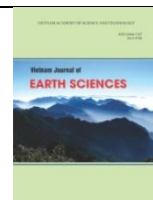




Vietnam Academy of Science and Technology  
**Vietnam Journal of Earth Sciences**  
<http://www.vjs.ac.vn/index.php/jse>



## Formation of anomalous gas fields of helium and hydrogen in the Cat Ba, Co To and Bach Long Vi islands, northern Vietnam

Syrbu Nadezhda<sup>1</sup>, Le Duc Luong<sup>2,3</sup>, Kholmogorov Andrei<sup>1</sup>, Nguyen Hoang<sup>2,3</sup>

<sup>1</sup>*V.I. Il'ichev Pacific Oceanological Institute Far Eastern Branch Russian Academy of Science, Baltiyskaya str., 43, Vladivostok, Primorsky Krai, 690041 Russia*

<sup>2</sup>*Institute of Geological Sciences, VAST, Hanoi, Vietnam*

<sup>3</sup>*Graduate University of Science and Technology, VAST, Hanoi, Vietnam*

Received 05 May 2021; Received in revised form 25 May 2021; Accepted 21 June 2021

### ABSTRACT

Data of methane, helium and hydrogen concentrations in the mineral waters, as well as in the subsurface atmosphere, of the Cat Ba, Co To and Bach Long Vi islands, shows that the regions belong to degassing zones of hydrogen and helium, and points at gas condensate potential of the Bac Bo sedimentary basin. A joint transit of these gases via the fault structures was established. Distribution patterns of hydrogen and helium concentrations from these islands (Tonkin Gulf) were obtained from the gas and water sample data. Thermogenic and metamorphogenic gases detected in hydrogeological wells on Cat Ba island and gas anomalies in subsurface gas indicate natural gas emission through permeability zones.

The work was carried out within the framework of the joint Russian-Vietnamese Laboratory on Marine Geosciences (V.I. Il'ichev Pacific Oceanological Institute FEB RAS and Institute of Marine Geology and Geophysics, VAST). The research involves the staff and scientific equipment of the new innovative Laboratory for Integrated Research of the Environment and Mineral Resources (LIREMR) of the POI FEB RAS, created within the framework of the SCIENCE national project.

*Keywords:* hydrogen, helium, methane, Cat Ba Island, northern Vietnam shelf.

©2021 Vietnam Academy of Science and Technology

### 1. Introduction

Studying deep structure features and geodynamic regimes related to the geological processes of North Vietnam is necessary for identifying the criteria of regional formation of oil and gas content and the areas being favorable for the generation of hydrocarbon

associations. This paper presents a set of data obtained with the support of the Institute of Marine Geology and Geophysics, Vietnam Academy of Sciences and Technologies (IMGG, VAST) in the framework of the joint Russian-Vietnamese Laboratory for Marine Geosciences, to create an objective zonal-regional picture of the ecological and gas-geochemical state in the Gulf of Tonkin. The

\*Corresponding author, Email: [syrbu@poi.dvo.ru](mailto:syrbu@poi.dvo.ru)

theoretical justification and systematization of long-term observations of gas-geochemical fields and sources in the Red River rift area are of scientific interest of not only geocology but also for practical petroleum geology, which is increasingly turning to the study of fluid dynamics processes both for the current state of oil and gas accumulations and rehabilitation of formation conditions of bearing strata and hydrocarbon accumulations itself.

The water-dissolved methane, hydrogen, and helium are used to decipher fault zones, forecast seismic activity, evaluate the environment's ecology, and prospect hydrocarbon fields. The spatially superimposed methane and helium anomalies may indicate the presence of ascending deep fluid.

The work aims to establish the main distribution features of hydrogen, helium, methane, and other gas components in the region of North Vietnam on the Cat Ba, Co To, and Bach Long Vi islands (Tonkin Gulf). The Tonkin Gulf (Song Hong sedimentary basin) is one of the least studied and interfaced to the Red River's largest and deepest rift system. The shelf of Vietnam is one of the most interesting and scrutinized regions with hydrocarbon pools in the basement. Some oil- and gas-bearing fields (the unique Red Tiger included) have been discovered in its southern part. The northern South China Sea accommodates hydrocarbon fields near Hainan Island (China).

Until recently, commercial hydrocarbon pools near coasts of northern Vietnam were unknown. In 2007-2016, the Bao Vang and Bao Den gas condensate fields and the deep-water Thang Bien hydrocarbon gas field were discovered on the Tonkin Gulf shelf (Bac Bo) in northern Vietnam. Total gas resources here are estimated at approximately 300 bln m<sup>3</sup>. Geological reserves in gas fields on the Bac Bo Gulf shelf are estimated at 890 bln m<sup>3</sup>. A joint group of PetroVietnam (Vietnam) and

Gazprom (Russia) is engaged in exploring, mining, reworking, transportation, and realizing hydrocarbons in this region.

In connection with great interest in hydrocarbon resources in northern Vietnam, the genesis and regularities of forming the background and anomalous gas-geochemical fields have become urgent (Duong Quoc Hung et al., 2019; Shakirov, 2018).

## 2. Materials and methods

The region of North Vietnam is tectonically active, and the main active fault zone of Southeast Asia, the Red River Rift, is located here. About 400 earthquakes were recorded annually in this area (Drogue et al., 2000). Movements along the main fault zones create conditions for increasing the flow of deep fluids and opening new channels for gas flow, especially if the region is under the influence of strong neotectonic activity.

The paper presents the complex joint Russian-Vietnamese expeditions in northern Vietnam, including the following islands: Cat Ba, Co To, and Bach Long Vi (Fig. 1). The work aims are to study the distribution of helium and hydrogen in the region with hydrocarbon potential and determine genesis and formation regularities of anomalous gas-geochemical fields.

The studied region of northern Vietnam is located in the Red River Rift domain. In the modern topography, the Red River Rift is a narrow and deep intermontane valley. Its continuation to the Gulf of Tonkin is the Song Hong Basin, a large Tertiary-age sedimentary basin in Southeast Asia. The basin was formed in Late Eocene or early Oligocene due to stretching during the transverse movement of the small Indo-Chinese plate along with the Song Hong fault system. The basin structure includes Quaternary sediments, Neogene, Paleogene formations, and Pre-Cenozoic rocks (the base complex of the tertiary basin, represented by Devonian and Permo-Carboniferous carbonates, metamorphosed Cambrian rocks, and Mesozoic granites). The

sedimentary cover is underlain by a predominantly carbonate complex of Late Paleozoic age (Devonian-Carboniferous), from which industrial oil inflows and numerous oil and gas occurrences were

obtained (Gavrilov, Leonova, 2011). The Song Hong basin and generally the water area of Bac Bo Bay are the least geologically studied areas among the Vietnam shelf sedimentary basins.

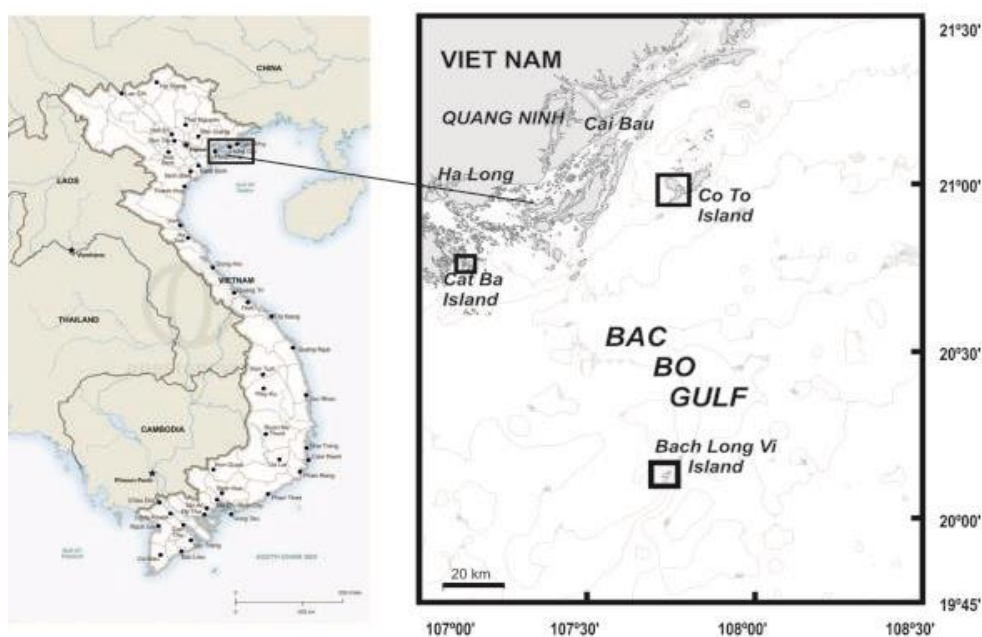


Figure 1. Study area in the Northern Vietnam and location of Cat Ba Island, Co To Island, and Bach Long Vi Island

Oil and gas promising evidence dated Oligocene and Miocene on the Tonkin Gulf shelf (Areshev, 2003). The study area is located in the bay, where the most alluvium and organic material from the rivers and islands are deposited in. According to the listed geological features, gas geochemical fields in the study area are complicated and various. Usually, seawater consists of a certain amount of methane, hydrocarbon gases, helium, hydrogen, and CO<sub>2</sub>. Differences in geological and geochemical conditions can change the concentrations of these gases from 5 to 20 times. These changes allow us to expose the geological structures, hydrocarbon accumulations, and seismo-tectonic. For example, high methane and hydrocarbon content are evidence of coal-gas – oil-bearing sediment, or knowing the carbon

isotope of methane allows us to determine the methane origin. The magma intrusion may produce hydrogen and CO<sub>2</sub> anomalies. Tectonic activities or earthquakes may create anomalies of hydrogen, helium, radon. Gases from these sources may considerably affect marine ecology, environment, and biodiversity. Though methane, hydrocarbon, and CO<sub>2</sub> from the depth may contribute considerably to the component of the seafloor fluid, there are very few research works concerning the origin and content of these gases aims at investigating geo-resources, especially natural gas and petroleum, geohazard and protecting marine environment and ecology system in Tonkin Gulf. Therefore, joint gas geochemical and geological surveys have been conducted by POI FEB RAS and IMG VAST since 2012.

Fieldworks included water sampling with a Niskin bathometer (bottle volume 0.5 L) from the mineral water resources. Gas was extracted by the equilibrium concentration and vacuum degassing methods in the Joint Russian-Vietnamese Laboratory based in the Institute of Marine Geology and Geophysics (Vietnam Academy of Sciences and Technology, Hanoi). Subsequently, the samples were transported to and analyzed in the Gas Geochemistry Laboratory of V.I. Il'ichev Pacific Oceanological Institute (Far Eastern Branch, Russian Academy of Sciences, Vladivostok).

The gas geochemical sampling of soils was accomplished based on the subsurface gas survey under the Russian State Standard GOST R 53239-2008 (2009) and methodical recommendations presented in Sokolov (1971). Gas samples taken from drill holes (depth 0.7-1.0 m) and small wells (1.5-2.0 m) were preserved in glass bottles (65 mL) using a conservant (supersaturated salt solution).

In addition, we obtained representative factual material during field works (Table 1). The majority of samples and specimens are unique because of the inaccessibility of regions and insufficient study of gas geochemical and geological parameters therein.

Table 1. Samples taken in the studied region

Object	Number of samples					Sampling year
	sediments	seawater (surface)	seawater (bottom)	subsurface gas	water	
Tonkin Gulf coast	-	-	-	11	-	2014
Cat Ba Island	-	-	-	-	14	2013
	-	-	-	-	25	2014
	-	-	-	-	27	2015
	-	10	12	-	14	2016
	-	8	4	-	14	2017
	6	4	18	69	56	2019
Co To Island	-	-	-	-	5	2013
	-	13	13	-	-	2015
Bach Long Vi Island	--	--	-	17	18	2014

The analysis of methane and carbon dioxide stable carbon isotopes was carried out using Finnigan MAT-252 mass spectrometer according to the CF-IRMS system at Nagoya University, Japan. The values ( $\delta$ ) were calculated as  $R_{\text{sample}}/R_{\text{standard}}$  ratio, where R is the  $^{13}\text{C}/^{12}\text{C}$  ratio for both the testing sample and the standard (VPDB). Hydrocarbon gases, nitrogen, oxygen, and carbon dioxide were analyzed using a CrystalLux 4000M two-channel gas chromatograph equipped with detectors of ionization flow and thermal conductivity (sensitivity  $10^{-3}\%$ ). Helium and hydrogen were analyzed with "Chromatec-Gazochrome 2000" gas chromatograph equipped with high-sensitive detectors of thermal conductivity (1-2 ppm for helium and hydrogen) and a vacuum degassing device.

Background gas concentrations were measured by special methods in compliance with the regulatory directives for the respective gases and the available methodical probabilistic-statistic references (Normativno-metodicheskoe..., 1995; Porotov, 1977; Smirnov, 1983). Gas Geochemistry Laboratory of V.I. Il'ichev Pacific Oceanological Institute holds the Russian Standard Certificate no. 41 to Laboratory Passport no. PS 1.047-18.

### 3. Results

Since 2012, within the joint Russian-Vietnamese Laboratory of Marine Geosciences, geoecological and gas geochemical monitoring of the Cat Ba, Co To, and Bach Long Vi islands on the northern

shallow Vietnam shelf (Tonkin Gulf) has been carried (Fig. 1).

In total, we took and analyzed more than 200 water samples from wells and springs, as well as 106 subsurface gas samples. Since 2012, at the largest island in the archipelago in the southwestern part of Ha Long Bay, Cat Ba Island, we have monitored water sources and wells with a depth of 50-60 used for local technical purposes. The wells are located within the development of complex structures composed of multiple-aged ancient rocks.

One important result was framing an area with sources (temperature up to +26°C) in the

northwest of the island with high methane concentrations up to 8018 nl/l (Table 2). Such concentrations are comparable to methane emissions from hydrocarbon accumulations of Sakhalin inshore (Shakirov et al., 2020). We found that Cat Ba Island was characterized by an increased background of methane concentrations in water with very high single anomalies (Table 2). Methane contents in wells on Cat Ba Island in 2019 were reported by previous studies (Shakirov et al., 2015; Shakirov et al., 2019) and marked new areas with abnormal gas concentrations in water.

Table 2. Water gas-geochemical composition of wells and springs on Cat Ba Island (gas extracted by equilibrium concentration method)

№	CH <sub>4</sub> ,nl/l	C <sub>2</sub> H <sub>4</sub> ,%	C <sub>2</sub> H <sub>6</sub> , %	O <sub>2</sub> +Ar, %	N <sub>2</sub> , %	CO <sub>2</sub> , %	He, ppm	H <sub>2</sub> ,ppm	δ <sup>13</sup> C-CH <sub>4</sub> , ‰	δ <sup>13</sup> C-CO <sub>2</sub> , ‰
2015										
1	544	0.00001	0	16.42	75.53	0.10	11.5	0.4		
2	507	0.00001	0	14.51	78.21	0.77	10	0.5		
3	563	0.00001	0	17.57	75.72	0.05	9	0.8		
4	1596	0.00001	0	16.59	77.41	0.25	11.4	0.2		
5	976	0.00001	0	15.66	75.06	0.18	11.2	0.9		
6	582	0.00000	0	14.57	77.49	0.33	9.5	0.1		
7	601	0.00001	0	14.81	78.48	0.22	11	0.8		
8	638	0.00003	0	14.93	76.89	0.19	10.7	0.6		
9	22378	0	0	14.65	76.90	4.17	12.9	0.3	-25.5	-20.7
10	3079	0	0	9.55	78.20	5.02	4.6	0		
11	14287	0	0	6.90	84.96	5.89	8.9	0.7		
12	27559	0.00002	0	10.91	81.91	1.46	11.1	0.6		
13	1671	0.00000	0	10.54	80.15	4.54	11.1	0.6		
14	24668	0	0	9.46	83.87	1.71	6.9	0.9		
15	4468	0	0	14.68	74.68	0.55	9.4	0.2		
16	8073	0.00001	0	16.46	74.27	0.21	8.6	0.6	-40.2	-21.3
17	1502	0	0	13.89	74.05	4.80	9.2	0.7		
18	432	0	0	10.74	81.75	2.14	9.6	0.4		
19	544	0	0	10.64	79.16	2.41	8.4	0.9		
20	1352	0	0	10.47	83.03	1.04	8.2	0.8		
21	1033	0	0	13.95	74.74	4.30	7.7	0		
22	695	0	0	12.86	81.05	1.06	9	0.9		
23	957	0	0	6.09	88.96	2.65	12.7	1.1		
24	10569	0	0.00004	14.63	76.89	1	9.7	0		
24	469	0	0	15.39	80.73	0.59	8.2	0.5		
2016										
1	645	0	0.00087	10.86	86.97	1.39	7.2	2.6		
2	2694	0	0	12.94	85.05	1.16	10.8	1.1		

№	CH <sub>4</sub> ,nl/l	C <sub>2</sub> H <sub>4</sub> ,%	C <sub>2</sub> H <sub>6</sub> , %	O <sub>2</sub> +Ar,%	N <sub>2</sub> ,%	CO <sub>2</sub> ,%	He, ppm	H <sub>2</sub> ,ppm	$\delta^{13}\text{C-CH}_4$ , ‰	$\delta^{13}\text{C-CO}_2$ , ‰
3	623	0	0	3.85	91.72	3.77	10.6	46		
4	7009	0	0.00001	14.32	75.7	2.27	8.8	1.9		
5	3315	0	0.00001	12.52	85.58	1.49	12.2	1.1		
6	1090	0	0.00001	13.09	85.16	1.38	6.6	1.1		
7	1936	0	0.00000	17.08	81.14	0.85	7.2	2.6		
8	1313	0	0.00001	14.39	83.21	1.06	9.3	1.7		
2017										
1	651	0	0	18.90	74.60	2.33	7.6	0		
2	163	0	0	18.60	77.80	0.45	7.2	0.4		
3	1201	0	0	18.90	76.70	0.98	6	0.4		
4	67	0	0	18.07	77.08	1.15	9.3	0.4		
5	59	0	0	17.98	76.10	1.73	4.3	0		
6	308	0	0	18.10	74.40	2.69	5.1	0.7		
7	107	0	0	18.20	77.70	0.16	5.4	0.1		
8	91177	0	0	16.86	74.79	2.50	2.8	0.1		
9	536	0	0	16.39	76.26	2.24	9.8	0.4		
10	256	0	0	16.40	77.40	1.50	5.2	0.3		
11	804	0	0	14.60	78.14	2.07	7.6	0.3		
12	1051850	0	0.0001	14.75	78.60	0.94	6.5	1.1		
13	27501	0	0	16.14	79.50	0.45	7.1	0		
2019										
1	1012	0.000001	0	84.3	5.5	0.1	0.0	0.4		
2	345	0	0	79.5	7.3	3.8	0.9	0.0		
3	1144	0	0	79.3	7.6	3.8	0.6	0.4		
4	1124	0	0	83.8	6.2	0.1	1.6	0.0		
5	324	0	0	83.1	6.1	1.0	2.1	0.4		
6	564	0	0	82.7	6.5	0.9	3.3	0.4		
7	1057	0	0	79.6	10.0	0.2	0.0	0.0		
8	936	0.000001	0	84.8	5.3	0.1	1.6	0.1		
9	213	0.000001	0	84.7	5.4	0.0	0.0	0.0		
10	279	0	0	82.8	6.3	1.2	3.2	1.5		
11	635	0	0	81.7	7.2	1.5	3.0	0.6		
12	437	0.000002	0.000001	83.9	6.1	0.0	4.7	0.2		
13	8018	0	0.000004	81.3	8.3	23	1.5	0.3		
14	5306	0	0	83.2	6.9	25	3.5	0.6		
15	361	0	0	82.2	7.2	1.1	1.7	0.7		
16	416	0	0	80.0	7.8	2.8	2.0	0.6		
17	882	0	0	79.6	7.6	3.9	1.6	0.1		
18	595	0	0	82.4	7.6	0.4	0.5	0.3		

Anomalously high methane values distinguish the southwestern part of the island in contrast to the increased background value in the groundwater. The geological scheme reflects a large number of intersecting faults in the area (Fig. 2). The areal subsurface gas survey carried out for the first time in 2019

revealed hydrogen anomalies in the subsurface gas. Still, the methane distribution was uniform, with an average value of 5 ppm (Fig. 3A).

The southwest part of the island has high-intensity methane anomalies in subsurface gas (Fig. 3A) in the area of mineral sources

discovered, where methane concentrations in water reach 5306-8018 nl/l. Also, in the area in 2015, values of stable carbon isotope in hydrogeological wells

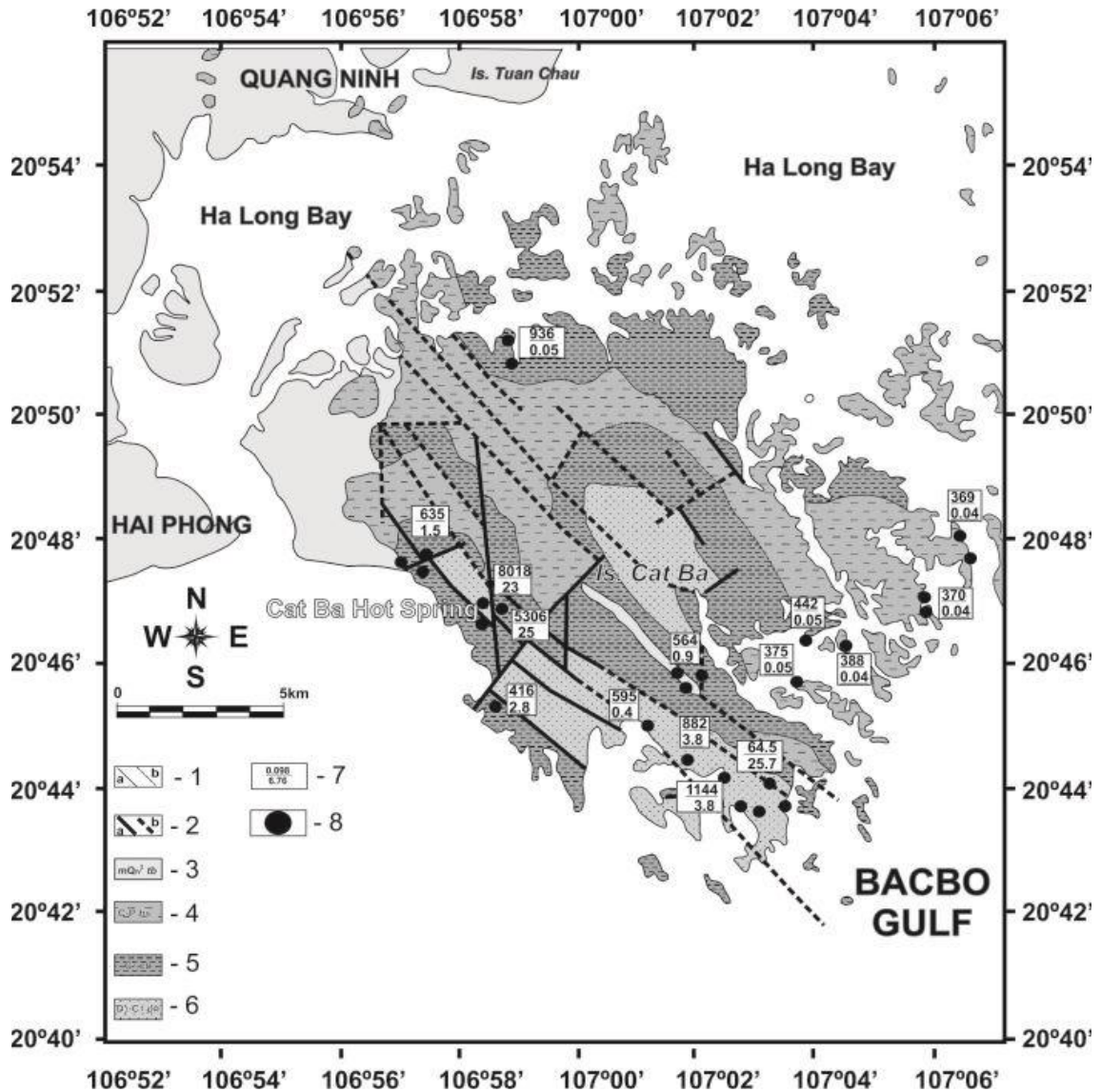


Figure 2. Geological map of Cat Ba Island and surrounding area

Legend: (1) Geological boundaries: (a) proven, (b) inferred; (2) nonclassifiable faults: (a) proven, (b) inferred; (3) Thai Binh formation-(am) clays, silts, and grayish brown sands; (bm) sands, silts, and dark gray clays: (a) quart sands, (ab) brown clays with black clay interlayers and plant remains, (m) fine and medium-grained black sands, (mv) fine-grained sands (thickness 1-5 m); (4) Bac Son formation: massive small limestones, oolitic limestones, calcareous clays, and siliceous limestones (thickness 600-950 m); (5) Cat Ba formation: black limestones, siliceous limestones, and siliceous mudstones (thickness 250-280 m); (6) Pho Han formation: thick limestone interlayers, siliceous limestones, siliceous shales, and gray calcareous clays (thickness 650 m); (7) CH<sub>4</sub> (ppm) and CO<sub>2</sub> (%) in the numerator and denominator, respectively; (8) sampling points in 2019

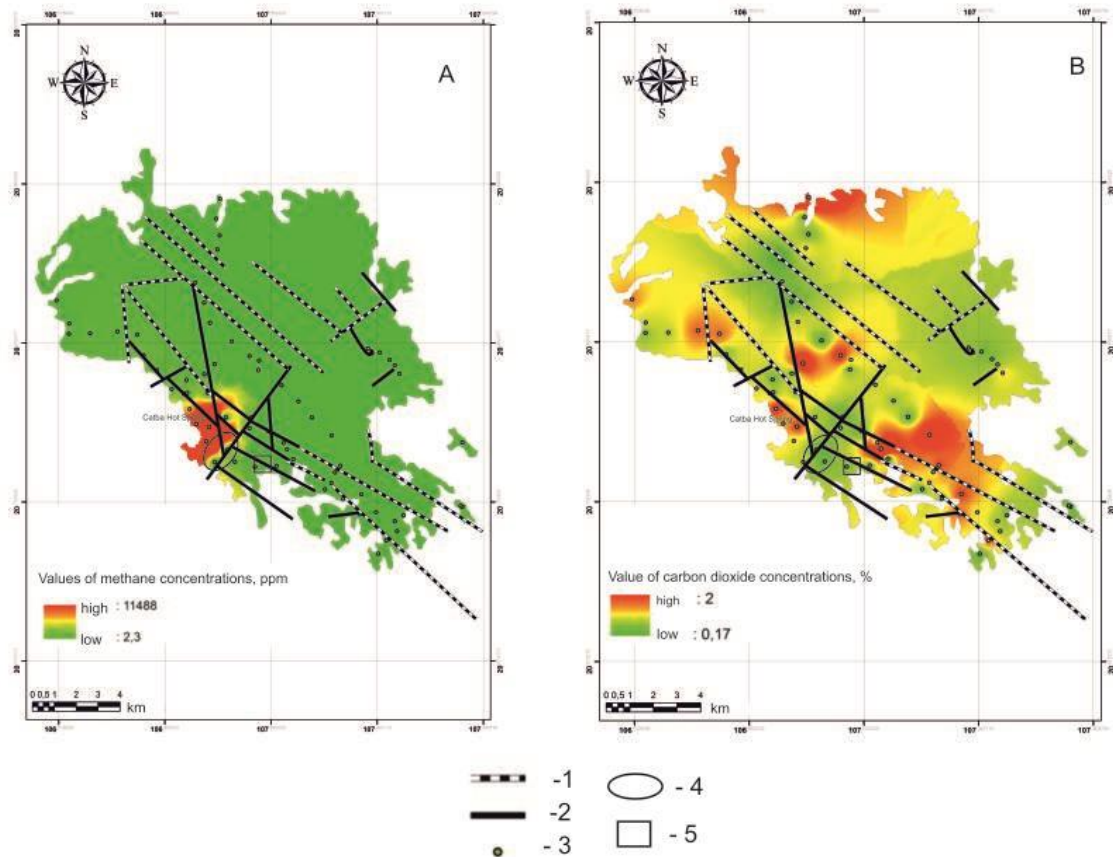


Figure 3. Distribution of methane (A) and carbon dioxide (B) in subsurface gas on Cat Ba Island and locations of discovered volcanic rocks and alluvial quartz on Cat Ba Island in 2019  
 Legend: 1 - inferred faults; 2 - faults; 3 - sample points; 4 - volcanic rock area; 5 - alluvial quartz area

were  $\delta^{13}\text{C-CH}_4$  -25.5 -40.2‰ and  $\delta^{13}\text{C-CO}_2$  -20.7 -21.3 ‰ (Table 1). In this part of the island, the main system of modern parallel deep faults of NW-SE direction formed in the late Cenozoic. Despite the small length, they dominate the structure of the island (Fig. 2).

All these facts directly indicate the migration of gas flow from the lower horizons of the folded base, shown by high-intensity anomalies of methane (up to 1052  $\mu\text{l/l}$ ) and carbon dioxide (up to 23-25%) in groundwater. Tectonic activity in Cat Ba Island is associated with the regional tectonics of northern Vietnam. It occurs at present, as indicated by the exits of mineral water in the valley, found in 2019 at increased helium concentrations carbon dioxide. Water sources

and wells on Cat Ba Island must be characterized by a very high concentration of carbon dioxide (18-28 ml/l) connected with the desalination of carbonate rocks and the intrusions interbedded in carbonate thicknesses.

Also, methane distribution on Cat Ba Island in subsurface gas and groundwater is influenced by coastal coal (anthracite) deposits. All coal types exclude anthracites, which cause methane accumulations inside coal layers and natural gas flux in permeable zones (Obzhirov et al., 2004). According to our data, sampling in the coal strata areas along the coast (subsoil and dissolved) shows methane pollution and revealed  $\text{CO}_2$  content peaks on Cat Ba Island (Table 2).



The concentrations of helium and hydrogen on Cat Ba Island are found at the background level. In contrast, some helium and hydrogen anomalies take place directly in the groundwater of Bach Long Vi Island (Figs. 4, 5; Table 3). Background concentrations of helium and hydrogen in

groundwater on Bach Long Vi Island were 14.5 ppm and 2-3 ppm, respectively.

The most important isotopic results are performed in Table 4. Three groups of gases are subdivided according to the isotope composition of methane carbon:

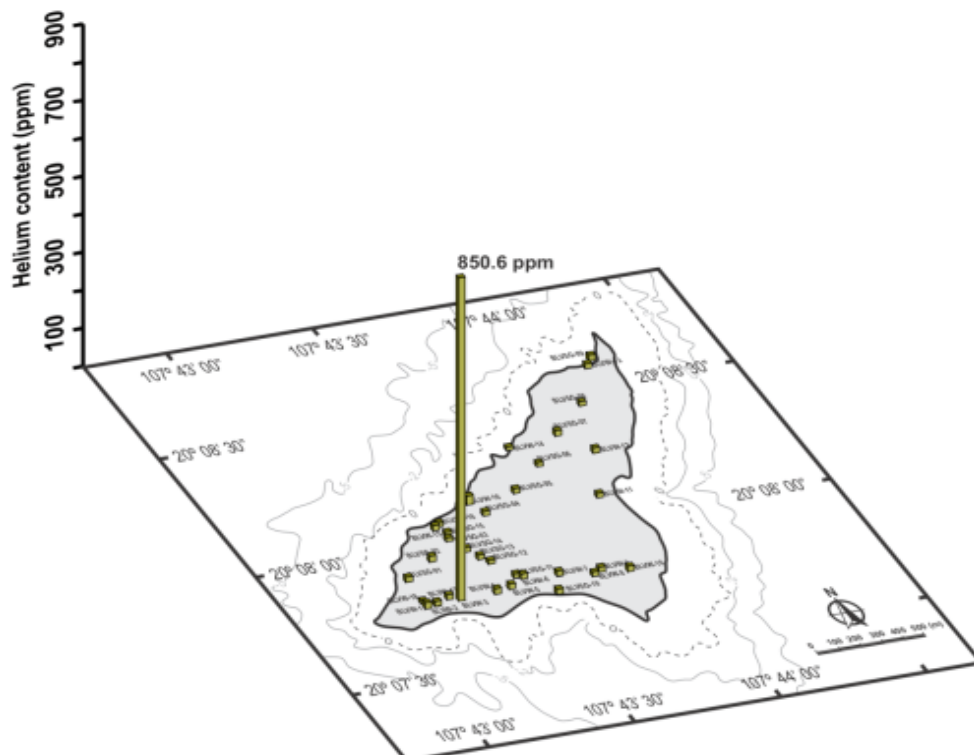


Figure 4. Concentration of helium in groundwater and sources on Bach Long Vi Island

(1) Microbial gases with values of  $-70.5\div-93.6\%$ . These were typical for superficial hydrological horizons and were found in the Red River mouth and the river and lake water on the islands.

(2) Mixed thermogenic and microbial gases in the sediments of the Tonkin Gulf have values  $-52.2\div-58\%$ . These values, accompanied by a high content of the hydrocarbon gases, pointed at the mainly thermogenic origin with non-significant additional microbial gases.

(3) Mixed thermogenic and metamorphogenic gases in the hydrological

wells on Cat Ba Island ranged  $-25.5\div-40.2\%$ . In this case, an obvious migratory gas inflow is observed from the folded basement of lower horizons defined by the high methane anomalies (up to 22378 nl/l). These indicate the gas-condensate hydrocarbon potential. That conclusion is also in good correlation to the gas-genetic diagram of China's coal-gas basins (Dai et al., 2014). With confidence, it is possible to conclude that islands and the coast of the Tonkin Gulf could open additional isotope and gas-geochemical characteristics which aren't shown so brightly in the marine sediments.

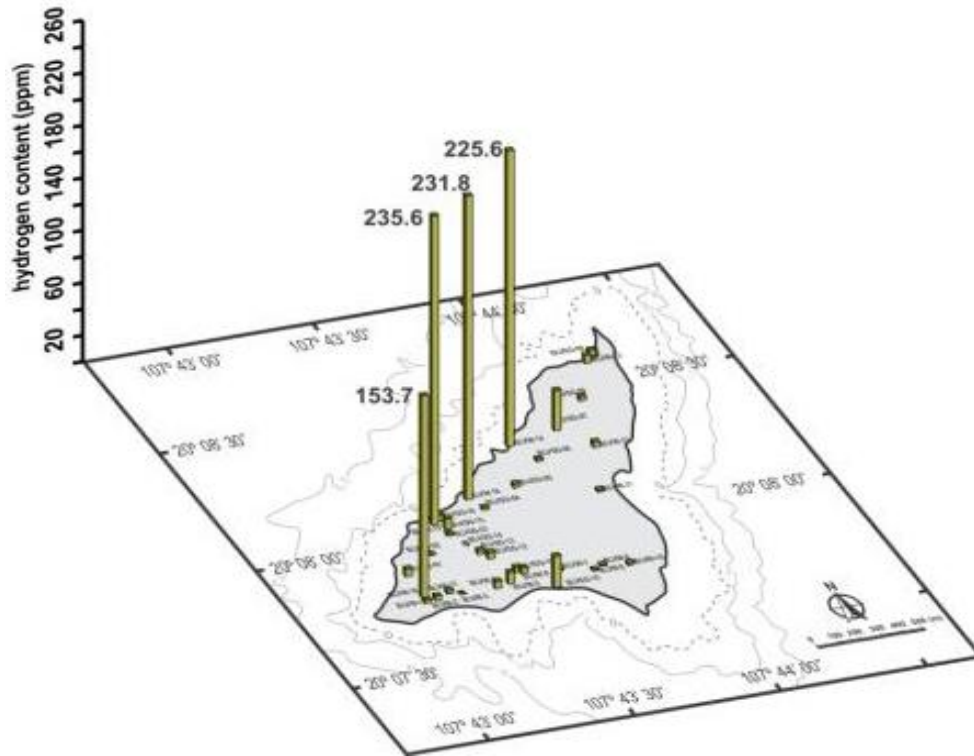


Figure 5. Concentration of hydrogen in groundwater and sources on Bach Long Vi Island

Table 3. Gas-geochemical composition of water in wells on Bach Long Vi Island in 2014 (gas was extracted by the equilibrium concentration method)

№	Station	CH <sub>4</sub> , nl/l	O <sub>2</sub> +Ar, %	N <sub>2</sub> , %	CO <sub>2</sub> , %	He, ppm	H <sub>2</sub> , ppm
1	14BLVW-01	9285	19.0	76.0	1.3	16	2
2	14BLVW-02	136	20.0	76.0	0.8	13	3
3	14BLVW-03	226	21.0	75.5	0.2	851	0
4	14BLVW-04	3715	20.9	75.7	0.4	15	6
5	14BLVW-05	159	18.8	77.1	1.0	15	9
6	14BLVW-06	92	20.0	76.3	0.5	14	4
7	14BLVW-07	69	21.1	75.5	0.3	13	1
8	14BLVW-08	1971	18.6	72.1	6.8	12	1
9	14BLVW-09	4454	19.7	76.1	1.5	13	1
10	14BLVW-10	1546	22.2	74.3	0.7	14	2
11	14BLVW-11	472	19.7	75.9	1.9	12	1
12	14BLVW-12	450	19.8	74.1	3.4	14	4
13	14BLVW-13	12059	20.1	76.5	0.8	13	6
14	14BLVW-14	1642	21.7	74.3	1.5	9	226
15	14BLVW-15	114	19.5	75.4	2.7	14	236
16	14BLVW-16	1491	18.2	74.1	5.5	24	232
17	14BLVW-17	467	20.6	75.7	0.9	13	3
18	14BLVW-18	4027	21.2	75.8	0.5	8	154

The isotope composition of the dissolved carbon dioxide carbon both at a headspace method and at vacuum degassing demonstrates similar values characterizing, in general, the carbon environment in the study area (Table 4). Thermogenic and metamorphogenic gases were found in the

hydrogeological wells on Cat Ba Island:  $\delta^{13}\text{C}-\text{CH}_4$  from -25.5 to -40.2‰. Those points at migration gas flows were transferred from the lower horizons of the folded base and corresponding to meso- and apocatagenesis zones. In this case, high helium concentrations indicate the presence of deep components.

Table 4. The carbon dioxide and methane carbon isotope composition of the Tonkin Gulf and its coastal and islands (2013-2014, the MS analysis was conducted at Nagoya University by Prof. U.Tsunogai)

No	Environment sampling	Place	Lat, °N	Long, °E	CH <sub>4</sub> , %	$\delta^{13}\text{C}$ CH <sub>4</sub> , ‰VPDB	CO <sub>2</sub> , %	$\delta^{13}\text{C}$ , ‰VPDB
2	fresh water (headspace)	Co To Island	2048.751	10721.377	0.05	-70.5	1.97	-23.3
5	fresh water (headspace)	Red River mouth	20 16.81667	106 32.233	5.0	-93.6	1.90	-24.2
K-2	fresh water (vacuum degassing)	Cat Ba Island (the well)	20.7359	107.044	0.003	-25.5	69.3	-20.7
K-6	fresh water (vacuum degassing)	Cat Ba Island (the well)	20.7368	107.043	0.030	-40.2	92.5	-21.3
17	sediment (headspace)	sediment	2059.796	1088.094	0.0006	-58.0	0.025	n.s.
45	sediment (headspace)	sediment	2022.464	10732.658	0.0004	-53.2	0.013	n.s.
71	sediment (headspace)	sediment	2037.65	10711.748	0.0008	-52.2	0.019	n.s.
79	sediment (headspace)	sediment	2035.514	1073.408	0.0005	-54.3	0.015	n.s.

n.s. - not specified

#### 4. Discussions

The carbon isotopic compositions of methane and carbon dioxide suggest an endogenous influence on carbonate strata in Cat Ba Island. Metamorphosed rock samples present in the endogenous development zone over an area of at least 6 km<sup>2</sup> (Syrbu et al., 2020). In addition, quartz mineral was discovered in this zone on the island from the river alluvial sediments (Table 5). All the facts obtained suggest an unknown igneous focus in the deeper path of Cat Ba Island (Shakirov et al., 2020). Previous studies of Vietnamese researchers pointed this fact out.

It has been established that all 2300 islands of the archipelago are composed of sedimentary rocks. Intrusive igneous rocks of a small outcrop can be found only on Cat Ba Island. For today, only a few forms of intrusive igneous rocks have been discovered. They are located in the southwestern part of the island (Ta Hoa Phuong et al., 2009).

The increased hydrogen field on Cat Ba Island can be undoubtedly associated with the processes of modern deep geodynamics. In the southwestern part of the island, the increased hydrogen content is most likely associated with its release through chemical

weathering in the intersection of tectonic faults. In this area, the weathering crust with nearby carbonates was found. Also, in the south of the island, we discovered a developed outcrop of metamorphosed sedimentary and volcanic rocks with the most intense helium and hydrogen anomalies (Fig. 6).

Table 5. Chemical analysis of quartz found in the alluvial river sediments on Cat Ba Island, 2019

Element	%	+/- 2 $\sigma$
Al	1.75	0.19
Si	44.95	0.22
Element	ppm	+/- 2 $\sigma$
S	650	150
Cl	1.748	0.033
K	4260	82
Ca	1056	36
Ti	470	180
Mn	387	29
Fe	3899	62
Ni	16	7
Cu	11	5
Zn	20	3
As	3	1
Rb	3	1.0
Sr	2	1
Y	3	2
La	85	54
LE	50.47	0.22

The formation of an abnormal hydrogen field on the island is probably influenced by the anthracite deposits, the Quang Ninh coal basin. This fact confirms some hydrogen anomalies (up to 3540 ppm) in seawater near Co To Island (Syrbu et al., 2020). The geodynamical active faults serve as channels for gas and fluids of molecular hydrogen produced either by high-temperature reactions in the asthenosphere (Sokolov, 1971) or by chemical reactions triggered by neotectonic movements at lower temperatures in the

lithosphere. Also, some microorganisms can release hydrogen during vital activity and have a possible influence on subsurface hydrogen.

High methane concentrations in waters were found up to 105058 nl/l and 12059 nl/l in Co To island and Bach Long Vi Island. These high concentrations can be explained by the islands' location in the zone of the Red River Fault, which is the most permeable for the gas migration and fluid flows.

Increased hydrogen concentrations may occur due to its transit from hydrocarbon accumulation zones in the region (gas condensate deposits of the Bac Bo basin, oil manifestations in the northwestern of Song Hong basin, and Quang Ninh coal basin with anthracites and semi-anthracites).

The main factors determining the vertical or sub-vertical gas migration (methane, hydrocarbon gases, helium, hydrogen, carbon dioxide) are diffusion seepage and tectonics, expressed in the extrusion structures of anticline folds, which are accompanied by migration channels formation in the form of faults, as well as displacements of geological structures (Shakirov et al., 2015; Truong Thanh Phi et al., 2018). The increased regional background of helium and hydrogen should be associated with these geological features and the modern tectonic activity of the Cat Ba archipelago. The main faults that form the gas permeability channels of ancient (Paleozoic) rocks on Cat Ba Island and the adjacent territory, most likely, are shear dislocations influenced by the tectonic regime of regional compression (Kasatkin et al., 2014).

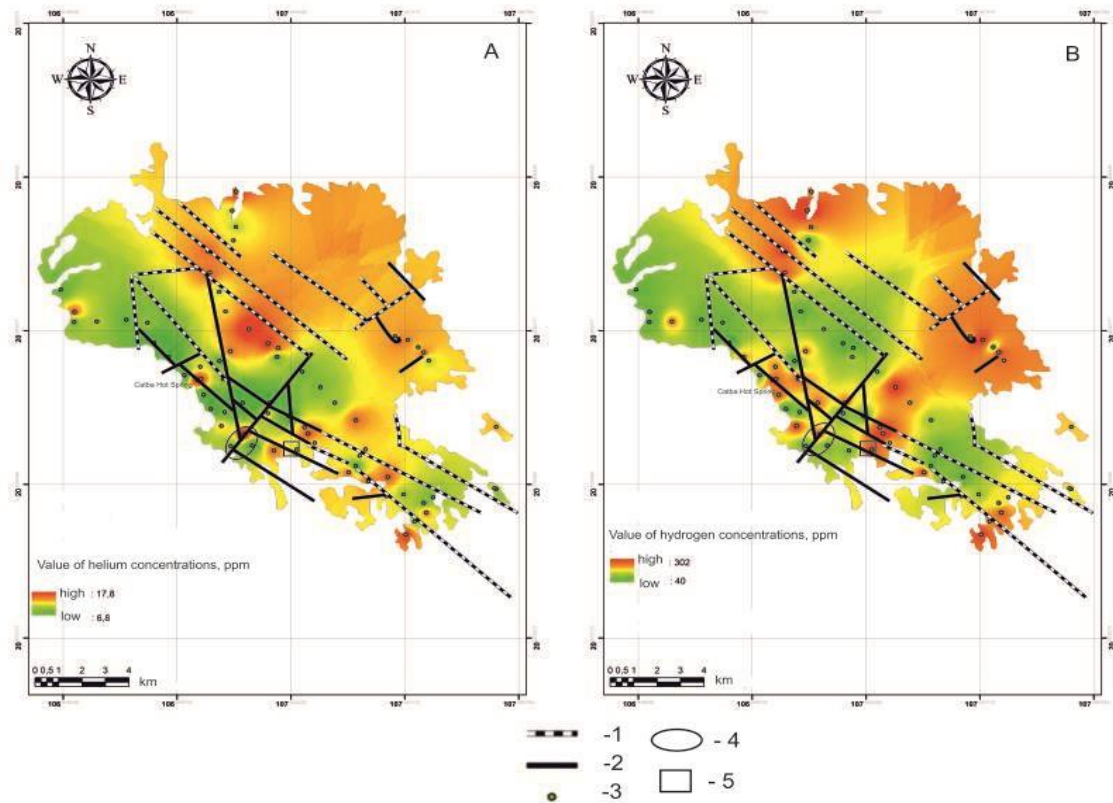


Figure 6. Distribution of helium (A) and hydrocarbon (B) in subsurface gas on Cat Ba Island and location of discovered volcanic rocks and alluvial quartz on Cat Ba Island in 2019  
 Legend: 1 - inferred faults; 2 - faults; 3 - sample points; 4 - volcanic rock area; 5 - alluvial quartz area

### 5. Conclusions

For the first time, large gas-geochemical and geological regional monitoring studies were carried out. As a result, we obtained unique data on the distribution of hydrocarbon gases, helium, and hydrogen in the north shelf of Vietnam, the islands of Cat Ba, Bach Long Vi, and Co To. Features of the degassing process by tectonic faults, hydrogen fields, and its control as one of the geodynamics indicators are considered.

Thermogenic and metamorphogenic gases detected in hydrogeological wells on Cat Ba Island and anomalies of methane, hydrogen, and helium in subsurface gas, show natural gas emission through permeability zones.

The data obtained (high concentrations of hydrocarbon gases, hydrogen and helium, heavy isotopic composition of methane carbon and carbon dioxide) indicate the gas condensate potential of the Bac Bo sedimentary basin. The contribution of the deep gas hydrocarbon and hydrogen fluid can be significant.

Bac Bo Bay (like the entire Song Hong basin), according to gas geochemical conditions, has the potential to form large gas condensate and oil deposits.

The interrelations of gas-geochemical fields with seismic and tectonic of the northwest South China Sea are uncertain today. Nevertheless, the raised background of thermogenic and metamorphogenic methane,

and hydrogen and helium peaks give evidence to thermogenic gases' steady inflow in the Gulf of Tonkin.

The increase in the quantity and intensity of abnormal gas-geochemical fields called by strengthening seismic activity can occur on the shelf of northern Vietnam in the future. Increasing seismic activity in all Vietnamese shelves will cause active natural thermogenic and microbial gas seepage like it observed in geological past herein, and nowadays in the Sea of Okhotsk and Japan Sea. According to helium and hydrogen anomalies deep metamorphic and magmatic sources (ultrabasic rocks) can be involved significantly.

#### Acknowledgments

The author thanks the Vietnamese colleagues from the Institute of Marine Geology and Geophysics VAST: Dr. Do Huy Cuong and Le Duc Anh, for the assistance in the research. Special thanks go to the deputy director of POI FEB RAS-Dr. Renat Shakirov for providing the expedition assistance in resolving organizational issues.

Expeditionary works were supported by the Ministry of Science and Higher Education of the Russian Federation in the framework of the state task of POI FEB RAS 0211-2021-0012. Work was supported by the RFBR (project no. 20-35-70014) and the President's grant MK-357.2021.1.5.

This work was carried out by the Joint Russian-Vietnamese Laboratory on Marine Sciences (V.I. Il'ichev Pacific Oceanological Institute-Institute of Marine Geology and Geophysics) under the Roadmap of Marine Studies by these two institutions (2018-2025). Information support was provided by the V.I. Il'ichev Pacific Oceanological Institute and the Primorye Branch of the Russian Geographical Society (ARIS RGS). This study complies with the Protocol of the Second Meeting of the Commission on Scientific-Technical Cooperation (Ministry of

Education, Russian Federation–Ministry of Science and Technology, Socialist Republic of Vietnam, 2019).

#### References

- Areshev E.G., 2003. Oil-and-gas content of the Far East and Southeast Asia shelf seas. Moscow, Avanti, pp.288.
- Dai Jinxing, Deyu Gong, Yunyan Ni, Shipeng Huang, Wei Wu. 2014. Stable carbon isotopes of coal-derived gases sourced from the Mesozoic coal measures in China. *Organic Geochemistry*, 74, 123-142.
- Drogue C., Cat N.N., Daz J., 2000. Geological factors affecting the chemical characteristics of the thermal waters of the carbonate karstified aquifers of Northern Vietnam. *Hydrology and Earth System Sciences*, 4(2), 332-340.
- Duong Quoc Hung, et al., 2019. A study on the relationship between gas-geochemical field and tectonic fault activities in the river mouth of Gulf of Tonkin. *Vietnam Journal of Marine Science and Technology*, 19(2), 191-198.
- Gavrilov V.P., Leonova E.A., Rybal'chenko V.V., 2011. Mud volcanism and petroleum potential in the Song Hong trough, northern shelf of Vietnam, in *Tr. Ross. Gos. Univ. Nefti Gaza*, 4, 28-37.
- GOST R 53239-2008, 2009. *Khranilishcha prirodnykh gazov podzemnye. Pravila monitoringa pri sozdanii i ekspluatatsii* (GOST R 53239-2008. Repository of Underground Gases: Monitoring Rules during Building and Exploitation). pp. 19, Moscow, Standartinform.
- Normativno-metodicheskoe obespechenie okhrany atmosfernogo vozdukha (Normative-Methodical Provisions for the Protection of Atmospheric Air). 1995. Perm, Intereko, 2, pp.249.
- Obzhairov A., et al., 2004. Relations between methane venting, geological structure and seismo-tectonics in the Okhotsk Sea. *Geo-Marine Letters*, 24, 135-139.
- Porotov G.S., 1977. *Matematicheskie metody pri poiskakh i razvedke poleznykh iskopaemykh* (Mathematical Methods in the Prospecting and Exploration of Mineral Resources). Leningrad. Leningr. Gorn. Inst., pp.106.

- Shakirov R.B., 2018. Gazogeokhimicheskie polya morei Vostochnoi Azii (Gas-Geochemical Fields in Seas of East Asia), Moscow, GEOS, pp.341.
- Shakirov R.B., et al., 2020. First complex Russian-Vietnamese geological-geophysical and oceanographic expedition in the South China Sea, R/V Akademik M.A. Lavrentev (Cruise 88, 2019). Vestn. DVO RAN, 3, 138-152.
- Shakirov R.B., et al., 2015. Peculiarities in the distribution of natural gases in bottom sediments and water in the northwestern Tonkin Gulf. Geogr. Prirodn. Resursy, 4, 178-188.
- Shakirov R.B., et al., 2019. Methane anomalies, its flux on the sea-atmosphere interface and their relations to the geological structure of the South-Tatar sedimentary basin (Tatar Strait, the Sea of Japan). Mar. Geophys. Res., 40, 581-600. <https://doi.org/10.1007/s11001-019-09389-3>.
- Smirnov B.V., 1983. Veroyatnostnye metody pognozirovaniya v inzhenernoi geologii (Probabilistic Methods of Prognosis in Engineering Geology), Moscow, Nedra, pp.134.
- Sokolov V.A., 1971. Geokhimiya prirodnykh gazov (Geochemistry of Natural Gases). Moscow, Nedra, pp.336.
- Syrbu N.S., et al., 2020. Formation of abnormal gas-geochemical fields of methane, helium and hydrogen in the area of northern Vietnam, coastal and adjacent area. Lithology and Mineral Resources, 55(6), 512-527.
- Ta Hoa Phuong, Tran Trong Hoa, Tran Duc Thanh, Nguyen Huu Cu, 2009. Diverse geology at Cat Ba archipelago - base to build a geopark. Journal of Sciences of the Earth, 31(3), 236-247 (in Vietnamese).
- Truong Thanh Phi, et al., 2018. Features of the Cenozoic deformation phases on Co To - Thanh Lan islands (Quang Ninh province, Tonkin gulf, Vietnam). Pacific Geology, 37(2), 87-101.