

Hydrogeochemical anomalies of fluorine in Transbaikalia, Russia

Leonid V. Zamana

(Institute of Natural Resources, Ecology and Cryology of Siberian Branch RAS, Chita, Russia 672014)

Abstract: Five types of hydrogeochemical anomalies of fluorine with difference in formation processes, sources of inflow in the water environment and level of concentration are determined and characterized in the article.

Key Words: Fluorine; types of hydrogeochemical anomalies; relative concentration; Transbaikalia

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1 Introduction

Fluorine is a basic chemical element necessary for a human organism. Drinking water satisfies up to 85 % of the physiological requirement of a person [1]. The lack of fluorine in water results in tooth decay, its leads excess to fluorosis. The increase of rF/rCa^{2+} ratio contributes to fluorosis progress. When its level is less than 0.25 and fluorine content is > 1.5 mg/L, according to the result of researches made in Republic Moldova, fluorosis is practically not discovered, whereas at $rF/rCa^{2+} > 2.0$ it afflicts over 70 % of the population [2]. Prolonged use of water with high level of fluorine results not only in dental fluorosis but also in other diseases of various organs and systems of a human organism [3]. In Russia the maximum allowable concentration of fluorine in drinking water is 1.2-1.5 mg/L depending on climatic conditions. Smaller level is characteristic of the territories with hot dry climate. The low limit of fluorine content in drinking water is not normalized but 0.5 mg/L is considered optimal.

2 The general laws of fluorine distribution in natural waters

Fluorine is a chemical element actively migrating in waters. The range of its concentration in natural waters changes from analytical zero (less than 0.01 mg/L) to 15.0 g/L. The specified maximum is established in ultra alkaline (pH 12.0) mining waters in apaitic syenites of Lovozerskiy massif on the Kola Peninsula [4]. The background content of fluorine in natural waters is influenced by landscape-climatic zoning and grows together with water total dissolved solids (TDS on the sum of ions) in the process of climate dryness increase and evaporation portion in water balance of territories. Thus its portion in the TDS or relative concentration (RC) at background levels remains less than 0.3 %.

3 Types of hydrogeochemical anomalies of fluorine in Transbaikalia

Transbaikalia is one of the largest fluorine

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Biography: Leonid V. Zamana, male, born in 1937, Dr Ph., Head of Laboratory Geoecology and Hydrogeochemistry, main study field—— hydrogeology of mountain territories, hydrogeochemistry, mineral and thermal waters; E-mail :lv.zamana@mail.ru.

bearing mineragenic provinces of Russia and is characterized by broad development of fluorite type and fluorite- or cryolite containing rare metal mineralization as well as rocks with high content of fluorine. Five types of hydrogeochemical anomalies of fluorine are identified in Transbaikalia depending on sources of fluorine and its formation features [5]. Fluorine in water samples was determined by potentiometric method[6].

Ore-genic anomalies are connected with fluorine containing mineralization. The fluorite deposits presented mainly by veined quartz-fluorite type in a mountain-taiga zone with prevalence of humidified permafrost landscapes form anomalies with fluorine content 0.24-1.6 mg/L at concentration, as a rule, not more than 0.20 mg/L. RC of fluorine in most cases is >0.5 % at the most frequent indexes up to 1.5 %-2.0 %.

The content of F in hydrogeochemical aureoles of fluorite mineralization of the same type reaches 2.5 mg/L in the forest-steppe landscape-climatic zone and in steppe -7.7 mg/L (Table 1). RC of fluorine decreases to 0.3, rarely exceeds 0.5 % , their background values are less than 0.2 % . The sulfide-fluorite type of ores in similar landscape conditions is fixed by higher concentration of fluorine

and sulfates at lower pH in comparison with quartz-fluorite mineralization.

In waters of dispersion streams of tungsten deposits in a mountain-taiga zone the fluorine content changed from 0.4 to 3.4 mg/L at background level of 0.1-0.2 mg/L. Higher F concentration in waters than that in fluorite deposits at its smaller content in wolframite ores is explained by sulphuric-acid decaying of fluorite at oxidation of associating sulphides. RC of F mainly varied within 1 %-4 %.

Tantalum-niobium mineralization localized to amazonite granites enriched by fluorite was accompanied by hydrogeochemical anomalies of fluorine to 1.4-1.7 mg/L (RC to 7.2 %). In inclosing shale-sand rocks its content was not higher than 0.15 mg/L. Cryolite containing Ta-Nb mineralization in conditions of permafrost bald mountain and mountain-taiga landscape was determined by anomalies of fluorine up to 40.9 mg/L[7]. In this regard it dominated in the structure of anions reaching 35 % -40 % of the TDS of water.

Aureole type of distribution of fluorine concentration is characteristic for ore hydrogeochemical anomalies. In aureole type they naturally decrease in the process of removal from

Table 1 Fluorine content in ore fields waters of quartz-fluorite mineralization^[5]

Deposit	F content			
	Ore anomalies		Background values	
	mg/L	RC, %	mg/L	RC, %
Mountain-taiga landscape zone				
Usuglinskoe	0.24-1.34	0.37-1.44	0.05-0.19	0.13-0.50
Uluntuiscoe	0.30-1.65	0.50-2.15	0.03-0.15	0.08-0.24
Solonechnoe	0.60-1.58	0.80-1.80	0.10-0.45	0.08-0.30
Forest-steppe landscape zone				
Duldurginskoe	1.58-2.51	1.90-3.84	0.13-1.04	0.06-0.27
Otsoluiscoe	1.62-4.31	1.37-4.07	<0.80	<0.30
Steppe landscape zone				
Abagaituiscoe	2.68-7.74	0.30-0.38	1.40-4.25	0.15-0.34
Urtuiscoe	2.50-7.74	0.70-1.45	1.60-2.28	0.30-0.50
Stepnoe	4.35-6.00	0.30-0.43	1.86-4.77	0.17-0.30

subtraction source.

Another type of fluorine distribution in waters (areal or disorderal) is characteristic for petrogenic anomalies conditioned by high, in comparison with clarke, content of fluorine in rocks containing water - granites, apatites bearing diorites, nephelinic syenites, etc.

Rare metal granites of intrusive complexes of Jurassic age are distinguished among acid rocks. The average content of fluorine in them is 0.15 %-0.28 % at ranite clarke of 0.08% . The basic stannum-tungsten-raremetal mineralization in Eastern Transbaikalia is genetically connected with such granites. As a rule, they compose small intrusions (maximum up to 300 km²) in watershed belt on mid- and low-mountain relief. Fluorine content in waters of two studied granite massifs changed from 0.57 to 3.79 mg/L (Table 2) at TDS generally up to 100 mg/L. The average RC of F on massifs was more than 4 % and quantity of fluorine in anions structure in separative cases exceeded 20 %-equivalent ^[8]. In waters of usual granites in similar landscape conditions the content of fluorine is not more than 0.2 mg/L.

Above-permafrost waters of intrusion of the rapakivi-similar granites of Kodar complex of Proterozoic in bald mountain and mountain-taiga

landscape zones contained fluorine to 3.5 mg/L at TDS to 110 mg/L (RC to 7.7 %), whereas in waters containing intrusion of metamorphic rocks its level was to 0.1 mg/L. Fluorine content in granites was approximately two times more than clarke level (0.15 %-0.17 %).

Abnormal fluorine bearing (0.57-2.23 mg/L) was characteristic to ultra fresh waters of subalkaline alaskites and granites massif TDS of which in most cases was less than 50 mg/L and fluorine level reached 10.4 %. In waters, extended in the bordering of the stock of ordinary biotite granites, the concentration of fluorine did not exceed 0.1 mg/L. In fracture waters of nephelinic syenites fluorine is determined in concentration to 5.0 mg/L and in diorites of a stock with industrial content of apatite it is to 1.84 mg/L.

High content of fluorine is fixed in the waters of some genetic types of friable Quaternary deposits. In particular, in the waters of fluvio-glacial deposits of Cenozoic depressions in Baikal rift zone (BRZ) in the north of the region it reached 4-8 mg/L at the TDS basically to 100 mg/L. In Charskaya depression such deposits were being collected due to the ablation of the fragmentary material of granites of the mentioned above Kodar intrusion. In Turgino-Kharanorskaya depression in the south of Eastern Transbaikalia

Table 2 Fluorine content in waters of rare metal granitoides^[8]

Index	Mean	Min.	Max.	s
Soktuy stock, *n=32				
F, mg/L	1.56	0.64	3.79	0.75
F, %-eq.	13.0	5.7	22.6	4.43
TDS, mg/L	30.2	13.9	143.0	26.0
Dotulur stock, n=33				
F, mg/L	1.35	0.57	2.39	0.41
F, %-eq.	23.9	3.3	36.4	0.10
TDS, mg/L	21.8	12.6	34.7	6.6
Kodar intrusion, n=38				
F, mg/L	0.94	0.19	3.53	0.63
F, %-eq.	15.1	4.3	54.3	9.11
TDS, mg/L	26.3	7.9	112.0	22.7

*n - number of samples.

accumulation of friable deposits occurred due to the rare metal granites of Suktuy massif destruction (Fig. 1).

Hydrothermal anomalies are connected with the nitric therms forming in seismic active faults. They spread in BRZ in the northern and northwestern part of the region as well as in the South of Eastern Transbaikalia within the territory of Khentey-Daurskoe arched uplift. In total more than 50 occurrences of therms with water temperature in sources to 83°C are

known. TDS of therms does not exceed 2.0 g/L, pH is 6.5-10.3. Fluorine content in therms changes in the range of 1.6-26.4 mg/L (Table 3), relative concentrations in most causes exceed 1.0 % and reach 6.8 %. The question on fluorine sources in thermal waters is being discussed for a long time. In our opinion, the main mechanism of therm enrichment with fluorine is its isomorphic replacement by OH group in micas. Positive correlation between F and pH

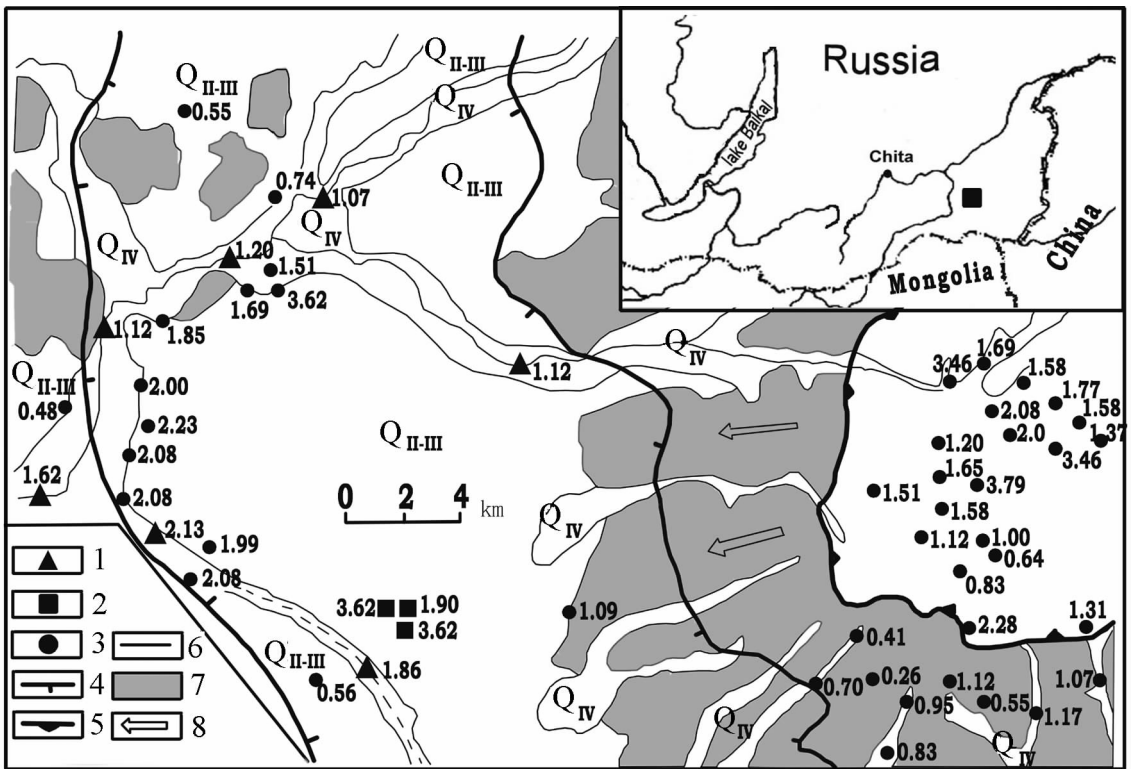


Fig.1 Fluorine content in waters of Quaternary deposits of Turgino-Kharanorskaya depression and granites of Suktuy stock

Legend: 1-3 - Points of sampling: rivers; 2 - Saline lakes; 3 - Underground waters in Turgino-Kharanorskaya depression, underground and surface waters in Suktuy stock; 4-6 - Boundaries; 4 - Turgino-Kharanorskaya depression; 5 - Suktuy stock; 6 - Geological complexes; 7 - Pre-Quaternary stratigraphic complexes; 8 - Direction of clastic material removal

Table 3 Fluorine content in hydrogeochemical anomalies of others types^[5]

Object research	Number of samples	Content of F, mg/L			s
		Mean	Min.	Max.	
Nitric therms	43	9.79	1.60	26.4	6.54
Saline lakes of Eastern Transbaikalia*	56	13.64	1.04	144.0	20.42
Snow cover, Chita city	42	2.28	0.10	4.56	1.03

*Data 2006-2009 year.

as well as hydrolysis of micas point to this fact^[9].

Evaporative (helio-genic) anomalies of fluorine are formed owing to evaporative concentration of surface and underground waters in arid (steppe and dry steppe) zone of region at low degree of relief drainage. This type of anomalies is typical anomalies for intermountain depressions of terrigenous and effusive-sedimentary rocks of Mesozoic and Cenozoic, especially in the south of Eastern Transbaikalia.

The maximum accumulation of fluorine occurs in waters of mineral (saline) lakes in which the water TDS varies within wide limits. During the drought periods it exceeds 300 g/L. In Eastern Transbaikalia the established maximum of fluorine concentration in lake waters is 144 mg/L, in Western Transbaikalia it is 150 mg/L. In latter case the lake is located on basalts with F content to 2 %. Fluorine accumulation in waters of mineral lakes is influenced favorably by high pH level, sodium composition and low content of calcium which limits fluorine concentration because of the formation of slightly soluble fluorite. In waters of the majority of salty lakes relative concentration of fluorine as well as in fresh waters is less than 0.3 %. With such RC anomalies are possible to consider as a result of waters concentration with background geochemical characteristics.

In underground waters zones of continental salinization fluorine concentration on separate territories reaches 3-5 mg/L, RC remaining <0.3 %.

Evaporative concentration most strongly occurs near the ground surface, up to 20-30 there is inversion of TDS and fluorine content (to 0.8-1.2 mg/L). In regard to RC criterion fluorine anomalies in the Datong basin (Shanxi Province, China) are formed most likely due to evaporation of waters with background F concentration but not because of ore sources as the authors of this paper supposed^[10].

Technogenic anomalies have various sources and formation ways.

The highest concentrations of fluorine are observed in acid waters of ore deposits forming both at the operation and after closing mines. In mine waters of the Kalanguy sulphide-fluorite deposit F content reached 186 mg/L, in drainage waters of tailing dam of the Bukuka tungsten deposit taken out of operation over 40 years ago it is revealed to 135 mg/L of fluorine. Fast growth of its concentration is marked at pH<4.0 (Fig.2). Simultaneously there was an increase in concentration of metals, in particular Al, Fe, Mn, Zn, Cu, etc.^[11]. Abnormal level of F concentration was observed in other mineral types of sulphide containing deposits under formation of acid waters condition. Fluorine migration in acid waters occurs mainly in metal-fluoride complexes mainly with Al (Fig.3). In case of high potential of neutralization with the presence of carbonates as a part of ores or enclosing rocks when waters pH is close to neutral values or alkaline, the concentration of fluorine remains low.

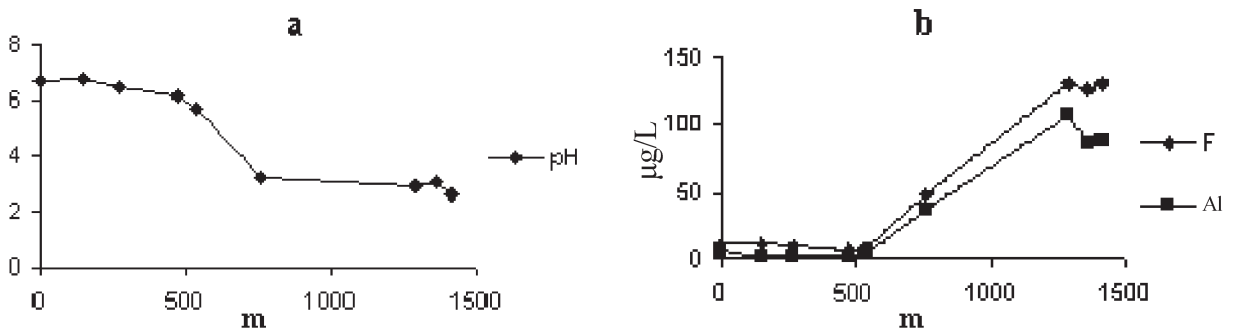


Fig.2 Change of pH values, F and Al concentration in waters of technogenic dispersion stream on Bukuka tungsten deposit

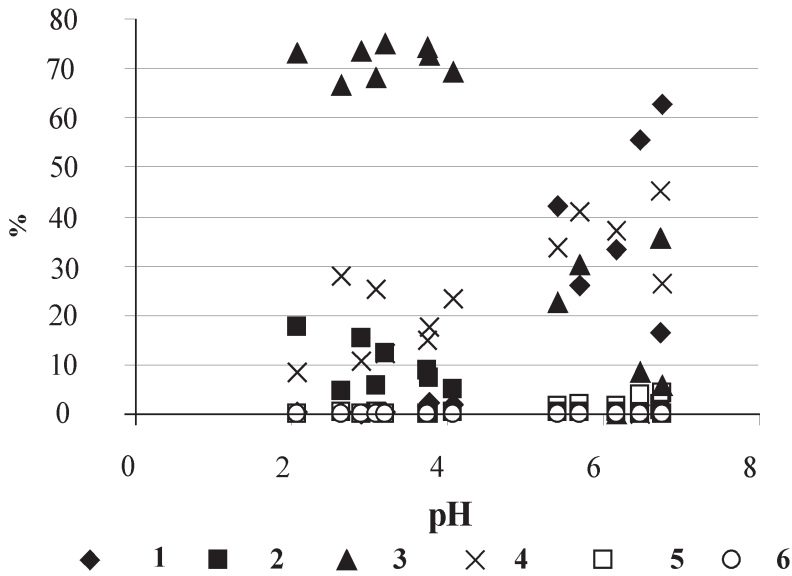


Fig.3 Migration forms of F in drainage waters of tungsten deposits in Eastern Transbaikalia^[12]
Legend: 1- F⁻, 2- (AlF)²⁺, 3- (AlF)⁺, 4-AlF₃, 5- (AlF₄)⁻, 6-(AlF₃)²⁻

Fluorine sources in technogenic anomalies of deposits are ores or enclosing rocks which sulfuric-acid decaying intensifies its subtraction. Other sources of fluorine and processes of its inflow in water environment in the anomalies are connected with the heat power enterprises working on coal. Pollution of waters by fluorine occurs owing to discharge of industrial wastes in surface waters. Pollution of underground waters is a result of sedimentation filtration, to lesser degree, through atmospheric transportation by gas-smoke emissions. Thus, the use of Kenon lake in Chita as a reservoir-cooler of a city heating station caused the increase of F content in lake water to 4-5 mg/L and on filtration sections from ash-disposal areas it reached 6-7 mg/L comparing with 1 mg/L level at the absence of pollution. In the snow samples selected at the end of the winter period content of fluorine (in thawing water) was to 4.6 mg/L (Table 3).

4 Conclusions

The given results show that hydrogeochemical anomalies of fluorine have various nature which defines the level of its content in waters, features of

spatial distribution, forms of presence in natural waters, etc. Accordingly there should be various approaches when economic-drinking water use planning of such waters or when working out actions for natural waters protection from pollution.

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俄罗斯外贝加尔氟的水文地球化学异常

Leonid V. Zamana

(Institute of Natural Resources, Ecology and Cryology of Siberian Branch RAS, Chita, Russia 672014)

摘要: 在本文中, 5 种类型的氟的水文地球化学异常被确定, 它们的形成过程、在水环境中的流入物源以及浓度水平各异。对它们的特征也进行了讨论。

关键词: 氟; 水文地球化学异常类型; 相对浓度; 外贝加尔

作者简介: Leonid V. Zamana, 男, 1937 年生, 教授, 地质生态学和人文地球化学实验室主任, 主要研究领域: 山地水文地质学、水文地球化学、矿物和热水; E-mail: l.v.zamana@mail.ru。