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Formation and harmfulness of high fluoride-bearing groundwater

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Abstract: According to the distribution of high fluoride-bearing groundwater in Liaoning Province, China, the cause of formation and hydrogeochemical characteristics as well as its relationship with human health and illness rate were discussed. Strategies to prevent and control fluoride pollution have also been outlined.

Key words: high fluoride-bearing groundwater; harmfulness; preventing and controling strategy; hydro-geochemical characteristics
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Introduction

In some special geomorphic, geological, litho-geochemical and hydro-geochemical environment, the groundwater and soil in some areas are often too rich of some elements, meanwhile those from other areas are too short of the elements, because of the element movement, diffusion and aggregation. The local people are susceptible to the diseases caused by the excessive or insufficient intake of some elements or chemical compounds through drinking water. This kind of diseases caused by natural environment factors is called endemic disease. The harmfulness or influence of chemical composition change to local people, ecological environment, industry and agriculture is called environment hydro-geochemical problem(Zhang, 1991).

The people are susceptible to the endemic fluoride disease which appear as spotted enamel teeth, teeth with being yellow, drab and black stain and emerge rupture and shedding of ones (slight illness) and fluor-base bones that appear hardening, softening and calcification of ones resulting in joint becoming deformed, humpback, and stiff waist vertebra, to bring about vertebra function hindrance or body paralysis at last (serious illness), if drinking high F (fluorine) groundwater for a long period. The research work on distribution, formation and hydro-geochemical characteristics of high F groundwater is of great practical importance to the prevention and control of endemic F disease, which can do good to human health, promote labor qualities and realize sustainable development of economic and social construction. And provides science foundation for the endemic fluoride disease control.

1 Methods

The research area concentrated in 14 cities, 44 counties and 2100 villages in Liaoning Province. We have made health investigations of the masses suffered from endemic fluoride diseases, geological investigations along the area of high F groundwater (Dandong, Kuandian, Huanren, Qingyuan in the Liaodong mountainous region and Kangping, Zhangwu, Fuxin, Jianping, Lingyuan, Jianchang in the Liaoxi low mountainous and hilly region), and detailed investigations of 52 thermal mineral springs. We combined the materials of the field investigations, results of samples (water and rock) determined and predecessors' works and carried out complex analysis. Combining quantitative and qualitative analysis, and geological information and human health information together, we studied the relationship between the high F groundwater distribution and its environment factors such as geomorphologic conditions, geological structure, litho-chemistry and hydro-geochemistry characteristic of the high F groundwater. By human health

investigation and hygienic index analysis, we inquired into the harmfulness of high F groundwater to human bodies, and advanced some workable preventative controling strategies.

2 Results and discussion

2.1 Distribution of high F groundwater

The high F groundwater has a higher fluorine content than the bottom limit of hygienic standard(1.0 mg/L), and is harmful to human beings and livestock. The high F groundwater in Liaoning Province is mainly distributed in the western part, which has low mountains and hills composed of high F volcanic rock, and belonging to half dry climate(Zhang, 1979; 1987; 1988; 1991), as well as the eastern and southern part, which has large area of apatite and warm springs (Zhang, 1979). In correspondence with geomorphology, it's mainly distributed in the low-lying land among mountains or half-close basins. The shallow groundwater usually has a higher F content than the deep groundwater.

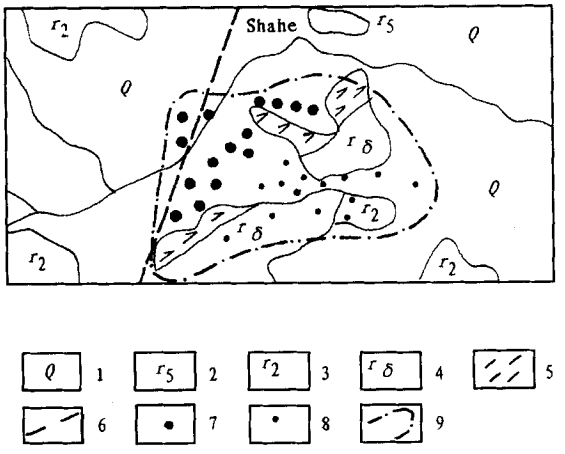

Fig. 1 Distribution of high F mineral groundwater of Wulongbei, Dandong

1. Quaternary alluvium; 2. Yanshan stage granite; 3. Luliang stage granite; 4. granodiorite; 5. limestone-calcite vein; 6. concealed fault; 7. high F thermal mineral groundwater; 8. abnormal points of high F thermal mineral groundwater; 9. distribution area of high F thermal mineral groundwater

2.2 Formation of high F groundwater

According to Berelman (Berelman, 1979) from high to low, the F content sequence is acidic rock, neutral rock and sedimentary rock, basic rock, and super basic rock. Because most of the rock in the volcanic areas is neutral or acidic, the F content is relatively high. The thermal mineral springs often expose at the joint belt of neutral or acidic rocks such as Yanshan stage and Zhendan period granite, metamorphic rock and Jurassic andesite rock, coarse rock and so on, which are abundant with high F minerals such as black mica, fluorine apatite and ordinary amphibole, some of which can have more than 20% of fluorine minerals (Zhang, 1982). The thermal mineral groundwater with high F of Wulongbei, Dandong, is one of them(Fig. 1).

Affected by the natural factors like water, CO_2 and temperature, the fluorine minerals provided as a source for F aggregation in the thermal groundwater. For an instance, during the solution process of fluorine minerals like fluoride or fluorite, and hydrolysis process of mica, the crystal structure of minerals is destroyed, thus F is liberated from the mineral and get into water. Take the weathering of mica as an example:

$$KAl_2[AlSi_3O_{10}](OHF)_2 \longrightarrow K_{<1}Al_{<2}[AlSi_3(OOH)_{<2}]_nH_2O$$

(white mica) (watered white mica)

$$KMg_2[AlSiO_3O_{10}](OHF)_2 \longrightarrow K_{<2}Mg_{<2}[AlSi_3(OOH)_{<2}]_nH_2O$$

(black mica) (watered black mica)

As a result of weathering, white mica turns into watered white mica, and black mica into watered black mica, fluorine then gets into water. Since the diversion rate of F in water is nearly equal to Na, Ca and Mg, but slower than Cl, Br, and I(the sequence is: Cl>I>Br>F>Na>K, Ca)(Berelman, 1974). Fluorine is liberated and get into water first during the weathering of fluorine bearing silicate. Another important source of fluorine contained gas produced by remnant

heat of recent magma activity.

2.3 Hydro-geochemistry of high F groundwater

2.3.1 Relationship between F and water chemical type

High F groundwater, especially hot water, has an intimate relation with water chemical type (Zhang, 1982): the content of F in HCO_3-Ca-Mg(Na, Ca) water, Cl-Na water, HCO_2-Na water and SO_4-HCO_3-Na water is 2, 4, 6 and 13 mg/L in average, respectively. The highest content in the last type can be 30 mg/L, as a result of the sulfide oxidation in the nearby sulfide mineral deposit. The most important chemical reaction heat in the earth crust is that from sulfide oxidation. An underground blind ore deposit of iron sulphide (FeS_2) needs only 70 g/m^2 iron sulphide disintegrated per year during the chemical reaction process to provide enough heat for the stratum at the depth of 50 m to raise its temperature 1℃ (Kapplelmeyer, 1974). The SO_4-HCO_3-Na and SO_4-Na water in Liaoning Province is mainly concentrated in the thermal spring area. The high water temperature makes it easy for the solution of F mineral in the surrounding rocks, thus increases the F content in water.

2.3.2 Relationship between F and mineralization degree

The F content in water increases with the mineralization as a parabola line, instead of a straight line (Zhang, 1982). When the mineralization degree is under 0.6 g/L, the F content increases with it very fast, but when mineralization degree passes over 0.6 g/L, the F content increases with it very slowly.

2.3.3 Relationship between F and temperature and pH value

Water temperature and pH are also important factors of F aggregation in water. F is positively related to water temperature and pH value, because they directly controls the solution and filtering intensity of fluorine ore (Zhang, 1982). Higher temperature can increase the vibration of mineral particles, decrease the ion bond strength in crystal structure, accelerate the speed of chemical reaction, and make more silicate dissolved in water. The water alkalinity increase when alkali metal silicate were hydrolyzed, and reversibly the alkaline water increases the solution of silicate, thus to intensify the movement and aggregation of F in water. High pH can also restrain the existence of Ca in water, in addition to its acceleration effect of mineral solution, therefore, it provides condition for the F aggregation in water.

2.3.4 Relationship between F and soluble SiO_2

The relationship between F and soluble SiO_2 appears positive (Fig. 1; Zhang, 1982). This is mainly because the solution rate of SiO_2 increases with water temperature. As is well known, there is little fluoride (such as NaF_3-NaF) in the earth's crust. Most of fluorine is in silicate containing it.

F and SiO_2 are liberated from silicate during weathering, and large amount of non-crystal SiO_2 is formed. The higher of pH value and temperature, the higher solution rate of non-crystal SiO_2, and the faster of F liberation from silicate. Therefore, alkali water, especially hog water, is favorable for the increase of F and SiO in water simultaneously.

2.3.5 The relationship between F and Na

Fluorine is positively related with Na(Fig. 3). The increase of Na in water (specially in hot water) is favorable for the increase of F(Zhang, 1982). When the (deep) cycling water contact with surrounding rocks, the high soluble elements F and Na in the rock dissolve in water quickly. Even some insoluble fluoride can give out F under the effect of hot alkaline water. Since NaF has a high solution rate, it can stay in water with high stability, thus contribute to the aggregation of F in water. That is, the increase of Na is good for the increase of F.

2.3.6 The relationship between F and Ca

I Liaoning Province, the high fluorine-bearing groundwater often contains Ca less than 100 mg/L while contains F more than 1 mg/L. Since F and Ca can form the insoluble sediment CaF_2, the increase of F detains the increase of Ca in water. Therefore F and Ca are negatively related

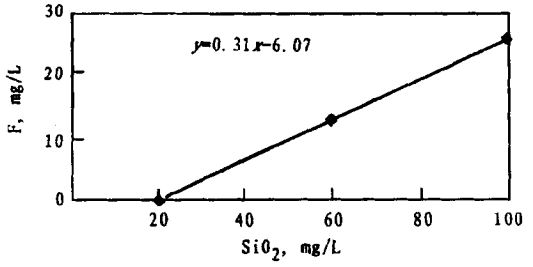

Fig. 2 Relationship between F and SiO_2

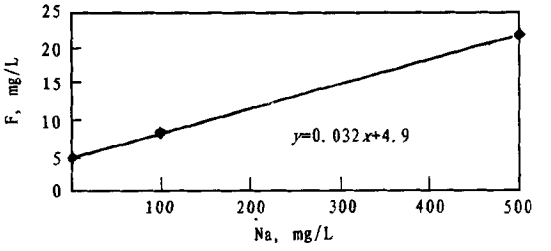

Fig. 3 Relationship between F and Na

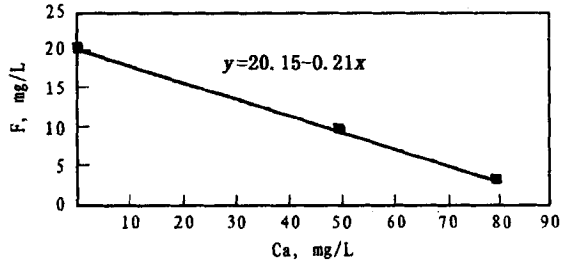

Fig. 4 Relationship between F and Ca

(Fig. 4).

Under natural condition, the Ca-HCO_3 water contains more Ca than Na, and thus has a relatively small amount of F (< 1 mg/L). Sometimes the fluorine in water is too low to provide enough F for human bodies. In Liaoning Province, although the high F (hot) groundwater belongs to HCO_3-Ca water, with the content of Ca higher than Na (Na/Ca = 0.13), it still has a high content of F, about 2 mg/L in average (4 mg/L in hot water). This is mainly because of high evaporation and temperature(Zhang, 1970).

2.4 Harmfulness of high F groundwater

People are susceptible to be poisoned if drinking high F groundwater for a long time. The intake of F is mainly from food and drink. The absorption rate of organism to water F is 90%, so drinking water becomes an important source of F in human body. It has been estimated that, F content high than 1 mg/L in drinking water will cause spotted enamel teeth, high than 3 mg/L, fluor-bones will also be caused (SASNAR, 1976).

More F gets in body to destroy the teeth first. It mainly effects on formation of prism crystal of teeth enamel, makes prism crystal materials and materials between the prism crystal emerging defect, to form stains and corrosion, then pigmentation makes teeth yellow, drab and black, to form spotted enamel teeth. According to abnormal construction, teeth will be easy to wear, split and come off. The higher F the drinking water contains, the heavier the fluorine poisoning is (Table 1). Children who have moved into the infected area after growing out the permanent teeth, will also suffer from the teeth disease. The incidence can even be higher than 28%.

Table 1 The influence of high F groundwater on human health

F content, mg/L	Incidence of teeth disease, %	F content, mg/L	Incidence of bone disease, %
1.5—5.0	3.5	1.5—5.0	41.6
>5.0	5.3—15.3	10.0	50.0
		11.8—21.8	58.8

It forms fluoride calcium combining more F and blood calcium in body. The fluoride calcium precipitates in bone organization and causes skeleton hardening and bone density increasing. A few fluoride calcium precipitates in soft organization to cause periosteum, tendon and ligament and other organization calcification. Because of change of the skeleton said above, it results in bone skin raising thickness and marrow cavity becoming small, then it make intervertebral hole or vertebra narrow to constrict the nerves and cause pain, the function obstruction and even body paralysis.

The metabolic disorder of calcium makes calcium dissociates from skeleton organization and results in its looseness and softness, to cause joint becoming deformed, humpback, stiff waist vertebra, and so on.

2.5 Strategies to prevent and control endemic fluorine poisoning

Deep layer groundwater, which usually has a lower content of F even in high F region, can be extracted as drinking water in the area with rich groundwater resources and better economic conditions. For those with bad water and economic conditions, the high F water can be previously treated with some chemicals or minerals such as alkali $AlCl_3$, activated Al_2O_3, $Al_2(SO_4)_3$, activated MgO and pumice stones and so on. Fluorine poisoned patients can be cured with medicines like Ca, licorice root, KF, or $Al(OH)_3$ gel and so on.

3 Conclusion

The high F groundwater is mainly distributed in the area where there are volcanic rock, apatite or warm springs with high content of F. Geomeorphologically it is mainly distributed in the low-lying land or half-close basins among dry or half dry hills.

From high to low, the rock F content sequence is: acidic rock > neutral and sedimentary rock > basic rock > super basic rock.

The main minerals containing F include black mica, white mica, apatite, ordinary amphibole, fluoride and fluorite and so on.

The way for F liberated from minerals to water is, mainly through weathering, which is extensively affected by water, CO_2 and temperature. Alkaline hot water is the best environment transference of F from mineral crystal to water.

In high F groundwater, F is positively related with Na, SiO_2, pH value, and temperature, but negatively related with Ca. It also has an intimate relation with water chemical types: SO_4-HCO_3-Na and SO_4-HCO_3-Na water has the highest F content, while HCO_3-Ca has the lowest.

In high F region, shallow water contains more F than deep groundwater.

The more F drinking water contains, the more harmful it is, and the higher disease incidence it causes. In high F area, drinking water should be extracted from the deep layer. The fluorine poisoned patients should be treated with suitable medicines and methods. These are main ways to prevent and control endemic fluorine disease.

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