Part 2

Fluoride

Chapter 4

The fluoride question

What is fluoride?

Fluoride is the name given to compounds which contain the gas fluorine and it is estimated to be the 13th most common element in the earth's crust.

Chemistry books teach us that;

"Fluorine is a yellowish gas, which is highly toxic, reacting and bonding readily with most inorganic and organic compounds, except helium and neon."

"It is the most chemically active non-metallic element and the most electro-negative of all the elements. It is a member of Group 17 (the halogens) of the periodic table". (1)

It was originally thought that fluorine gas could not exist in nature alone, only as a compound but, in 2012, the first source of naturally occurring fluorine was found in fluorite mines in Bavaria, Germany.

The three most common sources of fluorine as fluorides in the earths crust are 1) fluorite or fluorspar, 2) fluoroapatite, 3) cryolite.

1) Fluorite, (chemical formula, CaF2), is a compound of calcium and fluoride that crystallizes in the form of masses, cubic, and octahedral crystals. In its purest form it is transparent but impurities make it colourful. As a plentiful, affordable, and colourful gem, fluorite is popular with collectors worldwide. In the mining industry it is called fluorspar. It is found in veins, fractures and cavities of rocks particularly in limestone and dolomites. It can be well hidden often deep below the surface of the earth or it can be a constituent of sedimentary rocks, either as grains or as the cementing material in sandstone. Fluorite can exist within phosphate rock at the rate of 3–4%. Industrially, fluorite is used as a flux for smelting, and in the production of certain glasses and enamels. The purest grades of fluorite are used for hydrofluoric acid manufacture, which is the intermediate source of most fluorine-containing chemicals. Deposits occur in the USA, in Illinois and Kentucky; in the UK, Derbyshire; in southern Germany; in the south of France; and in Russia.

(Sedimentary rocks are types of rock that are formed by the accumulation or deposition of small particles and subsequent cementation of mineral or organic particles on the floor of oceans or other bodies of water at the Earth's surface).

2) fluoroapatite, (Ca5(PO4)3F), is a more complex compound, containing a variable amount of fluorine, calcium, phosphate and chlorine. It has a hexagonal crystal structure and is either transparent or opaque. Various colours arise due to the presence or absence of certain metal elements. It is in most rocks either as microscopic crystals but can occur as very large, well formed hexagonal crystals, in veins, fractures or pockets - these are often used as gemstones. Fluoroapatite is the most common and abundant apatite found in phosphate rock (15% to 20% on the basis of weight.) Phosphate rock is mined for the phosphorus within the fluoroapatite with the fluoride originally being an unwanted waste. However, the hydrogen fluoride by product is now one of the industrial sources of hydrofluoric acid, which in turn is used as a starting reagent for synthesis of a range of important industrial and pharmaceutical fluorine compounds. Phosphate rock is the world's largest source of fluoride. Phosphate rock comes from deposits in the USA (Florida, Tennessee, and South Carolina), in North Africa and the West Indies.

3) Cryolite, (Na3AIF6), is a compound of fluoride, aluminium, and sodium and is deposited through volcanic eruptions. Cryolite is the most fluorine-rich. It occurs as a glassy, colourless, white reddish to grey-black prismatic, monoclinic crystals. The mineral often resembles an ice block but it is a collector's curiosity item rather than a gemstone for jewellery. It is used as a solvent for bauxite in the electrolytic production of aluminium and has various other metallurgical applications, and it is used in the glass and enamel industries, in bonded abrasives as a filler, and in the manufacture of insecticides. Large deposits were once found in Greenland, smaller amounts in Spain, Russia, and Colorado USA. Due to excessive mining, it has become a rare mineral. In 1987 the Dutch were forced to close their mines in Greenland. However, cryolite can be produced synthetically from fluorspar. Aluminium manufacturing combines the Bayer and the Hall-Heroult process using bauxite ore and substitutes cryolite with a synthetic product of 'sodium aluminium fluoride'. The making of aluminium produces a quantity of fluoride waste: perfluorocarbons and hydrogen fluoride as gases, and sodium and alumimium fluorides and unused cryolite as particulates. (2)

4) There are many other sources of fluorides which contain varying amounts of fluorine, some samples are cut into gems, an example of which is;

topaz (Al2SiO4[F,OH]2). (3)

The fluoride that comes naturally in water and foods as calcium fluoride is different from the artificial fluoride that is the product of manufacturing processes. Natural, calcium fluoride in water and foods is usually combined with organic natural minerals and salts which, to some extent, counteract certain adverse reactions within the body. This is not the case with artificial fluoride.(4). More on artificial fluoride in chapter 7.

The History of fluoride

For centuries, fluorite was prized for its beauty, although pure fluorite is transparent, impurities make it colourful. It has been called 'the most colourful mineral in the world'. The most common colours are purple, blue, green and yellow. Due to fluorites relative softness, it was used for carvings, ornaments and jewellery. Fluorite carvings from about 1000 AD have been discovered in the Americas, in Indian burial grounds (Ref: Wikipedia). In the British Museum there are two Roman fluorite cups, the Barber Cup and the Crawford Cup. In Napoleonic times a variety of fluorite known as Blue John was exported from Devonshire, England, to France where it was worked into ornamental vases.

The usefulness of fluorite/fluorspar has been known for centuries. In 1529, the German physician and mineralogist, Georgius Agricola, described a crystalline material, fluorspar, that helped ores melt at lower temperatures, and called these stones 'fluxes' because they made metal ores 'flow' in the fire.

However, the search for the composition of fluorite took nearly two and a half centuries and was one of the chief unsolved problems in inorganic chemistry. It was slow because of the exceptional dangers of generating what was to be hydrogen fluoride (HF) as well as the pure fluorine gas - several early experimenters died or sustained injuries from their attempts

(Hydrogen fluoride is a chemical compound that contains fluorine. It can exist as a colourless gas or as a fuming liquid, or it can be dissolved in water and then named hydrofluoric acid. Solutions of HF are colourless, and highly corrosive. It is now used to make most fluorine-containing compounds; examples include the commonly used pharmaceutical antidepressant medication fluoxetine (Prozac) and the material PTFE (Teflon). Elemental fluorine is produced from it. It is commonly used to etch glass and silicon wafers.)

Hydrogen fluoride is the most dangerous acid known to man. If HF gets on the skin, it causes deep burns; it bonds with calcium ions and magnesium in the blood, making both unavailable for the body and, so, can easily kill.

Fluorine, the yellowish gas, as already mentioned, is also poisonous, dangerous and highly corrosive. Fluorine gas at low concentrations makes your eyes and nose hurt. At high concentrations it becomes hard to breathe and can cause immediate death due to lung damage.

It appears likely that crude hydrofluoric acid was first prepared by an unknown English glass worker in 1720 and used for glass etching. Andreas Sigismund Marggraf, a German chemist, formed the acid in 1764 when he heated fluorite with sulphuric acid, and the resulting solution corroded its glass container. In 1771 the Swedish chemist Carl Wilhelm Scheele, repeated this experiment, and named the acidic product, fluss-spats-syran (fluorspar acid). (5)

However, the French chemist Edmond Frémy (1814–1894) is credited with discovering hydrogen fluoride (HF), while trying to isolate fluorine.

It was Henri Moissan, Frémy's old student, who finally isolated fluorine gas on 26th June 1886. He continued to make a full study of the element and its reactions with other elements during which time he was poisoned several times. He was awarded the Nobel Prize in 1906 for Chemistry, for isolating the element fluorine and also for the development of the Moissan electric furnace, but unfortunately died two months later, on 20th February, aged only 54. His fluorine experiments may have contributed to his early death. It was said at the Nobel Prize ceremony in Stockholm that,

"he had opened the previously locked pathway to fluorine chemistry".

Those known to have also suffered injury because of their experiments on fluorite were Sir Humphrey Davy, English chemist; George Knox and his brother Thomas Knox, Irish chemists; Louis Gay Lussac, Louis Jacques Thenard and Jerome Nickles, all French chemists; and Paul Louyet, a Belgium chemist. They all suffered intensely from the effects of inhaling hydrogen fluoride (HE), experiencing severe pain. Davy's injuries included damage to his eyes and fingernails. George Knox was an invalid for three years and his brother Thomas Knox nearly died. Both Paul Louyet and Jerome Nickle, died during their investigations, it is presumed from the effects of inhaling HE.

Throughout the early part of the 20th century and up to the time of 'World War II' the element, fluorine, appeared to be only a laboratory curiosity although fluorine compounds were being emitted from coal-

burning electrical power plants and were by-products of industrial processes such as in the making of bricks, ceramics, and fertilizers; or used as 'fluxes' for the metal industry.

The big change came in the 1940s, when large amounts of fluorine was needed to produce the atomic bomb, (the use of uranium hexafluoride in the separation of uranium isotopes). This intense interest lead to the development of many organic fluorine compounds and soon fluorine became an industrial chemical of considerable use. Fluorides became utilized as refrigerants and aerosols; are instrumental in the making of plastics and Teflon; are used to fumigate cereals to stop them going mouldy and are often part of pesticides sprayed on fruit to stop pests. They continue to be used for etching and frosting glass and soon were developed to manufacture special lenses. They are used in the armaments industry and needed for rocket fuel. Pharmaceutical companies incorporate fluorine into many medications, e.g. Prozac, the antidepressant, and even some children's vitamin drops contain fluoride, see more on pharmaceutical use in Appendix 5. (6)

The temptation for profit proved overwhelming for industry at the time, so any negative data on health or on the environment was suppressed.

To explain how this happened the following history has been taken from Christopher Bryson's book, 'Fluoride Deception';

"Industry immediately saw the potential for the new fluorine chemicals. In 1928, in partnership with General Motors, DuPont patented the fluorine-based gas called Freon-12. It was initially to be used as a cooling gas in refrigerators. This new gas combined carbon, fluorine and chlorine (CFCs). The carbon and fluoride bond is one of the strongest bonds that can be made in chemistry, and these new chemicals become known as PFAS chemicals – short for poly and perfluoroalkyl substances. Used commercially since the 1940s, it was hoped that Freon-12 would replace previous toxic refrigerants such as PCBs (polychlorinated biphenyls). However, when exposed to a flame, Freon-12 decomposed into phosgene and hydrogen fluoric gases. Phosgene was the poison gas used so terribly in the trenches of World War 1, while Freon-12 was later found to be destroying the ozone layer."

"World War 2 created a weapons race, with fluorine as the key. Large-scale production of the elemental fluorine began, both in Germany and the US. Germany used high-temperature electrolysis to produce tons of chlorine trifluoride, a compound planned to be used as an incendiary. The US needed large-scale fluorine production for developing the atomic bomb. Because it was war-time and fluorine was needed in such large amounts, it was deemed necessary by the government of that time to suppress negative information regarding fluorine or fluoride."

"After the war, new household products relentlessly appeared, using fluorine-based mixes. These were called PFCs or perfluoro chemicals, they included plastics, aerosols, pharmaceuticals, water-proofers, pesticides, specialised lubricants, and firefighting foam. It was even to be found in greaseproof wrappers and in boxes to carry McDonald's French fries, in the coating of non-stick cooking ware – Teflon (PFOAs, perfluorooctanoic acid), in carpets to protect from spills and stains – PFOS or perflurooctane sulfonate is found in 'Scotchguard' for instance. The ability of these man-made PFC molecules to resist water, oil, and highly corrosive chemicals, seemed to make them perfect for a host of modern creature comforts. Unfortunately, the PFOS chemical found in Scotchguard does not just last a long time; it likely lasts for ever, says Scott A. Mabury of the University of Toronto." (7)

Others have confirmed the dangers of fluoride compounds. E.G. Vallianatos in his book, 'Poison Spring', pub. 2014 and, by Robert Bilott, in his book, 'Exposure' pub. 2019 where it has been explained that the chemicals PFCs (perfluoro chemicals), APFOs (ammonium perfluorooctanoate), PFOAs, (perfluorooctanoic acid) and PFOS (perfluoctane sulfonate) are all basically very similar, or 'kissing-cousins'. As persistent chemicals, they continue to build up in the environment and in animal and human life, and are now to be found in blood where they bind to protein and then accumulate in the liver and gallbladder.

There may be room for hope because as early as the 1960s, Rachel Carson's book, 'Silent Spring', highlighted concerns over the overuse of many chemicals, and because of her work some chemicals are now banned or are being 'phased out' from most countries. DDT was banned from most countries in 1972. Thirty years after Carson's book, Theo Colburn gave a further warning in her book, 'Our Stolen Future', pub. 1996, explaining the harm to both animals and humans from ever newer, and more toxic man-made chemicals. Her book may have prompted 3M (an American multinational conglomerate) and makers of PFAS chemicals (PFOS, PFOA and PFOS), in 2000, to promise a phase-out of such chemicals, while Canada proposed a complete ban in 2009. And manufacturers halted the production of Teflon, non-stick coating (PFOA) from cookware around 2002 because it produced a toxic gas when over heated - in one instance, a burning cigarette laid on some Teflon produced enough toxic gas to kill the smoke - but it took some more years before countries slowly banned its use. Unfortunately, this responsible beginning did not last as later the Teflon manufacturer slightly changed the non-stick formula in order to continue to sell the product.

T Vallianato's book, tells us that the bans on chemicals, as promised, has not happened. Vallianato discovered that the world is being contaminated with ever more unregulated noxious chemicals with no thought being given to the environmental and health consequences; if and when such concerns are raised, they are duly suppressed. The reason, he believes, is that: "Both individual people and entire bureaucracies are susceptible to corruption." Theo Colburn's has admitted, since writing her book, that the amount and extent of new persistent chemicals onto the market had been suppressed even from scientists.

The Childhood Cancer Prevention Initiative (CCPI) reported in 2020 that there were, to date, 85,000 manufactured chemicals used in the US, most of which have never been tested for safety or toxicity. (8)

Fluoride is not needed by the body

In 1979 the USA 's Food and Drug Administration (FDA) deleted two paragraphs that classified fluoride as an essential or probable essential for human consumption.

The US authority for recommended dietary intakes concluded in 1989 that contradictory studies in rats and mice in the 1970s,

"... do not justify a classification of fluorine [as fluoride] as an essential element, according to accepted standards." (9)

Because animal diets can be more stringently depleted in fluoride than human diets, studies in short-lived rats and mice are considered the best way to discover the possible essentiality of minerals in mammals. In its most recent publication on recommended dietary intakes, the same US authority makes no mention of fluoride essentiality in the diets of humans or animals. (10)

It was reported in 1994, in the UK that,

"No essential function for fluoride (F) has been proven in humans". (11)

The EU in 2013 reported,

"Fluoride has no known essential function in human growth and development." (12)

The Fluoride Action Network (FAN) submitted the following to the Environmental Protection Agency (EPA) in April 2011 on this point:

"Fluoride has no known role in nutrition or biochemistry. Fluoride is not considered by knowledgeable experts to be an essential nutrient for humans, and it has no known, beneficial role in human biochemistry." (13)

Human milk is extraordinarily low in fluoride, ranging from 0.007 ppm to 0.011 ppm (IOM, 1997) – 100 times less than in fluoridated water in the US (0.7 to 1.0 ppm). Human milk also has about three times less fluoride than the blood of the mothers producing it. (14)

"It seems clear that nature has evolved active mechanisms to limit the transfer of fluoride in humans – both from ingested food and water to blood, and from blood to breast milk. Thus, either by accident or intent, mothers' milk protects the baby from more than minimal exposure to fluoride. Water fluoridation removes that protection for bottle-fed babies," says Professor Paul Connett.

Fluoride in food and water

The following information has been taken from the 'Fluoride Alert' website, FAN, www.fluoridealert.org.

Over the past 100 years, the levels of calcium fluoride in foods, purchased at the grocery store have increased. The reasons for this increase include:

- 1. the mass fluoridation of water supplies in some countries
- 2. the introduction of fluoride-based pesticides
- 3. the use of mechanical de-boning processes, and, perhaps,
- 4. the use of Teflon in certain production processes.

The elevated fluoride levels that are now seen in most processed foods can make it seem that everything has fluoride in it. The good news, however, is that the naturally occurring, calcium fluoride, level of fluoride in most fresh fruits, fresh vegetables and fresh surface water, is very low. As can be seen in the tables below, the average level of fluoride in these products generally ranges from 0.01 to 0.1 ppm. Eggs and milk contain very low levels as well (0.01 to 0.03 ppm). By way of contrast, artificially fluoridated water contains 0.7 to 1.2 ppm, processed beverages and drinks generally contain 0.5 to 0.8 ppm, and juices (e.g. white grape juice) made from fruit sprayed with fluoride pesticide contain an average of 2.1 ppm.

As a general rule, therefore, one will receive very little fluoride when drinking fresh surface waters (e.g. spring water) and eating unprocessed fruits, unprocessed vegetables, eggs, and milk. While there are some exceptions to this rule (e.g. seafood, tea, water from deep wells, and fresh fruit/vegetables sprayed with fluoride pesticides), it is a good general rule to follow if you wish to reduce your fluoride exposure.

See: FAN's Grocery Store Guide: 7 Ways to Avoid Fluoride in Beverages and Food.

1. Fresh Water

	Average Fluoride Content (ppm)
Rain*	0.008
Surface Waters** (e.g., lakes, rivers, springs)	0.05
Bottled Water***	0.1

Fluoride in sea water is 1.4 ppm.

2. Raw fruit

	Average Fluoride Content (ppm)
Apple	0.03
Avocado	0.07
Banana	0.02
Cantaloupe	0.01
Cherries	0.02
Grapefruit	0.01
Peaches	0.04
Pears	0.02
Plums	0.02
Strawberries	0.04
Watermelon	0.01

3. Raw vegetables

	Average Fluoride Content (ppm)
Carrots	0.03
Celery	0.01
Cucumber	0.01
Green Pepper	0.01
Lettuce	0.05
Onions	0.01
Radishes	0.06
Tomato	0.02

4. Eggs & milk

	Average Fluoride Content (ppm)
Eggs	0.01
Milk, 1%	0.03
Milk, 2%	0.03
Milk, skim	0.03
Cream	0.03

(15)

Dr George Waldbott advised people to be careful in their assumptions, reporting in 1978, in his book 'Fluoridation' page 42, that talcum used to polish rice and peas had been found to raise their fluoride content to 10-14 ppm.

Waldbott also gave the example of a woman in England who consumed 6.3 to 9.3 mg fluoride a day from tea and water alone. She suffered with arthritis.

However, as a quick summary to fluoride in foods:

Professor Neil Jenkins, (pro WF advocate) maintained that fluoride is present in concentrations of up to 0.5 ppm in many foods, but that the total daily intake from this source rarely exceeds 1mg. However, people in a fluoridated area with 1ppm artificial fluoride added to the water supply could consume 5mg daily, enough to lower the thyroid activity in humans. (16)

George Waldbott lists the fluoride content of water from many sources, in his book Fluoridation the Great Dilemma on page 35, as fluoride levels can vary. For instance spring water in one area had been found to contain 7.5 ppm fluoride and sea water fluoride levels, in the Persian Gulf, was found to contain 8.72 ppm. F. (17)

For sources of fluoride that load our bodies - see Appendix 7

Chapter 4 References

(1) (Source: https://www.britannica.com/science/fluorine).

(2) (Source: Britannica.com; www.britannica.com/science/cryolite).

(3) (Source: George Waldbot, 'A Struggle Against Titans', page 73) and (https://www.britannica.com/science/fluorine - and Geomorphology), and ('An Introduction to the rock-forming mineral'. London: The Mineralogical Society. ISBN 978-0903056-27-4. OCLC 858884283), and (<u>https://geology.com/minerals/fluorite</u>).

(4) (Source: The Truth About Water Fluoridation by Charles Perkins, page 8.)

(5) (Source: britannica.com/science/fluorine).

(6) (Source: britannica.com/science/fluorine).

(7) (Ref: The Fluoride Deception by Christopher Bryson, Page 235).

(8) (Ref: https://www.cancerfreeeconomy.org/wp-content/uploads/2020/09/CFE_ChildhoodCancerPrevention_Report_F2.pdf)

(9) ((NRC, 1989).

(10) (IOM, 1997).

(11) (Ref: Department of health 'Report on Health and Social Subjects' No 41 Dietary Reference Values for Food, Energy and Nutrients 1994).

(12) (European Food Safety Authority. Scientific Opinion on Dietary Reference Value for Fluoride. EFSA J.2013:11(8):3332.)

- (13) (Ref: Nielsen, 1996; Hunt & Stoecker, 1996; NRC, 1989).
- (14) (Ref: Sener et al., 2007).
- (15) (SOURCE: USDA (2005). National Fluoride Database of Selected Beverages and Foods, Release 2).
- (16) (Ref: Page 488, of his book, 'The Physiology and Biochemistry of the Mouth', pub. 1954).
- (17) (Ref: G. Waldbott, 'Struggle with Titans', page 86).