



Stable carbon and oxygen isotope compositions of methane-derived carbonates from different fluid venting locations

E. Logvina, (1,5), **T. Matveeva** (1), L. Mazurenko (1), T.C.E. van Weering (3,4) , M. Ivanov (2), A. Stadnitskaia (3) and V. Blinova (2)

(1) All-Russia Research Institute for Geology and Mineral Resources of the Ocean (VNIIOkeangeologia), 190121, 1, Angliyskiy ave., St.Petersburg, Russia, (2) Moscow State University (MSU), 119899, Vorobjevy gory 1, Moscow, Russia, (3) Royal NIOZ, Landsdiep 4, 1797 SZ, 't Horntje, Texel, the Netherlands, (4) Department of Paleoclimatology and Geomorphology, Free University of Amsterdam, de Boelelaan 1085, 1081 HV Amsterdam, the Netherlands, (5) St.Petersburg State University (SPbSU), Universitetskaya naberegnaya 7/9, St.Petersburg, Russia (e-mail: Liza_Logvina@mail.ru)

This paper discusses stable carbon and oxygen isotope data for a sample collection of methane-derived carbonates. These carbonates were sampled during several national and international marine research cruises in various fluid venting areas. The aims of this study were to determine stable carbon and oxygen isotope compositions in different types of fluid venting (active and ancient gas seepages, discharges of gas-saturated water, mud volcanoes) and to clarify factors cause differences in the isotope composition at separate sites and environments. Several manifestations of methane-derived carbonates were studied: carbonate crust and concretions from mud breccias (Gulf of Cadiz (NE Atlantic)), dolomite and Mg-calcite chimneys on the seafloor resulted from ancient gas seepage activity (Gulf of Cadiz, North-western Black Sea), carbonate crusts, concretions, and nodules from sediments from active gas venting sites (the Sea of Okhotsk, Eastern Black Sea, Norwegian Sea (Vøring Basin)), carbonate concretions from site of barium-rich fluid discharge at the Sea of Okhotsk). More than 270 carbonate samples were analyzed in the Stable Isotope Laboratory (Faculty of Earth and Life Sciences, Free University of Amsterdam).

The obtained results revealed a wide range of methane seepage environments and related the carbonate precipitation. The studied samples as a whole were divided in two groups on the base of $\delta^{18}\text{O}$ determinations: sourced from seawater and those formed from ascending gas-saturated fluids with specific chemical and isotope compositions. The other factors controlling the isotope characteristics variations are recrystallization during long venting activity, diagenetic transformations, and specific temperature environment of the carbonate formation.

The first group represent by the carbonates from the active gas venting at the Eastern Black Sea and from the Gulf of Cadiz mud volcanoes with $\delta^{18}\text{O}$ values varying from +3.0 to -3.0‰, indicating that the precipitation of these carbonates were mainly in equilibrium with the ambient sea water.

The main part of the carbonates (second group) showed relatively ^{18}O -enriched characteristics: from +3.0 to +6.5‰. Such heavy values are typical for authigenic carbonates formed in the active venting sites of the Sea of Okhotsk, the Norwegian Sea and for chimneys discovered on the seafloor at the ancient seepage locations.

The stable carbon isotope signatures were also varied in the wide range, $\delta^{13}\text{C}$ ranges from +1.9 (Gulf of Cadiz) to -55.1‰ (Norwegian Sea) that testifies variety of the carbon sources taking part in the authigenic carbonate formation. Stable carbon isotope characteristics from carbonates revealed four potential carbon sources: (i) microbial methane, (ii) thermogenic, non-microbial methane, autochthonous to the host sediments DIC, and (iv) marine carbonate. The most common carbon source in the studied carbonates with $\delta^{13}\text{C}$ values from -55.0 to -30.0‰, is the carbon dioxide resulted from microbial oxidation of biogenic methane (active gas venting in the Norwegian Sea, Sea of Okhotsk, chimneys from ancient seeps at the North-western Black Sea). $\delta^{13}\text{C}$ values from 0 to -30.0‰, measured in the samples of crusts and dolomite chimneys from the Gulf of Cadiz, and in the samples from the Eastern Black Sea). One can suggests that an isotopic fractionation during recrystallization of calcium hexahydrate (ikaite [$\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$], $\delta^{13}\text{C} = -3.3\%$, (Domack et al., 2007) and -21.9‰, (Derkachev et al., 1999)) is resulted in formation of the carbonates with such isotopic values. This suggestion supported by the fact that the ikaite formation occurs at the decreased temperatures of the bottom waters (0 °C and lower) and at the considerable concentrations of organic matter.

Some carbonate samples from the Gulf of Cadiz and the Eastern Black Sea shows $\delta^{13}\text{C}$ values from 1.92‰, to 0‰. These values can result from input of carbon from ancient sediments that lost "light" carbon during either burial metamorphism or local hydrothermal activity. It means that this carbon was possibly washed out by the upcoming fluid and incorporated into the local ΣCO_2 -pool.

The study of stable oxygen and carbon isotope compositions allows reconstructing the environments where carbonates were formed.

This study was carried out as a part of the joint Dutch-Russian NWO/RFBR Dutch-Russian cooperative project (047.017.003) between the Royal NIOZ and the UNESCO/MSU Center for Marine Geology and Geophysics entitled "Evolution and Ecology of Cold Seep Structures in the Gulf of Cadiz".

References:

Derkachev, A.N., Nikolaeva, N.A., Obzhairov, A.I., Greinert, J., Suess, E., Bohrmann, G., Nurnberg, D. 1999. Glendonite concretions from island slope of north-Eastern Sakhalin. *Geology for Oceans and Seas, Abstract book XII International school for marine geology, vol.2, Moscow*. Pp. 154-155.

Domack, Eugene W., Halverson, Galen, Willmott, Veronica, Leventer, Amy, Brachfeld, Stefanie, Ishman, Scott. 2007. Spatial and temporal distribution of ikaite crystals in Antarctic glacial marine sediments. U.S. Geological Survey and The National Academies; USGS OF-2007-1047, Extended Abstract.015.