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The formation history of dolomite chimneys based on the δ^{18}O and δ^{13}C data (the Gulf of Cadiz, NE Atlantic)

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A large field of carbonate chimneys, named DIASOM, was discovered by the first time in the Gulf of Cadiz in 2000 (V. Diaz-del-Rio et al., 2003). A huge amount of the carbonate chimneys and crusts were discovered in the Gulf of Cadiz during the several Training Through Research cruises in 2001-2005 (TTR-11, 12, 14, 15), onboard of the R/V "Professor Logachev"(Ivanov et al., 2000; Blinova et al., 2002; Bileva et al, 2004; Sharapova et al., 2005).

Carbonate mounds, buildups and chimney-like structures, carbonate-cemented sediments, crusts and concretions are typical features that form around gas vents and cold seeps. Such methane-related carbonates have been reported in various cold venting locations: Oregon margin (Schroeder et al., 1987); North Sea (Hovland et al., 1987; Hovland and Judd, 1988); Gulf of Mexico (Baoshum et al., 1994; Roberts and Carney, 1997); Monterey Bay (Orange et al., 1999; Stakes et al., 1999); Sea of Okhotsk (Derkachev et. al., 2000; Matveeva et al., 2003); Kattegat (Jorgensen, 1992); Nankai Trough (Sakai et al., 1992); Otago continental slope, southern New Zealand (Orpin, 1997) and Makran accretionary wedge (Von Rad et al., 1996), etc. The precipitation of a carbonate results from excess carbonate generated by microbially-mediated process of anaerobic oxidation of methane (AOM; Ritger et al. 1987). Therefore, a fundamental requirement for the formation of these structures is the presence of methane used by microbes performing AOM as their carbon source. Formation of the authi-

genic carbonates occurs below the seafloor, in strict anoxic environments since AOM-performing microorganisms are obligate anaerobes (Fuex, 1977; Hathaway and Degens, 1968; Nissenbaum, 1984).

Two dolomite chimneys, sampled during the TTR-14 (2004) cruise were studied using stable carbon and oxygen stable isotopes. These chimneys were studied in details by measuring distribution profiles of δ^{13}C and δ^{18}O characteristic to reveal a probable sources of incorporated carbon and oxygen during the chimney formation. More than 70 samples were measured at the Stable Isotope Laboratory in the Free University of Amsterdam. Carbon, dioxide was extracted from the carbonates using 100 % phosphoric acid at 45˚C (for dolomite). Isotope ratios were measured using Finnigan Gasbench II consists of an auto-sampler, the Gasbench and the Finnigan DeltaplusXP .

Studied chimneys consist of dolomite mainly and classified (mineralogicaly) as the third type of the chimneys from the Gulf of Cadiz (Blinova, 2006). This type of chimneys is characterized by stable carbon and oxygen isotope composition from -1.9‰ to -24.7‰ and from 0.2‰ to 5‰, respectively (Blinova, 2006). The age of these crusts were determined by the U/Th techniques and composed ca.174 000 years (Blinova, 2006);

Our data revealed the growing history of the studied chimneys. It was possible to identify the top and the bottom part of the precipitant and to recognize both inside and outside an accretion direction. The obtained δ^{13}C values indicate three main carbon sources inherited by the carbonate: (1) AOM-derived carbon, (2) carbon from the ambient sea-water (δ^{13}C = 0‰), and carbon from the autochthonous organic matter (δ^{13}C = -27‰). The stable oxygen isotope composition varies from 2 ‰ to 5.5 ‰. This indicates that the studied chimneys were formed in the equilibrium with the ambient seawater. A small shift towards a depletion of δ^{18}O values can be explained by the recrystallization processes in the mineral consecution of calcite - Mg–calcite - dolomite.

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