Geophysical Research Abstracts
Vol. 14, EGU2012-4161, 2012
EGU General Assembly 2012

Past methane seepage and linked deep-water anoxia are logged in methane-derived carbonates

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The precipitation of carbonate in methane saturated environments is a common phenomenon that is caused by the increase of alkalinity due to the microbial process of anaerobic oxidation of methane (AOM) accomplished by a consortium of sulfate reducing bacteria and methanotrophic archaea (Boetius et al., 2000). Since the formation of such carbonates is irrespective to climate changes and to the depth of the carbonate compensation, they represent unique archives of the time and duration of methane seepage, adjacent sedimentary/water column environments and associated bionetwork.
The Nile Deep Sea Fan basin is known for the widespread occurrence of seabed methane/fluid seepage linked to mud volcanoes and pock marks. Massive accumulations of methane-derived carbonate pavements and up to one meter buildups were often encountered in the vicinity or even within mud volcano structures. Here we analyzed at high resolution the differences in stable carbon and oxygen isotope compositions and lipid biomarker composition, accompanied with U/Th dating of the topmost part of a ~1 m-high carbonate edifice sited at the margin of the Amon mud volcano. The uppermost part of the edifice has been dated at ~7.8 - 9.1 kyr B.P. This is synchronous with the increase of fresh-water fluxes in the Eastern Mediterranean resulting in density stratification of the water column (~ 10.5 - 5.0 14C kyr B.P.), with the formation of S1 sapropel (~9.7 – 5.7 14C kyr B.P.; De Lange et al., 2008), and with the Holocene warm climatic optimum (Rohling and Hilgen, 1991). Significant changes of [U+F064]13CCaCO_3 values, from -32 to -9‰ (VPDB), indicate swings in methane flux, which affected rates of AOM and the consequent production of 13C-depleted HCO_3-. Lipid biomarkers revealed the presence of methanotrophic archaea of the ANME-2 group due to the dominance of sn-2-hydroxyarchaeol over archaeol and the low abundance of tetraether lipids (Blumenberg et al., 2004). Ecologically these archaea are associated with elevated methane fluxes. Lipid biomarkers indicative of aerobic microorganisms were not detected.
The precipitation of AOM-related carbonates is limited to oxygen-free conditions since both AOM-performing microorganisms are so far known as obligate anaerobes. It is clear that the formation of carbonate build-ups above the seafloor is only possible in an anoxic water column. De Lange et al. (2008) reported that the whole Eastern Mediterranean Basin has been predominantly oxygen-free below ~ 1.8 km during 4 kyr of S1 sapropel formation. The Amon mud volcano is located at the water depth of ~ 1100 m. Our results thus potentially indicate that during the accretion of the studied carbonate build-up the oxycline was most likely shallower. The U/Th age determinations were only performed for the uppermost part of the structure, i.e. for the latest phase of the edifice development. Bayon et al. (2007) reported continuous carbonate precipitation over the last ~5000 years for a 5.5 cm thick crust in this area. The timing of the build-up formation is consistent with the period when bottom waters of the Eastern Mediterranean were anoxic. Most likely such carbonate edifices in the Nile Deep Sea Fan basin are fossil analogue of the currently existed microbial carbonate reefs in the Black Sea fuelled by AOM (Michaelis et al., 2002).

References:
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