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SHORT
COMMUNICATIONS

Factors Controlling Uranium Geochemistry in the Mixing Zone of River- and Seawaters

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When the transformations of the continental runoff in river mouths is studied, much attention is paid to the radioloecological aspect of the problem, in particular, to the identification of factors controlling the migration of radionuclides at the river–sea geochemical barrier. For trace elements with relatively low biological accumulation coefficients, a significant role is played by sorption–desorption processes, which are responsible for the redistribution of solute and particulate modes, because zones where riverine and marine waters are mixed are characterized by drastic changes in the concentrations of dissolved components and coupled changes in the composition of the adsorbed complex of riverine suspensions.

The behavior of U in river mouths varies: the Baltic Sea [1] and the mouths of the Volga [2], Gironde [3], Clyde, and Tamar rivers in Great Britain [4], Zaire [3, 5], Godavari [6], and Mahanadi [7, 8] are characterized by the strictly conservative behavior of this component, whereas the mouths of the Charente, France [3], and Forth [4] rivers and the Delaware and Chesapeake bays in the United States [9, 10] show the removal of significant amounts of dissolved U. The removal of U from the Forth and Charente river mouths was thought to be caused by sorption on riverine particulate matter, and U immobilization in the salty marshes of Chesapeake and Delaware bays can be related to the coprecipitation of U(IV), which is produced by the reduction of U(VI) by S-bearing compounds and/or organic matter, together with floccules of the latter or autochthonous Fe hydroxide.

However, even in the situation when U formally behaves conservatively, it cannot be ruled out that this element participates in sorption–desorption processes when riverine particulate matter interacts with seawater, a processes that sometimes cannot be identified during natural observations because of the low contents of particulate matter, which are insufficient for analytically significant changes in the U concentrations in the solutions. For example, a new quasiconservative type of distribution was recognized and described for F and B [11], when, in spite of the formal consistence of the results of natural observations with the conservative type of behavior, the interactions of riverine suspensions with seawater results in the sorption-related removal of much of the dissolved trace elements (7–18 and 67–80%, respectively, of the total F and B amounts introduced into the ocean with riverine runoff). This conclusion, which was rigorously confirmed in experiments, has notably modified the concept of the factors controlling the geochemical F and B balance in the ocean.

In order to elucidate the role of sorption–desorption processes in the transforms of the dissolved U runoff in the mixing zone of riverine and marine waters, we conducted an experimental simulation of the interactions of waters of various salinity that contain U(VI) with the predominant clay minerals, which represented the particulate matter of the continental runoff.

EXPERIMENTAL

Our experiments were conducted with samples of kaolinite clay from the Glukhovetskoe deposit in Ukraine, montmorillonite clay from the Askanskoe deposit in Georgia, and polymineralic clay from the Gzhel deposit in Moscow oblast, Russia, with a specific surface areas of 8.6, 112.7, and 23.4 m^2/g, respectively. According to XRD data, the samples had the following mineralogical composition: the kaolinite clay consisted of 9.6% quartz, 0.8% muscovite, and 89.6% kaolinite; the montmorillonite clay contained 0.6% biotite, 1.2% plagioclase, 66.1% Na-montmorillonite, and 32.1% amorphous phase; and the Gzhel clay was composed of 23.8% illite, 1.3% hydromica, 7.1% kaolinite, 19.7% microcline, 27.2% quartz, and 20.9% smectite.

In order to model a broad range of salinity, as is typical of waters in river mouths, normal seawater of salinity equal to 35‰ was mixed in various proportions with the water of the Moskva River, with the seawater proportion of mixture varied from 0 to 100%. In some of our experiments, the pH of the Moskva River water was within the range of 7.9–8.0, and in others it was increased to 8.4–8.5 by adding $NaHCO_3$–Na_2CO_3.

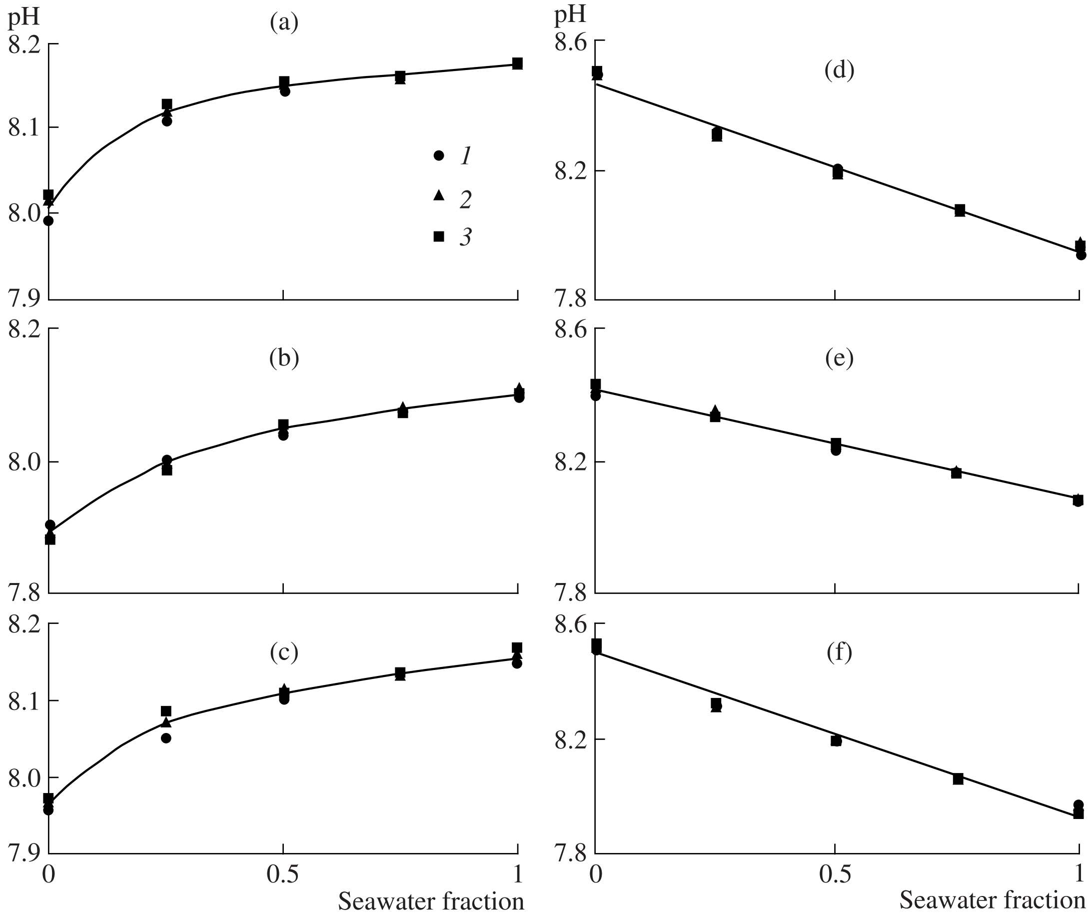

Fig. 1. Systematic variations in pH with increasing seawater fraction in the mixture. Normal riverwater: (a) kaolinite clay, (b) montmorillonite clay, (c) Gzhel clay. Alkaline riverwater: (d) kaolinite clay, (e) montmorillonite clay, (f) Gzhel clay. Initial U(VI) concentrations in the solution: (*1*) 2 μM, (*2*) 4 μM, (*3*) 6 μM.

Each of the clay samples was used in three sets of experiments with U(VI) concentrations in the river- and seawater equal to 2, 4, and 6 μM, separately for the "normal" and "alkaline" riverwater. The experiments with kaolinite and Gzhel polymineralic clays were carried out at the solid phase : solution proportions equal to 1 : 200, and the experiments with the montmorillonite clay were conducted at the solid phase : solution proportion of 1 : 1000 because of the strong influence of this clay on the pH of the solution. The exposure time was always equal to 2 months. Simultaneously we conducted replicate "blank" experiments in which the experimental solutions were mixed in the same proportions as in the main experimental sets but without adding clay.

Preparatorily to the analysis, the samples were filtered through dense paper filters. The filtrate of the "blanks" were analyzed for pH and the concentration of U(VI) by colorimetric techniques with arsenazo III. The relative errors in the measured pH and U concentrations were ±0.005 pH units and ±3%, respectively.

RESULTS AND DISCUSSION

Table 1 presents the results of our experiments. They indicate that the pH value increases nonlinearly with increasing percentage of seawater in the experiments with normal riverwater and linearly in the experiments with alkaline riverwater (Fig. 1).

For kaolinite clay, an increase in the percentage of seawater in the mixture led to a decrease in the U distribution coefficient

$$K_d = \Gamma/[U(VI)], \qquad (1)$$

where Γ is the specific sorption of U (nmol/g), and [U(VI)] is the equilibrium concentration of U(VI) in the solution (nM), which is described by linear dependences for the experiments with normal and alkaline water (Figs. 2a, 2d). The moduli of K_d in the experiments with riverwater of elevated pH were almost twice as low.

The sorption capacity of montmorillonite clay with respect to U was roughly an order of magnitude higher than that of kaolinite clay (Figs. 2b, 2e). Moreover, we

Table 1. Variations in the pH values and dissolved U(VI) concentration in the experiments modeling interactions between waters in river mouths with major terrigenous clay minerals

Seawater fraction	Solid phase/solution ratio	Equilibrium pH	U(VI) concentration, μM		K_d, l/g
			initial	equilibrium	
1	2	3	4	5	6
Kaolinite clay, normal riverwater					
0	0.005	7.99	2.00	1.67	0.040
0.25	0.005	8.11	2.00	1.70	0.035
0.50	0.005	8.14	2.00	1.77	0.026
0.75	0.005	8.16	2.00	1.82	0.019
1.00	0.005	8.18	1.99	1.88	0.013
0	0.005	8.02	3.99	3.24	0.046
0.25	0.005	8.12	4.01	3.42	0.034
0.50	0.005	8.15	3.99	3.59	0.022
0.75	0.005	8.16	4.00	3.71	0.016
1.00	0.005	8.17	4.02	3.78	0.012
0	0.005	8.02	6.00	4.87	0.047
0.25	0.005	8.12	6.00	5.10	0.035
0.50	0.005	8.15	6.00	5.39	0.023
0.75	0.005	8.16	5.99	5.57	0.015
1.00	0.005	8.18	6.00	5.60	0.014
Same, alkaline riverwater					
0	0.005	8.50	2.00	1.77	0.026
0.25	0.005	8.31	2.00	1.80	0.022
0.50	0.005	8.20	2.00	1.83	0.019
0.75	0.005	8.07	2.00	1.87	0.014
1.00	0.005	7.94	2.00	1.92	0.008
0	0.005	8.50	4.00	3.56	0.025
0.25	0.005	8.29	4.00	3.61	0.022
0.50	0.005	8.19	4.00	3.68	0.017
0.75	0.005	8.06	4.00	3.74	0.014
1.00	0.005	7.97	4.00	3.84	0.008
0	0.005	8.50	5.99	5.34	0.024
0.25	0.005	8.31	6.00	5.47	0.019
0.50	0.005	8.19	6.00	5.55	0.016
0.75	0.005	8.07	6.00	5.59	0.015
1.00	0.005	7.95	6.00	5.73	0.010
Montmorillonite clay, normal riverwater					
0	0.001	7.90	2.00	1.20	0.664
0.25	0.001	8.00	1.99	1.33	0.497
0.50	0.001	8.04	1.98	1.38	0.435
0.75	0.001	8.08	2.00	1.55	0.290
1.00	0.001	8.09	1.99	1.65	0.203
0	0.001	7.89	4.00	2.45	0.633
0.25	0.001	7.99	4.02	2.52	0.596
0.50	0.001	8.05	4.04	2.82	0.434
0.75	0.001	8.08	4.00	2.99	0.336
1.00	0.001	8.11	4.03	3.27	0.233
0	0.001	7.88	5.99	3.77	0.590
0.25	0.001	7.99	5.99	3.91	0.531
0.50	0.001	8.05	5.98	4.35	0.377
0.75	0.001	8.08	6.00	4.55	0.319
1.00	0.001	8.10	5.99	4.81	0.245

Table 1. (Contd.)

Seawater fraction	Solid phase/solution ratio	Equilibrium pH	U(VI) concentration, μM		K_d, l/g
			initial	equilibrium	
1	2	3	4	5	6
Same, alkaline riverwater					
0	0.001	8.41	2.00	1.95	0.024
0.25	0.001	8.34	1.99	1.82	0.094
0.50	0.001	8.24	1.98	1.72	0.152
0.75	0.001	8.17	2.00	1.65	0.212
1.00	0.001	8.08	1.99	1.58	0.255
0	0.001	8.43	4.00	3.86	0.038
0.25	0.001	8.35	4.02	3.71	0.081
0.50	0.001	8.25	4.04	3.62	0.118
0.75	0.001	8.17	4.00	3.29	0.217
1.00	0.001	8.09	4.03	3.33	0.211
0	0.001	8.43	5.99	5.80	0.033
0.25	0.001	8.34	5.99	5.54	0.081
0.50	0.001	8.25	5.98	5.30	0.130
0.75	0.001	8.16	6.00	5.06	0.185
1.00	0.001	8.08	5.99	4.82	0.241
Gzhel clay, normal riverwater					
0	0.005	7.96	2.00	1.77	0.026
0.25	0.005	8.05	2.00	1.78	0.024
0.50	0.005	8.11	2.00	1.78	0.024
0.75	0.005	8.13	2.00	1.81	0.021
1.00	0.005	8.15	1.99	1.85	0.016
0	0.005	7.96	3.99	3.54	0.026
0.25	0.005	8.07	4.01	3.54	0.026
0.50	0.005	8.11	3.99	3.61	0.021
0.75	0.005	8.13	4.00	3.68	0.017
1.00	0.005	8.16	4.02	3.71	0.017
0	0.005	7.97	6.00	5.29	0.027
0.25	0.005	8.09	6.00	5.40	0.022
0.50	0.005	8.11	6.00	5.48	0.019
0.75	0.005	8.13	5.99	5.57	0.015
1.00	0.005	8.17	6.00	5.51	0.018
Same, alkaline riverwater					
0	0.005	8.52	2.00	1.97	0.003
0.25	0.005	8.31	2.00	1.82	0.020
0.50	0.005	8.20	2.00	1.80	0.022
0.75	0.005	8.06	2.00	1.89	0.012
1.00	0.005	7.97	2.00	1.93	0.007
0	0.005	8.52	4.00	3.99	0.001
0.25	0.005	8.31	4.00	3.66	0.019
0.50	0.005	8.20	4.00	3.64	0.020
0.75	0.005	8.06	4.00	3.69	0.017
1.00	0.005	7.97	4.00	3.74	0.014
0	0.005	8.53	5.99	5.97	0.001
0.25	0.005	8.32	6.00	5.62	0.013
0.50	0.005	8.20	6.00	5.52	0.017
0.75	0.005	8.06	6.00	5.60	0.014
1.00	0.005	7.95	6.00	5.73	0.010

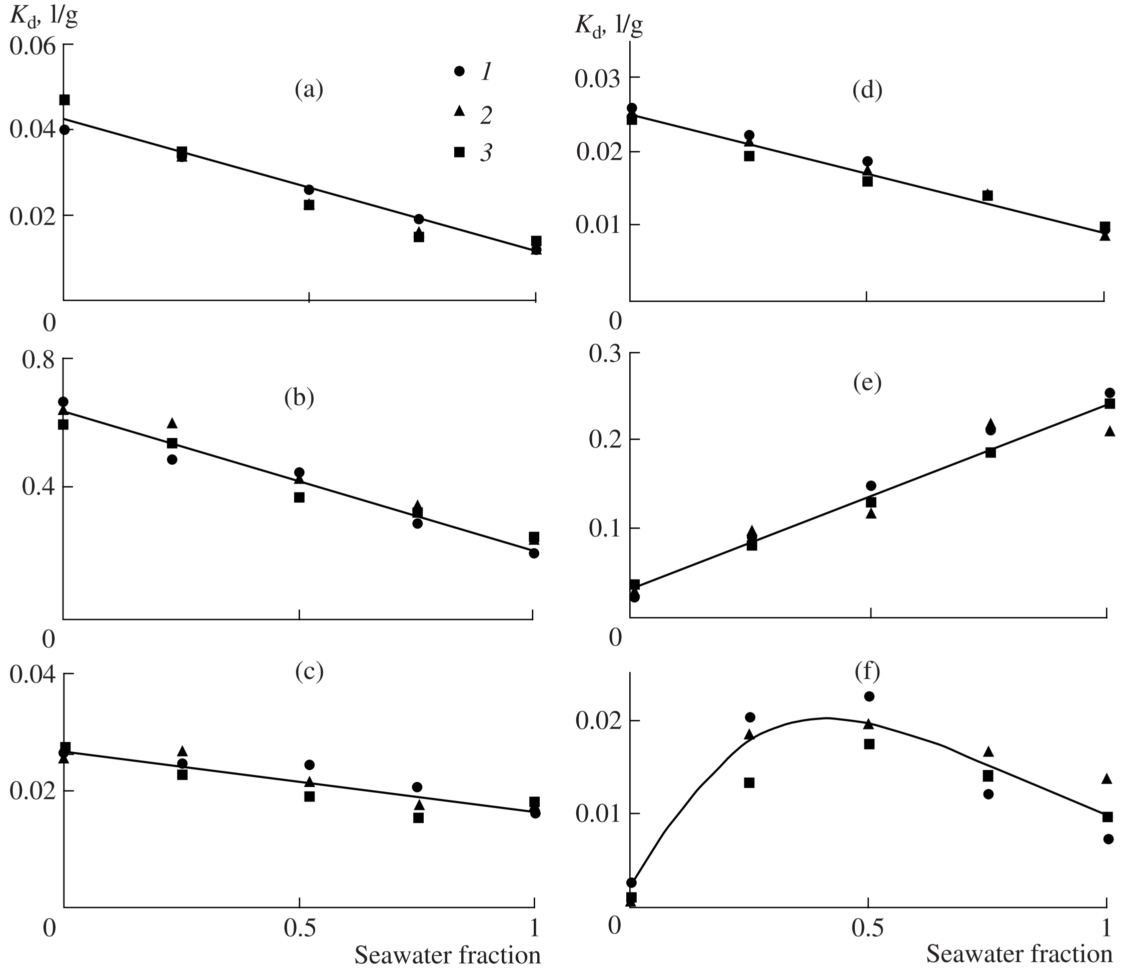

Fig. 2. Systematic variations in the U(VI) distribution coefficient between clays and solution with increasing seawater fraction in the mixture. Normal riverwater: (a) kaolinite clay, (b) montmorillonite clay, and (c) Gzhel clay. Alkaline riverwater: (d) kaolinite clay, (e) montmorillonite clay, and (f) Gzhel clay. Initial U(VI) concentrations in the solution: (*1*) 2 μM, (*2*) 4 μM, and (*3*) 6 μM.

determined that the K_d variations with increasing salinity are controlled mostly by the pH of the solution: K_d decreased when normal riverwater interacted with seawater and increased when alkaline water was used.

The U distribution coefficients for the polymineralic Gzhel clay were somewhat lower than those for the kaolinite clay and were prone to decrease with the transition from the riverine to marine water mass (Figs. 2c, 2f).

Using averaged K_d values for the experiments with various U concentrations (2, 4, and 6 μM), we calculated the specific sorption of U in a hypothetical zone where the global continental runoff mixes with seawater at variable salinity:

$$\Gamma = K_{\mathrm{d\,env}}[\mathrm{U(VI)}]_{\mathrm{cons}}, \qquad (2)$$

where $[\mathrm{U(VI)}]_{\mathrm{cons}}$ is the calculated U concentration at the conservative mixing of riverine runoff and seawater containing 2.1 and 12.6 nM dissolved U, respectively [12]. The difference between the U specific sorption from mixtures of various salinity and riverwater

$$\Delta\Gamma = \Gamma_S - \Gamma_{\mathrm{rw}} \qquad (3)$$

was used to evaluate the resultant effect of sorption–desorption processes on the transformation of the dissolved U runoff in the mixing zone of riverine and marine waters (Table 2).

The calculations indicate (Fig. 3) that the interaction of riverine suspensions of any mineralogical composition with saline waters results in the sorption removal of dissolved U, which reaches 0.07–0.08, 1.5–2.9, and 0.13–0.16 nmol/g for kaolinite, montmorillonite, and Gzhel clays, respectively, at the marine boundary of the mixing zone.

The relative abundance of clay minerals (except montmorillonite) in the Gzhel clay is close to that in the particulate matter in riverwaters around the world [13]. The difference in the total amounts of clay minerals in the Gzhel clay (53%) and global solid runoff (67%) can be taken into account by introducing a correction coefficients equal β to the ratio of the weight fractions of

Table 2. Estimated integral effect of sorption–desorption processes on the transformation of dissolved U runoff in the mixing zone of river- and seawater

Seawater fraction	$[U(VI)]^{*}_{cons}$, nM	$K_{d\,env}$, l/g	Γ, nmol/g	$\Delta\Gamma$, nmol/g
Kaolinite clay, normal riverwater				
0	2.1	0.044	0.093	0
0.25	4.7	0.035	0.164	0.071
0.50	7.4	0.024	0.174	0.081
0.75	10.0	0.017	0.167	0.074
1.00	12.6	0.013	0.164	0.071
Same, alkaline riverwater				
0	2.1	0.025	0.053	0
0.25	4.7	0.021	0.099	0.047
0.50	7.4	0.017	0.127	0.075
0.75	10.0	0.014	0.143	0.090
1.00	12.6	0.009	0.110	0.057
Montmorillonite clay, normal riverwater				
0	2.1	0.629	1.321	0
0.25	4.7	0.541	2.556	1.235
0.50	7.4	0.415	3.050	1.729
0.75	10.0	0.315	3.142	1.821
1.00	12.6	0.227	2.860	1.539
Same, alkaline riverwater				
0	2.1	0.032	0.067	0
0.25	4.7	0.085	0.403	0.336
0.50	7.4	0.133	0.980	0.913
0.75	10.0	0.205	2.042	1.975
1.00	12.6	0.236	2.970	2.903
Gzhel clay, normal riverwater				
0	2.1	0.026	0.055	0
0.25	4.7	0.024	0.113	0.058
0.50	7.4	0.021	0.157	0.101
0.75	10.0	0.018	0.177	0.121
1.00	12.6	0.017	0.214	0.159
Same, alkaline riverwater				
0	2.1	0.002	0.004	0
0.25	4.7	0.017	0.082	0.078
0.50	7.4	0.019	0.140	0.136
0.75	10.0	0.014	0.143	0.139
1.00	12.6	0.010	0.130	0.126

Note: * U concentration calculated under the assumption of the conservative mixing of continental runoff and seawater containing 2.1 and 12.6 nM of dissolved U, respectively [12].

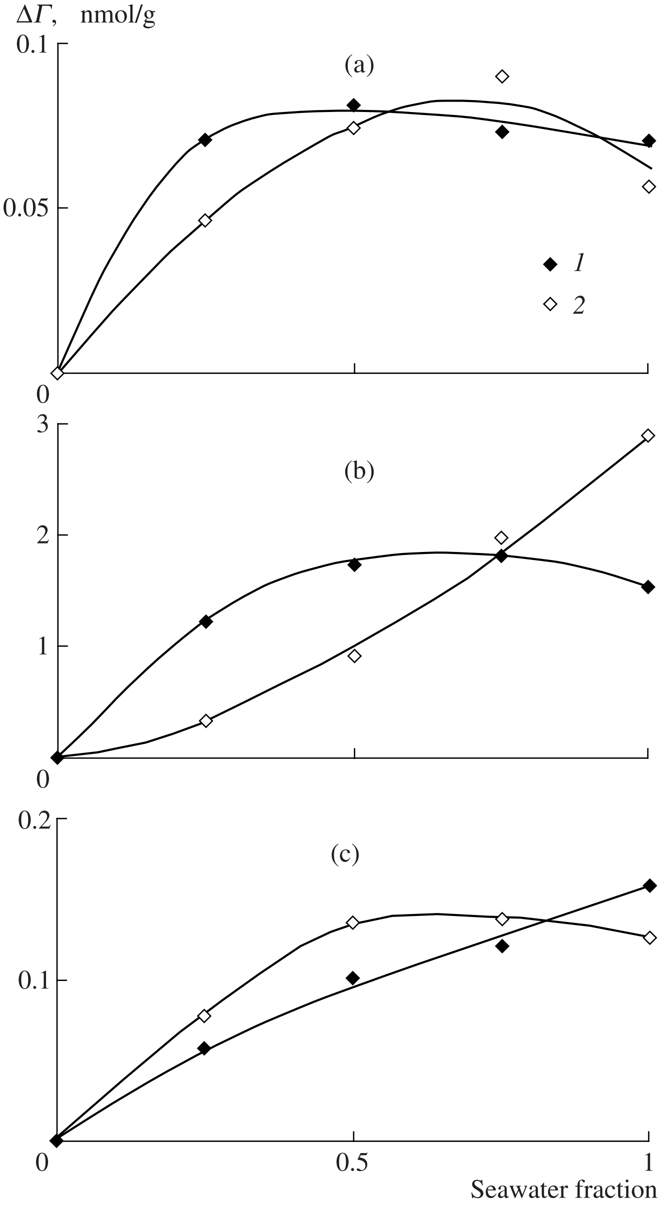

Fig. 3. Systematic variations in the specific sorption of U(VI) by clays with the transition from riverine to marine water masses: (a) kaolinite clay, (b) montmorillonite clay, and (c) Gzhel clay. (*1*) Normal riverwater; (*2*) alkaline riverwater.

pelitic material in the continental runoff and Gzhel clay ($k = 1.26$).

With regard for this correction, the experimentally determined specific sorption of U by the Gzhel clay with the transition from river- to seawater mass ($\Delta\Gamma$ = 0.13–0.16 nmol/g) increases to 0.16–0.20 nmol/g or 39–48 ng/g. According to the estimates [14, 15], the amount of particulate matter runoff from continents to the ocean is 15.7 and 18.5 bln. tons/year. This implies that the sorption removal of U at the river–sea geochemical barrier with the Gzhel clay (as an analogue of the particulate matter of continental runoff) amounts to 610–890 T U/year.

The resultant U sorption by montmorillonite clay in the mixing zone of river- and seawater ($\Delta\Gamma$ = 1.5–2.9 nmol/g) is roughly one order of magnitude higher than that of the Gzhel clay. Consequently, the presence of this mineral in the particulate matter results in significant U removal from the solution. According to [16], the montmorillonite concentration in riverine particulate matter amounts to 3% on average. In this situation, 170–380 T of U should be annually additionally removed with it, and this would result in an overall U sorption on terrigenous deposits equal to 780–1270 T U/year.

Compared to the supply of dissolved U with riverine runoff, which is estimated at 20000 thous. T/year [12], sorption U removal is insignificant and lies within 4–6%.

CONCLUSIONS

According to our experimental modeling data of U(VI) sorption–desorption processes on major clay minerals in the mixing zone of river- and seawater, the interaction of riverine particulate matter of any mineralogical composition with saline waters is associated with the sorption removal of dissolved U, a process that cannot be identified during natural observations because of low contents of particulate matter, which are insufficient for analytically significant change in the U concentration in the solution.

The assayed overall sorption removal of U with terrigenous material at the river–sea geochemical barrier is 780–1270 T U/year. Compared with the dissolved U supply with the global runoff, the sorption removal of this element is insignificant and is constrained within 4–6%.

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