

Contribution of methane seeps to the post-Marinoan cap carbonate? Evidence from carbon isotope and petrology in Yangtze Gorges area, South China

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Extremely negative methane-derived $\delta^{13}\text{C}_{\text{carb}}$ values from the Ediacaran Doushantuo cap carbonate (ca. 635 Ma) in the Yangtze Gorges area, South China, were taken as direct evidence for the hypothesis of methane hydrate destabilization. However, the methane-derived $\delta^{13}\text{C}_{\text{carb}}$ signatures were reported only from specific strata of the cap carbonate in three locations in the Yangtze Gorges area, South China. Here we report $\delta^{13}\text{C}_{\text{carb}}$ values as low as -44.36‰ (VPDB) in the calcitized structures in two strata from the Jiulongwan cap carbonate section in the Yangtze Gorges area, South China. These extremely negative $\delta^{13}\text{C}_{\text{carb}}$ values were obtained only from calcite components, while the dolomite components of cap carbonate usually showed relatively heavier $\delta^{13}\text{C}_{\text{carb}}$ values from -7.00‰ to 1.43‰ . Petrographic data show that the calcites with extremely negative $\delta^{13}\text{C}_{\text{carb}}$ value occur as blocky cements, veins, and usually replaced former precipitated dolomite at early diagenesis, suggesting that during or after the precipitation of cap dolomite, the methane hydrate destabilization and subsequent methane oxidation resulted dedolomitization of cap carbonate, leaved behind stratigraphically restricted distribution of calcite components with extremely negative $\delta^{13}\text{C}_{\text{carb}}$ values. Extremely negative carbon isotope values certify the destabilization of methane hydrate in post-Marinoan ocean, but stratigraphically and limitedly occurrence imply that the link between the formation of cap carbonate, mainly consisting of dolomite, and the destabilization of methane hydrate in postglacial ocean is still not clear.

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Microbial mineral carbonation in anaerobic fermentations

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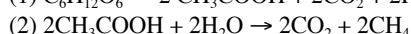
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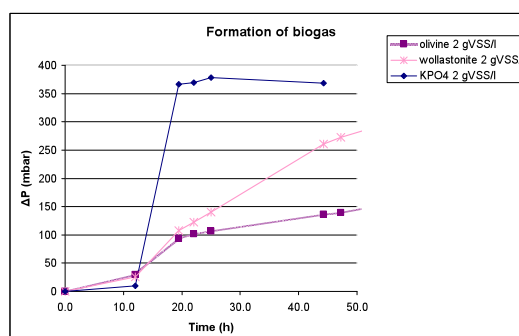
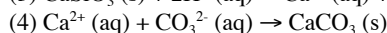
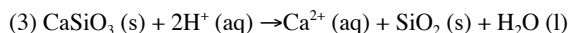
Mineral carbonation and Anaerobic fermentation

In anaerobic digesters organic waste is converted into biogas (65% CH_4) by micro-organisms according to the following simplified equations [1]:



Thus, production of CO_2 dilutes the caloric value of the biogas. Furthermore, production of acetic acid acidifies the reactor broth. Below a pH of 5.5 production of CH_4 -rich biogas is strongly inhibited [2].

Mineral carbonation reactions (with olivine and wollastonite) were used to prevent pH drop and directly sequester CO_2 , according to the following reaction equations [3]:



Discussion of results

Reaction rates of respectively 0.44, 0.21 and 0.12 gCOD- $\text{CH}_4/\text{g VSS}/\text{day}$ were obtained for phosphate, wollastonite and olivine buffer. Addition of wollastonite and olivine resulted in the dissolution of Ca^{2+} and Mg^{2+} and the precipitation of carbonate mineral according to reaction (4). Also significantly improved biogas composition ($>95\%$ CH_4) was measured. Wollastonite showed to be more reactive. Details on the experiment will be elaborated.

[1] Stams & Plugge (2009) *Nature Review Microbiology* **7**, 568–577. [2] Lettinga *et al.* (2000) *Biological wastewater treatment-part 1 Wageningen University* p. 200. [3] Kodama (2008) *Energy* **33**, 776–784.