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OBSERVATION OF MICROBIAL CARBONATE BUILD-UPS GROWING AT METHANE SEEPS NEAR THE UPPER BOUNDARY OF THE GAS-HYDRATE STABILITY ZONE IN THE BLACK SEA

Extensive dredge sampling carried out in May-June 2004 in the deeper part of the Dnepr paleo-delta area (NW Black Sea) yielded for the first time chimney-shaped carbonate microbial build-ups, which occur at methane seeps close to upper boundary of the gas-hydrate stability zone (~ 700 m). Carbonate samples taken with a benthic trawl represent fragments of the uppermost, middle and lowest parts of the build-up; they are similar morphologically to those found previously at the shallower and deeper methane seeps in the Black Sea. At the same time, the perforated, plate-like carbonates in the lowest parts of the build-up provide first indications that gas channels are formed during the earliest growth phase of these microbial structures. Stable carbon isotope analyses of the carbonates from the uppermost fragments gave the $\delta^{13}C$ values ranging from -33.7 to -36.6 ‰, while the $\delta^{13}C$ values of the lowest fragments are significantly lighter, varying between -42.0 and -44.6 ‰. Oxygen isotopic values also show differences between the samples from the uppermost part of the build-ups, which are composed of a mixture of aragonite and Mg-calcite ($\delta^{18}O$ = 0.7 to 0.94 ‰), and the only Mg-calcite cemented thin slabs of lowest carbonates ($\delta^{18}O$ = 1.35 to 1.57 ‰). The isotope data for carbon and oxygen suggests that carbonates formed as a result of anaerobic microbiological oxidation of methane supplied as a shallower-sourced fluid component from below. The difference in $\delta^{13}C$ and $\delta^{18}O$ values found in the upper and lowest parts of the build-ups may indicate that more carbon derived from seawater and less hydrate water are involved to the chimney formation during its growth, but this may be also a record of the long-term changes in the near-bottom environments related to evolution of salinity, temperature and anoxic conditions in the Black Sea.

Keywords: Black Sea, methane seepage, gas hydrates

Following the first hydroacoustic detection of gas seeps in the Black Sea in April 1989 [17], numerous seeps have been found by echo-sounding of plumes of emanating gas bubbles down to a water depth of 2070 m [1, 4-7, 14, 18, 23]. Most of these seeps are located along the shelf edge and on the upper slope, particularly at the paleo-deltas and canyons of the largest Black Sea rivers: the Danube, Dnepr, Dnestr and Don [7, 9, 21]. The deepest seeps have been discovered recently in association with faults and mud volcanoes in the central Black Sea basin [7, 14, 23].

Direct observations and sampling carried out in 1990 with the scientific submarine "Benthos-300" (USSR) revealed fields of chimney-like structures at methane seeps in permanently anoxic waters at depths of 200 – 230 m in the NW Black Sea [13, 18].

Comprehensive underwater inspection of this area and precise sampling were conducted in

2001 with the submersible "Jago" (Germany), finding the carbonate chimneys up to 4 m high at a depth around 230 m [16]. These structures represent carbonate build-ups, the upper part of which is covered by massive microbial mats consisting of methanotrophic archaea. Recent microbiological, isotopic, molecular and petrographic analyses showed that such microbial build-ups are formed as a result of anaerobic oxidation of methane seeping from the bottom sediments, which is operated by a consortium of archaea and sulphate-reducing bacteria [2, 16, 19, 25].

During observations conducted in greater water depths in 1993 with the submersible "Sever-2" (Ukraine), similar carbonate build-ups were found at a depth of 1738 m, in an area of deep faults and rock outcrops south-west of the Crimean peninsula [22]. During dredging in this area a carbonate chimney was recovered from 1555 m water depth [10, 23].

Thus, the methane-derived microbial build-ups sampled earlier were taken at depths much shallower [6, 13, 16, 18] or much deeper [10, 22] than the upper boundary of the gas-hydrate stability zone, which is located at 725 m water depth in the Black Sea [24], and below which the temperature-pressure conditions in the sediments are appropriate for hydrate formation [3]. Therefore, the purpose of this study was to investigate whether methane seeps and carbonate build-ups also occur at this key depth, and if so, what their general characteristics are.

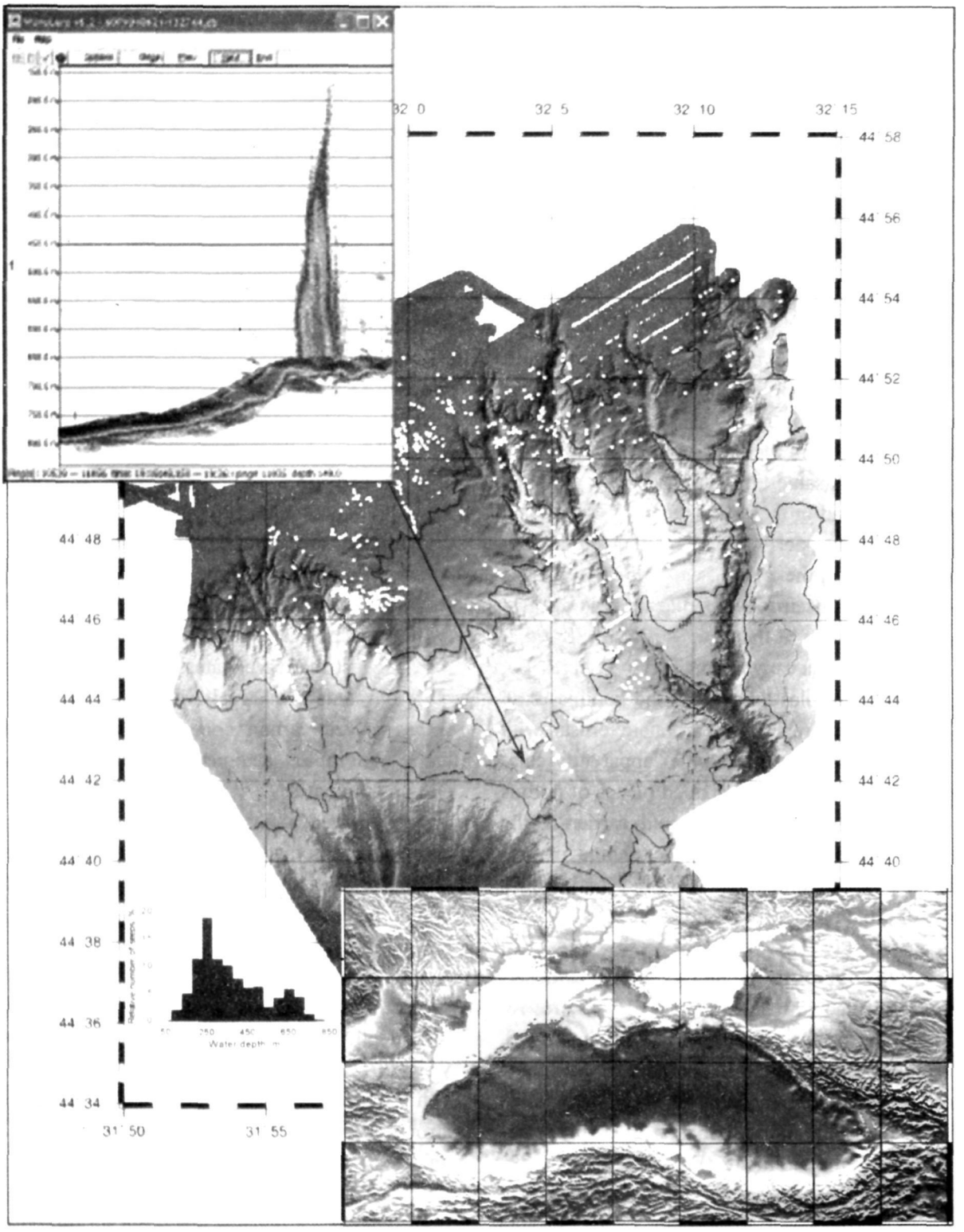
Materials and methods. The carbonate build-ups were sampled with a benthic trawl during the 60th cruise of R/V "Professor Vodyanitskiy" (Sevastopol, Ukraine) conducted within the framework of the EU-funded project CRIMEA in May/June 2004. Trawling was carried out in the deeper part of the Dnepr paleo-delta area (NW Black Sea) along a 600-m-long section from 44° 42.095' N – 32° 03.842' E, 730 m water depth, to 44° 42.215' N – 32° 04.265' E, 680 m water depth. Before the dredge sampling, this area was surveyed with the dual-beam scientific echosounder SIMRAD EK-500 and the SEABEAM-1050 swath bathymetry system for gas plume detection and bathymetric mapping [1, 9]. Visual sea-floor investigations at site of the trawling were carried out using the Ocean Floor Observation System (OFOS) operated by command via a deck unit.

The stable isotope composition of the retrieved carbonates was determined at IfM-GEOMAR (Kiel, Germany) using a Finnigan MAT 252 mass spectrometer connected to a Finnigan Kiel Carbo II preparation line (accuracy of ± 0.03 ‰ for $\delta^{13}C$; ± 0.06 ‰ for $\delta^{18}O$). XRD mineral analyses were undertaken with a Phillips goniometer (PW 1820) with Co X-ray tube (0.01° step interval, 2 sec. count time).

Results and discussion. The Dnepr paleo-delta is located on the shelf edge and the upper continental slope of the NW Black Sea, between 70 and 1200 m of a water depth (Fig. 1).

Fig. 1 Swath bathymetry map of the Dnepr paleo-delta study area acquired in 2003 during the CRIMEA cruise on RV "Professor Vodyanitskiy" (after [9]) with the detected seeps plotted as white dots. The lower right-hand inset shows the study area (yellow rectangle) at the Black Sea map with indication of all seeps found in 1989 - 2004 (red dots, after [7]). Upper inset shows the gas flare image obtained during the hydro-acoustic survey along the track line of the dredging performed during this study. The bar chart represent relative distribution of methane gas seeps vs. water depth over the Dnepr paleo-delta area (total number of seeps = 1549)

Рис. 1 Батиметрическая карта палео-дельты Днепра, полученная с помощью многолучевого эхолота в 2003 г. во время экспедиции на НИС «Профессор Водяницкий» по проекту CRIMEA [9] (белыми точками показано расположение обнаруженных метановых сипов). На правой нижней вставке этот район обозначен желтым прямоугольником на карте Черного моря (красные точки – локализация всех сипов, зарегистрированных в 1989 - 2004 гг. [7]). Верхняя вставка – эхограмма метанового сипа, обнаруженного во время гидроакустической съемки вдоль маршрута драгирования. На гистограмме представлены данные по частоте встречаемости сипов на разных глубинах в районе палео-дельты Днепра (общее количество сипов = 1549).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Bathymetric mapping carried out with the multi-beam system SEABEAM-1050 [9] has revealed that this area is characterised by a large Y-shaped canyon system to the east and a slope to the south. The border between these major features is a 150° striking ridge that starts as a broader saddle between ~120 and 400 m depth and becomes thinner with increasing depth (Fig. 1).

The echosounding of this area, which covered ~837 km^2, has allowed detection of 1549 gas seeps. This number was calculated from the initially obtained set of hydroacoustic flare images by excluding of the repeatedly crossed gas plumes. The most of the found seeps are located at a depth of 250 m in the upper anoxic water layers (Fig. 1). At the same time, an additional group of seeps was found in the depth range of 600 to 700 m, close to the upper boundary of the gas-hydrate stability zone in the Black Sea, probably because of a shallower occurrence of the underlying gas-charged sediments at this site, which is situated at the steep edge of a canyon adjacent to a ridge.

The samples taken with the benthic trawl at this location represent carbonate crusts with vents through which gas bubbles apparently emanated (Fig. 2), larger pipe-shaped pieces of porous carbonates similar to those found earlier at the shallower and deeper seeps (see photos in [16, 18]), and 2 – 4 mm thick plate-like carbonates, most of which show round holes of 0.5 – 1.5 cm in diameter (Fig. 3).

According to previous underwater observations fulfilled with submersibles [10, 13, 16, 18, 22], and during the present study with the OFOS, the typical Black Sea methane-derived carbonate structures form chimney-shaped build-ups with an intermediate pipe-like column on thick platforms embedded in the sediments (Fig. 4).

The upper parts of these chimneys are covered by bacterial mats with vents, through which irregular emanations of gas bubbles occur. Also, Shnukov et al. [22] have found plate-like carbonates in sediments subjacent to the deeper Black Sea chimney, which were identified as dolomites and which are very similar to those shown in Fig. 3, but without any holes.

Our XRD measurements have showed that carbonates from the upper part of the chimney taken during the present study (Fig. 2) are composed of a mixture of aragonite and Mg-calcite (12 to 13 mol % $MgCO_3$), and the only Mg-calcite cements thin slabs from the lowest part of this build-up depicted in Fig. 3 (15 mol % $MgCO_3$).

Stable carbon isotope analyses of the carbonates from the head of this chimney gave $\delta^{13}C_{CaCO3}$ values ranging from -33.7 to -36.6 ‰, which are very similar to those measured earlier in the upper and middle (piped) parts of the Black Sea build-ups from depths of 230 and 1555 m (-36.5 ‰ and -35.5 ‰, respectively). In contrast, the $\delta^{13}C_{CaCO3}$ of samples from the lowest part of the chimney are significantly lighter with values varying between -42.0 and -44.6 ‰. This difference of stable carbon isotope composition between the upper and lowest parts of the chimney may suggest that carbonates from the head of the build-up contain relatively higher amount of seawater-derived carbon compared to lower slabs, embedded in the sediments where CH_4-derived carbon dominates.

Indeed, it has been shown that authigenic carbonates, associated with the Black Sea methane seepages, incorporate variable proportions of carbon derived from the anaerobic oxidation of methane and from seawater [10, 15, 19].

Typical $\delta^{13}C$ values of bicarbonates dissolved in the Black Sea waters gradually decreases with depth from about -2 ‰ in the upper anoxic waters (~200 m) to -6.3 ‰ at depth ~2000 m [8], while the methane seeping from the chimneys is stronger depleted in ^{13}C, as indicated by $\delta^{13}C_{CH4}$ values of -58.2 ‰ [13] to -68.3 ‰ [16].

The abovementioned strong depletion of both types of carbonates taken during the present study (which show intermediate values between the seawater and methane carbon) implies that a major portion of these carbonates originates

from anaerobic microbiological oxidation of the of methane emanating from sediments [2, 10, 16], suggesting a lesser fraction of the methane-derived carbon in carbonate crusts from the head part of the chimney than in the lowest fragments of the build-up.

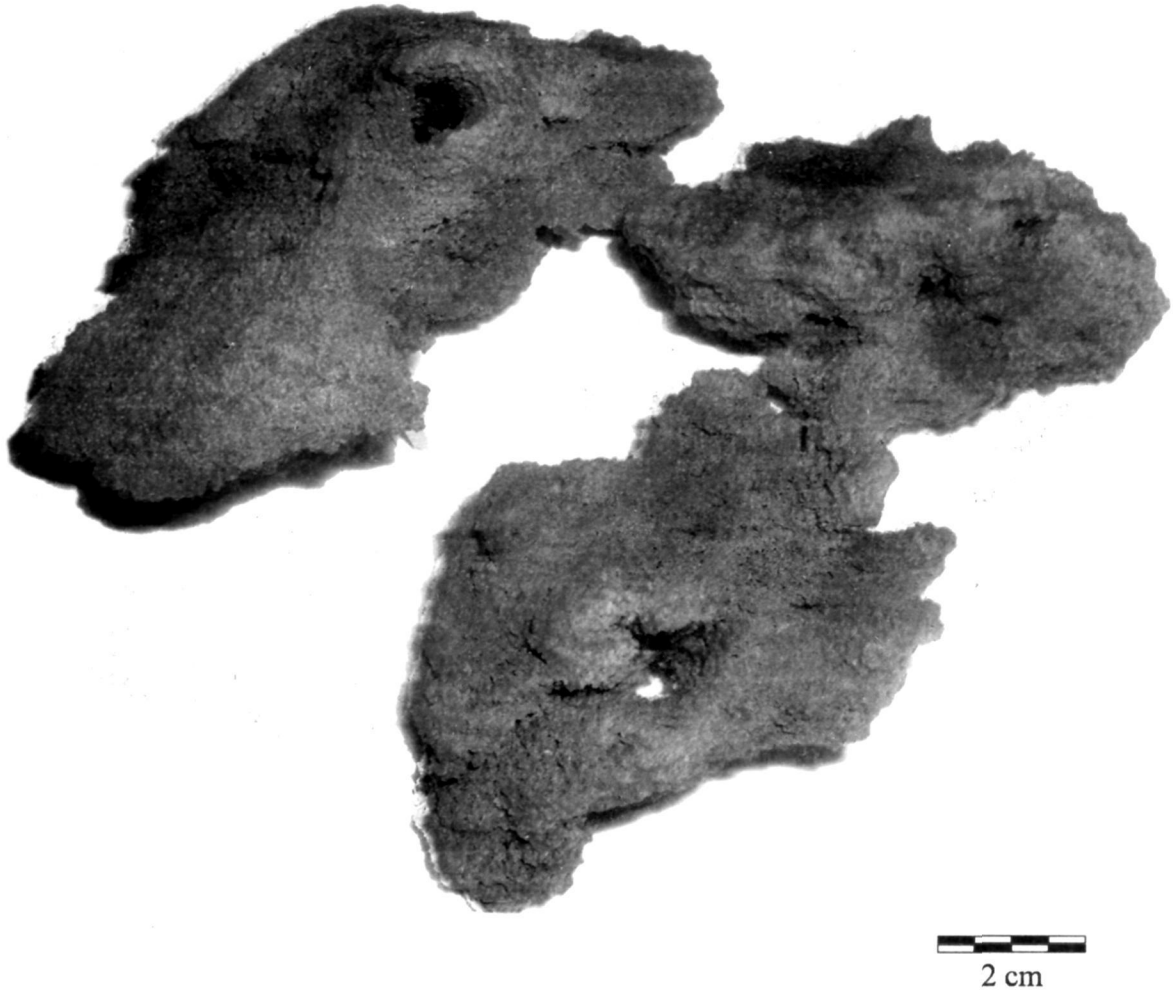

Fig. 2 Fragments of carbonate crusts with gas vents from the uppermost part of the methane-derived microbial build-up taken in June 2004 at depth near the upper boundary of gas-hydrate stability zone (~700 m) in the Dnepr paleo-delta area, NW Black Sea

Рис. 2 Фрагменты карбонатных корок с отверстиями для выхода газа из верхней части бактериальной постройки, обнаруженной в июне 2004 г. вблизи верхней границы зоны стабилизации газогидратов (~700 м) в районе палео-дельты Днепра (северо-западная часть Черного моря)

Oxygen isotopic values also show differences between samples from the upper and lowest parts of the chimney taken during the present study ($\delta^{18}O$ = 0.70-0.94 and 1.35-1.57 ‰, respectively).

Both types of these samples are slightly enriched in ^{18}O over the seawater, indicating an influence of ^{18}O-enriched fluid, saturated with methane and precipitating close or at the sediment/water interface [3, 12]. At the considered water depth (~700 m), which is the upper boundary of gas hydrate stability zone, this fluid may be influenced by the hydrate water from the partially dissociating gas hydrate, which is normally characterised by more negative than seawater $\delta^{18}O$ values [11].

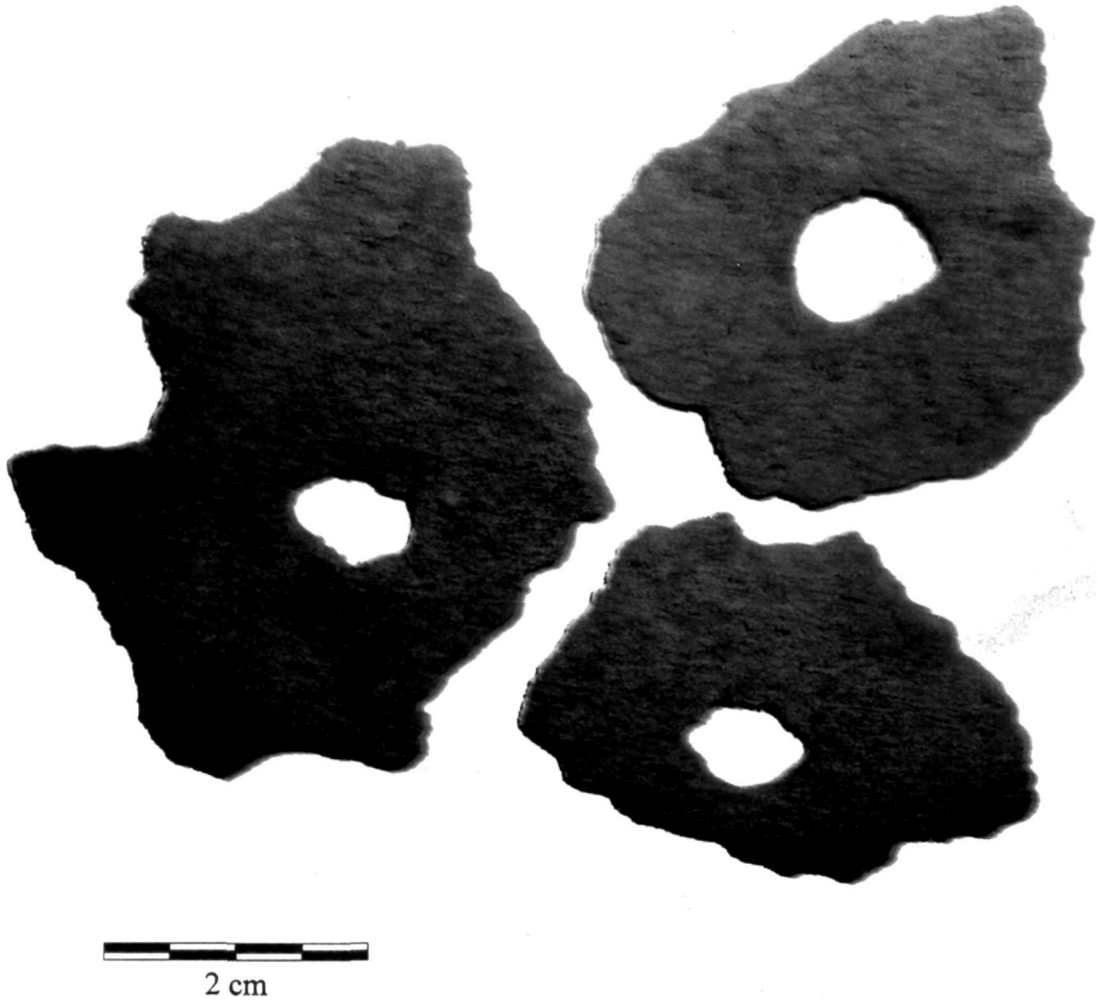

Fig. 3 Fragments of perforated plate-like carbonates from the lowermost part of microbial build-up taken in June 2004 at depth near the upper boundary of the gas-hydrate stability zone (~700 m) in the Dnepr paleo-delta area, NW Black Sea

Рис. 3 Фрагменты перфорированных пластинчатых карбонатов из нижней части бактериальной постройки, обнаруженной в июне 2004 г вблизи верхней границы зоны стабилизации газогидратов (~700 м) в районе палео-дельты Днепра (северо-западная часть Черного моря)

The lesser ^{18}O-enrichment found in the uppermost part of our chimney, as compared to its lowest part, may indicate that less hydrate water is involved to the carbonate formation at later phases of the chimney growths. On the other hand, such difference may reflect also the changes in the surrounding environment, as the oxygen isotopic composition of the carbonates may depend on the formation temperature, the oxygen isotopic composition of the precipitating fluid, and the pH [12]. Indeed, the recent ^{14}C-dating of the Black Sea methane-related build-ups has shown a gradual increase with depth of the age these chimneys corresponding to chronology of the anoxic conditions development in the abyssal basin [10]. The age of the deepest (from ~2000 m water depth) and shallowest (~200 m) build-ups was estimated as about 5300 and 2900 years before present, respectively. These dates correspond to the first appearance of hydrogen sulphide in the deepest Black Sea waters and to the stabilization of the upper boundary of the anoxic zone around the present day level.

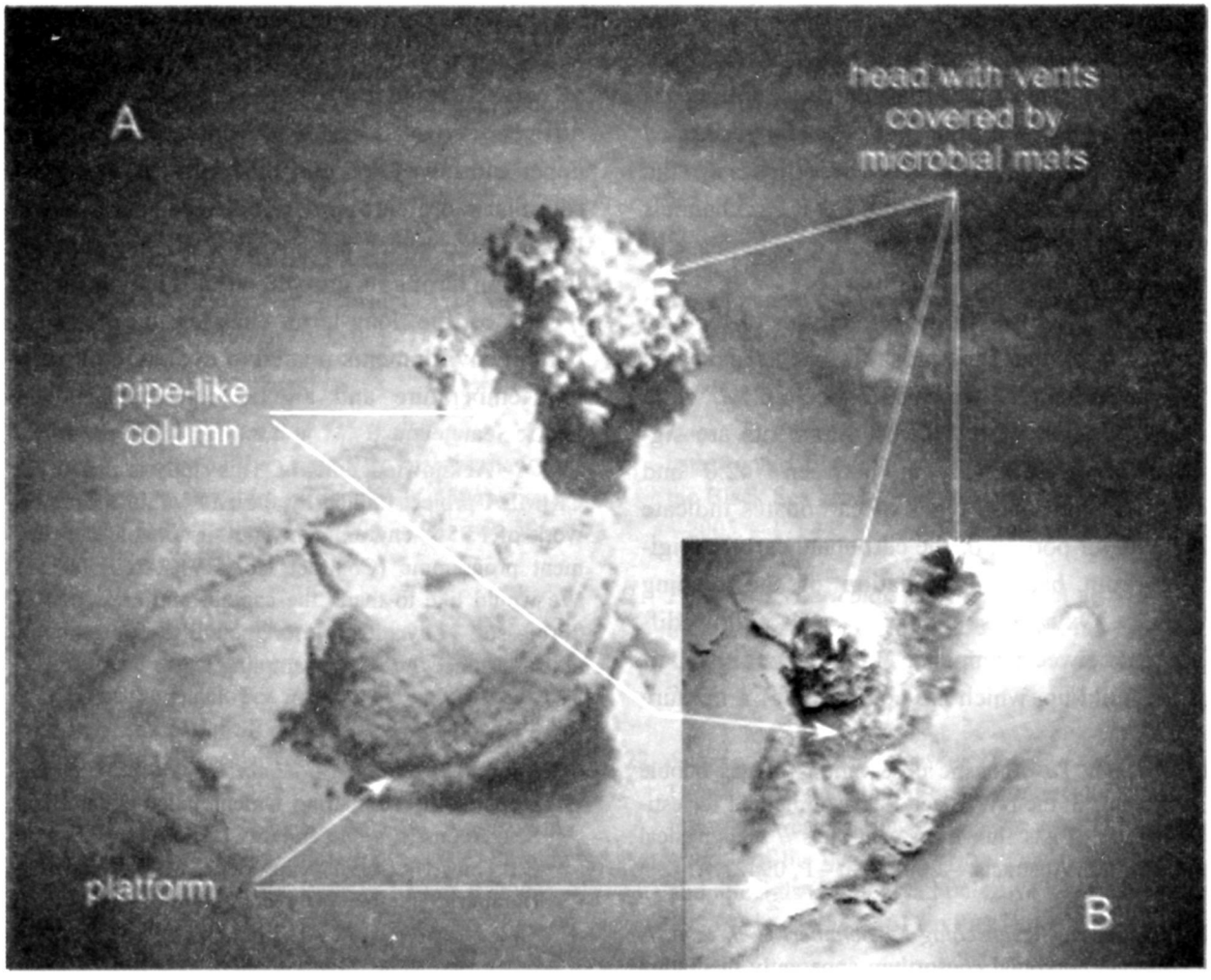

Fig. 4 Underwater photos of the methane-seep-related microbial build-ups growing at the upper slope of the NW Black Sea. The pictures were made from research submarine Benthos-300 in December 1990, water depth 230 m (A); and with the Ocean Floor Observation System (OFOS) at site of the dredging performed during the present study, water depth ~650 m, vertical view (B)

Рис. 4 Подводные фотографии бактериальных построек, расположенных в районах струйных выходов метана на континентальном склоне северо-западной части Черного моря. Фотографии были сделаны с борта научно-исследовательской подводной лодки «Бентос-300» в декабре 1990 г. на глубине 230 м (А); и с помощью подводной телекамеры Ocean Floor Observation System (OFOS) на участке драгирования, проведенного на глубине ~650 м в рамках данной работы - вид сверху (В)

Between these periods, the gradual salinization and warming of the Black Sea waters due to inflow of Mediterranean water have led to change of physiochemical water properties and had a large impact on the gas hydrate reservoir in the sediments [20].

Conclusions. The carbonate samples, taken in the deeper part of the Dnepr paleo-delta area (NW Black Sea) are fragments of the uppermost (crusts with vents), middle (pipe-like) and the lowest (holed plate-like) parts of a methane-derived chimney-shaped microbial build-ups occurring at the depth of the upper boundary of the gas-hydrate stability zone (~700 m water depth). Visual observation conducted with the OFOS system shows that build-ups at this depth are similar

morphologically to those found previously at the shallower and deeper methane seeps of the Black Sea. At the same time, the dredge sampling has allowed recovery, for the first time, the perforated plate-like carbonates in the lowest parts of the build-up provide first indications that gas channels may be formed during the earliest growth phase of these unique microbial structures.

Stable carbon isotope analyses of the carbonates from the uppermost fragments gave the $\delta^{13}C$ values ranging from -33.7 to -36.6 ‰, while the $\delta^{13}C$ values of the lowest fragments are significantly lighter, varying between -42.0 and -44.6 ‰. Both these types of carbonates indicate that a major portion of the carbonate carbon originates from bacterial oxidation of the seeping methane. Oxygen isotopic values also show differences between samples from the uppermost part of the build-up, which are composed of a mixture of aragonite and Mg-calcite ($\delta^{18}O$ = 0.7 to 0.94 ‰), and the only Mg-calcite cemented thin slabs of lowest carbonates ($\delta^{18}O$ = 1.35 to 1.57 ‰). The difference in $\delta^{13}C$ and $\delta^{18}O$ values found in the upper and lowest parts of the build-ups may indicate that more carbon derived from seawater and less hydrate water are involved to the chimney formation during its growth, but this may be also a record of the long-term changes in the near-bottom environments related to evolution of salinity, temperature and anoxic conditions in the Black Sea.

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Обнаружение бактериальных карбонатных построек, растущих вблизи верхней границы зоны стабилизации газогидратов в Черном море. С. Б. Гулин, Й. Грейнерт, В. Н. Егоров, М. Де Батист, Ю. Г. Артемов. Интенсивное драгирование, проведенное в мае-июне 2004 г в верхней части палео-дельты Днепра (северо-западная часть Черного моря), позволило впервые обнаружить коралловидные карбонатные постройки вблизи верхней границы зоны стабилизации газогидратов (~ 700 м). Образцы карбонатов, отобранные с помощью донного трала, представляют собой фрагменты верхней, средней и нижней части постройки, морфологически сходные с образцами, исследованными ранее в более мелководных и более глубоководных районах струйных выходов метана из дна Черного моря. Вместе с тем, обнаруженные впервые пластинчатые перфорированные карбонаты из нижней части постройки являются свидетельством того, что каналы для выхода газа формируются на самой ранней стадии роста этих структур. Анализ изотопного состава карбонатов показал, что дисперсия изотопов углерода ($\delta^{13}C$) в верхней части постройки варьирует от -33.7 ‰ до -36.6 ‰, тогда как в нижней части карбонаты характеризуются меньшим содержанием тяжелых изотопов углерода ($\delta^{13}C$ = -42.0 ÷ -44.6 ‰). Изотопный состав кислорода также показал различие в относительном содержании ^{18}O в верхней части постройки ($\delta^{18}O$ = 0.7 ÷ 0.94 ‰), и в ее нижней части ($\delta^{18}O$ = 1.35 ÷ 1.57 ‰). Данные по изотопному составу углерода и кислорода показали, что карбонатные постройки на исследованной глубине образованны в результате анаэробного окисления метана, поступающего из верхних слоев донных осадков. Различие в величинах $\delta^{13}C$ и $\delta^{18}O$, обнаруженное в верхней и нижней части постройки, может свидетельствовать о том, что по мере ее роста бóльшее количество бикарбонатов, растворенных в морской воде, используется метанотрофными археобактериями в процессе анаэробного окисления метана. Это может отражать, также, изменения солености, температуры и содержания сероводорода в придонной воде, происходившие в *течение длительного (2500-5500 лет) периода роста бактериальных карбонатных построек в Черном море.*

Ключевые слова: Черное море; метановые сипы; газогидраты

Виявлення бактеріальних карбонатних споруд, що ростуть поблизу верхньої границі зони стабілізації газогидратов у Чорному морі. С.Б. Гулін, Й. Грєйнєрт, В.М. Єгоров, М. Де Батіст, Ю.Г. Артемов. Інтенсивне тралення, виконане в травні-червні 2004 р. у верхній частині палео-дельти Дніпра (північно-західна частина Чорного моря), дозволило вперше знайти коралоподібні карбонатні споруди поблизу верхньої границі зони стабілізації газогідратів (~ 700 м). Зразки карбонатів, відібрані за допомогою донного трала, являють собою фрагменти верхньої, середньої і нижньої частини споруди, морфологічно подібні зі зразками, дослідженими раніше в більш мілководних і в більш глибоководних районах струминних виходів метану з дна Чорного моря. Разом з тим, уперше виявлені пластинчасті перфоровані карбонати з нижньої частини споруди є першим свідченням того, що канали для виходу газу формуються на самій ранній стадії росту цих структур. Аналіз ізотопного складу карбонатів показав, що дисперсія ізотопів вуглецю ($\delta^{13}C$) у верхній частині споруди варіює від -33.7 ‰ до -36.6 ‰, тоді як у нижній частині карбонати характеризуються меншим змістом важких ізотопів вуглецю ($\delta^{13}C$ = -42.0 ÷ -44.6 ‰). Ізотопний склад кисню також показав розходження у відносному змісті ^{18}O у верхній частині будівлі ($\delta^{18}O$ = 0.7 ÷ 0.94 ‰), і її нижньої частини ($\delta^{18}O$ = 1.35 ÷ 1.57 ‰). Дані з ізотопного складу вуглецю і кисню показали, що карбонатні споруди на дослідженій глибині сформовані в результаті анаеробного окислювання метану, що надходить з верхніх шарів донних відкладів. Розходження у величинах $\delta^{13}C$ і $\delta^{18}O$, виявлене у верхній і нижній частині споруд, може свідчити про те, що в міру її росту більша кількість бікарбонатів, розчинених у навколишній морській воді, використовується метанотрофнимі археобактеріями в процесі анаеробного окислювання метану. Також, це може відображати зміни солоності, температури і змісти сірководню в придонній воді протягом тривалого (2500-5500 років) періоду росту бактеріальних карбонатних споруд у Чорному морі.

Ключові слова: Чорне море; метанові сіпи; газогідрати