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# The Content of Gold in Vendian–Cambrian Phosphorite Concretions from the East European Platform

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**Abstract**—High Au contents in phosphorite concretions and Vendian–Cambrian enclosing shales are attributed to the concentration function of microbial biota of Precambrian epiplatformal basins. Microorganisms and organic detritus served as intermediate collectors of gold delivered with the continental runoff from provenances of the East European Platform.

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## INTRODUCTION

Clastogenic and chemogenic-sedimentary gold was discovered long ago in phosphorite concretions of the Volga phosphorite-bearing basin (Yasyrev, 1971). Gold flakes (0.05–0.22 mm) found in phosphorites of the Egor'ev deposit have a fineness of 900–920 (Kal'nichenko et al., 1995). Weathering crusts on platformal basement inliers (mainly, in the Baltic Shield) are considered the source of gold in both works cited above. The clastogenic gold delivered from provenances together with the river discharge was subsequently transformed into soluble compounds in the phosphate rock zone and incorporated into phosphorite concretions.

Conditions favorable the formation of auriferous phosphorites existed in the East European Platform not only in the latest Jurassic–Early Cretaceous and Paleocene (when phosphorites accumulated in the Volga Basin), but also in the latest Precambrian–Paleozoic. In the East European Platform, the Vendian–Cambrian epoch of phosphorite genesis is manifested as phosphorite-bearing horizons in Upper Vendian and Vendian–Cambrian sequences. It is worth mentioning that phosphorite concretions are known in the Kalyus beds (Nagoryany Formation) of the Vendian reference section in Podolia (southwestern Ukraine) since the 19th century. Intense chemical weathering in the East European Platform during the formation of phosphorite-bearing horizons has been revealed by the study of chemical compositions of Vendian–Cambrian shales (Felitsyn, 2004). Thus, both potential sources of gold (chemical weathering profiles on ancient shields) and its collectors (phosphorite concretions) existed in the East European Platform in the Vendian–Cambrian.

The present paper reports data on the Au content in Vendian–Cambrian phosphorites of the East European Platform, terrigenous sedimentary rocks of the Vendian–Cambrian section, as well as organic matter and associated iron sulfides from shales.

## MATERIALS AND METHODS

We studied phosphorite concretions from the Vendian reference section in Vendian–Cambrian boundary sequences of Podolia (Ukraine), in the central part of the Moscow syneclise, and at the western margin of the Russian Plate (Lublin slope). The concretions (1–20 cm) have spherical and botryoidal shapes. In the Vendian Podolian section, phosphorite concretions are abundant in the Kalyus beds of the Nagoryany Formation (Upper Vendian Kanilovka Group). They are being intensely investigated since the 1950s (Furman, 1954; Manilovskii, 1955) and considered a regional lithological marker for the correlation of Upper Vendian sections in the southwestern East European Platform (Velikanov, 1986).

We studied phosphorite (podolite) concretions from the Kalyus beds in borehole 60 (depth 520–480 m) in Rybnitsa (Moldova), borehole 3643 (depth 330–315 m) at the Settlement of Chukheli (Khmel'nitsk district, Ukraine), and natural outcrops at the Settlement of Borshchev-Yar (Vinnitsa district, Ukraine). Based on 31 analyses, the phosphorite concretions (4.5–11.0 cm) have the following average composition (wt %): $P_2O_5$ 34.1 ± 4.2, CaO 46.7 ± 2.6, and $SiO_2$ 3.6 ± 1.7. These values match the previous data on the composition of Kalyus phosphorite concretions in Podolia (Malinovskii, 1955). Fragments of spherical phosphorite (francolite) concretions, 2–6 cm in diameter, were detected in shales from the upper portion of the Nepeitsino Formation (Moscow syneclise) and boreholes Gavrilov-Yam 1 and Gavrilov-Yam 2 (Felitsyn, 2002). In terms of the $P_2O_5$ content (28–36 wt %) and petrography, Upper Vendian phosphorite concretions of

**Table 1.** The Au content (μg/g) in phosphorite concretions, organic matter, pyrite, and terrigenous rocks from Vendian–Cambrian sections of the East European Platform

| Object | Number of determinations | Average | Minimum | Maximum |
|---|---|---|---|---|
| Upper Vendian phosphorite concretions | 11 | 0.31 | 0.09 | 0.55 |
| Lower Cambrian phosphorite concretions | 4 | 0.14 | 0.13 | 0.16 |
| Sedimentary organic matter (kerogen) | 61 | 0.27 | 0.025 | 1.4 |
| Organic microfossils (vendotenid bands and sabelliditid tubes) | 17 | 0.097 | 0.022 | 0.18 |
| Sapropel films | 4 | 0.49 | 0.44 | 0.53 |
| Kerogen from the phosphorite-bearing horizon | 8 | 0.32 | 0.15 | 0.48 |
| Pyrite from the phosphorite-bearing horizon | 4 | 0.11 | 0.04 | 0.26 |
| Pyrite from phosphorite-free mudstones | 5 | 0.017 | 0.013 | 0.021 |
| Arkosic sandstone | 6 | 0.002 | <0.0005 | 0.005 |
| Shales from the phosphorite-bearing horizon | 25 | 0.043 | 0.004 | 0.14 |
| Vendian–Cambrian sandstones | 165 | 0.012 | <0.0005 | 0.081 |

the Moscow syneclise are similar to those in the Kalyus beds of the Podolian region.

Phosphorite concretions of the Vendian–Cambrian boundary beds of the East European Platform are present in the Cambrian Mazowsze Formation (Vendian–Cambrian section of the Lublin slope, eastern Poland, borehole IG-1, Bialopole area, depth 2783 m) and the Upper Vendian Wlodawa Formation (borehole IG-1, depth 2830 m). The spherical concretions (2–5 cm) contain 31–33 wt % $P_2O_5$. The stratigraphy and lithology of Upper Precambrian–Cambrian sections in eastern Poland are given in (Strauss et al., 1997).

Phosphorites are formed with the participation of organic matter. Therefore, we determined the Au content in various types of sedimentary organic matter from the Vendian–Cambrian sequence of the East European Platform. We investigated organic microfossils (sabelliditid tubes, lenticular remains of vendotenid bands, and sapropel films with fragments of cyanobacterial benthic communities). We also determined the chemical composition of organic matter dissemination extracted from the Vendian–Cambrian fine-grained terrigenous rocks by the acid maceration (kerogen) method. Methods of the extraction of organic matter, macrofossil morphologies, and sampling sites are presented in (Felitsyn and Pshenichnova, 1992a, 1992b; Felitsyn et al., 1998). In order to remove iron sulfides, all organic matter samples were treated in hot 8N $HNO_3$ for 30 s. Kerogens were subjected to repeated centrifuging and decantation in order to minimize the contamination with heavy mineral fraction and clastogenic gold.

We analyzed the distribution of Au in iron sulfide (mainly, pyrite) framboids from the Vendian–Cambrian section in the central Moscow syneclise (Gavrilov-Yam boreholes 1, 2, and 4). Pyrite framboids are 5 to 300 μm in size. In the Redkino horizon, pyrite is associated with organic matter. This mineral is rare in the overlying Povarovka Group (Afanas'eva et al., 1995).

Preliminary data on the Au content in Vendian shales (Felitsyn and Pshenichnova, 1992a) are supplemented with 65 new analyses that characterize the largest Vendian structures in the East European Platform (L'vov–Kishinev depression, Moscow syneclise, and Mezen depression).

Contents of minor, rare, and trace elements in phosphorite concretions, organic matter, sulfides, and enclosing terrigenous rocks were determined by the INAA (epithermal neutrons) method.

The air-dry samples (weight 11–60 mg) were placed in ampules made from analytical grade quartz and bombarded with neutron fluxes ($5 \times 10^{13}$ neut $cm^{-2}$ $s^{-1}$) for 48 h in research channels of a VVR-1 reactor (Petersburg Institute of Nuclear Physics, Gatchina). The Au content was determined based on the $^{198}Au$ radionuclide ([gamma] line, 411.5 keV) using a coaxial Ge–Li detector (volume 35 $cm^3$). The contents were calculated based on standards AGV-1 (andesite, USGS, attested Au content 0.0006 μg/g) and GSO-3 (quartz–gold–silver ore, TsNIGRI, attested Au content 0.94 μg/g). The average relative error of determination is <12% (at Au content <0.05 μg/g) and <5% (at Au content >0.05 μg/g).

## RESULTS

Table 1 shows the Au content in various sedimentary rocks of the Vendian–Cambrian cover of the East European Platform. The phosphorite concretions are significantly enriched in gold, relative to the enclosing shales. The Au content in concretions from the Upper Vendian phosphorite-bearing horizon is more than two times higher than that in the phosphorite concretions from the Vendian–Cambrian boundary rocks. The Au content shows positive correlation with the degree of

**Table 2.** The Au content (μg/g) in different parts of phosphorite concretions from Upper Vendian rocks of the East European Platform

| Sample no., diameter, and location | Au content at the concretion periphery | Au content at the concretion center |
|---|---|---|
| 718-29, 5 cm, Kalyus beds of the Nagoryany Formation, natural outcrops near the Settlement of Borshchev-Yar, Vinnitsa district (Ukraine) | 0.53 | 0.51 |
| Pod-1, 16 cm, Kalyus beds of the Nagoryany Formation, natural outcrops near the Settlement of Borshchev-Yar, Vinnitsa district (Ukraine) | 0.12 | 0.094 |
| 735-70, 4 cm, Kalyus beds of the Nagoryany Formation, borehole 60, the Rybnitsa area (Moldova), depth 559 m | 0.11 | 0.13 |
| 735-99, 4 cm, Kalyus beds of the Nagoryany Formation, borehole 60, the Rybnitsa area (Moldova), depth 511 m | 0.28 | 0.34 |
| 972-26, 2 cm, Nepeitsino Formation, borehole Gavrilov-Yam 1, Gavrilov-Yam 1 area, Yaroslavl district, depth 2409 m | 0.14 | 0.13 |

degradation of organic matter: the Au minimum is recorded in organic microfossils, while the Au maximum is observed in sapropel films. In this respect, the kerogen, a compound of various organic remains (microfossils, cyanobacterial benthic communities, organic detritus, and others), occupies an intermediate position between organic microfossils and sapropel films.

The average Au content in Vendian and Lower Cambrian shales is 0.012 μg/g. This is consistent with previous data (Felitsyn and Pshenichnova, 1992a). The Au content in mudstones of the Upper Vendian phosphorite-bearing horizon is more than three times higher than in the Vendian–Cambrian shales. In the Upper Vendian reference section exposed in the central Moscow syneclise (Gavrilov-Yam boreholes 1–4), we studied the Au distribution in pyrite and organic matter across the section. The results showed that kerogen and pyrite from mudstones of the phosphorite-bearing horizon are significantly enriched in gold, relative to analogous phases extracted from the over- and underlying shales.

The Au content in arkosic sandstones of the Redkino Group is 0.002 μg/g, which matches the Au content (0.002 μg/g) in agglutinated tubes of Early Cambrian *Platysolenites antiquissimus* (Lower Cambrian Lontova horizon, northwestern Moscow syneclise) that are composed of quartz and K-feldspar with a proportion of 5: 1 (Felitsyn, 1992).

The results obtained indicate that the Vendian–Cambrian phosphorite concretions are essential Au concentrators in the Vendian–Cambrian sedimentary cover of the East European Platform. The coefficient of Au enrichment in concretions (relative to shales and sulfides) is as much as 10–30. In terms of the Au concentration, the phosphorite concretions are similar to the sedimentary organic matter. Within the Vendian phosphorite-bearing horizon of the Nagoryany Formation of the Kanilovka Group (Ukraine and Moldova) and the Nepeitsino Formation of the Redkino Group (Moscow syneclise), the shales, kerogens, and sulfides are enriched in gold, relative to their sedimentary cover counterparts located below and above the phosphorite-bearing horizon. Based on the INAA data, the Au content is 0.63 μg/g in coalified *Vendotaenia* sp. bands extracted by the acidic maceration from the Kalyus beds (borehole Bolotino-1, depth 778.5–782.5 m) of the Kaushany Formation of the Moldova Plate, which is a stratigraphic analogue of the Nagoryany Formation in Podolia (Sokolov, 1997). The Au content decreases to 0.015 μg/g in vendotenid bands from the over- and underlying mudstones.

The Au content is <0.0005 μg/g in phosphate–siliceous ($SiO_2$ 62.4 wt %, $P_2O_5$ 14.6 wt %) concretions from the lower part of the Duoshantuo Formation (Upper Sinian of the Sinian reference section in the Three Gorges area of the Yangtze River, Hubei Province, China). The Au content is below the INAA detection limit (0.0005 μg/g) in the phosphate–siliceous ($SiO_2$ 70.3 wt %, $P_2O_5$ 9.3 wt %) concretion from the upper part of the Upper Vendian Tsagan Oloom Formation that underlies the *Anabarites trisulcatus* Zone in the Tsagan Gol section (Zavkhan basin, western Mongolia). The Au content is 0.086 μg/g in the phosphorite ($SiO_2$ 15.6 wt %, $P_2O_5$ 32.1 wt %) concretion (5 cm in diameter) from the Upper Vendian Estenilla Formation located 3 m below the Precambrian–Cambrian boundary in the Rio Huso section, central Iberia. These data indicate the relation of gold in phosphorite concretions with the parental phosphate material.

We determined the Au content in the peripheral and central parts of five concretions (Table 2). Chips were taken at ~0.5 cm from the outer edge of each concretion. The results do not reveal any regularity in the Au distribution between different parts of phosphorite concretions 4–16 cm in diameter. The Au content is virtually similar in both the peripheral and central parts of each concretion. At the same time, the bulk Au content in different concretions varies more than five times (from 0.1 to 0.55 μg/g).

## DISCUSSION

The average Au content in Vendian–Cambrian shales of the East European Platform is higher than the typical value for terrigenous rocks ($n \times 0.001$ μg/g based on numerous data). Based on the value obtained for minerals in sedimentary rocks from the central East European Platform, the average Au content in the sedimentary cover of the platform is 0.005 μg/g (Nikitin and Yasyrev, 1974). Among the clayey minerals, kaolinite and halloysite are characterized by the maximal Au contents (0.008 μg/g). Based on a limited number of determinations, the Au content in phosphorites is 0.0072 μg/g (Boyle, 1979). Thus, data presented in Table 1 indicate a significant Au concentration in the Vendian–Cambrian shales and phosphorite concretions therein. In the Vendian and Cambrian, the clastic material of epiplatformal basins of the East European Platform was mainly derived from the weathering crust, which was developed on stable inliers of the platformal basement (Baltic, Ukrainian, and Voronezh shields), and the volcanosedimentary complex of the platformal periphery (Sochava et al., 1992, 1994; Felitsyn, 2004). Obviously, gold was also transported to sedimentary basins as a result of erosion and denudation of the same sources.

In contrast to modern sedimentary basins where bacterial communities are confined to layers near the bottom and surface, Precambrian basins on ancient platforms are characterized by the presence of such communities in the whole watermass (Rozanov, 2003). Organic matter and products of its decomposition are efficient sorbents of gold (Dissanayake and Kritsotakis, 1984; Felitsyn and Pshenichnova, 1992b; Felitsyn et al., 1998; Mossman et al., 1993; Varshal et al., 2000). Therefore, we can consider microorganisms and organic detritus in the Precambrian epiplatformal basins as a mechanical and sorptional barrier for gold that enters the basins together with the continental runoff. Like benthic cyanobacterial mats of auriferous reefs of the Witwatersrand Complex (Yudovich and Ketris, 1988), benthic bacterial communities, which are typical of Late Vendian basins of the East European Platform in the Povarovka time (Afanas'eva et al., 1995; Felitsyn et al., 1998), could also serve as efficient Au concentrators (Yudovich and Ketris, 1988). This is supported by the high Au concentration in the Povarovka sapropel films in the central and northwestern regions of the Moscow syneclise (Table 1). The average content of organic matter (~2 wt %) in Vendian–Cambrian mudstones and shales of the East European Platform, as well as the Au content in the sedimentary organic matter (microfossils and kerogen), suggest that high Au concentrations in bulk samples are related to the enrichment of organic detritus in this element.

According to modern hypotheses of phosphorite genesis, organic matter is the major source of phosphorus for marine phosphorites, irrespective of the increase in bioproductivity (Baturin, 1999). These hypotheses suggest that concentration of nutrient-elements in water fosters its bioproductivity, creation of anoxic environment in the bottom water layer, and concentration of phosphates in mud waters as a result of the decay of organic matter (Cook and Shergold, 1984). Phosphorite concretions are formed in the nonlithified sediment below the water–sediment interface at depths ranging from several decimeters to a few meters (Morad and Al-Aasam, 1994). The syngenetic nature of Vendian phosphorite concretions in the East European Platform is supported by structural features of the enclosing clayey rocks. Gold can migrate as chlorides in mud waters (Yasyrev, 1971). Based on data obtained using an AVT-55 scanning electron microscope, apatite in the phosphorite concretions contain up to 0.2–0.3 wt % Cl, indicating that gold chlorides can form in the phosphorite formation zone.

Thus, the Au content is virtually similar in different parts of phosphorite concretions. Moreover, the Au content is not correlated with the dimension of concretions (Table 2). These facts suggest the existence of high Au concentrations in the entire concretion-forming medium, i.e., mud waters of deep sediments. Variations in the degree of Au concentration in the mud waters are indicated by different contents of this element in some concretions from the phosphorite-bearing horizon. In this respect, the phosphorite concretions differ from the biogenic apatite (Cambrian and Ordovician phosphate brachiopod shells and conodont elements in Baltoscandia). Based on 14 INAA analyses (unpublished data of the author of the present communication), the average Au content is 0.62 μg/g ($n = 22$) in the phosphate brachiopod shells (0.5–10 mm in size) and 4.0 μg/g ($n = 14$) in conodont elements (0.05–1.0 mm). Such a correlation between the dimension of biogenic apatite and Au concentration indicates that monomolecular interactions at the apatite–solution interface played an important role in the concentration of this element in the biogenic apatite. The mechanism of Au concentration in phosphorite concretions is probably different and similar to that in the case of REE concentration in them (Felitsyn and Morad, 2002).

The content of organic matter is 0.3 wt % in the Podolian phosphorite concretions (Malinovskii, 1955) and slightly higher (0.4–0.7 wt %) in concretions from the Gavrilov-Yam section. Therefore, the concentration of Au in phosphorite concretions is unrelated to the presence of Au-rich organic matter in the concretions. Instead, this is governed by the presence of Au, REE, and so on in the organic matter that serves as the source of phosphorus during the formation of concretions. Their decomposition in an anoxic setting produced soluble compounds of phosphorus and other elements. Pioneers of the investigation of gold potential of phosphorite concretions in the East European Platform (Yasyrev, 1971) had noted that organic matter can serve as an intermediate Au concentrator in nodular phosphorites.

The absence of correlation between Au, Sb, As, and Fe in phosphorite concretions indicate that gold in them cannot be related to authigenic iron sulfides. This conclusion is supported by the relatively low Au content in pyrite (Table 1). Based on INAA data, the concretions contain 0.48–2.35 wt % Fe, 0.8–4.3 μg/g Sb, and 10–47 μg/g As. The study of transverse sections of phosphorite concretions with an ABT-55 scanning electron microscope did not reveal clastogenic monomineral gold particles even at a magnification of 400 or 800. However, this fact does not rule out the presence of gold particles in a phosphorite concretion, but only testifies to their minor content (gold/phosphorite $<1/10^6$).

The Au content in kerogens, iron sulfides, and enclosing clayey rocks of the phosphorite-bearing horizon is higher than that in the over- and underlying beds (Table 1). Hence, a greater quantity of gold was delivered by the continental runoff into basins of the East European Platform during the Late Vendian phosphorite formation. Specific features of the chemical composition of clayey rocks with phosphorite concretions (Felitsyn, 2002, 2004) indicate that chemical weathering was intense during the formation of phosphorite-bearing horizons in the East European Platform. Moreover, weathering crusts on platformal shields played an important role as the source of clastic material. Thus, crusts of chemical weathering served as the primary source of gold accumulated in epiplatformal basins, as is supposed for the gold contained in nodular phosphorites of the Volga Basin (Kal'nichenko et al., 1995).

## CONCLUSIONS

Data reported in the present communication testify to high Au contents in various components of the Vendian–Cambrian sedimentary cover in the East European Platform. The highest Au concentration is recorded in the disseminated organic matter (kerogen), phosphorite concretions, and enclosing shales of the phosphorite-bearing horizon at the Upper Vendian Redkino/Povarovka boundary. The Au content in phosphorite concretions from the Vendian/Cambrian boundary beds is more than two times less than that in the Upper Vendian concretions. This discrepancy can be related to different intensities of the chemical weathering of provenance rocks in the Vendian and Early Cambrian.

High Au concentrations in various components of the sedimentary cover of the East European Platform are most probably related to the presence of organic matter that serves as a mechanical and sorptional barrier for gold delivered by the continental runoff from provenances. Specific features of the microbiota of Precambrian epiplatformal basins suggest that such barrier plays an essential role in the geochemistry of many elements (including Au) during the Precambrian sedimentation.

The detection of high Au contents in the Vendian–Cambrian phosphorite concretions of the East European Platform suggests that the gold potential of phosphorites is not limited by the well-known example of the Volga phosphorite-bearing basin. This feature may be typical of sedimentary phosphates in general. Of particular interest in this respect are phosphorite concretions from the Middle and Upper Devonian rocks in the northwestern East European Platform (Sammet, 1980).

The composition of provenance rocks and processes of continental weathering are correlated with the geochemistry and metallogeny of phosphorites (Kholodov and Paul, 2001). This relationship is a partial case of the more general regularity, i.e., the dependence of sedimentary ore genesis on the evolution of provenances (Kholodov, 1975, 1984, 1999).

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