GEOCHEMISTRY OF SULFUR AND SULFUR COMPOUNDS OF THE CAMBRIAN KUONAMKA COMPLEX (EASTERN SIBERIAN PLATFORM)

T.M. Parfenova
Trofimuk Institute of Petroleum Geology and Geophysics, Siberian Branch of the Russian Academy of Sciences, Novosibirsk, Russia

Abstract. New results of research of sulfur from rocks and organic matter (OM) for the Kuonamka complex of the Lower and Middle Cambrian in the eastern Siberian platform have been demonstrated. It has been shown that in the rocks enriched in organic matter the amount of organic carbon controls not only the total content of sulfur and sulfide sulfur, but also the content of sulphate sulfur. It has been revealed that the sulfur content in bitumen extracts of Cambrian black shales in the northeastern Siberian platform decreases with increasing carbon and hydrogen. It was hypothesized that during diagenesis the introduction of sulfur in the OM structure led to dehydrogenation and decarboxylation. The intensity of these processes is associated neither with the mineral composition of the sediment nor with its enrichment in OM. The paper discusses the structure and patterns of distribution of OM sulfur compounds in the rocks of the Kuonamka complex in the sections of the northern and southeastern Siberian platform.

Keywords: geochemistry, bitumen extract, sulfur, sulfur compounds, diagenesis, catagenesis, Kuonamka complex, Cambrian, Siberian platform

DOI: http://doi.org/10.18599/grs.19.1.8


Introduction
The black shale Kuonamka complex (formation) of the Lower and Middle Cambrian (Bakhturov et al., 1988; Kontorovich, Savitsky, 1970; et al.), widespread in the north and east of the Siberian platform, is considered by geologists as one of the main possible sources of oil and gas (Geochemistry of oil and gas..., 1972; Savitsky et al., 1972; Bazhenova et al., 1981; et al.), as well as the resource of oil shale (Geology of deposits ..., 1968; Gurari et al., 1987; Kashirtev, 2003; et al.) and the products of their chemical processing. The study of sulfur in rocks and organic matter (OM) is necessary to understand the conditions for the formation of the Cambrian rocks enriched with OM, the composition of oil and gas components generated by them.

According to methodological recommendations on the technical and environmental justification of the conditions for calculating reserves of coal and oil shale deposits (approved by the Russian Mining Union No37-r of the Ministry of Natural Resources of Russia of 05.06.2007), while developing the main parameters of the conditions, it is necessary to take into account associated components connected with the quality of oil shale (yield of tar, sulfur content, etc.). Thus, the study of sulfur in rocks and OM is necessary to assess the quality of black shale...
and "synthetic" petroleum products, to develop efficient and environmentally safe technologies for the extraction and processing of non-conventional hydrocarbon raw materials.

The purpose of this work is to reveal the regularities in the formation and distribution of sulfur and sulfur compounds in rocks and components of OM of the Kuonamka complex in the east of the Siberian platform.

**Materials and methods of research**

Materials for analysis were collections of rock samples from outcrops on the river Molodo (29 samples), well Khotochu-7 (43 samples from the intervals 309-332, 339-346 and 354-388 m). The sampling scheme is shown in Figure 1.

Analysis of the total sulfur content (S\text{total}), sulfur of sulfide and sulfate (S\text{sulfide}) in rocks is performed in the analytical center of the Institute of Geology and Mineralogy named after V.S. Sobolev of the Siberian Branch of the Russian Academy of Sciences.

A complex study of the OM components was carried out in the Laboratory of Oil and Gas Geochemistry of the Institute of Oil and Gas Geology and Geophysics named after A.A. Trofimuk of the Siberian Branch of the Russian Academy of Sciences. The content of organic carbon (C\text{org}) in rocks was determined on the AN-7529 express analyzer by incineration in oxygen of samples of an insoluble residue (HO), previously decarbonated with 10% hydrochloric acid. The bitumen was extracted from 50 grams of sample with chloroform at room temperature using a centrifuge. Purification of the extract from elemental sulfur was carried out with mercury.

To determine the elemental composition of the bitumen, the EA1110-CHNS analyzer (28 samples from the outcrop on the Molodo River) was used. The group composition of bitumoids was determined. To this end, asphaltenes were allocated from the bitumen by the excess of petroleum ether. Then the maltens were divided into fractions of saturated hydrocarbons (HC), aromatic compounds and resins. Sulfur compounds and high molecular hydrocarbons of aromatic fractions (29 samples from the outcrop on the Molodo River, 22 samples from the well Khotochu-7) were studied on an Agilent 5973N chromatography-mass spectrometer system (6890 gas chromatograph with a highly efficient mass-selective detector and a computer registration system) at a temperature of 100 to 320 °C. The chromatograph is equipped with a quartz capillary column 30 m long, 0.25 mm in diameter with the impregnated phase HP-5MS. The flow rate of the helium carrier gas is 1 ml/min. Identification of compounds was carried out by retention time by comparison with already known compounds and published data.

**Results and Discussion**

**Sulfur in the rocks.** According to the content of C\text{org} lithology, structural features, groups and subgroups of high-carbon and carbonaceous rocks are distinguished in the Kuonamka complex of the river Molodo (Parfenova et al., 2004), well Khotochu-7 – carbonaceous and low-carbon rocks (Parfenova et al., 2009). It was found that the total sulfur content (S\text{total}) in the rocks of the studied Molodo River varies from 0.3 to 2.7%, Stotal in the rocks of well Hotochu-7 varies from 0.02 to 2.6% (Table 1, 2). It should be noted that Stotal reaches values of more than 1% in rocks from well Khotochu-7 when the C\text{org} content is less than 5%.

It is known that, in comparison with the sediments of the Siberian platform depleted in OM, the rocks of the Kuonamka complex are enriched in sulfur (Savitsky et al., 1972; et al.). New and published materials (Bazhenova et al., 1981; Bakturov et al., 1988; Savitsky et al., 1972; Kontorovich et al., 2005) show that in the north- and southeast sections of the Kuonamka complex, the black shale deposition has regularity: with an increase in C\text{org} content, the concentration of Stotal and sulfur of sulfide in rocks increases. This is known to be an indirect evidence of the genesis of sulfur due to the microbiological reduction of sulfate dissolved in seawater.

Analysis of the mineral matter of samples from the outcrop of the river Molodo and core from well Khottochu-7 showed that the bonds of total sulfur content in rocks with HO, siliceous and carbonate constituents are not observed separately. The regular increase in S\text{total} like C\text{org}, occurs with a decrease in total content of the siliceous and carbonate substances. In most samples, the sulfur content of sulfate (S sulfate) is determined. It varies from 0% (in single samples) and trace amounts to 0.92% in rocks of the River Young and up to 0.12% – in the well Khotochu-7 (Fig. 2). As a rule, the content of sulfate is higher in high-carbon rocks with C\text{org} > 10% compared to rocks containing C\text{org} <10%.

In the finely dispersed fraction of the Kuonamka rocks from the section of the River Young by means of X-ray structural analysis, secondary sulfur-containing minerals (gypsum and jarosite) were found. It was revealed that they are mainly accompanied by rocks with C\text{org}>10%. These minerals were identified in small and trace amounts only in four samples of the collection, characterized by C\text{org}<10%. Gypsum and jarosite, apparently, are the products of destruction of inorganic sulphides and sulfur components of OM in the hypergenesis zone. Secondary mineralization of rocks of the Kuonamka complex is observed on outcrops (Fig. 3). The nature of the arctic hypergenesis of black shales has been studied for the regions of Pai-Khoi (Yushkin, 1980; Yudovich et al., 1998). The
researchers show the sequence of processes of sulfuric acid low-temperature oxidation of pyrite and other minerals. Apparently, in the regions of permafrost on the Siberian platform, black shales of the Kuonamka complex under near-surface conditions are subject to the same cryogenic weathering.

Analysis of the elemental composition of the kerogen collection from the River Molodo showed that the sulfur content in it varies from 0.5 to 6.4% (Parfenova et al., 2010). It does not depend on the content of $S_{\text{total}}$ and $C_{\text{org}}$ in rocks, and also on the content of carbon, hydrogen, oxygen and nitrogen in kerogen. This is confirmed by the well-known observation by VNIGRI researchers that there is no direct connection between the insensitivity of insoluble OM, reaching 10-15% (p. 39-40, Bazhenova et al., 1981), and some geochemical parameter of rocks or OM. The generalization and analysis of published materials on the elemental composition of kerogen (Parfenova et al., 2010) of the Kuonamka complex of the East of the Siberian Platform showed that the content of Skerogen

Table 1. Geochemical characteristics of rocks and bitumen of the Kuonamka complex (the Molodo River, the northeast of the Siberian Platform). Note. Above the line is the scatter of values, below the line is the mean. * Sample 9 is the only sample from subgroup IIa with $C_{\text{org}} > 10%$. ** – a quantitative assessment by (Kontorovich et al., 2004).

<table>
<thead>
<tr>
<th>Group</th>
<th>Subgroup</th>
<th>Lithology</th>
<th>Number of samples</th>
<th>$C_{\text{org}}$, %</th>
<th>$S_{\text{total}}$, %</th>
<th>Number of samples</th>
<th>$C_{\text{org}}$,DBT, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Ia</td>
<td>Clay-cherty rocks, cherts</td>
<td>13</td>
<td>2.2-7.5</td>
<td>0.7-7.6</td>
<td>7</td>
<td>17.4-71.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Dolomite limestones</td>
<td>3</td>
<td>2.9-5.0</td>
<td>0.3-0.5</td>
<td>6</td>
<td>19.2-66.1</td>
</tr>
<tr>
<td></td>
<td>Ib</td>
<td>Limestone</td>
<td>8</td>
<td>0.3-2.9</td>
<td>0.02-0.5</td>
<td>6</td>
<td>14.8-43.3</td>
</tr>
<tr>
<td></td>
<td>IIa</td>
<td>Clay-carbon-cherty rocks, cherts</td>
<td>11</td>
<td>3.1-9.2(14.2)*</td>
<td>0.6-1.5</td>
<td>9</td>
<td>6.7-44.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cherts</td>
<td>4</td>
<td>1.5-5.1</td>
<td>0.4-0.6</td>
<td>5</td>
<td>9.4-18.9</td>
</tr>
</tbody>
</table>

Table 2. Geochemical characteristics of the rocks and bitumen of the Kuonamka complex (Khotochu-7 well, southeast of the Siberian platform)

<table>
<thead>
<tr>
<th>Group</th>
<th>Subgroup</th>
<th>Lithology</th>
<th>Number of samples</th>
<th>$C_{\text{org}}$, %</th>
<th>$S_{\text{total}}$, %</th>
<th>Number of samples</th>
<th>$C_{\text{org}}$,DBT, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Ia</td>
<td>Clay-cherty rocks, cherts</td>
<td>13</td>
<td>2.2-7.5</td>
<td>0.7-7.6</td>
<td>7</td>
<td>17.4-71.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Dolomite limestones</td>
<td>3</td>
<td>2.9-5.0</td>
<td>0.3-0.5</td>
<td>6</td>
<td>19.2-66.1</td>
</tr>
<tr>
<td></td>
<td>Ib</td>
<td>Limestone</td>
<td>8</td>
<td>0.3-2.9</td>
<td>0.02-0.5</td>
<td>6</td>
<td>14.8-43.3</td>
</tr>
<tr>
<td></td>
<td>IIa</td>
<td>Clay-carbon-cherty rocks, cherts</td>
<td>11</td>
<td>3.1-9.2(14.2)*</td>
<td>0.6-1.5</td>
<td>9</td>
<td>6.7-44.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cherts</td>
<td>4</td>
<td>1.5-5.1</td>
<td>0.4-0.6</td>
<td>5</td>
<td>9.4-18.9</td>
</tr>
</tbody>
</table>

Fig. 2. Dependence of sulfate sulfur content on the concentration of organic carbon in the rocks of the Kuonamka complex of the Siberian platform: 1 – Molodo River, 2 – Khostochu-7 well.
lies in the range 1.03-3.29% in the sections of the River Olenek, River Nekekit, the interfluve of rivers Maiynda and Senkyu. Kerogen rocks from the outcrop on the river Sinyaya differs anomalously by high concentration of sulfur (S_kerogen = 6.8%).

Study of the kerogen from the Molodo river revealed several patterns (Parfenova et al., 2010). In connection with the study of the geochemistry of sulfur in the Kuonamka complex, we noted several of them. First, the moisture content in kerogens of the Kuonamka deposits from the section on the river Molodo, as a rule, increases with an increase in the content of secondary sulfate sulfur in rocks, which was formed during the oxidation of sulfur sulfides. Secondly, with an increase in the content of sulfate in rocks, the oxygen concentration in the kerogenes increases. Consequently, high humidity of kerogenes, varying from 3.5 to 5.0%, as well as increased concentrations of oxygen in samples of high-carbon rocks, indicate of exogenous oxidation of OM. It was suggested that the degree of secondary transformation in the hypergenesis zone is due to the structure of the rocks. The organic matter of light, loose fine-layered oil shales and fractured silicide is more oxidized in hypergenesis than other clayey-siliceous, carbonate or flinty denser rocks of the Kuonam complex of the Lower and Middle Cambrian.

**Sulfur in bitumen.** Investigation of the elemental composition of autochthonous (syngenetic) bitumen in OM from the outcrop on the River Molodo showed that, as a rule, in high-carbon rocks the content of S_{bitumen} varies from 1.57 to 3.25% (Table 1), in carbonaceous rocks it varies from 1.24 to 3.75%. Dependence of bitumen solubility on rock composition and C_organic enrichment is not observed.

An attempt to compare the contents of S_{bitumen} with the concentration in carbon and hydrogen in bitumen showed the presence of feedbacks with high correlation coefficients (Fig. 4a, 5a). Dependence between the content of S_{bitumen} and oxygen in the bitumen (O_{bitumen}) is absent. Apparently, the concentration of oxygen is related to the content of C_organic in the rocks. In high-carbon shale (C_organic > 10%), the values of the O_{bitumen} vary from 4.02 to 10.14%; in rocks with C_organic <10%, the value of the O_{bitumen} usually lies in the interval 1.37-4.34%, and in two samples it rises to 5.13%.

The author’s study of the elemental composition of bitumen presented in scientific publications (Bikkenina, 1964, 1966, Bogoroditskaya, 1966, Nevolin et al., 1974, Savitsky et al., 1972) confirmed the existence of a connection of bitumen with the content of hydrogen and carbon in bitumen from the sections of the East of the Siberian platform (Fig. 4b, 5b).

**Sulfur compounds**

The use of a quantitative estimate of relative concentrations for individual compounds with respect to the height of peaks, when 100% is taken as the sum of all the identified compounds (Kontorovich

---

**Fig. 3.** Secondary mineralization of rocks of the Kuonamka Formation in the outcrop on the Molodo River (photo of the author, 2008).

**Fig. 4.** Relationship between the content of sulfur and hydrogen in the bitumen rocks of the Kuonamka complex in the east of the Siberian platform: A – materials presented for the first time (1 – Molodo River); B – generalization of the published factual information (2 – River Olenek, watershed of the rivers Maiynda and Senkyu (Bogoroditskaya, 1966), 3 – River Olenek according to K.K. Makarov (1969) (Savitsky et al., 1972), 4 – River Olenek, (Bikkenina, 1964), 5 – River Maya (Nevolin et al, 1974)).
Fig. 5. Relationship between the content of sulfur and carbon in bitumen of rocks of the Kuonamka complex in the east of the Siberian platform: A – materials presented for the first time (1 – Molodo River); B – generalization of the published factual information (2 – River Olenek, watershed of the rivers Maynyd and Senkyu (Bogoroditiskaia, 1966), 3 – River Olenek according to K.K. Makarov (1969) (Savitsky et al., 1972), 4 – River Olenek, (Bikkenina, 1964), 5 – River Maya (Nevolin et al, 1974)).

et al., 2004), allowed us to establish a number of regularities for the OM of the Kuonamka complex from the section on the River Molodo (Kontorovich et al., 2005). Mass-chromatograms in m/z 184 and m/z 198 identified dibenzothiophene (C0DBT) and methylbibenzothiophenes (C1DBT) (Fig. 6A). It was found that the content of dibenzothiophenes (C0DBT + C1DBT) by the sum of the identified aromatic compounds increases with the growth in the rocks $C_{org}$ and $S_{total}$ (Table 1). A similar approach to quantitative analysis of aromatic components of well Khotochu No 7 is used in this work.

It also showed that the total content of dibenzothiophenes increases with increasing amounts of $C_{org}$ and $S_{total}$ in rocks (Table 2). But anomalously high values of dibenzothiophenes (up to 50-70%) are recorded not only for rocks with $C_{org}$ greater than 5%, but also for cherts and limestones with low $C_{org}$ content (at 1%) and $S_{total}$ (0.02-0.4%). Probably, the accumulation of large dibenzothiophene concentrations in precipitates relatively poorly enriched with OM, occurred in diagenesis with an excess of hydrogen sulfide in the waters and sediments of the Cambrian Sea.

The content of methylbibenzothiophene isomers in the samples from the collection of the River Molodo increase in the series (2-3) -C1DBT <1-C1DBT <4-C1DBT (Fig. 6A). This is typical for the marine aquatic OM (type II kerogen) (Radke et al., 1982; 1986: Schou et al., 1988). The average ratios of 4-C1DBT/1-C1DBT in high-carbon and carbonaceous rocks vary in the interval 1.6-2.3. Distributions of methylbibenzothiophenes of autochthonous bitumen of OM from the well Khotochu-7, as a rule, are the same as these compounds from the River Young (Fig. 6A), but sometimes different. The ratio of C1DBT isomers varies relative to each other in rocks regardless of the content of $C_{org}$, $S_{total}$ and lithology.

The predominance of 4-C1DBT and 1-C1DBT over the sum of (2 + 3)-C1DBT, as a rule, characterize the investigated samples of the Kuonamka complex of

Fig. 6. Typical chromatograms: A-dibenzothiophene (C0 DBT) in m/z 184, methylbibenzothiophenes (C1 DBT) in m/z 198 (the signature of peaks: 1-4-methylbibenzothiophene, 2-sum of (2 + 3) -methylbibenzothiophenes; 3-1-methylbibenzothiophene), ethyl- and dimethylbibenzothiophenes (C2 DBT) in m/z 212, the amount of carbon in the substituent varies from 0 to 2 (C0-C2), B – 4-alkylbibenzothiophenes in m/z 197 (1-13 is the amount of carbons in the substituent (R)), B – naphthobenzothiophenes in m/z 234 (4-6 – isomers and their structural formulas) of aromatic fractions of bitumen of the Kuonamka complex (east of the Siberian platform)
the southeast of the Siberian platform and confirm the aquatic OM (or type II OM). It has also been empirically established for the sedimentary basins of the world (Schou, Myhr, 1988) that reduced concentrations of 1-C1DBT with respect to the content of 4-C1DBT and (2 + 3)-CDBT indicate a high level of thermal transformation of OM or terrigenous type of OM, source of which was the highest terrestrial vegetation. In the studied collection from the well Khotchu-7 of aromatic fractions, samples are found with such values of the ratio of isomers of methyl dibenzothiophenes. Usually, the coefficient of 4-C1DBT/1-C1DBT varies from 0.5 to 2. Low values of less than 1 of this parameter are interpreted as evidence of immature OM (Schou, Myhr, 1988).

The superiority of 1-C1DBT over 4-C1DBT is noted in single samples of well Khotchu -7. We still have to explore how in this case variations in the distributions of methyl dibenzothiophenes are being controlled. Basically, the values of the ratio of methyl dibenzothiophenes confirm (Parfenova et al., 2009) that the rocks of the Kuonamka complex in the southeast of the Siberian platform reached the level of mesokatagenesis, the main zone of oil formation, and could generate oil components. The latter supplements the conclusions obtained by previous studies of the OM of this stratum (Bazhenova et al., 1981, Geochemistry of oil and gas bearing ..., 1972; Kashirtsev, 2003; Savitsky et al., 1972; et al.).

Today, the identification of sulfur compounds of the OM of the Kuonamka complex is actively continuing. Without the use of special techniques for isolating from OM of concentrates enriched in sulfur compounds, in aromatic fractions from the collections of the River Molodo and well Khotchu-7 we succeeded in revealing ethyl dibenzothiophenes and dimethyl dibenzothiophenes (C2DBT in m/z 212, Fig. 6A). Their total content is comparable to the concentration of methyl dibenzothiophenes (C1DBT in m/z 198).

It was found that a decrease in the content of homologues of 4-alkyl dibenzothiophenes for the collection of the River Molodo and the well Khotchu-7 occurs with an increase in their molecular weight. This is reflected in chromatograms in m/z 197 (Fig. 6B). The study of aromatic molecules made it possible to establish among the sulfide compounds of the Kuonamka complex two sections of naphthobenzothiophenes in m/z 234 with a close isomer distribution (Fig. 6B).

Detailed study by the method of chromatography-mass spectrometry of heteroorganic compounds of bitumen oil fractions from the rocks of the Kuonamka Formation of the River Molodo showed that the content of sulfur compounds predominates over the nitrogen and oxygen-containing structures identified in the oils (Min et al., 2009). Among the sulfur compounds, benzothiophenes are recognized in minimum amounts, dibenzothiophenes and naphthobenzothiophenes predominate.

The authors conclude that with increasing C_{org} usually dibenzothiophenes content increases and naphthobenzothiophenes concentration decreases, more alkylated benzothiophenes content increases and proportion of alkylated and dibenzo- and naphthobenzothiophenes decreases. The presence of methyl-, ethyl-, dimethylethyl- and tetramethyl substituted homologues of benzo- thiophenes, C_{7}-C_{9} dibenzothiophenes and other alkyl homologues of dibenzothiophene, as well as homologues of tetrahydronaphthobenzo- thiophene and tetracyclic naphthobenzo thiophenes was established in the oils Kuonamka Formation (Min et al, 2009; Kashirtsev et al., 2011).

**Conclusion**

New results of the investigation of sulfur and sulfurous compounds of the Kuonamka complex and published materials allow us to draw the following conclusions.

Rocks of the Kuonam complex are not homogeneous in the north and southeast of the Siberian platform by the degree of enrichment with OM and sulfur. The amount of C_{org} controls not only the total content of sulfur and sulfide sulfur, but also the content of sulphate sulfur.

The established regular increase in the sulfur content in bitumen with a decrease in carbon and hydrogen in them suggests a decarbonization and dehydrogenation of the chemical structure of OM in the diagenesis stage. The intensity of these processes, apparently, is not controlled by the content of the mineral and organic matter of the sediments.

The change in the content of sulfur and sulfurous compounds in the Cambrian sediments indicates that the rocks under study at the stages of sedimentation and diagenesis were formed under different oxidation-reduction conditions.

The increase in the content of sulfur compounds with increasing concentrations of C_{org} and S_{total} is characteristic for the rocks of the Kuonamka Formation. With deviation from this pattern, we should consider the hypothesis of hydrogen sulphide contamination of water and sediments of the marine basin, hypergenic destruction of the components of OM.

The composition and distribution of sulfur compounds of aromatic and oil fractions can be used to establish connections in the “oil producing rock-naphthide” system on the Siberian platform. Probably, bitumens and oils, genetically related to the OM of the Kuonamka complex, will be enriched with sulfur and sulfurous compounds.

It is known that sulfur degrades the quality of oil
shale, the development of deposits of this raw material can lead to negative consequences for the environment. In turn, sulfur compounds are valuable products, they are used in industry, agriculture and medicine. Considering the rocks of the Kuonamka complex in the east of the Siberian platform as an unconventional source of industrial power and petrochemicals, the results of studying the content and composition of sulfur and sulfurous compounds of OM must be taken into account for the successful extraction and processing of oil shale.

Acknowledgements

The work is performed in the framework of project No. VIII.73.4.3. of the Programm ONZ-1 of the Russian Academy of Sciences.

References


Geology of coal deposits and oil shale of the USSR. Oil shale of the USSR. Moscow: Nedra. 1968. Vol. 11. 607 p. (In Russ.)


About the Author

Tatyana M. Parfenova – PhD in Geology and Mineralogy, Senior researcher of the Laboratory of Geochemistry of Oil and Gas, Trofimuk Institute of Petroleum Geology and Geophysics, Siberian Branch of the Russian Academy of Sciences

Russia, 630090, Novosibirsk, Ak. Koptug ave., 3
Phone: +7 (383) 333-11-24
Email: ParfenovaTM@ipgg.sbras.ru

Manuscript received 9 September 2016;
Accepted 2 December 2016;
Published 30 March 2017