

Renat Shakirov · Anatoly Obzhairov · Erwin Suess
Anatoly Salyuk · Nicole Biebow

Mud volcanoes and gas vents in the Okhotsk Sea area

Received: 22 January 2003 / Accepted: 20 December 2003 / Published online: 6 May 2004
© Springer-Verlag 2004

Abstract Gas emissions from mud volcanoes on Sakhalin Island and water-column gas flares arising from cold seeps in the Okhotsk Sea appear to be related. They are likely activated by tectonic movements along the transform plate boundary separating the Okhotsk Sea Plate from the Eurasian and Amur plates. Gas vents (flares) and methane anomalies occur in the waters offshore Sakhalin Island, along with NE-SW-trending mounds and fluid escape structures on the seafloor. The intersection of the NE-striking transverse faults on land with the Central Sakhalin and Hokkaido-Sakhalin shear zones apparently determines the sites of mud volcanoes, a pattern that continues offshore where the intersection with the East Sakhalin and West Derugin shear zones determines the sites of the submarine gas vents.

Introduction

Mud volcanoes and submarine methane vents are among the most interesting, yet largely neglected phenomena related to natural seepage from the earth's surface. Mud volcanoes occur globally in terrestrial and submarine geologic settings (Kholodov 2001). Most of the terrestrial mud volcanoes are located within Alpine-Himalayan, Central Asian, Caribbean and Pacific mobile orogenic belts (Aliyev et al. 2002; Etiope 2002). In submarine settings they occur both along active and passive margins.

One of the main motivating factors in studying mud volcano processes is their hydrocarbon potential. The majority of published work shows that mud volcanoes occur only in the areas of deep burial of thick sedimentary sequences, either in marginal basins or fore-arcs of subduction zones (Ginsburg et al. 1999; Milkov 2000), especially due to compression regimes (Kopf 2002). This observation explains why the main source of large volumes of gas needed for the extrusion is believed to be generated at depth. Gas is formed usually at several kilometers depth (Kopf 2002), under pressure and temperature conditions high enough to force the gas-water-sediment mixture toward the surface. The basic extruding mass contains plastic clays, which are prevalent in sediments of the continental mobile- and marine-subduction zones.

Water plays an important role in the activity of the mud volcanoes. It permeates the interstices and pore space, and causes rocks to swell, turning them into a viscous mass. Mixed with gas, water promotes the ascent and extrusion of material toward the surface. Structural disruptions are one of the main factors in the initiation of mud volcanoes (Kholodov 2001). Mud volcanoes are confined to intersections of longitudinal and transverse faults. Collapse of sedimentary strata in anticlinal structures may also cause the generation of mud volcanoes.

The presence of thick sedimentary sequences with oil and gas deposits on Sakhalin Island and offshore in the Sea of Okhotsk, and the ongoing tectonic activity along eastern Sakhalin Island develop a complicated system of folded and disrupted strata both onshore and offshore. This tectonic setting makes this region a prime location for studying mud volcano phenomena and submarine gas emissions. Specifically, eastern Sakhalin Island represents a N-S-trending transform plate boundary (Baranov et al. 1999; Lüdmann et al. 2002). It is the dominant tectonic feature separating the Okhotsk Sea Plate from the adjacent Eurasian and Amur plates (Baranov et al. 2002; Lüdmann et al., 2002). The transform plate boundary is represented mainly by the

R. Shakirov · A. Obzhairov · A. Salyuk
V.I. Il'ichev Pacific Oceanological Institute FEB RAS,
Baltiyskaya 43, 690041 Vladivostok, Russia

E. Suess
Leibniz Institute of Marine Sciences (IFM-GEOMAR),
24148 Kiel, Germany

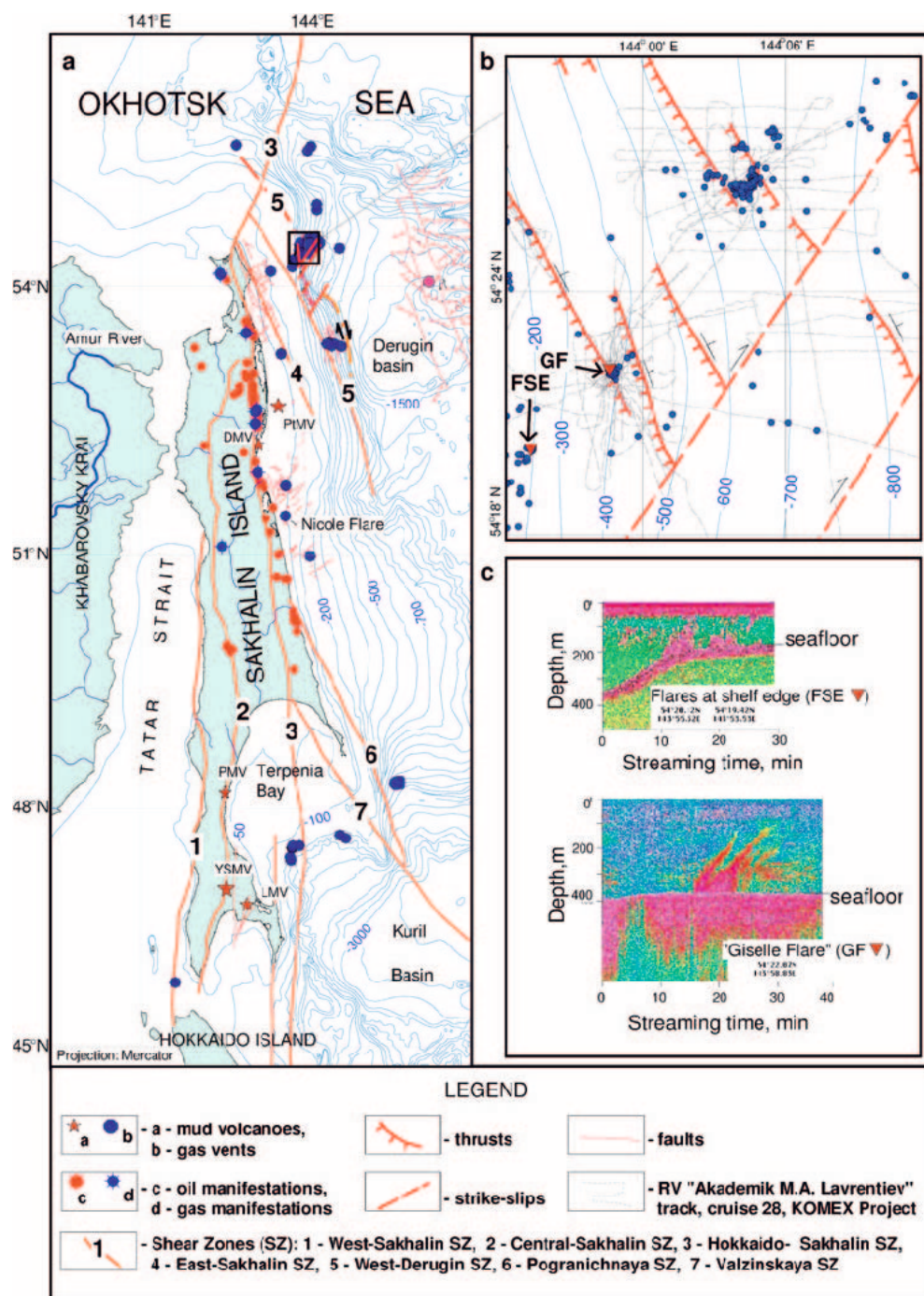
N. Biebow (✉)
Tethys Geoconsulting GmbH, 24148 Kiel, Germany
E-mail: nbiebow@ifm-geomar.de

Central Sakhalin and Hokkaido-Sakhalin shear zones (CSSZ and HSSZ) onshore, and the East Sakhalin and West Derugin shear zones (ESSZ and EWDZ) offshore (Fig. 1). The main tectonic features and faults shown on this map were investigated by V.V. Kharakhinov, N.A. Bogdanov, B.V. Baranov and others (Kharakhinov 1998; Baranov et al. 1999; Bogdanov and Khain 2000; Baranov et al. 2000, 2002; Kharakhinov 2002), the bathymetry by A.S. Svarichevsky (2001).

Numerous transverse faults cut across this plate boundary, offsetting several otherwise linear segments.

The offset is right-lateral, striking from 10° in the south to 40° in the north. Mud volcanoes occur in the northeastern part of Sakhalin Island, near Goryachie Klyuchi village, and also in the southern part (Fig. 1a). One is located 18 km NW of the Yuzhno-Sakhalinsk city, another 60 km from the city of Makarov between the villages Pugachiovo and Vostochni, and a third one is situated not far from the southwest coast of Terpeniya Bay. At these sites, gas sampling and monitoring were conducted during the period 12–24 July 2001.

Fig. 1 a Distribution of mud volcanoes and oil-gas manifestations (Aleksichik 1959) on Sakhalin Island and offshore vent sites in the Sea of Okhotsk in relation to the major submeridional on- and offshore tectonic features. b Detailed distribution map of flares off northern Sakhalin (bathymetry and tectonics; Baranov et al. 1999). c Acoustic images of the methane flares on the north-east Sakhalin upper slope



Gas flares have been known to dominate the outer shelf and upper slope off eastern Sakhalin Island (Obzhirov 1993; Ginsburg and Soloviev 1994; Obzhirov et al. 2002). Previous investigations of cold vents and seeps have suggested that the pattern of seep distribution is controlled by the offshore tectonic regime (Fig. 1a, b). In this report we document the distribution of gas flares offshore from northern Sakhalin Island, show that the flares are caused by the emission of methane bubbles, and suggest that onshore mud volcanoes and offshore gas emissions are both related to the pattern of transverse and longitudinal faults intersecting the Okhotsk Sea Plate and Eurasian Plate boundary.

Geologic setting

The Yuzhno-Sakhalinsky Mud Volcano (YSMV, Fig. 2a–e) is situated in the area of one of the thickest sections (up to 3,000 m) of high plasticity, argillaceous Cretaceous sediments, the Bikovskaya Suite (Mel'nikov and Il'yov 1989). It is confined to the largest and most distinct overthrust, the Central Sakhalin Fault (CSF), where upper Cretaceous rocks are thrust over Paleogene rocks. The CSF in the area of the YSMV dips to the west at an angle of 70°, and the vertical displacement of the CSF is 1.5–2 km (Zanyukov et al. 1982). Not only is the mud volcano confined to the fault plane, but mud extrusions and gryphons are distributed along transverse faults cutting the CSF. This distribution suggests a generic relationship between the mud volcano and the water–mud sources from within the fault zone.

The Pugachiovsky Mud Volcano (PMV) in many respects is like the YSMV. It contains a central mud pool located inside a big, circular elevated feature (Fig. 2f, h), with a number of mud vents (gryphons) less than 0.5 m in diameter (Fig. 2f, g, i). The PMV is situated in the same argillaceous formation as the YSMV and is also confined to the CSF (Mel'nikov and Il'yov 1989).

The Darginsky Mud Volcano (DMV) is of a different type. It consists of a group of small (up to 10–20 cm) gryphons on the coast of Darginsky Bay near a spa of the same name that is known for its mud baths. Here, on a small hill, there also is an argillaceous formation outcropping, perhaps of Neogene age, exhibiting a distinct fault pattern (Mel'nikov and Il'yov 1989).

The Lesnovsky Mud Volcano (LMV) is located east of the thrust fault where two faults merge, delineating a narrow zone (Fig. 1a) in which the Bikovskaya Suite outcrops. The outcrop represents the roof of a narrow anticline, possibly a diapiric structure. Not long before the LMV appeared on 10 June 1986, there had been an earthquake of magnitude 2.5 registered in this region, which possibly stimulated its formation (Mel'nikov and Il'yov 1989). When we observed the LMV, there was only a waterlogged plain in its place, and no elevated feature was recognizable.

Methane is emitted in the coastal zone, for example, on the beach near Darginsky Bay at the Darginsky Mud Volcano, in the tidal zone, and on the shallow shelf (Piltunsky Mud Volcano). Two offshore stations, Ga28-02 and Ga28-12, in 25 and 45 m of water depth, respectively, were investigated. The tectonic regime at this transition zone is difficult to assess because of the lack of suitable outcrops, and continuous wave erosion and runoff rapidly obliterate any evidence of mud, fluid, and gas extrusion. Farther offshore, the distribution of cold seeps occurs in clusters located at 53°25'N, and between 54°21.8'N and 54°26.8'N (Fig. 1b, c). The activity at the latter site is concentrated in two separate small regions (Fig. 1b). The tectonic setting around these clusters is characterized by a system of thrusts and reverse faults (Baranov et al. 1999) oriented in a NNW–SSE direction and, as shown in Fig. 1b, the two areas are located within narrow (1.3–1.5 km) zones between the traces of the thrusts. The faults exist over the entire shelf and downslope to 1,000 m water depth. They are the manifestations of the East Sakhalin and West Derugin shear zones. These faults are active, because they can be traced through the sedimentary column to the seafloor (Biebow and Hütten 1999).

Initially only a few vent sites were known in the area. Now, more than 100 active sites have been mapped at water depths of 400–800 m. At least one mound (mud volcano?) has also been found, coinciding with the northern area (54°26.5'N) at 620 m, which is also the area of intense flare activity. “Giselle Flare” is one of the prominent and stationary gas flares that has emitted methane over many years. Also present in the southern area is a mound (mud volcano?; 54°22'N, 144°20'E), but this mound has not yet been sampled.

Materials and methods

Geochemical data for the YSMV include 11 gas samples from different test stations and 44 monitoring gas samples (one sample for 6 h) from gryphon 9 (Figs. 2a, 3), six gas samples from the PMV, and five gas samples from the DMV.

Gas was sampled without contact with the atmosphere in glass test tubes sealed with rubber stoppers. For gas flow-rate measurements, we used a soft inflatable plastic bag (4-l volume). Gas analyses were done on a two-channel (SRI 8610C) gas chromatograph with flame-ionization detector (FID) with a sensitivity 10⁻⁶%. For calibration we used certified standard gas mixtures with methane concentrations of 100 ppm-v, 1,000 ppm-v and 1% by volume. The methane concentrations in the water column were determined following four basic steps: (1) seawater sampling by Niskin bottles; (2) sub-sampling of water from Niskin bottles to pre-evacuated plastic bottles (0.5 l); (3) gas extraction by a vacuum method; and (4) gas detection and quantification by gas chromatographic analyses using FID detection (Obzhirov 1993; Obzhirov et al. 2002).

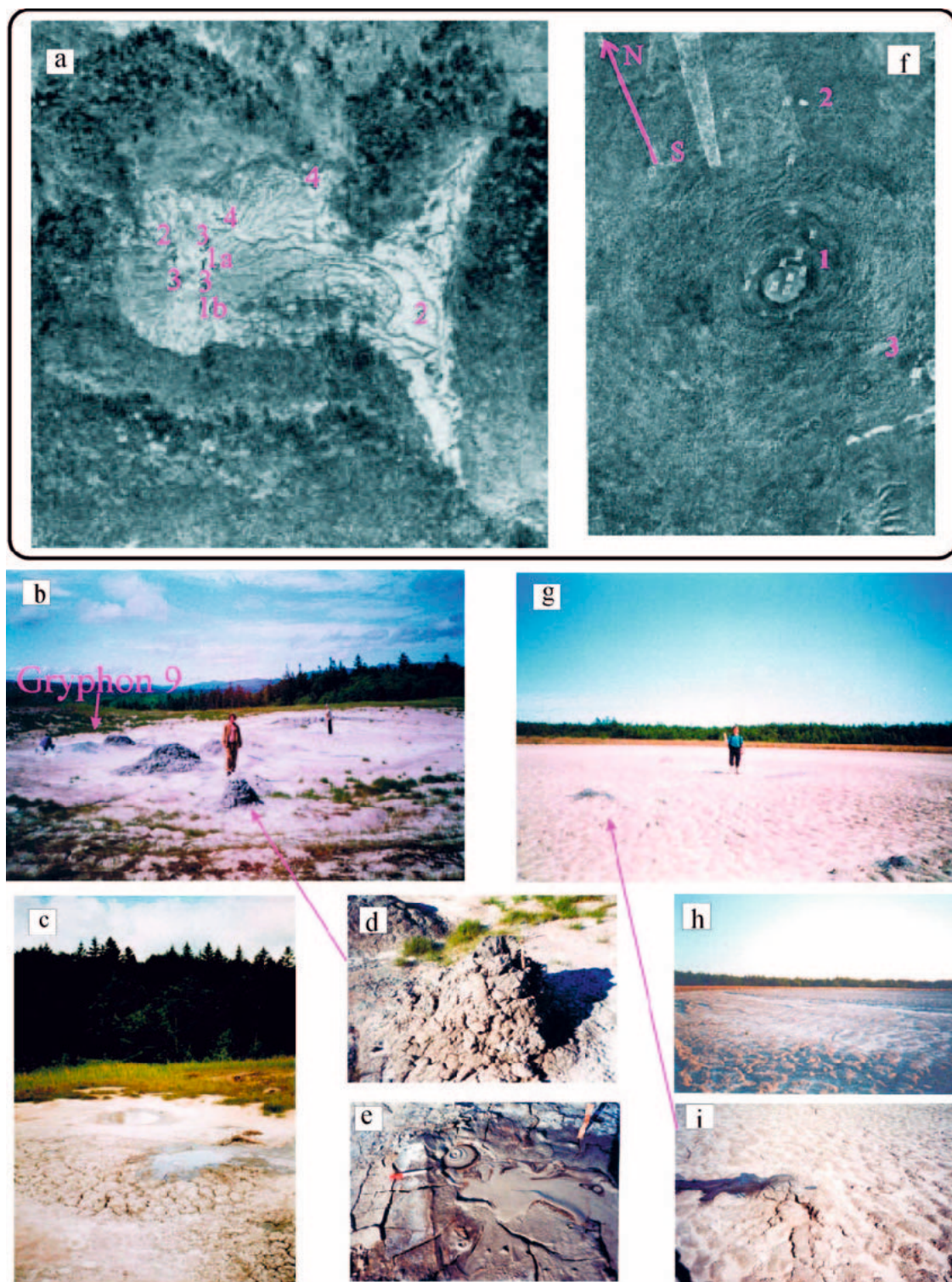


Fig. 2a-i Sakhalin mud volcano images (a-e YSMV, f-i PMV). **a** Aerial photograph of the YSMV (*1a, 1b* craters, *2* the biggest mud current of the 1959 explosion, *3* active gryphons, *4* small oval basins (Gurieva and Sharkov 1987). **b** Central part of the YSMV. **c** Mud water bath. **d** "Dry" gryphon", height 0.7 m. **e** Small mud bath. **f** Aerial photograph of the Pugachiovo group of mud volcanoes (*1* main PMV, *2* small northern PMV, *3* small southern PMV (Gurieva and Sharkov 1987). **g, h** PMV flat ring plane. **i** Small gryphon

This is the first time, to the best of our knowledge, that offshore and onshore gas concentrations are being compared, although different sampling protocol and methods of analyses were used. Hence, in interpreting the observed gas concentrations, the different methodologies need to be taken into account.

Results and discussion

Sakhalin Island

Yuzhno-Sakhalinsky Mud Volcano (YSMV)

During the observation period the YSMV was most active in regard to the discharge of gas, mud, water, and other products compared to the other Sakhalin mud volcanoes. Geochemical testing took place on actively degassing gryphons (3, 10, 13, and 19), and on mud and water pools (Table 1). It also included monitoring of gas flow rates at gryphon 9 (Fig. 2b).

Spontaneous degassing occurs in two modes: “dry” and “wet”. “Dry” degassing describes gas emissions without concomitant mud and water discharge. This mode was observed at several large gryphons at the YSMV, and took the form of periodic gas eruptions accompanied by loud hissing sounds (Fig. 2b, d). “Wet” degassing was in the form of bubbles that intermittently percolated from mud and water pools of several gryphons (Fig. 2c, e).

Gas chromatographic analysis showed that spontaneous dry gas emissions mainly consisted of CO₂, ranging from 66.4 (gryphon 9) to 94.6 vol% (gryphon 13). Methane ranged in concentration from 1.71 (gryphon 13) to 31.7 vol% (gryphon 3), oxygen from 0.2 (gryphon 10) to 7.4 vol% (water pool vent 22), and nitrogen from 28 (gryphon 13) to 27.7 vol% (water pool vent 22). Non-methane hydrocarbon gases up to pentane in composition were present in the spontaneous dry gas emissions (Table 1). The amount of non-methane hydrocarbons did not exceed 0.1 vol%.

According to our observations, the gas composition in comparison to published data, which had been obtained after the eruptions of 1959 and 1979 (Shilov et al. 1961; Zanyukov et al. 1982; Mel'nikov and Il'yov 1989), showed an increase in percentage of carbon dioxide relative to methane. Accordingly, after the eruption of 1959, the amount of CO₂ ranged from 28 to 46.9 vol%, and in 1979 it was 25.9 vol%. However, our data show that the amount of carbon dioxide was not lower than 70 vol% and increased to a maximum of 94.6 vol%. Methane decreased accordingly. In 1959 its concentration was 28–47 vol%, and in 1979 it measured 54.4 vol%. Currently, according to our results, methane concentrations do not exceed 32 vol%. Apparently, after a mud volcano eruption, there is a long-term decrease of methane in the spontaneous gas emissions, and an increase of CO₂.

The last eruption of the YSMV prior to our expedition was in 1996. Detailed shallow seismic investigations (Argentov et al. 2001) showed the presence of a mud volcano chamber at intermediate depth, situated close to the outcrop of the mud field (Fig. 3). This chamber is characterized by low seismic velocity, which indicates that the extruding material is of low density (Argentov et al. 2001). During the dormant periods of the YSMV,

the gryphons are mainly supplied from this chamber. The contribution of gas from the main strata must be from depths of up to 1–1.2 km (Zanyukov et al. 1982). The proximity of the chamber to the surface, the availability of cracks, and the elevated temperature of the mud–water material create favorable conditions for biogeochemical oxidation of methane. This methane oxidation may be the reason for the change in methane emission relative to carbon dioxide over the dormant five-year period from 1996 to 2001.

Monitoring of gryphon 9 of the YSMV

The emission of gas from wet gryphon 9 showed a smooth increase during the period of observation. At the same time, an increase of temperature was observed over the mud field surface (Astakhov et al. 2002; Fig. 4). The increase in flow rate and the increase in temperature may have resulted from the growth of stress just before the earthquake, which happened in early August 2001. We monitored gryphon 9 on 17 August 2001, soon after a magnitude 3 earthquake. Even though the discharge rate increased sharply, the gas composition did not change. This observation confirms that the source of gas during the dormant periods is from expansion of material at intermediate depths. For an increase in methane relative to CO₂, it would be necessary to open up deeper strata, which could occur with eruptions related to stronger earthquakes.

Pugachiovsky Mud Volcano (PMV)

The PMV was in a dormant state during the period of observations, as indicated by the fact that only six of the 20 gryphons located within the mud field were active. The others did not emit gas, water, or mud. The active gryphons very slowly extruded small mounds of silty mud, but bubble emissions of gas or water discharge were not observed.

The most representative sample was taken from dry gryphon 3 (Fig. 2g, i). It was located about 20 m from the center of the mud field, and it was nearly 20 cm high. Gas chromatographic analysis yielded the following gas composition: CO₂, 8.6 vol%; O₂, 18.4 vol%; CH₄, 12.61 vol%; and N₂, 60.4 vol% (Table 1). From published information (Sidorenko 1970), spontaneous gas of the PMV in the past consisted mainly of methane (63–83 vol%), carbon dioxide (6.4–27 vol%), oxygen (0.1–1.8 vol%) and nitrogen (0.2 vol%). These differences reflect the currently dormant condition of the mud volcano and the addition of atmospheric gas components.

Several samples contained small amounts of non-methane hydrocarbons: ethane, 3.7–92 ppm; propane, 0.8 ppm; butane, 2.5 ppm; and pentane, 1.1 ppm.

The similarity in gas composition of the PMV and YSMV suggests a genetic relationship. This suggestion is supported by the finding of the same lithotype of

Fig. 3 The structure of the YSMV with the seismogeological section (Argentov et al. 2001) across a cluster with large gryphons (1–1.5 m height). *Values* on the section are longitudinal wave velocity (km/s)

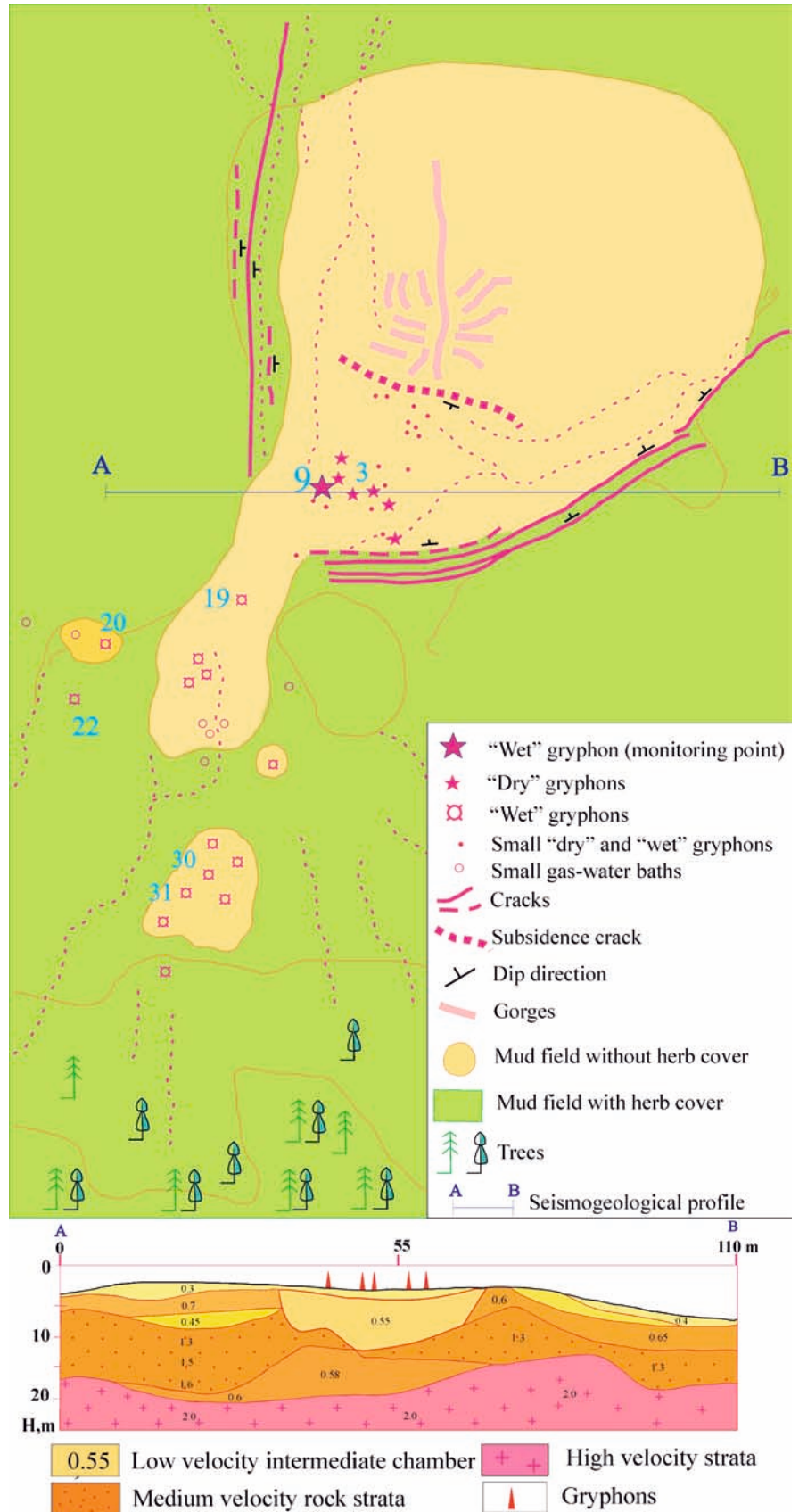


Table 1 Gas composition of the YSMV, PMV and Darginsky gas vent within the Darginsky area of mud volcanism on Sakhalin Island (*n.d.* not detected by GC)

Station	CO ₂	O ₂	N ₂	CH ₄	C ₂ H ₆	C ₃ H ₈	C ₄ H ₁₀	C ₅ H ₁₂
	(vol%)				(vol, ppm)			
Yuzhno-Sakhalinsky Mud Volcano								
Gryphon 13	94.6	0.9	2.8	1.7	371	70	11	22
Gryphon 19	92	1.4	5.2	1.6	278	7.5	15	<i>n.d.</i>
Gas water vent 22	42.9	7.4	27.7	22	1,624	241	27	15
Gryphon 3	65.6	0.3	2.4	32	3,758	401	109	17
Gryphon 10	76	0.2	2	22	2,204	276	76	<i>n.d.</i>
Gryphon 9	76.1	1.1	4.7	18.1	315	78.6	55.3	11.9
Pugachiovsky Mud Volcano								
Gryphon 3	8.6	18.4	60	12.6	92.8	<i>n.d.</i>	2.5	1.1
Darginsky Mud Volcano								
Darginsky gas vent	0.5	0.3	7.3	91.8	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>

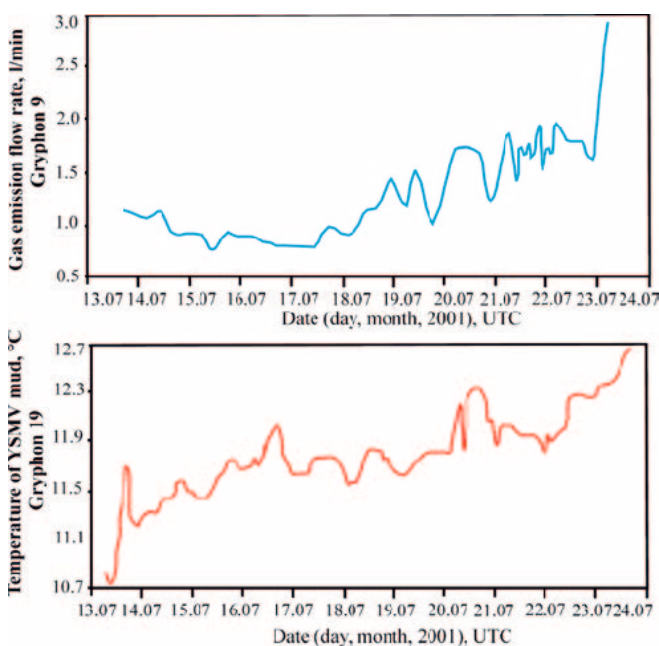


Fig. 4 Time series for 13–24 July 2001 of gas flow and temperature development on gryphons 9 and 19 located at the YSMV

erupted upper Cretaceous rocks, and the similar chemical composition of the brecciated rocks (Mel'nikov and Il'yov 1989).

Darginsky Mud Volcano (DMV)

Information on eruptions of the DMV is sparse, and this area showed the least activity during our investigation on Sakhalin Island. Published literature (Zanyukov et al. 1982; Mel'nikov and Il'yov 1989) describes several gryphons up to 10–20 cm high, which periodically extruded mud and gas; the gas consisted mainly of methane. From our observations we must conclude that the DMV is currently dormant. At the nearby coast during low tide, however, the seafloor of Darginsky Bay revealed numerous vents of natural gas in the form of bubbles rising from uniformly distributed, small water pools (1–3 m diameter). The gas of these bubbles is predominantly CH₄

(91.8 vol%) and contains insignificant amounts of CO₂ (0.5 vol%), N₂ (7.3 vol%) and O₂ (0.3 vol%).

Comparing the results of gas sampling of the DMV and YSMV (Table 1) reveals three general differences:

1. the basic gas component of the YSMV during the period of observation is CO₂, the levels of which reach 96 vol%, whereas the DMV showed only 0.5 vol% CO₂;
2. the gas from the DMV reached 91.8 vol% CH₄ whereas the gas of the YSMV contained no more than 32 vol% CH₄ during the period of observation; and
3. the gas of the DMV contained no higher hydrocarbons; however, these compounds were determined for the YSMV and PMV up to pentane.

These results are in good agreement with the data from other offshore gas vents described in the following sections.

Piltunsky Mud Volcano (PtMV)

An extension from onshore to offshore of mud and gas emissions is represented by the PtMV on the north-eastern shelf off Sakhalin Island (Fig. 1a, Obzhirov 1993). Although no gas samples were available from this mud volcano, we suspect their composition may be similar to that of the bubbles rising from water pools at the seafloor of Darginsky Bay. However, methane anomalies were detected in the water column of the eastern Sakhalin shallow shelf from the vicinity of the PtMV and DMV (Fig. 1a) at station Ga28-02 and station Ga28-12 (Nicole Flare). Concentrations of methane here ranged from 700 up to 4,000 nl/l (Fig. 5a). The change in concentrations is seasonally controlled and not influenced by depth or water column stratification. Comparison of emissions measured during June 1999 and May 2000 shows a factor of three differences whereas the water column at the eastern Sakhalin shallow shelf each time was homogeneously mixed. This distribution suggests direct emission of methane into the atmosphere. No heavier hydrocarbons were detected.

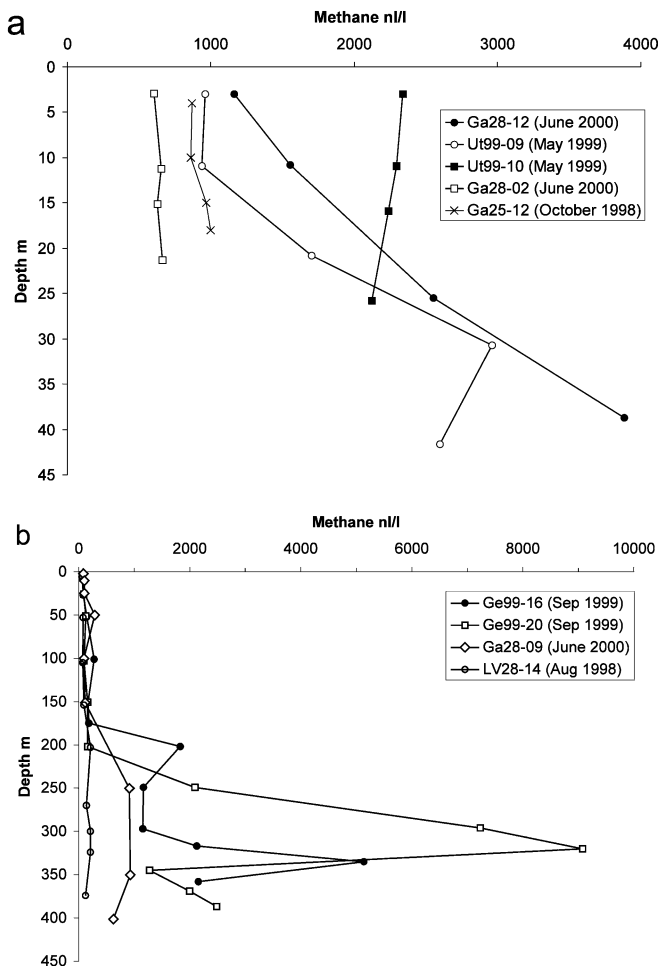


Fig. 5a, b Seasonal changes between October 1998 and June 2000 of methane in the water column **a** on the eastern Sakhalin shallow shelf (station Ga28-02) in the vicinity of the PtMV and DMV, and **b** at the “Giselle Flare” (station Ga28-09). The water column at station Ga28-02 is mixed and at station Ga28-09 stratified with regard to dissolved methane

Offshore Sakhalin Island

Gas flares and methane anomalies in the water column

Offshore gas flares over the shelf and upper slope off Sakhalin Island have been known for many years (Obzhirov 1993). They were imaged by hydroacoustic surveys based on the intensity of the return scattering of sound. There are many different types and shapes of flares recorded off Sakhalin Island using the SARGAN-IDM hydroacoustic system with an operational frequency of 20 kHz (Biebow and Hütten 1999; Biebow et al. 2000). The majority of the flares are elongated ellipsoids of varying width, ranging from a few meters up to about 300 m. They are rooted in the seafloor, indicating the sites from which they originate. The height of the flares is about 90–500 m above the seafloor, depending on their intensity. Repeated surveys have established that all major flares are stationary but often are deflected with increasing height above the bottom due to lateral currents.

The acoustic images are caused by methane bubbles rising from gas-saturated vent fluids at the seafloor. In other areas of flares, often referred to as acoustic plumes, it has been shown that their height in the water column terminates at about 300–400 m below the sea surface, regardless of the depth of the seafloor from which they originate. This depth of termination coincides with the upper limit of the stability field of methane hydrate in seawater (Rehder et al. 2002; Heeschen et al. 2003). These authors hypothesize that within the stability field of methane hydrate, the bubbles are shielded from dissolving by a hydrate skin, and hence are imaged acoustically. After they rise above that level, dissolution causes the bubbles to disappear, as does the hydroacoustic signal. The upper hydrate stability limit is a function of water depth and temperature, and since the water temperature at the shelf off Sakhalin is quite cold (-1.2°C), it is likely that the flares rise here to shallower depths than at other locations around the world. This phenomenon permits more sensitive acoustic detection of bubble vents as well as more accurate mapping of flare sites. Therefore, the abundant and well-defined flare distribution pattern offshore Sakhalin very likely reflects directly the subsurface structural regime.

Alignment of flares on the shelf upper slope edge

Typical flares are illustrated in Fig. 1c. Both examples are aligned regionally along the transverse fault direction, and span water depths of 400–180 m. One of these is known as “Giselle Flare” and has a well-defined, three-dimensional shape. It is one of the most prominent features from among more than 100 of such flares that have been identified offshore northern Sakhalin Island (Fig. 1a, b). The center of the most intense flare activity is oriented on a strike line of 40° that cuts across the East Sakhalin and West Derugin shear zones between $54^{\circ}22'N$ and $54^{\circ}28'N$ at $144^{\circ}05'E$ (Fig. 1b). High abnormal methane concentrations in the water column surrounding the flares have been detected. These measurements verify that the acoustic images are caused by bubbles of free methane.

Although in no case were the measured dissolved CH_4 levels anywhere near gas saturation, high persistent concentrations of CH_4 in the vicinity of the acoustic flares leave no doubt that both flares and high methane concentrations are different manifestations of the same phenomenon, i.e., cold seep venting. Concentrations of methane around the Giselle Flare over a two-year period (August 1998–May 2000) were not spectacularly elevated (<200 nl/l), but they increased to 6,000–10,000 nl/l in September 1999 (Ge99-16, Ge99-20; Fig. 5b). The maximum is not associated with the seafloor; instead, it appears to be the result of a lateral drift of highly CH_4 -enriched water from nearby. During the same time, a high methane (1,200 nl/l) incursion was also observed at site Ge99-13 (Obzhirov et al. 2002), suggesting that during the September season of 1999 another emission was most active. Such long-term dis-

tribution strongly suggests an inter-annual variability of methane emissions resembling those observed onshore during monitoring of gryphon 9 (YSMV).

Further examples of gas venting from nearshore sites are the Nicole Flare and the associated CH₄ anomaly at station Ga28-12 (Fig. 5b). Both locations are directly in line with onshore transverse faults striking 40° (Fig. 1a, b). Concentrations of methane around the Nicole Flare (station Ga28-12; Fig. 5b) ranged from about 1,000 nl/l at the surface up to 4,000 nl/l near the bottom of the rather shallow site. CH₄ concentrations remained the same from September 1999 until May 2000. No higher-molecular weight hydrocarbons were detected.

None of the gas samples taken from the DMV, from the vicinity of the PtMV, and from offshore cold vents contained heavy hydrocarbons (Obzhirov et al. 2002). Hence, the vents with highly anomalous methane concentrations on the shelf off northeastern Sakhalin Island may all emit natural gas of the DMV type. The absence of CO₂ may be due to the very high solubility of CO₂ in seawater, such that any fraction of it would immediately be stripped from the ascending bubbles and would leave only methane behind. On the other hand, if the CO₂ in the onshore mud volcano emissions is the result of methane oxidation during dormant or inactive phases, as proposed above, both gases may originate from the same source. Nevertheless, it would be interesting to ascertain whether or not CO₂ is initially also a component in the offshore gas vents; for example, its C-isotopic composition would not only confirm that relationship but would also indicate whether or not the carbon dioxide indeed results from oxidation of methane. All offshore sites coincide with or directly extend the orientation of the transverse fault pattern on land. It is highly likely that the intersection of the NE-striking faults on land with the Central Sakhalin and Hokkaido-Sakhalin shear zones determines the sites of the mud volcanoes. This pattern continues offshore where the intersection mainly with the East Sakhalin and West Derugin shear zones determines the sites of the gas vents.

Conclusions

During our observations, the Yuzhno-Sakhalinsky Mud Volcano was the most active with regard to gas emission and mud/water discharges relative to other Sakhalin Island mud volcanoes. The Pugachiovsky Mud Volcano was the next most active. The Darginsky Mud Volcano was dormant with respect to mud and water discharge whereas the least activity was shown by the Lesnovsky Mud Volcano, which has not been discussed. The main gas component of the YSMV during the observation period was CO₂. Its CO₂ concentration varied in the range 66–94 vol%. Correspondingly, the methane concentration showed a range of 2–32 vol%. A gradual and smooth increase of spontaneous gas emission and temperature increase over the mud field surface of the YSMV preceded an earthquake, which occurred in early

August 2001. This observation is evidence for increased tectonic stress in the crust before the earthquake that caused increases of these parameters.

The main source of spontaneous gas from gryphons of the YSMV during the observation period probably is an intermediate lenticular body. Therefore, the composition of the emanating gas is not representative of the gas components in the main deep gas reservoir, whose real gas composition can be observed after the volcano erupts. However, after the eruption the methane content of the spontaneously emitted gas decreases gradually, probably because of biogeochemical oxidation in the intermediate gas reservoir. This process also can cause the increase of CO₂ content of the gas emissions.

A gas reservoir of predominantly methane is the source of mud volcanism in the Darginsky area. Intensive emission of methane bubbles occurs in a wide area of the shallow gulf near the village of Goryachie Klyuchi. Anomalous concentrations of methane within the shallow shelf and upper slope off northeast Sakhalin Island are likely natural gas emissions of the DMV type.

All offshore sites coincide with or directly extend the trends of the transverse fault pattern on land. It is highly likely that the intersection of the NE-striking transverse faults on land with the Central Sakhalin and Hokkaido-Sakhalin fault zones determines the sites of the mud volcanoes, and that this pattern continues offshore where the intersection with the East Sakhalin and West Derugin shear zones determines the sites of the gas vents.

Acknowledgments The field expedition was carried out with funding from the Russian Fund of Fundamental Investigations, grant 01-05-64904a, and in cooperation with the program Integracia, grant E0252; the recipient of these grants is Dr. A.S. Astakhov, POI FEB RAS. The marine gas investigations were carried out within the framework of the German-Russian cooperative project KOMEX, grant 03G0535, jointly funded by the German Federal Ministry of Education and Research and by the Russian Ministry of Industry and Science. We are grateful for their financial support, which made this study possible. The manuscript benefited greatly from helpful reviews by Keith Kvenvolden and Bob Garrison. We greatly thank all Russian and German scientists who participated in the project KOMEX, especially R. Kulinich, B. Baranov, J. Greinert, B. Karp, and O. Vereshchagina.

References

- Alekseichik SN (1959) Geological structure and oil-gas potential of the northern part of Sakhalin Island (in Russian). Russian Oil Science and Research Institute for Geological Prospecting, Moscow
- Aliyev AA, Guliyev IS, Ivanov IS (2002) Catalogue of recorded eruptions of mud volcanoes of Azerbaijan (for the period of 1810–2001) (in Russian and English). Nafta-Press, Baku <http://www.gia.az/html/production/monographs>
- Argentov VV, Zhigulev VV, Melnikov OA, Patrikeev VN (2001) The experience of low depth seismics for structure studying of South-Sakhalin mud volcano (in Russian). Pacific Ocean Geol 20:3–11
- Astakhov AS, Sergeev KF, Mel'nikov OA, Prisyazhnyuk AV, Shakirov RB, Brovko PF, Kiselev VI (2002) The dynamics of the Central-Sakhalin Deep Fault defluidization processes at the

- seismic activation (results of the Yuzhno-Sakhalinsky Mud Volcano monitoring during July-August 2001) (in Russian). Rep Acad Sci (Dokl Akad Nauk) 386(2):223–228
- Baranov BV, Karp BYa, Wong HK (1999) Areas of gas seepage. KOMEX Cruise Report I RV Professor Gagarinsky, Cruise 22. Kiel, GEOMAR Rep 82 INESSA, pp 45–52
- Baranov B, Dozorova K, Karp B (2000) Tectonics of the Okhotsk Sea: extension vs compression. KOMEX Cruise Report V RV Professor Gagarinsky, Cruise 26. Kiel, GEOMAR Rep 88:67–80
- Baranov BV, Werner R, Hoernle KA, Tsoy IB, Van den Bogaard P, Tararin IA (2002) Evidence for compressionally induced high subsidence rates in the Kurile Basin (Okhotsk Sea). Tectonophysics 350:63–97
- Biebow N, Hütten E (eds) (1999) KOMEX Cruise Reports I & II. GEOMAR Rep 82:1–188 (85 appendices)
- Biebow N, Lüdmann T, Karp B, Kulinich R (2000) KOMEX: Kurile-Okhotsk Sea Marine Experiment. Cruise Reports KOMEX V and KOMEX VI, R/V Professor Gagarinsky Cruise 26 and M/V Marshal Gelovany Cruise 1. Kiel, GEOMAR Rep 88:1–296
- Bogdanov NA, Khain VE (eds) (2000) Explanation report for the tectonic map of the Okhotsk sea region, VE scale 1:250,000. Institute of Lithosphere of Border and Internal Sea RAS, Moscow
- Etiopie G (2002) Methane emission from the mud volcanoes of Sicily (Italy). Geophys Res Lett 29(8) 10/1029-2001-GL014340
- Ginsburg GD, Soloviev VA (1994) Submarine gas hydrates (in Russian). VNIIOkeangeologiya, St. Petersburg
- Ginsburg GD, Milkov AV, Soloviev VA, Egorov AV, Cherkashev GA, Vogt PR, Crane K, Lorenson TD, Khutorskoy MD (1999) Gas hydrate accumulation at the Haakon Mosby Mud Volcano. Geo-Mar Lett 19:57–67
- Gurieva ZI, Sharkov VV (1987) The Sakhalin Island mud volcanoes study with application of air photography (in Russian). Pacific Geol (Tikhookeanskaya Geol) 4:58–65
- Heeschen KU, Trehu AM, Collier RW, Suess E, Rehder G (2003) Distribution and height of methane bubble plumes on the Cascadia Margin characterized by acoustic imaging. Geophys Res Lett 30(12):1643 10.1029/2003GL016974
- Kharakhinov VV (1998) The tectonics of the Okhotsk Sea oil-gas province (in Russian). SakhalinNIPImorneft, Okha
- Kharakhinov VV (2002) The tectonics and oil-gas potential of the Okhotsk Sea region (in Russian). In: Alekseev MN (ed) Geology and mineral resources of the Russian shelf areas. GEOS, Moscow, pp 106–114
- Kholodov NV (2001) About the nature of mud volcanoes (in Russian). Nature (Russian) 11:47–58
- Kopf AJ (2002) Significance of mud volcanism. Rev Geophys 40(2):1005 10.1029/2000RG000093
- Lüdmann Th, Baranov BV, Karp BYa (2002) Cruise Report RV Professor Gagarinsky, Cruise 32, SERENADE. Kiel, GEOMAR Rep 105:1–40 (2 appendices)
- Mel'nikov OA, Il'yov AYa (1989) About new mud volcanism manifestations on Sakhalin (in Russian). Pacific Ocean Geol (Tikhookeanskaya Geol) 3:42–47
- Milkov AV (2000) Worldwide distribution of submarine mud volcanoes and associated gas hydrates. Mar Geol 167:29–42
- Obzhirov AI (1993) Gasgeochemical fields of the sea and oceans subbottom layer (in Russian). Nauka, Moscow
- Obzhirov AI, Vereshchagina OF, Sosnin VA, Shakirov RB, Salyuk AN, Lammers S, Suess E, Biebow N, Winckler G, Druzhinin V (2002) Methane monitoring in waters of the eastern shelf and slope of Sakhalin (in Russian). Geol Geophys Novosibirsk SB RAS 43:605–612
- Rehder G, Brewer PW, Peltzer ET, Friedrich G (2002) Enhanced lifetime of methane bubble streams within the deep ocean. Geophys Res Lett 29(15):1731 10.1029/2001GL013966
- Shilov VN, Zakhharova MA, Il'yov AYa, Podzorov AV (1961) Eruption of South Sakhalin mud volcano of spring 1959 (in Russian). Pap Sakhalin Complex Scientific-Research Institute, Russian Academy of Sciences, Siberian Branch, pp 83–97
- Sidorenko AB (ed) (1970) Mud volcanoes (in Russian). In: Geology of USSR vol 33, Sakhalin Island. Nedra, Moscow, pp 355–368
- Svarichevsky AS (2001) The bottom relief of the Okhotsk Sea (in Russian). In: Kazansky BA (ed) The problems of West-Pacific transition zone morphotectonics. Dal'nauka, Vladivostok, pp 82–97
- Zanjukov VN, Melnikov OA, Fedorchenko VI (1982) Eruption of Yuzhno-Sakhalinsky mud volcano (in Russian). Geol Geophys 2:127–130