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BRIEF COMMUNICATION

Patterns in the Organic-Acid Leaching of Fluorine from Rocks

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Abstract—Experiments were carried out on fluorine leaching from rocks (alkaline agpaitic granite, dacite, and feldspar–quartz aleurite with 0.005 M solutions of acetic, tartaric, citric, and oxalic acids. The previously revealed decrease of fluorine leaching with organic acids compared to distilled water under an acidity increase within the 6.3–3.5 range of pH values was confirmed. In terms of leaching ability related to distilled water, the organic acids constitute a series: oxalic > citric > acetic ~ tartaric. It has been proposed that a decrease of pH values causes the sorption of fluorides resulting from the substitution of adsorbed hydroxyl ions. In view of this, the less intense fluorine leaching in acids compared to distilled water might be ascribed to sorption immobilization of fluoride ions on a solid phase. A positive correlation between the levels of leached fluorine and magnesium points to the existence of some general but undetermined mechanism of the transition of these elements from minerals into aquatic solutions.

Keywords: fluorine, leaching, organic acids, rocks
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INTRODUCTION

Organic (carbonic) acids are of significant importance in the processes of chemical weathering for promoting the destruction of rock minerals and transition of macro- and microelements into a dissolved state (Drever and Stillings, 1997; Ginzburg et al., 1968; Hausrath et al., 2009; Huang and Keller, 1970, 1972; Savenko and Savenko, 2019; etc.). While the leaching effect of organic acids on the elements that occur as cations in natural waters is logically explainable by the formation of stable organic complexes, the data available for anionic elements are deficient, contradictory, and not easily explained. Thus, the increase of fluorine leaching from biotite in 0.01 M citric acid found in (Kularatne et al., 2012) was confirmed based on the examples of muscovite, ferriflogopite, and biotite in 0.01 M solutions of a number of organic acids, such as acetic, oxalic, citric, mandelic, phthalic, succinic, salicylic, and sulfanylic acids, but exclusively under low-alkaline conditions (pH 7.0–8.2), whereas the intensity of fluorine leaching decreased compared to distilled water at higher acidity (pH 7.0–5.1) (Savenko et al., 2014). Nevertheless, other experiments using a model solution to simulate the natural mixture of carbonic acids showed considerably higher fluorine leaching compared to distilled water for various rocks (meimechite, andesite basalt, albitized rhyodacite, and alkaline agpaitic granite) (Savenko and Savenko, 2017). The present study was intended to clarify the causes of these discrepancies and to determine the influences of organic acids on fluorine leaching from rocks.

MATERIALS AND METHODS

The procedures of the experiments. The experiments used three samples of powdered rocks, alkaline agpaitic granite, dacite, and feldspar–quartz aleurite, which contain roughly the same levels of fluorine (0.05–0.06 wt %). The chemical compositions are presented in Table 1. The grain size was 80 μm or less, with a 90% fraction of less than <40 μm. We used distilled water and 0.005 M organic acids (acetic, tartaric, citric, and oxalic) as the leaching solutions. The 0.8 g samples were placed into plastic test tubes and 40 mL of a solution was added into each of the test tubes. The suspended samples in closed test tubes were stirred with a shaker during 3 weeks for 8–10 h daily at room temperature until the changes in pH values ceased. The solutions were then filtered with a 0.22-μm pore size membrane filter. The pH values, fluoride concentrations via direct potentiometry (Savenko, 1986), and those of key ions (Na, K, Mg, Ca, Cl, and SO_4) were determined by capillary electrophoresis in the filtrates and initial solutions (Komarova and Kamentsev, 2006). The measurement errors were within ±3%.

Table 1. The chemical composition of the rock samples used in the experiments, wt % by (*Standartnye obraztsy*..., 1990, 2002)

Component	Agpaitic granite	Dacite	Aleurite
SiO_2	74.76	63.40	60.67
TiO_2	0.26	0.77	0.94
Al_2O_3	10.64	15.70	18.20
$Fe_2O_{3(total)}$	4.50	6.75	7.20
FeO	1.61	4.89	4.80
MnO	0.12	0.19	0.042
MgO	0.102	2.13	2.22
CaO	0.32	4.77	0.51
Na_2O	4.24	2.99	2.31
K_2O	4.64	2.37	3.43
P_2O_5	0.024	0.160	0.190
S_{total}	0.016	0.106	0.087
F	0.0620	0.0500	0.0600
Sum	99.68	99.40	95.86

RESULTS AND DISCUSSION

The results of the experiments presented in Table 2 showed that the effects of different carbonic acids on the fluorine leaching were similar for all three rock samples (Fig. 1). For each of the rocks, the maximum concentrations of fluorine were found in the solutions containing oxalic acid, along with the lowest calcium content. This effect might be caused by the formation of poorly soluble calcium oxalate CaC_2O_4, which is characterized by a solubility product of 2.3×10^{-9} (Lur'e, 1989). The product of the total concentrations of calcium and oxalate ions was more than 7×10^{-7}, which supported this assumption.[1] Hence, it is likely that the fluorine content in leaching solutions is determined by the concentration of calcium ions via the solubility of fluorite, which is one of the most widespread accessory fluorine minerals with a solubility product of 4.0×10^{-11} (Lur'e, 1989). However, the experiments found a value of the concentration product $[Ca^{2+}][F^-]^2$ below 1.6×10^{-13}, which excluded the presence of fluorite. Another widespread fluorine-containing accessory mineral, fluorapatite $Ca_{10}(PO_4)_6F_2$, could also not determine the concentration of fluorides in solution, since this concentration should then increase with the decrease in pH.

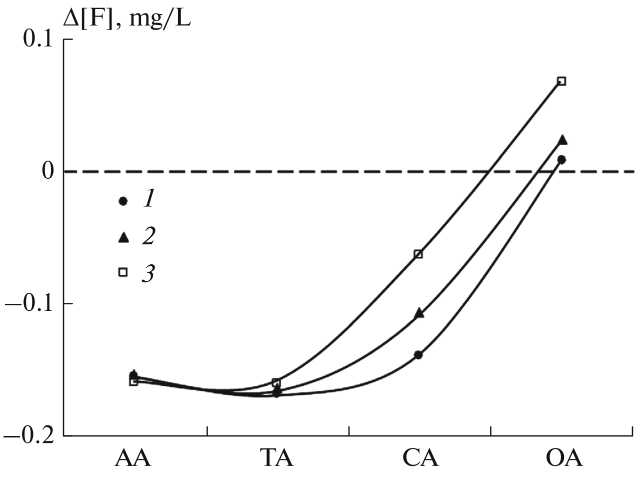

Fig. 1. Variations in the intensity of fluorine leaching under the interaction of agpaitic granite (*1*), dacite (*2*), and aleurite (*3*) with 0.005 M solutions of acetic, tartaric, citric, and oxalic acids (AA, TA, CA, and OA, respectively) related to the values for distilled water.

The leaching of fluorine in the presence of organic (excluding oxalic) acids is less than its transition to distilled water for all three rock types. Considering the leaching ability in distilled water, the organic acids are ranked in the series oxalic (0.03) > citric (–0.10) > acetic (–0.15) ~ tartaric (0.16).[2]

These data are consistent in general with the results of previous experiments on fluorine leaching from micas (Savenko et al., 2014): the release of fluorine from rocks decreases with a decrease of pH in the solutions, while this occurs to various degrees for different acids (Fig. 2). The inclination of the ΔF–pH dependence is at its maximum for oxalic acid, is considerably lesser for citric acid, is hardly visible for tartaric acid, and is even close to zero for acetic acid. The previously determined positive correlation of leaching intensities of fluorine and magnesium (Fig. 3) has been confirmed as well.[3]

The mechanism of the effect of organic acid on fluorine leaching from rocks is still not completely clear. One may suppose that the decrease of pH value causes the sorption of fluorides resulting from the reaction of ion exchange:

$$F^- + \overline{OH} \rightarrow \overline{F} + OH^-,$$

where the $\overline{F}$ and $\overline{OH}$ symbols denote the F^- and OH^- ions adsorbed on the surface of a solid phase. In view of this, the less intense fluorine leaching under acidic conditions compared to distilled water may be ascribed to the sorption immobilization of F^- ions on a solid phase.

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[1] In view of the complexation and correction for activity ratios, the product of activities of calcium and oxalate ions should be lower by approximately an order of magnitude, which would not be critical for this conclusion.

[2] In parentheses, the differences of the fluorine concentrations (the average for the treated rocks) in organic-acid leaching solutions and those in distilled water, mg/L.

[3] The deviation of two points from the linear relationship between the amounts of leached fluorine and magnesium for dacite and aleurite in the experiments on oxalic acid was caused by magnesium coprecipitation with calcium oxalate, with which these waters were supersaturated.

Table 2. The influence of organic acids on fluorine leaching from rocks*

Rock	pH	[F]	Δ[F]	[Na]	Δ[Na]	[K]	Δ[K]	[Mg]	Δ[Mg]	[Ca]	Δ[Ca]	[Cl]	$[SO_4]$
		mg/L											
Distilled water													
Agpaitic granite	8.05	0.20	–	6.18	–	5.29	–	0.36	–	7.57	–	0.44	4.00
Dacite	8.09	0.26	–	2.50	–	7.96	–	0.87	–	2.54	–	0.06	0.32
Aleurite	8.11	0.33	–	1.83	–	11.0	–	2.25	–	13.0	–	0.16	5.56
0.005 M acetic acid													
Agpaitic granite	4.73	0.05	–0.15	7.60	1.42	10.1	4.81	0.59	0.23	14.0	6.43	–	–
Dacite	4.90	0.11	–0.15	3.32	0.82	18.6	10.6	4.70	3.83	12.8	10.3	–	–
Aleurite	5.64	0.17	–0.16	1.99	0.16	17.1	6.10	7.68	5.43	32.2	19.2	–	–
0.005 M tartaric acid													
Agpaitic granite	3.70	0.04	–0.16	8.71	2.53	14.9	9.61	0.91	0.55	16.4	8.83	–	–
Dacite	4.63	0.10	–0.16	6.34	3.83	31.6	23.6	11.9	11.0	28.3	25.8	–	–
Aleurite	5.54	0.17	–0.16	2.23	0.40	23.4	12.4	18.4	16.2	36.0	23.0	–	–
0.005 M citric acid													
Agpaitic granite	3.48	0.07	–0.13	9.35	3.17	16.2	10.9	1.30	0.94	17.9	10.3	–	–
Dacite	4.30	0.16	–0.10	7.50	5.00	32.8	24.8	18.2	17.3	25.6	23.1	–	–
Aleurite	5.65	0.26	–0.07	2.51	0.68	24.7	13.7	27.1	24.8	33.6	20.6	–	–
0.005 M oxalic acid													
Agpaitic granite	5.37	0.21	0.01	9.73	3.55	16.4	11.1	1.98	1.62	11.5	3.93	–	–
Dacite	6.04	0.29	0.03	7.83	5.33	33.3	25.3	7.47	6.60	5.78	3.24	–	–
Aleurite	6.31	0.39	0.06	2.80	0.97	25.1	14.1	11.1	8.85	14.9	1.90	–	–

*Δ[*i*] is difference of the concentrations of an element *i* (F, Na, K, Mg, and Ca) in leaching solutions of corresponding organic acids and in distilled water.

The same mechanism of superposed sorption immobilization of F^- ions allows one to explain the more intense fluorine leaching from rocks (excluding meimechite) compared to distilled water in the experiments using a multicomponent solution of organic acid at the lowest pH values (2.56–3.58) (Savenko and Savenko, 2017). The dissociation constant of hydrofluoric acid

$$K^0_{\mathrm{HF}} = \frac{\left[\mathrm{H}^+\right]\left[\mathrm{F}^-\right]}{\left[\mathrm{HF}^0\right]}$$

is 6.2×10^{-4} under standard conditions, $\log K^0_{\mathrm{HF}} = -3.21$ (Lur'e, 1989). Hence, it follows that

$$\log\left(\frac{\left[\mathrm{HF}^0\right]}{\left[\mathrm{F}^-\right]}\right) = 3.21 - \mathrm{pH}.$$

It follows from this relationship that the bulk of dissolved fluorine at $\mathrm{pH} < 3.21$ occurs as undissociated HF^0 molecules. These are not adsorbed on solid phases and their fraction increases with the decrease in pH. In the experiments on multicomponent solutions of organic acids, excluding the series of meimechite, the final pH value was more than 3.21 (3.58) in the only experiment and the fraction of undissociated HF^0 molecules was less than that of F^- ions, amounting to 30%. Undissociated HF^0 molecules constituted the main form of fluorine in solutions in all the other experiments on fluorine leaching with multicomponent solutions of organic acids from andesite basalt, albitized rhyodacite, and alkaline agpaitic granite. In this case, low concentrations of F^- ions should prevent the sorption immobilization of fluorine and cause more intense leaching.

This concept is not in agreement with the results of experiments on meimechite (an ultrabasic rock with a

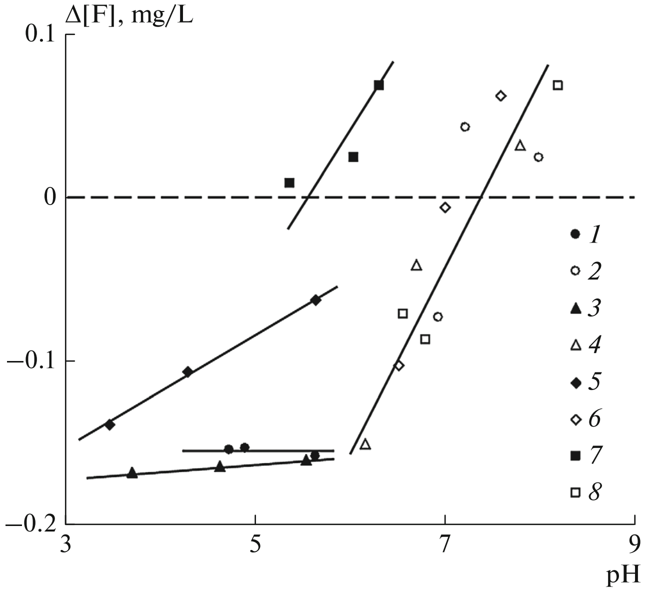

Fig. 2. The dependence of fluorine leaching from rocks and micas on the acidity of aquatic medium: (*1*) acetic acid, rocks; (*2*) acetic acid, micas, by (Savenko et al., 2014); (*3*) tartaric acid, rocks; (*4*) tartaric acid, micas, by (Savenko et al., 2014); (*5*) citric acid, rocks; (*6*) citric acid, micas, by (Savenko et al., 2014); (*7*) oxalic acid, rocks; (*8*) oxalic acid, micas, by (Savenko et al., 2014).

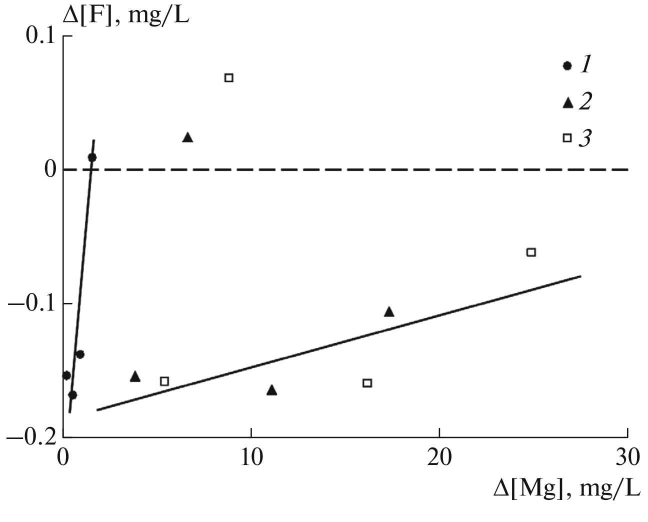

Fig. 3. The relationship between leaching of fluorine and magnesium from rocks with organic acids: agpaitic granite (*1*), dacite (*2*), and aleurite (*3*).

high magnesium content). The final acidity of a multicomponent solution of organic acids was within the pH range of 4.04–6.65; nevertheless, the fluorine leaching was much more intense compared to that under meimechite interaction with distilled water. It seems likely that another mechanism of fluorine mobilization occurs, which is somehow related to the leaching of magnesium and expressed in the positive correlation of the levels of fluorine and magnesium that transfer from the rocks to the solution. Evidence of the action of this mechanism, i.e., the positive correlations between the leaching of fluorine and magnesium, was seen in all of these experiments. The "magnesium" mechanism probably prevails for meimechite containing 30% MgO, whereas the contribution of sorption immobilization is of secondary importance.

CONCLUSIONS

The results of these experiments allow certain conclusions. First, the data of the experiments show that organic acids exhibit no specific influence upon fluorine leaching from rocks. The intensity of leaching at low-acid conditions in the presence of organic acids is less than that in pure distilled water. This effect is due to a decrease with an increase in the acidity of the concentration of hydroxyl ions competing with those of fluorine in a sorption–desorption equilibrium. The sorption immobilization of fluorides becomes minor and fluorine leaching increases considerably in a relatively acidic medium where undissociated HF^0 molecules constitute the key form of fluorine. Second, a positive correlation between the amounts of fluorine and magnesium leached indicates some general but unclear mechanism of the transition of these elements from rocks into aquatic solutions.

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