have high fluoride concentration and may be due to inter-trappean sediments with fluoride-rich minerals within volcanoes as a consequence of physicochemical conditions (Gupta et al. 2006). It was also presumed that the leaching of highly soluble villiaumite (NaF) within the volcanic traps into the entrapped water led to subsequent local dissolution in certain pockets.

## 2.11 Concluding Remarks

Based on the geochemistry, it is accounted that rocks such as metamorphic, sedimentary, and igneous are enriched with more fluoride content between several hundreds and thousands of mg per kg of water. Notable minerals, viz., apatite, topaz, cryolite, villiaumite, micas, clays, amphiboles, calcretes, sepiolite, and palygorskite, are reported to contain fluoride and tend to eject it into groundwater. Fluoride-containing granites under peralkaline, cretaceous, biotite, Mesozoic, and A-type

carboniferous categories have also been signified. The solubility product studies revealed that the dissolution of fluorite and calcite is in attribution with pH and other physical properties. In addition to the dissolution of fluoride-rich minerals, the influence of certain geochemical environments toward the enrichment of fluoride in groundwater has been ascertained by some researchers. The dynamics of fluoride in soils is well established by the fact associated to the presence of labile fluoride in soils which in turn decides the destiny of fluoride-enriched groundwater. The chapter has been dealt with the exploration of clay materials that serve as natural barriers to protect groundwater from fluoride and the magnitude of sorption is reported to be ten times higher in acidic conditions than in basic conditions. The relationship of fluoride with other physicochemical parameters ascertained the chemical composition of groundwater. Desorption and reductive dissolution under oxidizing and reducing environments of aquifers are two responsible processes for the co-contamination of fluoride and arsenic in groundwater and have been reported by many researchers across the world.

The deposition of evaporative salts in arid zones, semiarid climate with low rainfall, high rate of evaporation, and low groundwater hydraulic conductivity are the causative factors in the enrichment of fluoride in groundwater. Researchers corroborated that the residence time and temperature are the supporting factors which help in fluoride dissolution. Solubility of fluoride based on pH, anion and cation exchange capacities, residence time of water, temperature, and water softening was established by various researchers.

Fluoride contamination due to coal, steel, aluminum, copper and nickel smelting, glass, fertilizer, brick, and tile industries was also advocated and its presence in artesian wells has also been reported.

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