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Microbial carbonate build-ups at methane seeps near the upper boundary of the gas-hydrate stability zone in the Black Sea: results of EU project CRIMEA

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Extensive dredging carried out in May-June 2004 in the deeper parts of the Dnepr paleo-delta area (NW Black Sea) yielded for the first time chimney-shaped carbonate microbial build-ups, which occur at methane seeps close to upper boundary of the gas-hydrate stability zone (~ 700 m). Carbonate samples taken with a benthic trawl represent fragments of the uppermost, middle and lowest parts of the build-up, which are similar to those found previously at the shallower and deeper methane seeps in the Black Sea. At the same time, the holed, plate-like carbonates in the lowest parts of the build-up provide first indications that gas channels are formed during the earliest growth phase of these microbial structures. Stable carbon isotope analyses of the carbonates from the uppermost fragments gave the $\delta^{13}\text{C}$ values ranging from -33.7 to -36.6 pro mil, while the $\delta^{13}\text{C}$ values of the lowermost fragments are significantly lighter, varying between -42.0 and -44.6 pro mil. Both these types of carbonates indicate that a major portion of the carbonate carbon originates from bacterial oxidation of the seeping methane. Oxygen isotopic values also show differences between the more irregular and porous samples from the uppermost part of the build-up, which are composed of a mixture of aragonite and Mg-calcite ($\delta^{18}\text{O} = 0.7$ to 0.94 pro mil, and the only Mg-calcite cemented thin slabs of lowermost carbonates ($\delta^{18}\text{O} = 1.35$ to 1.57 pro mil. The difference in $\delta^{13}\text{C}/\delta^{18}\text{O}$ ratio found in the upper and lower parts of the build-up may reflect the changing of the water temperature and salinity during the chimney growth.