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GEOCHEMISTRY

Noble Metals in Recent and Ancient Phosphorites

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Noble metals (except Ag) in phosphorites are less studied than many other rare and trace elements. High Ag contents (4 g/t) were first reported from Missourian (Carboniferous) phosphorites in Alaska [1]. Subsequently, different contents of Au (<0.4–7 g/t) were detected in many of the world's Precambrian–Miocene phosphorite deposits, including Russia and the CIS [2–6]. For example, the Ag content is 1 g/t in Precambrian Tomalyk phosphorites and ~2 g/t in Cretaceous–Paleogene phosphorites of the Ukraine [4]. Generalization of data on 15 regions of the world showed that the average Ag content in phosphorites is 2 g/t, which is approximately 30 times higher than the average content in sedimentary rocks [6].

Information concerning the Au content in phosphorites is scanty. For example, the Au content is as much as 50–200 mg/t in phosphorites of the Kimov and Egor'ev deposits in the Russian Platform [5, 7]. The Au content is slightly lower (30–78 mg/t) in Cenomanian and Paleogene phosphorites of the Ukraine [4]. Higher Au contents have been reported in [8] from heavy fractions of some phosphorites in the Russian Platform. The Au content is maximal (1.1–4.7 g/t) in six samples of Cenomanian phosphorites from the Livnya–Boguchar zone of the Voronezh anteclise [9]. These samples also contain Pt (0.1–0.36 g/t) related to the delivery of metals by abyssal fluids to highly permeable zones in the Earth's crust.

Some information concerning the behavior of noble metals in oceanic phosphorites has been obtained with the application of modern scanning electron methods. For example, euhedral native gold crystallites associated with quartz have been detected in phosphorites from the Agulhas Bank [10]. Native platinum flakes and sternbergite (silver sulfide) have been found in phosphate sand grains from the giant phosphorite deposit on the Namibian shelf [11]. Phosphorite nodules from these sands contain three morphological varieties of gold: crystalline aggregates (<1 μm), platy particles, and elongate fusiform particles (<1 μm). The samples also include rounded and vermicular platinum particles associated with osmium and iridium particles 1–5 nm in size [12].

However, absence of data on the bulk content of noble metals in oceanic phosphorites hampers the understanding of their behavior in the process of oceanic phosphate accumulation. In order to fill this gap, we analyzed the general chemical composition and contents of five native metals (Ag, Au, Ir, Os, and Ru) in eight samples of oceanic phosphorites, three samples from very large continental phosphorite deposits, and four samples from recent and ancient marine phosphorites with abundant organic matter that is a constant component of phosphorites.

The oceanic phosphate material described in [13] is composed of the following varieties: recent phosphorites from the inner Namibian shelf (one nodule and two phosphatized coprolites of sea lion), Pliocene phosphorites from the outer Namibian shelf (two nodules from the phosphate sand deposit), a late Quaternary nodule from the Peru shelf, a Miocene nodule from the Yamato Seamount on the Sea of Japan floor, and probably Late Cretaceous material from the Mid-Pacific seamount system (phosphatized ferruginated breccia with inclusions of hyaloclastite detritus). Continental phosphorites are represented by samples from Miocene phosphorite deposits in Sechura (Peru) and Florida (United States) and from Late Cretaceous–Paleogene deposits in Morocco. Sediment samples include the recent diatom ooze from the inner Namibian shelf, late Holocene calcareous mud from the deep-water zone of the Black Sea, early Holocene sapropel mud from the Black Sea, and Ordovician black shale from northern Leningrad district.

Table 1 shows the major composition of material determined by the chemical and atomic absorption analyses at the Shirshov Institute of Oceanology. Table 2 presents contents of noble metals determined by the

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Table 1. Major chemical composition of phosphorites and sediments

Sample no.	P_2O_5	CaO	SiO_2	Al_2O_3	Fe_2O_3	CO_2	C_{org}	Co	Ni	Cu	Pb
48-8	32.41	43.0	0.03	0.014	0.048	6.36	0.87	1.1	4.2	6.7	0.64
48-10	30.49	49.0	0.07	0.04	0.073	5.47	0.90	0.73	6.9	3.9	0.51
48-12	31.19	50.0	0.12	0.035	0.053	6.21	0.71	0.91	11	6.7	0.84
L-6	26.22	43.2	9.31	1.6	2.4	4.35	1.01	10.3	57.3	13.6	16.6
546	22.3	41.50	12.22	3.59	1.2	7.80	0.80	6.3	44.7	27.7	3.4
3150	27.31	32.4	12.50	2.5	1.3	0.91	0.80	3.9	9.8	16.7	12.9
G-29	8.21	22.0	36.23	3.3	1.1	4.83	1.95	1.6	20	10	8.2
PR-8	33.5	52.0	2.8	0.39	0.19	4.9	0.37	0.34	31.2	34	3.6
FL-4	32.9	(45)	5.02	1.05	1.10	1.20	0.60	5.4	16.8	8.7	8.9
6369	5.20	7.80	46.7	17.94	7.6	2.90	0.10	20	85	81	12
48-1	0.82	7.3	58.9	1.9	0.93	2.62	5.54	<2	34.4	23.5	4.2
1309	0.09	42	6.98	2.8	2.1	30	4.5	28	59	43	7.2
862-2	0.25	4.0	22.42	9.6	3.8	3.15	8.5	21	180	200	18
DS	0.98	1.5	65.11	9.3	3.7	2.89	4.13	9.8	110	86	180

Note: Co, Ni, Cu, and Pb are given in ppm; other components, in %. Samples: (48-8) recent dense phosphorite nodule from the Namibian shelf; (48-10, 48-12) phosphatized coprolites of recent sea lions from the Namibian shelf; (L-3, L-6) Pliocene nodule (Namibian shelf); (546) nodule from the Peru shelf; (3150) nodule from the Yamato Seamount (Sea of Japan); (G-29) phosphate sand from the Sechura deposit (Peru); (PR-8) Moroccan phosphorite; (FL-4) phosphorite from Central Florida; (6369) phosphatized breccia from one of the Pacific seamounts; (48-1) recent diatom ooze from the Namibian shelf; (1309) recent calcareous mud from deep-water zone of the Black Sea; (862-2) ancient Black Sea sapropel mud; (DS) Ordovician Dictyonema shale (Leningrad district).

neutron activation analysis at the Vernadsky Institute of Geochemistry and Analytical Chemistry.

The results show that eight phosphate samples are mainly composed of calcium phosphate. The Sechura sample is dominated by diatomaceous opal, whereas the Pacific seamount sample is dominated by basaltic material and ferromanganese hydroxides.

Sediment samples are depleted in phosphorus (<1% P_2O_5) and enriched in C_{org} (4.1–8.5%), a biogenic admixture (diatomaceous opal on the Namibian shelf and coccolithophorid carbonate in the Black Sea), or clastic terrigenous material (ancient Black Sea sapropel and Dictyonema shale).

Phosphorites are slightly depleted in metals, such as Co (0.34–6.3), Ni (4.2–57.3), Cu (3.9–34), and Pb (0.51–16.6 ppm). However, one phosphorite sample from the Pacific seamount is enriched in Co, Ni, and Cu owing to high contents of ferromanganese hydroxides.

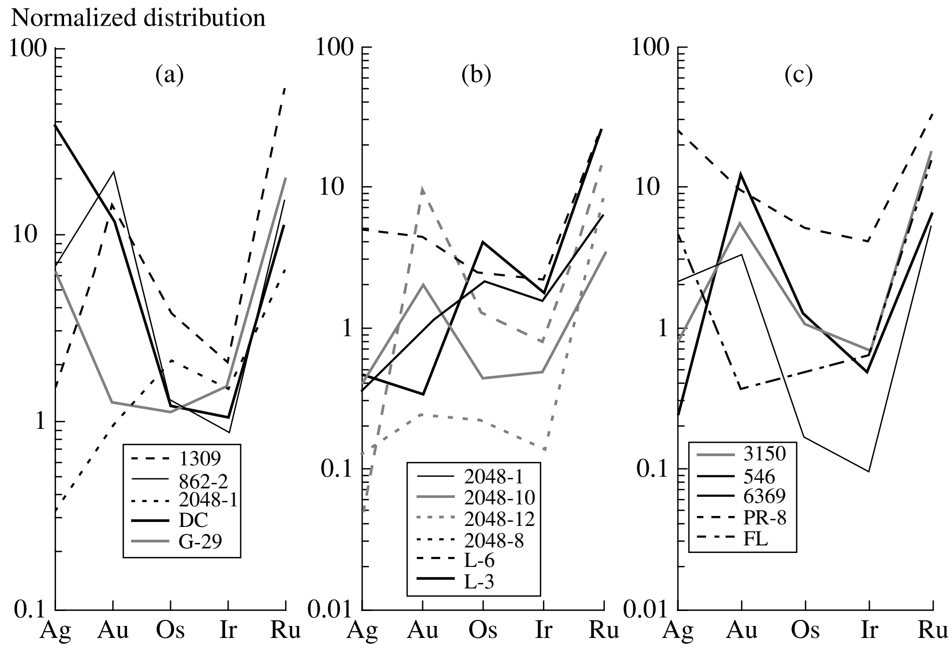
In this respect, the sediments differ significantly from the phosphorites. All sediments (except recent diatom oozes) are notably enriched in Co, Ni, and Cu. The ancient Black Sea sapropel and, particularly, Dictyonema shale are additionally enriched in Pb.

Table 2 shows that contents of noble metals in the phosphorites have the following variation range (mg/t): Ag from 1.98 (recent phosphatized coprolite) to 1020 (Moroccan phosphorite), Au from 0.49 (recent nodule) to 24.07 (phosphorite from the Pacific seamount), Ir from 0.029 (nodule from the Peru shelf) to 1.29 (Moroccan phosphorite), Os from 0.033 (Peru shelf) to 1.04 (Morocco), and Ru from 0.7 (recent phosphatized coprolite) to 6.6 (Morocco). Thus, the Moroccan phosphorite is characterized by higher contents of noble metals relative to all other shelf phosphorites. However, the Au content in the former sample is slightly lower than that in the seamount sample.

Variations in contents of noble metals in the sediments are as follows (mg/t): Ag from 13.8 (recent diatom ooze) to 1530 (Dictyonema shale), Au from 1.69 (diatom ooze) to 43.89 (ancient Black Sea sapropel), Ir from 0.266 (sapropel) to 0.625 (Black Sea coccolith mud), Os from 0.25–0.27 (ancient Black Sea sapropel and Dictyonema shale) to 0.80 (coccolith mud), and Ru from 1.34 (diatom ooze) to 12.8 (coccolith mud).

Thus, maximal contents of Ag, Au, and Ru are confined to sediments, while maximal contents of Ir are observed in the Dictyonema shale. The Os content in the Black Sea coccolith mud (0.80 mg/t) is comparable with that in the Moroccan phosphorite (1.04 mg/t). The discrepancy between the minimal and maximal concentrations of noble metals in the studied phosphorites is as follows: Ag 500 times, Au ~50 times, Ir 44 times, Os 30 times, and Ru 9 times. Variations in the sediments are as follows: Ag 110 times, Au 26 times, Ir 2.3 times, Os 3 times, and Ru 9.5 times.

Comparison of these data with the average contents of noble metals in recent oceanic sediments [14] shows that one-half of the studied phosphorites and three sediment samples (out of four) are enriched in Ag (from 2



Clarke-normalized distribution of noble metals in sediments and phosphorites. (a) Sediments; (b) recent phosphorites, phosphorite-enclosing diatom oozes, and Pleistocene phosphorites of the Namibian shelf; (c) older phosphorites.

to 50 times). The Ag depletion is noted in all recent sediment samples and two phosphorite samples from seamounts located in an oxidizing environment in the Sea of Japan and Pacific Ocean.

Gold is relatively concentrated in six phosphorite samples (2–12 times) and three sediment samples (9–16 times). Heavy rare earth elements (Ir and Os) are not concentrated in phosphorites and sediments, except for the Moroccan phosphorite (4–5 times higher concentrations of Ir and Os) and coccolith muds from the Black Sea (4 times higher concentration of Os). In contrast to other platinum group elements, Ru is concentrated in sediments (3 times in the recent phosphatized coprolite and 64 times in coccolith muds from the Black Sea). Figure shows the distribution of noble metals in oceanic and continental phosphorites and sediments.

Table 2. Contents of noble metals in phosphorites and sediments (mg/t)

Sample no.	Ag	Au	Ir	Os	Ru
2048-8	5.14	0.49	0.043	0.044	1.76
2048-10	15.9	4.14	0.146	0.089	0.7
2048-12	1.98	20.35	0.239	0.25	3.0
L-3	12.6	0.51	0.41	0.81	5.5
L-6	202.7	8.90	0.678	0.49	5.95
546	84.9	6.81	0.029	0.033	1.1
3150	31.6	11.31	0.213	0.22	3.85
G-29	256.5	2.57	0.466	0.23	4.15
PR-8	1020	19.68	1.29	1.04	6.6
FL	200.5	0.76	0.2	0.097	3.4
6369	9.22	24.07	0.146	0.26	1.36
2048-1	13.8	1.69	0.466	0.43	1.34
1309	60.2	28.73	0.625	0.80	12.8
862-2	276.8	43.89	0.266	0.27	3.2
DS	1530	24.47	0.319	0.25	2.4
Clarke	40	2	0.3	0.2	0.2

It is noteworthy that the phosphorite samples with the highest contents of heavy PGEs are also enriched in other associated elements. For example, the sample from the Pacific seamount is enriched in Co, Ni, and Cu; the Moroccan phosphorite, in Ni and Cu; and the nodule from the outer Namibian shelf, in Co and Ni. This PGE distribution pattern was noted in ferromanganese nodules and crusts in the World Ocean [14].

Thus, Ag and Au are typically concentrated in phosphorites genetically related to organic matter of bottom sediments [13] that extract these elements from seawater or mud water. Consequently, the phosphorites inherit Ag and Au from the enclosing sediments that are not always enriched in these elements. In contrast to other organic-rich sediments, the analyzed sample of recent diatom ooze from the Namibian shelf is not enriched in Ag and Au, although some sediments from this region are enriched in Au [15]. In addition to authigenic Au, allochthonous Au associated with quartz grains and micrograins can also be present in shelf phosphorites. This was observed in oceanic phosphorites of various types [10, 12, 13].

Anomalous Au and Fe contents recorded in one seamount phosphorite sample can be related to extraction of Au and nonferrous metals by ferromanganese hydroxides from seawater. This process can serve as one of the major mechanisms of Au delivery to ferromanganese crusts on seamounts [14].

Phosphorites and sediments are enriched in Ru simultaneously with U. Our data show that the U content varies from 17 (seamount phosphorite) to 887 ppm (Pleistocene phosphorite nodule from the Namibian shelf). This is probably caused by different types of behavior of light and heavy PGEs in the marine environment.

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