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Formation of dolomite catalyzed by sulfate-driven anaerobic oxidation of methane: Mineralogical and geochemical evidence from the northern South China Sea

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Abstract

It is very difficult to synthesize dolomite under Earth-surface conditions in the laboratory. However, multiple carbonate phases, including low-Mg-calcite (LMC), high-Mg-calcite (HMC), and dolomite, have been discovered in authigenic carbonate deposits that precipitated at cold methane seeps. The formation of such seep carbonates is triggered by the sulfate-driven anaerobic oxidation of methane (SD-AOM), which is mediated by a consortium of methane-oxidizing archaea and sulfate-reducing bacteria; this process releases bicarbonate and dissolved sulfide. Thus, the formation of Ca-Mg carbonate phases and, particularly, their respective $MgCO_3$ contents are likely to be intimately related to SD-AOM and the methane supply at cold seeps. Yet, the driving forces for $MgCO_3$ enrichment and the actual mechanism responsible for the incorporation of Mg^{2+} into the crystal lattice are not fully understood. Interestingly, recent laboratory experiments succeeded in synthesizing disordered dolomite under the catalysis of dissolved sulfide and extracellular polymeric substances (EPS) at low temperatures. To characterize the effect of these catalyzes on the formation of seep carbonates, we investigated mineral phases, microstructure, and contents of Ca, Mg, and rare earth elements of seep carbonates from the Shenhu area and the Southwest (SW) Taiwan basin of the northern South China Sea (SCS). The studied carbonates are composed of multiple Ca-Mg carbonate phases, including HMC, weakly ordered dolomite, and dolomite with a wide range of $MgCO_3$ contents. Transmission electron microscopy indicates that the microstructure of some Shenhu dolomite is almost stoichiometric, only a few domains exhibit the structure of Mg-calcite. Weakly ordered dolomite from the SW Taiwan basin contains less $MgCO_3$ than the Shenhu dolomite, and is composed of heterogeneously distributed domains of Mg-calcite and dolomite. A positive correlation between $MgCO_3$ contents, cerium anomalies, Nd_N to Yb_N ratios, and ^{13}C-depletion suggests that Mg^{2+} incorporation into the crystal lattice is favored by reducing conditions produced by pronounced SD-AOM. Based on previous studies, we put forward that SD-AOM derived sulfide and EPS produced by the SD-AOM consortium are the most plausible drivers for Ca-Mg carbonate formation at cold seeps. Precipitated under conditions similar to laboratory experiments, the initial Ca-Mg carbonates are apparently disordered nano-crystals with various $MgCO_3$ contents. In the course of maturation and recrystallization, the Ca-Mg carbonates evolve into weakly ordered dolomite or dolomite. This study contributes to the understanding of dolomite formation at cold seeps and the relationship between carbonate mineralogy, the supply of methane, and microbial activity.

Keywords: Dolomite, dolomite problem, authigenic Ca-Mg carbonate, SD-AOM, cold seep, South China Sea