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GEOCHEMISTRY

Rare Earth Elements as Indicators of Formation Conditions of Cretaceous Phosphorites: Evidence from the East European Platform

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Cretaceous phosphorites are abundant in the sedimentary cover of the central East European Platform as grains, pebbles, nodules, and economic-grade beds. We studied Cenomanian phosphorite deposits of the Voronezh anteclise (Polpinsk, Shchigrovsk, Svobodinsk deposits and several occurrences), the Campanian Unecha deposit, and the Valanginian Vyatka–Kama deposit in the Vyatka–Kama anteclise.

REE concentrations were measured by the ICP-MS method at the laboratories of the Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry and the Institute of Mineralogy, Geochemistry, and Crystal Chemistry of Rare Elements. The obtained data were analyzed using LREE–MREE–(HREE × 10) [10], La–(Nd + Sm)–(Y + Dy), La–(Ce + Nd + Sm)–(Y + Dy) diagrams [4, 5, 7], REE distribution patterns, and geochemical coefficients.

The platformal clay-normalized [1] REE distribution in phosphorites is primarily characterized by a uniform and weakly fractionated pattern with close contents of LREE, MREE, and HREE. Their distribution spectra are close to the sample/platformal clay curve. Individual phosphorites show a distinct positive Eu anomaly and enrichment in HREE (to a lesser extent, MREE) relative to LREE. In the LREE–MREE–(HREE × 10) diagram (Fig. 1), the phosphorites form a compact field, indicating similar facies conditions. Based on the diagrams, the Cretaceous phosphates were formed in a relatively shallow-water distal environment [8, 9].

The coefficients that characterize the facies conditions (table) [9, 11] are close to those in shelf waters of the present-day World Ocean: La/Yb = 13.1, La/Sm = 5.2, Ce/Sm = 13.0, Yb/Sm = 0.4, Y/Sm = 7.7 [1]. The average Eu/Eu* ratios in the Cenomanian and Valanginian phosphorites are close to those in sedimentary rocks (0.61–0.72) [2]. The average Eu/Sm ratio characterizes insignificant permeability of the Earth's crust within the sedimentation basin during phosphate formation. The Ce/Ce* ratio in phosphorites attests to epi- and pericontinental sedimentation environments with Ce/Ce* = 0.9–1.3 [12]. The Σ(REE + Y) content in the Cenomanian phosphorites is similar to that in the platformal clays (199.0 ppm) [1], while high values of the coefficient in the Valanginian and Campanian phosphorites correspond to the Σ(REE + Y) content in pericontinental settings [3].

The ΣCe/ΣY ratios characterize the type of lithogenesis. In [6], ΣCe/ΣY = 3 was proposed as the boundary

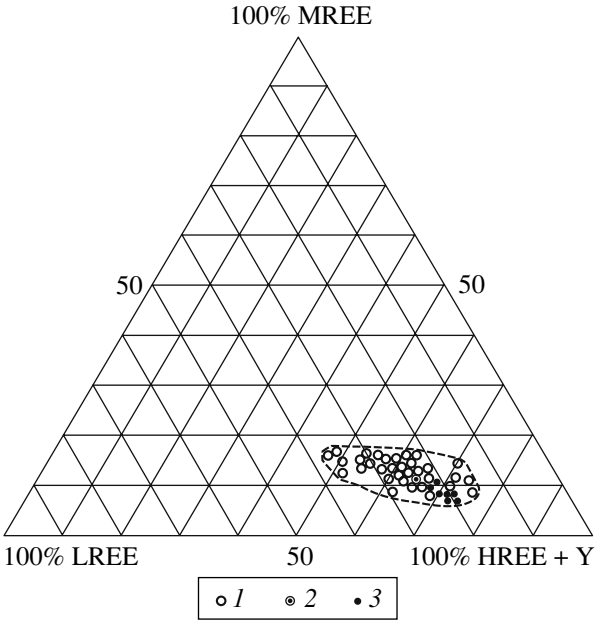

Fig. 1. LREE–MREE–(HREE × 10) diagram for phosphorites. Hereainafter, (*1*) Cenomanian, (*2*) Campanian, (*3*) Valanginian.

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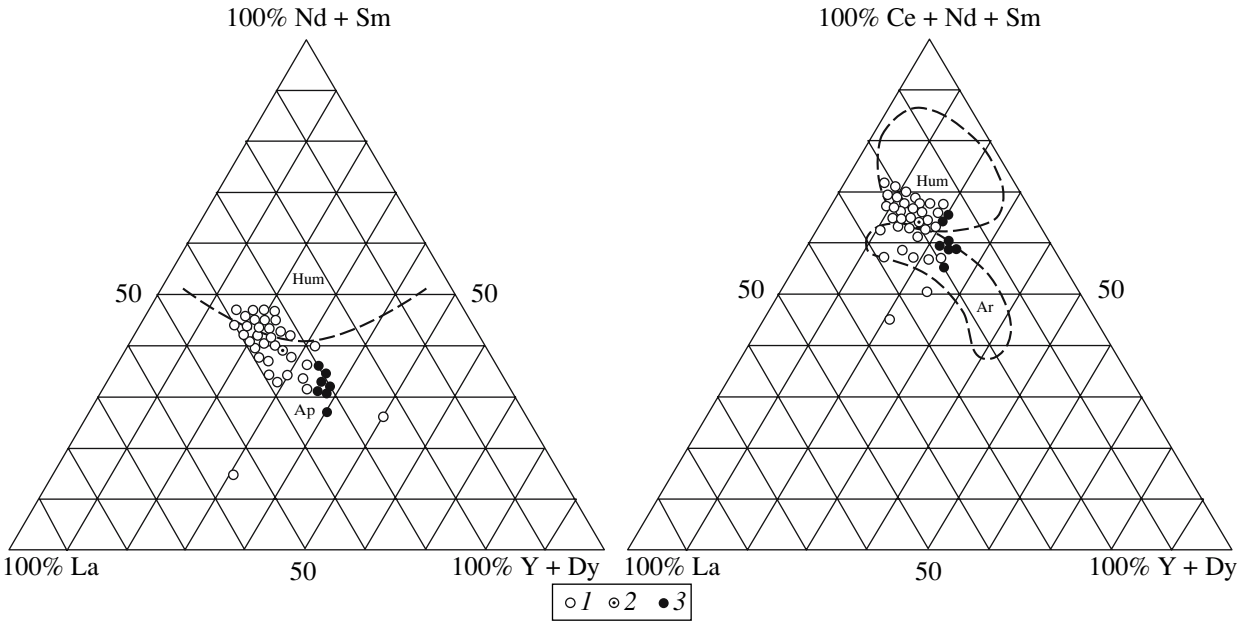

Fig. 2. La–(Nd + Sm)–(Y + Dy) and La–(Ce + Nd + Sm)–(Y + Dy) diagrams for phosphorites.

between the humid and arid conditions. Now this parameter has been specified: $\Sigma Ce/\Sigma Y = 2.5–4$ in semiarid–semihumid conditions; <2.5 in arid conditions; and >4 in humid conditions. Based on this ratio, the climatic conditions of phosphate formation are determined as semiarid–semihumid for Upper Cretaceous deposits and semiarid for Lower Cretaceous deposits. Using La–(Nd + Sm)–(Y + Dy) and La–(Ce + Nd + Sm)–(Y + Dy) diagrams (Fig. 2) compiled by the authors for climatic reconstructions of glauconite formation, the phosphates were formed under semiarid–semihumid conditions, with more arid conditions in the Valanginian as compared to the Cenomanian time. This is confirmed by the X-ray analysis data (the presence of palygorskite and gypsum in the Valanginian phosphorites and their absence in the Cenomanian phosphorites) and the lower average $\Sigma Ce/\Sigma Y$ values for phosphorites of the Vyatka–Kama deposit as compared to the Cenomanian phosphorites of the Voronezh anteclise (table). The validity of these diagrams for phosphorites is confirmed by compact swarms of data points, which almost do not fall beyond the fields of definite climatic conditions.

Geochemical coefficients (average values) in the Cretaceous phosphorites

	Voronezh anteclise		Vyatka–Kama anteclise
	Cenomanian stage (33 sample)	Campanian stage (1 sample)	Valanginian stage (7 sample)
Σ(REE + Y)	186.7	2246.9	793.0
Eu/Eu*	0.72	0.45	0.74
Eu/Sm	0.27	0.16	0.24
Ce/Ce*	1.04	1.04	1.36
$\Sigma Ce/\Sigma Y$	3.64	3.73	3.1
La/Yb	10.34	13.8	20.3
La/Sm	5.49	5.76	5.97
Ce/Sm	10.69	11.41	13.2
Yb/Sm	0.59	0.42	0.3
Y/Sm	2.85	3.86	6.44

Thus, the Cretaceous phosphates of the Voronezh and Vyatka–Kama anteclises were formed in an epicontinental shallow-marine distal environment under semiarid–semihumid conditions, with more arid conditions in the Valanginian time as compared to the Upper Cretaceous.

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