EXPERIMENTAL STUDY OF FLUORINE LEACHING BY WATER FROM ROCKS OF THE ORLOVKA AREA, EAST TRANSBAIKALIYA

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Key words: F, fluorine, experiment, leaching, rock. Orlovka

Fluorine at increased concentration in water is ecologically dangerous element. One of ways to get fluorine in earth and underground potable water are leaching from rocks. Despite of importance, the leaching process remains very poorly investigated and practically not characterized quantitatively [1]. The experimental data resulted below are aimed to fill this lack. Experimental study leaching of fluorine from rocks was carried out in water with powders prepared from rock samples collected in area of the Orlovka Ta deposit, the East Transbaikalia. A choice of the samples for experiments was not random. The big role of fluorine in formation of the Orlovka deposit has resulted in formation of the minerals, rocks, and soils with increased contents of fluorine in area of the deposit.

The new experimental data on leaching fluorine from various most widespread types of magmatic rocks (more than ten samples) from the area of the Orlovka deposit and containing the various amount of fluorine (Table) are discussed below.

Sample	Rock	S, m^2/g	F, wgt %	SiO_2	Al_2O_3	Na_2O	K_2O	FeO
Z-8	lamprophyre	1.7	0.038	55.34	14.98	3.24	0.74	7.12
A-24/01	bt granite	0.8	0.086	75.36	12.75	3.58	4.71	1.38
Z-20/95	ms granite	1.41	0.11	73.92	16.22	8.52	0.33	0.19
Sh-44	ab-ed granite	0.84	0.26	77.97	11.97	3.67	4.57	0.57
A-2	pegmatoid	1.0	0.51	71.76	16.3	6.25	3.78	0.38
Z-31b	Q-Be-Lep	1.59	0.56	85.41	7.38	0.89	2.74	1.59
A-81	"banded"	0.59	0.79	74.84	13.73	3.22	5.94	1.10
A-77	ab granite,with Fl	0.92	1.00	72.83	16.22	5.56	3.10	0.337
A-93	ab-lep granite	0.64	1.167	74.65	13.91	5.0	2.13	2.74
A-39	amz granite	0.51	1.433	75.08	15.43	4.87	3.11	0.29
Sh-18	"banded"	2.22	2.08	74.1	14.9	3.46	3.56	2.02

On the Orlovka deposit, the Li-F granite stock breaks through Khangilay massif composed of biotite and muscovite-biotite granite and cut a thick lamprophyre dyke. Among Orlovka Li-F granite: albite-amazonite and albite-Li-mica ones; intensive albitized zones; veins and zones of amazonite-quartz pegmatoids; and also specific rhythmically banded rocks combined by alternating layers, containing a topaz and beryl, and enriched or albite or by quartz with mica are widespread. Close dyke of lamprophyre, which could serve as a screen for hydrothermal fluids, veins or veinlet of quartz–lepidolite-beryl are met [2].

Experiments are carried out under room conditions at an initial water/rock ratio 5:1. Three - distilled water open for an atmosphere, with pH near 6.2, was used. The initial specific surface of powders tested by BET method was in an interval of 0.64-2.22 m^2/g. Duration of different series of experiments was 1, 3, 7, and 32 days. Concentration of fluorine after experiment was determined in a part of the solution by F-selective method with use of TISAB and a measuring complex "Ecotest-120-ATC" - a computer.

Experiments showed, that at water/rock interaction, pH of solution during experiment increases for the majority of rocks from 6.2 up to 7-7.5 after 1 and 3 days and up to 8-8.5 after 7 and 32 days. A clear relationship between final pH and F content of rocks is not marked. On separate samples at continuous record of pH values of solution, it is established, that they vary more than on unit within the first minute of the water- rock interaction and rearrange of equilibrium between the pH-electrode and the solution.

The most interesting experimental characteristics of leaching of fluorine from rocks are F concentration in water after experiment (M_{HF}. mole/dm) and a rate of leaching of fluorine from unit of a surface of rock in unit of time (V. g/m^2day). Changes of these characteristics concerning type of

rock, initial concentration F in rock, and duration of experiments are of the greatest interest. The experimental data showed, that among investigated rocks the lamprophyre with the lowest contents of fluorine (0.026 wgt %) are characterized both the least rates of leaching fluorine and the smallest HF concentration in a solution after experiments. For them the value lg M_{HF} after 32 days appeared close to (-5.2). Biotite and two-mica granite are characterized by higher concentration: in 32 days in a solution the value of lg M_{HF} is close to (–4). For rocks of the Orlovka stock (albite-amazonite and albite-Li-mica ones) and also ones from pegmatoid veins, concentration HF after 32 days are in short range. The lg M_{HF} was in a range (-3.51)÷(-3.16), i.e. concentration of fluorine in water was from 5.9 up to 13.1 mg/L. It is reminded, that in potable water physiologically safe concentration of fluorine should be in a narrow interval of 0.6-1.5 mg/L.

One of samples of the rhythmically banded rock, having the greatest contents of fluorine in the structure (2.08 wgt %), has shown concentration almost on the order above (lg M_{HF} = -2.56). As a whole, for all set of rocks, the tendency to growth of lg M_{HF} with increase in the content of fluorine in rock is observed. And, in comparison with variations of this value in experiments with the same sample, but different duration, this growth is more expressive. It speaks that leaching the great part of fluorine and growth of its concentration in water are observed in 1 day. Thus, the greatest changes M_{HF} were marked also for the richest by fluorine "banded" (Sh-18). Till 7 days, HF concentration in water continued to grow poorly for the majority of samples, and further - till 32 days changes insignificantly. Decrease of the concentration in separate experiments was relative shorter experiments, apparently, are connected to non-uniformity of leaching kinetic in different experimental series.

Average rate of leaching fluorine from rocks does not find out obvious dependence on the contents of fluorine in rock. It is appreciably lower only for lamprophyre. Average leaching rate is the highest in the first day for separate samples (A-2, pegmatoid); it achieved almost 0.01 g/m^{2}day. For the majority of rocks, it remained in the interval 0.02-0.04 g/m^{2}day and was much lower (near 0.0002 g/m^{2}day) for lamprophyre. For all rocks, experimental value of average rate leaching falls more than on the order for 32 days. The calculated differential rate, when the quantity of leached fluorine determined for the given sample in shorter experiment is excluded of rate calculation for next stage, for the same time falls almost on 2 orders. In separate experiments rate had negative value, that had more likely the kinetic reasons and is caused a little differing leaching kinetic in different series of experiments. Extrapolation of the experimental rates for infinite time allows estimate their value most corresponding to geological time scales. It appeared the least, equal about 0.00002 g/m^{2}day for lamprophyre. The maximal values were higher on the order. They have value near 0.0002 g/m^{2}day and were characteristic for biotite and two-mica granite of Khangilay massif. For the majority of the Orlovka rocks, the leaching rate was twice below, i.e. near 0.0001 g/m^{2}day is typical.

Thus, it is experimentally established, that water leached fluorine from granitoid rocks of the Orlovka stock in concentration, which in some times (from 5 up to 35 times) are higher, than allowable for potable water. Hence, such waters can be ecologically dangerous factor for the person if they will get ones on a regular basis without dissolution in drinking water.

Financial support by grants of INTAS 97-0721 (Principal investigator C. J. Stanley) and RFBR 02-05-65235 Principal investigator A. M. Aksyuk.

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Electronic Scientific Information Journal "Herald of the Department of Earth Sciences RAS" № 1(22)'2004
Informational Bulletin of the Annual Seminar of Experimental Mineralogy, Petrology and Geochemistry – 2004
URL: http://www.scgis.ru/russian/cp1251/h_dgggms/1-2004/informbul-1_2004/geoecol-1e.pdf
Published on July, 1, 2004