URANIUM AND YTTRIUM ACCUMULATION BY THE BONE DEBRIS IN CARBONACEOUS ROCKS OF THE KAMCHATSKY MYS PENINSULA

O.L. Savelyeva, D.P. Savelyev, T.M. Philosofova

Institute of Volcanology and Seismology FEB RAS, Petropavlovsk-Kamchatsky, Russia, 683006, savelyeva@kscnet.ru

The carbonaceous rocks composing the beds in the Cretaceous carbonate-siliceous paleoceanic sediments of the Kamchatsky Mys peninsula (Eastern Kamchatka) were studied using a scanning electron microscope. In the matrix, consisting of organic and siliceous matter, abundant bone debris and phosphate coprolites are found. In the fragments of fish bones, microinclusions, enriched in uranium and, to a lesser extent, yttrium, are revealed. The accumulation of these elements is associated with their sorption from seawater and from sediment by bone debris. The concentration of uranium was promoted by euxinic conditions in the near-bottom waters, caused by high biological productivity in the surface waters of the ocean, as well as low sedimentation rate, which prevented the dilution of organic matter and biogenic phosphates by terrigenous material and promoted long-term exposure of bone debris at the bottom.

Keywords: uranium, yttrium, bone debris, Kamchatka, carbonaceous rocks, bioproductivity.

INTRODUCTION

Carbonaceous rocks, also called black shales, often contain the increased amount of organogenic phosphates (bones, bone detritus and coprolites) (Baturin, Dubinchuk, 2011; Zanin et al., 2016; Chernyshov et al., 2012). Biogenic phosphates in young carbon deposits were recorded on the shelves of Namibia, Peru and Chile (Baturin, 2001, 2004; Kochenov, Baturin, 2002). The formation of these sediments is determined by high bio-productivity in upwelling zones. High concentrations of bone detritus could be associated with the fish and marine mammals abundance, which is typical for these zones, as well as, in some cases, with the ablation of bone material by currents. Another factor contributing to the black shales enrichment with organogenic phosphates is slow sediment accumulation rate. Bone phosphate is concentrated in these sediments due to its minimal dilution with terrigenous material (Yudovich, 2006), and in this case, high bio-productivity is not required. However, in some cases (for example, the Namibian Shelf), the combined effect of increased bioproductivity and slow sedimentation is also possible (Baturin, 2004; Yudovich, 2006).

Ancient analogues of carbonaceous sediments containing biogenic phosphates are known, for example, in Oligocene – Lower Miocene of the Mangyshlak Peninsula and the North Caucasus (Maykop series) (Baturin, Dubinchuk, 2011; Chernyshov et al., 2012; Sharkov, 2000); in the Tithonian–Early Berriasian Bazhenov Formation (West Siberian Basin) (Zanin et al., 2016); in the Phosphoria Formation (the western United States) of Permian age (Bushinsky, 1969); in the Chattanooga Formation (the eastern United States) of Upper Devonian age (Li, Schieber, 2015); in the Tulebuck Formation's oil shale (the northern Australia) of Cretaceous age (Patterson et al., 1986).

As such deposits usually contain high concentrations of various metals, including rare earth elements (REE) and uranium associated with phosphates they are well studied. It has been established that anoxic conditions in combination with high bio-productivity are most favorable for uranium concentration during sedimentation (Kochenov, Baturin, 2002). The main process of sediment's enrichment with uranium is the 

\[ \text{UO}_2\left(\text{CO}_3\right)_{4}^2- \text{diffusion from the water column,} \]

\[ \text{uranium reduction and sorption or deposition as independent minerals, mainly uraninite (Baturin, 2004; Tribovillard et al., 2006). Some issues related to the concentration of uranium by black shale phosphates require clarification. Researchers propose various models of uranium accumulation: substitution of calcium with uranium in the structure of apatite} \]
Savelyeva et al.

**GEOLOGICAL LOCATION OF THE SMAGIN ROCK ASSOCIATION**

The southern part of the Kamchatky Mys Peninsula is characterized by the complex cover and folded structure; predominantly volcanic-sedimentary rocks of Cretaceous age, ultrabasites, gabbroids and dolerites are developed here (Zinkevich et al., 1985, 1993). Geological surveys, allow us to refer volcanic-sedimentary deposits into the Smagin association (Savel'ev et al., 2007), enriched in comparison with the enclosing jasper, limestone and many ore elements, including uranium and yttrium (Savel'eva, 2009). This article presents the results of these carbon rocks research using the electron microscope. The mechanism of U and Y accumulation is considered.

**RESULTS**

Study of carbonaceous rocks in transparent thin sections and using the scanning microscope clearly show the lenticular-layered texture and skeletons of poorly preserved radiolarians composed by quartz-chalcedony (Fig. 2a). The electron probe microanalysis of carbonaceous rocks reveals the following phases: silica, pyrite, montmorillonite, apatite, barite, siderite, spalerite, iron sulfate, iron phosphate. Silica is dispersed in the rock and also forms isometric clusters, which are half-dissolved skeletons of radiolarians. Fine pyrite has been studied in details previously (Savel'eva et al., 2013). It is represented mainly by phramboids from 5 to 60 microns in size (Fig. 2b), polyphramboids of 40–45 microns in size, cubic crystals of 15–20 microns in size, and also irregular microcrystalline precipitates.

Often all these morphological types are confined to the inner part of the skeletons of poorly preserved radiolarians and to micro-coprolites, sometimes radiolarian skeletons are replaced by pyrite. Montmorillonite is observed in the form of spotted precipitates. Barite is observed in the form of crystalline grains up to 0.03 mm in size, circular-shaped concretions, irregular precipitates (Fig. 2c), and micro-veins up to 0.01 mm thick. Siderite fills micro-veins, grows on the walls of micro-hollows, and also composes individual grains. Spalerite was revealed in one grain of isometric shape with a size of 0.01 mm. Iron sulfate is often observed in concretions with pyrite; in addition, it fills micro-burners with a thickness of up to 0.01 mm. Iron phosphate forms nodular contractions (Fig. 2c).
Particular attention is paid to apatite inclusions. Bone detritus particles up to 0.2–1 mm in size dominate among them (Fig. 2d–h, 2j). These are probably fragments of fish bones. In some cases, their layered structure and internal pores are noticeable. In addition, the authors revealed oval-shaped nubbles of about 0.1×0.05 mm in size composed of phosphate material (Fig. 2i). They have a homogeneous fine-grained matrix in which larger fragments of bones with traces of etching are observed, which is a sign of coprolites according to (Anderson and Kowallis, 2005; Lamboy et al., 1994). Since the coprolites revealed by us contain bone remains of fish in the form of inclusions, we can assume that they were originally excrement of predatory fish. Microinclusions enriched in uranium and, to a lesser extent, yttrium were detected in bone detritus particles (Fig. 2k). The accurate chemical composition of microinclusions could not be determined because of their small size (<1 μm) and hosting apatite in the analyzed zone. Perhaps these microinclusions are composed of uraninite, in which yttrium impurity is common.

DISCUSSIONS

Our previous studies have shown that the mineral part (crozzle) of the carbonaceous rocks from the Smagin association, in comparison with the host jasper and limestone, is enriched in many impurity elements (Savelyeva, 2009, 2011). In particular, the average uranium content in carbonaceous ash is 97 g/t, which is 7–8 times higher than the average uranium content in siliceous black shales, which is 13 ± 2 g/t according to (Ketris and Yudovich, 2009). U contents that are close to the obtained U contents were recorded in carbonaceous rocks from some known formations, which contain bone detritus, for example, in the Bazhenov Formation (Zanin et al., 2016), the Chattanooga Formation (Li and Schieber, 2015), as well as in diatom silts of the Namibian shelf (Baturin, 2004; Kochenov, Baturin, 2002). At the same time, the U contents in the fish layers of the Mangyshlak (Chernyshov et al., 2012) and the Tulebak formation in Australia (Patterson et al., 1986), enriched by the removal of bone material, are several times higher than the U contents in our studied carbon rocks.

Thus, the environment of the open ocean, in which deposits of the Smagin association were formed, under certain conditions, favours U accumulation in sediments comparable to that observed in the coastal upwelling zones. The determining factors were the euxinic conditions in the bottom waters caused by the high biological productivity of plankton and nekton in the surface waters of the ocean, which is completely consistent with the common patterns of U concentration in sediments according to (Kochenov and Baturin, 2002). Sediments, subsequently turned into carbon interlayers as part of the Smagin association, were deposited at the top of the submarine hill during the time when the top of this hill was in the oxygen minimum zone (Savelyeva, 2009), which caused such unusual conditions for
Fig. 2. The position of the studied section (shown by a triangle) on the left tributary of Kamennaya River: a — lenticular lamination and skeletons of radiolarians; b — pyrite framboid; c — concretions of iron phosphate (Ph) with barite secretions (B); d–h, j — particles of bone debris; i — a coprolite; k — an enlarged fragment of a bone detritus particle with microinclusions of uranium and yttrium (bright dots), microprobe analysis of one of such microinclusions with capture of phosphate is shown.
sedimentation in the open ocean. No additional supply of uranium to the waters of the ocean within the region of the studied underwater elevation (for example, from hydrothermals) has been revealed. In addition to euxinic conditions, a low sedimentation rate played an important role in the concentration of uranium, which prevented the dilution of organics and biogenic phosphates with terrigenous and lithogenic materials. In this case, bone material was exposed continuously at the bottom and there was enough time for the diffusion of uranyl ions from the water column to the sediments.

The discovered microinclusions enriched with uranium in bone detritus are consistent with the conception that in the pore waters of restored sediments, finely dispersed precipitates of uranium minerals are formed, which can be captured (possibly sorbed) by a phosphate substance, including bone detritus during the fossilization process (Baturin, 2004).

The accumulation of Y and REE also occurs in bone remnants during their prolonged exposure at the bottom (Baturin, 2004; Dubinin, 2006; Ohta et al., 2016; Toyoda et al., 1990). The average yttrium content in the carbonaceous rocks in the Smagin association is 204 g/t (Savelyeva, 2009), which is almost by one order of magnitude higher than the average content in siliceous black shales, which is 25±2 g/t according to (Ketris and Yudovich, 2009). Yttrium in microinclusions in the bone detritus studied by us contributes to an understanding of the forms of yttrium in black shales. It is possible that REE, or at least some of them, are also associated with the discovered uranium minerals. The simultaneous enrichment of carbonaceous rocks in the Smagin association with uranium and rare earths suggests this idea (Savelyeva, 2009). Such a joint co-enrichment of U and REE in sediments is typical, for example, for the Namibian shelf, where it is explained by the fact that uranium oxides formed in the phosphate material capture dissolved REEs in the form of an isomorphic impurity (Baturin and Dubinchuk, 2003).

CONCLUSION

Carbon interlayers that are part of the Smagin kindred were studied using optical microscopy and electron probe analysis. In their composition, the remains of radiolarians, pyrite, montmorillonite, barite, iron phosphate and other minerals have been revealed. The authors have revealed phosphate coprolites and bone detritus in carbonaceous rocks. Microinclusions enriched in uranium and, to a lesser extent, yttrium were detected in bone detritus particles. This confirms the concept of G.N. Baturin (2004) that uranium forms its own minerals in reduced sediments and that they are captured by phosphates, including biogenic ones. The U contents in the carbonaceous rocks from the Smagin association are consistent with the contents in the layers of some black shale formations enriched with bone remnants and in young sediments of some upwelling zones. Euxinic conditions in the bottom waters, high bioproductivity in the surface waters of the ocean, and low sedimentation rate favoured the concentration of uranium.

The presented study may bring us closer to understanding the mechanism of syngenetic accumulation of metals in black shales.

References

Anderson A.D., Kowallis B.J. Storm deposited fish debris in the Cretaceous Mowry Shale near Vernal, Utah // Ed. by Dehler C.M., Pederson J.L., Sprinkel D.A., Kowallis B.J. Uinta Mountain geology: Utah Geological Association Publication 33, 2005. P. 125–130.

Baturin G.N. Phosphate accumulation in the Ocean / Ed. by Bogdanov Y.A. Moscow: Nauka, 2004. 464 p. (in Russian).

Baturin G.N. Uranium and thorium in phosphatic bone debris from the ocean bottom // Lithology and Mineral Resources. 2001. V. 36. Iss. 2. P. 99–108. https://doi.org/10.1023/A:100486215497.

Baturin G.N., Dubinchuk V.T. Origin of uranium and rare earth minerals in bone detritus from rare metal deposits // Doklady Earth Sciences. 2011. V. 438. Part 2. P. 766–769. https://doi.org/10.1134/S1028334X1106002X.

Baturin G.N., Dubinchuk V.T. The composition of phosphatized bones in recent sediments // Lithology and Mineral Resources. 2003. V. 38. Iss. 3. P. 265–274. https://doi.org/10.1023/A:1023987820590.

Baturin G.N., Kochenov A.V. Uranium in phosphorites // Lithology and Mineral Resources. 2001. V. 36. Iss. 4. P. 303–321. https://doi.org/10.1023/A:1010406103447.

Baturin G.N., Dubinchuk V.T., Fedorchuk A.V. Uranium and thorium in phosphatic bone debris from the ocean bottom // Lithology and Mineral Resources. 2001. V. 36. Iss. 4. P. 99–108. https://doi.org/10.1023/A:100486215497.

Boyarinova M.E., Veshnyakov N.A., Korkin A.G., Savelyev D.P. Gosudarstvennyaya geologicheskaya karta Rossiskoi Federatsii mashtaba 1:200 000 (State Geological Map of the Russian Federation to Scale 1:200000), 2nd ed., Seriya Vostochno-Kamchatskaya (Eastern Kamchatka Series), Sheet 0-58-XXVI, XXXI, XXXII (Ust’Kamchatsk), Explanatory Note, St.Petersburg: Kartograficheskaya fabrika VSEGEI, 2007, 226 p. (in Russian).
Ketris M.P., Yudovich Y.E. Estimations of Clarke's for Carbonaceous biolithes: World averages for trace element contents in black shales and coals // International Journal of Coal Geology. 2009. V. 78. P. 135–148. https://doi.org/10.1016/j.coal.2009.01.002.

Khotin M.Yu. Effusive–Tuff–Cherty Rock Association in the Kamchatsky Mys Peninsula. Moscow, Nauka, 1976, 196 p. (in Russian).

Khotin M.Yu., Shapiro M.N. Ophiolites of the Kamchatsky Mys Peninsula, Eastern Kamchatka: Structure, Composition, and Geodynamic Setting // Geotectonics. 2006. V. 40. № 4. P. 297–320. https://doi.org/10.1134/S0016852106040042.

Kochenov A.V., Baturin G.N. The paragenesis of organic matter, phosphorus, and uranium in marine sediments // Lithology and Mineral Resources. 2002. V. 37. Iss. 2. P. 107–120. https://doi.org/10.1023/A:1014816315203.

Lamboy M., Purnachandra Rao V., Ahmed E., Azzouzi N. Nannostructure and significance of fish coprolites in phosphorites // Marine Geology. 1994. V. 120. P. 373–383. https://doi.org/10.1016/0025-3227(94)90068-X.

Li Y., Schieber J. On the origin of a phosphate enriched interval in the Chattanooga Shale (Upper Devonian) of Tennessee – A combined sedimentologic, petrographic, and geochemical study // Sedimentary Geology. 2015. V. 329. P. 40–61. https://doi.org/10.1016/j.sedgeo.2015.09.005.

Ohta J., Yasukawa K., Machida S. et al. Geological factors responsible for REY-rich mud in the western North Pacific Ocean: Implications from mineralogy and grain size distributions // Geochemical Journal. 2016. V. 50. P. 591–603. https://doi.org/10.2343/geochemj.2.0435.

Patterson J.H., Ramsden A.R., Dale L.S., Fardy J.J. Geochemistry and mineralogical residences of trace elements in oil shales from Julia Creek, Queensland, Australia // Chemical Geology. 1986. V. 55. P. 1–16. https://doi.org/10.1016/0016-7037(86)90123-3.

Savelyev D.P., Lander A.V., Pronina N.V., Savelyeva O.L. Coalzy rocks first found in Cretaceous paleoceanic complexes of the Eastern Kamchatka // Vestnik KRAUNTS. Nauki o Zemle. 2007. № 10. P. 102–104 (in Russian).

Savelyeva O.L. The rhythmicity of sedimentation and footprints of anoxic events in the Cretaceous (Albian-Cenomanian) sediments of Eastern Kamchatka. Author's abstract of PhD Thesis. Moscow, 2009. 25 p. (in Russian).

Savelyeva O.L. Cretaceous paleoclimate. The rhythmicity of sedimentation and footprints of anoxic events in the Cretaceous (Albian-Cenomanian) sediments of Eastern Kamchatka. Saarbrücken: LAP LAMBERT Academic Publishing GmbH & Co. KG, 2011. 156 p. (in Russian).

Savelyeva O.L., Savelyev D.P., Chubarov V.M. Pyrite framboinds in carbonaceous rocks of Smagin Association of the Kamchatsky Mys Peninsula // Vestnik KRAUNTS. Nauki o Zemle. 2013. № 2(22). P. 144–151 (in Russian).

Sharkov A.A. Specific features of the structure and evolution of U- and REE-bearing organic phosphate deposits in the Southern Mangyshlak region // Lithology and Mineral Resources. 2000. V. 35. Iss. 3. P. 252–266. https://doi.org/10.1007/BF02821958.

Toyoda K., Nakamura Y., Masuda A. Rare earth elements of Pacific pelagic sediments // Geochemica et Cosmochimica Acta. 1990. V. 54. P. 1093–1103. https://doi.org/10.1016/0016-7037(90)90441-M.

Tribovillard N., Algeo T.J., Lyons T., Riboulleau A. Trace metals as paleoredox and paleoproductivity proxies: An update // Chemical Geology. 2006. V. 232. P. 12–32. https://doi.org/10.1016/j.chemgeo.2006.02.012.

Vine J.D. Element Distribution in Some Paleozoic Black Shales and Associated Rocks. Washington: United States Government Printing Office, 1969. 32 p.

Yudovich Y.E. Seven types of phosphogenesis // Vestnik IG Komi NC UrO RAN. 2006. № 6. P. 2–6 (in Russian).

Zanin Y.N., Zamirailova A.G., Eder V.G. Uranium, thorium, and potassium in black shales of the Bazhenov Formation of the West Siberian marine basin // Lithology and Mineral Resources. 2016. V. 51. Iss. 1. P. 74–85. https://doi.org/10.1134/S0024490216010077.

Zinkevich V.P., Kazimirov A.D., Peive A.A., Charakov G.M. New data on the tectonic structure of the Kamchatsky Mys Peninsula, eastern Kamchatka // Doklady Akademii Nauk SSSR. 1985. V. 285. № 4. P. 89–92.

Zinkevich V.P., Konstantinovskaya E.A., Tsukanov N.V. et al. Accretionary Tectonics of the Eastern Kamchatka. Moscow, Nauka, 1993, 272 p. (in Russian).