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Uranium in Supergene Phosphorites

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Abstract—The distribution of uranium was studied in supergene phosphorites from the zones of the weathering of sedimentary and endogenous rocks, as well as in nonmarine coprolitic phosphorites and, to a lesser extent, phosphorites from ocean islands. These phosphorites show a diversity of the composition of their carbonate-apatite and structural characteristics. The uranium content ranges mostly from 5 to 100 ppm, with minimum and maximum values of 0.5 and 790 ppm. There is no correlation between the uranium content of a phosphorite and the type of rock with which it is connected. Lacustrine coprolitic phosphorites show elevated uranium contents (about 200 ppm). The maximum uranium content was detected in finely laminated phosphorite encrustations. The correlation analysis of the whole data set (63 samples) showed that uranium content is not correlated with any other component of phosphorites at a confidence level of 0.95. In contrast, there is a correlation between U and P_2O_5, CaO, and F for the combined set of samples from southern Siberian deposits. The significant correlation of U with Na_2O and CO_2 is variable both for southern Siberia on the whole and for particular deposits from this region.

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INTRODUCTION

Phosphorites are widely used as a raw material for the production of fertilizers or directly as fertilizers. Their properties, including trace-element characteristics, have been extensively studied. Trace element studies are important for the elucidation of general relations in the behavior of elements in sedimentary rocks and for the practical agrochemical utilization of phosphorites, because some trace elements in phosphorites are microfertilizers, whereas others, for instance, uranium, are ecologically hazardous [1]. On the other hand, phosphorites may be important uranium ores, and a considerable portion of the uranium production of the United States is extracted from phosphorites [2].

Most studies of trace elements (including uranium) in phosphorites focused on marine phosphorites. Uranium in supergene phosphorites has been studied much less extensively. High uranium contents were reliably detected in calcium aluminophosphates of the crandallite group [3–10]. These publications were reviewed by us elsewhere [11]. The uranium content of phosphates of this type is beyond the scope of this study, which focuses on the distribution of uranium in apatite-group calcium phosphates, predominant in supergene phosphorites. Uranium was only sporadically analyzed in such phosphorites in some particular complexes and was never studied systematically. Moreover, only correlations between uranium and phosphorus were considered, whereas its relations with all other components of carbonate-apatite were never determined. The only inference on the content of uranium in supergene phosphorites was made by Levina et al. [12], who claimed that supergene (infiltration-related residual and redeposited) phosphorites are enriched in uranium compared with marine ones. At the present time, the general validity of this statement is debatable.

A number of studies (e.g., [13–24]) have been concerned with the characterization of the petrographic and mineralogical features of supergene phosphorites. The goal of this paper was to evaluate uranium contents in supergene phosphorites taking into account their genetic, chemical, mineralogical, and structural features.

METHODS

All the phosphorites analyzed for uranium were preliminarily examined using a petrographic polarization microscope and a scanning electron microscope (JSM-35). The results of these investigations were published elsewhere [22, 25, 26, etc.]. The chemical compositions of phosphorites were determined using routine methods. The abundances of P_2O_5, Al_2O_3, Fe_2O_3, TiO_2, FeO, and F were measured by spectral photometry; CaO, MgO, and MnO, by atomic absorption; K_2O and Na_2O, by flame photometry; CO_2, by the volumetric method; and SO_3, by the weighing method. Standard samples (120b, Ak, Ar, SG-1a, ST-1a, and SA) were used during analysis. Uranium content was determined by instrumental neutron activation analysis. The sensitivity of measurements was 0.1 ppm, and the possible relative error was 10%. The standard samples BCR-32

and CHC-2 were used for the calculation of uranium concentration. The plausibility of uranium contents obtained by this method was previously demonstrated by Gavshin and Zakharov [27]. The analyses were performed at the Analytical Center of the United Institute of Geology, Geophysics, and Mineralogy, Siberian Division, Russian Academy of Sciences.

GENERAL CHARACTERISTICS OF THE MATERIALS

The materials selected for our investigation were representative in three aspects: geologic factors, structural features of phosphorites, and phosphorite chemistry (Table 1). The geologic factors included the character of the parental rocks of supergene phosphorites, the morphological types of occurrence, and, in some cases, the environments of their formation. Both sedimentary and endogenous rocks served as parent materials for the supergene phosphorites. The former are represented mainly by carbonate and terrigenous–carbonate rocks or primary phosphorites, and the latter are mainly carbonatites and ultrabasic alkaline rocks [13–24]. Phosphorites of the first type were studied by the example of samples from the deposits and occurrences of southern Siberia (Belkinskoe, Obladzhan, Seibinskoe, Telek, and Irsym), Southern Urals (Ashinskoe), southern Kazakhstan (Dzhanytas in the Karatau Basin), central Kazakhstan (Mirnyi), Belgium (Liege region), Spain (Extremadura Province), India (Aravalli Basin), and the United States (land pebble phosphorites of Florida and brown phosphorites of Tennessee). Our collection included coprolitic phosphorites from caves of southern Siberia (Arkheologicheskaya Cave) and phosphate coprolites from the lacustrine deposits of the Lake Zaysan region, Kazakhstan. The zones of weathering of endogenous rocks were represented by supergene phosphorites from the Maymecha–Kotui province of ultrabasic alkaline rocks in northern Siberia (Magan, Yraas, and Essei massifs) and carbonatite massifs of the eastern Sayan (Belaya Zima) and the Kola Peninsula (Kovdor). The regions of coexisting endogenous and sedimentary rocks were exemplified by phosphorites from the Antonovsko–Lipovskoe occurrence in the Central Urals and the Lahn deposit in the Nassau region, Germany. Phosphorites from Christmas Island in the Indian Ocean were also analyzed (Fig. 1, Table 1).

Supergene phosphorites show the following structural types: massive, nodular, coprolitic (Fig. 2), and encrusting. The latter are subdivided into relatively coarsely laminated with centimeter- to millimeter-sized layers (Fig. 3) and finely laminated, in which tens to hundreds of consistent layers may be observed in a single sample or even a single thin section (Figs. 4, 5). In some cases, finely laminated phosphorites form large blocks. All these structural varieties of supergene phosphorites were represented in our collection (Table 1). The occurrences (deposits) of phosphorites have mainly depression–karst and apron morphologies, and the prevailing structural type of phosphorites is massive; brecciated phosphorites composed of fragments of earlier phosphorites and country rocks, as well as nodular and encrusting phosphorites were observed occasionally. Less common is the development of phosphorites along fractures; such phosphorites are encrusting by definition. Cave and lacustrine coprolitic phosphorites should be considered separately. The chemical compositions of supergene and marine phosphorites may be similar but never identical. Phosphate-rich marine phosphorites show very stable compositions, provided they are not affected by the processes of weathering and catagenesis. The abundances of characteristic components in them recalculated to a monomineralic or almost monomineralic composition are the following: 5.5–6.5% CO_2, 2.5–4.0% F, and 1.0–1.5% Na_2O, although there are a number of marine phosphorite occurrences with lower contents. As to supergene phosphorites, they may exhibit a considerable scatter in these components even within a single deposit (Table 1). Marine phosphate deposits contain fluorine-bearing carbonate-apatites, occasionally with a minor admixture of hydroxyl; their F content varies from 4.56% (Table 1, sample 4163 rl/L) to a few tenths of percent; occasionally, F is almost completely lacking, and the mineral is then hydroxycarbonate-apatite (Table 1; samples Ts-1, 4724 Isp, OR-1, and 4752-OR). All marine apatites are carbonate-apatites, whereas supergene apatite may contain less than 1% CO_2 (Table 1; samples 2011, 4931-r.l, 2854-Tl, 4761Tn, 4743 Ir, etc.) and are not carbonate-apatites according to the current classification. Their maximum CO_2 content is higher than 5% (Table 1; samples 1278-KG, 1295-z, and 1295-zh). The content of Na_2O in the marine phosphorites is relatively rare below 1%, whereas the supergene phosphorites have almost always <1% Na_2O. In the sample set studied, only one sample contains more than 1% Na_2O (sample 7778-Y), and a number of samples show less than 0.1% Na_2O (Table 1; samples 2011, 4931-r/l, 0109r/lI, 4163r/lL, 6209Ki, etc.). Finally, it should be noted that variations in P_2O_5 (24–40%) and CaO (34–57.67%) in our samples were significantly lower than variations in F (0–4.56%) and Na_2O contents (0.04–1.23%).

CONCENTRATIONS OF URANIUM IN THE PHOSPHORITES OF MAIN GENETIC AND MORPHOLOGICAL GROUPS

Coprolitic Phosphorites

This group is represented by phosphorite from the Arkheologicheskaya Cave in Khakassia (sample Ts-1) and Eocene lacustrine phosphorites from the Lake Zaysan region, Kazakhstan. Their uranium contents are distinctly different: 1.8 ppm in the former and 75–208 ppm in the latter (Table 1). The lacustrine coprolitic phosphorites show the maximum uranium contents among all the samples. Four of five samples contained more than 100 ppm U, averaging 141.6 ± 54.9 ppm for all

Table 1. Chemical compositions of supergene phosphorites

Sample	Region	Deposit, occurrence	Deposit type	Phosphorite structure	Concentration														U/P_2O_5 × 10^{-4}
					%													ppm	
					SiO_2	Al_2O_3	TiO_2	Fe_2O_3	CaO	MgO	MnO	Na_2O	K_2O	P_2O_5	CO_2	SO_3	F	U	
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
Cave coprolitic phosphorite																			
Ts-1	Southern Siberia	Arkheologicheskaya Cave	Cave	Encrustation, coarsely laminated	22.09	2.80	0.10	0.39	48.66	0.48	0.04	0.25	0.36	31.52	1.65	0.65	0.004	1.80	0.057
Lacustrine coprolitic phosphorites																			
2f	Eastern Kazakhstan, Lake Zaysan region	Eocene deposits	Lacustrine	Coprolitic, massive	0.82	0.13	0.00	0.77	52.59	0.19	1.09	0.53	0.03	34.2	2.85	2.85	3.44	75.0	2.21
32f					0.59	0.00	0.00	0.44	51.17	0.38	1.28	0.67	0.05	32.09	3.89	0.84	2.82	131.0	4.08
8sh					0.30	0.00	0.00	0.66	50.89	0.28	1.13	0.99	0.04	33.26	3.89	0.0	3.04	108.0	3.25
7293-1b					0.37	0.00	0.00	1.66	52.35	0.15	1.41	0.38	0.02	35.16	3.11	0.29	2.96	208.0	5.92
7293-1a				Encrustation, coarsely laminated	–	–	–	–	–	–	–	–	–	–	–	–	–	186.0	–
Supergene phosphorites in the areas of sedimentary rocks																			
2011	Southern Siberia	Belkinskoe	Depression–karst	Massive	4.04	0.61	0.00	0.44	53.72	0.13	0.05	0.04	0.05	38.41	0.78	0.0	3.6	8.0	0.21
6-Obl		Obladzhan			0.81	0.08	0.03	0.00	57.67	1.06	0.03	0.33	0.01	38.98	1.17	0.08	2.94	40.4	1.04
7-Obl					0.86	0.10	0.03	0.00	57.61	1.01	0.03	0.30	0.01	38.76	1.46	0.05	2.51	113	2.91
11-Obl					0.76	0.04	0.02	0.26	57.46	1.04	0.03	0.34	0.01	38.85	1.21	0.12	2.82	84.0	2.16
4-Dzh		Seibinskoe (Bolshie Djebarty section)			33.88	1.56	0.07	1.19	34.53	0.80	0.01	0.30	0.08	22.11	2.97	0.00	1.52	38.0	1.72
11-Dzh					19.52	1.43	0.10	0.00	43.53	0.83	0.14	0.30	0.11	27.25	3.42	0.00	1.00	40.0	1.47
14-Dzh					22.76	1.96	0.12	3.32	39.48	0.85	0.08	0.30	0.04	24.95	3.19	0.00	1.76	36.0	1.44

Table 1. (Contd.)

Sample	Region	Deposit, occurrence	Deposit type	Phosphorite structure	Concentration														$U/P_2O_5 \times 10^{-4}$
					%													ppm	
					SiO_2	Al_2O_3	TiO_2	Fe_2O_3	CaO	MgO	MnO	Na_2O	K_2O	P_2O_5	CO_2	SO_3	F	U	
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
1283-a		Seibinskoe (Karaul'naya gorka prospect)		Encrustation, coarsely laminated	1.86	0.76	0.00	0.33	53.18	0.00	0.00	0.35	0.16	35.47	3.84	0.00	2.87	45.0	1.27
1295-zh					1.50	0.41	0.00	1.00	53.91	0.04	0.09	0.45	0.18	34.60	5.19	0.00	2.99	33.5	0.97
1295-z					1.10	0.56	0.00	1.00	55.70	0.08	0.05	0.45	0.18	34.60	5.28	0.01	3.39	29.4	0.85
1278-KG				Massive	0.63	0.00	0.05	0.00	52.96	0.37	0.05	0.67	0.04	36.88	5.03	0.00	2.92	25.6	0.69
1277-KG					4.30	0.65	0.00	0.29	50.28	0.00	0.01	0.27	0.08	35.0	4.75	1.14	2.70	19.7	0.56
1283-b					1.44	0.28	0.00	0.35	55.18	0.00	0.00	0.40	0.19	35.54	3.29	0.00	2.82	32.0	0.90
2854-TL		Telek			0.20	0.16	0.00	0.36	55.36	0.01	0.03	0.19	0.05	40.89	0.55	0.00	2.81	11.9	0.29
2233-TL					0.15	0.37	0.00	0.71	54.04	0.15	0.25	0.16	0.05	40.00	0.55	0.03	3.00	10.2	0.25
2941-TL					0.07	0.26	0.00	0.41	54.64	0.13	0.02	0.22	0.05	39.14	1.10	0.01	3.00	7.9	0.20
2947b-TL					6.18	1.61	0.00	4.04	47.98	0.00	0.06	0.27	0.07	33.35	2.93	0.00	1.50	27.0	0.81
2271-TL					11.4	0.66	0.00	0.3	47.27	1.70	0.12	0.27	0.07	31.10	3.29	0.00	2.00	23.5	0.76
5055a-TL					2.74	3.32	0.00	0.84	50.34	0.00	0.00	0.24	0.03	35.80	2.56	0.00	3.42	28.0	0.78
5055b-TL				Encrustation, coarsely laminated	3.68	2.47	0.00	0.30	50.58	0.00	0.00	0.27	0.03	35.41	3.11	0.00	3.40	22.5	0.63
2271k-TL					8.40	0.86	0.00	0.33	47.20	3.40	0.00	0.30	0.09	31.15	3.29	0.00	1.25	29.0	0.93
2947a-TL					3.50	2.09	0.00	1.00	50.81	0.00	0.00	0.34	0.10	34.03	3.29	0.00	1.37	17.9	0.52
3539-Asha	Southern Urals	Ashinskoe	Depression–karst	Nodular	0.00	0.00	0.00	0.70	53.47	0.00	1.72	0.47	0.10	38.9	1.34	0.00	3.45	4.9	0.13
3545-Asha				Massive	2.01	0.00	0.00	0.28	53.47	0.00	1.33	0.52	0.07	36.8	2.01	0.00	3.65	6.3	0.17
4931-r/l	Southern Kazakhstan	Karatau Basin, Dzhanytas deposit	Fracture	Encrustation, finely laminated	0.37	0.00	0.00	0.00	55.42	0.40	0.01	0.04	0.03	39.47	0.78	0.00	3.74	5.8	0.15
4926-r/l					0.00	0.38	0.00	0.00	54.60	0.00	0.00	0.38	0.06	38.59	3.70	0.00	3.70	3.4	0.09
4929a-r/l					0.60	0.00	0.00	0.29	53.08	0.00	0.00	0.36	0.04	39.50	1.48	0.15	3.50	3.0	0.08
4929b-r/l					0.25	0.00	0.00	0.29	53.08	0.00	0.00	0.36	0.4	39.50	2.11	0.03	3.50	2.9	0.07
4915-k/m					2.50	0.60	0.00	0.00	54.28	0.00	0.00	0.40	0.10	34.20	3.59	0.10	4.00	17.0	0.50
4916-b					17.40	4.50	0.00	1.33	40.51	0.00	0.03	0.3	0.23	28.80	1.69	0.12	2.70	101.0	3.51
4916-k					2.85	0.90	0.00	0.74	52.61	0.00	0.00	0.40	0.10	38.00	1.48	0.05	3.50	12.0	0.32
4818M	Central Kazakhstan	Mirnyi occurrence	Fracture	Encrustation, coarsely laminated	5.63	1.80	0.00	1.68	48.69	0.00	0.34	0.26	0.30	33.16	3.21	0.00	1.50	23.1	0.70
4818 st				Encrustation, finely laminated	0.8	0.00	0.00	0.42	54.64	0.00	0.00	0.33	0.02	36.87	3.00	0.00	1.87	8.2	0.22

Table 1. (Contd.)

Sample	Region	Deposit, occurrence	Deposit type	Phosphorite structure	Concentration														$U/P_2O_5 \times 10^{-4}$
					%													ppm	
					SiO_2	Al_2O_3	TiO_2	Fe_2O_3	CaO	MgO	MnO	Na_2O	K_2O	P_2O_5	CO_2	SO_3	F	U	
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
Supergene phosphorites in the areas of sedimentary rocks																			
4724 Isp	Spain	Extremadura	Encrustation	Encrustation, finely laminated	0.10	0.28	0.00	0.14	54.34	0.00	0.00	0.48	0.06	40.50	1.11	0.00	0.02	0.9	0.02
4742 Liege	Belgium	Liege region	Depression–karst	Encrustation, finely laminated	6.59	1.52	0.06	0.22	52.59	0.17	0.00	0.60	0.34	32.42	3.11	0.00	3.96	31.8	0.98
4756 Fl	Florida	Region of land pebble phosphorites	Blanket-like	Massive, hard rock	–	–	–	–	–	–	–	–	–	–	–	–	–	87.0	–
4761-Tn	Tennessee	Region of brown phosphorites	Blanket-like	Massive	14.8	4.77	0.24	3.26	39.75	0.00	0.00	0.66	0.74	28.20	0.67	0.00	3.00	10.0	0.35
4762-a-Tn				Encrustation, coarsely laminated	2.20	0.85	0.00	0.00	54.45	0.00	0.00	0.33	0.12	37.10	2.58	0.00	3.50	6.0	0.16
4762-b-Tn				Encrustation, finely laminated	1.00	0.20	0.00	0.00	54.92	0.00	0.00	0.36	0.06	36.75	4.39	0.00	3.40	18.7	0.51
4743 Ir	Southern Siberia	Irsym	Unclear	Encrustation, finely laminated	0.7	0.15	0.00	0.00	55.56	0.00	0.00	0.33	0.06	40.27	0.17	0.00	3.45	115.0	2.86
0109r-l/I	India	Aravalli Basin, Jhamarkotra deposit	Fracture	Encrustation, finely laminated	0.22	0.00	0.00	0.00	57.62	0.09	0.02	0.03	0.01	39.40	1.81	0.00	3.74	72.0	1.82
0118r-l/I					1.50	0.00	0.03	0.00	54.96	0.24	0.02	0.36	0.14	37.00	2.59	0.00	3.30	790.0	21.35

Table 1. (Contd.)

Sample	Region	Deposit, occurrence	Deposit type	Phosphorite structure	Concentration														$U/P_2O_5 \times 10^{-4}$
					%													ppm	
					SiO_2	Al_2O_3	TiO_2	Fe_2O_3	CaO	MgO	MnO	Na_2O	K_2O	P_2O_5	CO_2	SO_3	F	U	
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
Supergene phosphorites in the areas of sedimentary and endogenous rocks																			
4163r-l/L	Germany, Nassau	Lahn	Blanket-like, pockets	Finely laminated	0.90	0.00	0.00	0.00	55.98	0.05	0.02	0.05	0.02	37.23	2.59	0.00	4.56	3.6	0.10
4163-L				Massive	19.5	0.34	0.00	5.43	41.85	0.7	0.22	0.04	0.17	27.55	1.81	0.00	3.10	3.6	0.13
PEB-L					7.63	3.63	0.37	1.66	48.07	0.13	0.30	0.06	0.38	30.56	3.11	0.00	3.88	5.8	0.19
4709a-AL	Central Urals	Antonovskoe–Lipovskoe	Blanket-like	Massive	0.00	0.33	0.00	0.26	52.24	0.00	0.00	0.36	0.07	38.27	0.86	0.00	2.20	17.3	0.45
4717-AL					16.6	8.59	0.08	2.54	35.63	0.38	0.06	0.12	0.39	24.45	1.55	0.05	3.12	15.5	0.63
Supergene phosphorites in the areas of endogenous rocks																			
7058-B.Z	Southern Siberia	Belaya Zima massif	Blanket-like	Massive	1.02	0.45	0.00	5.22	50.63	0.00	0.00	0.38	0.05	32.60	4.24	0.00	3.95	60.0	1.84
7060-B.Z					0.02	0.45	0.00	3.38	53.60	0.00	0.15	0.42	0.05	33.25	4.07	0.00	4.07	54.0	1.62
6005	Northern Siberia	Essei massif	Blanket-like	Massive	0.40	0.00	0.24	13.46	46.80	0.00	0.81	0.27	0.08	32.24	2.01	0.00	2.87	6.1	0.19
6007					0.6	0.00	0.20	6.65	51.36	0.00	0.51	0.37	0.70	33.60	3.25	0.00	2.50	2.8	0.08
7599-1Mag		Magan massif			2.17	0.17	0.00	0.88	54.32	0.48	0.19	0.08	0.04	35.31	3.11	0.00	2.76	1.7	0.05
7590Mag					0.30	0.00	0.00	1.60	53.90	0.00	0.06	0.48	0.08	36.50	3.57	0.06	2.75	0.5	0.02
7778-Y		Yraas massif			6.90	0.00	0.10	4.05	46.60	0.00	0.60	1.23	0.10	34.50	3.48	0.00	1.12	1.5	0.04
7878-Y					0.30	0.00	0.00	0.59	53.60	0.00	0.03	0.50	0.11	38.45	2.81	0.00	2.10	1.0	0.03
6241r/lK	Kola Peninsula	Kovdor massif	Blanket-like	Finely laminated	0.55	0.00	0.00	0.34	54.00	0.00	0.00	0.45	0.04	35.60	2.30	0.07	3.00	122.0	3.43
6209K				Massive	3.22	3.93	0.11	4.32	44.40	0.34	0.12	0.05	0.03	32.93	2.33	0.00	2.32	5.7	0.17
Island phosphorites																			
OR-1	Indian Ocean	Christmas I.	Blanket-like	Massive	2.10	0.90	0.00	0.57	51.68	1.00	0.00	0.61	0.03	38.00	2.53	0.45	0.23	5.7	0.15
4752-OR					0.60	0.00	0.00	0.17	53.04	0.00	0.00	0.82	0.04	38.60	4.01	0.04	0.00	2.1	0.05

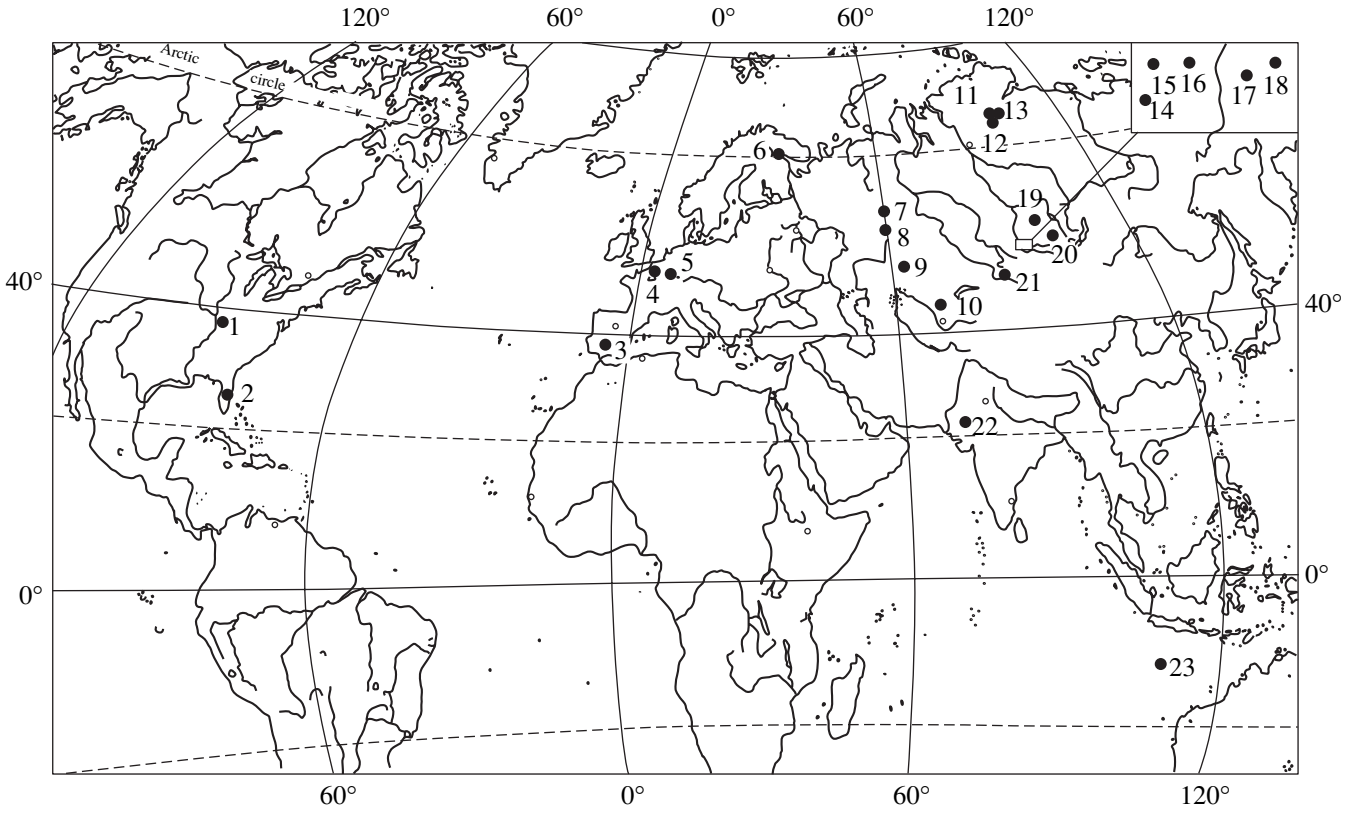

Fig. 1. Location of phosphorite deposits and occurrences considered in this study. Numbers on the map: 1, brown phosphorites of Tennessee; 2, hard rock phosphorites of Florida; 3, phosphorites of the Extremadura province, Spain; 4, phosphorites of the Liege region, Belgium; 5, Lahn deposit, Nassau region, Germany; 6, Kovdor massif, Kola Peninsula; 7, Antonovsko–Lipovskoe occurrence, Central Ural; 8, Ashinskoe deposit, Southern Ural; 9, Mirnyi occurrence, Central Kazakhstan; 10, Dzhanytas deposit, Karatau Basin, Southern Kazakhstan; 11–13, massifs (deposits) of the Maymecha–Kotui Province of ultramafic alkaline rocks: 11, Magan massif; 12, Essei massif; and 13, Yraas massif; 14–20, deposits and occurrences of southern Siberia: 14, Belkinskoe deposit; 15, Arkheologicheskaya Cave; 16, Obladzhan deposit; 17, Telek deposit; 18, Seibinskoe deposit; 19, Belaya Zima massif (deposit); 20, Irsym occurrence; 21, occurrence of Eocene coprolitic phosphorites from the Lake Zaysan region, Kazakhstan; 22, Jhamarkotra deposit, Aravalli Basin, India; and 23, Christmas I., Indian Ocean.

samples. These values are similar or identical to the uranium contents of granular marine phosphorites from the majority of relatively young (Cretaceous–Paleogene) deposits worldwide [28], including the deposits of northern Africa, which are considered by us and other authors [29, 30] as coprolites. In one sample, uranium was analyzed in brown phosphate from the inner part of coprolite (sample 7293-1b) and in a white phosphate crust on the surface of the coprolite (sample 7293-1a). In both cases, the phosphates are massive and cryptocrystalline. The contents of uranium in the phosphates were 208 ppm in the inner part of the coprolite and 186 ppm in the crust (Table 2).

Supergene Phosphorites from the Areas of Occurrence of Sedimentary Rocks

Most of the phosphorites from the zones of the weathering of sedimentary rocks are massive. In most phosphorite samples of this type, the uranium content ranges from 10 to 100 ppm, occasionally falling beyond these bounds. In particular, such uranium contents are characteristic of phosphorites from almost all karst deposits of southern Siberia, except for the aforementioned phosphorite from the Arkheologicheskaya Cave. For instance, an average uranium content of 30.9 ± 8.5 ppm was obtained for six samples from the Karaul'naya gorka prospect of the Seibinskoe deposit, 38.0 ± 2.0 ppm for three samples from the Bol'shie Dzhebarty prospect, 19.8 ± 8.1 ppm for nine samples from the Telek deposit, and 79.1 ± 36.5 ppm for three samples from the Obladzhan deposit. Uranium contents of 15.5 and 17.3 ppm were measured in two samples from the Antonovsko–Lipovskoe occurrence in the Central Urals; the phosphorites of the Liege region (Belgium) and the hard rock phosphorites of Florida contained 31.8 and 87 ppm U, respectively. On the other hand, some samples of massive phosphorites showed less than 10 ppm U. For instance, samples from the Belkinskoe and Ashinskoe (sample 3545) deposits contained only 8 and 6.3 ppm U, respectively. A sample of nodular phosphorite from the latter deposit (sample 3539) showed even lower U content of 4.9 ppm. In general, the phosphorites of this group from particular

Fig. 2. Coprolitic phosphorites from the Eocene deposits of the Lake Zaysan region, Kazakhstan. Diminution 0.7.

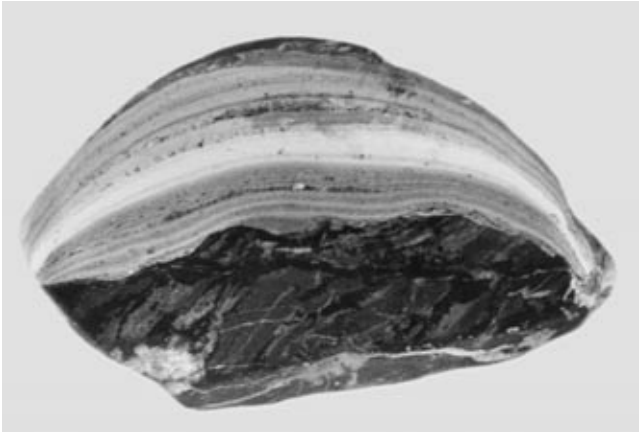

Fig. 3. Massive and encrustation supergene coarsely laminated phosphorites of the Seibinskoe deposit. Sample 1283, magnification 1.1.

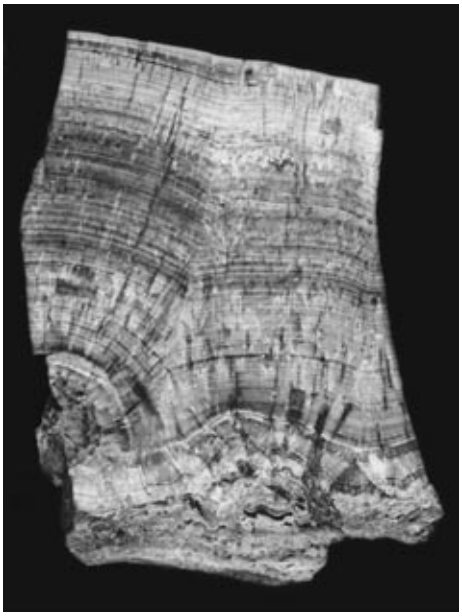

Fig. 4. Supergene coarsely laminated phosphorite encrustations from the Dzhanytas deposit, Karatau Basin. Diminution 0.7.

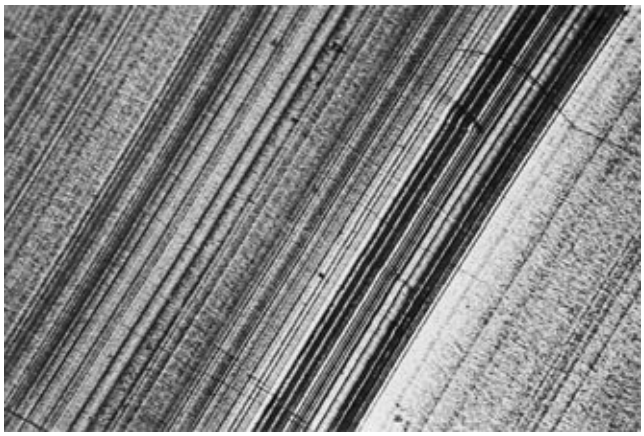

Fig. 5. Supergene finely laminated phosphorite encrustation from the Dzhanytas deposit, Karatau Basin. Sample 4931, thin section, magnification 50.

deposits or even regions (e.g., southern Siberia) have rather consistent uranium contents.

Encrustation phosphorites enclose fragments (nodules) of massive phosphorites or develop along the walls of fractures in them and in the country rocks. As was noted above, there are coarsely and finely laminated varieties. The thickness of layers in the former is from a few millimeters to a few centimeters. The U content and $U/P_2O_5 \times 10^{-4}$ ratio in crusts of this type is mostly somewhat higher than in the underlying massive phosphorites (Table 2; samples 1283, 2271, and 5055) or in the encrustations of an earlier stage. The latter is especially distinct in sample 4916 from the Dzhanytas deposit in the Karatau Basin (Table 2), where the U contents in the inner and outer parts of an encrustation were 12.1 and 101 ppm, respectively. This tendency is less pronounced in sample 1295 from the Seibinskoe deposit, where the uranium content varied from 29.4 ppm in the inner part to 33.5 ppm in the outer part of an encrustation. Only in sample 2947 from the Telek deposit, the uranium content in an encrustation (17.9 ppm) appeared to be lower than in the underlying massive phosphorite (27 ppm).

The thickness of individual layers in finely laminated crusts is usually no more than a few tens of micrometers. When such encrustations accompany coarsely laminated ones, they were always confined to the late stages of the formation of the phosphorite deposit. The uranium content of the finely laminated crusts may be both low and extremely high. For instance,

Table 2. Uranium contents in supergene encrustation phosphorites

Deposit, occurrence	Massive phosphorite at the base of phosphorite crust	Uranium, ppm	Encrustation phosphorite							
			Coarsely laminated				Finely laminated			
			Inner part of crust	Uranium, ppm	Outer part of crust	Uranium, ppm	Inner part of crust	Uranium, ppm	Outer part of crust	Uranium, ppm
Lacustrine coprolitic phosphorites from the Lake Zaysan region	7293-1b	208	–	–	7293-1a	186	–	–	–	–
Seibinskoe, Karaul'naya gorka prospect	1283-b	32	–	–	1283-a	45	–	–	–	–
Same	–	–	1295-z	29.4	1295-zh	33.5	–	–	–	–
Telek	2947b-Tl	27	–	–	2947-a-Tl	17.9	–	–	–	–
Same	2271-Tl	23.5	–	–	2271k-Tl	29	–	–	–	–
Same	5055b-Tl	22.5	–	–	5055a-Tl	28	–	–	–	–
Mirnyi, Kazakhstan	–	–	4818M	23.1	–	–	–	–	4818 st	8.2
Dzhanytas, Kazakhstan	–	–	–	–	–	–	–	–	4931-r/l	5.8
Same	–	–	–	–	–	–	–	–	4926-r/l	3.4
Same	–	–	–	–	–	–	4929b-r/l	2.9	4929a-r/l	3.0
Same	–	–	–	–	4915	17	–	–	–	–
Same	–	–	4916-k	12.1	4916-b	101	–	–	––	–
Irsym	–	–	–	–	–	–	–	–	4743	115.2
Extremadura, Spain	–	–	–	–	–	–	–	–	4724	0.9
Tennessee, USA	–	–	–	–	4762-a-Tn	6	–	–	4762-b-Tn	18.7
Belkinskoe					2011	8				
Aravalli Basin, India	–	–	–	–	–	–	–	–	0109	72
	–	–	–	–	–	–	–	–	0118	790
Kovdor massif	6209k	5.7	–	–	–	–	–	–	6241r/l	122
Lahn deposit, Nassau, Germany	4163	3.6	–	–	–	–	–	–	4163r/l	3.6

in the Dzhanytas deposit of the Karatau basin, finely laminated crusts (Table 2) contain from 2.9 to 5.8 ppm U. Very low U (0.9 ppm at a $U/P_2O_5 \times 10^{-4}$ of 0.02) was measured in a finely laminated phosphorite encrustation from an occurrence of the Extremadura Province, Spain (Table 2, sample 4724). A similar phosphorite from the Irsym occurrence in eastern Siberia (sample 4743) contained 115.2 ppm U. In the Jhamarkotra deposit of the Aravalli basin, India, the uranium content in a finely laminated phosphorite crust was 72 ppm in sample 0109 and 790 ppm in sample 0118, which is the highest value in the whole sample set.

The uranium content of a finely laminated encrustation may be different compared with the underlying phosphorite, including the inner part of the same encrustation (Table 2). In particular, sample 4762 from the region of so-called brown phosphorites of Tennessee contains a finely laminated encrustation with 18.7 ppm U underlain by a coarser laminated crust with only 6.0 ppm. In contrast, in sample 4929 from the Dzhanytas deposit in the Karatau basin, the uranium contents in the inner and outer parts of an encrustation were 2.9 and 3.0 ppm, respectively, at $U/P_2O_5 \times 10^{-4}$ of 0.73 and 0.76. These values are identical within the accuracy of the chemical analysis. However, in spite of the considerable scatter, it can be concluded that the highest uranium contents are confined to finely laminated encrustations.

Supergene Phosphorites in the Areas of Occurrence of Endogenous Rocks

A specific feature of the majority of phosphorites of this group is their low uranium content. In particular, it was detected in all phosphorites from the Maymecha–Kotui Province of ultramafic alkaline rocks in northern Siberia. Phosphorite samples from this province collected at the Essei, Magan, and Yraas massifs (Table 1) contained from 0.5 to 6.1 ppm U and showed $U/P_2O_5 \times 10^{-4}$ ratios of 0.04–0.19. The former uranium content and the corresponding $U/P_2O_5 \times 10^{-4}$ value are the lowest among all the samples studied. In contrast, supergene phosphorites from the Belaya Zima carbonatite massif in the eastern Sayan contained 54–60 ppm U, i.e., 1–2 orders of magnitude more than the phosphorites of the Maymecha–Kotui province. A supergene massive phosphorite from the Kovdor massif (Kola Peninsula) contained 5.87 ppm U, whereas a finely laminated encrustation from the same locality showed 122 ppm U (Table 2; samples 6209k and 6241r/l, respectively). The tendency is similar to that observed in a number of phosphorites from the zones of the weathering of sedimentary rocks, which, however, is not universal. For instance, in massive supergene phosphorites formed by weathering of schalstein in the Nassau region, Lahn deposit, Germany, the uranium contents in samples 4163 and PEB-1 were 3.6 and 5.8 ppm at $U/P_2O_5 \times 10^{-4}$ of 0.13 and 0.19, respectively (Table 2). A finely laminated phosphorite encrustation (sample 6241 r/l) contained 3.6 ppm U at a $U/P_2O_5 \times 10^{-4}$ of only 0.97, i.e., the U content of the finely laminated phosphorite appeared to be lower than that of the massive phosphorite from the same sample.

Supergene Phosphorites of Ocean Islands

Independent of the source of phosphorus, the phosphorites of ocean islands were formed in shallow lagoon environments. The phosphate rocks of many islands were altered under laterite weathering conditions with the development of iron- and aluminum-calcium phosphates, primarily crandallite; phosphatization of volcanic rocks is common in some islands. Phosphorites from ocean islands were described in many publications (e.g., [16, 18, 22, 31–33]). Two phosphorite samples from Christmas Island in the Indian Ocean showed U contents of 5.7 ppm (sample OR-1) and 2.1 ppm (sample 4752-OR) (Table 2). Uranium contents of 13–40 ppm were previously reported for several samples from this island [10]. Baturin [33] measured uranium contents in a series of phosphorites from ocean islands, including Nauru, Pacific Ocean (56.9 ppm); Sala y Gomez, Pacific Ocean (8.2–10.0 ppm); and Astov and African atolls, Seychelles, Atlantic Ocean (45 and 24.5 ppm, respectively).

CORRELATION ANALYSIS

The analysis of correlations between uranium contents and major components of phosphorites was carried out for three groups of samples. The first group included all the 63 samples considered in this paper (Table 1). This group shows a considerable scatter in the abundances of the major elements of phosphorites, which are dominated by carbonate-apatite. The phosphorites of this group show the following variations: 22.0–40.9% P_2O_5, 34.5–57.7% CaO, 0–4.07% F, 0.17–5.03% CO_2, and 0.04–1.23% Na_2O. The uranium content of these phosphorites ranges from 0.5 to 790 ppm. As was noted above, the geographic and geologic features of the areas where the supergene phosphorites were sampled, as well as their structural and textural features, are different. The second group (22 samples) included the phosphorites of the depression–karst deposits of southern Siberia (Belkinskoe, Telek, and Obladzhan deposits and the Bol'shie Dzhebarty and Karaul'naya gorka prospects of the Seibinskoe deposit). The concentrations of carbonate-apatite components in the samples from these deposits are less scattered compared with the whole data set. The ranges of P_2O_5 (22–40%) and CaO contents (34.0–57.67%) are similar to those of the first group, whereas variations in F and Na_2O are only 1.0–3.42% and 0.04–0.45%, respectively. The third group (nine samples) included phosphorites from the Telek deposit only. The phosphorites of this group contain 31.1–40.89% P_2O_5, 47.2–54.64% CaO, 1.25–3.42% F, and 0.18–0.34% Na_2O. As can be seen, in terms of major-component

Table 3. Characteristics of uranium correlation with the major chemical components of phosphorites for different sample sets

Set	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	CaO	MgO	MnO	Na_2O	K_2O	P_2O_5	CO_2	F	SO_3
All samples $n = 63$	–0.08	–0.11	–0.05	–0.12	0.12	–0.02	0.09	0.06	–0.06	0.03	0.05	0.12	–0.6
Southern Siberia $n = 22$	0.19	*0.50*	–0.49	*0.55*	*0.50*	0.18	0.37	*0.44*	0.34	*0.50*	*0.45*	*0.47*	–0.05
Telek deposit $n = 9$	*1.0*	*1.0*	–	0.52	*1.00*	0.45	*0.78*	–11	*0.81*	*1.00*	0.13	*0.99*	0.53

Note: The values shown in italics correspond to significant correlations at the 0.95 confidence level.

contents, the phosphorites of the second group are more homogeneous than the phosphorites of the first group, and the third group is more homogeneous than the second group. The phosphorites of the second and third groups show uniform structural characteristics (massive phosphorites or coarsely layered crusts) and similar conditions of formation and occurrence. The results of correlation analysis (Table 3) showed that the uranium content of first-group phosphorites is not correlated at a confidence level of 0.95 with any major component of phosphorites. Moreover, the pair correlation coefficients are in all cases very low. Different relations were observed for the second-group phosphorites from the deposits of southern Siberia. Significant pair correlation coefficients corresponding to a confidence level of 0.95 were obtained for elements and oxides composing carbonate-apatite: 0.50 for CaO and P_2O_5, 0.47 for F, 0.45 for CO_2, and 0.44 for Na_2O. High pair correlation coefficients were observed with alumina (1.0) and iron oxides (0.55). The pair correlation coefficients between uranium and the major components of supergene carbonate-apatite were even higher for samples from the Telek deposit: 1.0 for CaO and P_2O_5, 0.99 for F, and 0.81 for K_2O. The coefficients of pair correlation of uranium with silicon and aluminum oxides increased up to 1.0, whereas those with iron oxides, Na_2O, and CO_2 became insignificant at the 0.95 confidence level.

DISCUSSION

The uranium content in the phosphorite samples considered here varies within a wide range from 0.5 to 790 ppm at $U/P_2O_5 \times 10^{-4}$ between 0.014 and 21.35. In most samples, the uranium content is no higher than 50 ppm, and the $U/P_2O_5 \times 10^{-4}$ ratio is lower than 1 for at least two-thirds of all samples. In this respect, the supergene phosphorites are sharply different from marine ones, in which this ratio is higher than 1 for Mesozoic–Cenozoic and some Paleozoic phosphorites [28]. The $U/P_2O_5 \times 10^{-4}$ ratio is often lower than 1 only in Precambrian and Early Cambrian phosphorites; however, in our opinion, these phosphorites were depleted in uranium at the expense of its removal from the crystal lattice of carbonate-apatite during catagenesis [34].

The extreme uranium contents were detected in the coprolitic phosphorites from the Arkheologicheskaya Cave (sample Ts-1, 1.8 ppm) and the Eocene lacustrine coprolitic phosphorites from the Lake Zaysan region (75–208 ppm). The low uranium content in the cave phosphorites is attributed to the specific physicochemical conditions of their formation, which were highly acidic and oxidizing owing to the decomposition of bat guano. Uranium is highly mobile under such conditions [35, 36] and was transported by cave waters probably before the beginning of carbonate-apatite formation, which occurred under mildly alkaline conditions. The Eocene lacustrine coprolitic phosphorites from the Lake Zaysan region were formed in different environments. The mineralization of guano occurred under neutral or weakly alkaline conditions, and in contrast to the aerobic cave conditions, in a water environment, which implies a rather low oxidation potential. On the other hand, the system contained abundant organic carbon derived from the coprogenic material, the oxidation of which occurred much more slowly compared with the transformation of the same material in the cave. We believe that the high uranium contents in these phosphorites were related to this organic matter. The relation of uranium with organic matter in phosphorites from a number of deposits and occurrences is well known [12, 28, 34, 37].

The uranium content of massive supergene phosphorites from the regions of the weathering of sedimentary and igneous rocks and ocean islands is stable in particular deposits and even regions. For instance, phosphorites from the depression–karst deposits of southern Siberia very rarely contain less than 10 ppm U, and their $U/P_2O_5 \times 10^{-4} > 0.5$ in the overwhelming majority of cases. In contrast, the uranium content of phosphorite samples from the Dzhanytas deposit of the Karatau basin is mostly no higher than 10 ppm and $U/P_2O_5 \times \times 10^{-4} \le 0.15$. The uranium content of phosphorites from the zones of the weathering of the ultramafic alkaline rocks of the Maymecha–Kotui province varies from 0.5 to 6.1 ppm ($U/P_2O_5 \times 10^{-4}$ is no higher than 0.19). The Belaya Zima phosphorites contain 54–60 ppm U at a $U/P_2O_5 \times 10^{-4}$ of 1.62–1.84. We attribute these distinctions to the different abundances of uranium in the country rocks that served as sources for the formation of the supergene phosphorites.

Elevated uranium contents were also often observed in phosphorite encrustations, especially finely laminated ones, compared with the underlying massive and coarsely laminated phosphorites; however, this is not always the

case. The maximum uranium content of 790 ppm was measured in a finely laminated phosphorite (sample 0118, Jhamarkotra deposit, Aravalli Basin, India). The finely laminated phosphorites show not only higher uranium contents compared with massive varieties, but also much greater variations within particular deposits and areas.

Data from the literature on the abundance of uranium in supergene phosphorites are in general consistent with our results. The brown phosphorites of Tennessee contain 10–30 ppm U [6], which is in agreement with our data (Table 1), although Altshuler [3] reported a single analysis of phosphorite from this locality with 0.74 ppm U and 27.2% P_2O_5. Supergene phosphorite from South Carolina contained 740 ppm U and 25.9% P_2O_5 [3]. High uranium contents were detected in lacustrine phosphorites from various regions, but their genetic interpretation is not obvious. In particular, the phosphate-bearing layers of the Tertiary lacustrine deposits of Nevada showed uranium contents of 1000 and 1200 ppm at 6.7 and 11.0% P_2O_5, respectively. The Eocene lacustrine phosphorites of Wyoming contained 2700 ppm U and up to 19% P_2O_5 [6, 38]. Phosphorites from the Middle Paleozoic nonmarine deposits of the Khakassia and Tuva intermontane basins in southern Siberia contained up to 4000 ppm U and 20–25% P_2O_5 [39]. On the other hand, about 50 ppm U and 19.2% P_2O_5 were reported for phosphorite from the bottom deposits of Lake Baikal [40]. These phosphorites were not studied by us.

A comparative analysis of uranium contents in supergene phosphorites and primary marine phosphorites, the weathering of which produced the supergene phosphorites, did not reveal any regular relationship. The U content in the primary unweathered phosphorites of the Aravalli Basin, India was 3.6–4.2 ppm [34], whereas the supergene finely laminated phosphorites contained 72–790 ppm U (Table 2, samples 0109 and 0118). The primary phosphorites of the Dzhanytas deposit, Karatau Basin, Kazakhstan contained 5–43 ppm U (the upper limit is probably overestimated) [12, 34], whereas the supergene phosphorites contained 2.9 (sample 4929b-r/l) and 101 ppm U (sample 4196-b) (Table 2).

The relation of uranium to the phosphate matter of phosphorites has been actively discussed in the literature. The traditional concept postulates isomorphic substitution of tetravalent uranium for calcium in (carbonate)-apatite (e.g., [4, 41, etc.]). However, the determination of the oxidation state of uranium in marine phosphorites showed that tetravalent uranium accounts often only for a minor fraction of total uranium content [42]. These observations are in agreement with an earlier suggestion that hexavalent uranium can be sorbed by phosphate as uranyl species [43]. This suggestion was supported by experiments [44, 45]. Since in the waters of the supergene zone, uranium occurs mainly as U^{6+} in uranyl ions, which is not incorporated as an isomorphic admixture into minerals because of its large size [46], we believe that the major portion of uranium is sorbed as uranyl on supergene phosphorites. Uranium minerals proper were never found in the supergene phosphorites.

In our opinion [22], the massive phosphorites are products of single-stage sedimentation from colloidal solutions, whereas the finely laminated phosphorite encrustations were formed as a result of pulsed repeated crystallization from true solutions. The total sorption capacity of such thin layers precipitated each time from a new solution portion was presumably high, which was responsible for the elevated and, occasionally, extremely high uranium contents.

In addition to phosphates, uranium may be connected to other phases of supergene phosphorites. The high correlation of uranium content with silica and alumina observed in the Telek deposit suggests its relation to aluminosilicates. Levina et al. [12] noticed the presence of uranite in supergene ("secondary") phosphorites. Uranium could be in part sorbed by iron and manganese oxides in supergene phosphorites [47]. This suggestion cannot be rejected but should be considered with caution. For instance, sample 0118 is characterized by the maximum uranium content, but its chemical analysis showed no traces of aluminum and iron. The presence of uranium minerals (uraninite, ningyoite, and coffinite) was reported in the literature mainly on the basis of electron microscope investigations [33, 48]. Some of our samples of supergene phosphorites were extensively examined with an electron microscope, but such phases were never observed.

The results of correlation analysis showed (Table 3) that within the whole set of phosphorite samples, uranium shows no significant correlation (at the 0.95 confidence level) with any component of phosphorites. In this respect, calcium phosphates are fundamentally different from aluminum–calcium phosphates, the presence of aluminum in which is always correlated with elevated uranium contents (e.g., [4, 5, 11]). There is apparently no such uranium indicator element in the calcium phosphates of the apatite group.

Levina et al. [12] inferred that direct correlations between U and P_2O_5 in secondary infiltration-related residual and redeposited phosphorites are often disturbed. In reality, the relationships are probably somewhat different and more consistent with the conclusion of Gavshin et al. [39] on the absence of a direct global correlation between uranium and phosphorus in marine phosphorites. According to these authors [39, p. 122], the tendency of U and P correlation in marine phosphorites and phosphate-bearing rocks is manifested to a varying degree only in particular regions. This conclusion, drawn from the evaluation of uranium and phosphorus correlations in marine phosphorites, is fully applicable to the supergene phosphorites studied by us. It should also be noted that we observed similar degrees of correlation of uranium with phosphorus, fluorine, and calcium in supergene phosphorites. The values of pair correlation coefficients approach 1 for a particular

deposit (Telek), are much lower than 1 but significant at the 0.95 confidence level for the phosphorites of southern Siberia in general, and become insignificant for the whole set of phosphorite samples. In the Telek deposit, there is a significant, although lower than for P_2O_5, CaO, and F, correlation of uranium with elements incorporated into the structure of apatite as isomorphic impurities (Mn and K), and there is no significant correlation with such ubiquitous components of marine and supergene phosphorites as Na and CO_2, although a significant correlation between uranium and these components was obtained for all deposits of southern Siberia. Thus, it can be concluded that a significant correlation between uranium and components of carbonate-apatite may exist on a local and regional scale. This corresponds primarily to the relation of uranium to the major components of the mineral: P, Ca, and F. There is a weaker relation with components occurring in carbonate-apatite as isomorphic impurities: Na, CO_3^{2-}, and Mn. On the other hand, there is a very strong correlation (correlation coefficient is close to one) of uranium with silica and alumina in the Telek deposit phosphorite, which is consistent with the hypothetical uptake of uranium by aluminosilicate minerals.

CONCLUSIONS

(1) Uranium contents were determined in supergene phosphorites from a representative collection characterizing their main morphological, chemical, and genetic varieties. The phosphorites are rich in P_2O_5 (24–40%) and CaO (34.0–57.67%) and show considerable variations in F (0–4.56%), CO_2 (0.17–5.03%), and Na_2O (0.04–1.23%).

(2) The uranium content in the supergene phosphorites ranges from 0.5 to 790 ppm, with the most common values within 5–100 ppm (65% of all samples). Uranium contents below 5 ppm and above 100 ppm were measured in 21 and 14% of all samples, respectively. The uranium contents of supergene phosphorites formed by weathering of sedimentary and endogenous rocks lie in general within the same limits. As to coprolitic phosphorites, a sample of cave phosphorite showed a uranium content of only 1.8 ppm, whereas five samples of lacustrine phosphorites gave an average uranium content of 141.6 ppm. The uranium contents of the supergene phosphorites are close to those of many Mesozoic–Cenozoic marine phosphorites, but the U/P_2O_5 ratio of the former is lower at the expense of higher P_2O_5 contents. On the other hand, the supergene phosphorites are enriched in uranium compared with ancient marine phosphorites, the low uranium of which is assigned to its removal from the crystal lattice of carbonate-apatite during catagenesis. In particular deposits, uranium content in supergene phosphorites may be both higher and lower than that of primary marine phosphorites.

(3) The correlation analysis of the whole data set showed that uranium is not correlated with any component of carbonate-apatite at the 0.95 confidence level. A correlation with uranium content was detected for P_2O_5, CaO, and F only at the scale of a region (in our case, southern Siberia) and, especially, a particular deposit (Telek). A significant correlation of uranium with Na and CO_2 was observed, but it is unstable and may even be insignificant in a single deposit.

(4) It was suggested that the main mechanism of uranium concentration in supergene phosphorites is the sorption of uranyl by phosphate minerals.

(5) Phosphorite encrustations, especially finely laminated ones, often show higher uranium contents than the underlying massive phosphorites. The maximum uranium content (790 ppm) was found in a finely laminated phosphorite crust. In our opinion, the massive phosphorites are products of single-stage phosphate precipitation from a colloid solution, whereas the phosphate mineral of finely laminated crusts was formed by repeated chemical crystallization from true solutions, which was probably favorable for the accumulation of uranium in them. However, high uranium contents were not always observed in finely laminated phosphorite crusts and probably reflect the concentration of uranium in phosphate-forming solutions.

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