

Introduction

Fluorine, the lightest of the halogen elements, belongs to group 17 of the periodic table along with F, Cl, Br and I, and is one of most reactive of all elements. It has an atomic number of 9, an atomic mass of 19, one oxidation state (-1) and one stable isotope (^{19}F).

Fluorine is lithophile element with atmophile affinities, and occurs in many common rock-forming minerals, including fluorite CaF_2 , which occurs in both igneous and sedimentary rocks, apatite $\text{Ca}_5[\text{PO}_4]_3(\text{Cl},\text{F},\text{OH})$, topaz $\text{Al}_2\text{F}_2[\text{SiO}_4]$, simple halides such as carobbite KF , silicates such as muscovite $\text{KAl}_2(\text{OH},\text{F})_2[\text{AlSi}_3\text{O}_{10}]$ and a range of amphibole and mica minerals. Substitution of the F^- ion for the isoelectronic hydroxyl OH^- ion is commonplace, because of the similarity in ionic radii, although substitution will not occur if the OH^- ion is acting as a donor in hydrogen bonding (Wedepohl 1978).

Felsic igneous rocks, which contain relatively high concentrations of SiO_2 , tend to have higher concentrations of fluorine than mafic rocks. The average F content of rocks is: 1000 mg kg^{-1} in alkalic rocks, 400 mg kg^{-1} in intermediate rocks, dropping to 100 mg kg^{-1} in ultramafic rocks deficient in SiO_2 (Wedepohl 1978). In general, mica minerals tend to be the major source of fluorine in igneous and magmatic rock types, e.g., the mica phlogopite $\text{KMg}_3(\text{OH},\text{F})_2[\text{AlSi}_3\text{O}_{10}]$ is the main source of fluorine in ultramafic rock types (Rimsaite 1970). A strong association of F with phosphates is observed in both primary and secondary minerals (Kabata-Pendias 2001).

Fluorine is by far the most abundant halogen in sedimentary rock types. Clastic sediments can contain up to percentage level amounts of fluorine, whilst biogenic and chemical sediments range from <5 to $>800 \text{ mg kg}^{-1}$ F (Wedepohl 1978). As in igneous rock types, most fluorine in sedimentary rocks is contained within mica minerals (ca. 80–90%) with the remainder sourced from clay minerals, such as kaolinite and montmorillonite.

Fluorine is released as fluoride (F^-) during weathering. The chemical behaviour of F^- in natural water differs from that of the other halogen elements. In solution, F^- forms strong complexes with other ions, particularly Ca^{2+} , Al^{3+} ,

Fe^{3+} , PO_4^{3-} and $\text{B}(\text{OH})_4^-$. The concentration of F^- ions in solution is often controlled by the solubility of fluorite; hence, the concentration of F^- is often inversely proportional to that of Ca^{2+} . Fluoride also sorbs to mineral surfaces such as gibbsite, kaolinite, halloysite, and freshly precipitated amorphous $\text{Al}(\text{OH})_3$. Sorption to these solid phases may be favoured at lower pH.

Fluoride concentrations in natural water are generally less than 1 mg l^{-1} , with rivers typically containing a few tenths of a milligram per litre. The actual concentration of F in surface water depends heavily on the groundwater source, and may be higher in areas affected by volcanic activity. On average, sea water contains 1.3 mg l^{-1} F (Hem 1992). Fluoride concentrations in precipitation are generally low, typically $<50 \text{ } \mu\text{g l}^{-1}$, although levels can be higher where atmospheric deposition of F^- is enhanced by sources of industrial pollution.

Anthropogenic sources of fluoride include many industrial applications, most notably aluminium smelting and brick making (Debackere and Delbeke 1978), glass, china and steel works (Kabata-Pendias 2001), sewage, and the production and application of phosphate fertiliser and pesticides (Whalley 1976, Kabata-Pendias 2001).

Fluorine is an essential micronutrient for mammals, serving to strengthen the apatite matrix of skeletal tissues and teeth. The optimum range of F^- in drinking water is quite narrow, centred around 1 mg l^{-1} . Levels below 0.5 mg l^{-1} may lower dental health, while concentrations much above 1.5 mg l^{-1} may induce skeletal and dental disorders, and cause harm to kidneys, nerves and muscles. Fluorine in soil readily accumulates in plants. The amount taken up by plants depends upon the plant species, the soil type and the amount and form of fluorine. Even low concentrations of F can cause leaf damage and growth retardation in plants that are sensitive to fluorine exposure.

Table 28 compares the median concentrations of F^- in the FOREGS samples and in some reference datasets.

Table 28. Median concentrations of F⁻ in the FOREGS samples and in some reference data sets.

Fluorine (F)	Origin – Source	Number of samples	Size fraction	Extraction	Median mg kg⁻¹
Crust ¹⁾	Upper continental	n.a.	n.a.	Total	557
Water (F)	FOREGS	808	Filtered <0.45 µm		0.10 (mg l⁻¹)
Water ²⁾	World	n.a.	n.a.		0.1 (mg l ⁻¹)

¹⁾Rudnick & Gao 2004, ²⁾Ivanov 1996.

F in stream water

Fluoride values in stream water range over roughly two orders of magnitude, from <0.05 to 1.55 mg l⁻¹, with a median value of 0.1 mg l⁻¹. About 25% of data are less than the analytical limit of quantification (0.05 mg l⁻¹). Fluoride data tend to correlate most closely with chloride, with the exception of northern France and the Baltic states.

Lowest F values in stream water (<0.06 mg l⁻¹) are found throughout Norway, northern Finland, northern Scotland, Wales and south-west England, eastern Ireland, north-west part of the Iberian Peninsula, southern tip of Spain, western Pyrenees, south-central France, over much of the Alps and surrounding lowlands in northern Italy, Slovenia, northern Croatia and parts of Austria, and in northern Albania and some parts of Greece including Crete. The low F values in stream water observed in mountainous areas exposed to Atlantic rain in Norway, Scotland, Spain and northern Portugal, are the result of dilution by rainwater; streams in areas with flat topography in similar rain-exposed position receive additional groundwater by seepage, which contains more F.

Enhanced F concentrations in stream water (>0.36 mg l⁻¹) are found in south-east Sweden, southern Finland, central Poland, western Lithuania (linked to a natural F anomaly in deep groundwater, related to underlying Triassic deposits), eastern France, southern Portugal (probable mobile forms of F, which are slightly sorbed in clay minerals, pass to the fluid environment), Baetic Cordillera in southern Spain (associated with Pb-fluorite mining in Sierra de Lújar), in central and east Spain associated with Triassic sediments, and in parts of mainland central and southern Italy and Sicily. These values are associated with a range of lithologies.

In south-west and south-east Finland, the high values are linked to the occurrence of Rapakivi granite. In Italy, the anomalously high data in central and southern regions are associated with recent alkaline volcanics. A highly anomalous point value occurs in south-west Norway in an area where high F concentrations in groundwater were reported. Near the Czech-Austrian border high F values may be related to fluorine occurrences in contact with granitic rocks. In north-eastern France, fluoride anomalies in stream water are clearly connected with natural and human-induced salt dissolution from Keuper deposits.

As seen on the geochemical map, fluoride as an anion in stream water correlates well with the elements of the Major ions pattern which characterises the distribution of total dissolved solids in European stream water. This pattern is controlled by the climatic and geographical conditions of the continent, more than by its lithological composition. In addition, F is weakly associated with the elements typical for Felsic-alkaline rocks (Italy), and inversely with the Base metals elements type. For very high concentrations in southern Sweden and Finland the existence of fluoride- aluminium and -iron complexes might be suggested. Input through marine aerosols leads to variable results – along the rocky and mountainous coasts, F is very low in stream water, and around average or even high on low, sandy ones – which indicates specific processes of exchange with sea salts.

A more detailed description on the chemistry of F in stream water is given in Annex 1 of this volume by Ander *et al.* (2006), where the thematic interpretation of stream water chemistry is discussed (see section on fluorite solubility).