FLUORINE IN THE NATURAL ENVIRONMENT

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SUMMARY

Fluorine is found not only in all kinds of rocks, igneous and sedimentary, and in water in various amounts, but also in many organisms. Generally the content of water is not dangerous for human, but in some cases weathering of rocks, specially volcanic rocks increases its amount. Industrial dusts can also provoke some diseases.

INTRODUCTION

The fluorine, which we deal with here, is the one acting on human health, that means the one which we can drink, eat and breath. Everything we drink or eat is in direct relation with water. The concentrations of fluorine in natural waters result from the equilibrium between water and minerals, of the capabilities of minerals to release fluorine to the solution or, on the contrary, to absorb this element from the solution. Thus, it is necessary to consider not only the natural waters but also the minerals and rocks which are the first providers of fluorine.

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The major characteristics of fluorine are well known : this element is the lightest member of the halogen group, but its chemical behaviour is different from that of other halogens, and some of these differences are evident in its behaviour in natural water. Fluorine is the most electronegative of all the elements and in solution it forms F^- ions. Other oxidation states are not found in natural aqueous systems. This is the reason why the analyst reports fluoride concentration in terms of the free F^- ion. Nevertheless other varieties of dissolved fluorine can exist : at low pH the form HF° could occur; similarly in acid solutions the fluoride could well be associated with silica in six or four-coordinated structures as SiF_6^{2-} or SiF_4°, but the conditions required for stability of these species are very rarely reached in natural water except the case of volcanic condensates [1].

ABUNDANCE OF FLUORINE

In rocks

In *minerals* the ions F^- and $(OH)^-$ have very close ionic radii, and if F can be the major anion of some minerals like fluorite (CaF_2) and topaz ($Al_2F_2[SiO_4]$), it is also, in F-bearing minerals, an isomorphous replacement in the OH-position. For this reason very many minerals usually contain, or may contain, fluorine [2]. In some cases, fluorine is in OH-positions as a constituent of a mixed crystal varying from the pure OH^- to the pure F^- end member : apatite $Ca_5(PO_4,CO_3)_3(OH,F)$ is a good example. But, more generally fluorine is contained in relatively small amounts, camouflaged in the OH^- (or O^{2-}) position. This is the case of most of the silicate rock-forming minerals [3] as micas, amphiboles, ..., which have a very large range of contents, varying with the type of rock from 0,01 % in weight to several percentage points, however the average is less than 1 %.

These minerals form the rocks we have, now, to consider. In the *igneous rocks*, the major F-bearing minerals are apatite and fluorite. Apatite is more abundant but less rich in fluorine in the basic rocks (2% in gabbros) than in the acid ones (3 to 4.5% in granodiorites). Fluorite, a frequent mineral in hydrothermal veins, is present in a small proportion in the common igneous rocks. Actually, except the abnormal concentrations of F-bearing minerals, the major part of the fluorine content is brought by OH-rich minerals and there is more fluorine in the acid rocks, although there is more apatite in basic ones. Very briefly, the average content of igneous rocks is 800-1000 ppm for acid-, 400 for intermediate- and 100 for ultramafic-rocks. Some special types of igneous rocks, like pegmatites for example, can have a lot of fluorine due to the abundance of F-rich minerals (apatite, topaz, tourmaline, fluorite, ...). Fluorine is also abundant in some volcanic gases specially as HF which reacts quickly with the rocks and consequently in the hydrothermal waters. Veins of fluorite often associated with sulphides of metals, occur in the hydrothermal zone around igneous massives.

In *sedimentary rocks* there are few fluorine-bearing minerals, apatite, aragonite, clay minerals, opal, but only the apatite contains more than 1 % F by weight. The contents of the sedimentary rocks are similar, perhaps a little lower, than those of igneous rocks and there are a few fluorine-bearing minerals : apatite, aragonite, clay minerals, opal, of which only apatite contains more than 1 % F by weight. This is important because fluorine concentrations in natural waters are controlled by the solubility of these minerals. For example, the F-apatite, contained in igneous rocks, is less soluble than carbonate-F-apatite which is the major form of apatite in the sedimentary rocks.

<u>In water</u>

The content of *ground water* is generally lower than the critical limit of 1.5 mg/l or ppm, exceptionally it can reach some ppm. The ground waters associated with hot springs are special and can reach some tens of ppm. Many authors study *rivers and lakes* around the world ; their results give a content generally lower than 0.4 ppm F. For example, Hem [4] writes that most of U.S. rivers contain less than 0.5 ppm F, but some others contain up to 6.4 ppm F. We have to note that with increasing use of fertilizers today, the fluorine content of surface water can also increase. Approximately 20 to 400 g F per hect. are annually leached from soils, that means about the same amount which is added to the soil from the atmosphere... but fertilizing adds 5 to 30 kg F/hect. annually. A part of this fluorine can be adsorbed by the minerals of soils especially clay minerals and various oxides and hydroxides [5, 6] but we do not know how it is retained and this problem needs study. In *the oceans*, which are a regulator in the chemical equilibrium at the Earth's surface, the fluorine content of *sea water* varies from 0.03 to 1.35 ppm.

<u>In organisms</u>

The fluorine contents of *plants* are generally low except for tea (which can contain up to 400 ppm). Roots and leaves generally have higher fluorine content than fruits, seed, stems, woods or barks, but stay lower than 20-30 ppm. In *animals* the concentration in bones is, of course, higher. The organisms are sensitive to the pollution. In industrial areas with high emission of fluorine, content in vegetables is 2 to 250 times and in beef bones 2 to 75 times larger. All these organisms die and their fluorine is, with the other elements, more or less recycled, but some parts of these organisms are fossilized as bones and teeth. In fossils, apatite is the fluorine-bearing component, and, for F-apatite is the more stable mineral, fossilisation transforms OH- and carbonate-apatite of skeletons in carbonate-F-apatite to F-apatite [3, 7]. The content of fluorine increases during this transformation and a lot of fluorine is fixed; this is the same in the sedimentary phosphates which are an important element in the global budget of fluorine.

THE FLUORINE CYCLE

There is a necessary relation between all these raw data, which can be found by studying the fluorine cycle in Nature. The most common idea is that the fluorine goes from rocks to water by weathering. In this process the solubility and the hydrolysis of minerals are very important. These solubilities are different and, of course, the most soluble mineral provides more fluorine to percolating water. But these solubilities are generally low and the fluorine goes very slowly in solution and during its travel it can be temporarily fixed on clay minerals. For this reason, in the most common cases, continental waters contain a low amount of fluorine and the transportation from continent to ocean is probably more efficient through particles floating in the river than through solution. This is the opinion of Carpenter [8] who studied the factors controlling the marine geochemistry of fluorine. In the oceans the fluorine is injected by rains and rivers and removed by incorporation into the carbonate of organisms or fixation on clay minerals. Formation of phosphorites plays probably also an important rôle. The budget of fluorine in the oceans is with injection five to eight times more important than removal. Nevertheless, Carpenter thinks that the oceans can closely approach a steady state of fluorine and he explains the observed discrepancy by the loss of a lot of fluorine in particular forms escaping the cycle. He also estimates that industrial fluorine does not change the amount in the ocean.

Even if this global concept is true, local studies bring more nuances. Two examples, among others, show the influence of weathering.

In the Black Creek aquifer system of Harry and Georgetown Counties in South Carolina, Zack [9] observed variations of fluoride contents from 0.5 ppm to 5.5 ppm, the highest amounts being found with the highest amounts of sodium bicarbonate. The fluoride would be provided by the fluorapatite of fossil shark teeth contained in a neighbouring formation. Fluoride ions would be liberated to the ground-water system through anion exchange.

In East Africa, where the problem of excess of fluorine in water is well-known and worrying, Kilham and Hecky [10] examined lakes and rivers to elucidate processes of fluoride acquisition, concentration, removal, etc... The range of concentrations (0.02 to 1617 ppm) is the greatest found anywhere. A strong correlation is found between the concentration of fluoride and the predominant crystalline rocks of each particular drainage basin and the F/Cl ratio in surface waters. This fluoride is concentrated by evaporation in the lakes whereas it may be removed from pore waters as fluorite and possibly fluorapatite. In these countries, the high fluoride concentrations seem to have an influence on the distribution of zooplankton, phytoplankton and even on higher aquatic plants, but it is, of course, an extreme case. Nair <u>et al</u>. [11] give the content in ground waters of Kenya. Concentrations above 5 ppm are observed in 20 % of the 1286 boreholes studied, in close association with the distribution of volcanic rocks occuring in the Rift Valley area.

These examples show that it is difficult to deny the role of weathering of rocks, but generally the fluorine amount of river, and a fortiori of ground water, is dangerously high only in very peculiar cases and the average fluorine content exceeds 1.5 ppm only in the water in contact with alkaline rocks.

At first sight, the more dangerous sedimentary rocks for the water seem to be the phosphorites composed of carbonate-fluor-apatite rich in fluorine. This general and spontaneous assumption is not corroborated by Haikel et al. [12], who studied the area of Khouribga in Morocco, where a very important phosphate ore deposit occurs. They found that the ground water in this country has only a low content of fluorine (below 0.25 ppm) and that the endemic dental fluorosis is due to inhalation of fluorine-containing dust, discharged by the factories in the atmosphere. The low F-content of the water is not surprising, as the weathering of carbonate-F-apatite goes to more stable F-apatite, releasing CO_3^{2-} but not F [13].

In conclusion we can see that the global cycle of fluorine is relatively simple. The major part of fluorine originates in oceans and goes back to oceans through rains and rivers. The excess of fluorine introduced in ocean is neutralized inside particules. But the behavior of fluorine is more complicated in details ; it depends a lot on geological and human factors. Nevertheless, we observe a close relation between phosphorus and fluorine as soon as the latter is liberated from igneous rocks : it is used by animals more or less proportionally to its content in the water, and stocked in bones.

When fluorine is mineralized, it is essentially in apatite which can accumulate in giant deposits of phosphorites. This affinity for apatite is well seen in the *enrichment* of bones or teeth *in fossils*, and also in our synthesis of apatite obtained by biological activity, where fluorine is necessary to obtain good minerals [14]. But this association is, in a way 'against nature'. Phosphorus is a typical 'biological' element, but on the contrary, fluorine is a typical 'mineral' element. Without phosphorus life is impossible, an excess of fluorine makes life impossible. These two elements are opposite but they are also complementary as the quality of apatite, that means of our bones, depends on the amount of fluorine.

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