



Sulfate-driven anaerobic oxidation of methane catalyzes dolomite formation: A case study from the northern South China Sea

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Laboratory syntheses of stoichiometric and ordered dolomite at Earth-surface conditions have not succeeded. However, low-Mg-calcite (LMC), high-Mg-calcite (HMC), and dolomite have been discovered in authigenic carbonate precipitated at cold methane seeps. Sulfate-driven anaerobic oxidation of methane (SD-AOM), operated by the consortium of methane oxidizing archaea and sulfate reducing bacteria, converts methane and sulfate into bicarbonate and sulfide, stimulating the precipitation of multiple carbonate phases. From seabed to cold seep at Hydrate Ridge, the main carbonate phase changes from aragonite over LMC and HMC to dolomite. Recent laboratory work at low temperature show that dissolved sulfide and extracellular polymeric substances (EPS) could catalyze the precipitation of disordered dolomite which is a potential precursor of ordered dolomite. To test their catalytic effects on the precipitation of seep carbonates, we investigated the mineralogy, concentrations of Ca, Mg, and rare earth element (REE), and carbon isotope compositions of seep carbonates from Shenhu area and Southwest (SW) Taiwan basin. Multiple carbonate phases with a wide range of MgCO_3 contents are detected by X-ray diffraction analysis. Transmission electron microscopy indicates that Ca-dolomite and weakly ordered dolomite are the main dolomites in Shenhu and SW Taiwan samples, respectively. The microstructure of Ca-dolomite is mostly composed of dolomite structure, only a few domains show the structure of Mg-calcite. Weakly ordered dolomite, containing less MgCO_3 , shows heterogeneously distributed domains of Mg-calcite and dolomite structures. The geochemical results vary synchronously with the carbonate mineralogy. Positive relationships are shown between the Mg/Ca mole ratios, cerium anomalies, Nd_N to Yb_N ratios, and ^{13}C -depletion, indicating the incorporation of Mg^{2+} into carbonate lattice promoted by SD-AOM. Based on previous works, we believe that the catalytic effects of sulfide and EPS are the most possible factors for the formation of seep dolomite. Under the conditions enriched in bicarbonate, sulfide, and EPS released by SD-AOM, disordered nano-crystals of Ca-Mg carbonates may be firstly crystallized. The MgCO_3 content of them is positively related with the concentration of sulfide and EPS which correlates to the intensity of SD-AOM. After growth, recrystallization, and maturation, Ca-Mg carbonates with MgCO_3 content close to stoichiometric dolomite turn into Ca-dolomite, whereas those with relatively less MgCO_3 transform into weakly ordered dolomite. Our study contributes to the understanding of dolomite formation and the relationship between carbonate phases of seep carbonate deposits and the status of methane seep activity.