EXPERIMENTAL STUDY OF URANYL-IONS UPTAKE BY OCEANIC PHOSPHORITES

Savenko A.V., Baturin G.N.

Financial support by RFBR, grants NN 00–05–64762 and 02–05–06086.

Herald of the Earth Sciences Department RAS, № 1(20)′2002

URL: *http://www.scgis.ru/russian/cp1251/h_dgggms/1-2002/informbul-1.htm#geoecol-4.engl*

The concentration of uranium in oceanic phosphorites fluctuates in wide limits changing from less than 1 to hundreds ppm [1–3] being in most cases essentially higher as compared to average uranium concentration in marine and oceanic sediments (2–3 ppm [1]). It is assumed that uranium enrichment in oceanic phosphorites is related to its transition from VI to IV-valence state in reducing environment occurring in bottom sediments enriched in organic matter. In order to check this hypothesis we carried out experimental study of uranyl-ions uptake by oceanic phosphorites containing different amounts of organic matter and uranium.

In our experiments we used two samples of oceanic phosphorites namely Holocene phosphatized coprolite from the Namibian shelf and Late Cretaceous phosphatized limestone from one of the Mid Pacific Mountains. The specific surface value determined by crypton absorption method in the Institute of solid body physics, RAS, turned to be equal in both samples making 3.2 m^2/g. The chemical composition of both samples is shown in Table 1.

Table 1

Chemical composition of phosphorites studied

Sample type	Sample location	Chemical composition, %										
		U	P_2O_5	CaO	MgO	SiO_2	Al_2O_3	Fe_2O_3	Na_2O	K_2O	CO_2	C_{org}
Phosphatized coprolite	Namibian shelf	6×10^{-3}	30.00	51.90	1.32	0.30	0.38	0.14	2.70	0.12	6.21	0.80
Phosphatized limestone	Mid Pacific mountains	6×10^{-4}	27.90	50.60	n/d	1.62	0.83	0.57	1.89	0.55	10.17	0.15

The experiments were carried out in artificial sea water with 35 $^0/_{00}$ salinity and changing concentration (2.2–10.1 μM) of uranyl-ions at 1 : 100 solid/solution mass ratios. During 18 days, i.e. until the equilibration, the solutions were intensively mixed and then filtered through dense paper filter. Values of pH and residual concentration of uranyl-ions were determined in filtrate applying potentiometry and colorimetry with arsenazo III, correspondingly. Experimental results are presented in Table 2.

Table 2

Uptake of uranyl-ions by oceanic phosphorites from seawater

Sample type	Sample location	Concentration of UO_2^{2+}, μM		Specific uptake of uranium Γ, μmol/g	Distribution coefficient k in equation (1)	pH
		initial	equilibrium			
Phosphatized coprolite	Namibian shelf	2.20	1.40	0.080	0.057	8.10 ± 0.05
		3.99	2.49	0.150	0.060	
		5.75	3.59	0.216	0.060	
		8.00	5.15	0.285	0.055	
		10.10	6.66	0.344	0.052	
				Mean	0.057 ± 0.003	
Phosphatized limestone	Mid Pacific mountains	2.20	1.92	0.028	0.015	8.14 ± 0.02
		3.99	3.21	0.078	0.024	
		5.75	4.80	0.095	0.020	
		8.00	6.69	0.131	0.020	
		10.10	8.57	0.153	0.018	
				Mean	0.019 ± 0.003	

The experiments showed (fig. 1) that the increase of equilibrium concentration of uranyl-ions up to 7–9 μM was accompanied by linear growth of specific uranium uptake by phosphorite, which is described by equation:

$$\Gamma = k[\mathrm{UO}_2^{2+}], \qquad (1)$$

where Γ is the specific uranium uptake, μmol/g; $[\mathrm{UO}_2^{2+}]$ – equilibrium concentration of uranyl-ions in seawater, μM; k – distribution coefficient of uranium between solid phase and solution, l/g.

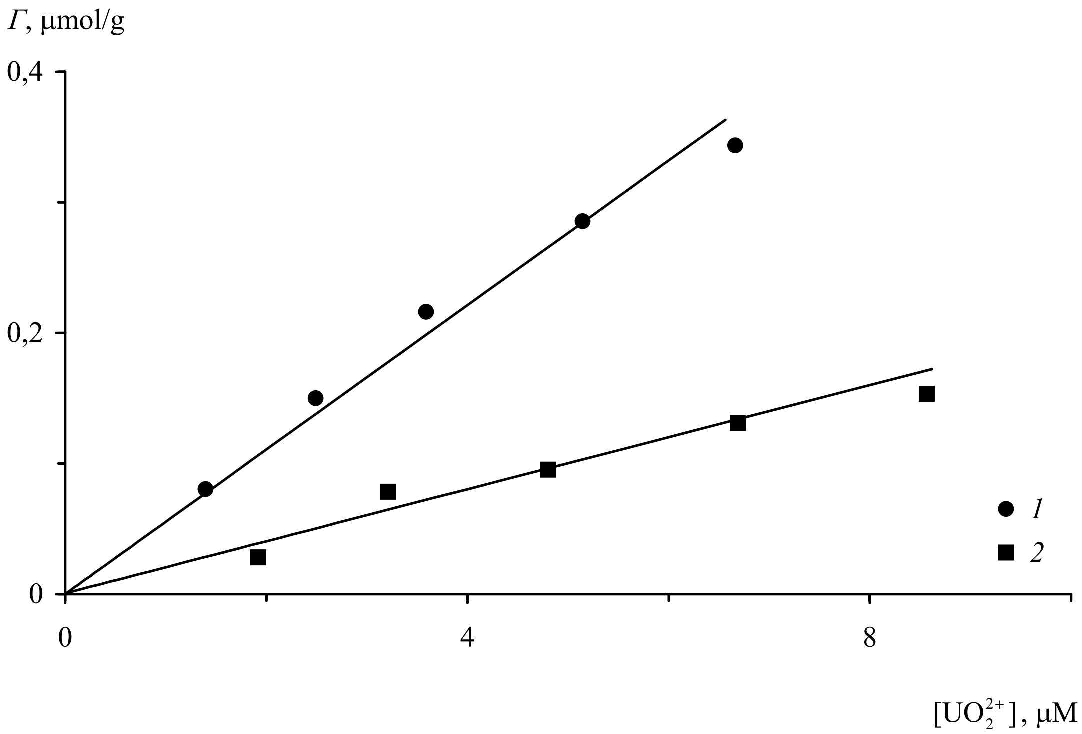

Fig. 1. The relationship between specific uranium uptake by oceanic phosphorites and equilibrium uranyl-ions concentration in seawater. *1* – phosphatized coprolite from the Namibian shelf, *2* – phosphatized limestone from the Mid Pacific mountains.

The uranium uptake by phosphatized coprolite is approximately 3 times higher as compared to phosphatized limestone: average values of distribution coefficient k in equation (1) for these samples are respectively 0.057 and 0.019 l/g (Table 2). The samples under study had equal specific surface area (3.2 m^2/g) and nearly the same P_2O_5 content (30 and 28 %), however, the concentration of organic matter and uranium in phosphatized coprolite (0.8 % and 60 ppm) was essentially higher than appropriate values in phosphatized limestone (0.15 % and 6 ppm). It shows that there is a link between enhanced uranium uptake by phosphatized coprolite and its organic matter enrichment despite the higher initial uranium concentration in this sample. These results may be considered as a proof of assumption [3] about important role of organic matter in accumulation of uranium by oceanic phosphorites occurring owing to reduction processes in enclosing organic-rich sediments.

References

1. *Baturin G.N.* Uranium in recent marine sedimentation. M.: Atomizdat, 1975. 152 p.
2. *Baturin G.N., Kochenov A.V.* Uranium concentration in oceanic phosphorites // Lithology and Miner. Resources. 1974. N 1. P. 124–129.
3. *Baturin G.N., Kochenov A.V.* Uranium in phosphorites // Ibid. 2001. N 4. P.353–373.
4. *Baturin G.N.* Phosphorites on the sea floor. M.: Nauka, 1978. 230 p.
5. *Baturin G.N., Dubinchuk V.T., Kochenov A.V.* Uranium in process or recent phosphorite formation // Geochemistry. 1986. N 9. P. 1277–1284.