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

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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 bio-productivity 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 $\text{UO}_2(\text{CO}_3)_3^{4-}$ diffusion from the water column, the 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

(Tribovillard et al., 2006) or calcite (Zanin et al., 2016), as well as the sorption relationship of uranium with organic matter (Baturin, Kochenov, 2001; Zanin et al., 2016). The question of uranium entering sources into the sedimentation basin is being discussed; it is supposed to be brought from hydrothermal (Chernyshov et al., 2012; Sharkov, 2000) or to be washed away from land (Baturin, Dubinchuk, 2011; Zanin et al., 2016).

The yttrium content in black shales often correlates with phosphorus content (Vine, 1969). Yttrium, along with REE, is often concentrated in sediments by organogenic phosphates (Ohta et al., 2016; Toyoda et al., 1990).

On the Kamchatsky Mys Peninsula (Kamchatsky Peninsula) (Eastern Kamchatka) carbonaceous interlayers are described as part of carbonate-siliceous paleo-oceanic deposits of the Smagin association (Savelyev et al., 2007), enriched in comparison with the enclosing jasper, limestone and many ore elements, including uranium and yttrium (Savelyeva, 2009). This article presents the results of these carbon rocks research using the electron microscope. The mechanism of U and Y accumulation is considered.

GEOLOGICAL LOCATION OF THE SMAGIN ROCK ASSOCIATION

The southern part of the Kamchatsky 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 of Alb-Cenomanian age (Boyarinova et al., 2007; Khotin, 1976). This association is composed of gray-green tuffosilicites, tuffites, tuffs, as well as rocks of red, red-brown and pink shades: hyaloclastites, jasper and limestone. Jasper and siliceous limestones usually form packages of rhythmic intercalation, sometimes lying on basaltic flows and including sills of the same composition (Boyarinova et al., 2007). However M.Yu. Khotin (1976) revealed that the Smagin association deposits are composed of genetically heterogeneous formations. Subsequently, it turned out that these formations have different ages. (Fedorchuk et al., 1989). This data resulted in two different rock associations in composition of the Smagin association. (Khotin, Shapiro 2006). The Smagin Association of Alb-Cenomanian Age and Paleo-Oceanic Genesis includes hyaloclastites, limestones, jasper and basalts, as well as carbonaceous rocks to which we pay our attention in this article. The Pikezh association of Santon-Campanian age and island-arc genesis is composed of tuffosilicites, tuffites and tuffs. The rocks of the Smagin association occur in the form of olistoliths and tectonic layers in the matrix composed of the Pikezh association rocks.

INITIAL DATA AND RESEARCH METHODS

The Smagin rock association is composed of up to 20 m thick layers of rhythmically interchanging reddish-brown radiolarian jaspers and pink nanoplanktonic limestones. Carbon rocks are present in several cross-sections; the C_{opr} content in these rocks varies from 18 to 53 wt.% (Savelyeva, 2009). We present the data obtained from the analysis of carbonaceous rocks samples from the cross-section on the left inflow of the Kamennaya River (Fig. 1a). The cross-section's thickness is about 10 m. Two layers of carbonaceous rocks with the 2 cm and 5–7 cm thickness are present in the middle and upper part of the cross-section (Fig. 1b).

Optical microscopy and electron probe analysis were used to study the mineral composition of the rocks. Microprobe analysis of carbon rock minerals in polished sections was carried out on the VEGA3 scanning electron microscope with the X-MAX80 analytical attachment at the Institute of Volcanology and Seismology, Far Eastern Branch of the Russian Academy of Sciences, Petropavlovsk-Kamchatsky.

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 revealed the following phases: silica, pyrite, montmorillonite, apatite, barite, siderite, sphalerite, 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 (Savelyeva 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. Sphalerite 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).

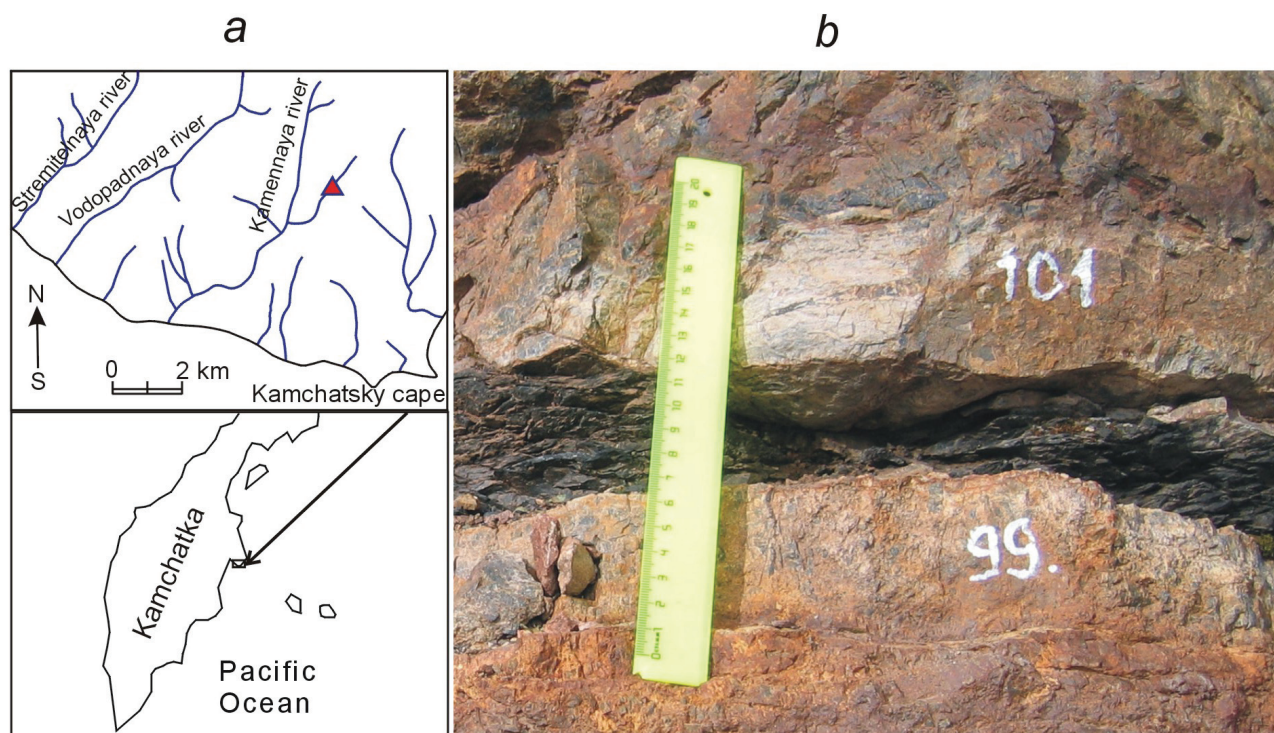


Fig. 1. The location of the studied section (denoted as a triangle) on the left tributary of the Kamennaya River (a) and photo of a carbonaceous bed (b).

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

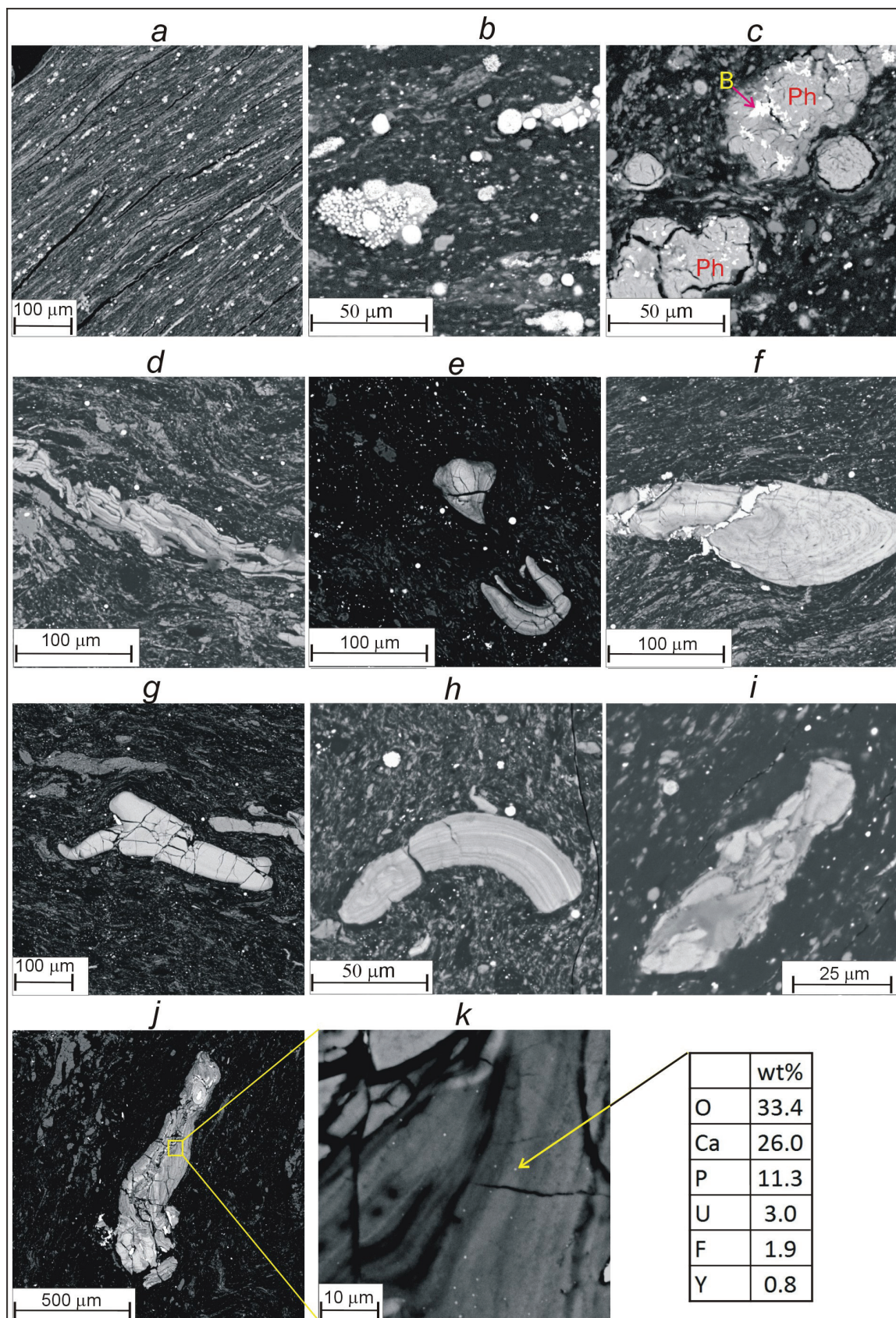


Fig. 2. The position of the studied section (shown by a triangle) on the left tributary of Kamennaya River: *a* — lenticular lamination and skeletons of radiolarians; *b* — pyrite framboid; *c* — concretions of iron phosphate (Ph) with barite secretions (B); *d–h, j* — particles of bone debris; *i* — 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 bio-productivity 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.

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