

AUTHIGENIC CARBONATES RELATED TO GAS SEEPAGE STRUCTURES IN THE SEA OF OKHOTSK (NE OFFSHORE SAKHALIN): RESULTS FROM THE CHAOS PROJECT

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ABSTRACT

Mineralogical and isotopic analysis of authigenic carbonates from different gas hydrate-bearing seepage structures in the Derugin Basin (Sea of Okhotsk) are presented. The analysis showed the existence of four morphological types of carbonates, with all of them mainly of Mg-calcite. $\delta^{13}\text{C}$ values of carbonates generally light owing to the inheritance of carbon from microbial methane. ^{13}C -enriched samples at the VNIIOkeangeologia structure with $\delta^{13}\text{C}$ values of up to +9.3‰ represent carbonate precipitation due to methanogenesis. The calculated equilibrium $\delta^{18}\text{O}$ values of carbonates in general correspond to measured values.

Keywords: gas hydrates, authigenic carbonates

INTRODUCTION

The Sea of Okhotsk is one of the biggest reservoirs of gas hydrates [1]. First gas hydrate-bearing structure was discovered in 1986 close to Paramushir Island [2]. Later, in 1991, the methane hydrates were retrieved within gas-venting areas in

the Derugin Basin on the continental slope offshore Sakhalin Island, Russia [3].

Multidisciplinary field investigations in the framework of the CHAOS project (Hydro-Carbon Hydrate Accumulation in the Okhotsk Sea) have revealed new, large hydrate-bearing seepage structures in the Sea of Okhotsk, a northwestern

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marginal sea of the Pacific Ocean [4]. The Derugin Basin at the central part of the Sea of Okhotsk, the zone of intensive gas seepage and hydrate accumulation, was studied during several cruises of the R/V *Akademik M.A. Lavrentyev*: CHAOS-2003 [4,5], CHAOS-2005 [6,7], and CHAOS-2006 [8].

Carbonates are probably the most common mineral precipitates at cold seeps, typically resulting from the anaerobic oxidation of methane. Several reports about the carbonate formation in the seepage structures of the Sea of Okhotsk were published [9-14]. However, these investigations covered only single seepage structures and didn't show the spatial variations in the isotopic and mineralogical composition of carbonates.

This paper is based on results of investigation of the carbonates taken from the 20 sites, located in the 17 seepage structures in the Derugin Basin. In our report we would like to show the mineralogy and isotope geochemistry of authigenic carbonates from the different hydrocarbon seep locations in the Derugin Basin. We present a comparative study that illustrates the processes associated with the gas seepage to the seafloor and the precipitation of authigenic carbonates at the various seeps.

METHODS

All carbonates were sampled during CHAOS-2003 [15], CHAOS-2005 [16], and CHAOS-2006 [17] expeditions on board RV *Akademik M.A. Lavrentyev* (31, 32, 36 and 39 cruises). Sediment coring was carried out using two types of corer (a gravity corer - 5 m and a hydraulic corer - 5.5 m) and dredge.

The mineralogical composition of carbonates was characterized by powder X-ray diffraction analyses at the Kitami Institute of Technology (Rigaku Rint 1200, monochromatic Cu K- α radiation). XRD patterns were obtained from 20° to 50° 2 θ (2 sec at each 0.01° step). Quartz was used as an internal standard for correction of the obtained peaks. Using the shift in d-spacing of the (104) reflection (3.035 Å for stoichiometric calcite), we estimated MgCO₃ content of the trigonal carbonate phases. Assuming that the shift was caused by Mg incorporation, Mg/Ca can be estimated by the standard calibration graphs [18] or using the following simple equation [19]:
$$\text{Mg (mol\%)} = 1/0.00298 (3.035 - d),$$
where d is a measured values of d(104).

Aragonite was defined based on 3.40Å peak. Carbonate mineralogy was determined separately for the inner and the outer parts of the concretions.

The isotopic composition of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ in carbonates was measured by mass-spectrometer Finnigan Delta plus XP at the Kitami Institute of Technology. The CO₂ extraction was carried out with pure H₃PO₄ at 70°C with a Gasbench on-line device connected to a mass-spectrometer. The NBS-19 limestone was used as a standard. All carbonate isotope values are given relative to PDB.

STUDY AREA

The Sea of Okhotsk is a large marginal sea at the northwestern rim of the Pacific and is surrounded by continental massifs (western Kamchatka and Okhotsk volcanic belt), Sakhalin, Hokkaido and the Kuril Islands. The Derugin Basin is the major bathymetric feature, located in the western, deepest part of the Sea of Okhotsk at water depths of about 1700 m. Its western flank (the northeast continental slope off Sakhalin Island) corresponds to oil- and gas-bearing fields. This area is filled with mainly Cenozoic sediment of several kilometers thickness and disrupted by numerous faults [20]. The uppermost Neogene-Quaternary sediments are composed mainly of diatomaceous and radiolarian ooze reflecting the high productivity of the Sea of Okhotsk [21].

The northern studied area 1 – “canyon field” was mapped by multibeam in KOMEX cruise (2004SO178) and later by side-scan sonar in CHAOS 2006 cruise. The width and depth of the channel are about 500 m and 100 m respectively. During the CHAOS 2005 and 2006 expedition, a carbonates were sampled in the gas hydrate-bearing structures VNIIOkeangeologia (station LV36-59) and Soloviev (station LV39-25) respectively (figure 1).

The central studied area 2 – “gas seepage field” contain a lot of gas flares in the water column and gas seepage structures on the seafloor. Water depths in the area range from 150 m to 1300 m. More than 40 gas seepage structures with crater shape are revealed on side-scan sonar mosaic [4]. Carbonates were taken from the following sites: Hieroglyph (LV32-14), KOPRI (LV36-15, -39), unnamed (LV36-17), Katyusha (LV36-19), CHAOS (LV36-25, LV32-16), Kitami (LV36-31),

Obzhirov (LV36-45), POI (LV36-55, -57), and Gisella (LV36-61).

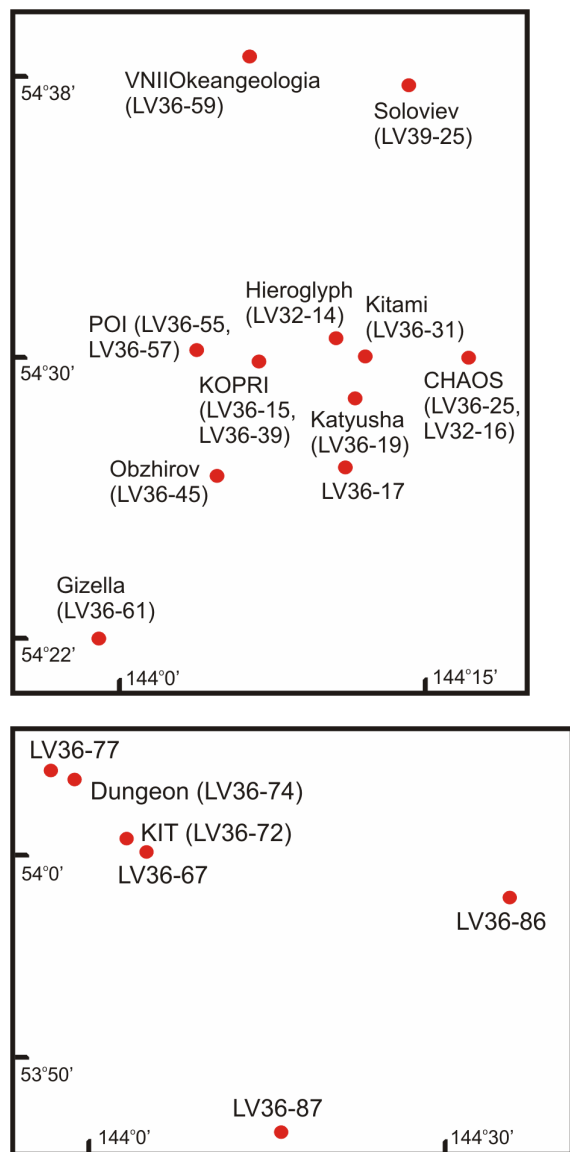


Figure 1. Location map of the study seepage structures (filled circles). Upper map: working areas 1 and 2. Bottom map: working area 3.

Working area 3 – “Lavrentyev Fault field” is located to the south from the “gas seepage field”, where a large-scale fault is the main geological structure. Carbonates were sampled from the KIT (LV36-72), Dungeon (LV36-74) and four unnamed structures (LV36-67, LV36-77, LV36-86 and LV36-87) (figure 1).

RESULTS AND DISCUSSIONS

Morphology and mineralogy

Based on morphology and density, carbonates can be subdivided into four main types. A first type of carbonates is poorly consolidated and fragile (Ia) or soft isolations (Ib), homogeneous in color (light green). They represent the initial stage of the formation of carbonate concretions. The second type of carbonates is dense concretions of dendritic or elongated shape which in some cases contain numerous protuberances. They display a zonality: gray or light-gray soft (or hard) crust, and dark-gray, very hard inner part. SEM observation showed, that the outer crust contains a considerable amount of diatoms, whereas the inner part includes a minor content of silica algae. The third type of carbonates is rounded or subangular dense concretions which have the same zone sequence. The fourth type is tubicolous carbonates formed by substitution of *Polychaeta* worms or burrows.

All types of carbonates are mainly composed of authigenic Mg-calcite with impurity of aragonite in some samples. External parts of carbonates are enriched in terrigenous component relative to the internal parts.

Results of chemical (EDS and ICP) and XRD analysis suggest that magnesium is the main divalent component, which displaces the calcium. The amount of Mg in the carbonate phases is not constant and varied at different sites and stratigraphic levels. The position of the measured $d(104)$ of calcite varies between 2.982 (Soloviev, 17.8 mol% Mg) and 3.034 (Kitami, 0.3 mol% Mg) angstrom. Concretions with highest content of Mg are mainly present in the homogeneous formations (types 1a). These formations are easily crumbled. The lowest concentrations of Mg were detected in the carbonates from structures at the limits of the Lavrentyev Fault area (e.g. LV36-87 – outer and inner parts of very hard zoned concretion, 5.5 and 5.6 mol% respectively; LV36-86 – homogeneous carbonate tile, 6.4 mol%) and also from the shell surface within the Kitami seep. Besides, inner and outer parts of concretions contain various quantities of magnesium with the internal part usually enriched in magnesium relative to the surface. Reversed situation is observed on the site LV36-77 (unnamed structure within the limits of Lavrentyev Fault area).

Stable Isotopes

The obtained isotopic values are generally consistent with values reported earlier from the Sea of Okhotsk [9-15]. The $\delta^{13}\text{C}$ values of carbonates presented here varies from -52.6 (Gisella) up to +9.3 (VNIIOkeangeologia) ‰ PDB. In spite of a wide spread of carbon isotopic values, almost all carbonate samples are ^{13}C -depleted and were produced by the anaerobic oxidation of isotopically light methane (figure 2). Only carbonates from the VNIIOkeangeologia structure (working area 1 – “canyon field”) are composed by the heavy carbon (with positive values) and were most likely formed due to methanogenesis (figure 2; top). It is clear from the figure 2, that the carbonates sampled from the “seepage field” (working area 2) were formed from the total dissolved carbon pool, which was almost ultimately released after anaerobic oxidation of methane (with exception of sample taken from the shell surface in the Kitami seep, $\delta^{13}\text{C} = -13.2\text{‰}$). Carbonates sampled from the Lavrentyev Fault field (working area 3) have a wider spread of carbon isotopic composition, reflecting the influence of additional carbon sources (e.g. oxidation of organic matter and/or shells destruction). Thermogenic gas was not detected in the investigated areas and, therefore, is not considered as a possible source for isotopically heavy carbon. It is important to note, that surface parts usually have heavier $\delta^{13}\text{C}$ values compared to the inner parts, but in some stratigraphic levels the reversed situation is observed (e.g. LV36-87, LV36-77).

Range of $\delta^{18}\text{O}$ values is narrow and is varying between 1.8 (Kitami) and 5.7 (Katyusha) ‰ PDB. Theoretical $\delta^{18}\text{O}$ values for carbonate precipitating in the present Derugin Basin bottom waters ($t = +2^\circ\text{C}$ [5]; $\delta^{18}\text{O} = -0.2\text{‰}$ SMOW [15]) have been calculated according to the experimental equation for Mg-calcite (assuming a 5.2-16.2% MgCO_3 content):

$$1000\ln\alpha = 2.78 \times 10^6 T^{-2} - 2.89 + 0.06\text{Mg} \text{ (mol\%)} \quad [22].$$

The results show that theoretical equilibrium $\delta^{18}\text{O}$ values of CHAOS carbonates varies from 3.6 up to 4.2‰ PDB, depending on the MgCO_3 content.

CONCLUSION

The basic mechanism of carbonate formation within the seepage structures at the studied area was anaerobic methane oxidation via sulfate reduction. Thus, the $\delta^{13}\text{C}$ values of carbonates are

generally light owing to inheritance of carbon from microbial methane. ^{13}C -enriched samples at the VNIIOkeangeologia structure (“canyon field”) with $\delta^{13}\text{C}$ values of up to +9.3‰ represent carbonate precipitation due to methanogenesis.

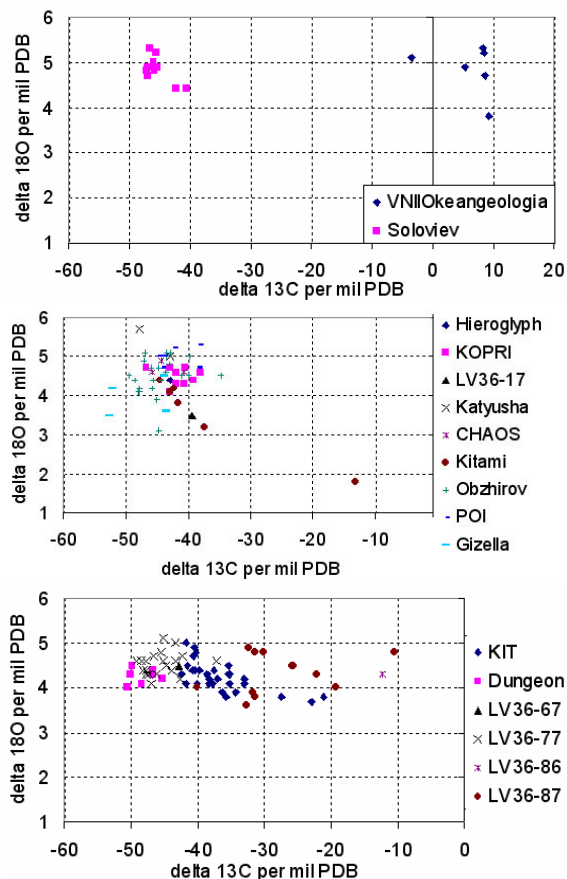


Figure 2. Isotopic composition of carbonates from the working areas 1 (top), 2 (middle) and 3 (bottom)

The calculated equilibrium $\delta^{18}\text{O}$ values of CHAOS carbonates in general correspond to measured values. All types of carbonates are composed mainly of Mg-calcite with minor admixture of aragonite in the several samples. Fluctuations in the ratio of Ca/Mg in the samples are caused by the influence of a “biogenic” source, pore water chemistry, chemical recrystallization during diagenesis and probably also by the composition of discharging fluid. The carbonate’s surface is usually heavier in ^{13}C compared to the inner part. It can be explained by the admixture of isotopically heavier carbon derived from dissolved

bivalve shells and/or from Okhotsk Sea water (pore water).

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