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Trace Elements in Supergene Phosphorites

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Abstract—Supergene phosphorites were analyzed for Sr, Ba, Zn, Cd, Sc, Cr, Ag, and V, i.e., elements incorporated in carbonate-apatite by isomorphic substitution. The phosphorites were subdivided into four groups: (1) phosphorites related to the weathering of sedimentary rocks, (2) phosphorites related to the weathering of endogenous rocks, (3) lacustrine coprolite phosphorites, and (4) phosphorites of ocean islands. In all the phosphorites groups, Sr, Zn, and Ba were the most abundant of the trace elements, whereas Cd, Ag, and Sc showed the lowest concentrations. Variations in trace element contents between supergene phosphorites of different genetic groups or within a single group can be explained by the different compositions of weathered rocks and geochemical environments of supergene phosphorite formation. At the same time, the contents of some trace elements are correlated with the structural type of phosphorite. In particular, phosphorite crusts or only their outer parts show elevated contents of chalcophile elements (Cd, Zn, and Ag), whereas massive phosphorites and inner parts of crusts are often enriched in such lithophile elements as Sc, V, and Cr. It was found that Cd, Zn, Ag, Sr, and Ba are positively correlated with CO_2 but show negligible correlations with other constituents of carbonate-apatite.

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INTRODUCTION

Phosphorites are typically characterized by a wide spectrum of trace elements [1–8]. Some elements occur as isomorphic admixtures in (carbonate)-apatite, the major mineral of phosphorite, while others form individual minerals or associate with the accessory mineral components of phosphorites. This study focuses on the abundances and distribution of the elements of the former group in phosphorites. The following elements are incorporated in (carbonate)-apatite by isomorphic substitution: Ag, Sr, Ba, Cd, Zn, Sc, Cr, V, U, Y, REE, Bi, As, Br [9], and, possibly, I. The contents of these elements are usually lower than 1%. There is an extensive literature on trace elements in phosphorites, but most publications address marine phosphorites, whereas relatively few data exist on trace elements in supergene phosphorites and concern only some of the above elements. This paper reports the results of the analysis of supergene phosphorites for Ag, Sr, Ba, Cd, Zn, Sc, Cr, and V. The distribution of U in supergene phosphorites was reported by us previously [10], and other elements will be considered in future publications.

Trace elements were analyzed in phosphorites representing different geologic settings, structures, chemical compositions, and compositions of the source rocks. The contents of the trace elements in supergene phosphorites were compared with those in marine phosphorites. The trace element contents of marine phosphorites were strongly affected by catagenesis and weathering [11–14]. In particular, most of the Mesozoic and Cenozoic phosphorites of Africa were strongly affected by weathering, and even the most comprehensive publications on this region could not be used for our purposes. In addition, data on trace element contents in marine phosphorites are scattered and not always consistent with each other. Therefore, only the most comprehensive literature sources were used for comparison.

METHODS

The supergene phosphorites whose trace element characteristics are reported in this paper were previously studied chemically and petrographically using an optical polarization microscope and a JSM-35 scanning electron microscope [15–19]. The contents of P_2O_5, Al_2O_3, Fe_2O_3, TiO_2, FeO, and F were determined by spectrophotometry; CaO, MgO, and MnO were analyzed by atomic absorption; K_2O and Na_2O, by flame photometry; CO_2, by the volume method; and SO_3, by the weight method. Standard samples 120b, BCR-32, Ak, Ar, SG-1a, ST-1a, and SA were used during analysis. Most trace elements were analyzed by atomic absorption on Unicum SP-9 and Perkin-Elmer HGA-600 instruments using the SGKhM-2, SGKhM-3, and SKR-2 standards. Only Sc was determined by instrumental neutron activation analysis. The detection limit was 0.1 ppm and up to 0.5 ppm for Cr at low contents. The possible relative error was 10%. All analyses were made at the Analytical Center of the Joint Institute of

Geology, Geophysics, and Mineralogy, Siberian Division, Russian Academy of Sciences.

CHARACTERISTICS OF THE MATERIALS

Based on geological characteristics, the supergene phosphorites were subdivided into four groups: (1) phosphorites formed in the areas of weathering of sedimentary rocks, (2) phosphorites formed in the areas of weathering of endogenous rocks, (3) lacustrine coprolite phosphorites, and (4) island phosphorites. The ancient weathering residues of sedimentary rocks were exemplified by karst and allied phosphorites from the following deposits and occurrence: Belkin, Telek, Obladzhan, Seibinsk, and Irsym in southern Siberia; Ashin in the southern Urals; Dzhantys in southern Kazakhstan; Mirnyi in Central Kazakhstan; Liege in Belgium; and deposits in Florida and Tennessee, United States. Supergene phosphorites from the areas of weathered endogenous rocks were studied by the example of the Magan, Yraas, and Essei massifs from the Maimecha–Kotui ultramafic alkaline province of northern Siberia, the Belaya Zima carbonatite massif of the East Sayan, and the Kovdor Massif of the Kola Peninsula. The phosphorites of the Antonov–Lipovsk occurrence in the Middle Urals and the Lahn deposit of the Nassau area, Germany, were presumably formed through weathering of sedimentary and endogenous rocks. Coprolite phosphorites were represented by the Eocene lacustrine deposits of the Zaisan Lake area in Kazakhstan. The coprolite phosphorites of the Arkheologicheskaya Cave in southern Siberia were considered together with supergene phosphorites developed in the areas of weathered sedimentary rock because of their resemblance in many components. Ocean island phosphorites were exemplified by the rocks of Christmas Island, Indian Ocean.

Structurally, the supergene phosphorites were subdivided into massive, nodular, coprolite, and crust varieties. The latter were additionally subdivided into relatively thick-bedded crusts with centimeter- to millimeter-thick layers and thin-bedded with layers thinner than 1 mm. Phosphorite crusts envelope phosphorite fragments of earlier generations or develop along fissures. Thin-bedded phosphorites occur occasionally as individual blocks up to several cubic meters in size. In some samples, trace elements were analyzed in the inner and outer parts of crusts or the trace element composition of massive phosphorites was compared with that of enclosing crusts.

ANALYTICAL DATA AND DISCUSSION

The major element compositions of the phosphorites are given in Table 1; their complete chemical compositions were reported elsewhere [10]. Most samples were almost monomineralic, but this requirement could not always be satisfied. As can be seen from Table 1, the main mineral of the phosphorites is carbonate-fluorapatite, with the exception of samples from the Arkheologicheskaya Cave and Christmas Island, which are practically free of fluorine and composed of carbonate-hydroxylapatite (dallite). In addition, carbonate-apatite from the phosphorites of the Maimecha–Kotui province contains oxygen substituting for monovalent anions. Some other phosphorites, primarily, those from the deposits of southern Siberia [16] and the Maimecha–Kotui Province in the northern part of the region [18] are characterized by a deficit of F. In general, carbonate-apatites contain more than 1% CO_2 in the form of a carbonate ion incorporated in the apatite structure [20]. As can be seen, most of our samples meet this criterion, with rare unsystematic exceptions. At the same time, the samples show considerable variations in CO_2 content, from less than 1% to more than 5%. The phosphorites have low Na_2O contents of a few tenths and occasionally even hundredths of a percent. Low Na content is a characteristic feature of supergene phosphorites [14], distinguishing them from marine phosphorites containing more than 1% Na_2O.

The contents of trace elements in supergene phosphorites are listed in Table 1 together with their major element compositions.

Lithophile Elements

Strontium and barium. In terms of Sr and Ba distribution, the material studied can be subdivided into four groups. The first group includes samples with Sr and Ba contents of tens and hundreds of ppm, with the predominance of either of these elements. This group involves supergene phosphorites related to sedimentary rocks. Only two samples (5055a and 5055b) from the Telek deposit have Sr contents of >1000 ppm. The average contents of Sr and Ba in this group are 397.4 ± 373 and 245.6 ± 155.5 ppm, respectively (Table 2). The average content of Sr is higher than that of Ba, but particular samples often show the opposite relation. The second group includes lacustrine coprolite phosphorites from the Zaisan Lake area. Their average Sr content is much higher than that of Ba (2932 ± 551 against 714 ± 115 ppm). It can be seen that the Sr content of this group is almost nine times that of the phosphorites of the first group, whereas the Ba content is only two times higher. The group of supergene phosphorites related to endogenous rocks contains 1289 ± 790 ppm Sr and 918 ± 516 ppm Ba. The fourth group comprises phosphorites from Christmas Island, which have the lowest Sr (176 ppm) and Ba (100–125 ppm) contents. The ranges of Sr and Ba variations for the groups are shown in Table 2. The lowest variations of these elements are observed in the Eocene lacustrine coprolite phosphorites of Zaisan Lake, the minimum and maximum values of which differ no more than by a factor of 1.6. The maximum-to-minimum ratios of Sr and Ba contents are 5–7 for the phosphorites formed after endogenous rocks and 24–26 for the phosphorites related to sedimentary rocks. According to Bliskovskii [21, 7], the Sr

Table 1. Chemical composition of supergene phosphorites

Sample No.	Region	Deposit, occurrence	Type of occurrence	Phosphorite structure	Content														
					%							ppm							
					SiO_2	Al_2O_3	CaO	Na_2O	P_2O_5	CO_2	F	Sc	Sr	Ba	V	Cr	Ag	Cd	Zn
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
Lacustrine coprolite phosphorites																			
2 f	Eastern Kazakhstan, Lake Zaisan area	Eocene deposits	Lacustrine	Coprolite massive	0.82	0.13	52.59	0.53	34.2	2.85	3.44	33.0	3465	524	43	18	<0.10	1.9	53
32f					0.59	0.00	51.17	0.67	32.09	3.89	2.82	15.2	3544	786	37	13	1.80	2.9	40
8sh					0.30	0.00	50.89	0.99	33.26	3.89	3.04	4.0	2808	802	31	13	5.00	1.3	39
7293-1b					0.37	0.00	52.35	0.38	35.16	3.11	2.96	17.70	2284	685	57	22	3.60	1.3	46
7293-1a				Crusted thick-bedded	–	–	–	–	–	–	–	124.0	2570	771	52	19	2.10	1.6	69
Supergene phosphorites related to sedimentary rocks																			
Ts-1	Southern Siberia	Arkheologicheskaya Cave	Cave	Crusted thick-bedded	22.09	2.80	48.66	0.25	31.52	1.65	0.004	n.d.	300	254	51	86	<0.10	8.1	1839
2011		Belkin	Basin–karst	Massive	4.04	0.61	53.72	0.04	38.41	0.78	3.6	1.08	105	171	279	24	<0.10	6.8	536
6-Obl		Obladzhan			0.81	0.08	57.67	0.33	38.98	1.17	2.94	0.14	682	171	74	27	0.32	15.0	93
7-Obl					0.86	0.10	57.61	0.30	38.76	1.46	2.51	0.17	840	150	48	12	3.10	11.3	114
11-Obl					0.76	0.04	57.46	0.34	38.85	1.21	2.82	0.10	604	107	105	14	1.40	3.6	124
4-Dzh		Seibin (Bol'shie Dzhebardy area)			33.88	1.56	34.53	0.30	22.11	2.97	1.52	4.10	735	465	218	64	4.30	16.2	700
11-Dzh					19.52	1.43	43.53	0.30	27.25	3.42	1.00	2.68	731	529	215	64	6.10	23.8	920
14-Dzh					22.76	1.96	39.48	0.30	24.95	3.19	1.76	4.49	577	3.58	149	48	5.00	29.0	1151
1283-a		Seibin (Karaul'naya Mount area)		Crusted thick-bedded	1.86	0.76	53.18	0.35	35.47	3.84	2.87	1.95	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
1295-zh					1.50	0.41	53.91	0.45	34.60	5.19	2.99	5.93	577	524	58	25	8.90	45.2	900
1295-z					1.10	0.56	55.70	0.45	34.60	5.28	3.39	4.14	630	396	46	23	8.30	10.0	944
1278-KG				Massive	0.63	0.00	52.96	0.67	36.88	5.03	2.92	1.15	367	465	44	17	7.60	16.1	915
1277-KG					4.30	0.65	50.28	0.27	35.0	4.75	2.70	1.37	369	635	72	77	14.4	9.1	1776
1283-b					1.44	0.28	55.18	0.40	35.54	3.29	2.82	1.03	682	669	68	34	12.30	64.0	2181
2854-Tl		Telek			0.20	0.16	55.36	0.19	40.89	0.55	2.81	0.19	67	150	39	12	11.90	6.2	572
2233-Tl					0.15	0.37	54.04	0.16	40.00	0.55	3.00	0.35	68	214	44	12	1.90	5.2	486
2941-Tl					0.07	0.26	54.64	0.22	39.14	1.10	3.00	0.12	80	112	97	12	1.10	6.7	851
2947b-Tl					6.18	1.61	47.98	0.27	33.35	2.93	1.50	7.70	568	171	72	40	0.17	5.3	465
2271-Tl					11.4	0.66	47.27	0.27	31.10	3.29	2.00	1.73	117	150	49	12	0.42	4.5	944
5055a-Tl					2.74	3.32	50.34	0.24	35.80	2.56	3.42	0.76	1328	317	49	25	1.70	7.3	700
5055b-Tl				Crusted thick-bedded	3.68	2.47	50.58	0.27	35.41	3.11	3.40	0.22	1420	342	56	17	0.17	8.7	658
2271k-Tl					8.40	0.86	47.20	0.30	31.15	3.29	1.25	0.63	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2947a-Tl					3.50	2.09	50.81	0.34	34.03	3.29	1.37	1.39	222	139	35	28	0.17	5.7	486

Table 1. (Contd.)

Sample No.	Region	Deposit, occurrence	Type of occurrence	Phosphorite structure	Content													
					%							ppm						
					SiO_2	Al_2O_3	CaO	Na_2O	P_2O_5	CO_2	F	Sc	Sr	Ba	V	Cr	Ag	Cd	Zn
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
3539- Asha	South Urals	Ashin	Basin–karst	Nodular	0.00	0.00	53.47	0.47	38.9	1.34	3.45	0.04	117	227	82	24	<0.10	1.5	26
3545-Asha				Massive	2.01	0.00	53.47	0.52	36.8	2.01	3.65	0.36	123	160	115	10	0.27	0.29	32
4931-r/l	Southern Kazakhstan	Karatau basin, Dzhanytas deposit	Fissured	Crusted thin-bedded	0.37	0.00	55.42	0.04	39.47	0.78	3.74	0.08	77	181	62	45	<0.10	1.1	76
4926-r/l					0.00	0.38	54.60	0.38	38.59	3.70	3.70	0.17	67	152	366	<5	<0.10	2.2	207
4929a-r/l					0.60	0.00	53.08	0.36	39.50	1.48	3.50	0.02	73	216	60	<5	<0.10	0.7	66
4929b-r/l					0.25	0.00	53.08	0.36	39.50	2.11	3.50	0.03	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
4915-k/m				Crusted thick-bedded	2.50	0.60	54.28	0.40	34.20	3.59	4.00	2.68	133	160	35	16	0.23	0.8	47
4916-b					17.40	4.50	40.51	0.30	28.80	1.69	2.70	7.69	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
4916-k					2.85	0.90	52.61	0.40	38.00	1.48	3.50	1.7	177	165	118	17	0.30	4.6	452
4818M	Central Kazakhstan	Mirnyi Occurrence	Fissured	Crusted thick-bedded	5.63	1.80	48.69	0.26	33.16	3.21	1.50	16.1	116	190	152	42	0.58	3.5	1322
4818 st				Crusted thin-bedded	0.8	0.00	54.64	0.33	36.87	3.00	1.87	1.50	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
4724 Sp	Spain	Estremadura	Crusted	Crusted thin-bedded	0.10	0.28	54.34	0.48	40.50	1.11	0.02	0.13	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
4742 Liege	Belgium	Liege area	Basin–karst	Crusted thin-bedded	6.59	1.52	52.59	0.60	32.42	3.11	3.96	6.50	150	192	29	22	0.32	7.4	474
4756 Fl	Florida	“Land pebble” phosphorites	Mantled	Massive solid	–	–	–	–	–	–	0.83	6.14	120	10	38	0.60	13.60	49	
4761-Tn	Tennessee	Brown phosphorites	Mantled	Massive	14.8	4.77	39.75	0.66	28.20	0.67	3.00	3.90	416	200	67	29	0.13	0.81	39
4762-a-Tn				Crusted thick-bedded	2.20	0.85	54.45	0.33	37.10	2.58	3.50	0.44	80	139	89	7	0.28	7.80	642
4762-b-Tn				Crusted thin-bedded	1.00	0.20	54.92	0.36	36.75	4.39	3.40	0.10	77	139	85	6	0.21	8.10	664

Table 1. (Contd.)

Sample No.	Region	Deposit, occurrence	Type of occurrence	Phosphorite structure	Content													
					%							ppm						
					SiO_2	Al_2O_3	CaO	Na_2O	P_2O_5	CO_2	F	Sc	Sr	Ba	V	Cr	Ag	Cd	Zn
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
4743 Ir	Southern Siberia	Irsym	Unclear	Crusted thin-bedded	0.7	0.15	55.56	0.33	40.27	0.17	3.45	0.87	1204	173	30	7	0.10	1.60	45
0109r-l/I	India	Aravalli Basin, Jhamarkotra deposit	Fractured	Crusted thin-bedded	0.22	0.00	57.62	0.03	39.40	1.81	3.74	0.05	60	160	104	<5	0.64	7.00	569
0118r-l/I					1.50	0.00	54.96	0.36	37.00	2.09	3.30	0.112	150	26	234	<5	0.80	4.70	672
Supergene phosphorites related to sedimentary and endogenous rocks																			
4163r/lL	Germany, Nassau	Lahn	Mantled–pocket	Thin-bedded	0.90	0.00	55.98	0.05	37.23	2.59	4.56	0.51	52	270	67	186	1.20		2000
4163-L				Massive	19.5	0.34	41.85	0.04	27.55	1.81	3.10	3.60	37	192	113	29	0.13	0.54	350
PEB-L					7.63	3.63	48.07	0.06	30.56	3.11	3.88	11.00	77	173	39	22	0.72	0.81	263
4709a-AL	Middle Urals	Antonov–Lipovsk	Mantled	Massive	0.00	0.33	52.24	0.36	38.27	0.86	2.20	6.30							
4717-AL					16.6	8.59	35.63	0.12	24.45	1.55	3.12	3.85	336	147	53	28	<0.10	1.90	168
Supergene phosphorites related to endogenous rocks																			
7058-B.Z.	Southern Siberia	Belaya Zima Massif	Mantled	Massive	1.02	0.45	50.63	0.38	32.60	4.24	3.95	6.41	778	611	74	5	1.5	3.10	511
7060-B.Z.					0.02	0.45	53.60	0.42	33.25	4.07	4.07	7.46	926	647	71	5	0.82	3.20	372
6005	Northern Siberia	Essei Massif	Mantled	Massive	0.40	0.00	46.80	0.27	32.24	2.01	2.87	18.90							
6007					0.6	0.00	51.36	0.37	33.60	3.25	2.50	16.20	433	564	62	<5	0.64	1.20	34
7599-1 Mag		Magan Massif			2.17	0.17	54.32	0.08	35.31	3.11	2.76	0.61	340	615	26	<5	0.63	1.8	49
7590Mag					0.30	0.00	53.90	0.48	36.50	3.57	2.75	6.31							
7778-Y		Yraas Massif			6.90	0.00	46.60	1.23	34.50	3.48	1.12	4.67	1814	1296	82	<5	0.14	1.3	265
7878-Y					0.30	0.00	53.60	0.50	38.45	2.81	2.10	4.17	2500	1588	34	8	0.64	2.50	171
6241 r/lK	Kola Peninsula	Kovdor Massif	Mantled	Thin-bedded	0.55	0.00	54.00	0.45	35.60	2.30	3.00	0.25	1481	353	71	<5	2.60	6.50	350
6209K				Massive	3.22	3.93	44.40	0.05	32.93	2.33	2.32	20.70	2037	1670	61	<5	0.85	2.40	115
Ocean island phosphorites																			
OR-1	Indian Ocean	Christmas Island	Mantled	Massive	2.10	0.90	51.68	0.61	38.00	2.53	0.23	0.47	176	125	20	<5	0.29	1.80	460
4752-OR					0.60	0.00	53.04	0.82	38.60	4.01	0.00	0.09	176	100	17	9	0.50	1.30	23

content of weathering-related continental phosphorites varies within 80–400 ppm, occasionally up to 800 ppm. These values are similar to those obtained by us for the majority of supergene phosphorites. However, some phosphorites from the areas of weathered sedimentary and endogenous rocks have significantly higher Sr contents (>1500 ppm), and coprolite phosphorites formed presumably in saline lakes contain up to 3500 ppm Sr. The Sr content of marine phosphorites unaffected by catagenesis and weathering reaches 3600 ppm and occasionally 5000 ppm [21] at normative contents of 2300–2500 ppm [7, 22]. These values are significantly higher than those of supergene phosphorites. A decrease in Sr and Na contents in supergene phosphorites as compared with marine ones was noted by Bliskovskii et al. [21] and McArthur [23]. The Ba content of coprolite phosphorites and phosphorites related to weathered endogenous rocks is in general higher than that of marine phosphorites (Table 2), whereas the supergene phosphorites related to sedimentary rocks are similar in this respect to marine phosphorites.

Vanadium. The vanadium content of the supergene phosphorites is typically tens and, occasionally, a few hundreds of ppm. In particular, the V content of the supergene phosphorites related to the weathering of sedimentary rocks ranges from 10 ppm ("hard" phosphorites of Florida) to a few hundreds ppm (some phosphorites from the Belkin, Seibin, Ashin, and some other deposits), averaging 94.76 ppm. The maximum values (279 ppm) are several tens of times higher than the minimum values (10 ppm). The V content of phosphorites related to the weathering of endogenous rocks ranges in a narrower range of 26–82 ppm, averaging 52.12 ppm. The lacustrine coprolite phosphorites of the Zaisan Lake area also show minor V variations from 31 to 57 ppm, averaging 44 ppm. Two samples of island phosphorites contain 17 and 20 ppm V. The V content of marine phosphorites varies from 7 to 300 ppm according to Altschuler [5] and from 10 to 1200 ppm according to Bliskovskii [7]. The average V content is 100 ppm in most deposits and may reach 300 ppm. The average V contents in all the distinguished types of supergene phosphorites are lower than 100 ppm. Most of the samples also showed less than 100 ppm V. Thus, the V content of supergene phosphorites is lower than that of marine phosphorites.

Chromium. The highest average Cr content was found in the hypergene phosphorites related to weathered sedimentary rocks (25.84 ppm), at minimum and maximum contents of 5 and 86 ppm, respectively. The Cr content of the supergene phosphorites from the areas of weathered endogenous rocks averages 5.38 ppm with the range from 5 to 8 ppm. The lacustrine coprolite phosphorites have significantly higher Cr contents from 13 to 22 ppm, averaging 17 ppm. Two samples from Christmas Island contain 5 and 9 ppm Cr (7 ppm on average). Similar to the supergene phosphorites, the minimum Cr contents of marine phosphorites are a few ppm, whereas the maximum contents reach hundreds of ppm (up to 300 ppm and even more) as compared with tens of ppm in the supergene phosphorites.

Scandium. The minimum Sc content of 0.09–0.47 ppm was found in the phosphorites of Christmas Island. The Sc contents of phosphorites from the areas of weathered sedimentary rocks vary within a wide range from 0.1 to 16.1 ppm at an average content of 2.05 ppm. The phosphorites from the areas of weathered endogenous rocks contain 0.25 to 20.07 ppm Sc at an average value of 7.27 ppm (Table 2). The highest Sr contents of 4–124 ppm (averaging 33.78 ppm) were observed in the lacustrine coprolite phosphorites. The maximum-to-minimum ratio of Sc contents is 31 in the lacustrine phosphorites, 80 in the phosphorites related to weathered endogenous rocks, and 161 in the phosphorites related to weathered sedimentary rocks. The Sc content of marine phosphorites varies from a few ppm to a few tens of ppm [5, 24], i.e., within the same range as most of the supergene phosphorites. It is noteworthy that the Sc content of one of our coprolite phosphorite samples (124 ppm) appeared to be the highest reported to date in phosphorites.

Chalcophile Elements

Zinc. Zn is the most abundant among the chalcophile elements analyzed in the supergene phosphorites. Supergene phosphorites developed in sedimentary rocks have the highest average Zn content (614.5 ppm), with the range from 26 to 2181 ppm. There is a clear discrimination between deposits in terms of Zn content. For instance, most samples from the Telek and Seibin deposits of the Altai–Sayan area contain more than 500 ppm Zn, whereas phosphorites from the Obladzhan deposit contain no more than 150 ppm Zn. Previously, we observed similar Zn contents in the phosphorites from the Seibin and Obladzhan deposits [25]. Significantly lower Zn contents were measured in all phosphorites related to endogenous rocks: from 34 to 511 ppm with an average value of 233.38 ppm. The Zn content of the lacustrine coprolite phosphorites ranges within 39–69 ppm and averages 49.4 ppm; none of the samples showed more than 100 ppm Zn. At the same time, two samples from Christmas Island contain 23 and 460 ppm Zn (241.5 ppm on average). Previously, the Zn content of ocean island phosphorites (Nauru, Oshen, and other islands) was estimated by Bliskovskii [7] as 200–1000 ppm, i.e., fairly close to our values. At the same time, supergene phosphorites from the areas of sedimentary rocks have an average Zn content of 614.5 ppm. This is significantly higher than that of marine phosphorites, which usually contain less than 300 ppm Zn [7, 5, 26, 27]. The extremely high Zn contents in the phosphorites of the Kuonam Formation of the Siberian Platform (more than 2000 ppm [26]) are related to the presence of sphalerite.

Cadmium. Similar to Zn, the highest average Cd content (10.09 ppm with the range from 0.29 to 64 ppm) was observed in phosphorites related to sedimen-

Table 2. Average contents and variations of trace elements in the distinguished genetic types of phosphorites, ppm

Genetic type of phosphorite	Content	Sr	Ba	Cr	Sc	Ag	Zn	V	Cd
Related to sedimentary rocks	Average	397.4	245.6	25.84	2.05	2.54	614.51	94.76	10.09
	Mean-square deviation	373	155.5	20.58	3.11	3.98	534.02	77.1	12.65
	from–to	60–1420	26–669	5–86	0.01–16.1	0.01–14.4	26–2181	10–279	0.29–64
Related to endogenous rocks	Average	1289	918	5.38	7.56	0.98	233.4	52.12	2.75
	Mean-square deviation	790	516	1.06	7.27	0.76	170.1	26.59	1.68
	from–to	340–2500	353–1670	5–8	0.25–20.07	0.14–2.6	34–511	26–82	1.2–6.5
Lacustrine coprolite	Average	2934	714	17.0	33.78	2.52	49.4	44	1.8
	Mean-square deviation	553	115	3.94	48.75	1.86	12.30	10.6	0.66
	from–to	2284–3544	524–802	13–22	4–124	0.1–0.5	39–69	31–57	1.3–2.9
Island	Average	176	112.5	7.0	0.28	0.39	241.5	18.5	1.55
	Mean-square deviation	–	17.7	2.83	0.27	0.15	309	2.1	0.35
	from–to	176	100–125	5–9	0.09–0.47	0.29–0.50	23–460	17–20	1.3–1.8
Marine*		2300–3000–5000 [22, 5, 21]	75–720 [5]	3–290 [7] 7–300 [5]	<2–22.7 [24, 5, 27]	<0.1–7 [5]	20–300 [26, 27, 5, 7]	7–300 [5] 10–1200 [7]	<0.10–80 [26–28]

* Unaffected by catagenesis and weathering.

tary rocks, although the absolute contents of these elements are very different: in most cases, the Cd content is tens or even hundreds of times lower than the Zn content. The maximum Cd contents, as well as the maximum Zn contents, were detected in the phosphorites of the Seibin deposit, southern Siberia. The contents of these elements in the Obladzhan deposit of the same region are significantly lower, which is in agreement with our previous results [25]. The supergene phosphorites related to endogenous rocks contain from 1.2 to 6.5 ppm Cd, with an average of 2.75 ppm, which is several tens of times lower than the Zn contents. Even lower average Cd contents (1.8 ppm) were determined in the lacustrine coprolite phosphorites (from 1.3 to 2.9 ppm) and island phosphorites (1.55 ppm on average and 1.3 and 1.8 ppm in particular samples). The Cd content of marine phosphorites varies from tenths to a few tens of ppm, occasionally higher [26–28]. In general, the Cd content of marine phosphorites is comparable with that of supergene phosphorites related to sedimentary and endogenous rocks but significantly higher than that of coprolite phosphorites.

Silver. The Ag content of the phosphorites is the lowest among the trace elements considered in this paper. Phosphorites from the areas of sedimentary rocks show a wide scatter from <0.01 to 14.4 ppm with an average value of 2.54 ppm. The highest silver contents (up to 10 ppm and more) were detected at Karaul'naya Mount in the Seibin deposit, southern Siberia. Five samples average 10.3 ppm Ag, with variations from 8.3 to 14.4 ppm. The average Ag content is 2.19 ppm for the Telek deposit (seven samples) and 1.6 ppm for the Obladzhan deposit (three samples). However, none of the supergene phosphorites related to sedimentary rocks beyond the Altai–Sayan area of southern Siberia contained more than 1 ppm Ag. The supergene phosphorites related to endogenous rocks also show low Ag contents: only four of eight samples contain more than 1 ppm Ag (minimum and maximum values of 1.3 and 2.6 ppm). The coprolite phosphorites show a relatively high average Ag content of 2.52 ppm (from 0.1 to 5 ppm). The phosphorites of Christmas Island contain 0.29 and 0.5 ppm Ag. The Ag content of marine phosphorites varies from <0.1 to 7 ppm [5], which is similar to those in most supergene phosphorites. At the same time, the Ag contents measured in the supergene phosphorites of the Seibin deposit, southern Siberia (up to 14 ppm) are higher than those of any marine phosphorite. Higher Ag contents in phosphorites reported from the Karatau basin (up to 210 ppm) are not related to carbonate-apatite [4].

The contents of the trace elements in different groups of supergene phosphorites decrease in the following sequence.

1. Supergene phosphorites related to sedimentary rocks:

Zn > Sr > Ba > V > Cr > Cd > Ag > Sc.

2. Supergene phosphorites related to endogenous rocks:

Sr > Ba > Zn > V > Sc > Cr > Cd > Ag.

3. Lacustrine coprolite phosphorites:

Sr > Ba > Zn > V > Sc > Cr > Ag > Cd.

4. Ocean island phosphorites:

Zn > Sr > Ba > V > Cr > Cd > Sc > Ag.

It is seen that the three highest scores in all the phosphorite groups belong to Sr, Zn, and Ba. Sr or Zn shows the highest content, Sr or Ba is the next highest, and Ba or Zn is the third highest. The fourth place is occupied in all cases by V; the sixth place, by Cd or Cr; and seventh and eighth places, by Sc, Cd, or Ag. The highest Sr and Ba contents were observed in the coprolite phosphorites and phosphorites related to weathered endogenous rocks, and the lowest contents of these elements are characteristic of island phosphorites. The highest Zn contents were measured in the phosphorites from the areas of weathered sedimentary rocks, and the lowest Zn contents, in the coprolite phosphorites. The highest V contents were observed in the phosphorites from the areas of weathered sedimentary rocks, and the lowest V contents, in the island phosphorites. The highest Cr and Cd contents are confined to the phosphorites related to weathered sedimentary rocks. The highest Sc contents were detected in the coprolite phosphorites, and the maximum Ag enrichment was observed in the phosphorites related to weathered sedimentary rocks and in the coprolite phosphorites (Table 2).

The above element sequences are similar, although not identical, to the distribution of the average abundances of trace elements in carbonate rocks (in %): $Sr(6.1 \times 10^{-2}) > Zn(2 \times 10^{-3}) > V(2 \times 10^{-3}) > Cr(1.1 \times 10^{-3}) > Ba(1 \times 10^{-3}) > Sc(1 \times 10^{-4}) > Cd(3.5 \times 10^{-6}) > Ag(x \times 10^{-6})$ [29]. This sequence is started with Sr and Zn and finished with Cd, Ag, and Sc. In the phosphorites, the second and third places are occupied by Ba, which is only fifth in abundance in carbonates. This can be explained assuming that Ba substitution for Ca is more extensive in the apatite crystal structure than in carbonate minerals. The concentrations of some trace elements (Sc, Ag, and, to lesser extent, Cd) in the phosphorites are higher than their average abundances in carbonate rocks, whereas Sr shows the opposite relation [21]. Significant variations in trace element contents were observed not only among phosphorites from different regions but also within individual deposits and occurrences. In particular, the lacustrine coprolite phosphorites contain from 4 to 124 ppm Sc and from <0.1 to 5 ppm Ag. The phosphorites of the Telek deposit contain 0.17–11.9 ppm Ag and 67–1420 ppm Sr. Other examples can be found. At the same time, some individual deposits and even regions are characterized by narrow variations in some elements. The lacustrine coprolite phosphorites show consistently high contents of Sr and, in part, Ba. Elevated contents of all chalcophile elements (Ag, Cd, and Zn) were

observed in the karst phosphorites of the Seibin and, in part, Telek deposits of southern Siberia.

The differences in the trace element composition of supergene phosphorites of various genetic groups are presumably related primarily to the compositions of weathered rocks and geochemical conditions of supergene phosphorite formation.

In particular, the elevated Sr content in the Eocene lacustrine phosphorites of the Lake Zaisan area is related, in our opinion, to the elevated salinity of this lake. This is supported by several observations. In particular, the average Na content of coprolite phosphorites is 0.64 ± 0.26 ppm, whereas lower contents were obtained for the supergene phosphorites related to sedimentary or endogenous rocks (0.33 ± 0.14 ppm) and phosphorites formed in karst cavities or similar environments and washed by "fresh" surface water (0.43 ± 0.36 ppm). It is known [17, 23] that relatively high Na contents are characteristic of marine phosphorites, which are generated in waters with higher contents of alkalis (more saline) as compared with continental phosphorites. This is also true for strontium. Indeed, the Sr content is 8100 μg/l in seawater, 88.7 μg/l in the continental leaching waters, and 183 μg/l in the underground waters of the supergene zone [30]. The Ba contents are 21, 14, and 18.3 μg/l, respectively. These values are in perfect agreement with the proposition of Katchenkov [31] that an increase in the Sr/Ba ratio of sedimentary rocks correlates with the increasing salinity of basin waters. In our case, the Sr/Ba ratio is 4.1 in the coprolite phosphorites, 1.62 in the supergene phosphorites related to sedimentary rocks, 1.40 in the phosphorites related to endogenous rocks, and 1.56 in the phosphorites of Christmas Island. There are grounds for believing that the Eocene lacustrine coprolite phosphorites of the Lake Zaisan area were formed under conditions of higher water salinity compared with other phosphorites.

The phosphorites related to endogenous rocks have higher contents of Na, Ba, and Sr compared with those related to sedimentary rocks (Tables 1, 2). This is presumably related to the composition of the weathered protolith, because the supergene phosphorites considered here are related to alkaline and alkaline ultramafic massifs [32, 33]. The geochemical features of weathered rocks are also responsible for the difference in the contents of V, Cr, and Sc in the supergene phosphorites. The elevated contents of Ag, Cd, and Zn in the supergene phosphorites of the Seibin deposit are explained by the regional enrichment of the source rocks of southern Siberia in these components. At the same time, the Cd and Zn of phosphorites from the Seibin deposit are not completely incorporated as isomorphic admixtures in supergene carbonate-apatite. It can be suggested that these chalcophile elements may occur in sulfide minerals, which could be present in these rocks. However, divalent Fe and (or) S were not found in samples 1283a, 1283b, 1278-KG, and 1295zh with elevated contents of Cd and Zn.

Let us consider the role of the structural factor on the trace element composition of phosphorites. The obtained data are ambiguous (Table 1). For instance, the inner part of one phosphorite coprolite from the Lake Zaisan area contains 2284 ppm Sr (sample 7293-1b), whereas the thick-bedded crust rimming this coprolite is significantly richer in Sr (2570 ppm). The same relationships were observed in this sample for other elements, including Ba (685 ppm in the massive phosphorite and 771 ppm in the crust), Cd (1.3 and 1.6 ppm, respectively), Zn (46 and 69 ppm), and, especially, Sc (17.7 and 124 ppm). The opposite relationships were observed for V (57 and 52 ppm), Cr (22 and 19 ppm), and Ag (3.6 and 2.1 ppm). Thick-bedded phosphorite crusts from the Telek deposit (sample 5055b-Tl) showed higher contents of Sr (1420 ppm) and Ba (342 ppm) compared with those in the massive phosphorites at the base of the phosphatic crust (sample 5055a-Tl, 1328 ppm Sr and 317 ppm Ba). In contrast, the Sr content of similar massive phosphorites in another sample from the same deposit (sample 2947b-Tl, 568 ppm) is more than two times higher than that in the thick-bedded phosphorite crust rimming the massive phosphorite (2947a-Tl, 222 ppm). At the Seibin deposit, the Sr content of phosphorite varied from 630 ppm in the inner part of a crust (sample 1295-3) to 577 ppm in its outer part (sample 1295-zh). The above examples concern thick-bedded crusts; however, thin-bedded crusts also show similar ambiguous relationships. In particular, a massive phosphorite from Tennessee (sample 4761) contains 416 ppm Sr, whereas thick-bedded and thin-bedded phosphorite crusts from the same locality contain only 80 (sample 4762-a-Tn) and 77 ppm Sr (sample 4763-b-Tn), respectively. Many other similar examples can be found.

Elevated content of chalcophile elements (Cd, Zn, and Ag) was observed in many phosphorite crusts or only in their outer parts relative to massive phosphorites or the inner parts of the crusts. The lithophile elements (Sc, V, and Cr) show the opposite tendency. The contents of Sr and Ba show both patterns. Thus, the contents of chalcophile elements tend to increase in phosphorite crusts or only in their outer parts, which is most distinctly expressed for Cd, whereas the lithophile elements, especially Cr, show the opposite relation.

Correlation analysis (Table 3) revealed two groups of trace elements showing significant positive correlations: (1) Sr and Ba and (2) Zn, Cd, and Ag. The elements of both groups show significant positive correlations with CO_2, i.e., with carbonate ions in the apatite structure. Correlations of these elements with other constituents of carbonate-apatite are poor. Sc shows a positive correlation with Na; Cr is negatively correlated with Ca and F and positively correlated with the chalcophile elements. The significant positive correlation of five trace elements with CO_2 deserves a detailed con-

Table 3. Correlations matrix for the contents of trace elements in supergene phosphorites and components of (carbonate)-apatite for the full dataset; values in bold correspond to correlations significant at a confidence level of more than 0.95

Element	P_2O_5	CaO	CO_2	Na_2O	F	Sr	Ba	V	Cr	Sc	Zn	Cd	Ag
P_2O_5	1												
CaO	*–0.30*	1											
CO_2	–.08	–0.17	1										
Na_2O	–.01	–0.00	0.17	1									
F	–.011	*0.58*	–0.14	0.06	1								
Sr	0.14	–0.09	*0.34*	0.25	–0.01	1							
Ba	–0.8	–0.16	*0.36*	0.26	–0.23	*0.61*	1						
V	0.28	–0.03	0.02	–0.03	0.03	*0.30*	–0.00	1					
Cr	–0.10	*–0.51*	0.15	–0.06	*–.43*	–0.23	–.08	–0.15	1				
Sc	–0.09	–0.11	0.24	*0.61*	–0.08	0.28	*0.44*	–0.02	0.00	1			
Zn	–0.06	–0.15	*0.38*	0.29	–0.25	–0.21	–0.03	0.04	*0.52*	–0.14	1		
Cd	–0.19	–0.10	*0.32*	–0.16	–0.21	–0.15	0.03	–0.07	*0.32*	–0.15	*0.60*	1	
Ag	–0.35	–0.03	*0.36*	–0.02	–0.17	–0.04	0.19	–0.16	*0.46*	–0.07	*0.65*	*0.55*	1

sideration. It is well known that the content of carbonate ion in the crystal structure of carbonate-apatite controls many physical and chemical properties of this mineral. An increase in CO_2 content leads to an increase in the relative distortion of the crystal lattice, size of coherent scattering domains, solubility in weak acids [11, 34, 12], and molecular water content [35]. The loosening of the carbonate-apatite structure with increasing carbonate ion content probably makes it more suitable for the incorporation of other ions, which was observed in our case. It is interesting that catagenesis leads to the partial release of carbonate ions from the apatite structure [11] and is accompanied by a decrease in the contents of some trace elements in the mineral [26, 36].

CONCLUSIONS

1. The distribution of isomorphic admixtures of Sr, Ba, Zn, Cd, Sc, Cr, Ag, and V was analyzed in (carbonate)-apatite samples [9] taken from supergene phosphorites related to the areas of weathered sedimentary and endogenous rocks, lacustrine coprolite phosphorites, and ocean island phosphorites. Most of the phosphorites have a monophosphate composition and contain more than 1% CO_2. Therefore, their apatite can be classified as carbonate-apatite [20].

2. Sr, Zn, and Ba show the highest concentrations in all the phosphorites: Sr is the first or second and Ba is the second or third most abundant element. Cd, Ag, and Sc are the lowest in abundance, and Ag is the last or next to last among them. This sequence resembles the distribution of average abundances of these elements in the carbonate rocks, in which Sr is the most abundant and Ag is the least abundant.

3. The concentrations of particular elements within the phosphorite groups may be either relatively consistent or strongly variable. Significant variations observed both within and between the genetic groups of supergene phosphorites can be explained by the different compositions of weathered rocks, geochemical environments of supergene phosphorite formation, mineralogical characteristics of carbonate-apatite, and structural features of phosphorites.

4. The distribution of trace elements in phosphorites shows correlations with their structural features. Phosphorite crusts as a whole or only their outer parts often show elevated contents of chalcophile elements (Cd, Zn, Ag), whereas massive phosphorites or inner parts of the crusts often have elevated contents of such lithophile elements as Sc, V, and Cr. The contents of Sr and Ba show no clear dependence on the phosphorite structure.

5. It was shown that the supergene phosphorites are similar to marine phosphorites in terms of Sc, Cd, and Ag contents. Exceptions are higher contents of Ag in the supergene phosphorites of southern Siberia and Sc in the coprolite lacustrine phosphorites. At the same time, the marine phosphorites are higher in Sr, V, and Cr than supergene phosphorites, and supergene phosphorites have higher Zn contents.

6. Correlation analysis showed a significant positive correlation of Cd, Zn, Ag, Sr, and Ba with CO_2 and negligible correlations with other components of carbonate-apatite. This is explained by the fact that an increase in carbonate ion content leads to the loosening of the

mineral structure, which is favorable for the incorporation of trace elements.

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