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Geological features for the formation of gas-geochemical fields, including helium and hydrogen, in the water and sediments at the Vietnamese part of the South-China Sea

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Abstract. The paper presents the results of a complex joint Russian-Vietnamese geological, geophysical and oceanographic expedition in the South-China Sea (R/V "Akademik M.A. Lavrentyev", cruise 88, 2019), as well as related joint Russian-Vietnamese marine and land researches in the area of north and south Vietnam under a series of local FEB RAS – VAST grants. The organizers of the marine expedition are the Ilyichev Pacific Oceanological Institute of the Far Eastern Branch of the Russian Academy of Sciences (POI FEB RAS) and the Institute of Marine Geology and Geophysics of the Vietnam Academy of Science and Technology (IMGG VAST). In comparison with the Sea of Japan and the Sea of Okhotsk, it can be noted that the active bottom degassing on the on the Vietnamese shelf and slope have is a local, although the intensity of gas-geochemical anomalies is comparable to similar zones in the Far Eastern Seas. For the first time, anomalous methane fields (up to 5000 nl/l) were found in the water column of the South-China Sea, which are comparable to anomalies on the oil and gas shelf and the gas-hydrate-bearing slope of Sakhalin Island.

Metamorphosed sedimentary and volcanic rocks were discovered for the first time in the southern part of Catba Island (Gulf of Tonkin), which indicates the introduction of an endogenous body into the sedimentary strata and its further transformation. In connection with the discovery in 2020 of the large Ken Bau gas field at the southern end of the sedimentary basin of the Red River, the forecast of POI scientists about the presence of significant hydrocarbon reserves in this area was confirmed.

The work was carried out within the framework of the joint Vietnam-Russia Laboratory for Marine Sciences and Technology (V. I. Ilyichev Pacific Oceanological Institute of the Far Eastern Branch of the Russian Academy of Sciences and the Institute of Marine Geology and Geophysics Vietnam Academy of Science and Technology). The expedition of the R/V "Akademik M.A. Lavrentyev" (cruise 88) is part of a series of expeditions in accordance with the UN Decade dedicated to the Ocean Science for Sustainable Development.

Keywords: helium, hydrogen, hydrocarbon potential, Nam Con Son basin, Phu Khan basin, Red River basin, South-China Sea

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Introduction

The South China Sea is central to understanding geophysical, geological, oceanographic, climatic and bioresource processes, occurring in the Western Pacific. It has been studied in the works of Russian, Vietnamese, German, French, Japanese scientists and a number of international scientific and industrial institutions. In the

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result, the modern geological structure, conditions and history of the basin formation, the prospects for oil and gas, and oceanographic features are generally known.

Despite the good knowledge of the shallow-water shelf, a number of important issues closely related to the natural resources of the water area of Vietnam are still remain poorly studied or insufficiently developed.

Especially, the area of the Red River sedimentary basin (the Song Hong and Quang Yen basins), is of the greatest interest at the present time including the shelf and continental slope, the central Vietnamese shelf and slope (Phu Khanh basin), where evidences of gas manifestations were recorded and the southwestern part of the South China Sea within the area of Nam Con Son basin. These areas are characterized by positive signs of hydrocarbon and other minerals. Their complex study will make it possible to compare the current state of the seabed and the water column with the integrated data obtained earlier and the data on the Far Eastern Seas of the Russian Federation.

In view of the active interest in the hydrocarbon resources of northern Vietnam, the questions of genesis and formation patterns of background and anomalous gasgeochemical fields are especially relevant (Shakirov, 2018; Duong Quoc Hung et al., 2019). Knowledge of the gasgeochemical and tectonic features of the region will be effectively used for forecast and prospecting for hydrocarbon deposits. For these and other purposes, complex geological and geophysical expeditions of Ilyichev Pacific Oceanological Institute of the Far Eastern Branch of the Russian Academy of Sciences (POI FEB RAS) on the shelf of Vietnam have been resumed (Shakirov et al., 2020).

The relation between the distribution of gas fluxes and modern geodynamic processes is beyond doubt (Kravtsov et al., 1967). Geodynamically active deep faults are the degassing channels of the Earth; these faults under the marine conditions exist in the form of gasgeochemical fields with anomalously increased concentrations of helium, hydrogen, methane and other gases in the water column and bottom sediments. The temporal variability of gasgeochemical fields reflects the dynamics of tectonic processes and changes in seismicity (Voitov, Dobrovol'skii, 1994).

Seismic activity can trigger gas fluxes in the Vietnam region of the South China Sea (Tuyen et al., 2018). The phases of tectonic deformations are contrastingly manifested on the islands of the Catba archipelago in the Gulf of Tonkin (Phi et al., 2018), in water sources of which high concentrations of hydrocarbon gases, carbon dioxide, helium and hydrogen were observed (Syrbu et al., 2020).

The aim of this work is to identify the main distribution features of the concentration fields (hydrogen, helium, methane and other gas components) on the North Vietnamese shelf of the South China Sea.

Materials and methods

The article presents the results of a series of complex joint Russian-Vietnamese expeditions in the area of the northern shelf of Vietnam, including the Gulf of Tonkin. In 2019, the first major geological, geophysical and oceanographic expedition onboard the R/V "Akademik M.A. Lavrentyev" was conducted in the exclusive economic zone of the Socialist Republic of Vietnam (SRV) (Fig. 1). The expedition obtained new data in the field of gasgeochemistry, geophysics, geomicrobiology, lithology, paleogeography, hydrooptics, hydrology,

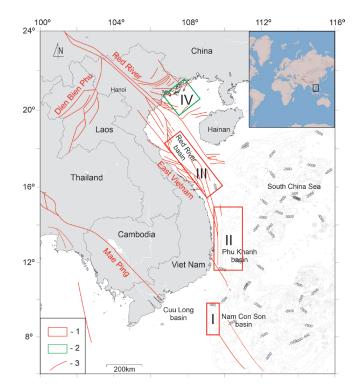


Fig. 1. Map of the study area. 1 - study areas of 88th cruise of the R/V "Akademik M.A. Lavrentyev": I - Southern area, Nam Con Son basin; II – Central area, Phu Khanh basin; III – Northern area, Red River basin; 2 - study area at the northern shelf of Vietnam, Gulf of Tonkin and Catba, Coto and Bach Long Vi islands; 3 - fault zones

mineralogy and other research fields on the Vietnamese continental shelf. In particular, gasgeochemical anomalies and groups of microorganisms, which are indicative of hydrocarbon accumulations, were observed in sediments at the stations within the shelf of northern Vietnam. It should be noted that the presence of hydrocarbon resources on the Vietnamese shelf has been already predicted by POI FEB RAS scientists in the late 1980s (Kulinich, Obzhirov, 1985; Obzhirov, 1993).

24 researchers from POI FEB RAS and 10 Vietnamese scientists from the Institute of Marine Geology and Geophysics, the Institute of Marine Resources and Environment, the Institute of Oceanography and the Institute of Geology of the Vietnamese Academy of Sciences and Technology (VAST), an employee from Center for Planning and Research of Marine Resources of the Ministry of Natural Resources of the Socialist Republic of Vietnam and an employee of the Center for Monitoring of the Marine Environment of the Vietnam People's Navy participated in the integrated research in the South China Sea onboard the R/V "Akademik M.A. Lavrentyev "(cruise 88).

Interest in oil and gas prospecting in Vietnam was caused by the discovery of a large oil reservoir in the granitoid basement of the White Tiger field in 1988 (Areshev et al., 1997). Later, oil deposits were discovered at the Dragon, Ruby, Daihung, Golden Lion and other fields. All these discoveries are related to the shelf structures of Southern Vietnam. Currently, the sedimentary basins of the Northern (Song Hong, the Gulf of Tonkin) and Central Vietnam (Phu Khanh) are of the greatest interest in the aspect of gasgeochemical studies; previously, these basins have not been considered promising for hydrocarbon prospecting.

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In the result of the research of the joint Vietnam-Russia Laboratory for Marine Sciences and Technology in the Gulf of Tonkin and the Red River sedimentary basin, isotopic and gasgeochemical data were obtained; on the basis of the data, conclusions about the presence of gas and condensate in the Red River basin were drawn (Obzhirov, 1993; Shakirov et al., 2015; Le Duc Anh et al., 2018; Duong Quoc Hung et al., 2019; Shakirov et al., 2019).

The basements of the Song Hong Basin (Red River) and the northern part of the Phu Khanh Basin are composed of two layers. Its lower layer (crystalline basement) is not exposed within the water area and is distinguished according to the data of geophysical studies and on the coast. On land, pre-Cambrian and early Paleozoic rocks form the Song Hong, Song Lo and other massifs. They are composed of complexes of magmatic and metamorphic rocks – gneisses, amphibolites, quartzites, vulcanites, granitoids, etc. (Shnip, 2012).

The study areas of the North Vietnamese shelf are in the zone of influence of the Red River Rift (Fig. 2), which had been formed in compressional environment (partly because of shear stresses), against the background of general rapid neotectonic uplift of the territory, which became a large mountainous country.

During the marine expeditions, gasgeochemical studies of methane, hydrocarbon gases, carbon dioxide, helium and hydrogen content in the deep, surface and subsurface layers of the water column, as well as in the bottom sediments of Nam Con Son, Phu Khanh and the Red River (including the Gulf of Tonkin) sedimentary basins were conducted .

For onboard water sampling, 6-position Rosette system (USA) combined with a CTD probe (Conductivity, Temperature and Depth) was used. The sounding complex was equipped with a cassette of NISKIN bottles (6 bottles). Water sampling was carried out at separate horizons, taking into account the vertical distribution of temperature, salinity and other hydrological parameters during CTD sounding. To study in detail, the distribution of methane concentrations in the water column, horizons characterized by significant gradients of oceanographic parameters (temperature, salinity, turbidity) were tested. Sampling was carried out at six horizons. Among them, the standard ones were 0 (surface), 20, 50, 200 and 600 meters. For gas chromatographic analysis of water, the "HeadSpace" method of equilibrium concentrations was used. For a more accurate and detailed analysis

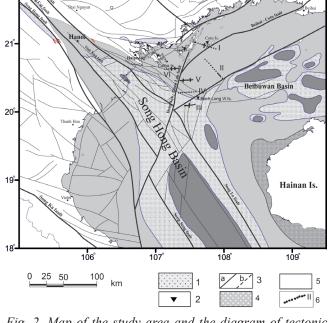


Fig. 2. Map of the study area and the diagram of tectonic structure of the Red River fault system according to (Geological map of Vietnam, 1986). 1 - Pliocene-Quaternaryrocks; 2 - sampling points at the islands; <math>3 - identified (a) and assumed (b) faults; 4 - the Red River sedimentary basin;5 - pre-Pliocene terrigenous formations; <math>6 - profiles of marine geological-geophysical and gasgeochemical works, 2013.

of concentrations of methane and a number of its homologues (ethane, propane, butane) in seawater, sampling to obtain the gas phase, using the vacuum degassing method, was also conducted.

The sediment sampling was carried out using gravity corer 6 meters long (in Gulf of Tonkin the sampler was 3 meters long) and up to 120 mm in internal diameter. Sampling for gasgeochemical analysis was carried out using 12-ml syringes with cut-off nozzles into 43 and 68 ml flasks filled with a saturated NaCl solution with a preservative (0.5 ml of chlorhexidine digluconate, 0.05 %). During the sampling, the lithological features of the sedimentary cores were taken into account.

The analysis of geological samples was carried out using Jeol JXA-8100 microanalyzer at the analytical center of the Far East Geological Institute (FEGI FEB RAS).

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 (Tsunogai et al., 2010). The values (δ) were calculated as $R_{sample}/R_{standard}$ ratio, where R is the ¹³C/¹²C ratio for both the testing sample and the VPDB standard (Vienna Pee Dee Belemnite).

During the work together with colleagues from the Institute of Marine Geology and Geophysics VAST on the Vietnamese shelf we obtained representative gr /m

factual material (Table 1). The overwhelming number of samples are unique due to inaccessibility of the regions and their little study in the gasgeochemical and geological aspects

The analysis of hydrocarbon gases, nitrogen, oxygen and carbon dioxide was carried out using two-channel gas chromatograph CristalLux 4000M equipped with ionization flow and thermal conductivity sensors (sensitivity is 10^{-5} %). For helium and hydrogen analysis, we used gas chromatograph "Chromatek-Gazochrom 2000" ("Chromatek", Yoshkar-Ola) with high-sensitivity thermal conductivity sensors (1-2 ppm for helium and hydrogen), as well as a vacuum degassing unit. Analysis duration for hydrocarbon gases was 20 min, for helium and hydrogen -5 min. To determine the background gas concentrations we used the methods, regulated by the current regulatory guidelines for measurement of background concentrations of substances (gases), and available methodological probabilistic and statistical published sources (Shakirov, 2016; Normative and methodical ..., 1995; Porotov, 1977; Smirnov, 1983).

Analyses were carried out at the Gasgeochemistry Laboratory of POI FEB RAS according to procedures approved by Rosstandart (Federal Agency on Technical Regulating and Metrology) Certificate No. 41 (Technical Data Sheet PS 1.047-18).

Object	Number of			
	sediments		seawater (bottom)	Year
Gulf of Tonkin	37	36	74	2014
	80	43	45	2016
Vietnam shelf R/V "Akademik M.A. Lavrentyev" (cruise 88)	499	101	204	2019

Table 1. Number of samples taken in the study are

Results and discussion

Helium and hydrogen distribution in the Gulf of Tonkin

In 2013, the surface sediments and sea water were sampled at 97 stations along 6 profiles in the study area of the Gulf of Tonkin (Fig. 3); sampling depths ranged from 7.5 m to 53.3 m (Shakirov et al., 2015).

The study area is located in the Beibuwan sedimentary basin, which occupies shallow water area (depths from 20 to 70 m). The basin had been formed as a result of polycyclic rifting processes in the Mesozoic and Cenozoic and was divided by faults, directed to the northeast. Tectonic depressions stretched in northeastern and, in more deep areas, western directions are spread in the bay. The basin is crossed by sub-latitudinal and sub-meridional faults; the faults directed from north-east

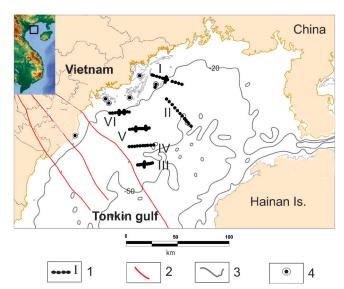


Fig. 3. Map of the study area for integrated geologicalgeophysical research in the Gulf of Tonkin, 2013 (Shakirov et al., 2015). 1 - profile and its number, 2 - faults of the Red River rift, 3 - isobaths, 4 - onshore water sampling stations. The inset square shows the position of the study area on the map of Vietnam.

to south-west prevail and are deeper. The sub-meridional faults are smaller, but occur more often (Shakirov et al., 2015).

Based on the results of a series of gas chromatographic analyses, the presence of methane in concentrations of 45.1–357 nM/dm³ was identified in all sediment samples. High background concentrations of methane in sediments (156 nM/dm³) were recorded over the entire area of the bay, which indicates diffusive seepages. Propane and butane were found in 80 % of the samples.

It is known that hydrogen and helium are characteristic gases for zones of deep faults and seismically active zones. The maximum concentrations of these gases in sediments and sub-bottom waters are confined to the rift zone of the Red River: in the sediments H_2 is up to 102 ppm (background values are 4–6 ppm), He is up to 20 ppm (background values are 10–11 ppm); in water H_2 is up to 300 ppm (background values are 5–6 ppm), He is up to 13 ppm (background value is 9 ppm) (Akulichev et al., 2015). This fact indicates the tectonic activity of the fault zone.

The distribution of high methane concentrations in bottom sediments, sub-bottom and surface seawater is relatively uniform, which is probably due to a system of cracks that cross the bottom surface.

On the coast of northern Vietnam (the Gulf of Tonkin), anthracite deposits were observed. Anthracite can be a source of hydrogen. This fact can explain the detection of abnormally high hydrogen concentrations (up to 3540 ppm) in seawater near the Coto Island (Syrbu et al., 2020).

Probably, the Gulf of Tonkin, another source, associated with hydrocarbon gases, can contribute to

Having different generating sources, helium and hydrogen have probably become companions of hydrocarbon gases, passing through joint deep filtration channels. If the Earth crust probably produces helium, then, in our case, migration channels of centers, generating hydrocarbon gases, is a source of hydrogen.

In (Shakirov et al., 2015), hydrogen and helium concentrations were compared with an interpreted crosssection of continuous seismic profiling, where the peaks of the hydrogen content over the sub-surface faults were clearly distinguished. The maximum was recorded over the faults that cross the sea floor, and the anomalies of lower intensity were recorded over the faults that don't reach the bottom surface.

Based on the results of the researches in the Gulf of Tonkin, it was found that increased hydrogen content in the sediments up to 100 ppm (profile V), hydrogen anomalies in the sub-bottom seawater layer up to 700 ppm (profile IV) and in the surface layer up to 300 ppm (profile I, III and V) are confined to the boundary of the east of the Red River rift and are caused by the migration of gases along tectonic faults from the deep horizons. The gasgeochemical regime with increased hydrogen content reflects fluid permeability of the subsurface. Before the research, the earthquakes (up to 3 points on the Richter scale) were recorded in the Gulf of Tonkin (Nguyen Nhu Trung, 2013). As is known, in most cases hydrogen is present in the gases of deep-seated faults, and is also an indicator of seismically active zones.

Dolginov and colleagues (Dolginov et al., 2010) detected the transformative character of the system of cracks, directed to the northeast, crossing all structures of the area in the Gulf of Tonkin. This is due to their penetration into sedimentary complexes of Triassic, Cretaceous, and Cenozoic rifts from older buried complexes.

Thus, the identified system of fluid-conducting zones is caused by a system of discontinuous structures in the region. Along these structures, conditions for the subvertical transit of gases and fluids towards the surface of the earth crust are most favorable. In this case, gases and fluids move towards the sedimentary cover of the Song Hong Trough, including marine sand-clay deposits. Cracks systems in geodynamically active rift structures of the Triassic, Cretaceous, and Cenozoic serve as favorable conditions for the migration of deep fluid (Perevozchikov, 2012). Thus, the relation between gasgeochemical anomalies and tectonic features reflects the increased gasfluid permeability in the North Vietnam region. According to the results of isotope analyzes, gases of thermogenic and metamorphogenic origins were revealed in hydrogeological wells of Catba Island $(\delta^{13}C-CH_4-25.5 \dots -40.2 \%)$. Methane with a similar isotopic carbon composition, for example, characterizes the Yuzhno-Sakhalinsky mud volcano (Sakhalin Island) (Ershov et al., 2010). The gas fluxes from the lower horizons of the folded basement is also manifested by high-intensity anomalies of methane (up to 1052 µL/L) and carbon dioxide (up to 25 %) in groundwater of the islands of the Gulf of Tonkin. With a low seismic activity of the region, this indicates high hydrocarbon potential of the subsoil (Shakirov et al., 2017).

The isotopic composition of carbon of methane and carbon dioxide suggests the presence of an endogenous source, having impact on carbonate strata on Catba Island. This source was first discovered in 2019, when samples of metamorphosed rocks were found in manifestation zone of endogenous processes over an area not less than 6 km² (Syrbu et al., 2020). In addition, for the first time, we discovered quartz in the river alluvial sediments in this area (Table 2). All the obtained facts suggest the presence of an unknown magma hearth beneath Catba Island (Shakirov et al., 2020).

In the south of the island, a manifestation of metamorphosed sedimentary and volcanic rocks was also discovered, where, according to (Syrbu et al., 2020),

Element	0/	+/- 2σ
Element	%	
Al	1.75	0.19
Si	44.95	0.22
Element	ppm	+/- 2σ
S	650	150
Cl	1.748	0.033
Κ	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

Table 2. Chemical analysis of quartz found in the river alluvial sediments (Catba Island, 2019)

the most intense hydrogen anomalies are observed. The rocks composing the outcrop are represented by silicified vulcanites and shales; the chemical composition, obtained with the use of microanalyzer, is presented in Table 3.

Figure 4 shows two quartz generations: volcanic glass (Qz 1 gen – quartz of the first generation) and pure quartz (Qz 2 gen – quartz of the second generation). Pure quartz is marked with a dotted line; it fills cracks in silicified vulcanite, which may indicate metasomatism after vulcanite formation.

Volcanic rocks are located in the southern part of Catba Island and are represented by silicified acidic vulcanites in contact with sericite-albite-quartz shales (Fig. 5). In the shale, zircons and phosphates were detected. Phosphates are presented by two generations, distinguished according to the presence of potassium. Potassium-free phosphate was formed later than potassium-containing phosphate.

The presence of metamorphic rocks according to sedimentary rocks, as well as volcanic formations, may indicate the magmatic intrusion in the sedimentary strata and its further transformation into sericite-albitequartz shales. Probably, magmatic intrusion took place in several stages that caused silicification of the vulcanites. Endogenous processes formed isotopically heavy carbon methane and carbon dioxide, as well as their anomalies and hydrogen and helium anomalies, which are manifested in water sources and subsurface gases.

Further marine operations in the Vietnamese part of the South China Sea, including the Red River basin, were continued in 2019; they expanded our understanding of the genesis and distribution of gasgeochemical fields of helium, methane and other gas components on the Vietnamese shelf.

No.	MgO	Al_2O_3	SiO_2	K ₂ O	Ti ₂ O	FeO
Shale	0.92	6.97	73.44	2.33	0.73	0.65
Silicified vulcanite	1.92	16.87	53.33	6.97	0.59	1.91

Table 3. Chemical composition of the samples (%), obtained using Jeol JXA-8100 microanalyzer

Helium and hydrogen distribution on the Vietnamese shelf of the South China Sea

During the marine research, the sampling was mainly carried out in three areas: Nam Con Son (Southern area), Phu Khanh (Central area), the Red River basin (Northern area) (Fig. 1). In total, 49 sediment cores were.

Hydrogen was identified in all sediment samples (concentrations from 0.01 ppm (Northern area, Red River basin) to 93 ppm (Central area, Phu Khanh basin)).

The most contrasting anomalies of helium and hydrogen were observed in the Central and Southern area: the southern part of the Phu Khanh basin, stations *LV88-16GC* (2220 m), *LV88-17GC* (2300 m), *LV88-20/1GC* (2400 m) in the deep-water part of the shelf and the northern part of the Nam Con Son basin, station *LV88-15GC* (236 m) (Fig. 6).

The highest hydrogen and helium concentrations were found in the deep-water part of the Phu Khanh basin; southerly, their concentrations in sediment cores gradually decrease. In the central area, signs of "local" fluid discharge zones were found in the northern and southern parts.

The deep-water stations of the central shelf of Vietnam are characterized by increased helium and hydrogen concentrations along the entire length of the core from the surface to the bottom (Fig. 7). This is probably due to the fact that sediments with helium and hydrogen anomalies were uplifted in the shear zone of the Tui Hoa fault zone, located to the southwest of the Phu Khanh Basin. This zone is an area having highamplitude faults. The shear zone is directed from NW to SE in a manner, similar to the Red River Fault System, which extends to the north of the Vietnamese mainland.

The results of a series of isotopic analyses (14 samples) of the Phu Khanh basin showed that the values of the stable carbon isotope lie in the range of 27.7–66.6 ‰ for methane, and 15.4–25.9 ‰ for carbon dioxide (Table 4), which indicates predominantly thermogenic origin of gas (depths more than 2 km) with the presence of gases of microbial origin. The most "heavy" isotopic composition of methane and CO_2 carbon was observed in sediments of the deep-water part of the Phu Khanh basin and the northern part of the Nam Con Son basin.

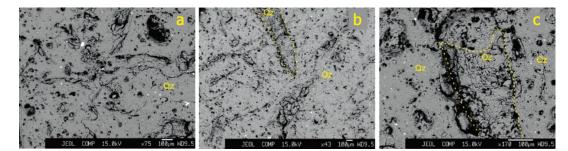


Fig. 4. Volcanite from the outcrop on Catba island (the Gulf of Tonkin), 2019. The photo was taken on an electron probe microanalyzer Jeol JXA-8100 (DVGI FEB RAS): a) almond-stone structure; b) crushing zone with introduced quartz; c) crushing zone with introduced quartz. Qz 1 gen – quartz of the first generation, Qz 2 gen – quartz of the second generation.

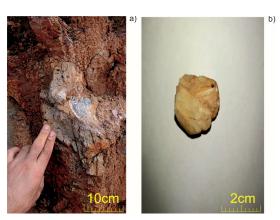


Fig. 5. a) weathered vulcanite; b) poorly rounded quartz found in a brook in 2 km from the supposed source of volcanism

In the same areas, anomalous concentrations of helium and hydrogen were recorded in sediments (Fig. 6), which proves the gas origin (thermocatalytic decomposition of organic matter).

In difficult conditions of gas mixing, the informativeness of the isotopic method can be significantly increased if the isotopic composition of methane is considered together with other gas indicators, which include methane and its homologues, as well as helium and hydrogen concentrations. In the Phu Khanh basin, the isotopic composition of δ^{13} C–CH₄ (66 ‰) at station *LV88-27GC* and δ^{13} C-CH₄ (66.6 ‰) at station *LV88-43GC* (Table 4) indicates the predominance of microbial gas in the methane flux. This is primarily due to the fact that in the presence of an intense upward natural gas flux favorable conditions for microbial processes are created and ¹³C/¹²C isotopic ratio of thermogenic methane can be masked by the presence of a significant amount of microbial gas from the upper sedimentary horizons. Thus, at the considered stations in the Phu Khanh basin, high methane concentrations (up to 666.4 nM/dm³) and the presence of methane homologues up to and including propane were identified in the sediments. In the sediments of the nearest stations, methane content is even higher – up to 3422 nM/dm³.

In such cases, accompanying helium and hydrogen measurements are necessary to identify the nature of the gas flux.

The lowest helium and hydrogen concentrations were observed in the north (the area of the Song Hong sedimentary basin). The profile is represented by "shallow-water" stations (depth up to 60 m).

Low hydrogen concentrations in sediments of the Red River basin are probably explained by the location of sampling stations in the sedimentary basin far from

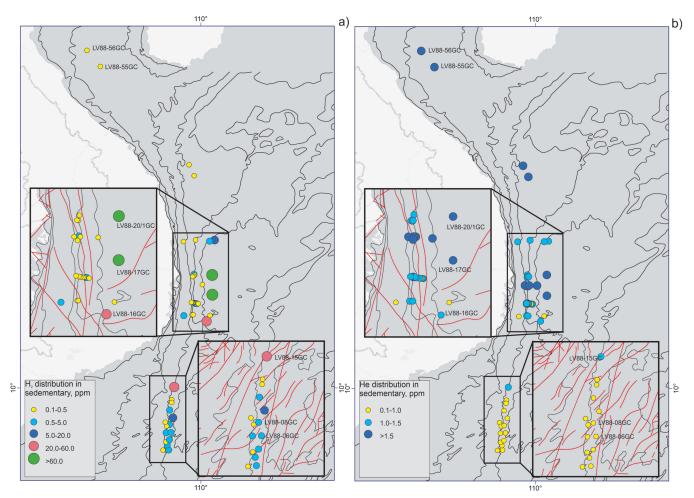


Fig. 6. Hydrogen (a) and helium (b) concentrations in sediment cores on the Vietnamese shelf, R/V "Akademik M.A. Lavrentyev", cruise 88, 2019.

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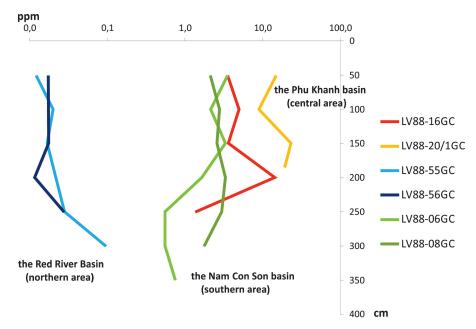


Fig. 7. Distribution of hydrogen concentrations in sediment cores (R/V "Akademik M.A. Lavrentyev", cruise 88, 2019)

the faults. So, in the most permeable zones – channels of rapid vertical migration of endogenous gases – free hydrogen and helium migrate in the form of gas fluxes. Such highly permeable zones are rifts – oceanic and continental, regional deep faults, and zones of modern volcanism.

Among the deep-seated faults, the most permeable and, therefore, the most promising for hydrogen and helium will be those, activated in the neotectonic stage and, especially, the newest ones, framing the zones of active modern tectonic deflections (troughs or grabens) with a reduced crustal thickness (Kudrin et al., 2006).

The Red River Rift is potentially helium-hydrogenbearing not throughout its entire length, but, apparently, only in segments with the maximum heat flux, since, according to the Le Chatelier principle, in the Earth inhomogeneous thermal field, gases with high specific heat capacity are concentrated in zones of abnormally

Station	Sample	CO ₂ , %	δ^{13} C-CO ₂ , ‰	CH4, %	δ ¹³ C-CH ₄ , ‰
Northern area (Red River Basin)					
LV88-55GC	84	1.49	-23.7	0.0053	-46.0
LV88-56 GC	87	1.88	-23.8	0.0040	-40.4
LV88-55GC	105	0.02	-18.3	0.0013	-64.0
LV88-55GC	104	0.15	-17.4	0.0010	-60.2
		Central area (Phu Khanh Basin))	
LV88-18GC	30	2.44	-24.4	0.0039	-27.7
LV88-22GC	36	1.78	-15.9	0.0027	-40.3
LV88-22GC	37	2.33	-25.9	0.0095	-43.7
LV88-22GC	47	0.14	-20.2	0.0067	-51.1
LV88-23GC	48	0.07	-17.9	0.0039	-59.6
LV88-27GC	42	2.59	-23.4	0.0076	-40.7
LV88-27GC	51	0.23	-15.4	0.0097	-66.0
LV88-31GC	52	1.03	-22.9	0.0015	-29.1
LV88-31GC	59	0.32	-22.4	0.0021	-58.7
LV88-37GC	67	0.01	-20.4	0.0021	-57.0
LV88-42GC	67	0.42	-23.9	0.0005	-46.5
LV88-43GC	69	0.06	-24.5	0.0006	-48.4
LV88-42GC	80	0.03	-20.6	0.0286	-49.8
LV88-43GC	83	0.02	-16.8	0.0021	-66.6
Southern area (Nam Con Son Basin)					
LV88-02/1GC	6	0.03	-18.9	0.0042	-64.6
LV88-12GC	29	0.15	-19.7	0.0115	-25.7
LV88-5GC	3	0.11	-17.6	0.0151	-28.0
LV88-12GC	20	1.10	-24.8	0.0032	-29.4

Table 4. Isotopic composition of methane and CO_2 carbon in sediments of the Vietnamese part of the South China Sea (the analysis was executed at Nagoya University under the guidance of Prof. Urumu Tsunogai)

high temperatures; these gases are, first of all, hydrogen and helium (as well as nitrogen, methane, carbon monoxide); and at the periphery of these anomalies are gases with low specific heat capacity (hydrogen sulfide, water vapor, carbon dioxide, etc.). According to (Pollak et al., 1991), heat flow value of $80-100 \text{ mW/m}^2$ was observed in the area of the Red River rift. Numerous heat flow measurements in the region show that the highest values (over 100 mW/m²) correspond to deep-water depressions; this indicates active processes occurring in the mantle, which are expressed at the surface in the manifestation of anomalous gasgeochemical fields of helium, hydrogen and methane.

This conclusion was also confirmed by the patterns of the CO₂ distribution in the area of the Red River rift system (northern area). At stations LV88-56GC and LV88-55GC, the maximum concentration of carbon dioxide was recorded at 137606 nM/dm³ (LV88-55GC, horizon 275 cm) and the concentration increases with depth and beyond the horizon of 200 cm. These sampling points lie at a distance from the deep fault, but are located in the zone of influence of the Red River rift system.

Carbon dioxide at this polygon has a negative correlation with methane and hydrocarbon gases. At 200 cm horizon (stations LV88-56GC and LV88-55GC), there is a sharp decrease in concentrations of methane, hydrocarbons and an increase in carbon dioxide concentration. All this gives reason to believe that within the deep-seated fault zone, helium and hydrogen anomalies are of a local nature and appear in the segments with the maximum heat flow, close to the zone of deep-seated fault.

Differences in the degassing of helium, hydrogen and hydrocarbon gases are reflected in the geological features of the Song Hong Basin: the northwestern part of the basin includes the Hanoi Trough and numerous faults of Bacbo Bay, which form complex folded structures, accompanied by the Miocene tectonic inversion; the central part of the Song Hong Basin is a structurally complex region with a tectonically stable basement, where the sedimentary column exceeds 14 km. In the southern part, there is a narrowing of the sedimentary basin when it reaches the continental slope, which is controlled by fault zones (Fig. 8).

In 2020, specialists from a Vietnamese oil company discovered a large gas and condensate field in this area - Ken Bau. In 88th cruise of the R/V "Akademik M.A. Lavrentyev" in the vicinity of the discovered field (Fig. 8) elevated helium concentrations, manifestations of authigenic sulfides, and geomicrobiological signs of gas migration were detected (Eskova et al., 2020).

Compare to the Sea of Japan and the Sea of Okhotsk, it can be noted that the active degassing zones of the bottom of Vietnamese shelf and slope are local, although the intensity of gasgeochemical anomalies in them is

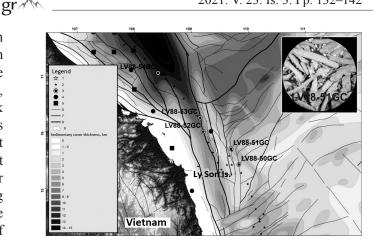


Fig. 8. Map of the stations of the R/V "Akademik M.A. Lavrentyev" (cruise 88, 2019) on the tectonic scheme of the southern part of the Red River sedimentary basin. 1 - 1running water sampling; 2 – surface water sampling; 3 – sediment sampling stations; 4-5 stations for sub-bottom water sampling (Obzhirov, 1993); 6 – faults of the third order; 7 – faults of the second order; 8 – faults of the first order, 9 – contours of the Ken Bau field. The inset shows the photography of sulfides (station LV88-51GC) under a binocular microscope (LOMO HS 1349 binocular, magnification x3).

comparable to similar zones in the Far Eastern seas. Hydrogen anomalies on the oil- and gas-bearing shelf and gas hydrate-bearing slope of Sakhalin Island according to the data (Shakirov et al., 2016) are comparable to the established anomalies on the Vietnamese shelf of the South China Sea.

The concentration mechanism of free (or dissolved) hydrogen and helium in the earth crust is apparently close to the mechanism of concentration of methane and hydrocarbon gases – in structural, tectonic, lithological, and other traps. Hydrogen and helium, coming from the depths, are screened in traps by low-permeability covers, which differ from covers that capture hydrocarbons generally by greater depth and permeability. The permeability of such covers is determined by the diffusing abilities of hydrogen and helium (Kudrin et al., 2006).

Since the origin of most of hydrogen and helium beneath the Earth is unambiguously endogenous, not associated with biogenesis, promising hydrogen- and helium-bearing structures are spatially localized in smaller zones (along deep faults serving as channels for hydrogen migration from the mantle), compare to hydrocarbons.

Conclusion

For the first time in the last 30 years, POI FEB RAS and IMGG VAST carried out a large-scale complex geological-geophysical, geochemical and oceanographic research in the Vietnamese water area of the South China Sea, as a result of which unique data on the distribution of helium and hydrogen, methane, hydrocarbon gases gr

in the region of continental shelf and slope of Vietnam were obtained. The degassing features of the lithosphere were considered in relation to tectonic faults, outflows of hydrogen and its control as one of the indicators of the gasgeochemical regime.

In the result of the research, the spatial distribution of helium and hydrogen in sediments in three sedimentary basins (the Red River basin, Phu Khanh basin and the Nam Con Son basin) was studied.

As a result of the study, the patterns of the distribution of the helium and hydrogen gasgeochemical fields in the Vietnamese part of the South China Sea were revealed, the gasgeochemical background was clarified, and the possible genesis of the gas fluxes was specified.

Based on the results of gasgeochemical and isotopic studies, it can be concluded that within the Red River deep fault zone (northern area), helium and hydrogen anomalies are local and appear in the segments with the maximum heat flow, close to the fault zone. This fact is confirmed by the results of oil and gas prospecting works.

During intensification of seismotectonic activity, tectonic shift along the main fault zones occurs; this shift contributes to increase in permeability and the transport of thermogenic gases towards the bottom surface and into the water column.

Manifestations of volcanomagmatic processes within the Catba archipelago are most likely the cause of isotopically heavy methane and CO_2 carbon in the water sources of the islands of the Gulf of Tonkin.

High concentrations of hydrogen and helium, hydrocarbon gases, and methane in the Gulf of Tonkin and its islands tend to decrease from the Red River rift zone towards the Song Hong sedimentary basin, where carbon dioxide reaches its maximum concentration.

The presence of metamorphosed sedimentary and volcanic rocks on Catba Island (Gulf of Tonkin) significantly contributes to the history of the geological development of the region, to the search and forecast of hydrocarbon and ore deposits.

The discovered features of the distribution of gasgeochemical fields must be investigated and detailed in subsequent expeditions.

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References

Akulichev V.A., Obzhirov A.I., Shakirov R.B., Mal'tseva E.V., Syrbu N.S., Polonik N.S., Van Phach P., Trung N.N., Hung D.Q., Anh L.D. (2015). Anomalies of natural gases in the Gulf of Tonkin (South China Sea). *Doklady Earth Sciences*, 461(1), pp. 203–207. https://doi.org/10.1134/S1028334X15030010

Areshev E.G., Gavrilov V.P., Dong Ch.L., Zao N., Popov O.K., Pospelov V.V., Shan N.T., Shnip O.A. (1997). Geology and oil and gas content of the Sunda shelf basement. Moscow, 285 p. (In Russ.)

Dolginov E.A., Bashkin Yu.V., Belousov T.P., Kao D.T., Le V.Z. (2010). Rift and epirift structures of northwestern Vietnam and their probable analogues. *Izvestiya vuzov. Geologiya i razvedka = Proceedings of higher educational establishments. Geology and Exploration*, 5, pp. 3–8. (In Russ.)

Duong Quoc Hung, Renat Shakirov, Iosif Iugai, Nguyen Van Diep, Le Duc Anh, Mai Duc Dong, Bui Van Nam, Yury Telegin (2019). A study on the relationship between gas-geochemical field and tectonic fault activities in the rivermouth of Gulf of Tonkin. *Vietnam Journal* of Marine Science and Technology, 19(2), pp. 191–198. https://doi. org/10.15625/1859-3097/19/2/14036

Ershov V.V., Shakirov R.B., Mel'nikov O.A., Kopanina A.V. (2010). Variations in the parameters of mud volcanic activity and their relationship with the seismicity of the south of Sakhalin Island. *Regional 'naya geologiya i metallogeniya* = *Regional Geology and Metallogeny*, 42, pp. 49–57. (In Russ.)

Es'kova A.I., Ponomareva A.L., Legkodimov A.A., Kalgin V.Yu., Shakirov R.B., Obzhirov A.I. (2020). The Characteristics and Distribution of Indicator Microorganisms in the Marine Sediments from the South-China Sea. *Izvestiya Irkutskogo Gosudarstvennogo Universiteta. Seriya: Nauki o zemle = The Bulletin of Irkutsk State University. Series Earth Sciences*, 33, pp. 33–43. (In Russ.) https://doi.org/10.26516/2073-3402.2020.33.33

Geological map of Vietnam. (1986). Scale 1: 1 500 000. General Dpt. of Geology, Hanoi.

Kravtsov A.I., Voitov G.I., Fridman A.I. et al. (1967). Hydrogen content in free jets in the Khibiny. *Doklady Akademii Nauk SSSR*, 5, pp. 1190–1192. (In Russ.)

Kudrin I.V., Orlyankin V.N., Kudrin K.I. (2006). Method of searching of gaseous hydrogen and helium clusters in earth interior. Patent RF RU2316028. (In Russ.)

Kulinich R.G. Obzhirov A.I. (1985). On the structure and current activity of the junction zone of the Sunda shelf and the South China Sea

basin. *Tikhookeanskaya geologiya* = *Russian Journal of Pacific Geology*, 3, pp. 102–106. (In Russ.)

Le Duc Anh, Nguyen Hoang, Phung Van Phach, Malinovskii A. I., Kasatkin S. A., Golozubov V. V. (2018). Geochemistry and petrogenesis of volcanic rocks and their mantle source in the East Vietnam Sea and adjacent regions in the Cenozoic. *Vietnam Journal of Marine Science and Technology*, 17(4), pp. 406–428. https://doi.org/10.15625/1859-3097/17/4/9258

Nguyen Nhu Trung. (2013). Basement structure of the Bac Bo Basin based on the 3D interpretation of satellite gravity and magnetic data. *Proceedings of the 11th SEGJ International Symposium*. https://doi.org/10.1190/segj112013-034

Regulatory and methodological support for the protection of atmospheric air (1995). Perm: Intereko, 249 p. (In Russ.)

Obzhirov A.I. (1993). Gas-geochemical fields of the bottom layer of seas and oceans. Moscow: Nauka, 139 p. (In Russ.)

Perevozchikov G.V. (2012). PHydrogen field at the Gazli field according to geochemical studies in the oil and gas region of Central Asia. *Neftegazovaya geologiya. Teoriya i praktika = Oil and gas geology. Theory and practice*, 7(1), pp. 1–13. (In Russ.)

Pollak H.N., Hurter S.J., Johnson J.R. (1991). New global heat flow compilation. University of Michigan, USA.

Porotov G.S. (1977). Mathematical methods in searching and prospecting for minerals. Leningrad: Leningrad Mining Institute, 106 p. (In Russ.)

Shakirov R.B. (2016). Gas-geochemical fields of the marginal seas of the Far Eastern region: distribution, genesis, connection with geological structures, gas hydrates and seismotectonics. Abstract Sci. Diss. Vladivostok: Il'ichev POI FES RAS, 49 p. (In Russ.)

Shakirov R.B. (2018). Gas-geochemical fields of the seas of East Asia. Moscow: GEOS, 341 p. (In Russ.)

Shakirov R.B., Hung D.Q., Anh L.D., Syrbu N.S., Obzhirov A.I., Borzova O.V., Okulov A.K., Nam B.V., Diep N.V., Dong M.D., Legkodimov A.A., Shakirova M.V., Ponomareva A.L., Bakunina M.S. (2019). Features of the gasgeochemical abnormal fields distribution in the Red River rift (Tonkin gulf, South-China sea). *Doklady Earth Sciences*, 484, Part 2, pp. 181–184. https://doi.org/10.1134/S1028334X19020065

Shakirov R.B., Li N.S., Obzhirov A.I., Valitov M.G., S''edin V.T., Telegin Yu.A., Proshkina Z.N., Okulov A.K., Storozhenko A.V., Ivanov M.V., Shvalov D.A., Legkodimov A.A., Es'kova A.I., Lipinskaya N.A., Bovsun M.A., Makseev D.S., Kalgin V.Yu., Yakimov T.S., Nguen Chun Tkhan', Le Dyk An'. (2020). Integrated Russian-Vietnamese geological-geophysical and oceanographic expedition in the South China Sea (R/V "Akademik M.A. Lavrentyev", cruise 88, 2019). *Vestnik of Far Eastern Branch of Russian Academy of Sciences*, 3, pp. 138–152. (In Russ.)

Shakirov R.B., Obzhirov A.I., Syrbu N.S., Nguen Nu Chung, Zyong Kuok Khyn, Mal'tseva E.V., Sorochinskaya A.V., Yugai I.G., Le Duc Anh, Fueg Van Fat, Polonik N.S., Bui Van Nam, Nguen Van Diep. (2015). Features of the distribution of natural gases in bottom sediments and water in the northwestern part of the Gulf of Tonkin (South China Sea, Vietnam). *Geografiya i prirodnye resursy*, 4, pp. 178–188. (In Russ.)

Shakirov R.B., Sorochinskaya A.V., Syrbu N.S., Nguen Nu Chung, Fung Van Fat, Le Duc Anh, Chon Tkhan' Fi. (2017). Gas-geochemical features of sediments in the Tonkin Gulf (South China Sea). *Vestnik of Far Eastern Branch of Russian Academy of Sciences*, 4, pp. 33–42. (In Russ.)

Shakirov R.B., Syrbu N.S., Obzhirov A.I. (2016). Distribution of helium and hydrogen in sediments and water on the Sakhalin slope. *Lithology and Mineral Resources*, 51(1), pp. 61–73. (In Russ.) https://doi.org/10.1134/S0024490216010065

Shnip O.A. (2012). Composition and oil and gas content of the basement of the shelf of Northern and Central Vietnam. *Trudy RGU Nefti i gaza imeni I.M. Gubkina*, 31, pp. 53–55. (In Russ.)

Smirnov B.V. (1983). Probabilistic forecasting methods in engineering geology. Moscow: Nedra, 134 p. (In Russ.)

Syrbu N.S., Shakirov R.B., Le Duc Anh, Kholmogorov A.O., Iakimov T.S, Kalgin V.Yu. (2020). Formation of abnormal gasgeochemical fields of methane, helium and hydrogen in Northern Vietnam, its coastal and adjacent

water areas. Lithology and Mineral Resources, 55(6), pp. 512–527. https://doi.org/10.1134/S0024490220060097

Tsunogai U., Kosaka A., Nakayama N., Komatsu D., Konno U., Kameyama S., Nakagawa F., Sumino H., Nagao K., Fujikura K., Machiyama H. (2010). Origin and fate of deep sea seeping methane bubbles at Kuroshima Knoll, Ryukyu forearc region, *Japan. Geochemical Journal*, 44, pp. 461–476. https://doi.org/10.2343/geochemj.1.0096

Tuyen N.H., Phach Ph.V., Shakirov R.B., Trong C.D., Hung Ph.N., Anh L.D. (2018). Geoblocks Recognition and Delineation of the Earthquake Prone Areas in the Tuan Giao Area (Northwest Vietnam). *Geotectonics*, 52(3), pp. 359–381. https://doi.org/10.1134/S001685211803007X

Voitov G.I., Dobrovol'skii I.P. (1994). Chemical and isotopic carbon instabilities of natural gas flows in seismically active regions. *Fizika Zemli* = *Izvestiya, Physics of the Solid Earth*, 3, pp. 20–31. (In Russ.)

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