Biomimetic Formation of Monohydrocalcite

YU-YING WANG¹, QI-ZHI YAO²*, AND GEN-TAO ZHOU¹*

¹School of Earth and Space Sciences, University of Science and Technology of China, Hefei 230026, P. R. China (gtzhou@ustc.edu.cn)
²School of Chemistry and Materials, University of Science and Technology of China, Hefei 230026, P. R. China (qzyao@ustc.edu.cn)

Monohydrocalcite (MHC) is a thermodynamically metastable polymorph of CaCO₃ and has already been found in a variety of organisms. The investigation for the calcareous corpuscles of Mesocestoides corti showed that MHC is the major component of the corpuscles and coexists with amorphous calcium carbonate (ACC) and organic matrices. It is widely found that the formation of crystalline biogenic CaCO₃ (calcite, vaterite and aragonite) during biomineralization often occurs via an ACC precursor phase. Almost all the known biogenic ACCs contain appreciable level of Mg²⁺. Further investigations also revealed that the structure of most biogenic ACCs is analogous to MHC. In addition, the inorganic synthesis experiments also demonstrate that ACC and MHC have similar chemical composition, precipitation condition, and thermal behavior. Therefore, some studies indicate that MHC may form from ACC. Nevertheless, these researches cannot fully explain the formation mechanism of MHC in organisms. Herein, a series of Mg-ACCs with different contents of Mg²⁺ were first synthesized and then dispersed into aqueous solution to investigate their transformation under different conditions. Our results show that Mg-ACC with >24 mol % of Mg can transform into MHC at room temperature, and the MHC can be stabilized in aqueous solution for a long time, whereas the low Mg ACCs form Mg calcite and aragonite. The transformation from Mg-ACCs to crystalline polymorphs may all follows the initial precursor Mg-ACC dissolution and then crystallization of secondary mineral phases. Therefore, high Mg ACC may act as the transient precursor and be responsible for the formation of biogenic MHC. The current effort also helps to understand the origin mystery of MHC in nature.