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Gold in biogenic apatites of the Baltic-Ladoga phosphorite basin

Sergey B. FELITSYN[1]✉, **Nadezhda A. ALFIMOVA**[1,2]
[1] *Institute of Precambrian Geology and Geochronology, Russian Academy of Sciences, Saint Petersburg, Russia*
[2] *Institute of Earth Sciences, Saint Petersburg State University, Saint Petersburg, Russia*

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Abstract. The distribution of gold in biogenic apatites from the Ordovician deposits in the northwest of the East European Platform shows that the maximum concentration of gold in apatites is found within the Ladoga-Baltic suture zone. Gold mineralization has a superimposed character, which is confirmed by the dependence of the gold content on the size of apatite particles and a number of isotope geochemical systematics in biogenic apatites. Gold is present in the form of high fineness particles to 20 μm in size on the surface of biogenic apatite fragments (phosphate brachiopod shells and conodont elements) and is easily extracted. In 10 % of samples of biogenic apatites, the total content of rare earth elements is more than 1 wt.%.

Keywords: biogenic apatites; Baltic-Ladoga phosphorite basin; Ordovician; gold; isotopic systematics

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Introduction. For many centuries, gold has been a measure of the value of goods and services. It has served as a universal monetary unit, as well as a symbol of wealth and power. In our time, gold is increasingly being used not only in jewelry, but also in industry. Russia is one of the ten largest gold mining countries along with China, Australia, and the United States. In the material mineral deposites of Russia, gold reserves significantly predominate part in primary deposits, with a gradually decreasing amount of gold in placers. The average gold content in Russian placer deposits over the past 30 years has decreased by 2.5 times [1, 2]. Thus, the search for new sources of high-grade and affordable deposites seems to be a relevant task.

Industrial concentration of apatite develops in two processes, magmatic (alkaline and alkaline-ultramafic rocks) and during the formation of sedimentary phosphorites. The phosphorites contains such minerals as quartz, glauconite, dolomite, clay substance and others from the non-phosphate mineral series, as well as biogenic apatite, similar in composition to hydroxylfluorapatite. In Russia, the apatite deposits are known in the Kola Peninsula, Eastern Siberia, and the Urals. Apatite and phosphorite concentrate are used mainly for the production of phosphate fertilizers. In the Leningrad Region, phosphorite accumulations are confined to the Pakerort Horizon of the Lower Ordovician [3].

Phosphorite basins of the shell type formed during the Ordovician and Silurian. At present, the Baltic-Ladoga, Lena-Tunguska, South Swedish, and North Wales basins are known [4]. A useful component of shell-type phosphorites is the shells of phosphate brachiopods, consisting of hydroxylfluorapatite. Sedimentary phosphorites have certain prospects not only as a raw material for phosphorus, but also as a possible source of rare earth elements and yttrium [5, 6].

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The association of gold with nodulous and granular phosphorites has been known for a long time: clastogenic and chemogenic-sedimentary gold was found in phosphorite nodules of the Volga phosphorite basin [7]. In phosphorite nodules of the Ediacaran and Cambrian of the East European Platform, the average gold content is 0.3 μg/g [8]. In phosphorites of the Yegoryevsk deposit, gold grains to 0.22 mm in size and fineness of 900-920 were found [9].

In the ore concentrate from the Kingisepp deposit of the Baltic-Ladoga basin, whose productive stratum is a layer of quartz sands 1-5 m thick incorporating to 40 % of brachiopod shells, gold grains with a fineness of 775-910 and to 2 mm in size were found [2]. A subsequent study of biogenic apatites (fragments of phosphate brachiopod shells and conodont elements) revealed an increased gold content in them, to 20 μg/g. Gold is present on the surface of biogenic apatites in the form of particles 3-20 μm in size with a fineness of 865-985 [10, 11].

The article presents data on the distribution of gold in biogenic apatites from the Ordovician deposits from the southern Ladoga region to southern Sweden, i.e., within two phosphorite basins, the Baltic-Ladoga and South Swedish.

Methodology. The structure of the studied region contains both ancient, Archean-Proterozoic rock complexes, and relatively young, Paleozoic ones. Ediacaran, Cambrian, and Ordovician sedimentary complexes with a total thickness to 500 m lie on the basement rocks. All Lower Paleozoic deposits lie horizontally or near-horizontally, often separated by small unconformities or occur conformably. Most outcrops of the Ordovician rocks (sands, limestones, and mudstones) are confined to the so-called Baltic-Ladoga glint, which can be traced along the southern coast of the Gulf of Finland and further south of the Neva and Lake Ladoga [12-15]. The Ordovician shell phosphorites, attributed to the Pakerort horizon in the Leningrad Region [12], are quartz sandstones rich in brachiopod shells. The overlying Koporye black shales, enriched in uranium and vanadium, belong to the same horizon.

Data on the location, species composition, and stratigraphic position of the studied samples are given in [16]. The elemental composition (including Au and rare earth elements) of biogenic apatites was determined using neutron activation analysis (instrumental technique, INAA). Air-dry weighted samples of phosphate material were placed in ampoules of highly pure quartz, sealed, and then irradiated for 48 h in the research channels of the VVR-1 reactor at the St. Petersburg Institute of Nuclear Physics (Gatchina) in a neutron flux with a density of 5×10^{13} neutron/cm$^{-2}\times$s^{-1}. To determine the gold content, the 411.5 keV γ-line of the ^{198}Au radionuclide was used. The measurements were carried out on a coaxial Ge-Li detector with a volume of 35 cm^3. Gold content was calculated using standard samples AGV-1 (andesite, USGS, certified Au content = 0.0006 μg/g) and RZS-3 (gold-silver quartz ore, TsNIGRI, certified Au content = 0.94 μg/g). The average relative error in the determination of gold was less than 12 % at a concentration of less than 0.05 μg/g and less than 5 % at a concentration of more than 0.05 μg/g; for REE at the concentrations observed in the studied biogenic apatites, the average error of determination was less than 7 %.

Results. The average Au content in the shells of phosphate brachiopods is 0.88 μg/g (from 0.052 to 2.99 μg/g, 112 determinations); in conodont elements it is 5.0 μg/g (from 0.33 to 22.1 μg/g, 36 determinations). The given values are close to those previously obtained for biogenic phosphates of the Baltic-Ladoga phosphorite basin [17].

The research identified that the maximum gold content in fragments of phosphate brachiopods and conodont elements from the Ordovician deposits in the northwest of the East European Platform is observed in the areas of intersection of the productive strata with large linear zones: the Trans-Scandinavian magmatic belt and the Ladoga-Bothnia suture zone (Fig.1).

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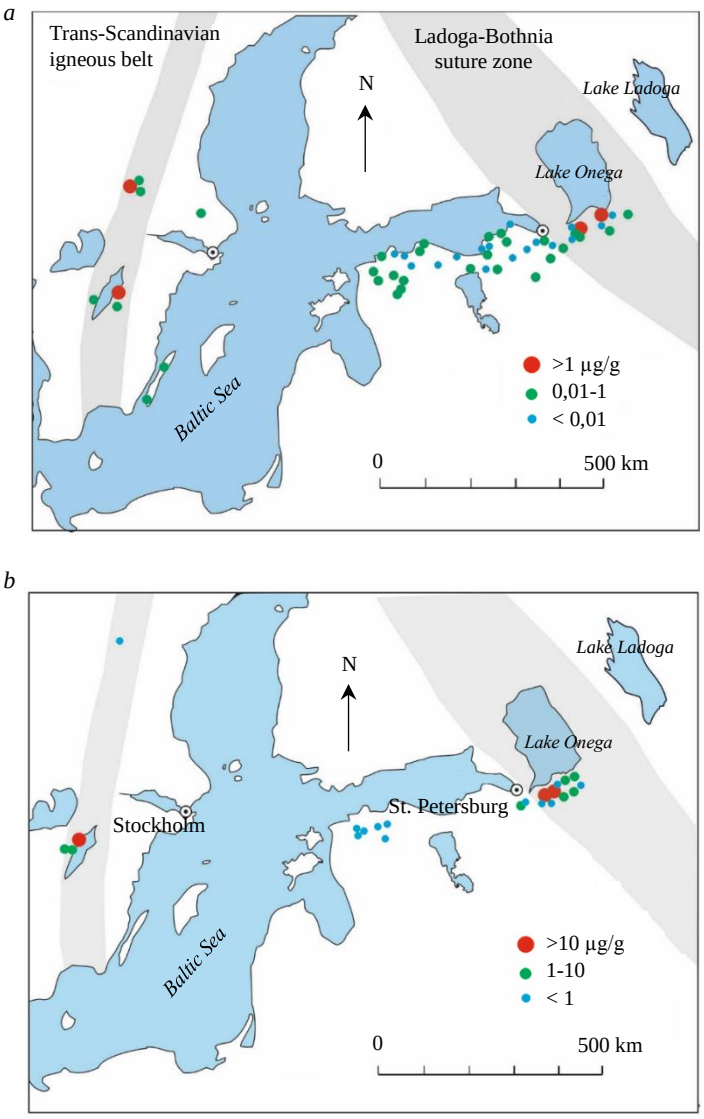


Fig.1. Gold content in biogenic apatites of the Baltic-Ladoga phosphorite basin according to instrumental neutron activation analysis (INAA): *a* – shell fragments of phosphate brachiopods; *b* – conodont elements

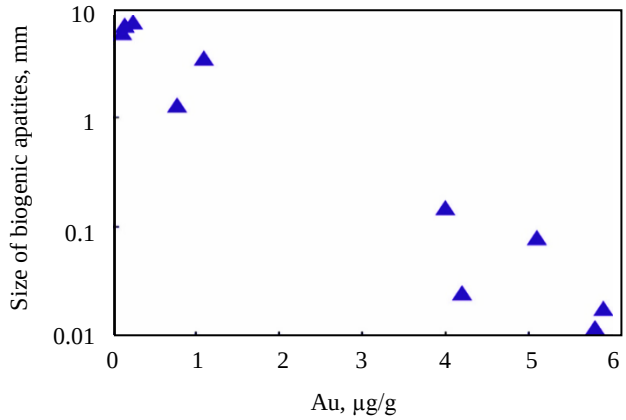


Fig.2. Dependence of gold concentration on the particle size of biogenic apatite from the Baltic-Ladoga phosphorite basin

We found a dependence between the size of fragments of phosphate brachiopod shells and conodont elements and the gold content: the smaller the size of biogenic apatite fragments, the higher the gold concentration in them (Fig.2).

The distribution of REE in the studied biogenic apatites is characterized by a pronounced enrichment in light and medium REE (Fig.3). Since INAA determined an incomplete list of REEs, it is impossible to quantify the total content of all REEs in phosphate brachiopod shells and in conodont elements. Nevertheless, it should be noted that in 10 % of the studied samples of biogenic apatites, the concentration of La, Ce, Nd, Sm, Eu, Tb, Yb, Lu exceeded 1.0 wt.%

Gold was extracted from the phosphate brachiopod fragments of the phosphorite ore from the Kingisepp deposit under laboratory conditions. To do this, 5 kg of phosphate brachiopod fragments were placed in a container with a volume of 20 dm^3 and a chlorine-air mixture was supplied in a ratio of 1:5 at a temperature of 1200 °C for 72 h. Then, AM-2B10P ion-exchange resin was loaded into the resulting hydrochloric acid solution for 15 hours as a sorbent. After annealing of the sorbent, we analysed the residue, which showed the degree of gold extraction under laboratory conditions of 70-75 %. Details of the procedure are available in the description of patent N 2386708 of the Russian Federation [18].

Discussion. The studies of isotope geochemical systematics of biogenic apatites from the Baltic-Ladoga basin [19] showed the presence of a statistically significant correlation of the gold content with the following geochemical signatures:

• the gold content increased with the increase in biogenic apatites of sodium, the total content of La + Ce + Nd + Sm + Eu + + Tb + Yb + Lu, and the Th/U value.

• the maximum concentrations of gold (over 1 μg/g) were found in the group of samples of biogenic apatites with $^{87}Sr/^{86}Sr$ ratio of 0.7064-0.7072 [20, 21]. In the

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group of samples with $^{87}Sr/^{86}Sr$ from 0.7086 to 0.7092, the gold content is more than an order of magnitude lower and amounts to 0.07 μg/g. The strontium isotope composition in the samples of this group corresponds to the strontium isotope composition of a marine reservoir in the Ordovician.

Solid tissues of modern marine organisms consisting of calcium phosphate contain no more than $n\times10$ ng/g [22, 23]. The enrichment of biogenic apatites in REE (especially with medium and light ones) is traditionally associated with their replacement of calcium in the crystal lattice of calcium phosphates at the early and late diagenesis stages [24, 25]. The result of such a substitution is the so-called hat-shaped form of the REE distribution with a low value of the La/Sm ratio and high values of the Sm/Yb ratio. It is this type of REE distribution that is observed in the studied biogenic apatites from the Baltic-Ladoga phosphorite basin (Fig.3). It indicates the modification of geochemical systematics in biogenic apatites under the influence of secondary processes.

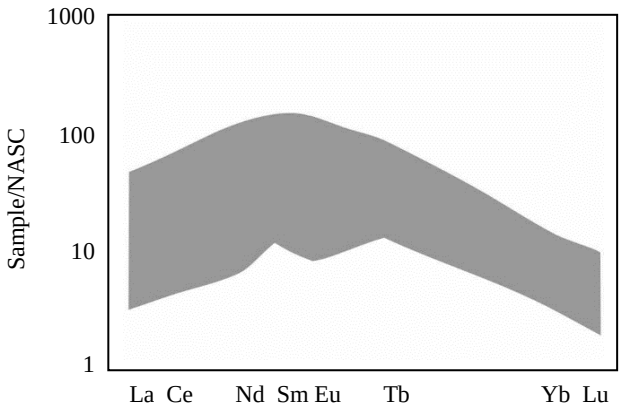


Fig.3. Distribution of REE values normalized to standard composite shale in 220 samples of biogenic apatites from the Baltic-Ladoga phosphorite basin according to INAA results (minimum and maximum concentrations are shown). In 10 % of samples, the total content of 8 rare earth elements exceeds 1 % wt., in 50 % of samples, more than 0.5 % wt.

Uranium and thorium do not accumulate in the tissues of living organisms and do not participate in physiological processes [23]. Accumulation of thorium and uranium by biogenic phosphates (bones, teeth, shells) occurs exclusively at the *post-mortem* stage (after burial in the sediments) and is associated with the replacement of calcium by Th and U in the hydroxylfluorapatite lattice during its recrystallization [26]. U^{4+} is easily oxidized to U^{6+} and leached from apatite upon contact with oxidizing solutions. Therefore, the correlation between Au and Th/U shown in [11] should also be considered as evidence of gold enrichment of biogenic apatites at the late diagenesis/epigenesis stage.

Studies of Rb-Sr and K-Ar systematics of bulk samples of clay shales from the Upper Precambrian-Lower Paleozoic section in the central part of the Russian Plate revealed differences in the isotope geochemical composition of mudstones in the lower and upper parts of the section. This fact can be explained by the epigenetic transformation of rocks in the upper part of the section under fluid impact at the turn of 390 Ma [27, 28]. The appearance of such fluids is associated with the tectonic-magmatic activation of the East European Platform at the final stage of the Caledonian cycle and/or at the beginning of the Hercynian epoch. Data on the gold distribution in the scattered organic matter of the sedimentary cover of the East European Platform, in combination with the isotope geochemical characteristics of kerogens and organic macrofossils [11], confirm the assumption of epigenetic transformations of the sedimentary cover in the Hercynian stage. The nature of the modification of the isotope geochemical signatures of biogenic apatites from the Baltic-Ladoga phosphorite basin makes it possible to evaluate some fluid parameters, namely, the oxidative nature of the medium, which led to the removal of uranium in the form of U^{6+}, a high sodium content, and the $^{87}Sr/^{86}Sr$ ratio less than 0.705.

The correlation of Au with the sizes of biogenic apatite fragments suggests that the reason for the biogenic apatites enrichment in gold was the redistribution of gold in the sedimentary sequence during the Hercynian stage of tectonic-magmatic activation of the East European Platform. The gold enrichment of biogenic apatites from the Baltic-Ladoga phosphorite basin with anomalously low $^{87}Sr/^{86}Sr$ values for the Ordovician confirms the stated assumption. The probable mechanism of this process is sorption, which is confirmed by the dependence between the size of biogenic apatite fragments and the gold content in them (Fig.2).

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No gold grains were found on the surface of quartz and clay particles. The high fineness of gold particles on the surface of biogenic apatites and the extremely low content of admixtures (copper, lead, silver) in them, according to [10], sharply distinguishes them from gold particles previously found in the apatite concentrate from the Kingisepp deposit of the Baltic-Ladoga phosphorite basin [29]. One may reasonably assume that the source of gold on the surface of biogenic apatites was clastogenic gold in the Ordovician strata, mobilized during the post-Ordovician history of the northwest of the East European Platform. Probably, the ease of gold extraction by the chemical method under laboratory conditions is determined by the composition and texture of gold accumulated on the surface of biogenic apatites.

Conclusions. Data on the areal distribution of gold content in biogenic apatites from the Ordovician deposits in the northwest of the East European Platform showed that the maximum concentrations (to 20 μg/g) are confined to zones of increased permeability corresponding to large linear zones: the Trans-Scandinavian magmatic belt and the Ladoga-Bothnia suture zone. Gold is present on the surface of phosphate brachiopod shells and on conodont elements in the form of particles of high fineness and is easily extracted under laboratory conditions. The enrichment of biogenic apatites in gold in the Baltic-Ladoga phosphorite basin and the high content of rare earth elements in them allows us to consider them as a potential source of gold and rare earth elements.

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REFERENCES

1. Geology and minerals of Russia. Vol. 1. West of Russia and the Urals. St. Petersburg: Izd-vo VSEGEI, 2006, p. 528 (in Russian).

2. Mikhailov B.K., Ivanov A.I., Vartanyan S.C., Benevolskii B.I. Raw material base of gold in Russia: state and development prospects. *Mineralnye resursy Rossii. Ekonomika i upravlenie*. 2014. N 6, p. 9-13 (in Russian).

3. Kiselev I.I., Proskuryakov V.V., Savanin V.V. Geology and minerals of the Leningrad Region. St. Petersburg: Peterburgskaya kompleksnaya geologicheskaya ekspeditsiya, 1997, p. 197 (in Russian).

4. Yanshin A.L., Zharkov M.A. Phosphorus and potassium in nature. Novosibirsk: Nauka, 1986, p. 190 (in Russian).

5. Emsbo P., McLaughlin P.I., Breit G.N. et al. Rare earth elements in sedimentary phosphate deposits: solution to the global REE crisis? *Gondwana Research*. 2015. Vol. 27. Iss. 2, p. 776-785. DOI: 10.1016/j.gr.2014.10.008

6. Hein J.R., Koschinsky A., Mikesell M. et al. Marine phosphorites as potential resources for heavy rare earth elements and yttrium. *Minerals*. 2016. Vol. 6. Iss. 3, p. 88-98. DOI: 10.3390/min6030088

7. Yasyrev A.P. Nodular phosphorites of the Russian Platform, an intermediate gold collector during placer formation. *Doklady Akademii nauk*. 1971. Vol. 199. N 2, p. 452-455 (in Russian).

8. Felitsyn S.B. the content of gold in vendian-cambrian phosphorite concretions from the East European Platform. *Lithology and Mineral Resources*. 2006. Vol. 41. N 5, p. 417-422 (In Russian).

9. Kalnichenko S.S., Ivanov N.M., Karimova N.A. et al. Main types of gold-bearing deposits in the sedimentary cover of the central part of the East European Platform. *Rudy i metally*. 1995. N 6, p. 5-15 (in Russian).

10. Felitsyn S.B. Gold in the Lower Paleozoic conodont elements of Baltoscandia. *Doklady Akademii nauk*. 2008. Vol. 419. N 2, p. 247-249 (in Russian).

11. Felitsyn S.B. Gold in vendian-cambrian organic macrofossils of the East European platform. *Lithology and Mineral Resources*. 2008. Vol. 43. N 6, p. 542-548 (In Russian).

12. Biske Yu.S. Geology of Russia. St. Petersburg: Izd-vo Sankt-Peterburgskogo universiteta, 2019, p. 228 (in Russian).

13. Geological map of Russia and the adjacent water areas. 1:2 500 000. St. Petersburg: VSEGEI, 2004 (in Russian).

14. Jaanusson V. Faunal dynamics in the Middle Ordovician (Viruan) of Balto-Scandia the Ordovician System: Proceedings of a Palaeontological Association Symposium, September 1874, Birmingham. University of Wales Press and National Museum of Wales, Cardiff, 1976, p. 301-326.

15. Jaanusson V. Confacies differentiation and upper middle ordovician correlation in the Baltoscandian. *Proceedings of the Estonian Academy of Sciences*. Geology. 1995. Vol. 44. N 2, p. 73-86.

16. Sturesson, L.U., Popov L., Holmer M. et al. Neodymium isotopic composition of Cambrian – Ordovician biogenic apatite in the Baltoscandian Basin: implications for palaeogeographical evolution and patterns of biodiversity. *Geological Magazine*. 2005. Vol. 142, p. 419-439.

17. Felitsyn S.B. the content of gold in lower paleozoic phosphatized biogenic remains in Baltoscandia. *Lithology and Mineral Resources*. 2007. Vol. 42. N 4, p. 400-402 (In Russian).

18. Dotsenko V.I., Felitsyn S.B. Patent N 2386708 RF. The use of biogenic apatite from phosphorite ore of the Baltic-Ladoga basin as an ore for gold production. Publ. 20.04.2010. Bul. N 27 (in Russian).

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19. Felitsyn S.B., Bogomolov E.S. Isotope-geochemical systematics of gold-bearing biogenic apatites from lower paleozoic deposits of Baltoscandia. *Doklady Akademii nauk*. 2013. Vol. 451. N 2, p. 879-881 (In Russian). DOI: 10.1134/S1028334X13080266

20. Denison R.E., Koepnick R.B., Burke W.H., Hetherington E.A. Construction of the Cambrian and Ordovician seawater 87Sr/86Sr curve. *Chemical Geology*. 1998. Vol. 152. Iss. 3-4, p. 325-340. DOI: 10.1016/S0009-2541(98)00119-3

21. Veizer J., Ala D., Azmy K. et al. 87Sr/86Sr, δ13C and δ18O evolution of Phanerozoic seawater. *Chemical geology*. 1999. Vol. 161. Iss. 1-3, p. 59-88.

22. Elderfield H., Pagett R. Rare earth elements in ichthyoliths: variations with redox conditions and depositional environment. *Science of the Total Environment*. 1986. Vol. 49, p. 175-197.

23. Trueman C. N., Tuross N. Trace Elements in Recent and Fossil Bone Apatite. *Reviews in Mineralogy and Geochemistry*. 2002. Vol. 48. Iss. 1, p. 489-521. DOI: 10.2138/rmg.2002.48.13

24. Haley B.A., Klinkhammer G.P., McManus J. Rare earth elements in pore waters of marine sediments. *Geochimica et Cosmochimica Acta*. 2004. Vol. 68. Iss. 6, p. 1265-1279. DOI: 10.1016/j.gca.2003.09.012

25. Reynard B., Lécuyer C., Grandjean P. Crystal-chemical controls on rare-earth element concentrations in fossil biogenic apatites and implications for paleoenvironmental reconstructions. *Chemical Geology*. 1999. Vol. 155, p. 233-241.

26. Neruchev S.G. Uranium and life in the Earth's history. St. Petersburg: Izd-vo VNIGRI, 2007, p. 326 (in Russian).

27. Vinogradov V.I., Buyakaite M.I., Muravev V.I. et al. Isotopic evidence of the Paleozoic stage of the epigenetic reworking of the Vendian deposits in the Russian Platform. *Litologiya i poleznye iskopaemye*. 2002. N 5, p. 525-534 (in Russian).

28. Vinogradov V.I., Golovin D.I., Bujakaite M.I., Burzin M.B. Stages of the Epigenetic Alteration of Upper Precambrian Rocks from the Central East European Platform: Evidence From Rb-Sr And K-Ar Isotope-Geochemical Investigations). *Litologiya i poleznyye iskopayemyye*. 2003. N 2, p. 209-214 (In Russian).

29. Konstantinov V.M., Kazakov A.A., Novikov V.M., Trubkin N.V. Gold in phosphorites of Kingisepp deposit, Russian Platform. *Otechestvennaya geologiya*. 2005. N 6, p. 48-51.

***Authors*: Sergey B. Felitsyn,** *Doctor of Geological and Mineralogical Sciences, Chief Researcher, felitsynsergey@gmail.com, https://orcid.org/0000-0003-3688-9326* (*Institute of Precambrian Geology and Geochronology, Russian Academy of Sciences, Saint Petersburg, Russia*), **Nadezhda A. Alfimova,** *Candidate of Geological and Mineralogical Sciences, Associate Professor, https://orcid.org/0000-0003-4168-5176* (*Institute of Precambrian Geology and Geochronology, Russian Academy of Sciences, Saint Petersburg, Russia*; *Institute of Earth Sciences, Saint Petersburg State University, Saint Petersburg, Russia*).

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