Authigenic Carbonate Formation in the Ocean

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Abstract—Oceanic authigenic carbonates are classified according to the origin of carbonate carbon source using a complex methodology that includes methods of sedimentary petrography, mineralogy, isotope geochemistry, and microbiology. Mg-calcite (proto-dolomite) and aragonite predominate among the authigenic carbonates. All authigenic carbonates are depleted in heavy carbon isotope ^{13}C and enriched in heavy oxygen isotope [18]O (in PDB system), indicating biological fractionation of isotopes during the carbonate formation. Results obtained show that authigenic carbonate formation is a biogeochemical (microbial) process, which involves carbon from ancient sedimentary rocks, abiogenic methane, and bicarbonate-ion of hydrothermal fluids into the modern carbon cycle.

Carbonate formation in ocean is a powerful sedimentary process that annually removes from the carbonate cycle about 1 Gt of $CaCO_3$ (Lisitsyn, 1978). This process maintains equilibrium in the carbon dioxide balance of the lithosphere-ocean-atmosphere and system the global calcium balance. After a prolonged domination of chemogenic hypotheses, based on abundant experimental data, Lisitsyn proved that biogenic carbonate sedimentation prevails over processes of chemical precipitation (Lisitsyn, 1978, p. 233).

Scale and mechanisms of the authigenic carbonate formation in oceanic sediments were ignored by researchers for a long time. Strakhov (1951) examined the principal mechanism of diagenetic carbonate formation with reduced Black Sea sediments as example. He believed that "CO_2 generated during diagenetic decay of buried organic matter must play an important role in the migration and redistribution of carbonates in sediments. Content of CO_2 generated during diagenesis, the amount of carbonate dissolved in pore solution, and the redistribution and concentration of carbonates in the form of local segregations have a direct correlation with the organic matter content (Strakhov, 1962, p. 545). However, Strakhov denied the role of bacteria in calcium precipitation. He believed that "bacterial calcite formation" is insignificant, whereas chemical precipitation of $CaCO_3$ and its transport in suspended form are a dominant process" (Strakhov, 1962, p. 102).

Interest to processes of authigenic carbonate formation in ocean increased after the 1960s when a new specific type of authigenic carbonates (methane-derived carbonates) related to methane oxidation in both recent and ancient (mainly Pleistocene) oceanic sediments was first described in (Fuex, 1977; Hathaway and Degens, 1968; Nissenbaum, 1984).

Methane seeps, *i.e.* discharge of methane-bearing solutions and gas jets from bottom sediments discovered in 1984 represent a new natural phenomenon in the ocean (Suess *et al.*, 1985). More than 30 active fields of methane seeps are already known to date. They are marked by the development of specific biological communities (Sibuet and Olu, 1998) and various morphological types of authigenic carbonates, including carbonate buildups ("chimneys" or "reefs"), plates, crusts, and so on. The authigenic carbonate mineralization is described with various details in several publications (Aloisi *et al.*, 2000; Hackworth and Aharon, 2000; Paull *et al.*, 1992; Von Rad *et al.*, 1996; and many others).

Since 1979, several active hydrothermal fields have been discovered in rift zones of mid-oceanic ridges. These fields are marked by the discharge of endogenic gases (CH_4, CO_2, and others) and the formation of authigenic carbonate minerals (dispersed and veinlet mineralization). Massive carbonate buildups are also formed in some cases.

In summer 2001, a hydrothermal field (the Lost City field) with low-temperature solutions and approximately 30 columnar carbonate buildups, up to 10 m across and 60 m high, was discovered at the intersection of the Mid-Atlantic Ridge with a transform fault in the North Atlantic 30° N area (Kelley *et al.*, 2001; Lein *et al.*, 2002a). Carbon dioxide and Ca^{2+} in these carbonates are derived from seawater and hydrothermal fluid, respectively. This type of authigenic carbonates represents a new phenomenon in ocean.

Since 1975, we have regularly studied processes of authigenic carbonate formation in sediments of the modern ocean (Fig. 1, Table 1). This article is aimed to summarize materials of different years and determine the role of microbial activity in the authigenic carbonate mineralization.

We studied authigenic carbonates in seven large regions of active carbonate precipitation (Fig. 1, Table 1).
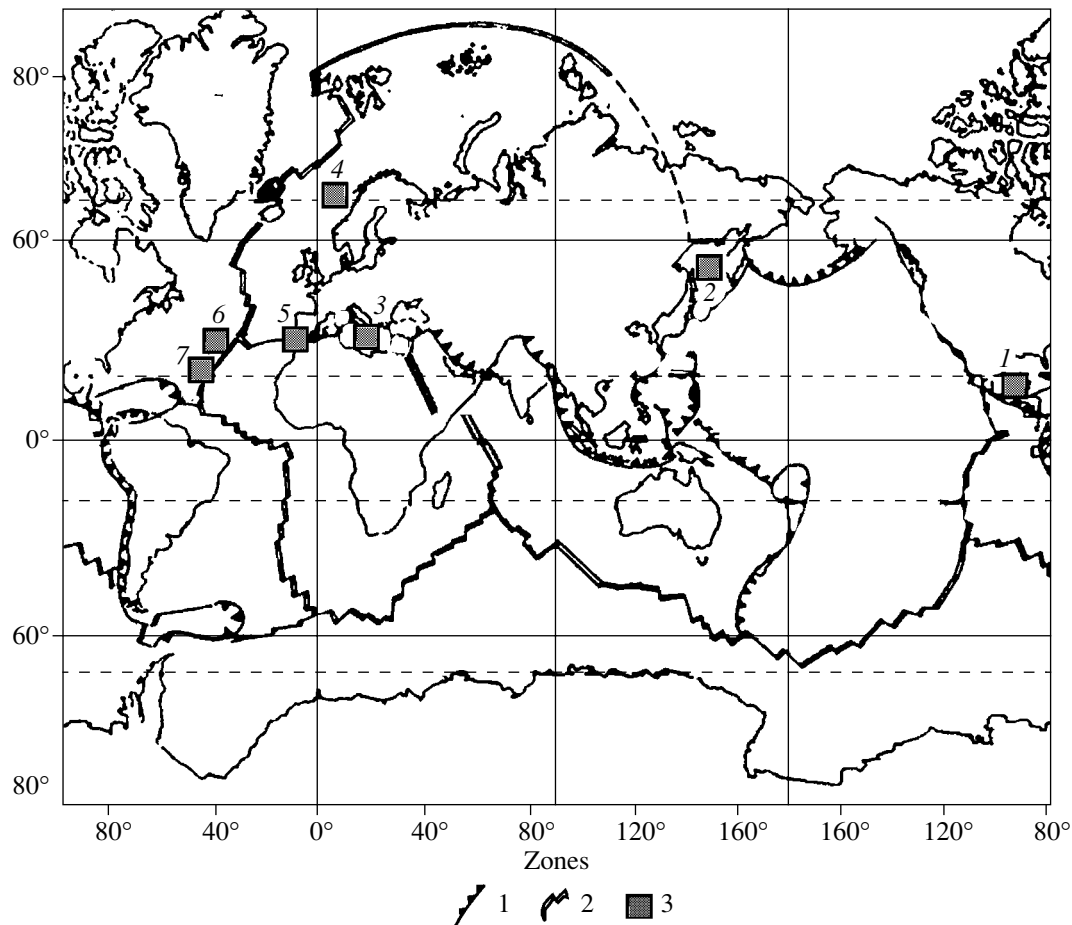
Fig. 1. Location of the studied regions with authigenic carbonates in the ocean. (1) Subduction zones; (2) spreading zones; (3) study regions; (*1*) Gulf of California; (*2*) Sea of Okhotsk, Paramushir Isl. area; (*3*) Black Sea, Dnepr canyon; (*4*) Norwegian Sea, Haakon Mosby mud volcano (HMMV); (*5*) mud volcanoes of the Gulf of Cadiz; (*6, 7*) active hydrothermal fields of the Mid-Atlantic Ridge (MAR): (*6*) Lost City (30° N); (*7*) Logachev (14° N).

As follows from the table, authigenic carbonate is formed at various depths ranging from several meters (the Black Sea shelf area) to 3400 m (mid-oceanic ridges) and in different climatic environments varying, from the polar zone to tropics.

We studied of the authigenic carbonate formation based on a unified complex methodology that includes methods of sedimentary petrography, mineralogy, isotope geochemistry, and microbiology (Table 2). These methods are scrutinized in our previous publications (Lein *et al.*, 1998, 2000a, 2000b, 2002a, 2002b; Pimenov *et al.*, 2000).

TYPE I. AUTHIGENIC DIAGENETIC CARBONATES FORMED DUE TO THE DECAY OF MICROBIAL ORGANIC MATTER IN SEDIMENTS

In 1972, Strakhov initiated studies of sediments along the Transpacific transect including reduced sediments from the Gulf of California with high organic carbon (C_{org}) content (*Geokhimiya...*, 1980). Tiny anhedral and euhedral crystals and crystalline aggregates of carbonate minerals paragenetically associated with sulfides were found in all studied cores of reduced sediments from the Gulf of California and the Pacific margin off Mexico, whereas carbonate crusts and nodules (Fig. 2) were recovered in the Gulf of California at Station 666 (Lein, 1978; Lein *et al.*, 1975, 1979).

Several mineral phases were detected among finely dispersed carbonates by means of X-ray analysis: (1) common low-magnesian calcite; (2) calcium dolomite (protodolomite); (3) high-magnesian calcite; and (4) aragonite. Unlike monophase shell carbonate, the finely dispersed carbonates contain several mineral phases and can be defined as newly formed minerals (Lein *et al.*, 1979).

Results of their mineralogical study well correspond to isotope-geochemical data. The authigenic carbonates are depleted in heavy carbon isotope ^{13}C relative to carbon of shell carbonate, marine limestones, and seawater bicarbonate (Table 3, Fig. 3).
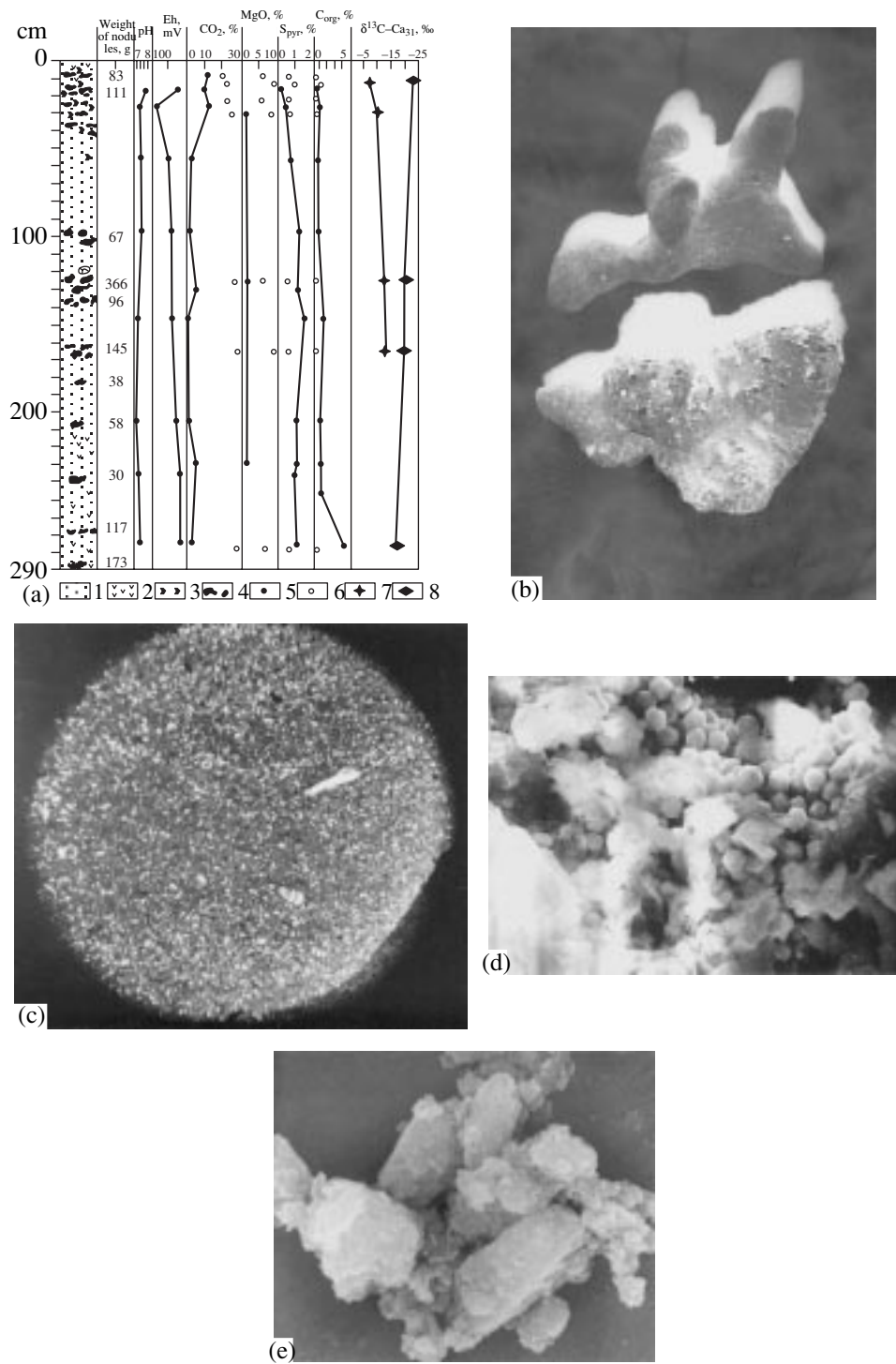
Fig. 2. Lithologeochemical characteristics of sediments enclosing carbonate nodules and morphology of nodules. (a) Lithogeochemical characteristics of sediments from the Gulf of California shelf (Station 666) enclosing carbonate nodules: (1) terrigenous mud; (2) volcanoclastic material; (3) shell fragments; (4) carbonate nodules; distribution of CO_2, MgO, S_{pyr}, and C_{org} in (5) sediments and (6) nodules; distribution of $\delta^{13}C$-CO_3 in (7) sediments and (8) nodules. (b) Authigenic carbonate nodules (1/2 of nat. size). (c) Authigenic carbonate nodules from the interval 5–45 cm (thin section, magn. 14, crossed nicols, (d, e) SEM images of (d) sulfides and (e) authigenic carbonates from carbonate nodules: (d) cavern incrusted by pyrite crystals on the nodule surface, magn. ×14000; (e) aggregate of anhedral and euhedral Mg-calcite crystals, magn. ×7000.

**Table 1.** Regions of authigenic carbonate investigation

Region	Coordinates	Depth, m	Specific benthic community, mats	CH_4-gas hydrates	CH_4 seeps, CH_4 transport	$\delta^{13}C–CH_4$, ‰	Source
Gulf of California: Shelf	24°53.7 N 108°42′ W	120	–				Lein *et al.*, 1978, 1979, 1999
Continental slope	27°09′ N 111°08′ W	up to 3260	–				
Black Sea: shelf	44°46′–44°52′ N 31°50`–31°59′ W	60–180	Mats	None	Diagenetic CH_4	−68	Lein, 1991; Lein *et al.*, 2001, 2002b
Continental slope	44°46′–44°41′ N 31°47′–31°59′ W	200–500	Mats		Bubble-stream		Ul'yanova *et al.*, 1995; Thiel *et al.*, 2001
Norwegian Sea: Continental slope	72° N	1200	Mats, symbiotrophic polychaeta	At and below bottom surface	Thermogenic + diagenetic diffusion	−60	Lein *et al.*, 1998, 1999, 2000a, b Pimenov *et al.*, 1999
Sea of Okhotsk: Continental slope	49° N	800	Symbiotrophs and mats	~1-cm-thick layer	Thermogenic, bubble-stream	−54 average	Lein *et al.*, 1989
Gulf of Cadiz: continental slope	35°30′ N 7°10′ W	960	Mats, benthic animals	Within sediments	Thermogenic + diagenetic + hydrothermal, not determined	−32…−63 From −32 to −63, up to −19.2 in homologues	Stadnitskaia *et al.*, 2001; Lein *et al.*, 2003
Logachev, MAR	14° N	3400	Mats, symbiotrophic mollusks	None	Hydrothermal, diffusion	−14.6	Lein *et al.*, 2000a, c, 2001, 2003
Lost City, MAR	30° N	860	Mats and symbiotrophic animals (?)	None	Hydrothermal, diffusion	−16	Lein *et al.*, 2002b

Note: (–) Not known, no data.

Table 2. Analytical methods used in this work for the determination of chemical, isotopic, and mineral composition, as well as for the estimation of the microbial process rate (Lein *et al.*, 1998, 2000a, 2003)

Determination object	Method	Precision, %
SO_4^{2-}	Ion chromatography (stationary lab.)	3
C : Hydrothermal : N	CHNS-O analyzer (stationary lab.)	0.3
Cl^-	Direct titration with $AgNO_3$ (on board the ship)	0.25
$Ca^{2+} + Mg^{2+}$	Trilonometric (B) titration with black eriochromium for $(Ca^{2+} + Mg^{2+})$ determination and murexide for Ca^{2+} determination (stationary lab.)	3.0
Dissolved phosphorus	Photometry based on the formation of phosphorus-molybdenum heteropolyacid complex and its reduction to molybdenum blue by the ascorbid acid (on board the ship)	3.0
Dissolved silicon	Photometry based on the interaction of silicon and ammonium molybdate with the subsequent reduction by Metol (on board the ship)	3.0
Water content	Gravimetric (on board the ship)	1%
pH, Eh	Ionometer pH 320/set, Germany (on board the ship)	0.1; 10 mV
Total alkalinity	Potentiometric titration (on board the ship)	3.0
$FeS_{n-1}FeS_2$	Iodometric titration (acid-soluble forms) and trilonometry (stationary lab.)	5.0
$\delta^{18}O$	Mass spectrometry: equilibration with CO_2 at 25°C, *Micromass 602 D* (stationary lab.)	0.1–0.5 (‰)
$\delta^{13}C$	Mass spectrometry: oxidation to CO_2, *Micromass 602 D, MI-1202 B* (stationary lab.)	0.5 (‰)
$\delta^{34}S$	Mass-spectrometry: oxidation to SO_4, *MI-1202 B* (stationary lab.)	0.1 (‰)
Silicates	X-ray emission (stationary lab.);	Standard
Mineral composition	X-ray diffraction (stationary lab.) SCAN JEM-5300 + LINK ISIS; JEM-1002	Standard
SO_4^{2-} reduction	Radioisotopy $Na_2^{35}SO_4$ (10 µCi) (stationary lab.)	
CO_2 assimilation	Radioisotopy $Na_2^{14}CO_3$ (5 µCi) (on board the ship)	
CH_4 formation on $CO_2 + H_2$	Radioisotopy $Na_2^{14}CO_3$ (5 µCi) (stationary lab.)	
CH_4 oxidation	Radioisotopy $^{14}CH_4$ (2 µCi) (on board the ship)	
Total number of bacteria	Fluorescence with fluorescamine (stationary lab.)	
Tissues of pogonophora	Electron microscopy (stationary lab.)	

The formation of authigenic carbonates in a constant paragenesis with sulfide mineralization is related to microbial reduction of sulfate ion in seawater and pore water accompanied by the extraction of isotopically light bicarbonate and hydrogen sulfide according to the reaction:

$$SO_4^{2-} + 2C_{org} + H_2O \longrightarrow H_2S + 2HCO_3^-.$$
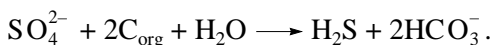
This reaction leads to increase in total alkalinity due to the appearance of H_2S, its hydrolysis, and carbonate precipitation. High concentration of bicarbonate ion and precipitation of calcium and magnesium carbonates from the pore water of reduced sediments are documented in sediment cores where active microbial sulfate reduction is observed (Table 4).

Based on results of microbiological, radiocarbon, and stable isotope studies, we calculated the value of total ΣHCO_3^- production during the microbial reduction of sulfate ion in pore water using the equation of isotope–mineral balance. Results obtained show that the average contribution of dispersed authigenic carbonate minerals to the total carbonate carbon is about 40% (Lein, 1983).

Nodules from different depth levels of the core at Station 666 vary in morphology, isotopic composition (δ^{13} ranges from –18.1 to –24.9‰, Table 3), and age of their carbonate carbon (from 5 ka at 5–40 cm to 14 ka at 160–200 cm, Table 5). These carbonates were formed from the carbon dioxide as a result of the decomposition of organic matter (OM) buried in sediments and sulfate reduction (Lein, 1983; Lein *et al.*, 1975, 1983).

Young nodules from upper levels of the core existed in the littoral environment for some time where the

Table 3. Isotopic composition of pyrite sulfur and carbonate carbon in carbonate nodules and enclosing mud (Station 666) from the Gulf of California (Lein *et al.*, 1979)

Interval, cm	δ^{34}S, ‰		δ^{13}C-CaCO$_{3\ auth}$, ‰		δ^{13}C-C$_{org}$, ‰		δ^{13}C-CaCO$_{3\ shell}$, ‰		Sulfate reduction rate, g S/kg day
	mud	nodules	dispersed in mud	nodules	mud	nodules	mud	nodules	
5–45	–28.0	–10.8	–6.5		–21.2	–	1.7	–	4.67
		–8.6	–9.1	–24.9	–		–0.4		
90–110	–	–	–	–18.5	–	–	3.1	–	–
120–140	–6.7	–7.5	–14.5	–18.1	–23.3	–	–0.2	–	0.3
160–170	5.5	5.2	–15.6	–19.9	–	–21.0	2.2	2.4	–
270–280	–	8.8	–	–18.6	–22.0	–21.6	0.8	0.1	0.16

Note: (–) no data.

enclosing mud was washed out. Carbonate nodules underwent mechanical and chemical destruction. They often served as a hard substrate for oysters and other benthic animals, whose remains occur on the nodule surface (Lein *et al.*, 1979).

Nodule-bearing sediments were buried at the depth of 120 m, and sulfate reduction was restored of postglacial transgression. Consequently, isotopically light (δ^{34}S = –28‰) younger sulfides were formed within the upper layer of sediments (Table 3; Figs. 2d, 3).

Reduced sediments from the Gulf of California and the Pacific margin off Mexico are considered a typical model that illustrates the formation of dispersed diagenetic carbonates and carbonate nodules due to active decay of microbial OM and carbon dioxide generation during the reduction of marine sulfate ion. We did not detect any contribution of CH$_4$ to carbonate formation in the studied sediments.
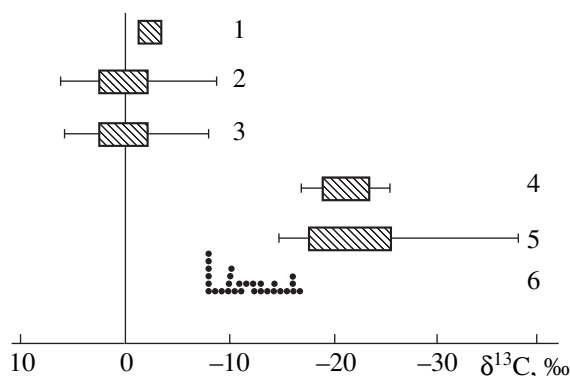

Fig. 3. Variations in carbon isotopic composition of different compounds. (1) Seawater HCO$_3^-$; (2) marine limestones; (3) shells of marine animals; (4) OM carbon in sediments of the Gulf of California; (5) carbon of carbonate nodules in sediments of the Gulf of California; (6) carbon of dispersed authigenic carbonates in sediments from Pacific and Indian oceans (Lein *et al.*, 1980).

Reduced sediments of the Black Sea represent another spectacular example of the formation of metabolic carbon dioxide in pore water and dispersed authigenic carbonate in sediments. The upper mud layer, where the contribution of CH$_4$ carbon to total ΣHCO$_3^-$ does not exceed 10%, is characterized by a high sulfate reduction rate ranging from 3.62 to 8.89 mg/kg day (Lein *et al.*, 1986, 1997, 2002c) or from 0.65 to 1.43 mmol/m^2 day (Jorgensen *et al.*, 2001).

The δ^{13}C value in dispersed authigenic carbonates varies from –2.0 to –15‰, whereas the δ^{13}C value of organic carbon ranges from –20 to –26‰ (Lein *et al.*, 1997). These data suggest that 40% or more of dispersed carbonate minerals in the terrigenous mud from the Black Sea are formed due to the reduction of microbial sulfate ion within the upper sediment layer during OM decay, as was described above for mud from the Gulf of California.

The formation of dispersed authigenic carbonates due to microbial OM destruction takes place with various intensities in the majority of reduced Quaternary terrigenous sediments on shelves and continental slopes of the ocean (Lein *et al.*, 1980, 1983) and in marginal and intercontinental seas (Aloisi *et al.*, 2000).

Such authigenic carbonates are characterized by a variable mineralogy, heterogeneous isotopic composition with relatively low δ^{13}C values (from –3.6 to –15.6‰, Table 3), active sulfate reduction (Table 4), and CH$_4$ concentration close to the background value. All these features indicate that the contribution of CH$_4$ to authigenic carbonate formation is negligible in the sediments described above. However, we cannot rule out the possibility that a minor part of dispersed authigenic carbonates in sediments of shelf and continental slope zones may be formed by both aerobic and anaerobic oxidation of methane generated *in situ* during diagenesis. Example of the Gulf of California, where the sulfate reduction rate in the upper mud (20 cm) is higher than the methane generation rate (Table 4), suggests that the diagenetic methane formation in young

Table 4. Changes in chemical composition of pore water from reduced sediments of the Gulf of California and δ^{13}C-CaCO$_3$ of dispersed authigenic carbonates (Ivanov and Lein, 1980; Shishkina and Pavlova, 1976)

Station no., depth, m	Interval, cm	SO$_4^{2-}$, mgeq/kg	Alk, mgeq/kg	Ca^{2+}, mgeq/kg	Mg^{2+}, mgeq/kg	H$_2$S, mgeq/kg	δ^{13}C-CaCO$_3$, ‰
664; 1170	0–5	55.3	2.8	20.3	104	–	–
	60–70	–	–	–	–	0.75	–11.0
	100–140	51.1	2.8	20.0	102	–	–
	150–155	–	–	–	–	0.09	–
	180–208	50.2	7.9	18.4	104	–	–
	260–275	–	–	–	–	0.07	–12.0
	275–310	47.6	9.6	17.5	104	0.01	–11.8
665; 3260	5–20	54.5	4.2	20.2	103	–	–
	40–45	–	–	–	–	112.7	–12.3
	103–135	38.0	15.5	17.5	106	12.5	–13.4
	206–245	31.8	22.3	11.2	100	–	–12.0
	265–305	22.6	27.5	9.8	100	1.7	–

Note: (–) No data.

Table 5. Age of authigenic carbonates

Region	Interval, cm	Morphology	Age, ka	Source
Gulf of California shelf, 120 m	5–40	rounded concre-tions and crusts	11 ± 1.2	Lein et al., 1979
	90–140		14 ± 1.2	
NW shelf of Black Sea, Dnepr canyon	0–10	plates and coral-shaped buildups	3.4 ± 0.6	Ivanov et al., 1991
	0		5.1 ± 1.2	
Norwegian Sea, caldera of Haakon Mosby mud volcano		buildups	8.7 ± 0.16	Lein et al., 2000b
			11.4 ± 0.53	
			10.7 ± 0.24	
			10.7 ± 0.62	
			7.96 ± 0.41	
Sea of Okhotsk, off Para-mushir Is.	0–5	crusts	from 1 to 10	Zonenshain et al., 1987

marine sediments is less intense than sulfate ion reduction (Belyaev and Finkelstein, 1976; Jorgenson et al., 2001; Lein, 1983; Rusanov et al., 1994). The CH$_4$ oxidation with CO$_2$ generation, and authigenic carbonate precipitation may be more significant in sediments of freshwater basins.

TYPE II. METHANE-DERIVED AUTHIGENIC CARBONATES

Methane carbon rather than organic carbon serves as the main source of carbon for these carbonates. Microbial oxidation of methane produces carbon dioxide that participates in the formation of type II carbonates (Hathaway and Degens, 1968). As a rule, this methane enters the sediments from the outside. Discovery of methane seeps in the subduction zone off the Oregon coast (Suess et al., 1985) revived the interest to study of the authigenic carbonate formation. It was ascertained that carbonate buildups are formed in the zones of methane-bearing solution discharge during CH$_4$ oxidation.

Results of the study of sediments with methane gas hydrates from the northern Gulf of Mexico were published in 1984 (Brooks et al., 1984). It was suggested that isotopically light carbonates (δ^{13}C-CaCO$_3$ ranges from –26.8 to –47.5‰) in sediments are formed by the microbial oxidation of biogenic methane hydrates, whereas another portion with δ^{13}C-CaCO$_3$ varying from –17.7 to –33‰ is generated during oil biodegradation.

A detailed study of the area with methane seep near Paramushir Island (Sea of Okhotsk) at the water depth of 786–796 m was carried out with the help of the
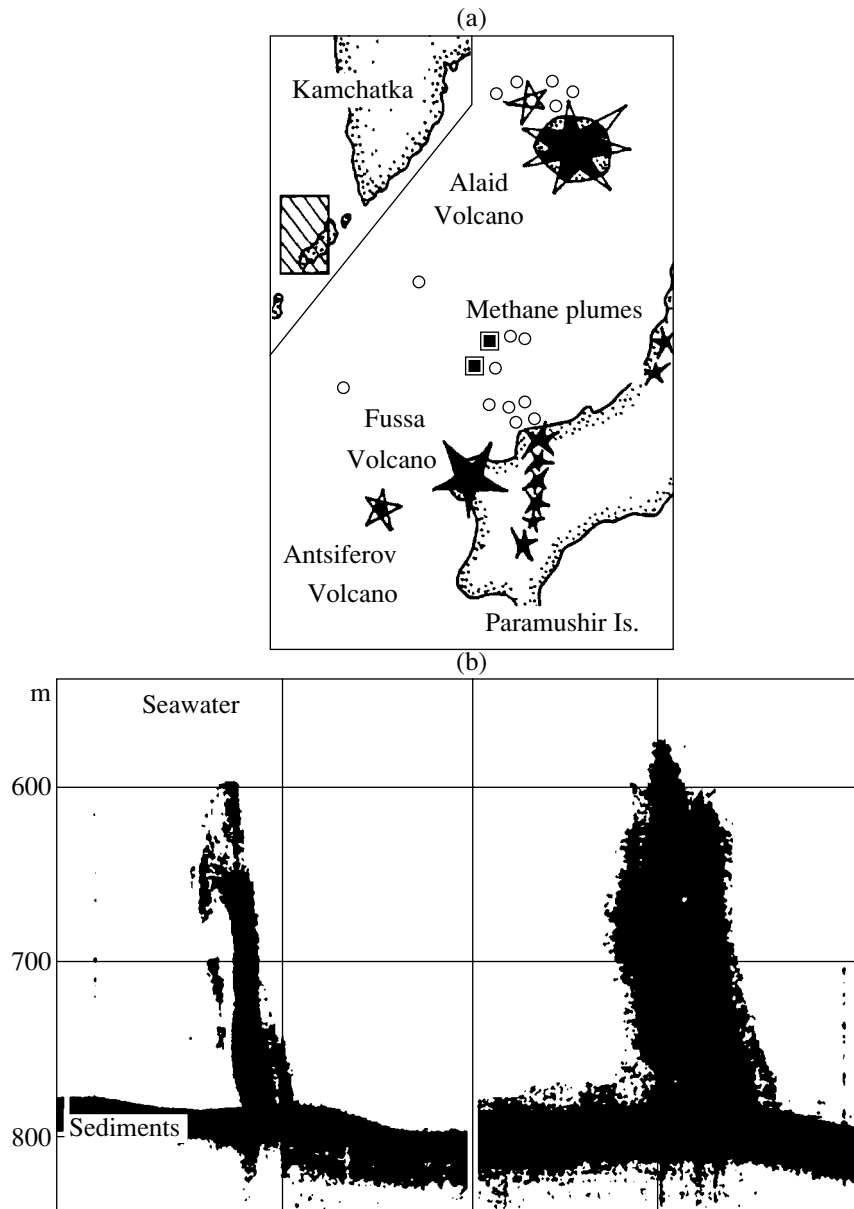
Fig. 4. (a) Location of the methane seeps age area off the Paramushir Island, Sea of Okhotsk and (b) echo sounding image of gas plumes. Submarine and subaerial volcanoes are marked by stars; methane plumes are marked by circles; framed circles indicate studied plumes.

manned submersible *Pisces* during the expedition of R/V *Akademik Mstislav Keldysh* in summer 1986 (Fig. 4). The methane seepage site was 20–25 cm across. The gas bubble emanation rate was about 0.2 m/s, and the bubbles were less than 1 cm in diameter (Zonenshain *et al.*, 1987). Black reduced mud containing free H_2S indicated the proximity of methane seep. The sediment is cemented by carbonate material and locally covered by carbonate crusts. About 2-cm-thick interbed of methane gas hydrates was recovered at the core bottom (180–205 cm). Small gas hydrate lenses occurred within the Holocene mud in a sediment core from the seepage area. The gas contained 97.8 vol % CH_4 ($\delta^{13}C$-CH_4 = −54.6‰), 1.61 vol % N_2, and traces of methane homologues, argon, hydrogene, and carbon dioxide. White patches of microbial mats were observed on the black mud surface. The mats mainly consisted of thionic bacteria oxidizing hydrogen sulfide (Lein *et al.*, 1989). Carbonate cementation was only observed at the bubble discharge site. The active decay of gas hydrates is proved by a freshwater admixture in pore solution and high rate of microbial methane oxidation that exceeds the rate of microbial methane formation (Figs. 5a, 5b; Tables 4, 6) in strongly reduced sed-

iments from the Sea of Okhotsk (Fig. 5b). The total number of four methanotrophic bacteria species (*Methylomanas methanica*, *Methylobacter capsulatus*, *Methylobacter chrooccum*, and *Methylobacter vinelandii*), which are most widespread in marine ecosystems, was counted in bottom water samples (Fig. 5b).

The $\delta^{13}C$ values of carbon in authigenic carbonates from the Paramushir seep site are rather uniform throughout the 2-m-thick mud section and range from −47.5 to −49.2‰. These values are close to those for the gas hydrate methane with $\delta^{13}C = -54.6$‰ (Lein *et al.*, 1989). Isotopically light authigenic carbonates were later found at other sites in the Sea of Okhotsk in a close paragenesis with authigenic pyrite and barite (*Monitoring...*, 2002).

Numerous submarine gas exhalations were discovered in the Black Sea in 1989 at depths from 60 to 650 m, *i.e.*, in both aerobic and anaerobic zones (Polikarpov *et al.*, 1989). Detailed biogeochemical investigations were carried out on a *Benthos-300* submersible laboratory in the northwestern Black Sea in 1990 at 226–230 m (Station 1) and 176–180 m (Station 2) (Ivanov *et al.*, 1991). The study showed that methane is the main component of submarine gas exhalations (~80 vol %). Methane concentration in the bottom water exceeded the background value by two to three orders of magnitude. Observations in the gas discharge area revealed light-colored patches of microbial mats on the monotonous gray mud surface and carbonate buildups of various morphological types: hummocky round plates (diameter 0.5–1.5 m), plates with coral-shaped overgrowths, and high (more than 1 m) free-shaped buildups. Breaking of buildups by a *Benthos* grab resulted in gas bubble exhalation from their cavities and channels. Plates consist of mud cemented by Mg-calcite. Coral-shaped and free-shaped buildups attached to the plates consist of 99.6% aragonite (Lein, 1991; Ul'yanova *et al.*, 1995).

Carbonate buildups contain pyrite. The $\delta^{13}C$ values of carbonate carbon measured in 13 aragonite samples from different parts of a 30-cm-high buildup vary from −32.5 to −40.4‰. The age of buildups is about 5000 yr (Table 5).

The buildups are covered by thick mucous microbial mats. The $\delta^{13}C$ values of biomass carbon in mats range from −75.6 to −83.8‰ (Ivanov *et al.*, 1991). Microbiological study of ultrathin sections of the mats revealed abundant morphologically variable microorganisms, cysts (resting spores), and remains of lysis cells. Only rare methanotroph cells of genus *Methylobacter* and *Methylomonas* occur in the microbial consortium (Ivanov *et al.*, 1991).

Studies carried out in 1991 raised many problems, among which the mechanism of microbial methane oxidation in anaerobic conditions represents a cardinal problem of methane cycle in the biosphere.

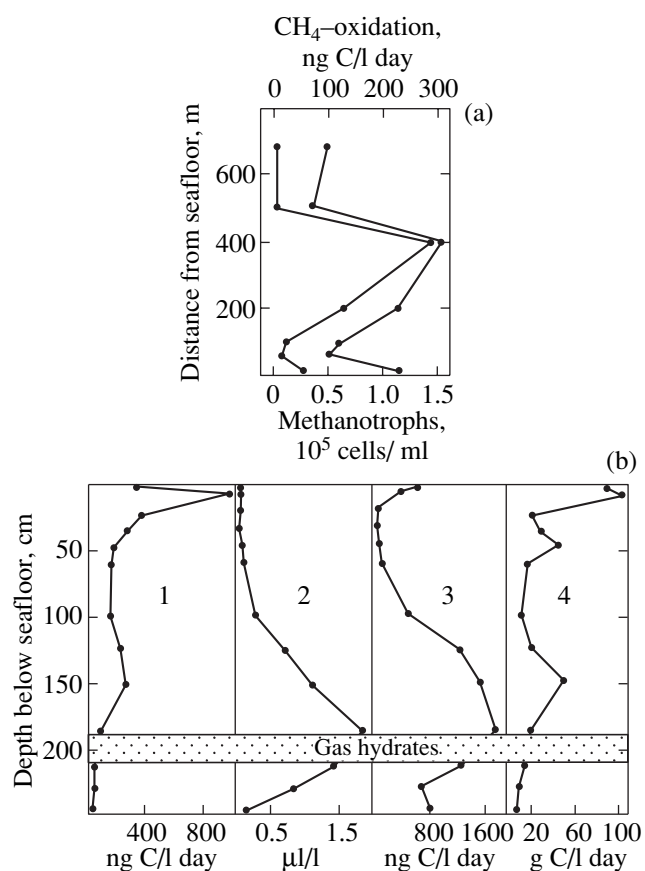We have to emphasize that aragonite buildups are formed in the Black Sea within the stable anaerobic

Fig. 5. Intensity of methane oxidation and methane generation. (a) (1) variation in intensity of methane oxidation and (2) number of methanotrophs in the water column over a methane seep in the Sea of Okhotsk, (b) (1) Profiles of methane generation intensity, (2) methane concentration, (3) methane oxidation intensity, and (4) CO_2 assimilation in sediments from a methane seepage area, Sea of Okhotsk (Gal'chenko, 2001).

zone. Thus, they represent an ideal object for the study of methane oxidation in anaerobic conditions. Investigations of methane seeps and related authigenic carbonates in the Black Sea were continued during expeditions in 1994, 1995, and 2001 (Lein *et al.*, 2002b; Pimenov *et al.*, 1998).

Table 6. Summary intensity values of methane generation and methane oxidation in sediments (thickness 200 cm) and water column in the methane seepage area of the Sea of Okhotsk (Gal'chenko, 2001)

Station no. (studied object)	Intensity, gC/m^2 day	
	CH$_4$ generation	CH$_4$ oxidation
1395 (sediments with gas hydrate interbeds)	212	878
1392 (bottom water in CH$_4$ plume area)	traces	67332

Detailed data on the mineral and isotopic composition of carbonate buildups from the northwestern Black Sea are presented in (Lein *et al.*, 2001, 2002b; Peckman *et al.*, 2001).

Coral-shaped buildups consist of more than 90% aragonite (Figs. 6a–6c), whereas Mg-calcite is cementing terrigenous mud mainly composed of quartz and aluminosilicate minerals (Figs. 6a–6c). Aragonite is represented by spheroidal aggregates with radial-fibrous structure (Figs. 6d–6l) and rodlike growths of prismatic, pyramidal, and spicular crystals (Figs. 6d–6l). Twins and trillings also occur.

Aragonite aggregates from the coral-shaped buildups contain less than 0.3% $MgCO_3$, 0.5–1.5% $SrCO_3$, and 1.13–1.63% C_{org}. The high Sr content in aragonite is explained by a preferential incorporation of strontionite into the crystal lattice of aragonite.

Aragonite aggregates of coral-shaped buildups are literally hidden in thick gel-type microbial mats. The mat surface commonly contains hydrotroilite that stains the outer coating (1–2 mm) of pink mats into black color. Less than 1% CaO and MgO, as well as a negligible admixture of sodium sulfate and P_2O_5 (0.26–1.34%), are detected in the biomass of mats. Phosphate is absent in aragonite crystals.

Some photomicrographs show radial-fibrous and sheaflike aragonite growths with micritic carbonate nuclei enriched in C_{org} (Figs. 6d–6l).

Pyrite occurs in paragenesis with Mg-calcite (Fig. 6b). Barite was found in a carbonate sample from the seep at 1500 m.

As mentioned above, Mg-calcite and aragonite are typical minerals of many well-known methane-derived carbonate buildups. However, such a distinct coral-shaped (free-shaped) morphology of buildups consisting of monomineral aragonite was first recorded in the Black Sea at 170–230 m (Ivanov *et al.*,1991). Further studies in the Dnepr canyon region revealed that most of the methane seeps and high (up to 4 m) buildups composed of authigenic carbonate occur just at these depths (Fig. 7). Comparison of the methane carbon isotopy in recent sediments and gas samples collected by the manned submersible *Jago* directly from exhalations at the Dnepr canyon floor (Fig. 8) suggests that methane is produced as a result of the microbial CO_2 reduction by hydrogen during the diagenesis of Paleoeuxinian and Neoeuxinian sediments (Lein *et al.*, 2002b).

Investigation of the isotopic composition of seep methane showed that the $\delta^{13}C$-CH_4 value varies from −65 to –70.5‰ and the δD-CH_4 value ranges from −132 to –201‰ (Fig. 9). The $\delta^{13}C$ value of Mg-calcite and microcrystalline carbonate minerals in the mud cement ranges from –25.2 to –38.1‰ (Fig. 8). The $\delta^{13}C$ value of aragonite varies from –35 to –46.4‰. Carbonates most depleted in $\delta^{13}C$ occur in microbial mats (Fig. 8). An extremely light isotopic composition of organic carbon ($\delta^{13}C$ from –61.2 to –83.8‰) characterizes the biomass of microbial communities (Fig. 8). Measurements of the carbon isotopic composition of lipid biomarkers (Fig. 8d) indisputably prove the methane oxidation by a microbial consortium in anaerobic conditions.

Oxygen isotopic composition ($\delta^{18}O$) varies from 0.9 to 1.2‰ in microcrystalline carbonate of the mud cement and from 0.2 to 0.8‰ in the monomineral aragonite of coral-shaped buildups (Fig. 10). Enrichment of authigenic carbonates in heavy isotope ^{18}O results, first of all, from isotope fractionation of initial bicarbonate ion during the carbonate formation. The oxygen isotopic composition of carbonates less depends on water temperature.

Investigation of methane seeps in the Dnepr canyon provided several pieces of evidence in favor of a large-scale microbial methane oxidation in the anoxic (H_2S-rich) environment of the Black Sea.

Organic carbon of microbial mats and aragonite buildups is considerably enriched in light ^{12}C relative to the methane carbon used for intermediate (e.g., methanol or formiate) and final (carbon dioxide) methane oxidation products in processes of biological isotope fractionation during fermental synthesis of the methane-oxidizing microbial biomass (Fig. 8).

Microbiological nature of methane oxidation with the subsequent methane-derived carbonate precipitation is proved by distribution patterns of oxygen and carbon stable isotopes in carbonates and OM (Figs. 8–10), radiocarbon estimates of linked methane oxidation and sulfate reduction rates (Table 7, Fig. 11), and molecular-biological studies of microbial mats (Ivanov *et al.*, 1991; Michaelis *et al.*, 2002; Pimenov *et al.*, 1997; Turova *et al.*, 2002).

Thus, we considered the isotope geochemistry of authigenic carbonates formed as a result of the oxidation of diagenetic methane delivered from underlying sediments to the Dnepr canyon of the Black Sea. This

Fig. 6. SEM images and energy-dispersive spectra of authigenic carbonates. Mg-calcite and paragenetic sulfides and sulfates: (a) fine-grained carbonate (Peckman *et al.*, 2001) cementing terrigenous mud, (a_1) energy-dispersive spectrum of carbonate represented by authigenic Mg-calcite (silica and aluminosilicates are derived from the terrigenous material of enclosing sediment), (b) framboidal pyrite (light-colored spherules) as patches within carbonate plates, (b_1) energy-dispersive spectrum of pyrite, (c) authigenic barite (light) in carbonate matrix, (c_1) energy-dispersive spectrum of barite; monomineral authigenic aragonite in coral-shaped buildups from anaerobic zone: (d) radial-fibrous aragonite, (d_1) energy-dispersive spectrum of aragonite, (e) radial-fibrous aragonite, detail of (d), (f) radial-fibrous growths of yellowish aragonite with intense fluorescence (enriched in organic matter), (g) spicular aragonite crystals with numerous twins; (h) long-prismatic aragonite crystals; (i) radial-fibrous and fibrous aragonite with high microbial biomass content (black); (j) the same as (i), microcrystalline carbonate with intense fluorescence (Peckman *et al.*, 2001); (k) microcrystalline carbonate (dark) and radial-fibrous aragonite; (l) energy-dispersive spectrum of a sample of aragonite buildup impregnated with microbial biomass.
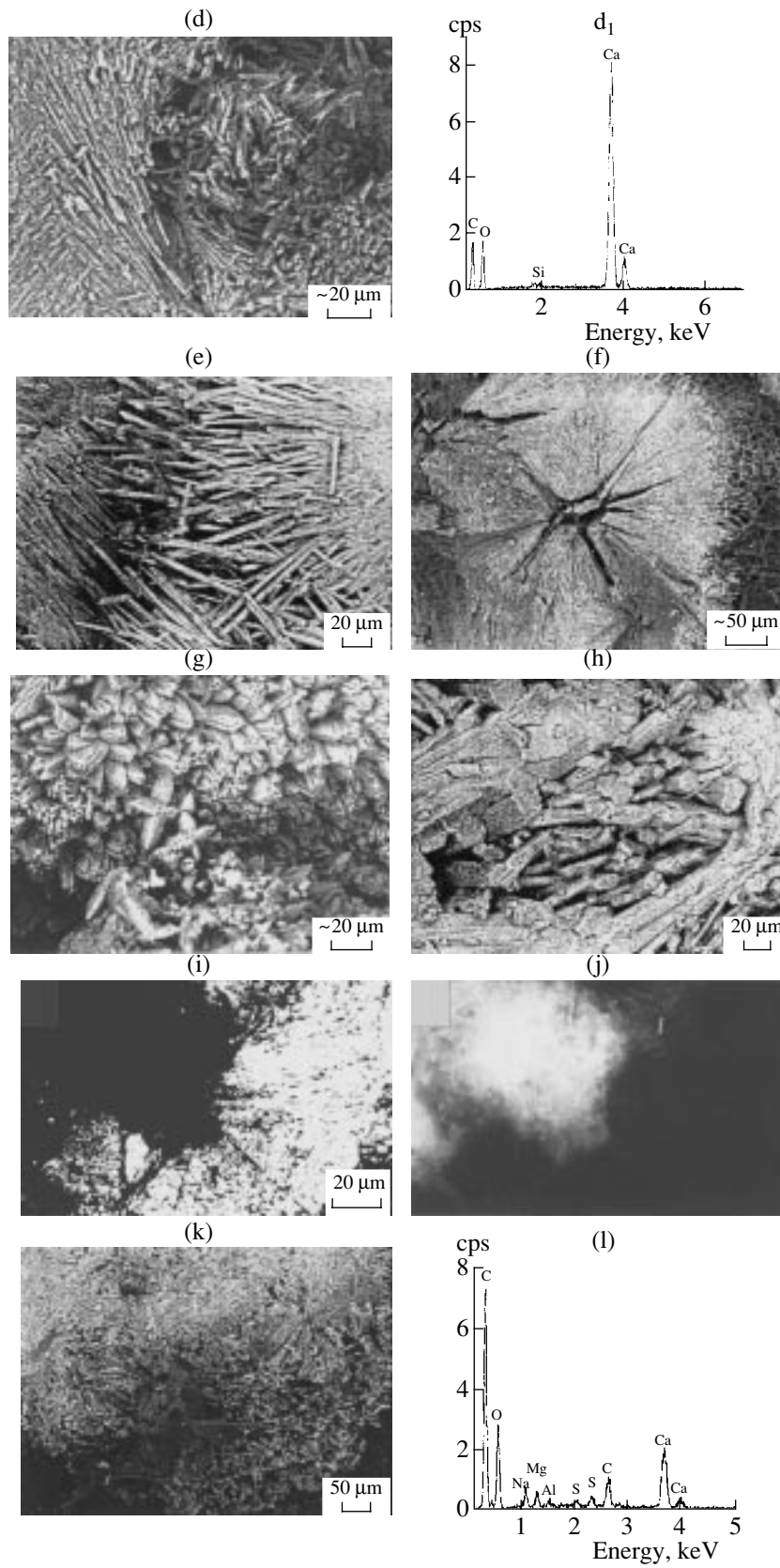
(d)

d_1

(e)

(f)

(g)

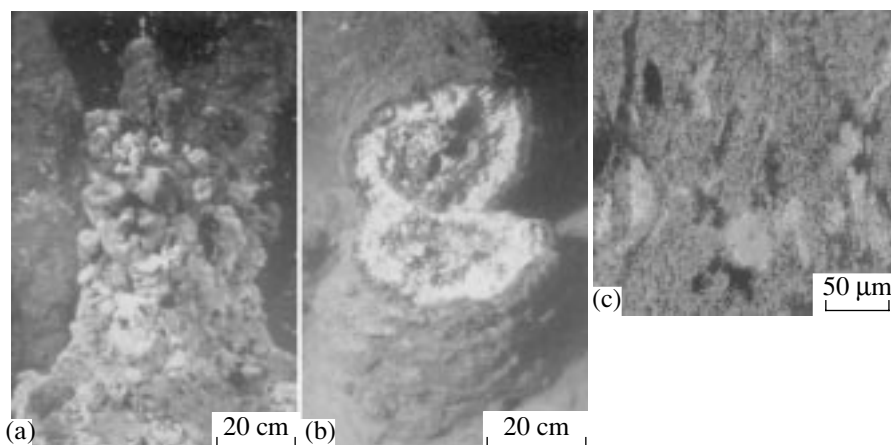(h)

(i)

(j)

(k)

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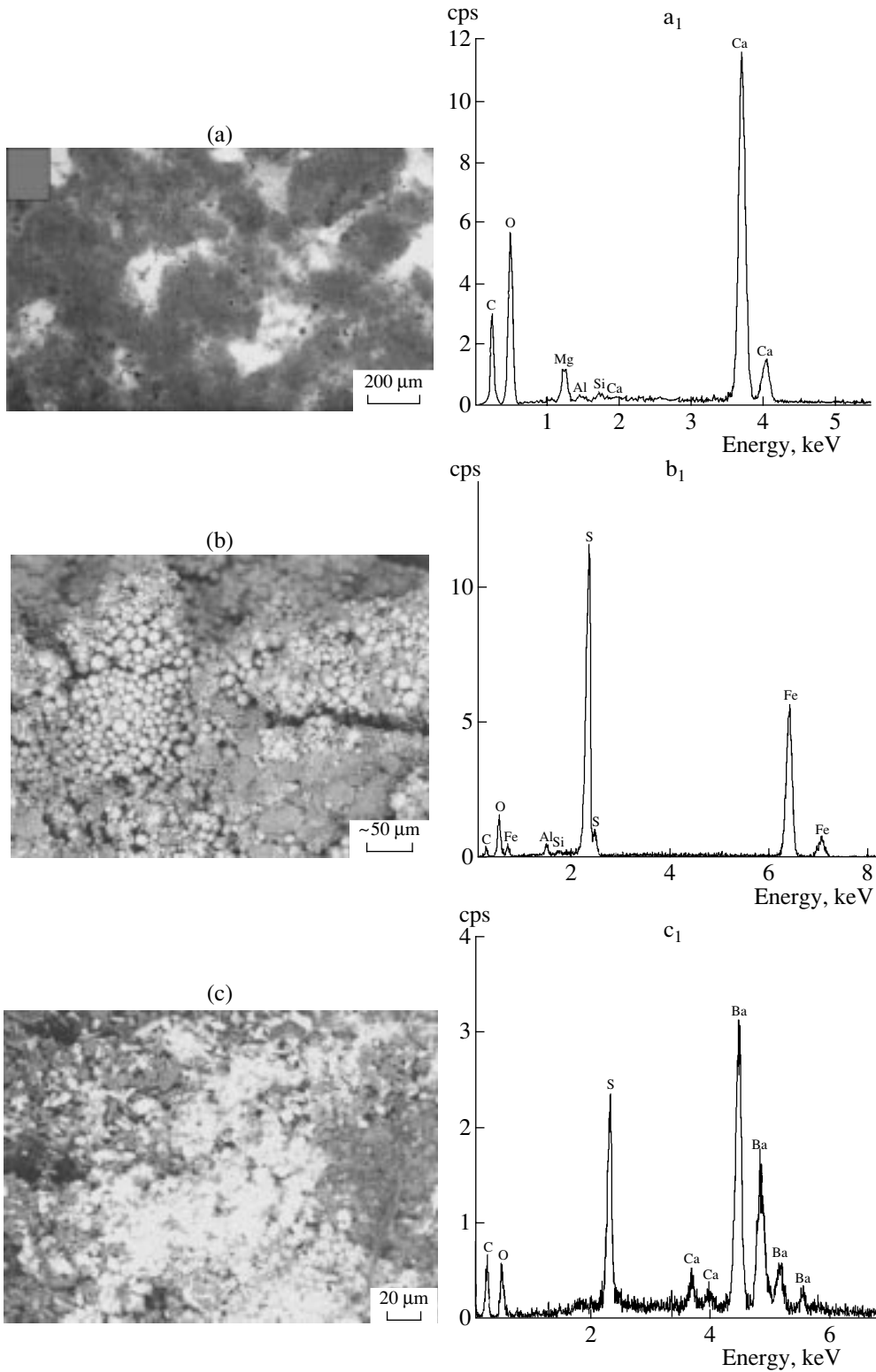
Fig. 6. (Contd.)

Fig. 7. Authigenic carbonate buildups composed of jelly-like microbial biomass and aragonite on the Dnepr canyon floor, Black Sea (Michaelis *et al.*, 2002). (a) Top of a buildup; free methane is releasing as bubbles into anaerobic seawater; (b) internal structure of a disturbed buildup; the outer cover is darker owing to hydrotroilite (FeS_{n-1}) precipitation; the internal zone is composed of pink microbial mat with carbonates transformed into gray porous mixture of microbial biomass and carbonates; (c) microcolony of sulfate-reducing bacteria (coccoids) surrounded by clusters of methanotrophic archeabacterial cells (ANME-1).
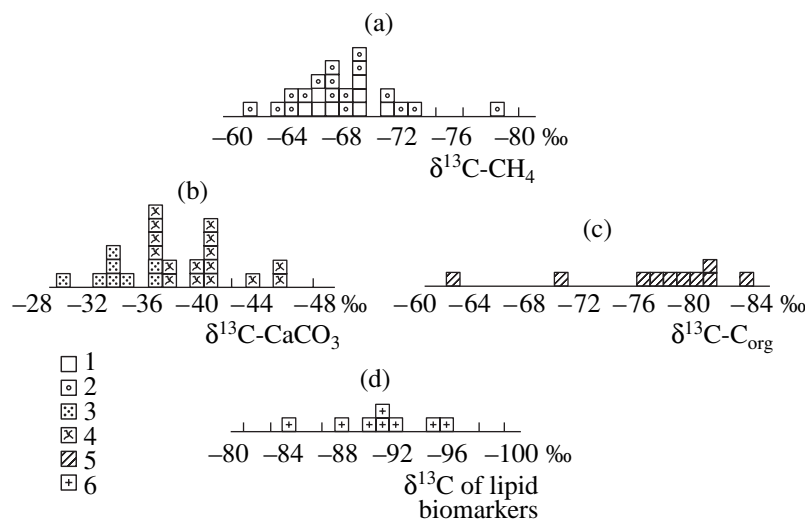

Fig. 8. Histograms of $\delta^{13}C$ values of (a) methane, (b) authigenic carbonates, (c) organic carbon, and (d) lipid biomarkers in carbonate buildups from active methane seepage fields in the Dnepr canyon, Black Sea. (1) Carbon of diagenetic methane in bottom sediments; (2) methane carbon of bubble-stream gas discharges from carbonate buildups and sediments; (3) carbon of authigenic carbonate plates; (4) carbon of authigenic carbonate buildups; (5) carbon of microbial biomass developed on carbonate buildups; (6) carbon of *n*-alkanes and other lipids extracted from microbial mats.

raises the question of the main difference between these carbonates and methane-derived carbonates generated during the oxidation of migrational thermogenic methane (including the gas hydrate variety) in the Black Sea. Methane gas hydrates are widespread in ocean below water depths of 600–700 m. According to various estimates, they contain 10^6 Tg CH_4 (Ginsburg and Solov'ev, 1994; Milkov and Sassen, 2002). If the stability condition of gas hydrates is disturbed, their deposits are destroyed and methane migrates to the seafloor.

Mud volcanism is a common cause of the destruction of gas hydrate deposits at passive continental margins. Mud volcanism results in the discharge of methane-bearing fluids, methane oxidation, and authigenic carbonate formation.

The genesis of authigenic carbonates has been scrutinized in the caldera of the active Haakon Mosby mud volcano (HMMV) in the Norwegian Sea. Along with mineralogical and isotope-geochemical analyses of the
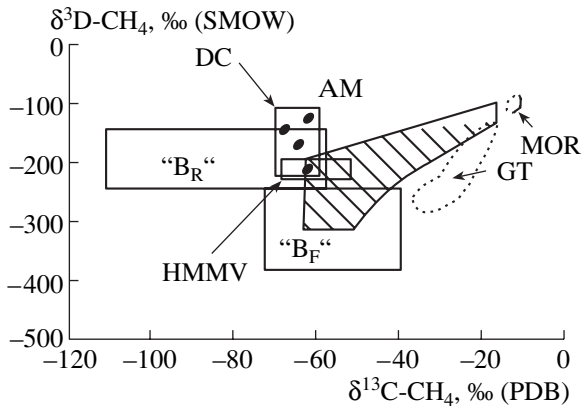
Fig. 9. Diagram of the relationship between δD-CH$_4$ and δ^{13}C-CH$_4$ (Schoell, 1988). Fields of δD and δ^{13}C for methane: (HMMV) Haakon Mosby mud vocano, Norwegian Sea; (DC) Dnepr canyon bubble-stream, Black Sea.
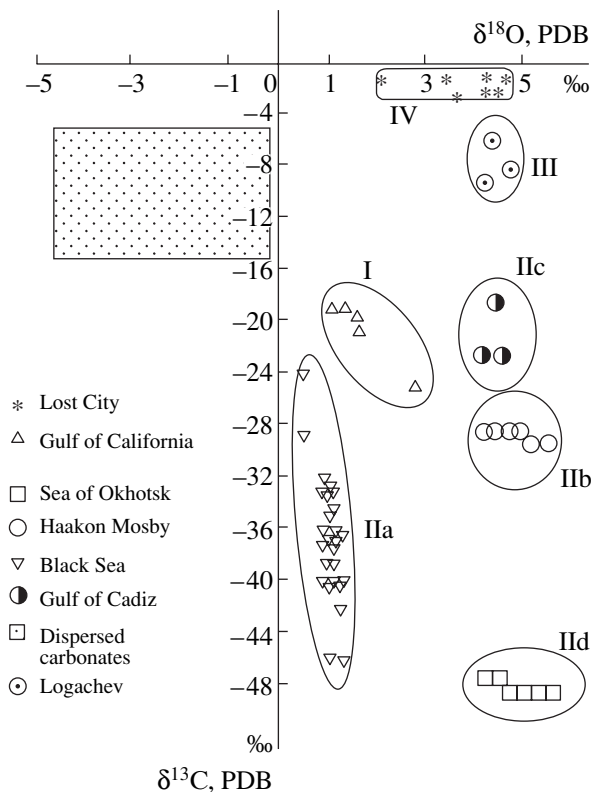

Fig. 10. Diagram showing relationship between isotopic compositions of carbon and oxygen in authigenic carbonates of different origins. (I) Diagenetic carbonates formed due to organic matter decay; (II) methane-derived carbonates: (a) diagenetic methane, (b) thermogenic methane, (c) mixed (thermogenic + hydrothermal) methane; (III–IV) hydrothermal authigenic carbonates; (III) oxidation of hydrothermal methane; (IV) seawater ΣHCO$_3^-$ and Ca^{2+} of hydrothermal fluid.

carbonates, biogeochemical processes of sulfur and carbon cycles related to the activity of various microbial groups were studied here both within sediments and at the water–bottom interface (Lein *et al.*, 1997b, 1998, 2000a, 2000b; Pimenov *et al.*, 2000).

Authigenic carbonates make up conical, columnar, and crustal buildups on the caldera floor and slopes and summits of mounds surrounding the caldera. Their height ranges from several centimeters (plates) to 30 cm. The buildups are subdivided into "living" ones which are overgrown with benthic fauna and located within the most active zone of the caldera, and inactive ones occurring at the caldera margin. The base of living buildups is buried in black reduced sediments containing CH$_4$ and H$_2$S. In addition to carbonate (37–50%), the buildups contain silica and clay mineral components. The chemical composition of authigenic buildups calculated on the carbonate-free basis is similar to that of methane-bearing mud and mud volcanic breccia in the caldera (Lein *et al.*, 1998). Rock fragments of various sizes are cemented by micritic carbonate and clay minerals (Fig. 12). The detrital material consists of quartz (~25%), feldspars (~10%), mica (2–5%), and organic remains (up to 5%) represented by pogonophora tube fragments, sponge spicules, benthic foraminiferal tests, and shell fragments.

Calcite occurring as micrometer-sized aggregates is the dominant mineral phase of authigenic carbonates (Fig. 13). Diagenetic pyrite, zeolites, and Sr-barite are detected in paragenetic association with the carbonate (Fig. 13). Magnesium, a common component in marine authigenic carbonates, was not detected in any of the energy-dispersive spectra (Lein *et al.*, 2000b; Suess *et al.*, 1998; Von Rad *et al.*, 1996).

The X-ray diffraction data confirmed that calcite (Ca$_{0.85}$C$_{1.2}$O$_{3.32}$) is the only authigenic carbonate mineral in buildups of the Haakon Mosby caldera (Lein *et al.*, 2000b).

The δ^{13}C value of authigenic carbonate carbon varies from –28.4 to –29.6‰ (Table 8). The δ^{18}O (δ^{18}O = 4.3–5.4‰ values relative to PDB) also show minor variations (Fig. 10). These carbonates are enriched in ^{18}O relative to the dispersed carbonate from mud-volcanic rocks and oxygen of seawater, pore water, and CH$_4$-gas hydrate water (Fig. 14).

Carbonate buildups are located at the boundary between bottom water and strongly reduced (Eh = –300 mV) methane-bearing mud-volcanic rocks with free H$_2$S (Lein *et al.*, 1998, 1999).

The major salt composition of pore water from rocks is characterized by an anomalously low concentration of Cl$^-$, SO$_4^{2-}$, Ca^{2+}, and Mg^{2+} and high content of biogenic elements (Fig. 15). Almost total reduction of sulfate ion in the upper 10-cm-thick layer of sediments, where SO$_4^{2-}$ concentration decreases from 28 to 0.86 mM, seems especially unusual.

Table 7. Rates of microbial processes in surface sediments and microbial mats within active methane seep age fields in the Dnepr canyon, Black Sea

Depth, m	Reaction rate		Source
	sulfate reduction, M S/dm^3 day	methane oxidation, M CH$_4$/dm^3 day	
sediments from the seep area, interval 0–2 cm*			
77 (3 samples)	6–17	0.21	Dando, Niven, 1998; Rusanov *et al.*, 1994 Lein *et al.,* 2002
195	17.5	–	
260	2.9	0.1–2.5	
590	11.0	–	
microbial mats			
230	M S/g day	M CH$_4$/g day**	Michaelis *et al.,* 2002
	19 ± 1	18 ± 12	
190	g S/dm^3 day	g C/dm^3 day	Pimenov *et al.*, 1997
	608 (maximum value)	252 (maximum value)	

Notes: Reaction rates are given in units used by authors of the cited publications (unification of the units may lead to considerable errors); (*) sulfate reduction rate below 0–2 cm does not exceed 1.5 M S/dm^3 day; (**) calculated per 1 g of dry sediment; (–) no data.

The total alkalinity value is up to 23.0 mg eq/l. Concentrations of Br and I are 4–5 times higher than the background ones. The ammonium nitrogen concentration (~3 mM) is high throughout the entire studied core section. The Ca concentration falls precisely at the water–sediment interface (Fig. 15).

Based on geochemical data, we can propose the following model of pore water formation in the surface layer of HMMV caldera sediments. The methane-bearing fluid, which is characterized by low H$_2$S concentration and salinity owing to gas hydrate decomposition, ascends to the sediment surface and mixed with the bottom water to form pore solution containing sulfate ion.

Presence of sulfate ion strongly enhances the microbial sulfate reduction and generation of HS$^-$ and HCO$_3^-$ ions. Along with the anaerobic methane oxidation, this promotes the precipitation of calcium carbonates from the solution and the formation of authigenic carbonate buildups that contain isotopically light CO$_2$ carbon generated during the microbial methane oxidation (δ^{13}C-HCO$_3^-$ up to –31.6‰) and organic matter decay as a result of sulfate reduction in surface sediments (δ^{13}C-HCO$_3^-$ = –18.7‰).

Negative Eh values even in the upper sediment layer (0–2 cm) indicate anaerobic methane oxidation with the formation of microbial mats on methane-bearing sediments. Active oxidation of reduced compounds with a dominating contribution of large filamentous sulfur-rich bacteria *Thriotrix, Beggiatoa* and sulfur-free *Leucothrix* takes place on the surface of mats. Such bacteria may reach up to 100 µm in length and up to 8 µm in diameter (Pimenov *et al.*, 2000). Authigenic carbonates and microbial mats are not observed in sediments with the normal reducing diagenesis beyond the seep field where methane discharge is absent.

Microbiological studies showed that the total number of microorganisms in the surface layer (0–10 cm) of methane-bearing sediments reaches 1.2×10^9 cells/cm^3, including the number of sulfate reducers equal to 10^7 cells/cm^3 and the number of methanotrophs equal to 10^6 cells/cm^3 (Pimenov *et al.*, 2000). The average rate of anaerobic methane oxidation estimated in 9 samples was 744 ml C/dm^3 day, whereas the average sulfate reduction rate was 10 mg S/dm^3 day (Fig. 11). In some cases, the rate of these microbial processes in the surface layer of sediments reached ~1.6 ml C/dm^3 day and 17 mg S/dm^3 day, respectively (Fig. 16). Anaerobic microbial processes of sulfate reduction and methane oxidation in the surface layer of methane-bearing sediments from the caldera explain the additional input of bicarbonate ion into the pore solution. This provides favorable conditions for the precipitation of authigenic carbonates with a mixed carbon isotopic composition (methane oxidation + OM decay during sulfate reduction + seawater bicarbonate) and domination of methane carbon.

In addition to isotope and microbiological data, ^{14}C dates of carbonate carbon equal to 8–11 ka (Table 5), which are lower than the age of gas hydrate methane (~18 ka) (Bogdanov *et al.*, 1999), also support the dominating role of methane carbon in the authigenic carbonate formation. The younger age of methane-derived carbonates in the buildups is a result the contribution of modern sources of carbon dioxide to the carbonate formation.

Thus, carbon in the authigenic calcite is derived from mixed sources, including bicarbonate of the pore water and carbon dioxide generated during the OM decay and anaerobic and aerobic oxidation of methane.
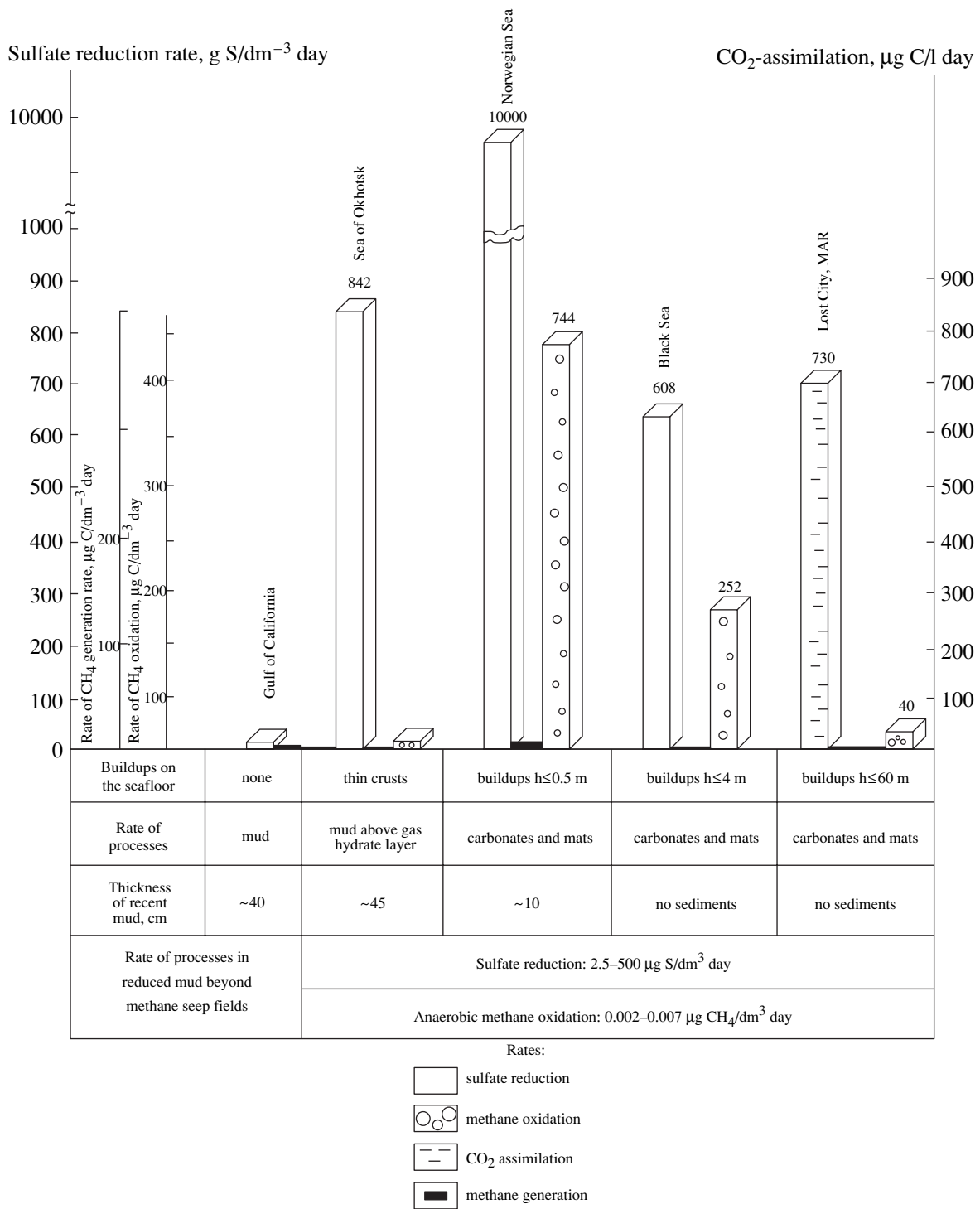
Fig. 11. Rates of microbial processes (average values) in sediments from active methane seepage areas.
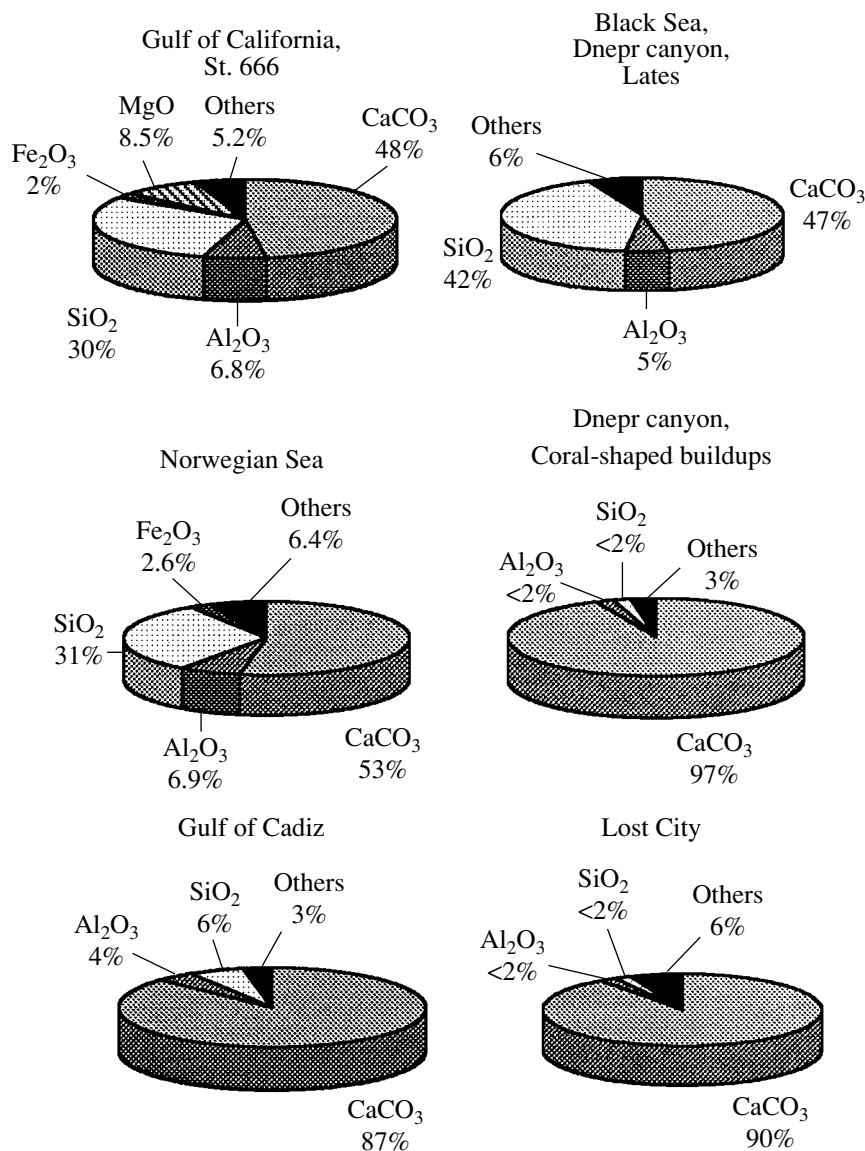
Fig. 12. Major components of authigenic carbonate buildups from different regions of the ocean.

Bicarbonate of seawater and/or pore water serves as the main oxygen source of oxygen for calcite (Fig. 14).

Microbiological processes of methane oxidation and sulfate reduction create physicochemical conditions necessary for the carbonate precipitation. At the site of a living buildup, the pore water becomes oversaturated in bicarbonate that results in the extraction of Ca^{2+} from the pore solution to form calcite. Geochemical parameters in such areas are as follows $Mg^{2+}/Ca^{2+} = 3.3/1$; ΣCO_3^{2-} (Alk)/Ca^{2+} = 5.7/1. These parameters characterize the field of Mg^{2+}-free calcium carbonate precipitation at ~0°C at the caldera bottom of the Transpolar mud volcano (Lein *et al.*, 2000b).

The living buildup is overgrown with symbiotrophic animals, including pogonophora *Scleronimum sp.* that cannot live without methane inflow (Pimenov *et al.*, 1999). The occurrence of authigenic carbonate buildups at the water–bottom interface is related to input of seawater sulfate ion into the surface layer of sediments, because only traces of sulfate ion are present in the methane-bearing fluid and subsurface caldera deposits. Biomass of methane-oxidizing organisms serves as an additional substrate for the vital activity of sulfate reducers.

The authigenic carbonate formation related to methane-bearing mud volcanic fluids was first discovered in the Gulf of Cadiz at a depth of 956–961 m in 2000 (Stadnitskaia *et al.*, 2001; Vermeesch *et al.*, 2000). The study region includes a methane seepage zone. Like the HMMV caldera, this region is marked by the formation of authigenic carbonates at the geochemical barrier
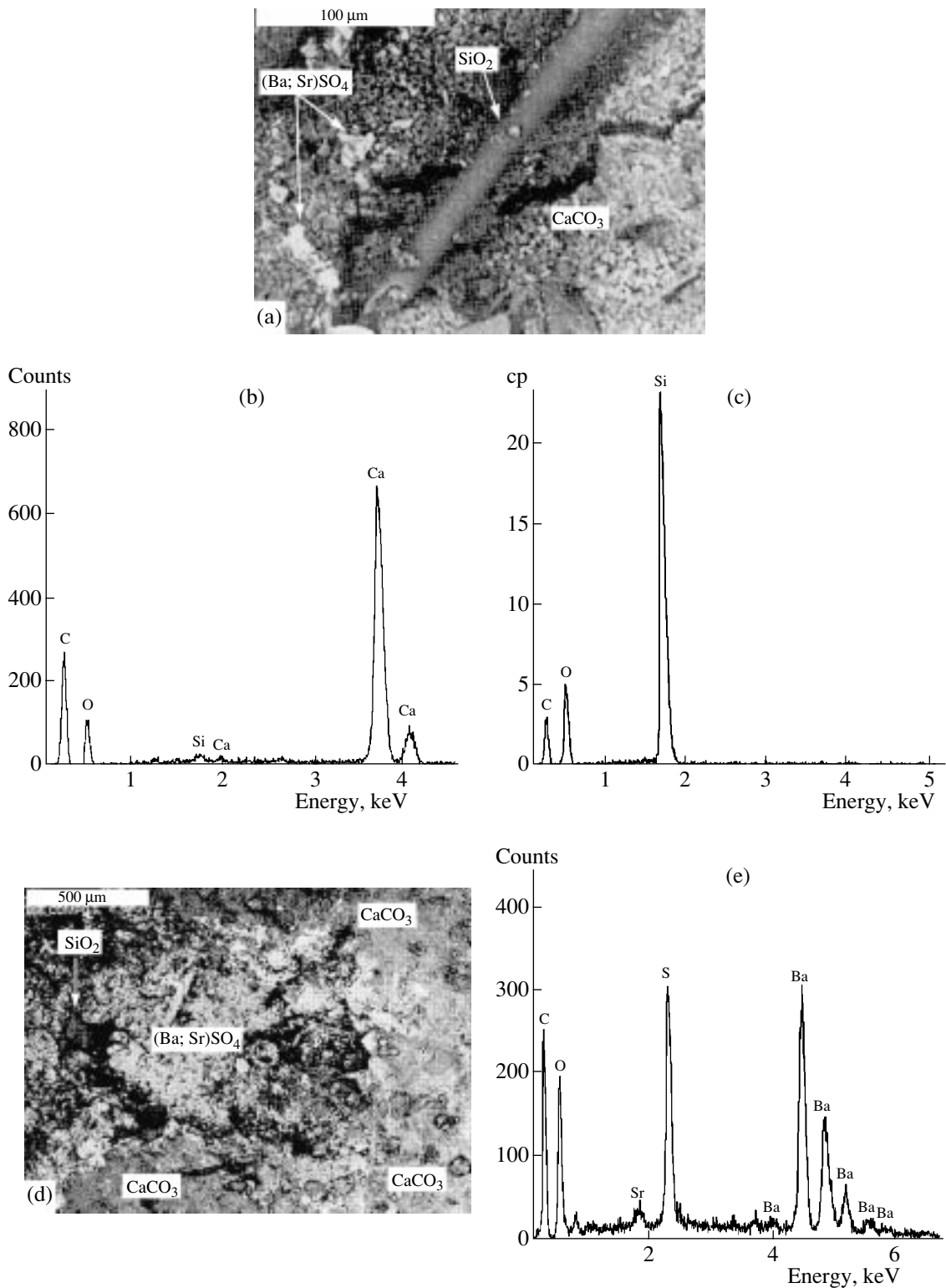
Fig. 13. SEM images and energy-dispersive spectra of the major mineral phases of authigenic carbonates. (a, d) SEM images; energy-dispersive spectra: (b) carbonate, (c) silica, (e) Sr-barite.

between the bottom water and reduced (H_2S^- and CH_4-bearing) sediments.

Along with calcite, carbonates contain Mg-calcite (Figs. 12, 17). Study of authigenic carbonates from the Gulf of Cadiz revealed the following characteristic features of the methane-derived carbonates: (1) typical morphology of buildups; (2) specific mineral composition and structure of the carbonate; (3) light carbon isotopic

composition of carbonates and OM in the buildups; and (4) enrichment of carbonate oxygen in ^{18}O (Fig. 10).

However, carbonates from the Gulf of Cadiz display some specific features relative to other methane-derived carbonates. Among them, a relatively high content of heavy carbon isotope (^{13}C) in the carbonate carbon ($\delta^{13}C$ ranges from –11.0 to –23.1‰) seems to be the most important.

The high ^{13}C content in authigenic carbonates from the Gulf of Cadiz may be explained by the higher ^{13}C value of carbon, at least in a part of the migrating methane ($\delta^{13}C$-$CH_4 \sim$ –32.0‰) and its homologues ($\delta^{13}C$-C_2–C_5 varies from –19.2 to –29.0‰) (Stadnitskaia *et al.*, 2001). The polygenetic nature of the migrated methane is also possible in this case. It may be represented by thermogenic (+diagenetic) methane from sedimentary rock masses and by abiogenic methane related to hydrothermal processes in basaltic (or ultramafic rocks) of the oceanic crust. The Gulf of Cadiz is located within the southeastern part of the Azores–Gibraltar fracture zone located south of the Cadiz–Alicante fault, i. e., in the complicated interaction zone of African and Eurasian lithospheric plates (Kazmin *et al.*, 1990). Hydrothermal processes related to serpentinization of ultrabasites commonly accompany the compression tectonics typical of this region. Such hydrothermal processes have been reported from in this region. We may assume that methane and other hydrocarbons in methane seep fluids of the Gulf of Cadiz are related to both mud volcanism and hydrothermal processes, which commonly promote the synthesis of methane with $\delta^{13}C$ ranging from –14 to –21‰ (Lein, 2001).

TYPE III. AUTHIGENIC CARBONATES FORMED DURING THE MICROBIAL OXIDATION OF HYDROTHERMAL METHANE

Participation of abiogenic methane in authigenic carbonate formation within the Logachev active hydrothermal field (14°45′ N, Mid-Atlantic Ridge) was first recorded in 1998. The $\delta^{13}C$-CH_4 value reaches –14.4‰ [Lein, 2001]. The $\delta^{13}C$ values in the fine-grained carbonate, which cements terrigenous material of surface sediments in the diffuse low-temperature methane discharge area ("Anin Sad") vary from –4.4 to –11.0‰.

Authigenic carbonate of crusts is observed as fine-grained aragonite (Fig. 18a). Crusts and buildups occur within a small field of reduced dark gray coarse-grained sediments and silty mud. Fluids with a high methane content (1375.22×10^{-3} ml/l) discharge at this site. This area also contains symbiotrophic mollusks (Fig. 18b) with the ^{13}C value of their biomass (legs and branchiae) equal to –14‰, which is close to that of the hydrothermal methane. Carbon of organic matter in crusts appeared to be isotopically light $\delta^{13}C_{org\ crust} = -27.6$‰) relative to C_{org} in enclosing sediments ($\delta^{13}C_{org\ sed} = -22.2$‰).

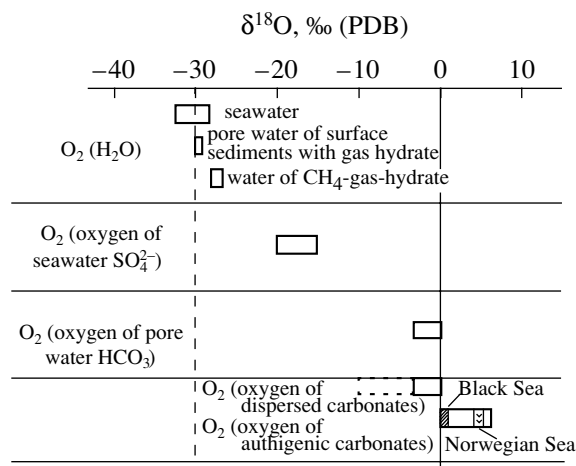**Fig. 14.** $\delta^{18}O$ values of oxygen in seawater, pore water, gas hydrate water, sulfate ion, dispersed carbonates, and authigenic carbonates.

Hence, OM of carbonate buildups mainly represents microbial biomass participating in the oxidation of reduced compounds (CH_4, H_2S, H_2, and others) in the hydrothermal fluid. In other words, ^{13}C depletion of OM from authigenic carbonates is explained by the microbial oxidation of CH_4, OB, H_2S, and other compounds with the generation of chemosynthetic OM. Lipid biomarkers typical only for microbial biomass were identified in the C_{org} composition of sediments with carbonate buildup fragments.

It is worth mentioning that the discovery of authigenic carbonates in the Logachev field did not attract a proper attention. Further observations showed that this kind of authigenic carbonate formation may represent a large-scale process at sites of hydrothermal fluid discharge in mid-oceanic ridges. Methane and carbon dioxide of the fluids are not obligatory carbon sources for carbonates in these processes.

TYPE IV. AUTHIBENIC CARBONATES FORMED DURING THE MIXING OF HYDROTHERMAL FLUID WITH SEAWATER

In 2000, American expedition of the R/V *Atlantis* with the *Alvin* submersible on board discovered light-colored columnar hydrothermal carbonate buildups in the MAR at a depth of 700–850 m (Kelley *et al.*, 2001). Summits and walls of living buildups were washed by warm (40–75°C) solutions. This hydrothermal field, about 100 m in diameter, was named the Lost City. It is located at 30° N, 15 km away from the MAR junction with the Atlantis transform fault. The Atlantis Massif composed of black ultramafic rocks rises from the transform fault floor (depth 3800 m) to a depth of less than 1000 m (Lein *et al.*, 2002a). Beginning with a depth of about 1000 m, its slopes become gentler. Fragments of these rocks are cemented by the lithified carbonate sediment on the exposed black bedrock surface
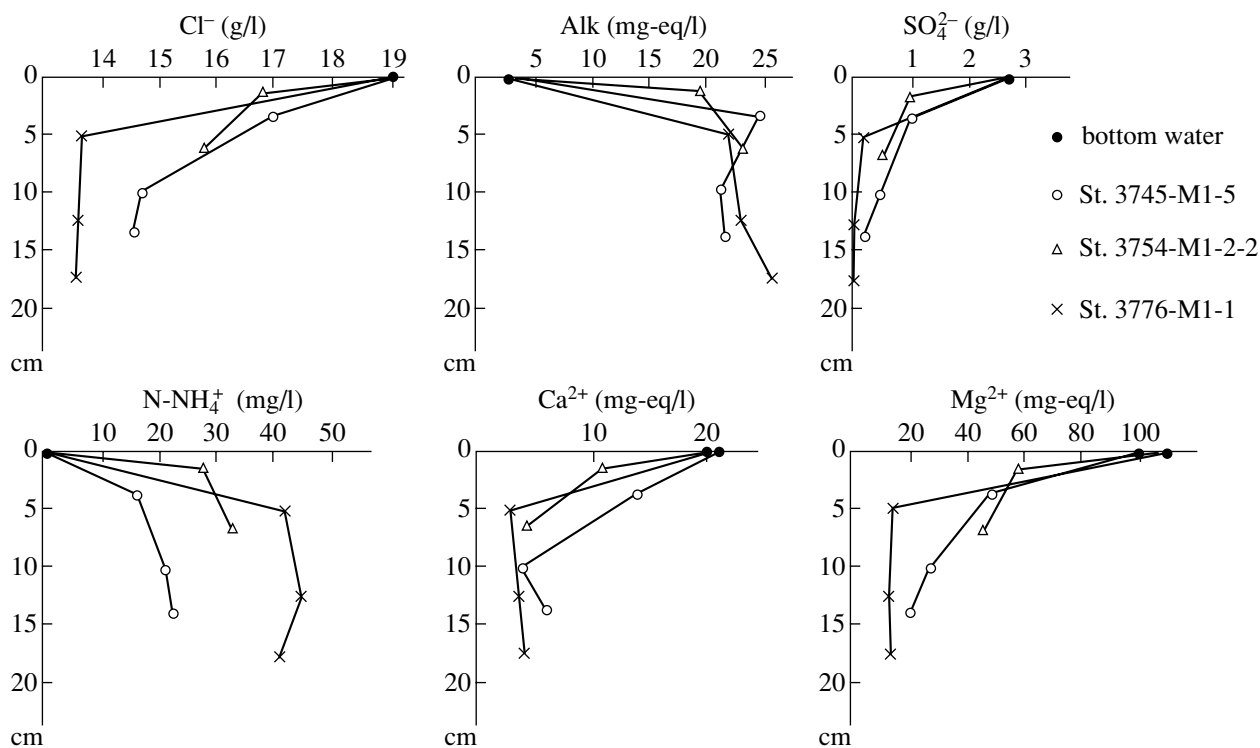
Fig. 15. Distribution of Cl^-, alkalinity, SO_4^{2-}, $N-NH_4^+$, Ca^{2+}, and Mg^{2+} in bottom water and pore water of the upper sediment layer (0–20 cm) from the caldera of Haakon Mosby mud volcano, Norwegian Sea.

with rare light-colored aragonite veinlets ($\delta^{13}C = -4‰$; $\delta^{18}O = 0.4$–5.4‰, PDB). Numerous carbonate plates persist to appear at the depth of about 900 m where the Lost City hydrothermal field begins. Approximately 30 light-colored columnar carbonate buildups rise here above the carbonate plates. Large buildups are up to 60 m high and 10 m in diameter (Fig. 19). The columns consist of aragonite (with minor calcite), brucite $Mg(OH)_2$, and Na–Ca-carbonate (Table 9). Strontium is present among trace elements (0.18–2.74%).

Carbonate columns of the Lost City field represent a new phenomenon in the ocean. Their origin is related to the discharge of strongly altered hydrothermal solutions. Relative to seawater, seeps of alkaline solution (pH = 8.14–9.9) are characterized by decreased concentrations of Mg^{2+} and SO_4^{2-} ions, twofold Ca^{2+} excess (Table 10), and increased concentrations of Cl^-, Na^+, Ba^{2+}, and some other cations. The solution contains CH_4, H_2S, and H_2.

Isotope ratio $^{87}Sr/^{86}Sr$ suggests a mixed origin of the fluid (seawater + deep-seated source). Judging by isotope values δD and $\delta^{18}O$ of the fluid, seawater predominates in its composition. At discharge sites of the low-temperature fluid, buildups are overgrown with dense microbial mats composed of various microbial groups dominated by colorless filamentous H_2S-oxidizing bacteria (Lein *et al.*, 2002a). Carbonates in the columns are

impregnated by hydrothermal solutions, which fill thin (0.5–3 mm) channels and cleavage joints. Bright white jellylike accumulations of microorganisms and their metabolism products (primarily, mucus) are widespread in the internal part of columns, especially on flattened buildup summits with flickering warm water outflows. The amount of jellylike and filamentous microbial biomass may reach 3–5 and 0.3–0.5 g/kg of rock mass, respectively. Active processes of microbial CO_2 assimilation and methane oxidation are detected in jellylike clots (Fig. 11). Considerable amounts of CO_2, CO, and hydrocarbons are identified in decrepitograms of inclusions in carbonates (V.B. Naumov, private communication). Distinct maxima of even low-molecular alkanes C_{12}–C_{16} indicate a microbial nature of *n*-alkanes in hydrocarbons from the carbonate buildups. Abundant cycloalkanes almost totally composed of microbes are also typical of the carbonates and solutions.

Based on geological and mineralogical–geochemical investigations, the formation model of hydrothermal carbonate buildups in the Lost City is as follows (Fig. 20). In the subsurface zone of bedrock crushing, the ascending hot hydrothermal solution enriched in methane and, especially, hydrogen meets the oceanic bottom water and cools down to a temperature below 100°C. As a result, the fluid composition considerably changes to form a secondary mixed solution. Metals are virtually absent in the secondary solution, but it con-
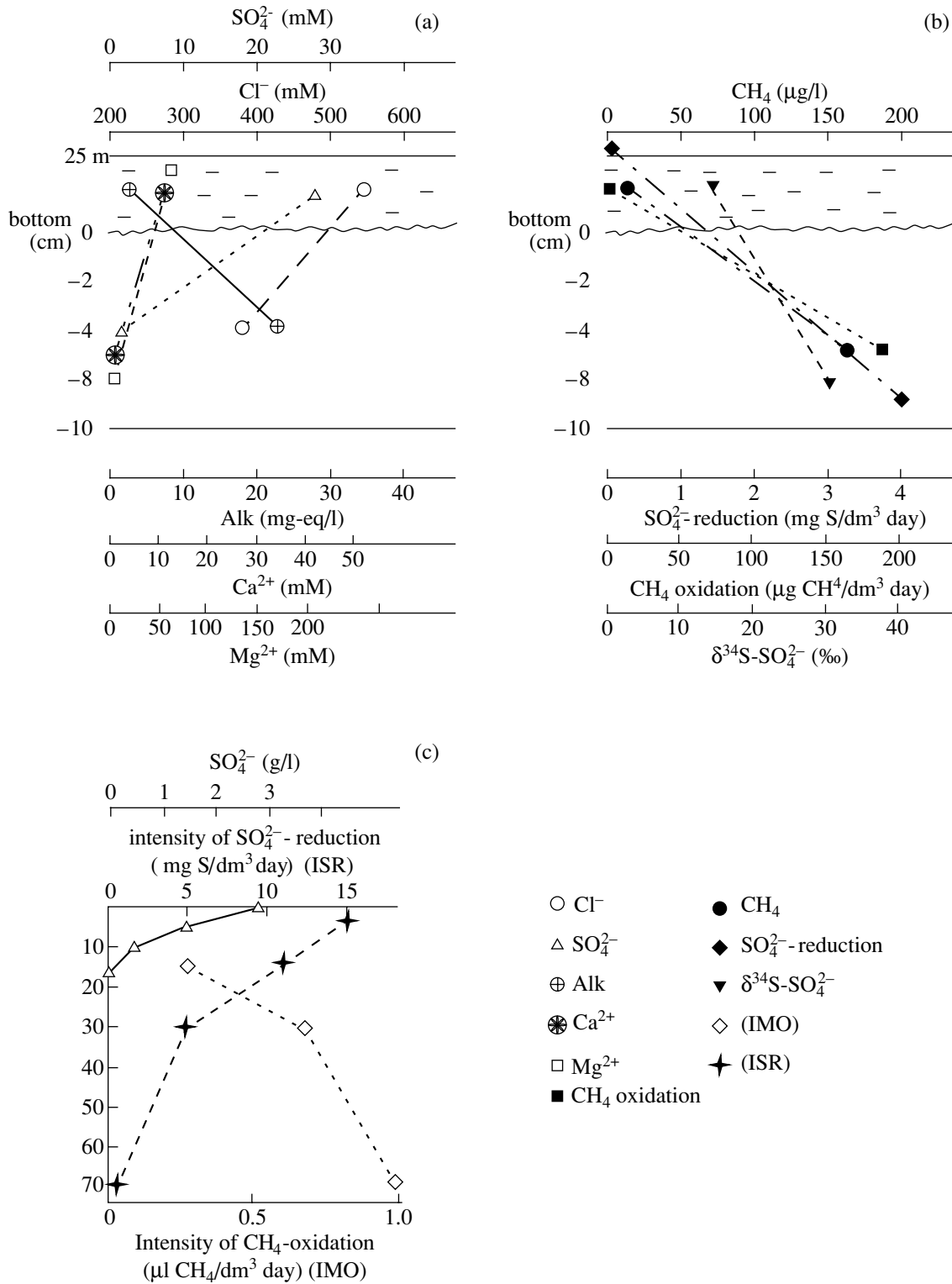
Fig. 16. Changes in (a) salt composition, (b) intensity of microbial processes and $\delta^{34}S$-SO_4^{2-} at the bottom water–sediment interface, and (c) sequence within the caldera of Haakon Mosby mud volcano.
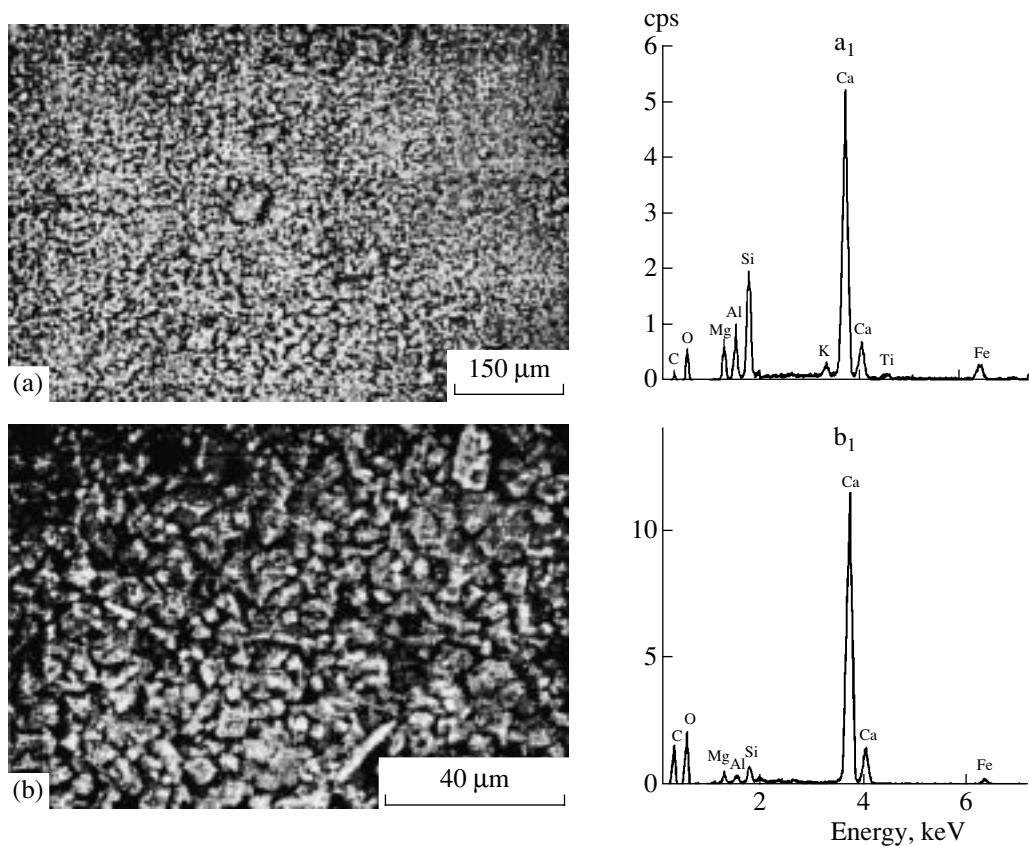
Fig. 17. (a, b) SEM images and (a_1, b_1) energy-dispersive spectra of authigenic carbonates. (a) Microcrystalline, locally fine- and medium-crystalline authigenic Mg-calcite; (b) crystalline authigenic calcite with an admixture of aluminosilicate minerals.
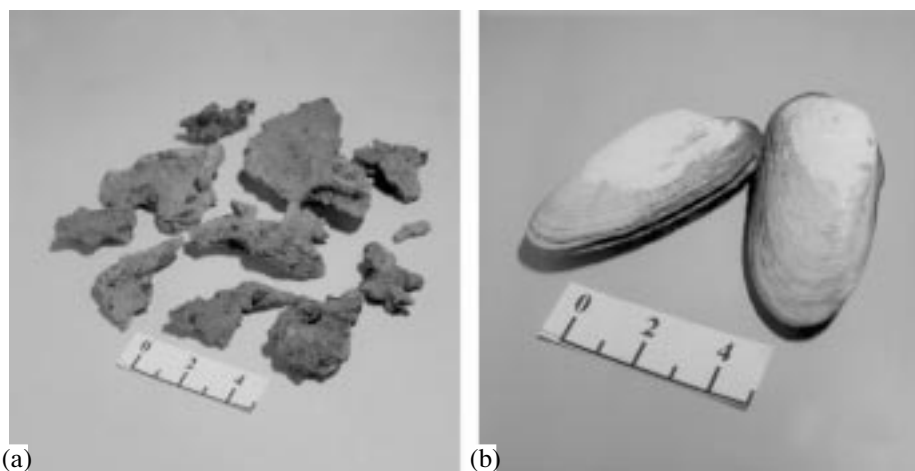

Fig. 18. (a) Aragonite crusts and (b) mollusk shells from the discharge zone of warm (about 60°C) methane-bearing solution at the Anin Sad site within the Logachev-1 hydrothermal field (14° N, MAR).

tains minor Mg^{2+} and SO_4^{2-}, which cannot occur in the primary fluid. Concentrations of Na^+ and Cl^- practically do not change, as compared to the seawater composition.

Low sulfate concentration in the Lost City solution, as compared to that in the surrounding oceanic water, indicate that hydrogenic sulfate reduction takes place in the mixing zone of hot hydrogen-bearing fluid with sulfate ion-bearing seawater. Thermophyle microbes possibly belonging to the archaebacteria group participate in the sulfate reduction according to the following reaction:

$$CaSO_4 + 4H_2 \longrightarrow CaS + 4H_2O.$$
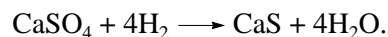
The subsequent hydrolysis of the calcium sulfide
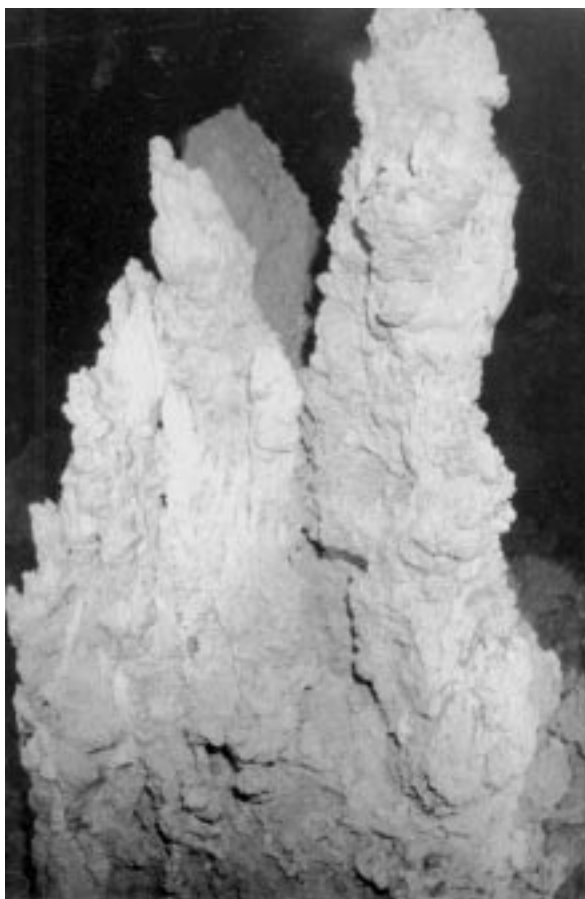
Fig. 19. Carbonate "columns" in the Lost City hydrothermal field, 30° N, MAR (Lein *et al.*, 2002a).

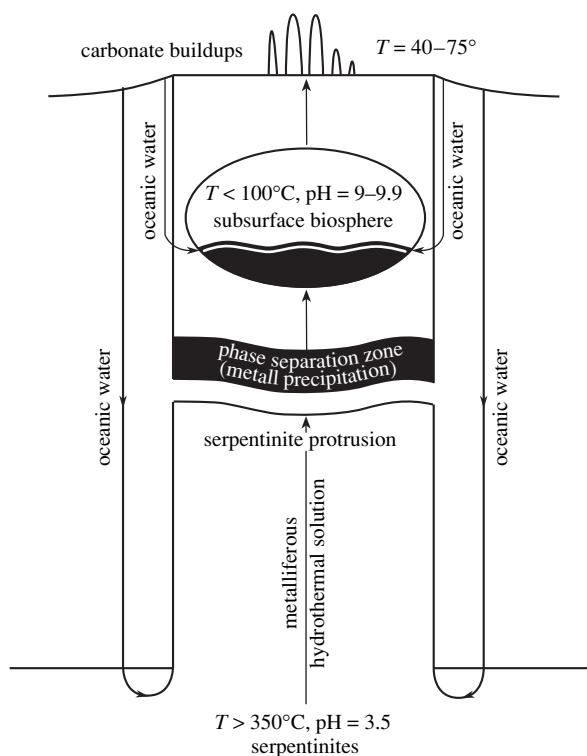**Fig. 20.** Evolution of abyssal hydrothermal fluid in the Lost City field during the formation of carbonate buildups (Lein *et al.*, 2002a).

$$CaS + 2H_2O = H_2S + Ca(OH)_2$$

explains the higher alkalinity of the solution (pH up to 9.0–9.9) relative to that of the surrounding seawater. Outflow of this solution to the bottom surface creates favorable conditions for calcium carbonate precipitation.

CONCLUSIONS

It became clear during last decades that the ocean sphere inhabited by living organisms, which participate in the carbon cycle, extends from the atmosphere–ocean interface and encompasses the entire thickness of oceanic crust where water exists in the liquid state. Authigenic calcium carbonate formation is a major process of interaction of organic and inorganic carbon cycles with the calcium cycle. Calcium carbonates are responsible for the bicarbonate equilibrium, since they restrict pH decrease by dissolution of carbonates and pH increase by precipitation of $CaCO_3$. The inorganic carbon cycle is connected with the organic carbon cycle via labile forms CO_2 and HCO_3^- during autotrophic CO_2 assimilation (photosynthesis or chemosynthesis) and CO_2 extraction (OM destruction and CH_4 oxida-

tion). In other words, the Ca cycle governs via carbonate formation acidic–alkaline and redox conditions of the biosphere, in general, and the ocean, in particular.

The large scale of authigenic carbonate formation is becoming more and more evident. As a matter of fact, Strakhov (1951, 1962) considered only one mechanism of authigenic carbonate formation related to OM decay with HCO_3^- and CO_2 generation during diagenesis (Fig. 21). Such carbonates are widespread in ocean and related to the organic carbon cycle. We investigated details of their formation mechanism (supplemented with isotope data that were not available during the works of Strakhov) for the Gulf of California. In the framework of this mechanism, anaerobic sulfate reduction is the main biological process and carbonates and iron sulfides make up the major mineral paragenesis.

Obligatory conditions for the formation of Type I authigenic carbonates include high labile C_{org} content and enhanced heterotrophic microbial activity in sediments. Organic matter decay in sediments results in the precipitation of carbonates depleted in heavy carbon isotope ^{13}C, by up to 10–15%, relative to dispersed marine carbonates (Fig. 10) as a result of the input of isotopically light CO_2 that inherited the isotopic composition of primary C_{org}. The $\delta^{18}O$ value in carbonates depends mainly on the oxygen isotopic composition of bicarbonate ion in pore water or seawater and less on

**Table 8.** Characteristics of morphological types of authigenic carbonates

Morphological types	Size	Minerals	Enclosing medium	$\delta^{13}C\text{-}CaCO_3$, ‰	$\delta^{18}O\text{-}CaCO_3$, ‰	Carbon source	Examples
			Shelf and continental slope				
Dispersed mineralization	0.001–0.5 mm	Calcite, Mg-calcite	Reduced sediments	−6.5…−15.6	−	C_{org}; $2C_{org} + SO_4^{2-} + H_2O = H_2S + 2HCO_3^-$	Shelf off California HMMV
				−3.6…−8.3	−5.1…−9.8		
				−6.2…−12.2	−		Gulf of Cadiz
				−5.3…−12.6	−		Sea of Okhotsk
Crusts, nodules, concretions, gennoishi	From 1–2 cm to 5–10 cm	Calcite, Mg-calcite, protodolomite, ikaite	Reduced sediments	−18.1…−40	−	$C_{org} + (CH_4\ ?)$	Shelf off California, HMMV
				−28.4…−29.6	4.3–5.4		HMMV
				−22.0…−23.1	4.4–5.4	$CH_4 + (HCO_3^-)$	Gulf of Cadiz
				−47.5…−49.2	2.9–3.2		Sea of Okhotsk
Cementation of sediments	Thickness 5–30 cm, width up to 1–3 m	Calcite, Mg-calcite, aragonite (minor)	Surface layer of reduced sediments and sediment–water interface	−26…−34.0	0.6–1.2	$CH_4 + (HCO_3^-)CH_4$	Black Sea shelf up to depth 130 m
Buildups	From 0.3 × 0.2 m to 4.0 × 1.5 m	Aragonite, calcite, Mg-calcite (minor)	Sediment–anaerobic water interface	−33…−46	0.2–0.5	$CH_4 + (HCO_3^-)$	Dnepr canyon, Black Sea
	0.3 × 0.5 m	Calcite, Mg-calcite		−29…−31	4.0–5.0	$CH_4 + (HCO_3^-)$	HMMV
			Mid-oceanic ridges				
Buildups		Aragonite, calcite	Serpentinite–water interface	1.0–2.1	1.9–4.8	ΣHCO_3^-	MAR, 30° N
Crusts, cement	From 1–3 cm to 5–7 cm	Aragonite, calcite	Serpentinite–water interface	−14.0	0.6–5.4	$CH_4 + (\Sigma HCO_3^-\ ?)$	MAR, 14° N

the water temperature. Mg-calcite predominates in carbonates of this type.

Generally, migratational methane of various origin participates in the formation of methane-derived carbonates of type II (Fig. 21). Methane seeps are related to large-scale tectonic and geomorphological phenomena in ocean. We examined the authigenic carbonate formation on the following types and subtypes of methane seeps: (IIa) with the diagenetic methane (Black Sea); (IIb) with the thermogenic methane (mud volcanism in passive continental margins, e.g., Haakon Mosby mud volcano in the Norwegian Sea); (IIc) the same as IIb, but with an assumed contribution of hydrothermal methane to the fluid (Gulf of Cadiz); (III) with the hydrothermal methane (Logachev field, MAR); (IV) with the hydrothermal Ca^{2+}, seawater CO_2, and carbon compounds of the fluid (Lost City field).

Methane seeps in the Dnepr canyon (Black Sea) showed that methane may be oxidized in both aerobic and anaerobic conditions, but the microbial activity is obligatory for oxidation in any case. The group of so-called methanotrophs participate in the aerobic oxidation.

The mechanism of anaerobic methane oxidation and the role of different physiological groups of anaerobic microorganisms in this process are actively discussed since the first publications by Zehnder and Brock (1979, 1980). Based on laboratory experiments with pure methanogene cultures these authors demonstrated that if substrates (CO_2, H_2) are exhausted and the methane content is high, methanogenes begin to realize the process of anaerobic methane oxidation according to the reaction:

$$CH_4 + 2H_2O = CO_2 + 4H_2. \qquad (1)$$
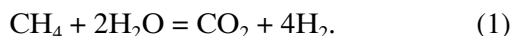
Since this process proceeds very slowly in pure cultures owing to hydrogen accumulation, the researchers (Reeburgh and Alperin, 1988; Valentine and Reeburgh, 2000; and others) assumed that reaction (1) takes place simultaneously with reaction (2) in natural anaerobic ecosystems with the involvement of sulfate-reducing bacteria:

$$4H_2 + SO_4^{2-} + H^+ = HS^- + 4H_2O. \qquad (2)$$

The formal summation of Eqs. (1) and (2) yields the mechanism of sulfate-dependent methane oxidation (SDMO):

$$CH_4 + SO_4^{2-} = HCO_3^- + HS^- + H_2O. \qquad (3)$$
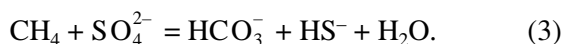
The hypothesis of direct methane oxidation by sulfate-reducing bacteria, which allegedly use methane as a donor of electrons for sulfate reduction, existed in the literature for a long time (Barnes and Goldhaber, 1976; Reebourgh, 1976; Reebourgh and Heggie, 1977).

Microscopic study of mat samples from the surface of carbonate buildups and inoculation on elective nutrient media revealed abundant and diverse microflora, including sulfate reducers, aerobic methanotrophs, and large filamentous microorganisms morphologically

Table 9. Mineral and chemical compositions of carbonate buildups in the Lost City hydrothermal field (Lein *et al.*, 2002a, with additions)

Oxides, %	Minerals (number of samples)			
	Aragonite + calcite (6)	Brucite + aragonite (2)	Aragonite + brucite (14)	Na–Ca-carbonate (10)
	Sample 6	Sample 2	Sample 14	Sample 10
CaO	45.4	5.87	22.7	46.8
MgO	0.63	26.80	12.3	0.11
SrO	2.74	0.181	0.62	0.49
Na_2O	0.45	<0.05	<0.05	9.92

Table 10. Chemical composition of real solution and primary hydrothermal fluid of the Lost City field

Components, M, parameters	Oceanic bottom water	Real solution	Primary fluid
$T°C$	7	40–75	~360
pH	7.8	9.0–9.8	~3.0
Mg	54.0	59.8	9–19
Ca	10.4	12.4	21.0–23.3
Na	475	–	479–485
Cl	553	555.1	546–549
SO_4^{2-}	28.6	25.9	5.9–12.9
H_2S	–	0.0012	0.064
CH_4	4×10^{-7}	0.093	0.13–0.28
H_2	4×10^{-4}	0.683	0.25–0.43
CO_2	2.3	–	–
$\delta^{13}C$-CH_4, ‰	–	–17.0	–
Depth, m	700–850		
Primary rock	Peridotite + Gabbro		

Note: (–) No data.

similar to methanogenes (Ivanov *et al.*, 1991; Pimenov *et al.*, 1997). Results of molecular-biological studies, which revealed typical archaebacterial biomarkers, also indicate the presence of methanogenes in the mats (Pimenov *et al.*, 1997; Turova *et al.*, 2002). The $\delta^{13}C_{org}$ value in carbon of lipids decreased to –120‰ (Michaelis *et al.*, 2002; Thiel, 2001).

Based on experiments with radioactive markers, Pimenov *et al.* (1997) detected active processes of sulfate reduction, autotrophic methane generation, and anaerobic methane oxidation in the mats. Coupled with data on isotopy of carbonates and organic matter in mats, all these data support the microbial nature of anaerobic methane oxidation. However, they are insufficient to decipher the mechanism of this process.
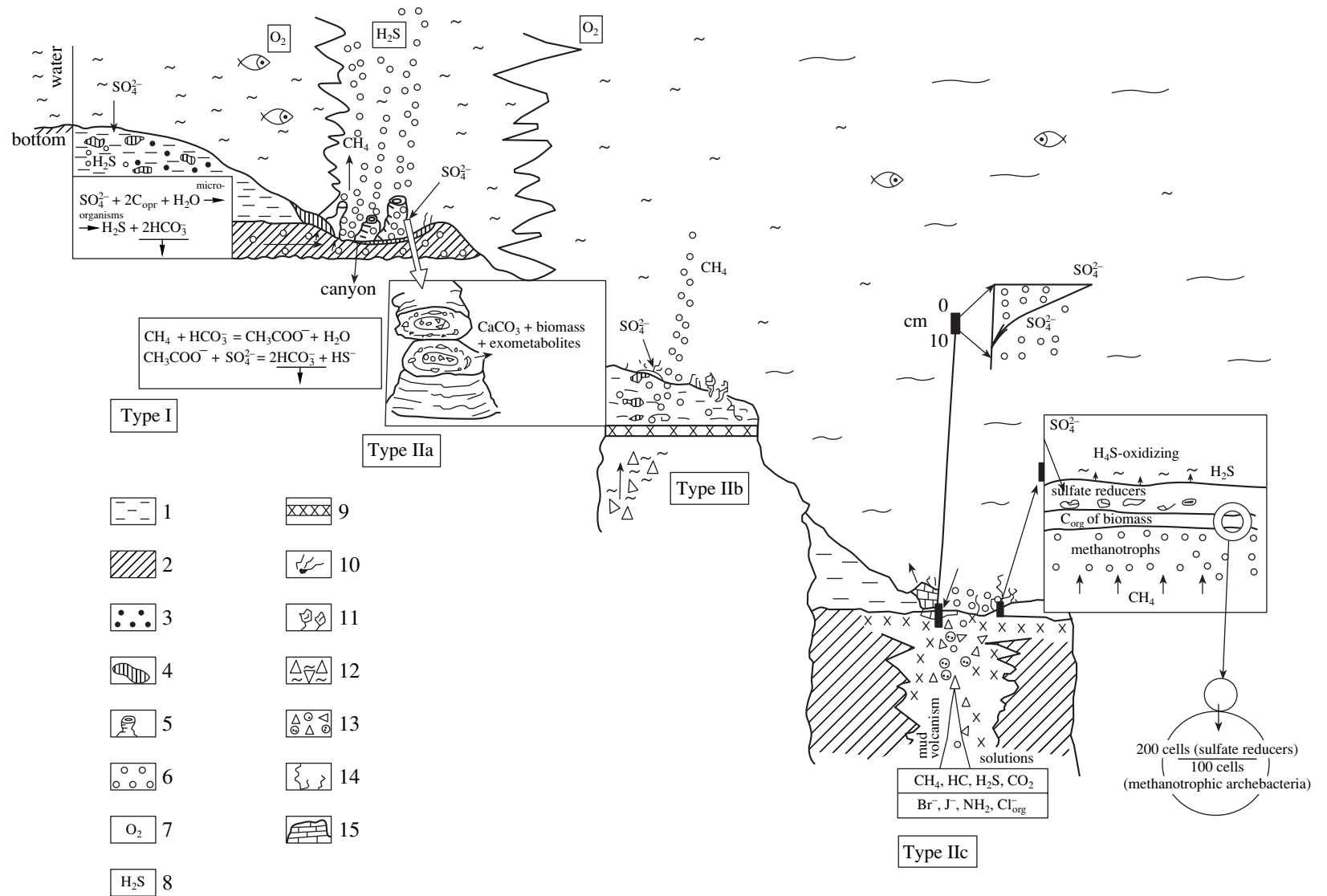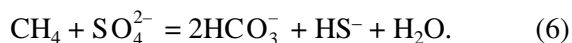
LEIN

water

bottom

O_2

H_2S

O_2

$\sim SO_4^{2-}$

H_2S

$SO_4^{2-} + 2C_{opr} + H_2O \longrightarrow$

micro-

organisms

$\longrightarrow H_2S + 2HCO_3^-$

CH_4

SO_4^{2-}

$CH_4 + HCO_3^- = CH_3COO^- + H_2O$

$CH_3COO^- + SO_4^{2-} = 2HCO_3^- + HS^-$

canyon

$CaCO_3$ + biomass
+ exometabolites

Type I

Type IIa

CH_4

SO_4^{2-}

Type IIb

cm

0

10

SO_4^{2-}

SO_4^{2-}

SO_4^{2-}

H_4S-oxidizing

H_2S

sulfate reducers

C_{org} of biomass

methanotrophs

CH_4

mud volcanism

solutions

CH_4, HC, H_2S, CO_2

Br^-, J^-, NH_2, Cl_{org}^-

Type IIc

200 cells (sulfate reducers)

100 cells

(methanotrophic archebacteria)

1   9

2   10

3   11

4   12

5   13

6   14

O_2 7   15

H_2S 8

Fig. 21. Formation schemes of two main authigenic carbonate types (I and II) in the ocean. (1) Holocene mud; (2) Holocene–Pleistocene sediments; (3) dispersed carbonate mineralization; (4) carbonate plates; (5) coral- and free-shaped aragonite buildups; (6) bubble-stream gas discharge (CH_4); (7) aerobic conditions in the basin; (8) anaerobic conditions in the basin; (9) CH_4 gas hydrates; (10) microbial mats; (11) mollusks; (12) mud-volcanic breccia; (13) deposits of backarc volcanism; (14) polychaeta; (15) carbonate buildups in the caldera of mud vocano.

We used data on oxygen isotopy of authigenic carbonates to understand the nature of ultimate electron acceptor involved in the anaerobic methane oxidation. The $\delta^{18}O$ values of carbonates substantially differ from the $\delta^{18}O$ values of seawater and sulfate dissolved therein, thus eliminating their participation as oxygen donors in the anaerobic methane oxidation according to Eqs. (1) and (3).

The $\delta^{18}O$ values in authigenic carbonates from the Black Sea are close to the $\delta^{18}O$ value of bicarbonate dissolved in pore water of the upper sediment layer (Fig. 14). Therefore, oxygen of bicarbonate ion is the agent than might be used in the anaerobic methane oxidation.

According to (Valentine and Reeburgh, 2000), such reaction may proceed by the mechanism of methane oxidation to acetate and water (Eq. (4)) owing to the activity of acetoclastic methanogenes with the subsequent participation of sulfate-reducing bacteria and anaerobic oxidation of acetate (5):

$$CH_4 + HCO_3^- = CH_3COO^- + H_2O, \qquad (4)$$

$$CH_3COO^- + SO_4^{2-} = 2HCO_3^- + HS^-, \qquad (5)$$

$$CH_4 + SO_4^{2-} = 2HCO_3^- + HS^- + H_2O. \qquad (6)$$

Equation (6), i.e., summation of reactions (4) and (5) realized by methanogenes and sulfate reducers, is similar to the SDMO reaction (3). However, the oxygen source (HCO_3^-) and the intermediate oxidation product (CH_3COO^-) are substantially different.

Contribution of marine bicarbonate with a rather heavy carbon isotopic composition ($\delta^{13}C = -2.1‰$) may explain the above considerable difference in $\delta^{13}C$ values between carbonates and organic carbon of authigenic carbonate buildups. The carbon isotopic composition of carbonate buildups is a mixture of isotopically light carbon formed during the methane oxidation and isotopically heavy bicarbonate carbon of seawater.

Thus, anaerobic oxidation is realized by a microbial consortium mainly including methanogene archae and sulfate reducers. According to the modern classification, a part of the sulfate reducers belongs to archae rather than bacteria (Michaelis et al., 2002; Pimenov et al., 1998).

Methane of hydrothermal fluids (type III) discharging onto the bottom surface as any other methane undergoes the microbial oxidation to form carbonate crusts. Carbon isotopy of authigenic carbonates inherited from the hydrothermal methane is a geochemical evidence of the carbonate origin, as shown by the example of carbonate crusts cementing sediments within the Logachev hydrothermal field ("Anin Sad").

Authigenic carbonates from the Lost City field represent a specific type IV. Bicarbonate of seawater or fluid serves as carbon and oxygen source for these carbonates, whereas calcium and partially strontium are derived from the hydrothermal solution. Carbonates of this recently discovered type are also related to microbial activity. A complicated microbial consortium impregnates the carbonate buildups and maintains the reduced (Eh = –120 mV) alkaline (pH = 9.0–9.9) environment in the hydrothermal fluid, which give rise to carbonates.

Microorganisms (more precisely, prokaryotes) with a specific calcite-forming function have not been found in nature up to date. However, it is these microbial communities that increase the pH value of seawater and create favorable conditions for calcium carbonate precipitation.

Carbon in authigenic carbonates of types I and II is depleted in isotope ^{13}C ($\delta^{13}C$ values vary from –15 to –50‰). Unlike carbonates dispersed in mud characterized by negative $\delta^{18}O$ values ranging from –5.1 to –9.8‰, these carbonates shows positive $\delta^{18}O$ values varying from 1.0 to 5.4‰ (Fig. 14).

According to the data on ^{90}Sr distribution as a result of the Chernobyl catastrophe, the growth rate of Black Sea carbonate plates in which the authigenic carbonate cements terrigenous mud, is 0.65 mm/yr (Lein et al., 2002b). The growth rate of coral-shaped buildups is considerably higher and may reach several millimeters per day. The growth rate of carbonate buildups in aerobic ecosystems varies from 0.02 to 0.37 mm/yr (Table 5).

Experiments with radioactive isotopes allowed us to estimate quantities of oxidized methane and produced bicarbonate using Eq. (6). The average methane oxidation rate in the surface layer (0–10 cm) ranges from 150 ml CH_4/m^2 day in the HMMV caldera to 1200 ml CH_4/m^2 day in the Black Sea seeps (Lein et al., 2000a; Pimenov et al., 2000). About 80% of the methane is oxidized to HCO_3^- (120–1000 ml/m² day). As was previously shown, about 0.5 t CH_4 is consumed to form a carbonate buildup of 1 m³ in the Dnepr canyon in the Black Sea (Polikarpov et al., 1992). According to the latest estimates, about 27×10^6 t CH_4/yr is supplied from deep-sea mud volcanoes onto the bottom (Milkov and Sassen, 2002). Therefore, up to 0.5×10^6 m³ of carbonates may be annually formed only in regions of methane seeps related to the mud volcanism. Of course, these are very rough estimates presented here to emphasize the large scale of anaerobic methane oxidation and authigenic carbonate formation.

We should also emphasize another important circumstance. Owing to microbial activity, the organic carbon from ancient sedimentary deposits, which is transformed into CO_2, methane, and methane homologues during thermogenic processes, is involved in the present-day carbon and calcium cycles during the formation of methane-derived carbonates. Abiogenic carbon compounds, methane first of all, are involved in the modern biogeochemical carbon cycle in mid-oceanic ridges.

Data given in this work certainly testify to the participation of microbial activity in the authigenic carbonate formation. Microbial communities occur in all types of authigenic carbonates considered here. Carbon sources may be different: OM, methane, bicarbonate ion of seawater and/or pore water, and even inorganic carbon compounds of hydrothermal solutions. The authigenic carbonate formation is a combination of biogeochemical (microbial) processes that ensure the interaction of calcium, organic carbon, and inorganic carbon cycles.

The above presented materials suggest the following conclusions.

(1) Based on the carbonate carbon source, authigenic carbonates in the ocean can be divided into four major types: (I) organic carbon of bottom sediments; (II) carbon of methane, including (IIa) diagenetic, (IIb) thermogenic, and (IIC) thermogenic + hydrothermal subtypes; (III) carbon of hydrothermal methane; and (IV) carbon of ΣHCO_3^- in seawater and hydrothermal fluid. Authigenic carbonates of types I and II are most widespread in the ocean (Fig. 21).

(2) All types of authigenic carbonates are formed with an obligatory participation of microorganisms, among which many groups of sulfate reducers and methanotrophs (archae and bacteria) are most important.

(3) Unitary models of microbial processes participating in the authigenic carbonate formation are absent. According to the first well-known model, microbial decay of organic matter in sediments to HCO_3^- results in alkalinity increase due to H_2S formation during sulfate reduction in the pore water. The second model (participation of microbial processes in the carbonate formation under strongly anoxic conditions) was proposed in 2002 (Lein *et al.*, 2002b). This process is controlled by the activity of different microbial groups, which produce intermediate products of methane oxidation. Bicarbonate of seawater and/or pore water participates in the process as a main oxygen source for carbonates. The third model is valid in the case of discharge of low-temperature hydrothermal fluids with a high concentration of H_2, which is a good substrate for the specific group of sulfate reducers stimulating the increase in alkalinity of solutions and the formation of carbonate buildups at seepage sites. The whole variety of microorganism-mediated processes of the authigenic carbonate formation in ocean is not exhausted by these three models.

(4) Mg-calcite (+ protodolomite), calcite, and aragonite dominate among the authigenic carbonates. Holocene buildups (younger than 10 ka) at methane seepage sites on the seafloor mainly consist of monomineral aragonite. Sediments are commonly cemented by authigenic Mg-calcite. Carbonate nodules also mainly consist of Mg-calcite. Carbonate buildups and nodules contain Sr and Ba.

(5) All authigenic carbonates are depleted in heavy carbon isotope ^{13}C and enriched in heavy oxygen isotope [18]O. This is possible only if the isotopes undergo biological fractionation during the carbonate formation.

(6) The growth rate of carbonate buildups ranges from 0.65 mm/yr to several millimeters per day under anaerobic conditions and from 0.02 to 0.37 mm/yr at the boundary between aerobic and anaerobic environments.

(7) Old radiocarbon ages obtained for carbonate buildups and nodules produced by the oxidation of migrational thermogenic methane are likely inherited from near-surface methane gas hydrate deposits formed during the Last Glacial Maximum. Up to 0.5 Tg m^3/yr of authigenic carbonates may be produced in calderas of submarine mud volcanoes of the ocean.

(8) Authigenic carbonates are formed at water depths ranging from several meters to thousands of meters in different (polar to tropical) climatic zones.

(9) Authigenic carbonate formation is a microbiologically mediated geochemical process in the modern carbon cycle with the involvement of recent and ancient OM, abiogenic methane, and ΣHCO_3^- of hydrothermal fluids.

ACKNOWLEDGMENTS

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