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Association of gas hydrate formation in fluid discharges with anomalous hydrochemical profiles

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Numerous investigations worldwide have shown that active underwater fluid discharge produces specific structures on the seafloor such as submarine seepages, vents, pockmarks, and collapse depressions. Intensive fluxes of fluids, especially of those containing hydrocarbon gases, result in specific geochemical and physical conditions favorable for gas hydrate (GH) formation. GH accumulations associated with fluid discharge are usually controlled by fluid conduits such as mud volcanoes, diapirs or faults. During last decade, subaqueous GHs become the subject of the fuel in the nearest future. However, the expediency of their commercial development can be proved solely by revealing conditions and mechanisms of GH formation. Kinetic of GH growth (although it is incompletely understood) is one of the important parameters controlling their formation among with gas solubility, pressure, temperature, gas quantity and others.

Original large dataset on hydrate-related interstitial fluids obtained from different fluid discharge areas at the Sea of Okhotsk, Black Sea, Gulf of Cadiz, Lake Baikal (Eastern Siberia) allow to suggest close relation of the subaqueous GH formation process to anomalous hydrochemical profiles. We have studied the chemical and isotopic composition of interstitial fluids from GH-bearing and GH-free sediments obtained at different GH accumulations. Most attention was paid to possible influence of the interstitial fluid chemistry on the kinetic of GH formation in a porous media. The influence of salts on methane solubility within hydrate stability zones was considered by Handa (1990), Zatsepina & Buffet (1998), and later by Davie et al. (2004) from a theoretical point of view. Our idea is based on the experimentally proved fact that fugacity coefficient of methane dissolved in saline gas-saturated water which is in equilibrium with hydrates, is higher than that in more fresh water though the solubility is lower. Therefore, if a gradient of water salinity exist under conditions of hydrate stability, diffusion of methane induces hydrate formation by segregation on the outside a boundary fresher/saline water.

Geochemical analysis of the interstitial fluids was used to define the mechanisms of GH accumulation and spatial distribution pattern of GHs in sediments from gas seeps abundant off NE Sakhaline Island (Sea of Okhotsk) (Matveeva et al., 2005; Mazurenko et al., submitted). A model of the ascending fluid discharge along one of the seeps named CHAOS was made based on the measured chlorinity (salinity function) of the pore waters and calculated chlorinity gradients. The chloride ion distributionprofiles with depth at the CHAOS site represent alike increasing and decreasing trends both in hydrate-bearing and hydrate-free cores. The model testifies an upward water infiltration of more saline water in vicinity of coring stations recovered GHs and relatively desalinated water mostly around those hydrate-free. It was established that GH formation at the CHAOS site is focused at the locations of intensive ascending flow of water enriched by salts that is probably function of gas solubility in water in the equilibrium with hydrate supposing that the feature is responsible for the hydrate formation just at the locations of the saline water up flows (other conditions being equal).

Another case study supporting direct relation of GH formation with anomalous fluids and possible GH formation just on the interface of water flows with different salinity (defining chemical potentials of the water) is fresh-water GH accumulation at the Malenkiy fluid vent in the southern basin of Lake Baikal (Matveeva et al., 2003). The GH accumulation characterizes by heterogeneity in the spatial distribution of GH within a very small vent area. The spatial distribution of the GH-bearing and gas-saturated sediments suggests that several small fluid vents exist within the Malenkiy structure. Based on coring results, the size of these vents should not exceed a few meters. Interstitial water chemistry data indicates that water discharged within the Malenkiy vent is enriched with salts, especially Ca, Cl, and SO_4 ions. The ascending water delivering gas into the GH stability zone is thought to be the main GH-forming fluid. Geochemical data suggest that the GH in the subsurface sediments of Lake Baikal originated from a deep source of water with anomalous composition assumed to be derived from buried paleolakes. As a whole, the GH accumulation corresponds to the area of the Malenkiy structure and is represented by several small scale GH occurrences coincident with local fluid discharge manifestations.

The data obtained may serve as useful tool for development of geological and hydrogeochemical models of separate GH accumulations forming in the fluid discharge areas. The models on may also serve as a base for the gas inventory of the GH accumulations.