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Origin of Cenomanian Nodular Phosphorites in the Dnieper–Donets Depression (Paleogeographic Aspect)

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Abstract—Paleogeographic settings of the Dnieper–Donets Depression are discussed with consideration of its Cenomanian provenance, land–sea proportions, and paleoclimate. The role of the Jurassic–Cretaceous weathering crust that stimulated the formation of phosphate solutions and the accumulation of apatite–ilmenite placer deposits is emphasized. Based on global regularities in the phosphorite formation, it is stated that weathered areas of adjacent land, rather than the World Ocean, represented the main source of phosphorus in ancient platform basins.

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It is well known that the Dnieper–Donets Depression of the East European Platform represents a large NW-oriented syncline located between the Ukrainian crystalline shield in the southwest and Voronezh Massif in the northeast.

The structure is bordered by the Belarus Massif in the northwest and the Donets Paleozoic massif and Don–Donets threshold in the southeast (Shatsky, 1946; Sobolevskaya, 1951; Bogdanov, 1964; *Tektonika…*, 1975; Khain, 1977; and others).

The Dnieper–Donets Depression is filled with thick Paleozoic and Mesozoic sediments. Cenomanian terrigenous–clayey and terrigenous–carbonate sediments in the sedimentary cover of the depression enclose numerous ore occurrences and deposits of nodular phosphorites. These deposits are scrutinized in works of A.D. Arkhangelsky, G.I. Bushinskii, P.P. Drozhzhevaya, B.M. Gimmel'farb, M.I. Karpova, V.I. Belyaev, A.D. Savko, S.V. Manukovskii, V.I. Fominskii, S.Yu. Malenkina, and others. As was previously emphasized (Kholodov and Paul, 2001), Polpin (Bryansk) and Shchigry (Kursk) nodular phosphorite deposits are the largest ones. In addition, similar occurrences of Cenomanian phosphorites are known in the western Voronezh and Smolensk regions and at the middle course of the Dnieper River (Ukraine).

Paleogeographic formation settings of Cenomanian phosphorite deposits in the Dnieper–Donets Depression are now sufficiently well studied. They clarify to a significant extent the origin of "platformal" nodular phosphorites and, therefore, their analysis is the main purpose of this work.

GENERAL CENOMANIAN PALEOGEOGRAPHY OF THE SOUTHERN EAST EUROPEAN PLATFORM

Land and Sea Proportions

The distribution of land areas and sea basins in the East European Platform during the Cenomanian has been studied by A.D. Arkhangelsky, V.N. Sobolevskaya, A.P. Vinogradov, A.B. Ronov, and other scientists. The most substantiated scheme of Cenomanian paleogeography was compiled by Sobolevskaya (1951) on the basis of geological map (scale 1: 5000000). The scheme is based on 108 lithofacies sections located in different areas of the region. They were studied and generalized by outstanding experts in platform geology using the common stratigraphic scheme. This paleogeographic map (Fig. 1) shows that the entire northern part of the region represented in the Cenomanian a land area extending in the near-latitudinal direction conformable with the "Caucasian" strike.

Its central part located between Velikie Luki, Tula, and Tambov represented a peninsula corresponding to the northeastern flank of the Voronezh Massif. The area located southeast of the Voronezh peninsula was occupied by a sea basin corresponding to the Dnieper–Donets Depression. In the southwest, the basin was bordered by the elevated Ukrainian crystalline shield that extended from Pinsk to Dnepropetrovsk. The southeastern continuation of the shield was represented by a large island located in the present-day Severnyi Donets scroll area. The island was surrounded by the Cenomanian sea, which probably covered the Dnieper–Donets Depression and spacious areas of the Ciscaucasian and Caspian regions.

When considering facies peculiarities of Cenomanian marine sediments developed in the Dnieper–

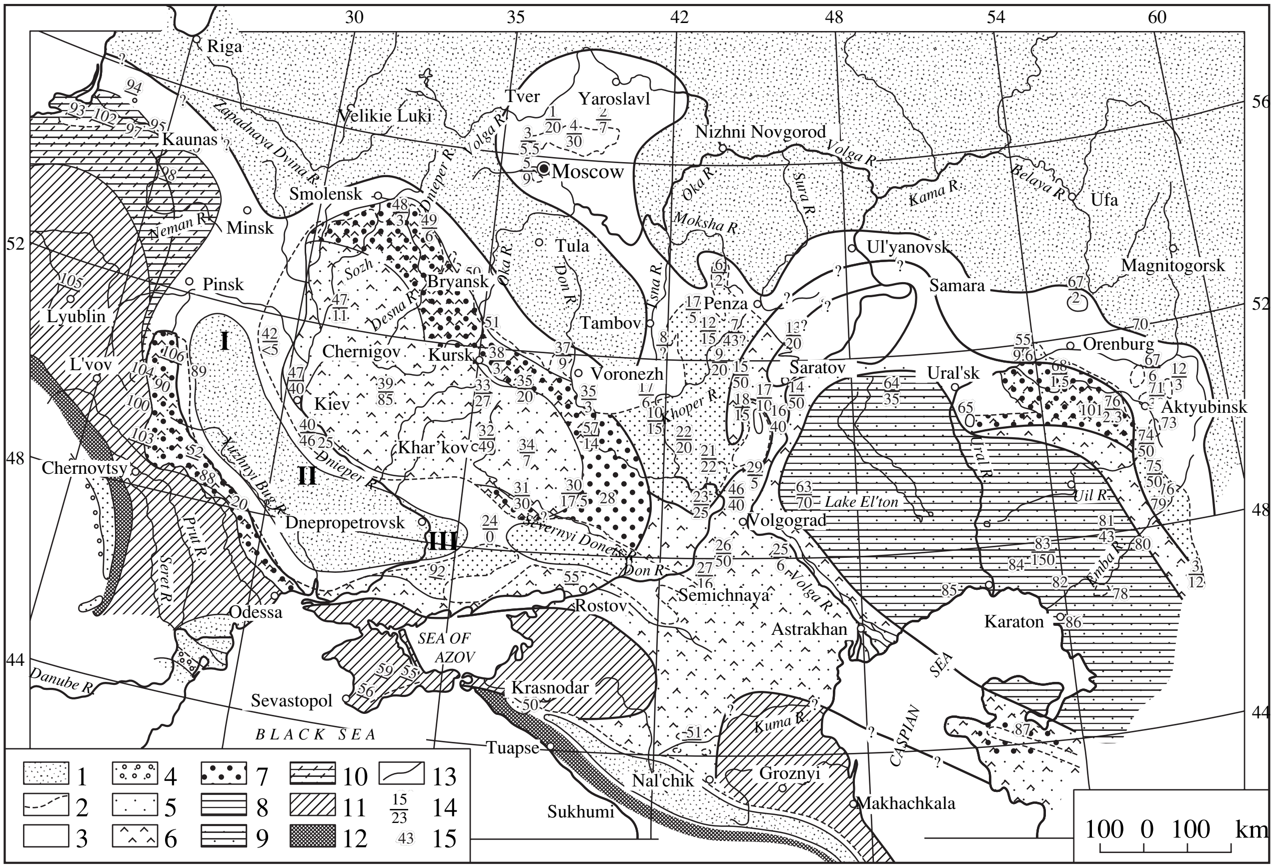

Fig. 1. Cenomanian paleogeography and facies of the East European Platform (Sobolevskaya, 1951). (1) Erosion area (land); (2) boundary of the present-day field of Cenomanian sediments; (3) assumed initial field of Cenomanian sediments eroded later; (4) coarse-grained clastic material (conglomerate, pebble gravel, gravel, and others); (5) quartz sand; (6) glauconite; (7) phosphorites; (8) clay; (9) sandy clay; (10) marly clay; (11) marl; (12) Upper Cretaceous flysch; (13) conditional boundaries between facies; (14) sampling site (numerator) and thickness of Cenomanian sediments, m (denominator) (15) sampling site number. (I–III) intrusions: (I) Korosten, (II) Korsun–Novomirgorod, (III) Oktyabr'sk.

Donets Depression, we should keep in mind that their section is almost universally characterized by a two-member structure. The lower part is composed of terrigenous sandstones and siltstones containing quartz, glauconite, and phosphorites. The upper part consists of sandy chalk ("surka"). Sobolevskaya devoted the main attention to facies relationships in the lower part of the section and arbitrarily considered the surka as a permanent constituent of the Cenomanian sequence.

The analysis of the relevant paleogeographic map reveals the circum-continental distribution of facies zones. The central part of the syncline is dominated by terrigenous–glauconitic sediments that make up an oval spot near Chernigov and Khar'kov. Locally, they are replaced by pure oligomictic quartz sands and sandstones that represent typical sediments of ancient platforms closely associated with humid weathering and maturing.

Terrigenous–phosphorite facies make up an external ring around the oval spot closer to the Cenomanian shore. Following probably the bathymetric pattern of the Dnieper–Donets paleobasin, these facies are more widespread in its northern part, as compared with southern and southwestern segments. The southwestern coast of the paleobasin is locally marked by coarse-grained pebble gravel and gravelstones that often make up regular fans, which mark Cenomanian rivers flowing from the Ukrainian crystalline shield.

The Cenomanian sea of the Dnieper–Donets Depression was surrounded by islands or continental land. According to (Sobolevskaya, 1951), this sea area could be isolated notably from its main part. In the southeast, it was bordered by the underwater Don–Donets threshold, which hindered free migration of the benthic fauna. For example, inarticulate brachiopods *Lingula krausei Dam.*, which were widespread in Cenomanian marine sediments of the Caspian region, are extremely rare or absent in the Dnieper–Donets part of the paleobasin. There are also differences in faunal communities of the Polish–German and Dnieper–Donets Cenomanian paleobasins.

Based on materials of the VNIGNI (O.V. Flerova, Ya.S. Eventov), Saratov University (N.S. Morozov), Academy of Sciences of the Ukrainian SSR

(E.Ya. Kraeva), Academy of Sciences of the Belarussian SSR (V.S. Akimets), and Central Research Laboratory of the Volgograd Council for National Economy (A.V. Smirnov), A.B. Ronov compiled a principally similar paleogeographic map at a scale of 1: 5000000 (*Atlas…*, 1961). However, this map is distinguished from Sobolevskaya's version by the synthesis of several more detailed paleogeographic maps available for different areas and regions. Therefore, it is less reliable.

In principle, the paleogeographic map compiled by Ronov corresponds to Sobolevskaya's version, but the role of land areas surrounding the Dnieper–Donets Depression is underestimated. The southeastern Ukrainian land consists of several islands, while the northeastern Voronezh Peninsula is shown as an island.

In Sobolevskaya's version, the main attention is paid to sedimentation settings during the early Cenomanian. The map compiled by Ronov reflects relationships between the lower and upper parts of the Cenomanian section. It demonstrates that the surka facies prevails in the northwestern part of the depression, while the remainder of the Dnieper–Donets paleobasin is largely covered by terrigenous sediments with glauconite and phosphorites,

The thickness of Cenomanian sediments, which form an isolated lenticular sedimentary body, increases generally from surrounding uplifts toward the central part of the depression. This inference confirms Sobolevskaya's interpretations.

Cenomanian Climate and Dominant Landscapes

Main reconstructions of global paleoclimatic epochs are considered in numerous works of F. Lotze, M. Schwartzbach, E. Dorf, E.S. Barghorn, R. Kreisel, A.H. Smith, V.A. Vakhrameev, L.B. Rukhin, N.M. Strakhov, A.B. Ronov, and others.

Summarizing these studies, Strakhov (1947, 1960) formulated the following three principal postulates that keep their significance until now.

(1) Global paleoclimatic zones of the Earth are always symmetrical relative to the equatorial tropical humid zone.

(2) The spatial position of global paleoclimatic zones is reconstructed by mapping lithological or biotic climate indicators. The lithological indicators are as follows: bauxites, iron ores, peat, coal, kaolinite, and oligomictic sandstones (*humid* region); evaporites, and chemogenic carbonates, Cu–Pb–Zn deposits (*arid* region); and tillites, tilloids, and varves (*glacial* region). The biotic indicators are as follows: different fossil plants, their spores and pollen, and remains of animal organisms closely associated with particular past settings.

(3) Paleoclimatic reconstructions should always be based on lithological climatic indicators. The less certain floral and faunal indices allow us to specify only the general paleoclimatic situation of the particular geological epoch.

Subsequently, these principles were used to compile global paleoclimatic maps for the Cenomanian and late Cretaceous based on the traditional (Braitsch, 1968; Zharkov, 1978; Sinitsyn, 1980; Ronov and Balukhovskii, 1981, and others) and mobilistic (Chumakov, 1984; Chumakov et al., 1995; Zharkov et al., 2004; Herman, 2005) concepts.

Based on the study of glacial epochs in the Earth's history and the analysis of dynamics of paleoclimatic zonality in the Phanerozoic, Chumakov (1995) formulated the concept of alternating glacial and ice-free warm epochs, which could differ in both glaciation scales and types of the climatic zonality. According to Chumakov (1984), the warm biosphere and thermal climatic zonality were typical of the Cambrian–Ordovician, Devonian, and Jurassic–Cretaceous. In contrast, the Silurian, Carboniferous, partly Permian, and Tertiary–Quaternary periods corresponded to periods of the sporadic distribution of global glaciation, which developed around poles, substantially transformed the general climatic zonality of the planet, and made it similar to the present-day one.

According to (Schwartzbach, 1955; Krishtofovich, 1957; Sinitsyn, 1980), northwestern Europe was characterized in the Late Cretaceous by high annual mean temperatures and high atmospheric precipitation. Instead of the present-day northern humid zone, this region was occupied by spatially associated subtropical and boreal zones. The polar glacial zone typical of present-day high latitudes was almost missing at that time. According to Krishtofovich (1957), angiosperms, ferns, and conifers were spread in the Cenomanian at the latitude of Greenland and palms grew in the Arctic part of America at that time.

The Cenomanian–Campanian climate warming is well illustrated by the map of climatic zonality (Fig. 2) based on the modern geographic map at a scale of 1 : 25 000 000 (Ronov and Balukhovskii, 1981).

The analysis of the climatic zonality map reveals that the entire East European Platform was located in two paleoclimatic zones during the Cenomanian. The tropical–subtropical humid and temperate humid zones were located in the south and north, respectively. The boundary of the northern arid zone passed along the northern coast of the Mediterranean Sea and extended to boundaries of present-day Iran and Afghanistan, where it turned sharply to the northeast and further to northern boundaries of present-day Mongolia. The boundary separating the subtropical and temperate humid zones crossed the East European Platform from the Middle Urals (approximately the Tagil area) toward Narvik and Budeu (Norway).

Thus, the entire land area surrounding the Dnieper–Donets Depression was located in the Cenomanian within the warm subtropical zone, where the annual mean temperature varied from +20 to +21°C and the

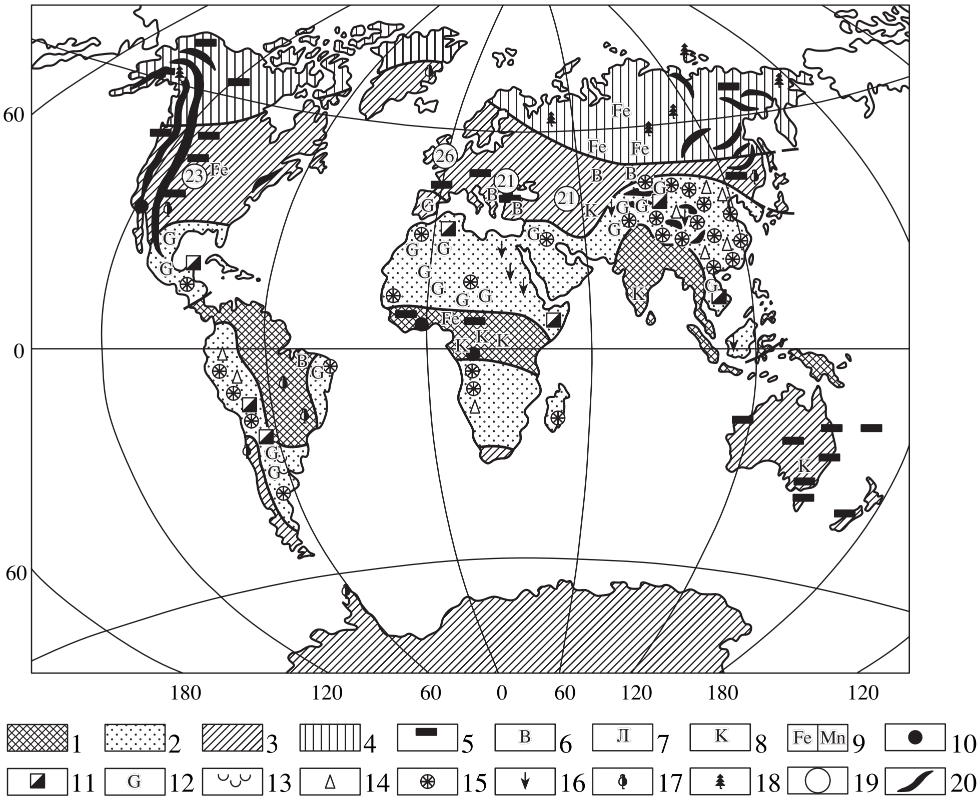

Fig. 2. Map of climatic zonality of continents in the Cenomanian (Ronov and Balukhovskii, 1981). (1) Equatorial humid zone; (2) arid zones; (3) tropical and subtropical humid zones; (4) temperate humid zones; (5) coal and lignite; (6) bauxite (B); (7) laterite; (8) kaolinite (K); (9) sedimentary iron and manganese ores; (10) weathering crust, redbeds, and variegated sediments; (11) salt; (12) gypsum (G) and anhydrite (A); (13) eolian desert sediments; (14) terrestrial carbonate sediments with gypsum; (15) carbonate redbeds and variegated sediments; (16) xerophyte flora indicating arid climate; (17) flora of the humid tropical and subtropical climate; (18) flora of the humid temperate climate; (19) oxygen isotope paleotemperatures; (20) mountainous systems.

atmospheric precipitation ranged from 2000 to 2500 mm/yr (for comparison, the atmospheric precipitation in the present-day tropical zone is estimated at 2500–3000 mm/yr, annual mean temperature varies from +25 to +26°C). It goes without saying that exposed bedrocks were subjected to intense chemical decomposition and weathering in such climatic environments.

It should be emphasized that the climatic zonality defined for the Cenomanian remained stable for a long time. Similar spatial relationships between the subtropical and temperate humid zones are also outlined in separate paleoclimatic maps compiled for three Jurassic and Cretaceous epochs (Ronov and Balukhovskii, 1981).

Similar inferences are obtained from reconstructions based on the consideration of the continental drift. According to (Chumakov et al., 1995; German, 2005), paleoclimatic estimates reconstructed for the southern part of the East European Platform with the consideration of the continental drift appear to be identical to the zonality in the map compiled by Ronov and Balukhovskii (1981). In addition, according to German (2005), all the 12 paleoclimatic maps compiled for different periods of the Early and Late Cretaceous indicate the lack of glaciation at high latitudes and two-member patterns of the northern humid belt that includes the subtropical and temperate humid zones.

Hence, land areas of the southern East European Platform were located in the zone of subtropical forests.

According to (Yarmolenko, 1935; Baikovskaya, 1953; Vakhrameev, 1952, 1959), the northern part of the platform was covered with coniferous–broadleaved forests dominated by platans (*Platanus, Protophyllum, Credneria*, and others). The conifers were largely represented by genera of the Taxodiaceae (*Sequoia, Cephalotaxopsis*, and others) and Pinaceae (*Pinus, Picea, Cedrus, Abies*) families. The lower level of forests was represented by ferns (*Asplenium, Gleichenia, Aneimia*) and Cicadophycaceae species. Vegetation of southern areas of this forest zone included abundant evergreen forms, such as magnolia, laurel, and myrtle.

It is remarkable that maritime plains were occupied by numerous lowmoors and peats, which were transformed in the post-Cretaceous time into coal seams and

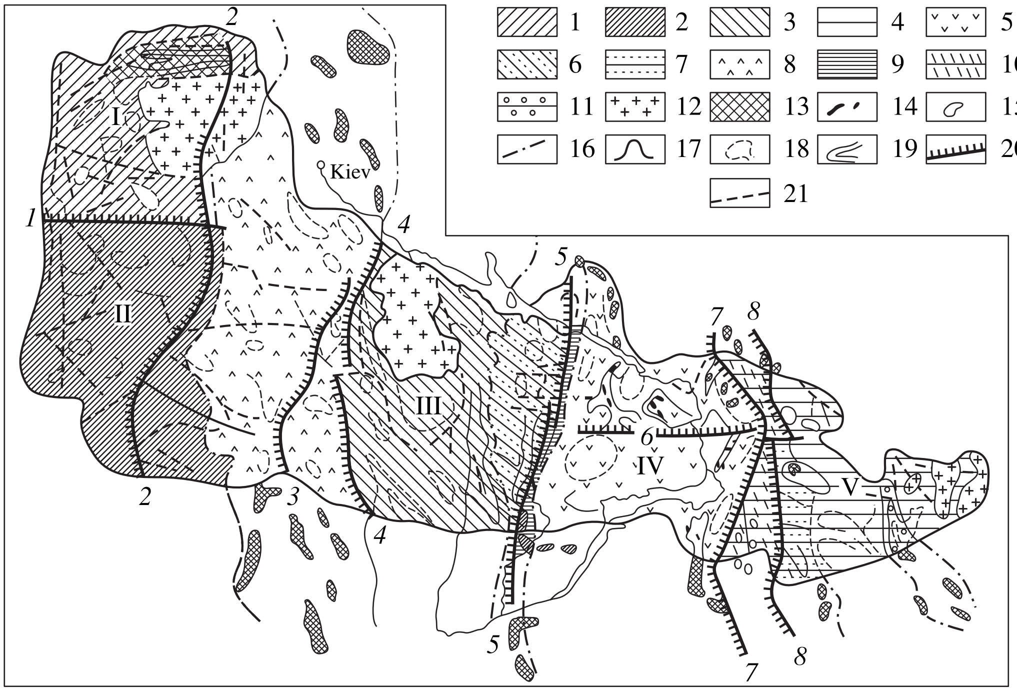

Fig. 3. Schematic structure of the Ukrainian Shield (Khain, 1977). (1–5) Blocks consolidated in the terminal Archean: (1) Volyn (I), (2) Bug–Podolia (II), (3) Kirovograd (III), (4) Dnieper (IV), (5) Azov (V); (6, 7) margins of Archean blocks involved into geosynclinal subsidence in the Early Proterozoic: (6) Western Ingulets, (7) Western Azov; (8–11) Early Proterozoic protogeosynclines: (8) Odessa–Kanev, (9) Krivoi Rog–Kremenchug, (10) Orekhov–Pavlograd, (11) Mangush; (12) plutons of rapakivi granites and mafic rocks; (13) Late Proterozoic Ovruch intracratonic trough; (14) outcrops of ferruginous quartzites; (15) intense positive magnetic anomalies corresponding to unexposed ferruginous quartzites; (16) boundaries of structural zones; (17) contours of the shield; (18) conditional contours of anticlinal basement structure; (19) the same of synclinal structures; (20) major hidden faults; (21) regional faults: (*1*) Andrushov, (*2*) Western Zhitomir, (*3*) Western Uman, (*4*) Buz'ko–Mironov, (*5*) Krivoi Rog, (*6*) Devlad, (*7*) Orekhov–Pavlograd, (*8*) Azov–Pavlograd.

deposits widespread throughout the Cenomanian land (Ronov and Balukhovskii, 1981).

Geological Structure and Composition of the Adjacent Land

The Ukrainian crystalline shield and Voronezh Massif served as a provenance for the Cenomanian Dnieper–Donets paleobasin and played a significant role in its geochemistry.

The *Ukrainian crystalline shield* composed of Precambrian crystalline rocks extends in the northeastern direction over more than 1000 km (width 250–300 km). Figure 3 adopted from the monograph by Khain (1977) illustrates its geological structure.

The shield is mainly composed of Archean (less commonly, Lower Proterozoic) gneisses, crystalline schists, amphibolites, quartzites, marbles, and migmatizing granitoids and ultramafic rocks. The entire Precambrian rock complex is intricately deformed and disintegrated into several blocks. These blocks originated in the Katarchean and are separated by near-meridional deep-seated faults, which form a system of graben-synclines filled with lower Proterozoic rock complexes enclosing ferruginous quartzites and jaspilites. The Volyn and Bug–Podolia blocks, as well as the Dniester and Azov megablocks, are defined from the west to east.

Igneous rocks constituting the shield were the main sources of ore material for the adjacent paleoseas. Ore components were primarily delivered by the following rocks: (1) mafic–ultramafic complexes of the Korosten Pluton the intrude Archean rocks of the Volyn and Kirovograd blocks; (2) mafic–ultramafic complexes of the Mirgorod Pluton located in the Kirovograd block; (3) alkali granites of the Oktyabr'sk Pluton and carbonatite occurrences in the Azov region; and (4) Proterozoic iron ore formations of suture zones (particularly, ferruginous quartzites of Krivoi Rog).

The *Korosten Pluton* located in the northwestern part pf the Volyn block is composed of intricate combination of rapakivi granites and ultramafic rocks that intrude Archean gneisses, crystalline schists, amphibolites, quartzites, and marbles. The massif, 12000 km^2 in size, includes ultramafic rocks in its southern part in the form of isolated bodies with a total area of 1300 km^2. Igneous rocks of the mafic complex are represented by the dominant gabbro anorthosites and the subordinate anorthosites, gabbro norites, and norites (Moshkin and Dagelaiskaya, 1974).

Table 1. Composition of igneous and metamorphic rocks of the Ukrainian crystalline shield (Dodatko et al., 1975)

Oxides, %	Gabbro–anorthosite, Korosten massif	Amphibolite, Middle Dniester region	Peridotite, Davlatovo massif, Middle Dniester region	Serpentinite, Nikolaev massif, Middle Dniester region
SiO_2	51.21	51.40	42.40	29.20
TiO_2	0.62	0.76	0.21	0.05
Al_2O_3	23.18	12.33	3.18	1.14
Fe_2O_3	1.40	5.25	4.71	0.99
FeO	4.17	6.62	5.73	5.51
MnO	0.04	0.18	0.14	
MgO	1.60	8.00	34.70	0.13
CaO	8.46	10.10	2.42	34.40
Na_2O	4.70	1.84	0.45	–
K_2O	1.17	0.16		0.95
P_2O_5	0.35	0.055	0.032	0.018
SO_3	Not determined	0.099	0.102	0.24
CO_2	1.10	1.06	0.66	18.48
H_2O	0.76	1.00	0.24	0.20
LOI	2.27	2.43	5.85	26.25
Nb_2O_5	–	0.024	–	–
Cr_2O_3	–	0.08	0.33	0.15
NiO	–	–	0.23	0.85
Total	100.42	100.32	100.73	100.69

Table 1 presents the most typical composition of gabbro anorthosites. It is seen that ultramafic rocks are characterized by high Fe, Ti, and P contents.

Semenenko et al. (1960) define three age series among igneous rocks in the Korosten intrusion: old ultramafic rocks, intermediate rapakivi granites, and young alkali syenites and vein–dike alkali rock complexes. The age of ultramafic intrusions of the Korosten Pluton is estimated at 1750–1850 Ma (Semenenko et al., 1960) or 1.7–1.9 Ga (Shcherbak, 1975).

The *Korsun–Novomirgorod Pluton* located in the northwestern part of the Kirovograd block represents a spacious Middle Proterozoic layered pluton of gabbro and rapakivi granites. Like in the Korosten Pluton, gabbro anorthosites and anorthosites here form isolated bodies with the total area of 5400 km2. In the Novomirgorod, Gorodishche, and Smelyansk ultramafic bodies, anorthosites distinctly prevail over gabbro anorthosites and gabbroids (Moshkin and Dagelaiskaya, 1974). The rocks contain titanomagnetite, magnetite, and apatite that make up commercial accumulations in some places (Dagelaiskii, 1988). The ultramafic rocks are 1.84 Ga old (Birkis and Koshik, 1984).

Middle Proterozoic *alkali plutons* are distributed in the eastern part of the Azov block as the Oktyabr'sk (Mariupol), Malo-Tersyaw, Pokrovsko-Kireevsk, and Kal'mius massifs of syenites, juvites, shonkinites, and other alkali igneous rocks. According to Tsarovskii (1968), the apatite potential of these massifs is low because of the low content of P_2O_5 and rare accumulations of vein apatite along fissures.

Alkali rocks and carbonatites of the Novaya Poltava apatite–rare metal deposits, which mark the hidden Chernigov fault, are prominent among rocks in this area. The deposit (1.8–2.0 Ga) is represented by a very large dike (0.9 km wide and 13 km long) composed of alkali and nepheline syenites (external zone) and carbonatites (inner zone). Carbonatites constitute nine large and seven smaller lenticular bodies of apatite–dolomite–calcite and apatite–pyroxene–feldspar ores. They contain apatite (12%) and magnetite (1–6%) accompanied by fergusonite ($(Y,Er,Ce,U)(Nb,Ta,Ti)O_4$) and other rare earth minerals.

Proterozoic iron ore formations are widespread in the Krivoi Rog suture that separates the Dniester and Kirovograd blocks. It is composed of the Krivoi Rog metabasic rock complex (up to 8 km thick, 2100–1800 Ma) that encloses the sequence of ferruginous quartzites. Hematite–martite–magnetite ores of this region contain >58% of Fe and <14% of SiO_2. The Krivoi Rog basin is characterized by huge reserves of magnetite. Taking into consideration Proterozoic jaspillites in other suture zones of the Ukrainian Massif, the Ukrainian Shield could serve as an important sup-

Table 2. Thickness of the weathering crust developed after rocks of the Ukrainian crystalline shield (Bass et al., 1975)

Region	Area (% of the total)	Thickness of the weathering crust, m				
		0	0–10%	10–20%	20–40%	40–60%
Volyn–Podolia	41	18	48	22	11	1
Central	28	46	32	11	9	2
Dnieper	24	21	40	25	12	2
Azov	7	21	62	11	6	–
Total for the shield (200000 km^2)	100	21.6	42.6	18.9	10.4	1.5

plier of Fe and Mn to the adjacent paleoseas during the Jurassic–Cretaceous erosion epoch.

Thus, the Precambrian land of the Ukrainian Shield, which bordered the Cenomanian sea basin of the Dnieper–Donets Depression, was characterized by intricate metallogeny.

In contrast, the northern insular and continental land areas, which represented the northeastern flank of the *Voronezh Massif* and southwestern flank of the *Moscow Syncline*, were remarkably sterile with respect to metals. These areas were occupied by Devonian terrigenous–redbed, evaporitic, and carbonate rocks, as well as Carboniferous carbonate and terrigenous–clayey sediments (Savko, 2000). They provided carbonate and, to a lesser extent, terrigenous material to the Cenomanian basin.

Weathering Crusts and Their Geochemical Specialization

Weathering crusts of the Ukrainian Shield have been studied by many Ukrainian geologists (Yu.B. Bass, N.I. Buchinskaya, E.G. Kukovskii, Yu.A. Rus'ko, A.D. Dodatko, V.G. Pogrebnoi, M.D. El'yanov, E.K. Lazarenko, Yu.P. Mel'nik, M.G. Berger, V.Yu. Kondrachuk, M.B. Slavutskii, and others). They have shown that this region passed through several stages of weathering crust formation. The weathering crust was best developed in the Middle Jurassic–Early Cretaceous periods of the Middle Mesozoic.

The Middle Jurassic–Early Cretaceous weathering crust is developed over the entire shield. The crust usually overlaps crystalline rocks of the Precambrian basement and is overlain by Upper Cretaceous or, less commonly, Paleogene–Neogene sediments. Its thickness varies from 20 to 60 m (Table 2).

The Middle Jurassic–Early Cretaceous weathering crust is characterized by the following features: (1) dominant clayey composition; (2) well-developed vertical zoning; (3) laterite profile in mafic igneous rocks and kaolinite profiles in granitoids; (4) inheritance of textural, structural, and geochemical properties of parent rocks; and (5) grain-size heterogeneity of eluvium.

The weathering crust of the Ukrainian Shield is usually characterized by the following zonal structure (from the base to top): (1) disintegrated parent rocks; (2) intermediate weathering products (montmorillonite, nontronite, hydromica, and halloysite); (3) stable weathering products (kaolinite and iron hydroxides); and (4) ultimate weathering products (laterites with alumina and iron minerals).

The weathering crust is spatially very heterogeneous, with geochemical and metallogenic characteristics determined by the composition of underlying bedrocks. Figure 1 shows that the Korosten and Korsun–Novomirgorod plutons and alkali intrusions of the Azov block were the main suppliers of ore components to the adjacent paleoseas.

Lisitsyna (1973) scrutinized geochemical properties of weathering crusts developed after the Korosten gabbro anorthosites and divided them into different mineralogical–geochemical zones. Based on the absolute mass method, she calculated the rate of the removal of different components from eluvium (Table 3).

It is obvious that the formation of the montmorillonite zone in the weathering crust is accompanied by the intense removal of Al, Ti, and Si from the crust and the accumulation of Al, Ti, and Fe in the upper kaolinite zone. This is typical of the laterite process, an indicator of tropical weathering.

The behavior of phosphorus is interesting. The major share of this chemical element in parental anorthosites occurs as stable crystalline apatite. In the course of eluvium formation, a part of apatite (50–82%) is dissolved in water and removed from the weathering crust to the adjacent sea basins. The other part (insoluble residue) is accumulated in the weathering crust and redistributed during its reworking (formation of colluvium, talus, and proluvium). Thus, placers can be formed.

The group of Irsha ilmenite–apatite placers spatially confined to the Stremigorod ultramafic pluton, which is a constituent of the Korosten massif, is of particular interest.

The Stremigorod massif of gabbro, gabbro norites, and gabbro monzonites is highly enriched in disseminated ilmenite ($FeTiO_3$), magnetite ($FeFe_2O_4$), titanomagnetite ($FeFe_2O_4$ with admixture of TiO_2), and apa-

Table 3. Distribution of absolute masses and intensity of the output of ore components from gabbro anorthosites of the Korosten Pluton (Lisitsyna, 1973)

Weathering crust zones	Al		Ti		Si		Fe		P	
	absolute mass, mg/cm^3	% of output	absolute mass, mg/cm^3	% of output	absolute mass, mg/cm^3	% of output	absolute mass, mg/cm^3	% of output	absolute mass, mg/cm^3	% of output
Kaolinite zon	+82.49	input	+2.38	input	54.53	91.8	17.86	input	0.281	82
Montmorillonite zone	180.53	62	1.71	60	278.05	68	2.60	93	0.790	50
Parent rock (labradorite–anorthosite)	380.02	100	4.29	100	664.73	100	38.91	100	1.547	100

tite ($Ca_3(PO_4)_3CaF_2$). According to Malyshev (1957), rocks of the massif contain TiO_2 (7%), ilmenite (5–11.5%), FeO (~16%), Fe_2O_3 (~2%), and P_2O_5 (~2%).

The Irsha placers are associated with the Stremigorod weathering crust and the overlying Mesozoic–Cenozoic sedimentary sequences, which are widespread in the triangle defined by Korosten, Zhitomir, and Novograd-Volynskii. This area hosts more than twenty ilmenite–apatite placers that are distinctly confined to left tributaries of the Teterev River (Irsha, Uch, Zlobich, Lemna, Trostyanka, and other rivers). They are discussed in works of M.F. Veklich, M.G. Dyadchenko, A.Ya. Khatuntseva, I.L. Lichak, and S.I. Gurvich. The more recent works dedicated to this problem include (Zubkov and Patyk-Kara, 1997). Figure 4 illustrates the lateral distribution of these placers in the Irsha ore field. It is clearly seen that some placers are localized at river watersheds and associated with the weathering crust eluvium, while other placers extend along river channels and display their association with alluvium.

The ilmenite–apatite placers began to form in the Jurassic simultaneously with the development of weathering crusts on ultramafic rocks. This is evident from the localization of ore bodies in the Verkhnyaya Irsha deposit in the lower part of the weathering crust at its contact with disintegrated gabbro anorthosites. The weathering process stimulated the accumulation of stable apatite and ilmenite in different zones of eluvium. However, apatite was probably dissolved in the Torchinsk deposit, and the hydrogene francolite was concentrated in placers of this area (Zubkov and Patyk-Kara, 1997).

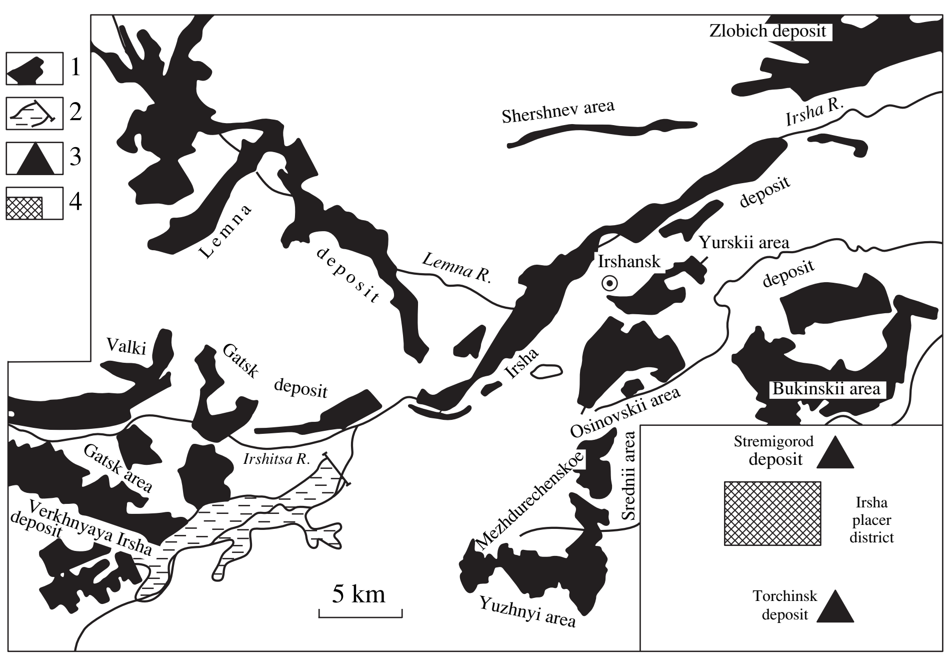

Fig. 4. Schematic distribution of ilmenite–apatite placers in the Irsha area based on the data of the Irsha ore dressing plant (Zubkov and Patyk Kara, 1997). (1) Placers; (2) dams and ponds; (3) bedrocks and their weathering crusts; (4) location of the Irsh placer district. Inset shows positions of the Irsha placers relative to the Stremigorod and Torchinsk deposits.

Subsequently, placers formed continuously in the Irsha area. This process was particularly intense during the Early Cretaceous (terrestrial), Late Cretaceous (marine), Paleogene Poltava (marine), and Quaternary (terrestrial) periods. According to Zubkov and Patyk-Kara (1997, p. 245), "…placers formed in the area during a long period beginning from the Early Cretaceous (Late Jurassic?) and they reactivated after short intervals as a result of the stable tectonic regime that stimulated the multiple reworking of ore matter from the ore-bearing eluvium and older sediments."

This process fostered the formation of intricate placers with a uniform composition. The main component is ilmenite (100–200 kg/m^3). Apatite, siderite, and titanomagnetite are subordinate.

Of particular interest are Cenomanian–Turonian placers that closely associate with coastal-marine glauconite–quartz sands. The Lemna deposit area incorporates such a placer with the following maximum contents of useful minerals (kg/m^2): ilmenite 212, siderite 112, apatite 25, and titanomagnetite 15. Leucoxene and rutile are accessory minerals.

The Lemna placer indicates that the Korosten Pluton of the Ukrainian crystalline shield undoubtedly served in the Cenomanian time as a source of P, Fe, and Ti, which were intensely transported to the Dnieper–Donets Depression. Phosphorus migrated to Cretaceous seas in the form of both stable apatite and dissolved phosphates.

Intrusions of the Azov block of the Ukrainian crystalline shield overlain by a thick Jurassic–Cretaceous weathering crust also delivered substantial quantities of ore components to Cenomanian seas. Of particular interest is the above-mentioned Novaya Poltava apatite–rare metal deposit associated with carbonatites. In this deposit, apatite–dolomite–calcite and apatite–pyroxene–feldspar dikes were subjected to intense weathering. They are overlain by the apatite-bearing kaolinite weathering crust (100–360 m thick), which represents an important commercial phosphorus deposit.

The Jurassic–Cretaceous weathering crust is overlain by the Mesozoic–Cenozoic sequence (300 m). It consists of ferruginated debris, which overlies the bedrocks, and clay–ochre–apatite zone up to 60–70 m thick. The ores are divided into the ochre–hydromica–clay–apatite and apatite–hydromica–feldspar–clay varieties.

Stratiform-lenticular orebodies within the weathering crust contain apatite (20–65), kaolinite (18), hydrophlogopite (15), and iron hydroxides (2–46%), as well as dolomite, magnetite, ilmenite and rare earth minerals. The P_2O_5 content averages 9% with the maximal value amounting to 25% (Fil'ko et al., 1985).

The weathering crust of the Azov block undoubtedly contributed much to the enrichment of the Dnieper–Donets paleobasin in apatite and dissolved phosphates.

Correlation between Erosion of Weathering Crusts of the Ukrainian Crystalline Shield and Sedimentation in Adjacent Paleoseas

Phosphorite-bearing sediments of the Dnieper–Donets Depression border the Ukrainian Shield in the northwest (Fig. 1). In the southeast, this spacious structure is surrounded by a band of Cenomanian phosphorite-bearing terrigenous sediments described in detail by D.N. Kovalenko, V.G. Semenov, N.K. Burgel, A.Yu. Senkevich, I.V. Gukovskii, M.P. Mel'nikov, and other Ukrainian geologists. According to (Sen'kovskii et al., 1989), Cenomanian phosphorites in sedimentary sequences of the North Black Sea Depression, which borders the Ukrainian Shield in the south, are very similar to their age analogues from the northern Dnieper–Donets Depression. These sections are particularly similar in the structure and composition of nodular phosphorites, the abundance of various phosphatized organic remains (wood fragments, sponge remains, fish and mammalian bones), and the close association of phosphorite-bearing glauconitic sands with opoka, tripoli, and chalk members.

The structure of Mesozoic–Cenozoic sections of the Dnieper–Donets and North Black Sea depressions, which surround the Ukrainian Shield, are scrutinized in (Kondrachuk et al., 1971, 1975).

These authors demonstrated that the Mesozoic–Cenozoic sequences in these depressions are characterized by cyclic lithology that is typical of wide stratigraphic intervals. This is particularly well manifested in their Cretaceous and Paleogene–Neogene cycles. Each cycle is composed of two members.

The first stage (lower part of the cycle) is composed of poorly sorted terrigenous sediments that include pebbles, sands, kaolinite, amorphous silica, and bauxites. These sediments frequently enclose coalified remains and even brown coal. They represent the shallowest coastal facies of paleoseas genetically associated with the erosion of the continental weathering crust on land.

The second stage (upper part of the cycle) includes the finer-grained carbonate, carbonate–clayey, or clayey–siliceous sediments. According to (Strakhov, 1960, 1963), they represent a mixture of terrigenous suspended particles with the typical sedimentary matrix. These sediments represent deepwater facies of sea basins, probably, with the contribution of several sources, including areas without direct link with the Ukrainian crystalline shield.

Four cycles can be distinguished in Mesozoic–Cenozoic sequences of the Dnieper–Donets and North Black Sea depressions. The most prominent Lower–Upper Cretaceous and Paleogene–Neogene cycles are observed on the northeastern, southern and western

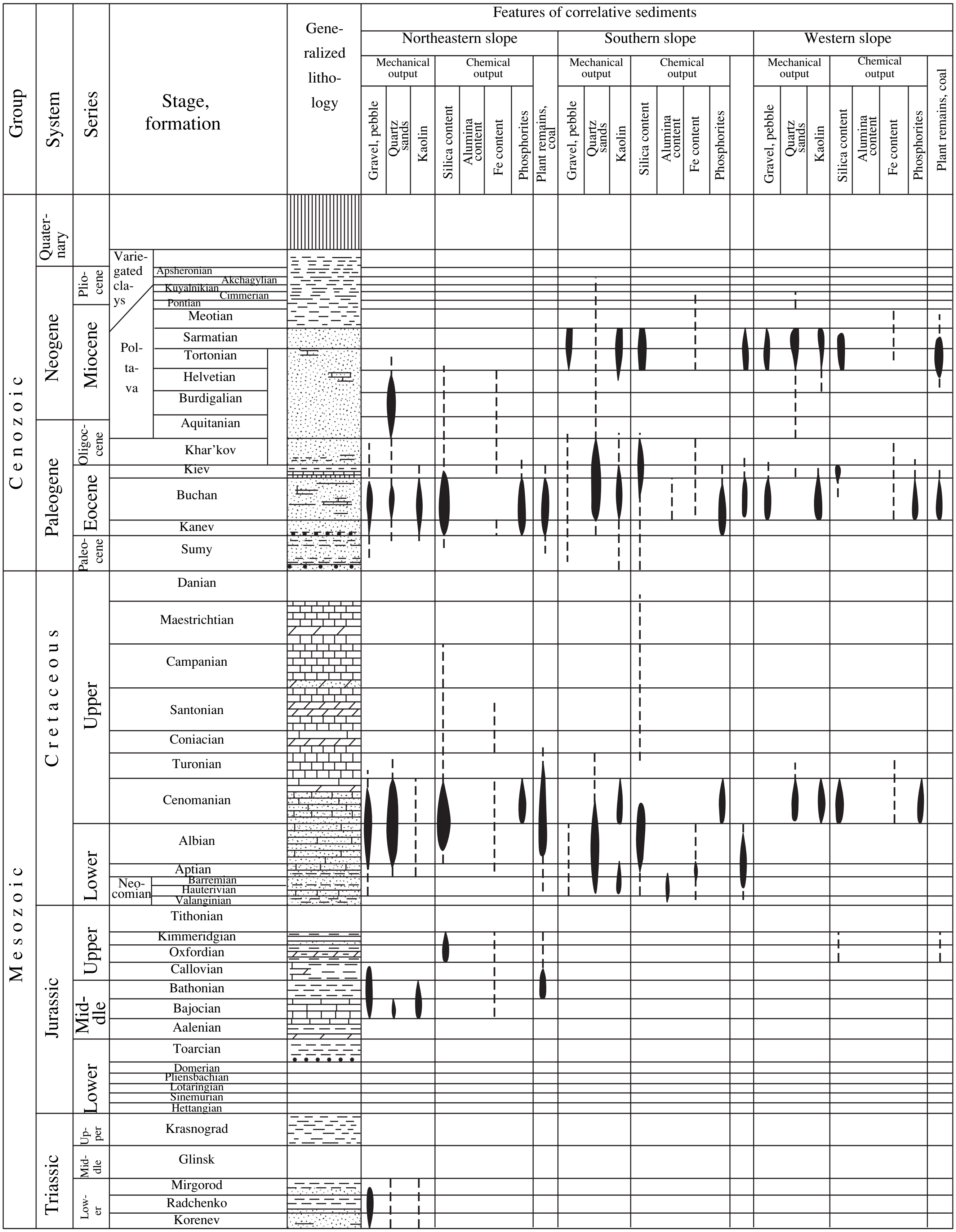

Fig. 5. Distribution of sediments correlated with the erosion of weathering crusts of the Ukrainian crystalline shield (Kondrachuk et al., 1976).

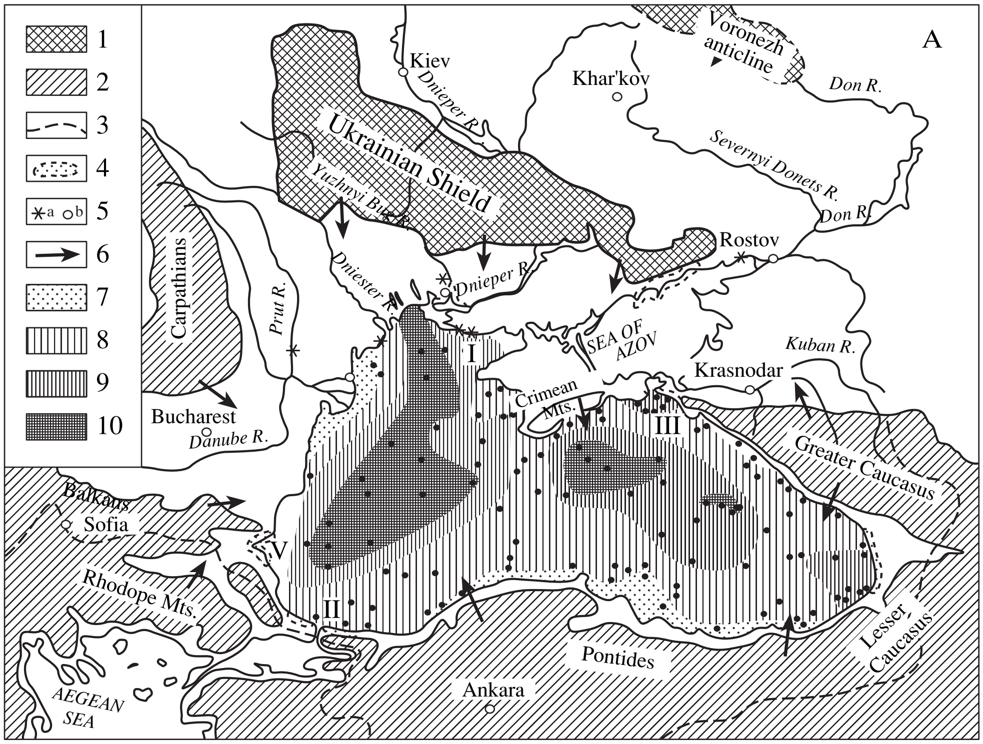

Fig. 6. Phosphate sources of recent coastal-marine placers (Shnyukov, 1983) and distribution of phosphorus in bottom sediments of the Black sea (Strakhov et al., 1971). (1) Precambrian shields; (2) Alpine folded structures; (3) watershed lines; (4) ilmenite–rutile–zircon placers with apatite admixture: (I) Dzharylgan Island and Dnieper–Bug estuary, (II) northern coast of the Sea of Azov; magnetite placers with apatite admixture: (III) Anapa area, (IV) Chorokh–Rioni area; (5) finds of (*a*) diamonds and (*b*) gold; (6) direction of terrigenous material transport; (7–10) the P content (%) calculated on the carbonate-free basis: (7) <0.04, (8) 0.04–0.07, (9) 0.07–0.10, (10) >0.1.

slopes of the Ukrainian Shield (Kondrachuk and Kornienko, 1971; Kondrachuk et al., 1973).

Results presented in Fig. 5 suggest the following conclusion. The first stage of each cycle was probably associated with erosion of the weathering crust of the Ukrainian crystalline shield in the Albian–Cenomanian and Eocene, respectively. This stage was marked by the accumulation of the universal nodular phosphorites and iron ores, coupled with sediments that serve as lithological–geochemical indicators (gravel, pebble, sand, kaolin, bauxitic alumina, cherts, and coalified plant remains).

The above fact suggests the following conclusions. Phosphorus is derived from the continental source. In nature, ultramafic and apatite-rich alkali igneous rocks, as well as weathering crusts that enclose apatite placers and generate dissolved P_2O_5, are often genetically associated with the adjacent paleoseas that concentrate apatite and dissolved P_2O_5. These components are subsequently transformed into nodular platform phosphorites.

The influence of apatite-bearing intrusions and phosphorite-bearing weathering crust, which overlie crystalline rocks of the Ukrainian Shield, on geochemical properties of the adjacent sea basins was retained for a long geological period. The author of the present paper has shown that recent and Quaternary regularities in the behavior of P_2O_5 are largely related to the redistribution of phosphates by present-day rivers (Kholodov, 2002, 2003a, 2003b).

Indeed, as is evident from Fig. 6, right tributaries of the Dnieper River (Irsha, Uzh, Zlobich, Lemna, Trostyanka, Teterev) and left tributaries of the Yuzhnyi Bug River (Sob, Gniloi, Tikich, Gornyi Tikich, Sinyukha, Ingul, and others) drain the apatite-bearing Korosten intrusion area and transport a large quantity of terrigenous suspended material, the composition of which is close to that of eroded placers, to the Dnieper–Bug Estuary of the Black sea. Consequently, the present-day beach, littoral, and shelf sediments of the Bug–Dnieper Estuary are enriched in ilmenite, sphene, rutile, and apatite. Such areas incorporate Quaternary coastal-marine placers (Shnyukov, 1983; Markovskaya, 1990).

It is remarkable that phosphorus is concentrated as apatite not only in the coastal sediments, but also in the deeper recent sediments of the estuary and Ukrainian shelf (Maslov, 1929). Subsequently, the phosphorus is gradually replaced by colloidal hydrogene phosphates and organophosphoric compounds (Volkov and Sevast'yanov, 1968; Volkov, 1984). As is shown in the map based on materials of M.A. Glagoleva (Strakhov, 1976), high P_2O_5 contents in recent sediments are traceable within a wide band extending from the Bug–Dnieper Estuary to the western halistase of the Black

Sea, which is also enriched in phosphates. The geochemical situation illustrated in Fig. 6 is undoubtedly related to the erosional activity of rivers that currently drain the Ukrainian crystalline shield.

Sources of Phosphorus in Phosphorite Genesis

The source of phosphorus is one of the most important problems in the theory of phosphorite genesis. The formation of phosphorite deposits is usually attributed to three factors: (1) volcanic or hydrothermal activity; (2) discharge of waters of the World Ocean; and (3) continental weathering of igneous rocks.

The *volcanosedimentary hypothesis* was first proposed by Mansfield (1940) and actively supported by Shatsky (1955). It was further developed in works of Eganov (1964), Shkol'nik et al. (1966), Brodskaya and Il'inskaya (1968), Brodskaya (1974), and, partly, Yanshin (1993). These researchers considered that submarine hydrothermal solutions are the main source of phosphorus, and their geochemical influence is spread over great distances. The concept of siliceous phosphorite-bearing formations, which appear at a distance of many tens of kilometers from the areas of hydrothermal solution discharge into seawater, was criticized by Strakhov (1960, 1971). The concept of the decisive role of volcanogenic–hydrothermal source in the formation of subaqueous phosphorites was rejected by many researchers (Bushinskii, 1966; Kholodov, 1970a, 1970b, 1973, 1975; Il'in, 1973; Baturin, 1978, Eganov and Sovetov, 1979, and others).

In the 1990s, the volcanogenic–hydrothermal phosphorite formation hypothesis was ultimately discarded. Attempts to reanimate this concept from the position of plate tectonics and phosphorite-formation epochs (Sokolov, 1999; Frolov and Sokolov, 1995; Sokolov et al., 2001) can hardly be viewed as successful. They are overviewed in previous papers (Kholodov, 2002, 2004; and others).

Kazakov (1937, 1939, 1950) was the first researcher to propose the hypothesis of phosphorite formation from *World Ocean waters* largely based on oceanographic works of British and German researchers (Murray and Renard, 1891; Wattenberg, 1927). Initially, this hypothesis attributed the formation of phosphate deposits to upwelling and chemical precipitation of phosphates from CO_2-rich cold deep waters. This interpretation was supported by McKelvey (1959) and partly shared by Strakhov (1960, 1963), Sheldon (1964), and others. Subsequently, chemical precipitation was, however, rejected. In the subsequent works (Cook and McElhinny, 1979; Baturin, 1989, 1993, 2004), waters of the World Ocean and their upwelling are still considered the principal source of P_2O_5 in phosphorite genesis, but its precipitation is assigned to biochemical functions of marine organisms. However, these researchers continue to believe that waters of the World Ocean are the major source of phosphorus, and they provide the main reserves of dissolved phosphates.

The hypothesis of *continental origin* of phosphorites explains the formation of phosphorite deposits in a slightly different way (Bushinskii, 1963, 1965; Kazarinov, 1969; Bgatov et al., 1969; Zanin, 1969, 2001; Kholodov, 1970, 1981, 1997, 2002, 2004; and others).

According to this hypothesis, igneous rocks exposed on land serves at present (and served in the past) as the main source P_2O_5. Their primary phosphate potential was enhanced by weathering. In the course of fluvial erosion, this potential was imprinted as nodular, granular, and pelletal phosphorite deposits in sediments of the adjacent paleoseas.

The terrestrial origin of phosphates contained in the major portion of ancient phosphorite deposits and basins is confirmed by the following global regularities:

(1) Almost all the ancient phosphorite deposits formed in paleoseas isolated from the World Ocean. This is evident from paleogeographic reconstructions and the frequent association of phosphorites with evaporites, sediments of carbonate platforms, and accumulations of shallow-water stromatolites.

(2) Epochs of phosphorite formation manifested synchronously in different, frequently isolated from each other paleoseas are closely related to the evolution of magmatism on continents. Moreover, paragenetic associations of phosphorite-bearing sediments reflect geochemical properties of weathered igneous rocks. For example, Vendian–Cambrian phosphorite-bearing basins are universally characterized by the SiO_2 excess, which is typical of weathered ultramafic rocks (gabbro, gabbro anorthosites, and gabbro monzonites). In the Cretaceous–Paleogene phosphorite-bearing basins, phosphorites are often associated with rare metal placers, which are characteristic mineralogical indicators of igneous alkali rocks (syenites, shonkinites, and others).

(3) The main mass of phosphates is undoubtedly concentrated in the Earth's continental blocks. This is evident from estimates of the P_2O_5 content carried out by Kholodov (2002) based on (Ronov, 1980, 1998; Yanshin and Zharkov, 1986; and Kaplan-Diks and Alekseeva, 1988):

The P_2O_5 Content, t

Continents

Soils 2.29×10^{11}

Stratisphere 3.6×10^{15}

Phosphorite reserves 5.7×10^{9}

Granite envelope 1.05×10^{16}

Mantle (basalts) 2.6×10^{16}

Total ~4.04×10^{16}

World Ocean

Water column 2.24×10^{11}

Sedimentary cover 9×10^{14}

Mantle 1.14×10^{16}

Total $\sim 1.23 \times 10^{16}$

It is obvious that the total P_2O_5 content in the continental block is four times higher than that in the World Ocean.

(4) The distribution of organic matter in recent oceanic sediments is characterized by the circum-continental zonality (Romankevich, 1977, 1990), which emphasizes the significance of the continental source of phosphorus and other biogenic elements. Unfortunately, the input of P_2O_5 by river waters is usually ignored in studies of recent accumulations of phosphorites on shelves.

Taking into consideration results of the paleogeographic analysis of the Cenomanian phosphorite formation in the East European Platform and Dnieper–Donets Depression, as well as general comparative estimates of phosphorus production on continents and in the ocean, we should admit that the role of land in the contribution of phosphorus to the adjacent paleobasins is underestimated so far.

In this connection, the further study of phosphorite deposits should compulsorily be supplemented with complex paleogeographic investigations, which would foster the reconstruction of physicogeographic environments and compositions of bedrocks in the adjacent land. Thus, the problem of the input of phosphorus and associated ore components to areas of future phosphorite deposits could be solved on the basis of an alternative approach.

In our opinion, such a complex systemic approach to the study of genetically intricate phosphate deposits in sedimentary formations might shed light on the problem of their genesis and raise the lithological science to a new level.

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