

Formation of carbonate minerals at early stage of sulfate-driven anaerobic oxidation of methane

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Precipitated by sulfate-driven anaerobic oxidation of methane (SD-AOM) at cold-seep sites, authigenic carbonates, including aragonite, low-Mg-calcite (LMC), high-Mg-calcite (HMC) and dolomite, archive different stages of seep activity. We previously found that HMC and dolomite were formed under reducing conditions [1] indicating late-stage seep activity. Here, we study carbonates from Haima area and site TVG11 to characterize the carbonate phases at early stage of cold-seep activity.

Carbonate phases are microcrystalline aragonite and a few HMC at Haima area and micritic HMC with isopachous aragonite at site TVG11. Pyrites are scattering between carbonates as framboids. Although rare earth element patterns reveal reducing pore water conditions for both sites, lower contents and sulfur isotope values of chromium reducible sulfur (CRS) in Haima samples than in TVG11 samples indicate more open system with sufficient sulfate supply from seawater. Thus, we suggest that microcrystalline aragonite from Haima area were precipitated at the initial interaction between seep pore water and seawater while micritic HMC of TVG11 were formed at slightly later stage. Contents and sulfur isotope values of CRS positively correlate with MgCO₃ contents of carbonates, supporting the sulfidic catalysis formation of HMC and dolomite [1, 2]. At early seepage stage as for Haima samples, sulfide was oxidized, resulting in microcrystalline aragonite. In the following stage as for TVG11 samples, accumulated sulfide catalyze the precipitation of micritic HMC.

Our work suggests (1) microcrystalline aragonite as the phase precipitated at initial stage of cold-seep activity, caused by the absence of catalysis by dissolved sulfide, and (2) contributes to the understanding of dolomite formation.

[1] Lu et al. (2018) *AM. Mineral.* 103(5), 720-734.

[2] Zhang et al. (2012) *GCA* 97, 148-165.