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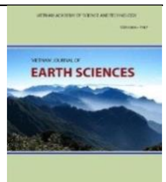

Gas-geochemical studies of gas fields and increased metal concentrations in the East Siberian Sea

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ABSTRACT

Paper presents the results of complex gas-geochemical studies of bottom sediments of the East Siberian Sea along the meridional profile from Cape Billings to the Mendeleev Ridge. Abnormal concentrations of methane (up to 2.4% vol.) and hydrogen (up to 600 ppm) are controlled by neotectonic faults and are typical for the areas of gas hydrate formation. The carbon isotope composition indicates the predominance of the thermogenic component. When studying the chemical composition of sediments, the data helped to identify the permeability zones of neotectonic faults that have favorable conditions for the concentration of a number of elements: Mn, Cu, Ag. Such zones are characterized by the gas anomalies in sediments (methane, hydrogen, etc.). The accumulation of anomalous metal contents is facilitated by specific geological conditions that occur in zones of gas anomalies within tectonically active structures, where fine-grained sediments enriched with organic matter are present. The gas-geochemical fields formed in this pattern can be applied as indicators in forecasting of hydrocarbon accumulations, for mapping permeable fault zones, and for the environmental impact assessing of hydrocarbon anomalies. This approach could be especially effective in the basins with low seismic activity such as seas of East Siberian shelf and some of the marginal seas of Pacific Ocean, for instance, East Sea.

Keyword: bottom sediments; gas content; isotopy; organic carbon; metals; East Siberian Sea.

1. Introduction

A sharp increase in oil and gas demand in the world stimulates the study of sedimentary basins of the Arctic Ocean, which have almost untouched reserves of hydrocarbon and minerals and represent a huge resource reserve. According to the estimates of VNIIOkeangeologia and VNIGRI, more than 75% of the explored reserves of the entire Russian shelf are concentrated in the Russian part of the West Arctic shelf, e.g., 8.2 billion tons of conv. fuels (Burlin et al., 2008). The seas of the Russian zone of the eastern Arctic (East Siberian and Chukchi seas) are less

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studied. But in the US sector of the Arctic, in the immediate vicinity of the Russian economic zone, about 40 oil and gas fields have been discovered (oil reserves are estimated at about 15 million barrels, gas - over 2 trillion).

Currently, 20% of US oil production comes from the Prudho Bay field on the northern coast of Alaska. In the Canadian sector in the Mackenzie River Delta, 49 oil and gas deposits and 15 deposits in the Arctic Islands were discovered (Kontorovich et al., 2010). According to present estimates (Khain et al., 2009), the Russian East Arctic shelf has a high industrial potential for oil and gas exploration. In this regard, the Chukchi and East Siberian seas are currently being actively studied. A program has been developed for geophysical (seismic, gravimetric, magnetometric) and geochemical work in the East Siberian Sea. Gas geochemical studies in water areas are of particular interest, since they allow quickly and efficiently identifying and locating possible hydrocarbon gas deposits, to establish their relationship with tectonic structures, including deep ones.

The East Siberian Sea is the least studied among the Arctic seas due to severe climatic conditions and the length of the ice period. It is the shallowest with 72% of the water area has a depth of less than 50 m, depths of less than 30 m occupy half the sea area. Another sea feature is that a stable sedimentogenic environment is on the vast continental shelf, so bottom sediments generally have a fine-grained structure (Palidis, Scherbakov, 2000).

This paper presents the results of a study of the gas-geochemical specifics of sediments in the East Siberian Sea based on data from a complex geological and geophysical expedition on the R/V “Akademik M.A. Lavrentyev” (Cruise 45), which employees of the V.I. Il'ichev Pacific Oceanological Institute FEB RAS and Federal State Unitary Scientific Industrial Company for marine exploration "Sevmorgeo" took part in.

2. Study area

The gas-geochemical profile in the East Siberian Sea from south to north is 550 km long from station 10 (69°58.07’N, 175°48.38’E) to station 560 (74°42.63’N, 179°36.41’E) included 56 bottom stations by 10 km distance from each other. Depth range at sampling stations varies from 19 to 200 m below sea surface (Fig. 1).

In the neotectonic structure of the East Siberian Sea, a number of main structures are stand out. Its boundaries, as a rule, are the latest various faults, mainly faulting and strike-slipping dislocations (Verba et al., 2011; Mazarovich, 2005; Neotectonic structures,… 2004; Khain et al., 2009). The gas geochemical profile crosses the following structures from south to north: Long Basin (stations VS-50-VS-80), Wrangel Rise (stations VS-100-VS-120), Wrangel graben (stations VS-130-VS-220), North-Shelagh uplift limited by the faults of surrounding structures (stations VS-230-VS-370), Kolpacinski Graben-rift (stations VS-380-VS-430), North Chukchi trough and shelf edge (stations VS-440-VS-560), which are separated from the southern part of the Mendeleev Rise by the sublatitudinal Mendeleev-Bering Fault (Neotectonic structures,… 2004). The thickness of the sedimentary cover in the study area can reach 7 km with the wide development of positive structures (Malyshev et al., 2010).

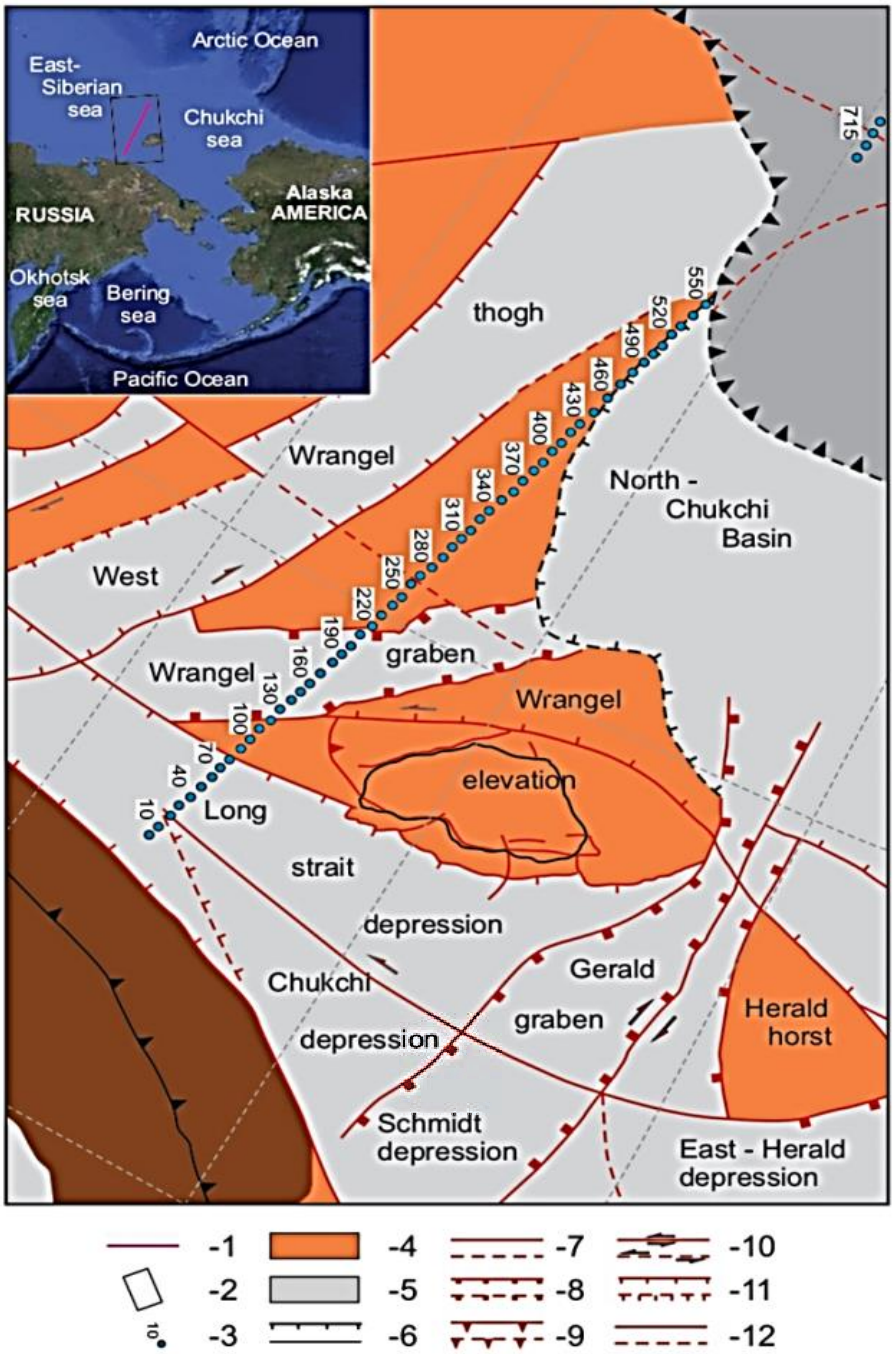

Figure 1. Research area. The location of bottom sediment sampling in the East Siberian Sea on the map of neotectonic structures expressed in the relief of the Arctic shelf (Neotectonic structures,… 2004). Legend: 1-work profile; 2-study area; 3-sampling stations; 4-uplifts and horsts; troughs, 5-grabens, ramps; 6-reliable/estimated boundaries (strokes are directed towards the troughs). The latest faults: (the main faults are shown by thickened lines): 7-reliable/estimated; 8-faults; 9-up thrust fault; 10-shifts; 11-unspecified type; 12-without an established shift

3. Materials and methods

Bottom sediment was sampled at 56 stations along a regional profile from Cape Billings to the underwater Mendeleev Ridge. Bottom sediment sampling was carried out by a direct-flow shock pipe (length 420 cm, inner diameter 90 mm) and bottom grab Ocean-2, followed by a lithological description and study of the distribution of hydrocarbon gas concentrations. Concentrations of methane and heavy hydrocarbon gases in the sediments were determined by the method of equilibrium concentrations (headspace) on board and by the method of thermal vacuum degassing in laboratory (Hachenberg, Schmidt, 1979). Gas from the sediment was previously desorbed in an ultrasonic bath for 2-4 hours. Methane and hydrocarbon gases (saturated and unsaturated homologues up to pentane) were determined on the gas chromatograph CrystalLux-4000M. Gas standards were used with concentrations of methane 10, 100, 1000 ppm, and 1% CO_2, ethane (SCOTTY, ALLTECH GmbH, Germany) for calibration. Measuring error was less than 5%. The extraction of helium and hydrogen from bottom sediments and water was by the method of equilibrium concentrations. Portable gas chromatograph Gasochrome 2000 (Chromatek, Yoshkar-Ola, Russia) with a high sensitivity thermal conductivity detector-2 ppm (2 × 10-4% vol.) was used for analysis of helium and hydrogen. Calibration mixtures of gases produced by UGRA-PGS were in service. Measuring error were 0.05 ppm for helium and 0.03 ppm for hydrogen.

Grain-size analysis of sediments and determination of the elemental composition of bottom sediments were performed under stationary laboratory conditions. Grain-size analysis was done by a laser dispersion method on a Microtrac-100 setup. Sediment elemental composition (gross contents) was determined at the Analytical Center of the Far Eastern Geological Institute, Far Eastern Branch of the Russian Academy of Sciences. The methods of atomic emission spectrometry with inductively coupled plasma (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS) were respectively applied for analysis of macroelements (Ti, Fe, Ca, Mg, Mn, K, Na) and microelements. The accuracy of the element determination was confirmed by the analysis of SSC (standard sample composition) of sediments including terrigenous clay OOPE101, volcanic terrigenous silt OOPE201, siliceous silt OOPE402 and international standard - basalt JB-3 (Japan).

The organic carbon content was measured on a TOS-V_{CPN} analyzer with a device for solid sample burning SSV-5000A from SHIMADZU at the Pacific Oceanological Institute of the Far Eastern Branch of the Russian Academy of Sciences. The analytical principle of operation is based on the method of measuring the absorption of infrared radiation by carbon dioxide formed during the combustion of organic and inorganic compounds. When determining the TC, the relative standard deviation was 1.2%, for IC-1.7%. The natural stable isotopic composition of methane, ethane, and carbon dioxide, represented by its $\delta^{13}C$, were measured using CF-IRMS (Continuous-Flow Isotope Ratio Mass Spectrometry) system in Nagoya University (Tsunogai et al., 2000; Tsunogai et al., 2010). The delta (δ) values are calculated as $R_{sample}/R_{standard}$ - 1, where R is the $^{13}C/^{12}C$ ratio for $\delta^{13}C$ in both the sample and the respective international standard (VPDB for carbon).

4. Study results and discussions

4.1. Gasgeochemical studies

Hydrocarbon gases. The gasgeochemical survey in bottom sediments by the profile revealed the presence of methane in all samples: from 2.0 ppm to 2.4% (Table 1).

Table 1. The content of methane, helium and hydrogen in the sediments (ppm) at different intervals and the carbon isotopic composition of CH_4, C_2H_6 and CO_2 (‰ VPDB) along the profile in the East Siberian Sea

Station	Interval of sediment core, cm	CH_4	He	H_2	$\delta^{13}C$ V-PDB		
					CH_4	C_2H_6	CO_2
10	0-20	-	-	-	-56.8		-21.7
	30-60	$\frac{54,8}{35,1-74,5(2*)}$	-	-	-	-	-
	80-120		-	-	-	-	-
20	0-20	$\frac{3.2}{2.3-4.0(2*)}$	12.8	8.4	-	-	-
	30-60	5.7(1*)	-	-	-	-	-
	80-120		-	-	-	-	-
30	0-20	$\frac{3.0}{2.3-3.7(2*)}$	18.4	33.3	-	-	-
	30-60	6.6(1*)	-	-	-	-	-
	80-120	-	-	-	-	-	-
40	0-20	$\frac{6.2}{3.7-8.6(2*)}$	-	-	-45.8	-29.1	-22.8
	30-60	6.6(1*)	-	-	-	-	-
	80-120	-	-	-	-	-	-
50	0-20	3.6(1*)	20.3	30.8	-	-	-
	30-60	5.9(1*)	-	-			
	80-120	-	-	-	-	-	-
60	0-20	$\frac{4.1}{3.2-5.0(2*)}$	12.9	8.4	-	-	-
	30-60	$\frac{9.8}{7.8-11.7(2*)}$	-	-	-	-	-
	80-120	$\frac{19.4}{15.4-23.4(2*)}$	-	-	-	-	-
70	0-20	3.8(1*)	19.9	4.3	-	-	-
	30-60	$\frac{10.6}{6.7-14.4(2*)}$	-	-	-	-	-
	80-120	23.2(1*)	-	-	-	-	-
80	0-20	3.6(1*)	-	-	60.8	-	-22.0
	30-60	$\frac{19.4}{9.8-29.1(2*)}$	-	-	-	-	-
	80-120	$\frac{25.0}{19.1-31.0(2*)}$	-	-	-	-	-
90	0-20	3.0(1*)	-	-	-29.5	-24.6	-17.7
	30-60	16.9(1*)	-	-	-	-	-
	80-120	$\frac{46.0}{42.5-49.4(2*)}$	-	-	-	-	-
100	0-20	9.1(1*)	15.5	32.2	-56.1	-	-21.9
	30-60	151.7(*)	-	-	-	-	-
	80-120	220.9(1*)	-	-	-	-	-
110	0-20	2.4(1*)	-	-	-	-	-
	30-60	12.8(1*)	-	-	-	-	-
	80-120	$\frac{14.8}{14.6-15.0(2*)}$	-	-	-	-	-
120	0-20	6.6(1*)	-	-	-	-	-
	30-60	13.8(1*)	-	-	-	-	-
	80-120	$\frac{17.1}{15.0-19.2(2*)}$	-	-	-	-	-

130	0-20	3.1(1*)	-	-	-	-	-
	30-60	$\frac{9.8}{5.4-14.3(2*)}$	-	-	-	-	-
	80-120	29.2(1*)	-	-	-	-	-
140	0-20	4.0(1*)	16.0	11.7	-	-	-
	30-60	$\frac{5.4}{4.2-6.5(2*)}$	-	-	-	-	-
	80-120	4.9(1*)	-	-	-	-	-
150	0-20	7.9(1*)	-	-	-	-	-
	30-60	2.6(1*)	-	-	-	-	-
	80-120	$\frac{10.8}{10.0-11.6(2*)}$	-	-	-	-	-
160	0-20	9.7(1*)	13.4	9.5	-	-	-
	30-60	$\frac{30.8}{8.8-52.7(2*)}$	-	-	-	-	-
	80-120	-	-	-	-	-	-
170	0-20	4.6(1*)	-	-	-	-	-
	30-60	$\frac{7.8}{7.4-8.2(2*)}$	-	-	-	-	-
	80-120	-	-	-	-	-	-
180	0-20	5.7(1*)	-	-	-	-	-
	30-60	19.4(1*)	-	-	-	-	-
	80-120	-	-	-	-	-	-
190	0-20	2.1(1*)	-	-	-53.6	-26.1	-22.9
	30-60	-	-	-	-	-	-
	80-120	-	-	-	-	-	-
200	0-20	2.0(1*)	-	-	-	-	-
	30-60	-	-	-	-	-	-
	80-120	-	-	-	-	-	-
210	0-20	2.5(1*)	-	-	-	-	-
	30-60	-	-	-	-	-	-
	80-120	-	-	-	-	-	-
220	0-20	5.3(1*)	-	-	-	-	-
	30-60	13.7(1*)	-	-	-	-	-
	80-120	-	-	-	-	-	-
230	0-20	5.9(1*)	-	-	-	-	-
	30-60	$\frac{35.6}{30.9-40.6(2*)}$	-	-	-	-	-
	80-120	40.4(1*)	-	-	-	-	-
240	0-20	3.7(1*)	19.7	23.7	-	-	-
	30-60	9.4(1*)	-	-	-	-	-
	80-120	10.0(1*)	-	-	-	-	-
250	0-20	5.1(1*)	-	-	-	-	-
	30-60	7.3(1*)	-	-	-	-	-
	80-120	-	-	-	-	-	-
260	0-20	5.6(1*)	-	-	-59.0	-31.8	-22.6
	30-60	14.6(1*)	-	-	-	-	-
	80-120	19.5(1*)	-	-	-	-	-
270	0-20	41.9(1*)	-	-	-	-	-
	30-60	1278(1*)	-	-	-	-	-
	80-120	23787.8(1*)	-	-	-	-	-
280	0-20	13.0(1*)	-	-	-72.2	-	-23.5
	30-60	21.2(1*)	-	-	-	-	-
	80-120	16.2(1*)	-	-	-	-	-

290	0-20	4.5(1*)	-	-	-	-	-
	30-60	13.6(1*)	-	-	-	-	-
	80-120	$\frac{17.7}{14.9-20.5(2*)}$	-	-	-	-	-
300	0-20	4.5(1*)	-	-	-	-	-
	30-60	15.6(1)	-	-	-	-	-
	80-120	22.3(1*)	-	-	-	-	-
310	0-20	2.4(1*)	-	-	-	-	-
	30-60	12.4(1*)	-	-	-	-	-
	80-120	$\frac{12.8}{11.2-14.5(2*)}$	-	-	-	-	-
320	0-20	3.9(1*)	17.0	8.1	-60.1	-	-23.7
	30-60	6.3(1*)	-	-	-	-	-
	80-120	$\frac{14.0}{10.8-17.3(2*)}$	-	-	-	-	-
330	0-20	2.6(*)	-	-	-	-	-
	30-60	9.7(*)	-	-	-	-	-
	80-120	16.6(*)	-	-	-	-	-
340	0-20	3.1(1*)	14.8	8.3	-	-	-
	30-60	$\frac{10.1}{7.2-13.0(2*)}$	-	-	-	-	-
	80-120	-	-	-	-	-	-
350	0-20	3.3(1*)	16.2	1.5	-	-	-
	30-60	$\frac{6.0}{5.3-6.8(1*)}$	-	-	-	-	-
	80-120	8.9(1*)	-	-	-	-	-
360	0-20	6.4(1*)	-	-	-	-	-
	30-60	$\frac{10.6}{8.9-12.3(2*)}$	-	-	-	-	-
	80-120	-	-	-	-	-	-
370	0-20	-	-	-	-58.8	-	-22.4
	30-60	$\frac{36.8}{16.5-57.1(2*)}$	-	-	-	-	-
	80-120	101.8(1*)	-	-	-	-	-
380	0-20	2.6(1*)	-	-	-	-	-
	30-60	4.8(1*)	-	-	-	-	-
	80-120	-	-	-	-	-	-
390	0-20	2.7(1*)	17.8	3.4	-	-	-
	30-60	4.4(1*)	-	-	-	-	-
	80-120	-	-	-	-	-	-
400	0-20	3.0(1*)	-	-	-	-	-
	30-60	4.4(1*)	-	-	-	-	-
	80-120	9.1(1*)	-	-	-	-	-
410	0-20	3.8(1*)	16.1	603.9	-	-	-
	30-60	13.4(1*)	-	-	-	-	-
	80-120	11.7(1*)	-	-	-	-	-
420	0-20	4.4(1*)	-	-	-	-	-
	30-60	8.6(1*)	-	-	-	-	-
	80-120	8.3(1*)	-	-	-	-	-
430	0-20	5.7(1*)	-	-	-60.3	-	-24.3
	30-60	13.4(1*)	-	-	-	-	-
	80-120	$\frac{23.8}{20.0-27.5(2*)}$	-	-	-	-	-
440	0-20	6.1(1*)	-	-	-	-	-

	30-60	12.0(1*)	-	-	-	-	-
	80-120	-	-	-	-	-	-
450	0-20	4.8(1*)	13.9	18.4	-62.0	-	-
	30-60	14.3(1*)	-	-	-	-	-
	80-120	$\frac{43.1}{37.8-48.4(2*)}$	-	-	-	-	-
460	0-20	5.4(1*)	-	-	-	-	-
	30-60	19.0(1*)	-	-	-	-	-
	80-120	30.1(1*)	-	-	-	-	-
470	0-20	5.8(1*)	-	-	-	-	-
	30-60	15.6(1*)	-	-	-	-	-
	80-120	24.2(1*)	-	-	-	-	-
480	0-20	7.4(1*)	-	-	-	-	-
	30-60	8.2(1*)	-	-	-	-	-
	80-120	-	-	-	-	-	-
490	0-20	11.1(1*)	-	-	-62.0	-	-23.4
	30-60	20.9(1*)	-	-	-	-	-
	80-120	$\frac{28.4}{24.9-32.0(2*)}$	-	-	-	-	-
500	0-20	13.8(1*)	14.0	148.1	-	-	-
	30-60	26.3(1*)	-	-	-	-	-
	80-120	$\frac{33.2}{31.3-35.2(2*)}$	-	-	-	-	-
510	0-20	7.9(1*)	15.7	9.4	-	-	-
	30-60	8.8(1*)	-	-	-	-	-
	80-120	12.0(1*)	-	-	-	-	-
520	0-20	3.8(1*)	-	-	-	-	-
	30-60	8.8(1*)	-	-	-	-	-
	80-120	$\frac{10.7}{10.3-11.1(2*)}$	-	-	-	-	-
530	0-20	4.9(1*)	-	-	-	-	-
	30-60	8.8(1*)	-	-	-	-	-
	80-120	$\frac{17.2}{16.8-18.0(2*)}$	-	-	-	-	-
540	0-20	4.1(1*)	13.9	8.0	-	-	-
	30-60	$\frac{8.4}{7.5-9.2(2*)}$	-	-	-	-	-
	80-120	-	-	-	-	-	-
550	0-20	2.8(1*)	-	-	-50.3	-17.0	-23.0
	30-60	$\frac{5.6}{3.7-7.5(2*)}$	-	-	-	-	-
	80-120	$\frac{22.9}{22.5-23.6(2*)}$	-	-	-	-	-
560	0-20	4.7(1*)	-	-	-	-	-
	30-60	$\frac{9.3}{4.3-14.3(2*)}$	-	-	-	-	-
	80-120	$\frac{25.2}{20.2-30.3(2*)}$	-	-	-	-	-

Note: * - the number of samples in the interval; in the numerator is the average value; in the denominator is the range of concentrations

Background methane concentrations were 3-4 ppm, which is comparable to background methane concentrations in the sediments of the Sea of Okhotsk. Methane seepage structure, controlled by the neotectonic fault, (CH_4, 2.4 % vol., Station VS-270) is in the central part of the profile (Fig. 2). Such methane concentrations are characteristic for gas hydrate sediments of the Sea of Okhotsk (Shakirov, Obzhirov, 2009). Heavy hydrocarbons in bottom sediments are represented by ethane (maximum value is 0.43 ppm), ethylene, propylene (max is 0.61 ppm), propane (max is 0.33 ppm), butane (max is 0.7 ppm) and pentane (max is 17 ppm). The maximum methane concentrations in bottom sediments are observed at the boundaries of tectonic structures, which are usually separated by faults. Methane anomalies are associated by genetic, as a rule, with underlying coal-bearing deposits, and methane migration occurs along tectonically weakened fault zones (Gresov et al., 2017).

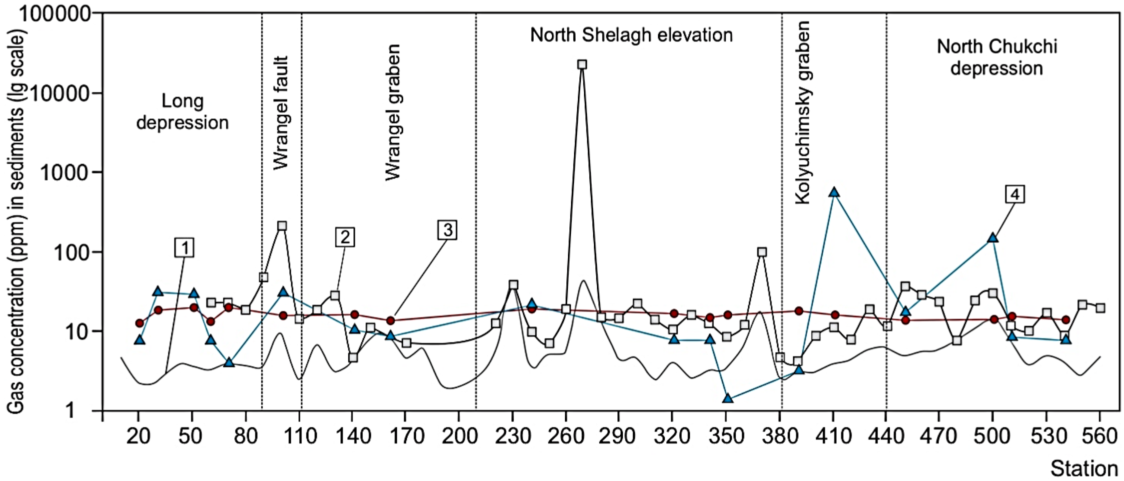

Figure 2. Concentrations of methane, helium and hydrogen in sediments (ppm): 1-methane concentrations in sediments, interval 0–5 cm; 2-methane concentrations in sediments, interval 80–120 cm; 3-helium concentrations; 4-hydrogen concentrations

The carbon isotopic composition of methane, ethane, and carbon dioxide was determined for 14 gas samples from various sections of the profile. The isotopic composition of methane carbon varies from -27.7 to -72.2 ‰ VPDB; ethane from -17.0 to -31.8 ‰ VPDB; carbon dioxide from -17.7 to -23.7 ‰ VPDB.

The obtained data on the carbon isotopic composition are within the range of values characteristic for gas-bearing and gas-and-oil-bearing sedimentary formations in northeastern Russia (Gresov et al., 2011).

Based on the results of studies of deep-sea gas vents in the pre-arc Ryukyu basin, Japanese scientists concluded that gases with the carbon isotopic composition of methane -40 ‰ VPDB and ethane -28 ‰ VPDB should be assigned to hydrocarbons that were formed during thermal metamorphism of the sediment organic matter (Tsunogai et al., 2010). In the diagram (Fig. 3), the carbon isotopic composition of methane and ethane from the studied regions falls into the gas field with a mixed genesis (thermogenic and bacterial) with a predominance of thermogenic fraction.

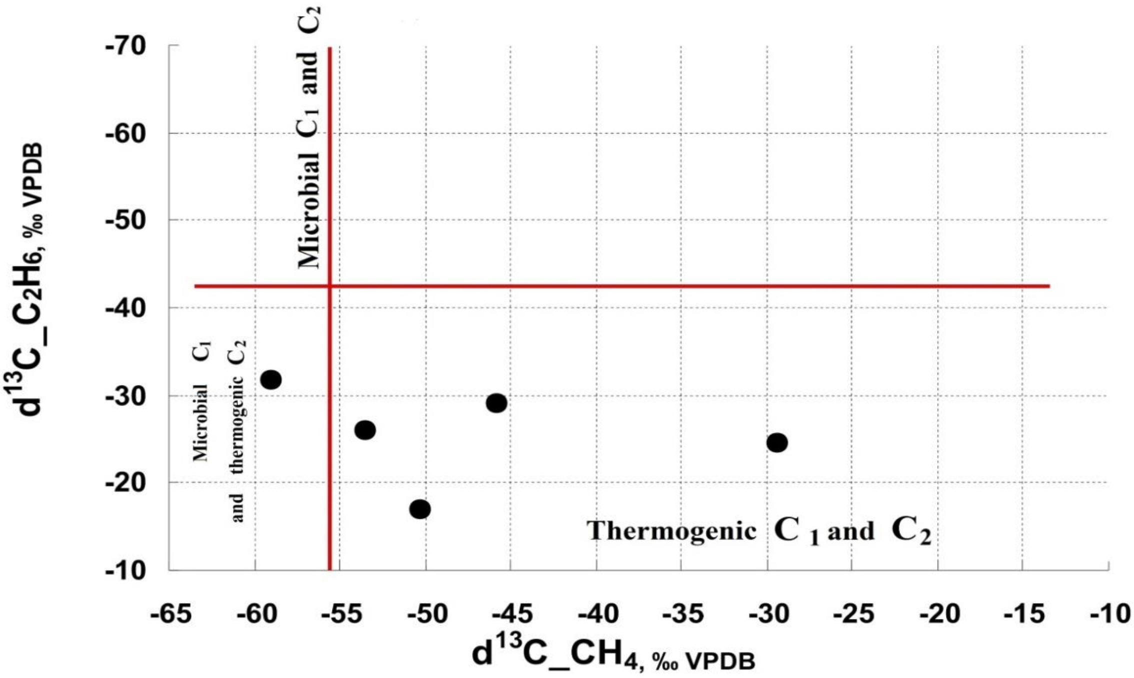

Figure 3. The isotopic composition of carbon methane and ethane in the sediments of the East Siberian Sea

Methane with a carbon isotopic composition from -45.8 to -56.1‰ VPDB (stations VS-40-VS-60) is characteristic for coal-bearing formations. The most "heavy" methane in carbon was detected at station VS-90: -27.9‰ VPDB..Such kind of methane is close to methane of Sakhalin mud volcanoes (Ershov et al., 2011). The "lightest" methane (-72.2‰ VPDB) was recorded at VS-280 station, in the zone with its maximum concentration in the sediments.

In the general, when unloading natural gas from a hydrocarbon accumulation zone, the thermogenic component should prevail. However, in places of active methane shows (such as gas hydrate), gas with a relatively light carbon composition is often found, for example, on the northeastern slope of Sakhalin Island ($^{\delta}C_{13}$-CH_4 from -55 to -77.5 ‰ VPDB). This feature is explained by active microbial processes in the upper layers of bottom sediments, where multiple fractionation of carbon occurs, including that coming from thermogenic sources and feeding microbiological communities. It can be assumed that methane with a light carbon composition in the permeability zones is not typically microbial but indicates the presence of hydrocarbon fluids from the deep horizons of the sedimentary thickness. Perhaps this explains the presence of "light" methane in carbon isotopic composition at VS-280 station, as this section is controlled by a neotectonic fault. This is also confirmed by the values of the carbon isotopic composition of carbon dioxide of -23.5‰ VPDB. The values are comparable with the average carbon isotopic composition of carbon dioxide from samples, where the thermogenic component prevails in the isotopic composition of methane carbon.

The average carbon isotopic composition of carbon dioxide coincides in genesis with the same of coal-bearing strata with a high degree of metamorphism (for example, coal deposits of Sakhalin). The molecular mass of the gas hydrocarbon fraction (M_{HH} - the weighted average value by weight of the individual members of the C1-C5 series) and the weight concentration of hydrocarbons normalized towards M_{HH} were studied as a single quantitative indicator of the genesis characteristics of hydrocarbons (Gresov, 2011). The average M_{HH} value of 25.3 as a whole is typical for gas-oil and oil deposits. In this connection the weight concentrations of C1-C5 (600-6-8-27-360) confirm that the gas-geochemical field is a polygenesis formation. The gas components of this field are formed by mixing the deep gases of the primary generation of the coal-and-gas and oil-and-gas series formed during the secondary migration processes.

Thus, according to the results of gas-geochemical studies in the East Siberian Sea, conditions for gas and gas condensate deposits search are primary task. At that a significant contribution of organic matter is likely, and the migration inflow to the near bottom sediments creates favorable conditions for the formation of gas hydrates within the permeability zones.

Helium and hydrogen content. Hydrogen and helium are migratory gases forming at the considerable depths and enter to sediments by disjunctive faults. The helium content in the surface sediments layer varies from 12.8 to 20.3 ppm, background concentrations are 16 ppm. Values of hydrogen concentrations are vary in wide range from 1.5 to 604 ppm, background concentrations are 13 ppm (for comparison: the background helium contents in the sediments of the Sea of Okhotsk are 4.5 ppm, and hydrogen are 4 ppm).

The maximum hydrogen content at VS-410 station (604 ppm) was recorded in the Kolpacinski Graben at the border of the North-Shelagh uplift and the North Chukotka Basin (depression). The increase in concentrations is marked at the VS-500 station (up to 148 ppm). Figure 2 shows that helium anomalies are fixed on the sides of the graben, where helium and hydrogen can be delivered along deep faults.

Hydrogen, most likely, migrates with methane through the thickness of sedimentary deposits by the systems of tectonic faults. Helium anomalies indicate the presence of even deeper gas sources. The coincidence of helium and methane anomalies in the fault zone and the presence of hydrogen indicate the activity of the geological structure within fluid transfer occurs. Faulting systems in geodynamically active rift structures serve as favorable conditions for the supply of deep fluid (Perevozhikov, 2012).

4.2. Sediment study results

The East Siberian Sea is a typical shelf sea of the polar regions where sediment formation occurs mainly due to mechanical weathering of rocks and with predominance of the terrigenous component. For interpretation the results of the grain-size analysis, a three-component classification was used according to the ratio of the fraction content of psammite (1-0.1 mm), silt (0.1-0.01 mm) and pelit (< 0.01 mm) (Likht et al., 1983). The main type of sediment in the profile is pelitic silt. The sediment is represented by psammite silt and silt pelit respectively at the station located in the Wragel graben and at the stations farther from the coast (Fig. 4). Significant contents of the pelitic fraction (21-72%) are presented in all samples along the profile, which is associated with the subglacial-marine sedimentation conditions. The water area is covered almost all year round with ice field, and the main process of sedimentation is the gravitational settling of clay particles

(Pavlidis, Scherbakov, 2000; Dudarev et al., 2006). The content of aleurite component in sediments along the profile varies from 26-58%, psammite from 0 to 36%.

According to the results of the description of microscopic preparations, the presented bottom sediments can be classified as terrigenous with an insignificant admixture of biogenic material. The main component of sediments in the East Siberian Sea is silicon due to the sharp prevalence of terrigenous sedimentation. A high positive correlation of this element with the content of the psammitic fraction (0.76) is noted. The maximum SiO_2 contents were recorded in the Wrangel graben (station VS-200).

The content of basic oxides in the samples varies in the following ranges (%): SiO_2 - from 51 to 80, Al_2O_3 - from 8.6 to 16, Fe_2O_3 - from 2 to 7, MgO- from 0.9 to 3, CaO- from 1 to 1.5, K_2O- from 1-3, TiO_2- from 0.4-0.6, MnO- from 0.02-0.93.

TOC concentrations in samples of bottom sediments vary from 0.29 to 2.27% of dry matter (average 1.6%) (Fig. 4). This is coicident with data from previous studies (Vetrov et al., 2008; Pavlidis, Scherbakov, 2000). A significant positive correlation is shown between the contents of organic carbon and the pelite fraction (0.65). Sediments are represented by practically carbon-free differences (IC-0-0.06%), which is typical for bottom sediments of the Arctic seas and is due to the features of the polar biocenosis and its biotype (Romankevich, Vetrov, 2001). A high degree of correlation connects TOC with a number of elements: Fe (0.87), Mg (0.88), V (0.75), Cr (0.86), as they are able to form stable organometallic complexes (Varshal et al., 1994). The average content of chemical elements and statistical parameters of their distribution are presented in Table 2.

Normalization of the element contents to their average content in clays and slates (Vinogradov, 1962; Grigoriev, 2002) shows that in the studied sediments, most of the elements are presented in concentrations below clarke - (0.2-0.7) × K_k (where K_k is the concentration coefficient expressing the ratio concentration of the element in the sediment to its clark). The contents of Mo, Pb are comparable with their contents in sedimentary rocks. Above the clarke values are Fe, V, Cr, Ba, Zn (Table 2).

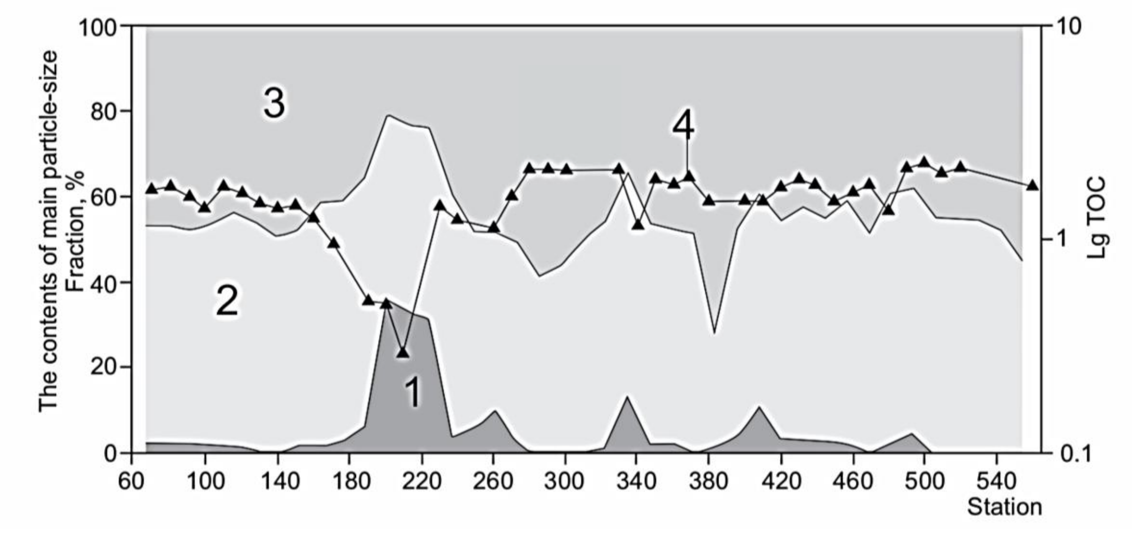

Figure 4. Diagram of the sediment grain-size composition and distribution of TOC (logarithmic scale): 1-psammite; 2-aleurite; 3-pelite; 4-Lg TOC

Table 2. Average contents of chemical elements in the bottom sediments of the East Siberian Sea, statistical parameters of their distribution and concentration coefficients (K_k) in comparison with clarke contents

Elements	Units	Content				Average grade (sedimentary rocks)	
		Max	Min	Average	Standard deviation	Content	$K_к$
Si	%	37.21	23.9	29.01	2.74	23.8*	1.22
Ti	-«-	0.38	0.23	0.33	0.03	0.45*	0.72
Al	-«-	8.46	4.55	6.51	0.61	10.45*	0.62
Fe	-«-	5.15	1.62	3.92	0.74	3.33*	1.18
Ca	-«-	1.13	0.79	0.97	0.10	2.53*	0.38
Mg	-«-	1.88	0.54	1.35	0.28	1.34*	1.01
K	-«-	5.13	1.90	1.98	0.70	2.28*	0.87
Na	-«-	5.13	1.90	2.94	0.70	0.66*	1.45
Mn	-«-	0.72	0.02	0.02	0.15	0.097**	0.81
P	-«-	0.32	0.06	0.12	0.05	0.08*	1.70
$C_{орг}$	-«-	2.27	0.39	1.66	0.41	-	-
V	10^{-4} %	276.8	59.8	161.5	41.0	120**	1.35
Cr	-«-	82.7	31.2	69.8	10.9	76**	1.52
Co	-«-	34.0	4.8	11.7	7.0	19**	0.62
Ni	-«-	67.1	11.6	33.2	11.0	47**	0.71
Cu	-«-	467.8	7.2	35.5	90.2	36**	0.99
Zn	-«-	185.9	37.7	109.5	30.9	52**	2.11
Sr	-«-	197.7	150.9	171.2	11.5	240**	0.71
Y	-«-	18.4	11.8	15.8	1.2	31**	0.51
Zr	-«-	77.8	49.0	66.7	5.9	190**	0.35
Mo	-«-	3.1	0.4	1.5	0.8	1.6**	0.95
Ag	-«-	0.21	0.12	0.17	0.02	0.2**	0.85
Cd	-«-	2.12	0.06	0.29	0.42	1.0**	0.29
Ba	-«-	706.2	575.3	665.3	29.7	460**	1.45
Pb	-«-	19.9	9.6	15.9	2.5	14**	1.14

Note: *-average content for sedimentary rocks by Vinogradov (1967), **-average content for sedimentary rocks by Grigoriev (2002)

The distribution of most elements depends on the grain-size distribution of the sediment. Sediments enrichment of Al, Mg, Fe, K, TOC correlates with the content of the pelitic fraction, since these elements are part of clay minerals (hydromica, chlorite, smectite, etc.) that make up these fractions. Clay minerals are also concentrators of many trace elements (Co, Ni, Cu, Zn, V, etc.).

Minimum concentrations of most elements were observed at VS-200 station, located in the Vragel graben. Here, in sediments, the maximum content of the psammite fraction (33%), the minimum content of pelite (23%) and the minimum values of TOC. When moving towards the open sea (towards the North Chukchi Trough), the proportion of silica decreases and the proportion of pelitic material in the sediment increases. At stations in the northern part of the profile, located on the border of the continental shelf and controlled by the sublatitudinal Mendeleev-Bering fault, anomalous contents of Mn, V, Mo, Cu, Co, Cd, Ag are noted (Fig. 5). The abundance of elements is considered to be abnormal when the concentrations exceed a value equal to the average content of the element plus a triple value of the standard deviation (Voroshilov, 2011).

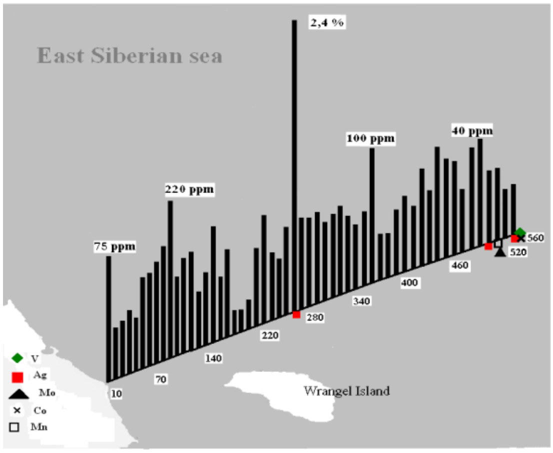

Figure 5. Methane content in bottom sediments of the East Siberian Sea and locations of anomalous metal contents

In the bottom water at these stations, elevated methane contents (3-4 times relative to the background) and abnormal hydrogen contents (10-fold excess of the background) were recorded (Table 1) according to the results of gas-geochemical studies. That indicates the activity of the fault zone separating tectonic structures. An active tectonic structure, the presence of fine-grained sediments with a high concentration of organic matter is favorable prerequisites for the formation of specific hydrochemical conditions, which leads to the accumulation of a number of elements. An important factor contributing to the concentration of these elements in sediments is the biochemical processes that are activated at the sites of methane vents (Varshal et al., 1994).

The calculated lithochemical modules characterizing the geological processes in sediments (Yudovich, Ketris, 2000) also indicate specific conditions of sedimentation in the northern part of the profile. The manganese module Mn/Fe fixes the difference in the intensity of water migration of Mn and Fe. The behavior of Mn and Fe in sea water is different, so $Mn(OH)_2$ dissolves much more easily than $Fe(OH)_3$ (Vinogradov, 1967). For sediments of the southern and central parts of the profile, the Mn/Fe value does not exceed 0.01, which is typical for terrigenous clastic-clay sedimentary rocks. For the sediments of the northern part of the profile, the Mn/Fe ratio reaches its maximum value -0.159; such values are already characteristic of pelagic aquatic clays. The maximum shift in the Mn/Fe ratio may indicate the accumulation of suspended forms of Mn in bottom waters as a result of its gradual oxidation: $Mn^{+2} + O_2 \rightarrow MnO_2$ (Yudovich, 2001).

The values of the titanium module (Mn + Fe)/Ti, which is considered as one of the criteria for the exhalation effect on the sediment, vary from 7 to 17. These values are more characteristic for terrigenous sediments than for metal-bearing (Strakhov, 1967), but there is an increase in this module at stations in the northern part of the profile.

The aluminosilicate module (Al_2O_3/SiO_2) reflects the degree of chemical differentiation of sedimentary material and the level of the matter geochemical transformation, which is determined by the tectonic regime (Rusakov et al., 2010). The module values increase (from 0.11 to 0.27) at stations in the northern part of the profile, in the zone of an active tectonic structure. With an increase in the Al_2O_3/SiO_2 ratio, the content of Fe, Mg, Co, Ni, Cu, Zn, V in the sediment increases (Fig. 6).

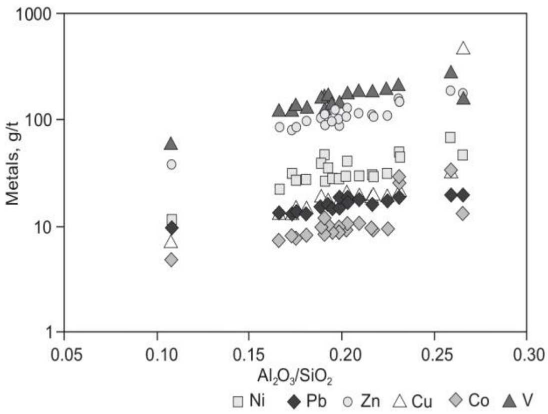

Figure 6. The content of some metals (logarithmic scale) in the sediment surface layer along the profile relative to the aluminum-silicon module

5. Conclusions

The conducted gas geochemical studies in the East Siberian Sea made it possible to characterize the distribution of saturated and unsaturated hydrocarbon gases, hydrogen and helium in bottom sediments along a regional profile of 550 km long from Billings Cape to the Mendeleev Ridge. The most contrasting gas geochemical anomalies recorded in sediments are obviously associated with tectonic faults of various specializations. The presence of hydrocarbon gases (up to pentane) with typical anomalies in the sediments along the profile allows to consider the continental shelf of the East Siberian Sea as promising for hydrocarbon potential, while the contribution of carbonaceous matter is possible. The migratory inflow of thermogenic gases to the upper part of the section creates favorable specific conditions for the formation of gas hydrates in permeability zones.

The investigation results of the sediment elemental composition show that most of the elements are present in lower concentrations relative to their average content in sedimentary rocks - (0.2-0.7) × K_k. Contents of Fe, V, Cr, Ba, Zn are above the clarke values. Sediments are enriched with organic carbon; and the TOC content correlates well with the pelitic component.

The grain-size distribution and high concentration of organic matter are the main factors controlling the concentration of metals in the sediments. Stations with abnormal metal contents in the sediment (Mn, V, Mo, Cu, Co, Cd, Ag) are identified in the northern part of the profile. The accumulation of anomalous metal contents is facilitated by specific geological conditions that occur in zones of gas anomalies within tectonically active structures, where fine-grained sediments enriched with organic matter are present. The gasgeochemical fields formed in this pattern can be applied as indicators in forecasting of hydrocarbon accumulations, for mapping fault zones, and for the environmental impact assessing of hydrocarbon anomalies.

This approach could be especially effective in the basins with low seismic activity such as seas of East Siberian shelf and some of the marginal seas of Pacific Ocean, e.g., East Sea.

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