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Fluorine

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Element Data

Atomic Symbol: F
Atomic Number: 9
Atomic Weight: 18.998 g/mol
Isotopes and Abundances: ^{19}F 100%
1 Atm Melting Point: $-219.67\text{ }^{\circ}\text{C}$
1 Atm Boiling Point: $-188.11\text{ }^{\circ}\text{C}$
Common Valences: -1
Ionic Radii: 130 (III), 131 (IV), and 133 (VI), in pm (coordination number)
Pauling Electronegativity: 3.98
First Ionization Potential: 17.4428 eV
Chondritic (CI) Abundance: $60.7\text{ }\mu\text{g}\cdot\text{g}^{-1}$
Silicate Earth Abundance: two estimates:
 $18\pm 8, 25\pm 10\text{ }\mu\text{g}\cdot\text{g}^{-1}$
Crustal Abundance:
(continental) $\sim 550\text{ }\mu\text{g}\cdot\text{g}^{-1}$
(oceanic) $130\sim 1000$ (est. 400) $\mu\text{g}\cdot\text{g}^{-1}$
Seawater Abundance: $1.3\text{ }\mu\text{g}\cdot\text{g}^{-1}$
Core Abundance: considered as 0

Properties

In its elemental form, fluorine exists as a diatomic molecule of highly toxic, corrosive, pale yellow gas with a pungent smell in ambient conditions. As the most electronegative element, fluorine is reactive, and commonly found in nature as ionic compounds bonded to metal cations or hydrogen. Fluorine can dissolve into solution forming F ions.

History and Use

Fluorite (CaF_2) has been known and used in the metal smelting process to lower the melting temperature of metal ores since the

16th century. It was then known as *fluores* or *flusse*. The element was later isolated in 1886 (Moissan, 1886), 330 years after fluorite was first described by Agricola (1556). Today, 6.2 million metric tons of fluorite is mined for industrial use (British Geological Survey 2010-2014 report) in metallurgy, ceramics, and chemistry, with applications including the production of aluminum, fluorocarbons, and fluorine gas. For example, fluorine is used to separate uranium in the nuclear power industry, and to produce high-performance plastics such as polytetra-fluoroethene (PTFE, commonly known as Teflon[®]) and the Gore-Tex[®] membrane.

Geochemical Behavior

Fluorine plays an important role in geochemical and biogeochemical systems, despite its relative low overall abundance on Earth and in the Cosmos. For example, fluorine can exert a significant control on the behavior and composition of magmas, the composition of hydrothermal fluids, and the transport of ore metals in the crust. The distribution of fluorine in various geological samples is therefore of interest in geochemical investigations, including: tracing the evolution and source of hydrothermal fluids active in ore deposit formation; metamorphism and subsolidus alteration; and tracking subduction-related mantle to crust mass transfer.

Fluorine has a strong tendency to bond with silica and other cations and is therefore

considered a lithophile element. Reflecting this characteristic, a dominant fraction of F on Earth, ~99%, is estimated to exist in the solid Earth. However, fluorine is also referred to as a magmatic volatile element, as it is found as HF gas in volcanic edifices and fumaroles. A small quantity of F is found in surface waters. On the contrary, F is thought to play a role in forming ligands and increasing metal solubility in high-temperature fluids (hydrothermal fluids, diagenetic formation waters, metasomatic fluids).

Considerable effort has been put into the advancement of analytical techniques to accurately determine the fluorine content of geological materials. Such analytical techniques include anion chromatographic column, selective electrode, neutron activation, electron microprobe, ion probe (SIMS), and irradiated rare-gas analysis (Hanley and Koga, in prep.).

Abundances

Fluorine, having the single isotopic species ^{19}F , was produced by nucleosynthesis in stars and supernovae pre-dating the sun, through neutrino spallation of ^{20}Ne and hydrogen-helium burning involving ^{14}N , ^{18}F , ^{18}O , and ^{15}N . (Woosley and Haxton 1988; Forestini et al. 1992). At the time of the formation of the solar system, F is considered to have been moderately volatile with a 50% condensation temperature of 734 K for fluorapatite (Lodders et al. 2009). The solar abundance

has been assessed by measurements of volatile element-rich CI chondrites and spectrometry of the Sun's photosphere. While heavier halogen elements tend to be less abundant, the lightest halogen, Fluorine, is notably less abundant than the heavier element Cl. In addition, F is 3 to 4 orders of magnitude less abundant than neighboring elements, namely C, N, O, and Ne due to a small probability of production and its destruction in supernovae (Clayton, 2003).

Meteoritic F abundances vary by a factor of 20; CI and EH chondrites show higher abundances among the different chondrite classes (i.e. CM, CO, CV, H, and L, while EL and LL show the highest abundances; Wasson and Kallemeyn, 1988). Fluorine contents of the Moon, Mars and Vesta are also reported. The Moon's mantle is reported as 5.3 ppm F, based on glass samples (approximately 30% of Earth mantle). Bulk F abundance for Mars is 21 ± 13 ppm, estimated from shergotite meteorites (Taylor, 2013). The eucrite parent body, Vesta, probably contains some volatile elements since F-rich apatites have been found in this class of meteorites.

The abundance of trace elements in the Earth's mantle is commonly assessed through compositional correlations among primitive basalt, peridotite xenoliths, and chondritic meteorites. The modeled F content of the bulk silicate earth (BSE) ranges from 18 to 25 ppm, with different estimates agreeing within reported uncertainty. MORBs are derived from a

depleted mantle source with F contents ranging from 6 to 22 ppm. Limited data on the bulk F content of mantle xenoliths shows significant variability from 7 to 400 ppm (Hanley and Koga, in prep).

Laboratory experiments show that F has a stronger affinity to silicate melt than to metals, metal alloys, and sulfides (*e.g.* Mungall and Brenan, 2003). Based on a comparison of chondritic and BSE abundances, F abundance in the core is negligible (McDonough 2003).

Seawater, representing only 0.02% of Earth's mass, is a negligible F reservoir as it contains less than 1% of the total F budget of the bulk Earth. The preferred mean abundance of F in seawater is 1.3 ppm. Fluorine in river water is reported as 10 to 20 ppb. Formation water in sedimentary basins and well waters in crystalline basements typically ranges from 0.5 to 10 ppm (Hanley and Koga, in prep). Hydrofluoric acid is present in high temperature volcanic gases, with concentrations typically in the range of 100 to 300 ppm, in which F is the least abundant of the five elements (H, C, O, S, Cl, and F) constituting volcanic gas (Symonds et al. 1994).

Fluorine abundance in the bulk continental crust is estimated as 553 ppm; this value is a volumetric average of upper (611 ppm) and lower crustal (429 ppm) average abundances. The upper continental crust is enriched in fluorine, relative to the

lower continental crust, by a factor of 1.4 - 2.3 (Rudnick and Gao 2004).

Fluorine contents in magmatic rocks are in the 100s to 1000s of ppm range. Highly fractionated peraluminous and peralkaline granitoids, and some basaltic rocks, show the highest abundances, as F is generally concentrated into magmas during crystal fractionation. In addition, F is incorporated into silicate melt by bonding to Si and Al, resulting its higher solubility in felsic than mafic melts (Dalou et al. 2015).

During the weathering of volcanic products, glass devitrication results in mobilization of F (*e.g.*, Stix et al., 1995). F is particularly rich in phosphatic shales, caliche (nitrate) deposits (up to ~4000 ppm; Salminen et al., 2005) and evaporites.

Fluorine can be locally concentrated in mantle as halides and hydroxyl minerals. Carbonatites from Ol Doinyo Lengai, Tanzania, contain between 1.2 to 3.5 wt. % F, occurring as immiscible halide melt (Teague et al., 2011); halide melt inclusions in magmatic minerals are found in intrusive carbonatites (St.-Honoré, Quebec, Canada). Furthermore, fluoride melt has been reported in peridotite xenoliths (Klemme, 2004). Similarly, F-rich micas and amphiboles are reported from various mantle nodules (*e.g.* up to 8 wt. % F for phlogopite found in peridotite nodules).

Mineralogical hosts

There are 427 naturally occurring Fluorine-hosting minerals registered in the

IMA inventory, in which halides, oxyhalides, silicates and other groups are listed. Nearly all silicate minerals with hydroxyl (OH) sites can potentially have F-bearing species, such as mica, amphibole, apatite, and norbergite. Fluorite (CaF_2) contains 48.7 wt. %. Up to a few weight percent F can be found in micas, amphiboles, and apatites (e.g. 4.5 wt.% phlogopite, 4.6 wt. % fluorrichterite; 3.8 wt. % fluorapatite). Trace quantities of F can be incorporated into minerals without crystallographic site accommodation because of its similar ionic size to oxygen. For example, olivine and orthopyroxene in mantle peridotites are reported to contain 2.9 – 30.3, and 12 – 30 ppm, respectively (Beyer et al., 2012).

Biological Utilization and Toxicity

The teeth of some sharks are enameloid (in contrast to common dentin), which consists of fluoroapatite, contrary to hydroxyapatite in human teeth. The lattice parameters of enameloid are close to those of the geological fluoroapatite single crystal, with enameloid F content being 3.1 wt.%, similar to the F content of geological fluoroapatite (3.64 wt.%; Enax et al., 2012). Incorporation of F in benthic foraminifera shells ranges from 0.00016 to 0.0016 F/Ca by weight, a maximum of 650 ppm F (Rosenthal et al., 1997). Corals contain 700 ~ 1200 ppm F.

In low concentrations, fluoride (F) strengthens the teeth and bones of

vertebrates, and less than 2 ppm is added to toothpaste and drinking water in some countries. The human body contains on average 3 mg of F.

Elemental fluorine is highly toxic. Studies have found that a single ingestion of just 0.1 to 0.3 mg F/kg (i.e., milligrams of F for every kilogram of bodyweight) can cause the first symptoms of poisoning, including nausea, vomiting, abdominal pain, and diarrhea. Ingested fluoride is transformed in the stomach to hydrofluoric acid, which has a corrosive effect on the epithelial lining of the gastrointestinal tract. Fluoride consumed in excess is an endocrine disruptor that can affect your bones, brain, thyroid gland, pineal gland and even your blood sugar levels (Akiniwa, 1997).

Cross-References

- Halogens
- Halide Minerals
- Nucleosynthesis
- Volcanic gases
- Weathering Chemical
- Chlorine
- Chlorine isotope
- Magmatic volatile elements
- Ore Deposits
- Hydrothermal fluids
- Chondrites
- Meteorites
- Silicate Minerals
- Cosmic Element Abundances
- Lithophile elements

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