ISSN 0145-8752, Moscow University Geology Bulletin, 2013, Vol. 68, No. 2, pp. 123–128. © Allerton Press, Inc., 2013.
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SHORT COMMUNICATIONS

Rhenium in the Dictyonema Shale of the Baltic Basin

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Received October 29, 2012

Abstract—The data on the Re-bearing Dictyonema shale in the Baltic basin within the Leningrad Region are reported. The material and petrographic black-shale composition is studied to establish rhenium identification features, Dictyonema shale formation conditions, and the effect of volcanism on the development of rhenium mineralization. The relationship of rhenium with other metals, especially, uranium, is investigated.

Keywords: rhenium, Dictyonema shale, Baltic basin, petrographic composition, mineral reserve base, formation conditions, and rhenium genesis

DOI: 10.3103/S0145875213020117

INTRODUCTION

The rhenium content in the earth's crust is 0.0007 g/t, i.e., six times less than the gold content. Rhenium occurs as an impurity at different metal deposits and in carbonaceous rocks; thus its production is related to great financial costs and technological problems. Nevertheless, the commercial need for rhenium is increasing, and the world market cannot satisfy the demand. Rhenium as a very expensive metal is of the greatest commercial and industrial interest. The Russian Federation as one of the world's leading countries in the production of aviation, space, atomic, and oil-processing equipment has an acute rhenium deficit, because advanced aircraft engines and oil-processing equipment cannot be produced without this metal. Currently, a rhenium mineral reserve base is absent in Russia, in spite of the fact that it is a strategic metal. At the Sora molybdenum deposit, rhenium passes into the molybdenum concentrate (up to 86.97%) under ore beneficiation, but then it is entirely lost in the course of concentrate processing at the Chelyabinsk Ferroalloy Plant due to a lack of the necessary extraction technology. To satisfy the current demand, rhenium is imported to Russia largely from Kazakhstan (4–5 t/year). The world's rhenium production is about 45 t/year.

To create a mineral reserve base (MRB) in Russia, rhenium can be searched for in uncommon sources, such as black shales. The average rhenium content in the Dictyonema shale in Estonia reaches 0.11 g/t (Naumov, 2006).

MATERIALS AND METHODS

The Dictyonema shale (DS) of the Baltic basin occurs as dark brown, almost black when wet, commonly fine-layered argillite. The DS obtained its name due to the occurrence of numerous Dictyonema residues in its composition. The shale contains 10–20% kerogen.

The basin that contains the Dictyonema shale spreads from Norway, Denmark, Southern Sweden, and Estonia to the Leningrad Region up to the Syas' River. Shale makes up the Lower Ordovician sediments (Pakerort level, Tremadocian) with a thickness from a few meters to 20 m. The Dictyonema shale overlies obolus sands. The DS-bed thickness varies from 5.0 m in the western part of the Leningrad Region to 0.5 in its east.

Dictyonema shale is a potential power low-grade fuel and also a raw material for the production of uranium, as well as rare and trace elements. The forecast for DS resources at average bed thickness of 2 m (to the depth of 100 m) gives an estimate of 5.7 Gt (only at the Izhora site).

Having studied thirty hand specimens and trench samples by mass-spectrometry in the Central Laboratory of the Karpinsky Russian Geological Research Institute of the Russian Academy of Sciences, we obtained new data on the concentrations of rhenium and associated metals in the Dictyonema shale (Vyalov, Mironov, and Nezhenskii, 2010). It was the first time when a commercial Re concentration (up to 3.6 g/t) was acquired at the average grade of 0.25 g/t. Shales also contain other rare and trace elements, such as Rb, Cs, Sc, occasionally, Te, Ag, and Au; V, Ti, Cu, and Mo below commercial concentrations. The U

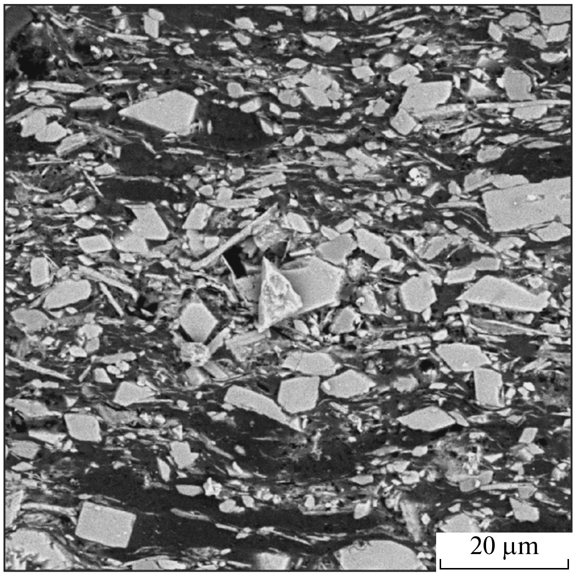

Fig. 1. A picture of the Dictyonema shale. Minerals and organic matter (black), sulfides as rare white grains.

content is at the outbalance or between the outbalance and commercial level.

The commercial Re concentration in the ores (as an accompanying element) reaches 0.045 g/t (Gordienko, 2008). The material–petrographic composition and structure of the Dictyonema shale are demonstrated in Figs. 1–4. Monazite, zircon, and apatite are sporadic (Figs. 4a, 4b).

Major DS minerals include quartz and K-feldspar (sanidine and microcline). Accessory minerals include illite, goethite, cerussite, gypsum, mackinawite, and jarosite. According to the X-ray phase analysis data that were obtained after Dictyonema shale processing with benzene, the shale residue consists of quartz (60 ± 4%), K-feldspar (24 ± 3%), illite (6 ± 3%) and iron sulfides, such as pyrite, marcasite, and mackinawite (2% in total), and also an X-ray amorphous phase (~1%).

The Dictyonema shale contains up to 10–20% organic matter (largely, residues of *Dictyonema flabellioformis* Eichw. and some amount of *Cyanobacteriae*).

To study the distribution of rhenium and foreign-metal impurities, we carried out Dictyonema shale extraction with different solvents (HNO_3, hydrogen peroxide, and benzene) as well as the recovery of humic acids (15 wt % on average). The results are given in Table 1: (B-1) humic acids, (B-2) residue after HNO_3 processing, (B-3) residue after hydrogen peroxide processing, (B-4) residue after benzene extraction, (B-5) residue after the removal of humic substances, (B-6) water-soluble carboxylic acids, including fulvic acids (activated carbon was used).

As follows from Table 1, 7% Re passes into humic acids. Meanwhile, with a humic acid yield of 15% and a rhenium concentration of 0.77 g/t the Dictyonema shale can be regarded as a Re-bearing ore.

Rhenium and several accompanying elements in Dictyonema shale are suggested to be related to sulfide mineralization. The Dictyonema shale can contain 8–10% pyrite and marcasite. Pyritization is widespread over the area and along the section of the Dictyonema shale that forms compact pyrite interlayers or chains of pyrite concretions with poorly preserved host rocks. This type is related to the sand–aleurolite interlayers in the lower and middle parts of the shale bed. There are also pyrite segregations of up to 3 × 8 cm in size with vague boundaries that contain well-preserved rel-

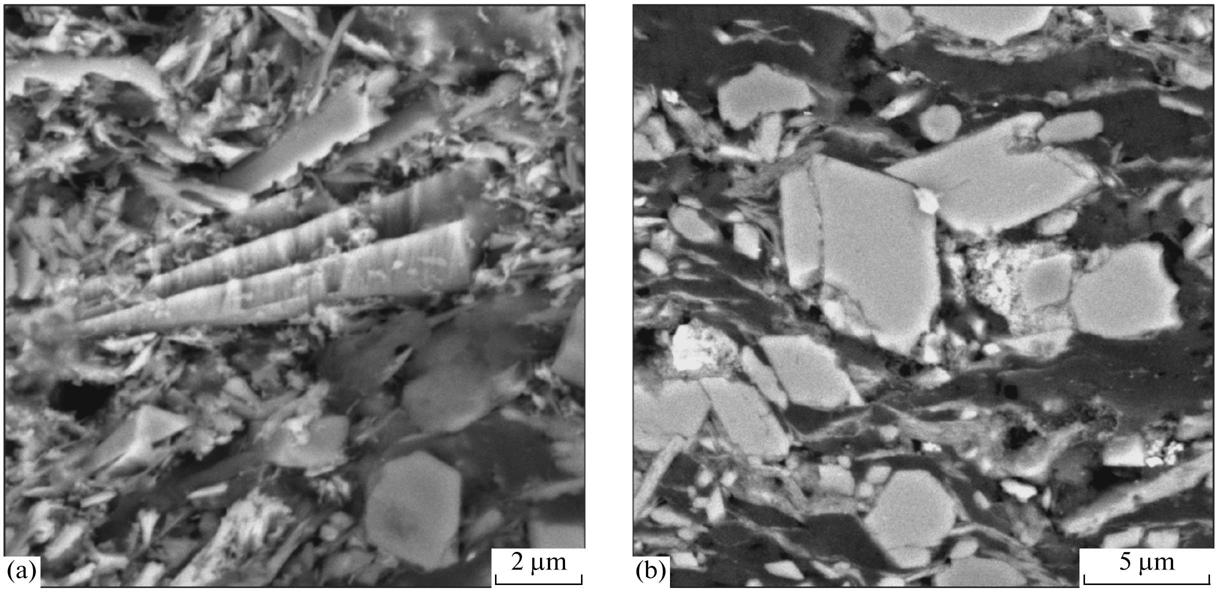

Fig. 2. The Dictyonema shale: (a) algae (black) and sulfides (white); (b) characteristic microcline crystals and quartz grains.

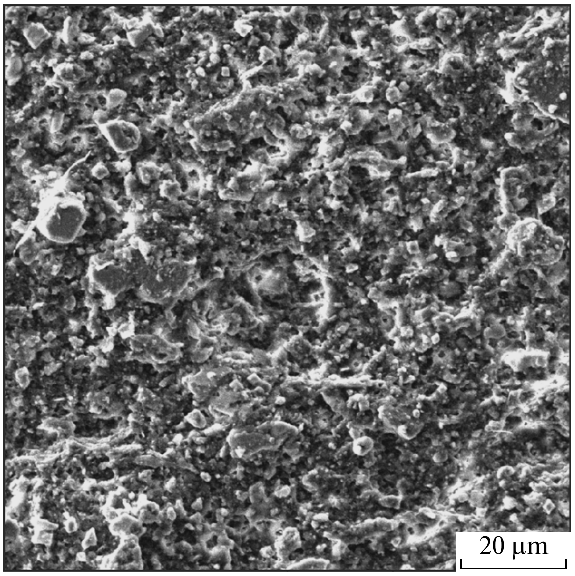

Fig. 3. The Dictyonema shale: fragmental and porous structure.

ics of layered host rocks. The fine-grained pyrite veinlets are confined to the periphery of anthraconite concretions with sporadic sphalerite crystals.

Fine pyrite lenses are observed in argillite in the upper part of the Dictyonema shale bed. Fine pyrite dissemination is widespread throughout the section. The pyrite concretions, which are ellipsoid and bun-shaped in form, commonly occur in argillite that contains fine aleurolite interlayers. Pyrite is often associated with marcasite and replaces it. The Dictyonema shale also contains galena-forming pockets in anthraconite concretions and individual layer-by-layer veinlets.

The studied massive (macroscopically) sulfide sample from the lower part of the Dictyonema shale is observed as a sulfide-cemented fragmental rock (Figs. 5a, 5b) that contains a galena pocket in addition to pyrite (Fig. 5a). Further magnification reveals well-defined rounded quartz grains, and more rarely, feldspar crystals (Fig. 5b).

Figure 6 demonstrates three sulfide generations: pyrite, marcasite, as well as galena (the predominant white cementing material) and chalcopyrite (in the rim around quartz grains) crystals (in the center).

According to the laser-ablation mass-spectrometry data that were obtained at seven points (1 × 1 mm) of a polished sample, the Re content is 0.4–2.1 g/t. The Re/U relationship is 0.83, while Re/Mo is 0.59. It should be noted that molybdenite was not detected in the Dictyonema shale.

Rhenium can be extracted from fine mackinowite (pyrite) crystals with an aqueous solution, because they are readily dissolved with the release of Re and other sulfide-associated elements. ReO_7 is readily dissolved in water. Under drying of nanofractions, rhenium is identified in the thus-formed gypsum. Hence, rhenium and some accompanying precious metals can be easily extracted at levels of 32% and higher, and the Re MRB in Dictyonema shale can be of real and great importance. This is the reason that we studied the rhenium mineralization formation conditions in Dictyonema shale.

SEDIMENTATION CONDITIONS

Having applied the geochemical indicators (Table 2) that were proposed by (Panov and Akhmedov, 2011)

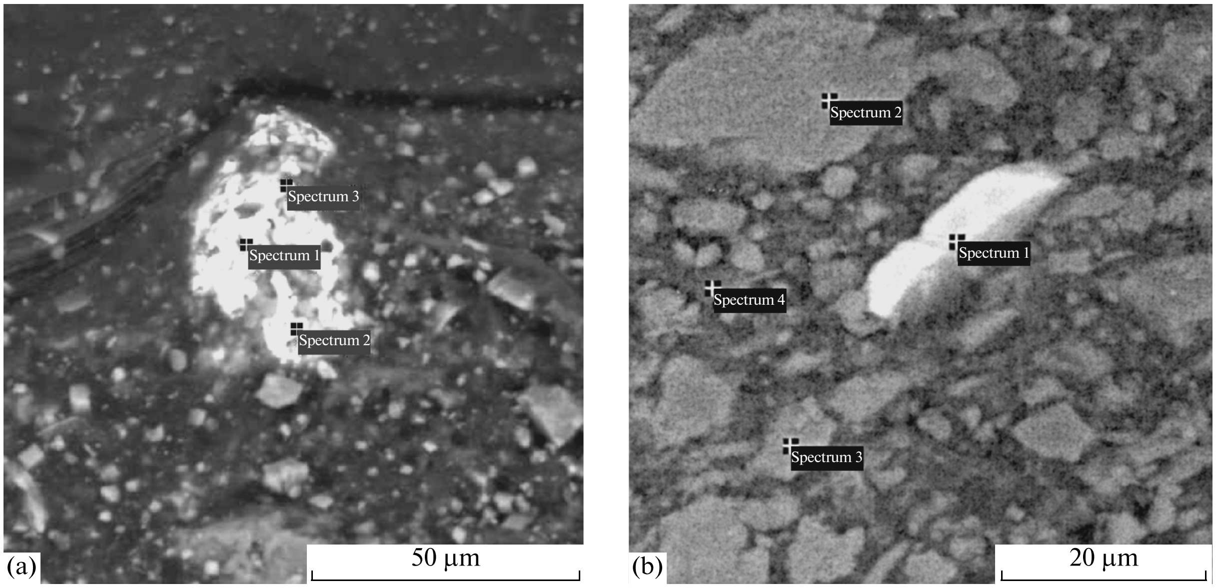

Fig. 4. Minerals in the Dictyonema shale: (a) monazite and (b) zircon.

Table 1. The chemical compositions of Dictyonema shale fractions

Sample	Element							
	Re (1.7)	Ag (4.11)	Ni (45.9)	Cu (55.2)	Cr (94.5)	Mo (420)	U (156)	V (1410)
B-1	**0.77**	**13.70**	142.50	74.05	165.00	**413.50**	64.45	**540.50**
B-2	0.00	**5.36**	18.15	30.60	52.45	0.05	3.48	59.00
B-3	**0.08**	n.d.	14.05	38.45	55.85	84.05	72.20	**1435.00**
B-4	**1.57**	″	44.40	53.60	55.75	**387.50**	**169.00**	**1595.00**
B-5	**0.17**	″	48.40	**396.50**	61.95	56.55	**163.50**	**1615.00**
B-6	**0.05**	0.87	9.97	9.09	2.84	1.89	0.49	9.85

Note: The shale concentration in an ordinary sample subject to extraction is shown in brackets. Significant concentrations are in bold.

Table 2. Geochemical indicators

Ti/Mn	ΣCe/ΣY	Fe/Mn	Sr/Ba	Ce/Ce*	V/Cr	Mo/Mn	V/(V + Ni)	U/Th	La/Yb	Eu/Eu*	La/V
12	2.9	109	0.2	3.7	12.6	1.1	0.8	8.4	10.6	0.2	0.01

and taking the facial and climatic sedimentation conditions into account, in particular, the water salinity in ancient basins, great distance from land, depth, and temperature, as well as the distribution and migration of chemical elements, we reconstructed the rhenium mineralization formation conditions in the following manner.

The Dictyonema shale was deposited in a coastal–maritime environment of the shallow marine shelf under normal salinity. The continental interruption in the Late Cambrian was accompanied by a sea transgression in the Early Ordovician and the formation of an epicontinental bay–strait-like basin. The basin initially accumulated the sand sediments with phosphate valves of *Obulus* inarticulate brachiopods, and then Dictyonema silts, with the maximum thickness in the central part (Baukov and Kotlukov, 1973). Two belts can be distinguished by the distribution of different organic organisms in the Ordovician. One of them united North America, Arctic Archipelago, Greenland, Scotland, Scandinavia and the Baltics. The belt that enclosed the Ordovician near-equatorial regions was characterized by a hot climate and a great diversity of the organic world. The great amount of nutrient substances in the photosynthesis zone was favorable for the development of biological microorganisms in

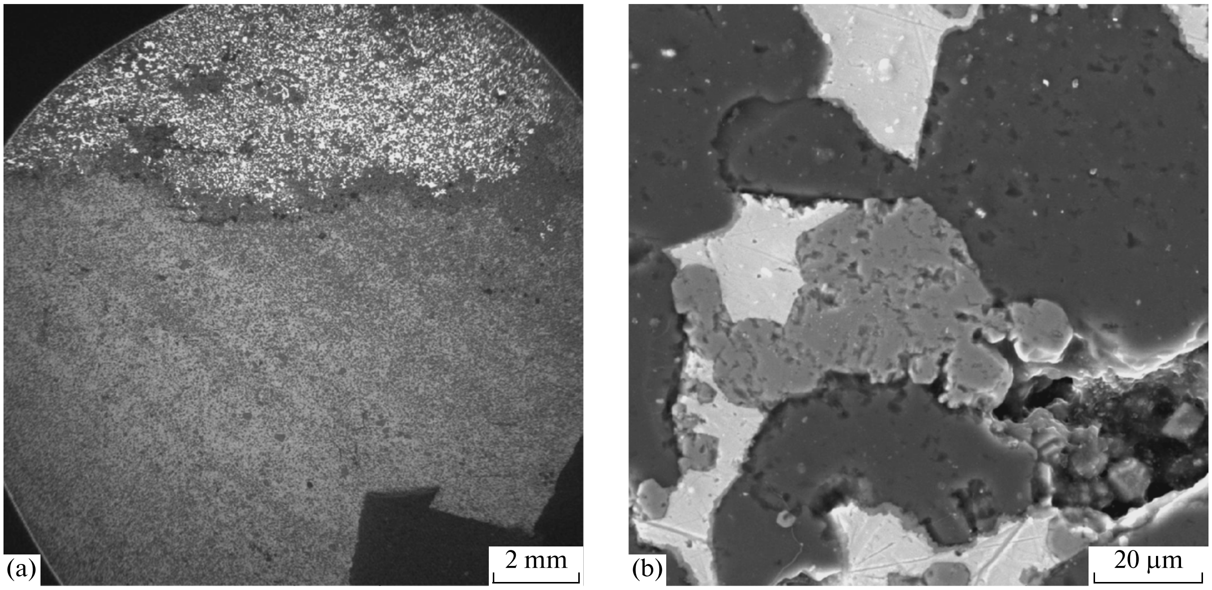

Fig. 5. A “Massive sulfide” sample with a galena pocket (above) (a) and quartz grains cemented by sulfides (b).

the sea (abundant plankton, in particular, graptolites). Dead organisms were buried in the bottom sediments, where the decomposition of organic matter led to the reducing environment formation. The initial organic matter of the sediment was subject to complex transformations (likely due to bacterial action) up to a state that was stable against further destruction.

The metal content of black shales is related to the sedimentary–diagenetic transformation of sea sediments that were enriched in organic matter (graptolites) and the phosphatized detritus of brachiopods. The paleobasin silt waters were characterized by a reducing hydrosulfuric environment that was favorable for the deposition of heavy-metal sulfides, uranium, and rare earth sorption (Boitsev, 1989).

RESULTS AND DISCUSSION

Rhenium is localized in the Dictyonema shale in a complicated way. Rhenium and a number of accompanying elements occur in sulfides as impurities (in pyrite, marcasite, chalcopyrite, and galena) which provide a relatively high concentration.

In organic matter, Re is observed in humic acids that are characterized by sorption, ion-exchange, and biological active properties. In the natural conditions, Re is distinguished by a high selective ability that is expressed in its accumulation in oil organic compounds (Poplavko et al., 1978).

Some part of Re is scattered and does not form its own mineral forms. Re is likely localized in rock fractures and pores, because it is readily extracted with water.

It is suggested that volcanism is a major reason for rhenium mineralization formation in the Dictyonema shale. Re is a high-melting heavy metal: it is the second among metals after wolframium in its melting temperature (3180°C) and the first in its boiling temperature (5900°C). Re is resistant to repeated heating and cooling. Its strength at 1200°C is higher than that of wolframium and is much higher than that of molybdenum. The physical properties of this metal are indicative of the fact that it is originated from high-temperature deep magmatic melts that formed due to volcanic activity, for example, the Kudryavyi Volcano (Iturup Island).

The Dictyonema shale contains high-temperature K-feldspar, viz., sanidine, which is characteristic of volcanic rocks. Hence, it can be suggested that rhenium appeared in the shales owing to volcanism. The rhenium deposition, phosphate rock and Dictyonema shale formation were syngenetic and are related in time and space to volcanic activity in the Caledonian Orogeny period (tectogenesis) that resulted in the development of the Caledonian structures of the British Islands and Scandinavia, as well as Northern and Eastern Greenland. According to Stille, the Caledonian period started between the Ordovician and Silurian (the Taconic Orogeny). Meanwhile, different researchers later distinguished two more folding phases, viz., the Bohemian at the end of the Late Cambrian and the Tresilian at the beginning of the Ordovician in Norway (*Geologicheskii* ..., 1973). The last event was simultaneous with the formation of the Baltic Dictyonema shale and phosphate rocks, while their spatial position is close to the Scandinavian Region.

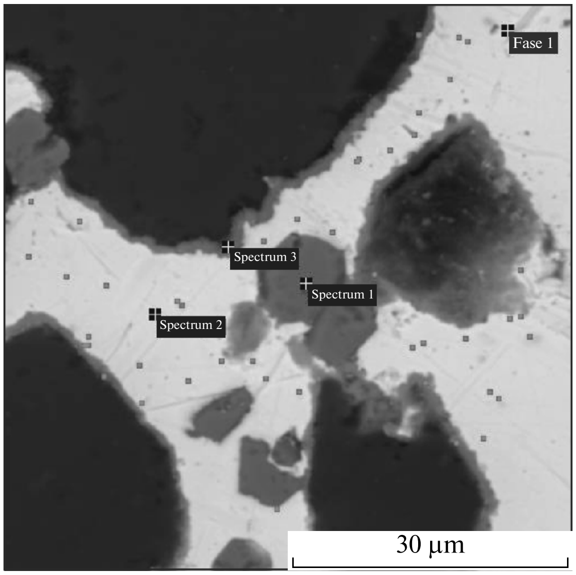

Fig. 6. Quartz (dark grey), galena (white), pyrite, and marcasite (grey).

The Japetus Ocean formed in the Early Cambrian and separated North America (Laurentia) and Europe (the Baltics) expanded, thus drawing them aside. This ocean was 2000 km in width in the Early Ordovician. The tectonic movement of the plates was accompanied by numerous volcanic eruptions, whose products as tuffs, lavas, and ash filled the sea basins (Kuzmin and Korolkov, 2000).

The terrigenous rocks, which are currently observed as conglomerates, sand, sandstone, and clay shale, were deposited in the active continental margins of Western Europe and in the north of the Scandinavian Peninsula. Abundant volcanic rocks which, along with the terrigenous rocks, made up the layered Cambrian and Ordovician sequences are indicative of intense volcanic activity (Gordienko, 2008).

The Ordovician rocks of Northern England are composed of argillite similar to shale, coarse-grained sandstone, and volcanic rocks with a thickness of up to 4000–5000 m (Wales) (Gordienko, 2008). Fragments of volcanic glass, cinders, and melt metal balls are frequently found in the Lower Paleozoic sediments of the Leningrad Region. All these facts confirm the occurrence of active volcanoes in the Baltic Region at that time. Rhenium that was delivered into sea waters was deposited along with uranium in shallow sediments (the future Dictyonema shale) (Al'tgauzen, 1992).

CONCLUSIONS

Hence, simultaneous volcanism and sedimentation resulted in the formation of rhenium mineralization in the Dictyonema shale.

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Translated by E. Maslennikova