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Section I
Fluorine in Context

CHAPTER 1

Fluoride in the Context of the Environment

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1.1 Fluoride in the Environment and Health Implications

Fluoride has interesting properties related to human health, particularly in preventing dental caries. However, when it is concentrated in drinking water at levels higher than 1 mg l^{-1}, a clinical condition called dental fluorosis may appear. This consists of a dental enamel hypomineralization that manifests through greater surface and subsurface porosity than in normal enamel, a condition that develops as a result of excessive fluoride intake (Burt and Eklund, 1992). Typical symptoms of dental fluorosis are fine white stripes to dark stains in the teeth surface. Endemic fluorosis is known to affect many millions of people around the world due to chronic exposure to high levels of fluoride in drinking water. The incidence of this illness is also closely correlated with climatic conditions, eating habits, and the social status of the population.

The effects of fluoride are best predicted by the dose and the duration of exposure. For example, the F requirements set for drinking water in temperate climates are not directly applicable to hot humid regions, where significantly more water is consumed. However, most epidemiological studies concerning the effects of fluoride on teeth and bone have correlated the effects with the concentration of fluoride in drinking water (Fawell *et al.*, 2006). The World

Health Organization has established a maximum concentration of 1.5 mg l^{-1} 1
F as a guideline value for drinking water (Fawell *et al.*, 2006) and most coun-
tries have adopted this value in their corresponding national regulations.

Long-term intake of high doses of fluoride can also produce alterations
in the musculoskeletal, reproductive, developmental, renal, endocrine, neu- 5
rological, and genotoxic systems. Bones and teeth are the target organs of
fluoride, as they tend to accumulate it with age (Ayoob and Gupta, 2006).
Hydroxyapatite is the mineral deposited in and around the collagen fibrils of
skeletal tissues to form bone (Ozsvath, 2009). In the presence of F-rich solu-
tions, hydroxyapatite is transformed into the more stable and less soluble 10
fluoroapatite, *via* a process of ion exchange. When the exposure to fluoride is
high, a dose-related disruption of enamel mineralization is produced, result-
ing in anomalously large gaps in its crystalline structure, excessive retention
of enamel proteins, and increased porosity (Aoba and Fejerskov, 2002).

Fluorine (F) is a univalent poisonous gaseous halogen that occurs under 15
standard conditions (*i.e.*, room temperature and normal vapor pressure) as
a light yellow-green, pungent, acrid gas. Fluorine has the atomic number 9
and a molecular weight of 18.998 g mol^{-1}. It is the most electronegative ele-
ment in the Periodic Table and the most chemically reactive of all elements.
Fluorine readily forms compounds with most other elements, including the 20
noble gases krypton, xenon and radon. The superb reactivity (*i.e.,* oxidizing
capacity) of fluorine is due to its high electronegativity, its unusually low dis-
sociation energy in relation to other halogens, and the great bond strength
of its compounds. Fluorine compounds are characterized by an oxidation
state −1. In soil, water, plants, foods and even in air, fluorine is present in its 25
ionic form. During weathering, fluorine can be leached out and dissolved
into water, where its natural concentration depends on the geological, chem-
ical and physical characteristics of the reservoir.

Fluorosis, along with other diseases produced by the intake of fluoride-rich
waters, is a major health concern. Understanding the causes of elevated 30
fluoride concentrations in natural waters is therefore essential in order to
define appropriate protocols of exploitation and management of the water
resources, as well as to design adequate methodologies of remediation. To
achieve this goal, it is necessary to identify the sources of fluorine and the
mechanisms that control its mobility and biodisponibility in natural media. 35

1.2   Natural Sources of Fluoride

In pristine areas, the source of solutes can be mostly attributed to lithology.
When rocks are exposed to the weather agents, a series of chemical processes 40
start. These chemical processes lead to the alteration of the rock minerals
and the release of dissolved components.

Minerals are characterized by their definite chemical composition and
distinctive crystalline structure. Some elements dominate the chemical
composition of a mineral, while some others may be incorporated into lat- 45
tices as impurities, which neither affect the chemical or physical properties
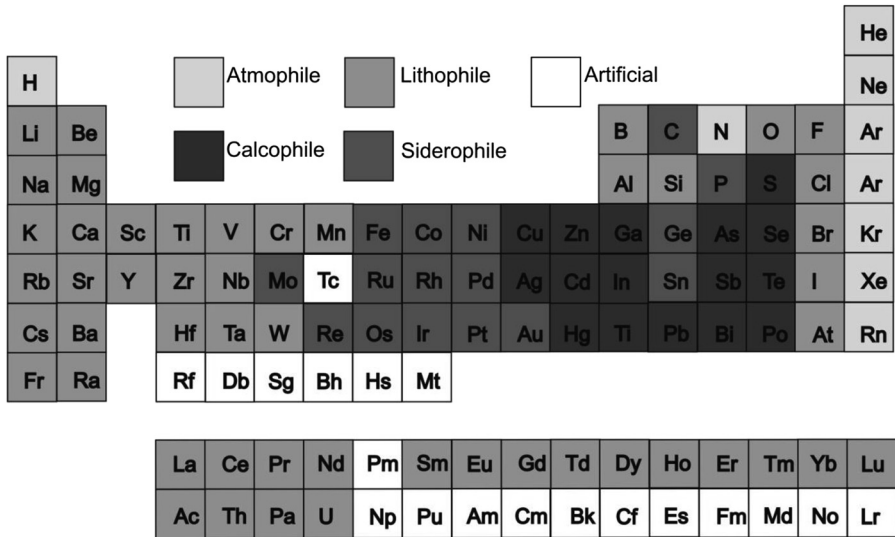
Figure 1.1   Periodic table showing the Goldschmidt's classification of elements.

of the system as a whole or to a significant extent. This process, known as substitution, depends on two physical properties such as ionic radius and electronegativity. Based on these two properties, the prestigious geochemist Goldschmidt recognized four categories of elements: atmophile, lithophile, chalcophile, and siderophile (Figure 1.1). Atmophile elements are, in general, extremely volatile and concentrated in the atmosphere and hydrosphere. Lithophile elements are those that show an affinity for silicate phases and are concentrated in the silicate portion – crust and mantle – of the Earth. Siderophile elements have an affinity for a metallic liquid phase. They are depleted in the silicate portion of the earth and presumably concentrated in the core. Chalcophile elements have an affinity for a sulfide liquid phase, so they too are depleted in the crust and may be concentrated in the mantle and core.

Fluorine is an incompatible lithophile element that preferentially partitions into silicate melts as magmatic crystallization proceeds. The geochemical behavior of F determines its accumulation in the Upper Continental Crust, where its average abundance is 611 mg kg^{-1} (Wedepohl, 1995).

## 1.2.1   F-Bearing Minerals

A large number of minerals contain F in their chemical formulas as a primary constituent or include it as an impurity. Among primary minerals, biotite and muscovite may contain about 1 wt% of F, while contents are higher in accessory minerals, such as fluorapatite (~3.8 wt%), topaz (~11.5 wt%), and fluorite (~48 wt%). Rare minerals such as cryolite may contain up to 54 wt% F.

As fluoride ions have the same charge and nearly the same radius as hydroxyl ions, they may replace each other in the octahedral sheet of mineral structures (Brigatti and Guggenheim, 2002). This kind of substitution is a common process in micas lattices, where the halogen is found at the same level as the apical oxygens of the tetrahedral sheets where they are bonded to octahedral cations (Figure 1.2).

Minerals of the apatite group are some of the other important F-bearing minerals associated with igneous rocks. The apatite-group minerals, which have a general chemical formula, $Ca_{10}(PO_4)_6X_2$, include three accepted species: fluorapatite (where X = F), chlorapatite (X = Cl), and hydroxylapatite (X = OH). Fluorapatite, in particular, is a ubiquitous accessory phase in igneous, metamorphic, and sedimentary rocks (Pan and Fleet, 2002). Along with hydroxylapatite and their carbonate-bearing varieties, it is an important mineral component of bones, teeth and fossils (Ivanova *et al.*, 2001).

Fluorite (CaF_2) is a common mineral that forms in hydrothermal systems usually with a cubic shape but can also form into octahedral or other suboctahedral shapes, depending on the temperature and composition of the solution where the crystals grow (Zidarova, 2010). It is also found as a cement in
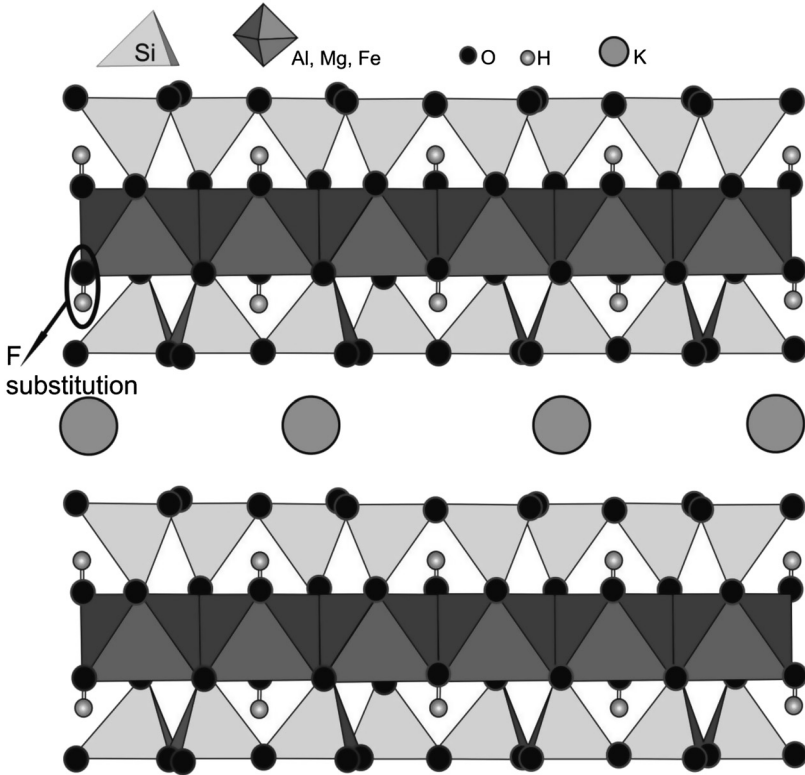
Figure 1.2   Crystalline structure of micas showing the substitution of OH⁻ by F⁻.

carbonate rocks (limestones and dolomites), and less often as an accessory mineral in pegmatites and granites or as a precipitated salt associated with hot springs.

Other F-bearing minerals that are much less abundant include amphiboles (*e.g.*, hornblende, tremolite), topaz ($Al_2SiO_4(OH,F)_2$), and cryolite (Na_3AlF_6). Villiamite (NaF), an almost infinitely soluble mineral, may contribute considerably to fluoride concentrations in groundwater associated with certain peralkaline intrusive bodies, such as the Lovozero Massif in Russia (Kraynov *et al.*, 1969).

1.2.2   Volcanic Sources

Fluoride is also commonly associated with volcanic activity and fumarolic gases. As magmas ascend and decompress their volatile species exsolve into a vapor phase. Trace elements diffuse through the liquid and partition into the vapor, to be liberated during degassing from volcanoes, fumaroles and solfataras.

Active volcanoes emit a variety of gases, including H_2O, CO_2, SO_2, HCl, NH_3, H_2S, HF and a few other minor constituents. It is estimated that the annual global emissions of gaseous fluoride compounds from volcanic sources range from 60 000 to 6 million tons (Symonds *et al.*, 1988). The emitted gases interact rapidly with the ash particles of the volcanic plume and form extremely thin salt coatings. This material is composed of relatively soluble sulfate and halide salts mixed with sparingly soluble fluorine compounds (Delmelle *et al.*, 2007), such as CaF_2, AlF_3 and $Ca_5(PO_4)_3F$. As a consequence, the water in contact with volcanic ash deposits usually contains high concentrations of fluoride (*e.g.*, Wolff-Boenisch *et al.*, 2004; Ruggeri *et al.*, 2010).

Additionally, the (calc-) alkaline volcanoes, typical of continental rift (East Africa), hot spot, continental margin (Andes) or island arcs (Japan), produce relatively fluorine-rich lavas (Rosi *et al.*, 2003).

1.2.3   Geothermal Sources

Geothermal waters are associated with active areas of volcanic activity. Geothermal fluids that rise to the surface include hot water and steam both containing dissolved solutes and gases. They may be discharged from hot springs, fumaroles, hot-water wells and wet- and dry-steam wells. Although a small amount of geothermal water may be derived from gases that were originally dissolved in magmas, most correspond to rainwater that descends through faults to considerable depths, and then is heated by the magma attaining high temperatures (>250 °C) and pressures.

The most common types of geothermal water are alkali-chloride solutions with near-neutral pH values (Edmunds and Smedley, 2013), although a great variability in the chemical composition and in the range of pH can be observed worldwide. Features that are common to most high-temperature waters include unusually high proportions of Li, Rb, Cs, Si, B, As, F and NH_4^+.

The concentration of fluoride in geothermal waters is closely linked to the solubility equilibria of fluorite (Nordstrom and Jenne, 1977), which in turn, also depends on the fluid temperature.

1.2.4   Seawater

The average abundance of fluorine in seawater is 1.3 mg l^{-1}. The aqueous speciation of marine waters reveals that fluorine is mainly found as F$^-$ and MgF$^+$ ions; these account for about 51 and 47%, respectively, of the total F concentration in seawater. Fluorine's removal from seawater is produced as aerosol sea spray and through the incorporation into marine sediments, either as part of marine organisms, such as in shells or fish bones (Carpenter, 1969) or by the precipitation of authigenic minerals, especially carbonate fluorapatite (Van Cappellen and Berner, 1988). This is the most abundant authigenic marine phosphate phase and consists of a highly substituted apatite with a formula $Ca_5(PO_4)_{2.5}(CO_3)_{0.5}F$ that contains ~3.90 wt% F.

1.2.5   Natural and Anthropogenic Sources in the Atmosphere

Fluoride contributions from natural sources like volcanic eruptions, rock dust or the marine environment are relatively small in the atmosphere. Most of these derive from anthropogenic sources, which include aluminum smelters, fertilizer factories, and industrial activities such as brick and ceramic industries, iron and steel production, fossil fuel burning, cement works, and glass manufacture. These pollution sources release fluorine to the environment as gaseous (*e.g.*, HF, SiF$_4$, F$_2$, and H$_2$SiF$_4$) or particulate (*e.g.*, CaF$_2$, NaF, and Na$_2$SiF$_6$) species (Ozsvath, 2009). Atmospheric chlorofluorocarbons also contribute fluoride to the atmosphere, however, the measured concentrations in rainwater are insignificant when compared to natural background levels. Fluoride concentrations in precipitation are generally low, typically <50 µg l^{-1}, although levels can be higher where atmospheric deposition of fluoride is enhanced by sources of industrial pollution, volcanic activity or in coastal areas.

Several cases of fluorosis due to indoor pollution have been reported in many regions of SW China, where they were attributed to coal-burning practices (*e.g.,* Liu *et al.*, 2007). Although the F-bearing phase in coal has not yet been identified, many authors suggest that it likely occurs in minerals that are commonly present in this material, such as apatites, fluorites, amphiboles, clays and mica.

1.3   Controls on Fluoride Mobilization

The occurrence, distribution, and mobility of fluorine in aqueous reservoirs depend on the interplay of a number of geochemical processes that determine its removal or release into the solution. Environmental conditions, such as water pH, the chemical composition of the system (*e.g.,* water chemical

composition, lithology, *etc*.), and the reaction kinetics strongly influence all
these processes.

1.3.1   Adsorption

Colloids in the environment play a fairly important role in controlling pollut-
ant cycling and transport, as they may retain or release ions through adsorp-
tion and desorption processes. Adsorption may be defined as the transfer of
ions (adsorbate) from the solution phase to the solid phase (adsorbent) *via*
various mechanisms, such as physical and chemical adsorption and surface
precipitation. Adsorption is described in terms of a set of reactions between
solutes and functional groups existing at the solids surfaces. The variety of
natural colloid compositions leads to the occurrence of a broad spectrum of
surface functional groups that form during the water–solid interaction.

The metal ions on the surface layer have a reduced coordination number,
and therefore behave as Lewis acids. In the presence of water, the surface
metal ions may first tend to coordinate with water molecules (Figure 1.3(a))
and the dissociative chemisorption of water leads to the formation of sur-
face of hydroxyl groups (Figure 1.3(b)). As they can be either deprotonated or
exchanged readily for an anion in aqueous solution, these functional groups
are highly reactive (Stumm, 1992).

These kinds of OH groups are found on metal (hydr)oxides, clays minerals
and amorphous silicates, where they may form two types of complexes with
ions at the solid/water interface (Figure 1.4):

a) Inner sphere complexes (specific adsorption): complexation occurs
   through short range bonding between the solute complex and surface
   oxygens. This type of interaction is also called chemisorption.
b) Outer-sphere complexes (nonspecific adsorption): complexation occurs
   between aqueous ions and the surface functional group through-
   out electrostatic interactions. This type of interaction is also called
   physisorption.
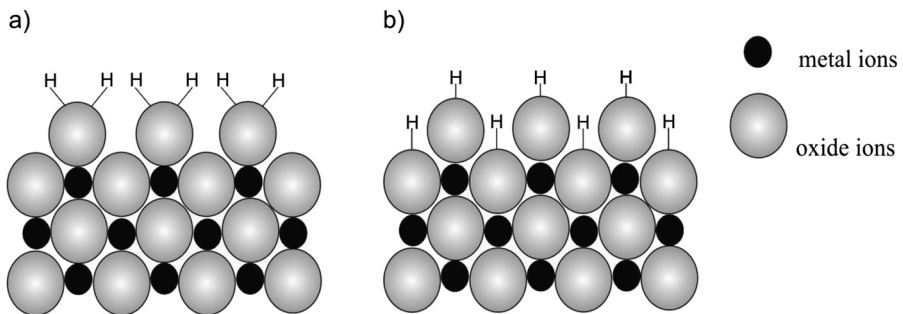
Figure 1.3   Surface functional groups normally present at the water/solid inter-
face of metal oxides, oxyhydroxides, hydroxides, clays minerals and on
amorphous silicates.

AQ1
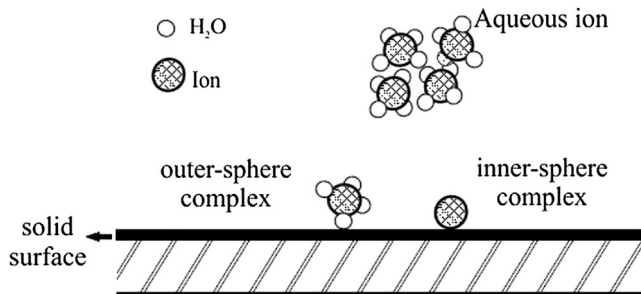
AQ2 **Figure 1.4**   Inner- and outer-surface complexes on solid surfaces.

It is important to note that even if the ion and surface have the same charge, the chemical affinity of an ion for the surface can override the electrostatic repulsion (*i.e.*, if there is a sufficiently strong chemical interaction, a negatively charged ion can adsorb onto a negatively charged surface). Ions retained strictly by electrostatic forces are more likely to be easily displaced by ions of a similar charge and thus, are termed exchangeable. Exchangeable ions are essential in the maintenance of plant nutrient levels, but are not strong enough to immobilize environmental pollutants. Chemically retained ions form very strong associations with solids that are often considered to be irreversible. As a result, chemically bound ions will have a diminished potential for release and should therefore pose a lower risk than ions held by only electrostatic forces.

A number of studies have been carried out in order to characterize the interactions of fluoride with different mineral surfaces. The identification of the factors that control the adsorption and desorption of fluoride from mineral surfaces is crucial to understanding its mobility in aquatic environments, where the most reactive minerals are metal (hydr)oxides, carbonates and clays.

1.3.1.1   Adsorption Onto Metal (Hydr)Oxides and Calcite

The adsorption of fluoride onto Fe (hydr)oxides has been studied extensively (*e.g.*, Hiemstra and Van Riemsdijk, 2000; Sujana and Anand, 2010). The kinetics of adsorption is relatively fast (10 min to 10 h, depending on the oxide crystallinity) and the process is pH dependent, as higher adsorption occurs at lower pH values. Optimum removal is determined in the range from pH 4 to 8. The interaction between surface groups and fluoride is by inner sphere surface complexes and involved a replacement of the fluoride with the surface hydroxyl groups (Hiemstra and Van Riemsdijk, 2000) and the consequent release of OH$^-$ into the solution as show in eqn (1.1).

$$\equiv FeOH^{-1/2} + F^- = \equiv FeF^{-1/2} + OH^- \tag{1.1}$$
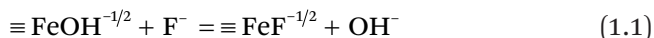
Farrah *et al.* (1987) first investigated the interaction of fluoride with aluminum (hydr)oxides over a range of pH from 3.0 to 8.0. The obtained results indicated that under strongly acid conditions, the oxides dissolve and form F–Al complexes, while maximum adsorption occurs in the pH range from 5.5 to 6.5 (~170 mg g^{-1}). As the adsorption of fluoride onto Al oxides is low (~0.2–0.4 mg g^{-1}), this material needs to be activated by heating in order to become an effective adsorbent.

Calcite is another important fluoride sink in soils and sediments, where this mineral may be present as either dentric grains or cement. Due to the strong affinity of fluoride for calcite sites, this mineral has largely been used as an adsorbent in wastewater-treatment technologies (*e.g.*, Turner *et al.*, 2005).

1.3.1.2 Adsorption Onto Clay Minerals and Soils

The electrical charge in natural clay minerals is generally negative, which makes these materials unsuitable for anion removal. However, this condition is altered in soils and sedimentary deposits, where clays are usually associated with metal (hydr)oxide coatings, particularly Fe (hydr)oxides (Zhuang and Yu, 2002). Thus, the presence of these coatings increases their capacity for fluoride adsorption (Bia *et al.*, 2012). The formation of Al–F complexes also enhances the adsorption of fluoride in soil systems (Harrington *et al.*, 2003; Zhu *et al.*, 2004). Harrington *et al.*,(2003) indicated that fluoride complexation to surficial Al and Fe *via* ligand exchange with surficial OH^{-} groups and water molecules appears to be a dominant mechanism of adsorption.

Competitive adsorption is a common mechanism in soils and sedimentary environments. Fluoride usually competes with other anions such as phosphate, arsenate, chloride, sulfate and carbonate for surface sites in aquatic environments (*e.g.*, Zhu *et al.*, 2007; Bia *et al.*, 2012).

1.3.2 Precipitation

The main authigenic F-bearing minerals that may precipitate from saturated solutions in the aquatic environments are fluorite, fluorapatite and, depending on the alkalinity of the media, carbonate fluorapatite. Table 1.1 shows the solubility constant of some of these minerals.

Table 1.1 Solubility constants at 25 °C for most common F-bearing minerals.

Mineral	Chemical Formula	log k_{ps}
Fluorite	CaF_2	−10.0370
Fluorapatite	$Ca_5(PO_4)_3F$	−24.9940
Carbonate-fluorapatite	$Ca_{9.316}Na_{0.36}Mg_{0.144}(PO_4)_{4.8}(CO_3)_{1.2}F_{2.48}$	−114.4

1.3.3   Dissolution and Desorption

As mentioned above, the main F-bearing minerals in the natural environment are amphiboles, micas, fluorite and apatite, and, to a lesser extent, topaz and cryolite. All these phases show marked differences in regards to their solubility in water, as shown in Figure 1.5. Cryolite and fluorite are much more soluble than fluorapatite and micas in the range of pH of natural water (4–9) and their solubilities are almost constant across the entire pH range. On the contrary, the solubilities of fluorapatite and micas are highly pH dependent in the range from pH 2.5 to 12.5.

Fluorapatite is more soluble under acidic pH, but is still one to two orders of magnitude less soluble than fluorite and cryolite, respectively. Chaïrat *et al.* (2007) determined that fluorapatite dissolution rates decreased at pH ≥ 3, remained constant between 7 ≤ pH ≤ 10 and decreased again at pH ≥ 10.

Despite their low solubilities, the dissolution of biotite and muscovite in granitic terrains has been considered an important source of fluoride in water that is in contact with such rocks. Leaching experiments performed with suspensions of biotite in pure water at pH 7 and 25 °C revealed that fluoride is released after 200 h of reaction reaching concentrations in water of about 6–10 mg l^{-1} (Chae *et al.*, 2006)

It is commonly accepted that dissolution of fluorite is the main cause of elevated concentrations of fluoride in groundwater in many parts of the world (*e.g.*, Currel *et al.*, 2011; Edmunds and Smedley, 2013). The dissolution of this mineral is usually favored by the co-occurrence of mechanisms that promote the scavenging of Ca^{2+}, such as calcite precipitation and cation exchange. For
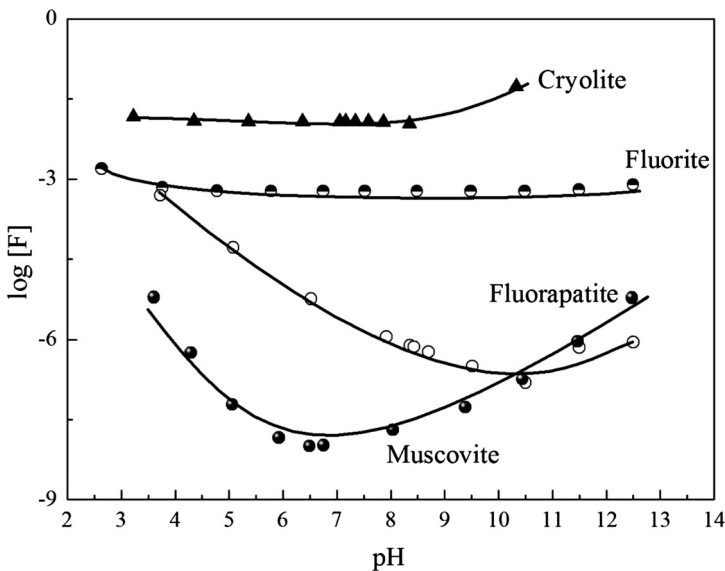

Figure 1.5   Solubility diagram of most common F-bearing minerals.

this reason, in such reservoirs, it is usual to observe inverse trends between Ca^{2+} and fluoride concentrations along the flow path.

Desorption from Fe, Al and Mn (oxy)hydroxides has usually been considered a secondary source of fluoride in groundwater reservoirs where alkaline conditions predominate (*e.g.*, Currel *et al.*, 2011; Borgnino *et al.*, 2013).

1.4 Fluoride in Natural Waters

1.4.1 Speciation of Fluoride in Natural Waters

Fluoride, as a strong ligand in water, may form soluble complexes with polyvalent cations, such as Mg^{2+}, Fe^{3+}, Al^{3+}, and Ca^{2+} depending upon the water pH (Nordstrom and Jenne, 1977), as well as with trace elements present in water, such as B, Be, Si, U, V, and rare earth elements. Free fluoride, however, is the predominant species in most groundwater reservoirs worldwide, while metal complexes with Ca, Mg, and Na, along with the neutral species HF, are only present in low concentrations under acidic conditions (*i.e.*, pH < 3.5). Table 1.2 summarizes the thermodynamic data and the aqueous speciation of some fluoride species commonly found in natural aquatic reservoirs.

1.4.2 Concentration and Speciation of Fluoride in Natural Environments

1.4.2.1 *Igneous and Metamorphic Terrains*

Many of the world's high-fluoride districts (Figure 1.6) are underlain by crystalline igneous and metamorphic rocks (*i.e.*, parts of India, Sri Lanka, Senegal, Ghana, Cameroon, Tanzania, South Africa, the Pampean ranges in southern South America, and Scandinavia). The average fluorine concentration in crystalline rocks can range from 100 mg kg^{-1} up to over 1000 mg kg^{-1}, because these contain a large proportion of F-bearing minerals. In affected areas, fluoride concentrations in natural water have been reported to be higher than 0.5 mg l^{-1} and up to 40 mg l^{-1} (*e.g.,* Chae *et al.*, 2007; Fantong *et al.*, 2010; Reddy *et al.*, 2010; Berger *et al.*, 2012; Garcia *et al.*, 2012; Padhi and Muralidh, 2012; He *et al.*, 2013; Vikas *et al.*, 2013). Most of these works attribute the elevated fluoride concentrations in water to the dissolution and weathering of F-bearing minerals present in the dominant rocks. Among them, fluorite is one of the more soluble, but it is just an occasional accessory mineral in these crystalline rocks. On the other hand, apatite, micas, and amphiboles are much less soluble than fluorite (Figure 1.5) but they are considered to be the more likely source of fluoride in natural water in granitic terrains. Recently, on the basis of experimental results, Borgnino *et al.*,(2013) determined that fluoride is preferentially released under acidic pH and low Ca^{2+} concentrations from fluvial sediments of the granitic Pampean ranges of Argentina. When equilibrium conditions are reached, water typically shows high pH and alkalinity, which in turn promotes the precipitation

of calcite and further enhances the dissolution of Ca- and F-bearing minerals present in the rocks (*i.e.*, fluorapatite). The combination of these processes results in water with high fluoride concentrations along with low levels of Ca, Mg and total hardness.

1.4.2.2   Volcanic and Geothermal Domains

In volcanic areas, drinking-water sources often have inputs from geothermal activity related to volcanic and/or hydrothermal processes. Consequentially, aqueous reservoirs in the Pacific volcanic belt, the largest volcanic area in the world, are affected by high fluoride concentrations (Figure 1.6). For example, in the Andean cordillera, concentrations as high as 8.5 mg l^{-1} have been measured in thermal springs from the Puna/Altiplano region (*e.g.*, Hudson-Edwards and Archer, 2012) In the western USA, fluoride

Table 1.2   Thermodynamic data for aqueous speciation of fluoride species.

|	Aqueous species	Reaction	log k
Al	AlF^{+2}	$F^- + Al^{3+} = AlF^{2+}$	7.0
	AlF_2^+	$2F^- + Al^{3+} = AlF_2^+$	12.6
	$AlF3$	$3 F^- + Al^{3+} = AlF_3$	16.7
	AlF_4^-	$4 F^- + Al^{3+} = AlF_4^-$	19.1
B	$BF_2(OH)_2^-$	$F^- + H^+ + B(OH)_3 = BF2(OH)_2^- + H_2O$	6.62
	BF_3OH^-	$3F^- + H^+ + B(OH)_3 = BF_3OH^- + H_2O$	13.2
	BF_4^-	$4F^- + 3H^+ + B(OH)_3 = BF_4^- + 3H_2O$	18.0
Ba	BaF^+	$F^- + Ba^{2+} = BaF^+$	−0.18
Cu	CuF^+	$F^- + Cu^{2+} = CuF^+$	1.2
Eu	EuF^+	$F^- + Eu^{2+} = EuF^+$	−1.3
	EuF^{+2}	$F^- + Eu^{3+} = EuF^{2+}$	4.4
	EuF_2	$2 F^- + Eu^{2+} = EuF_2$	−2.04
	EuF_2^+	$2F^- + Eu^{3+} = EuF_2^+$	4.0
	EuF_3	$3 F^- + Eu^{3+} = EuF_3$	10.2
	EuF_3^-	$3 F^- + Eu^{2+} = EuF_3^-$	−2.5
	EuF_4^-	$4F^- + Eu^{3+} = EuF_4^-$	12.1
	EuF_4^{-2}	$4 F^- + Eu^{2+} = EuF_4^{2-}$	−2.8
Fe	FeF^+	$Fe^{2+} + F^- = FeF^+$	1.3
	FeF^{2+}	$Fe^{3+} + F^- = FeF^{2+}$	4.1
	FeF_2^+	$2F^- + Fe^{3+} = FeF_2^+$	8.3
H	HF_2^-	$H^+ + 2F^- = HF^-$	3.76
	H_2F_2	$2H^+ + 2 F^- = H_2F_2$	6.8
Mn	MnF^+	$Mn^{2+} + F^- = MnF^+$	1.4
Pb	PbF^+	$Pb^{2+} + F^- = PbF^+$	0.82
	PbF_2	$2F^- + Pb^{2+} = PbF_2$	1.61
Sm	SmF^{2+}	$Sm^{3+} + F^- = SmF^{2+}$	4.36
	SmF_2^+	$2F^- + Sm^{3+} = SmF_2^+$	7.63
	SmF_3	$3F^- + Sm^{3+} = SmF_3$	10.02
	SmF_4^-	$4F^- + Sm^{3+} = SmF_4^-$	11.97
Sn	SnF^+	$Sn^{2+} + F^- = SnF^+$	4.08
	SnF_2	$2 F^- + Sn^{2+} = SnF_2$	6.68
	SnF_3^-	$3F^- + Sn^{2+} = SnF_3^-$	9.46

concentrations up to 50 mg l⁻¹ were determined in thermal waters collected from Yellowstone National Park (*i.e.*, Deng *et al.*, 2011), while in New Zealand and Taiwan, deep geothermal waters have shown concentrations as high as 12 mg l⁻¹ (Cronin *et al.*, 2003; Bernal *et al.*, 2014)

The speciation of fluorine in high-temperature geothermal waters is usually quite different from that found in cold groundwater, since several complexation reactions may occur between F and other constituents that are usually present in geothermal water, such as Al, Fe and B (Guo, 2012). In these systems, fluoride concentrations are typically in the range of 1–10 mg l⁻¹, although concentrations as high as 1000 mg l⁻¹ can be found under acidic conditions. In such solutions, HF, HF_2^- and SiF_6^{2-} species are present and may escape into the air as HF and SiF_4 gases at atmospheric pressures (Nordstrom and Jenne, 1977).

The region occupied by the East African Rift is a large tectonic depression with volcanic activity that encompasses several countries in East Africa, including Sudan, Ethiopia, Uganda, Kenya and Tanzania. Natural waters here are characterized by anomalous concentrations of fluoride that mostly exceed the World Health Organization guideline value for drinking water. This is the cause of prevalent endemic fluorosis disease in the region (*e.g.*, Rango *et al.*, 2009).

A thick layer (up to 1500 m) of basaltic rocks covers an extensive area over the Parana River basin, in southern Brazil, eastern Paraguay, northern Uruguay and Argentina (Figure 1.6). These rocks, known as Serra Geral Formation, overlay the formations of the Guarani Aquifer System, one of the most important reservoirs of fresh water in the world. Thermal waters extracted from deep boreholes located along the Uruguay River show fluoride concentrations of up to 13 mg l⁻¹. Despite these elevated concentrations, fluorosis has not been identified in the region, most likely because water use is generally limited to recreational purposes.
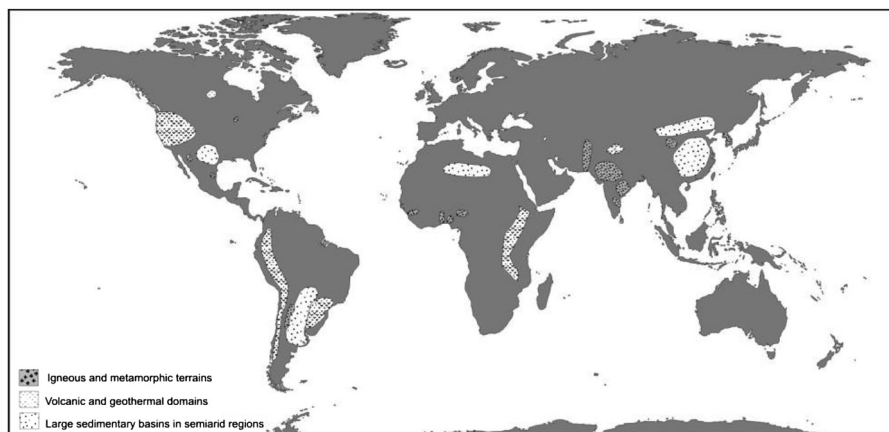
Figure 1.6 Worldwide distribution of fluoride-rich districts.

1.4.2.3   *Large Sedimentary Basins in Semiarid Regions*

In large sedimentary basins located in semiarid regions of the world, such as in the Chacopampean Plain in South America, the Yellow River Basin in China, and the arid and semiarid regions of Southern USA and Northern Mexico, groundwater constitutes one of the main drinking-water sources. Common features in these aquifers are the predominance of oxidizing conditions, alkaline pH, and a chemical composition of water dominated by Na^+ and HCO_3^- ions. Elevated concentrations of fluoride are typically found, along with other hazardous elements such as As, Mo, V, and U (*e.g.*, Currel *et al.*, 2011; Edmunds *et al.*, 2011; Nicolli *et al.*, 2012).

It is estimated that about 1.2 million inhabitants in the Chaco Pampean Plain drink groundwater with fluoride levels that exceed the guideline value of 1.5 mg l^{-1} for drinking water. The primary sources of fluoride have been traditionally attributed to the presence of volcanic shards and some scarce fluorapatite grains spread within the loessic sediments that are in contact with these water reservoirs. However, the association of fluoride in the volcanic glass still remains unknown. The concentration of this ion in groundwater is considered to be the result of the release from these primary sources, as well as from desorption from Fe and Mn (hydr)oxide coatings (*e.g.*, Borgnino *et al.*, 2013).

High concentrations of fluoride and arsenic are also found in groundwater that is in contact with loess sediments accumulated in arid and semiarid river basins in northern China (*e.g.*, Guo *et al.*, 2007; Currel *et al.*, 2011). The mechanism that mainly controls the mobility of fluoride is attributed to desorption from Fe, Al and Mn oxides present in the loess sediments that compose the aquifer (Currel *et al.*, 2011).

In the desert area along the border between Mexico and USA, groundwater also shows high contents of As and F (*e.g.*, Scanlon *et al.*, 2009; Vinson *et al.*, 2011). The sources of both natural pollutants has been attributed to lithology, mainly composed of alluvial sediments that contain fragments of volcanic rocks such as rhyolites, tuff, and volcanic glass (Reyes Gomez *et al.*, 2013).

Summary Points

- More than 70 million people suffer from fluorosis worldwide.
- Although anthropogenic sources account for some important contributions, the sources of this element in water are primarily geogenic.
- Minerals such as micas, apatites and fluorite are responsible for the release of elevated concentrations of fluoride to natural waters.
- Fluoride is associated with volcanic activity.
- The dynamics of fluoride in natural environments depend on the dissolution and precipitation of F-bearing minerals, along with the adsorption/desorption from metal (hydr)oxides and clay minerals.
- Most of the world's high-fluoride districts coincide with areas affected by volcanic activity, regions underlain by crystalline igneous and metamorphic rocks, and large sedimentary basins in arid and semiarid conditions.

Key Facts

Key Features of Weathering

1. Weathering is the process by which rocks originally formed at higher temperatures and pressure deep in the Earth come to equilibrium with water at temperatures prevailing at the surface of the Earth.
2. Weathering produces two kinds of products: secondary minerals, formed by the chemical alteration of primary minerals, and dissolved components.
3. The global reaction that resumes the chemical weathering can be expressed as: rock + H_2O + $CO_{2 \ atm}$ → secondary minerals (altered rock) + solutes.
4. During weathering, rock minerals may completely dissolve without leaving a solid residue. For example, calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$), dissolve congruently in slightly acidified water, while silicate minerals are usually altered, forming a solid residue, generally a clay mineral and/or amorphous Fe or Mn (hydr)oxides.

Key Terms

Accessory minerals: Any mineral in an igneous rock not essential to the naming of the rock. They usually constitute less than 1% of a rock by volume.

Authigenic minerals: Minerals that form *in situ* within the depositional site in response to geochemical processes. Typical examples are calcite, halite, and gypsum.

Basaltic rocks: Dark colored, fine-grained, igneous rock, with low contents of silica and comparatively rich in iron and magnesium. It most commonly forms as an extrusive rock, such as a lava flow.

Cratonic area: Tectonically stable areas composed of crystalline rocks that make up the oldest part of a continent.

Igneous rocks: Rocks formed from the solidification of magma, which is a hot (600 to 1300 °C) molten or partially molten rock material. Rocks formed from lava at the Earth surface, are extrusive or volcanic rocks, while rocks formed from magma at depth are intrusive, or plutonic rocks.

Incompatible element: Elements that tend to partition into the melt phase when melting or crystallization occurs.

Lewis acids: Elements or compounds that behave as electron-pair acceptors.

Primary minerals: Minerals that form by solidification from magma under conditions different from those at the surface of the Earth.

Secondary minerals: Minerals that form through processes such as weathering or by hydrothermal alteration.

Rift: Wide valley formed at a divergent plate boundary.

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