

Supporting information

Crystallization and oriented attachment of monohydrocalcite and its crystalline phase transformation

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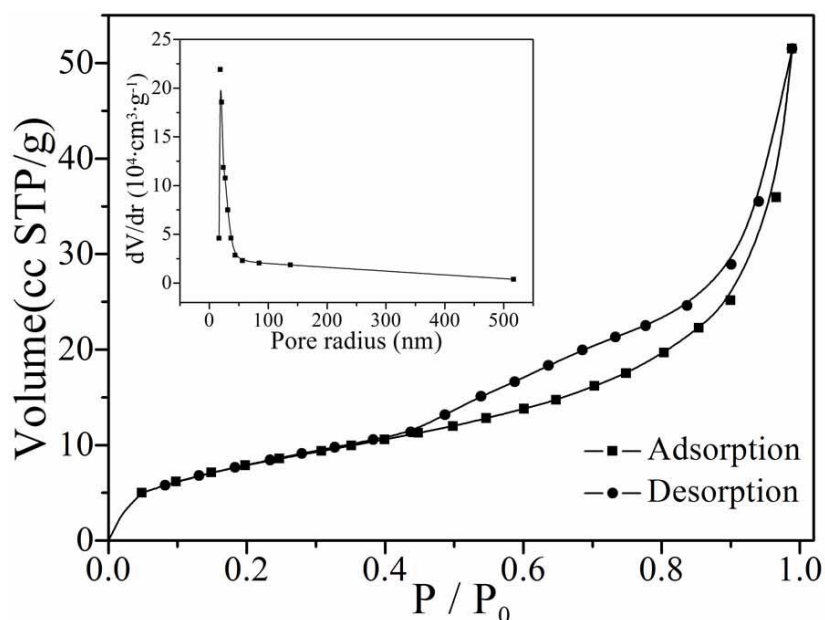


Fig. S1. Nitrogen adsorption-desorption of calcite obtained after the N₂-atmosphere calcination of monohydrocalcite (MHC) dumbbells at 300°C for 3 h. Inset is the corresponding pore volume distribution curve.

The average Brunauer-Emmett-Teller (BET) surface area (S_a) was 27.7 m²·g⁻¹, and the pore radius was 18.5 nm. The relatively high S_a value shows a porous nature of calcite dumbbells, which proves the aggregation of tiny CaCO₃ nanoparticles for the formation of hierarchical superstructures.

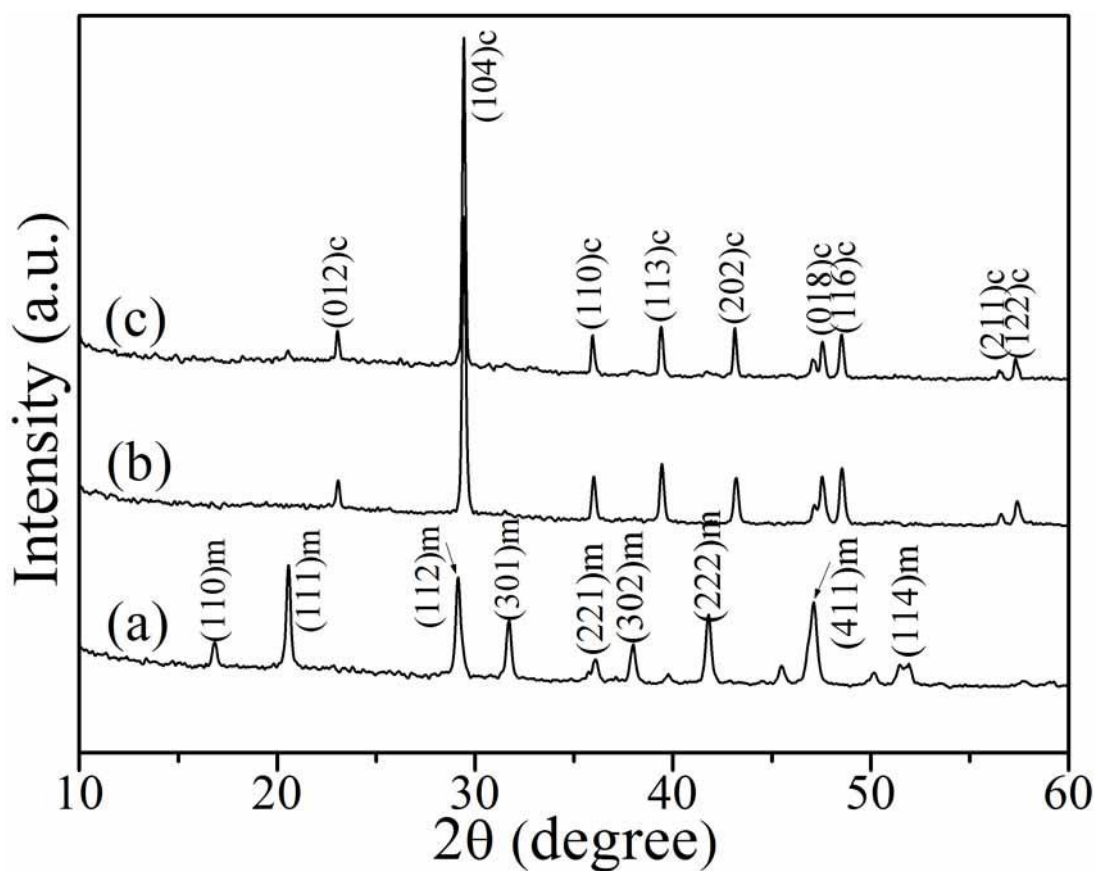


Fig. S2. XRD patterns of CaCO_3 collected from NaCl aqueous systems in the presence of NaOH at 30°C for 24 h: (a), pH 10.0; (b), pH 12.0; (c), pH 13.0. The subscripts *c* and *m* denote the crystal phases of rhombohedral calcite and hexagonal MHC, respectively.

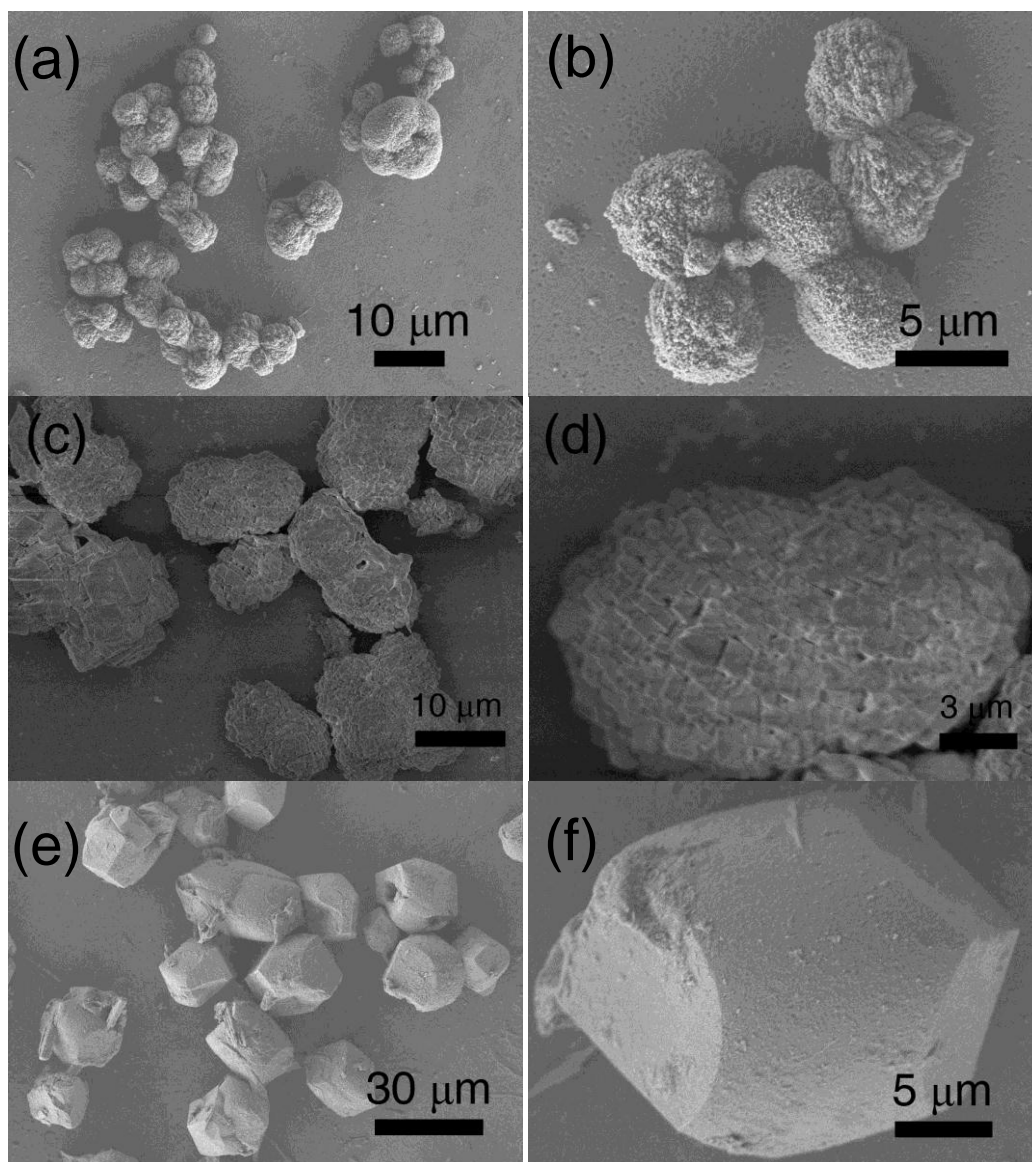


Fig. S3. SEM images of CaCO₃ crystals collected from NaCl aqueous systems in the presence of NaOH at 30°C for 24 h: (a, b), pH 10.0; (c, d), pH 12.0; (e, f), pH 13.0.

As shown in curve (a) of *Fig.S2* and in the panels (a) and (b) of *Fig.S3*, the original dumbbell-like superstructures of MHC did not experience a phase transformation of MHC to anhydrous calcite (and/or aragonite) at pH~10.0 after the 24-h incubation at 30°C. Perhaps, the slight presence of NaOH into NaCl aqueous solution (pH~10.0) is helpful for the stability of MHC.

As for the abnormal phase transformation of MHC to calcite, the released Mg²⁺ ions can be rapidly consumed by hydroxide ions at the first time, resulting in dumbbell-like structures of calcite (panel c and d of *Fig.S3*). The relatively high pH value (i.e., pH~13.0) may modify the supersaturation degree of Mg(OH)₂, then accelerates the dissolution (or transformation) rate of MHC, and then facilitates the nucleation and crystal growth of anhydrous calcite.

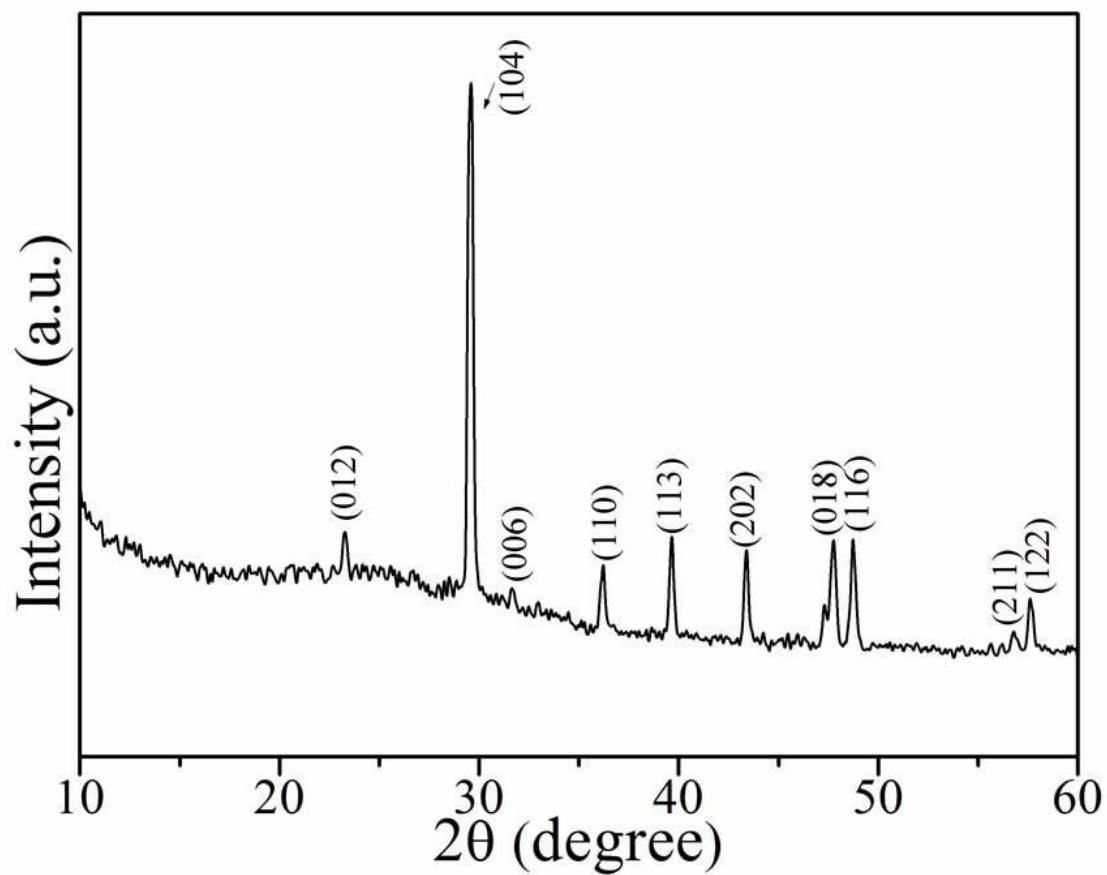


Fig. S4. XRD pattern of anhydrous calcite crystals collected from a NaCl incubation system in the presence of 200.0 mM acetylacetone at 60°C for 24 h.

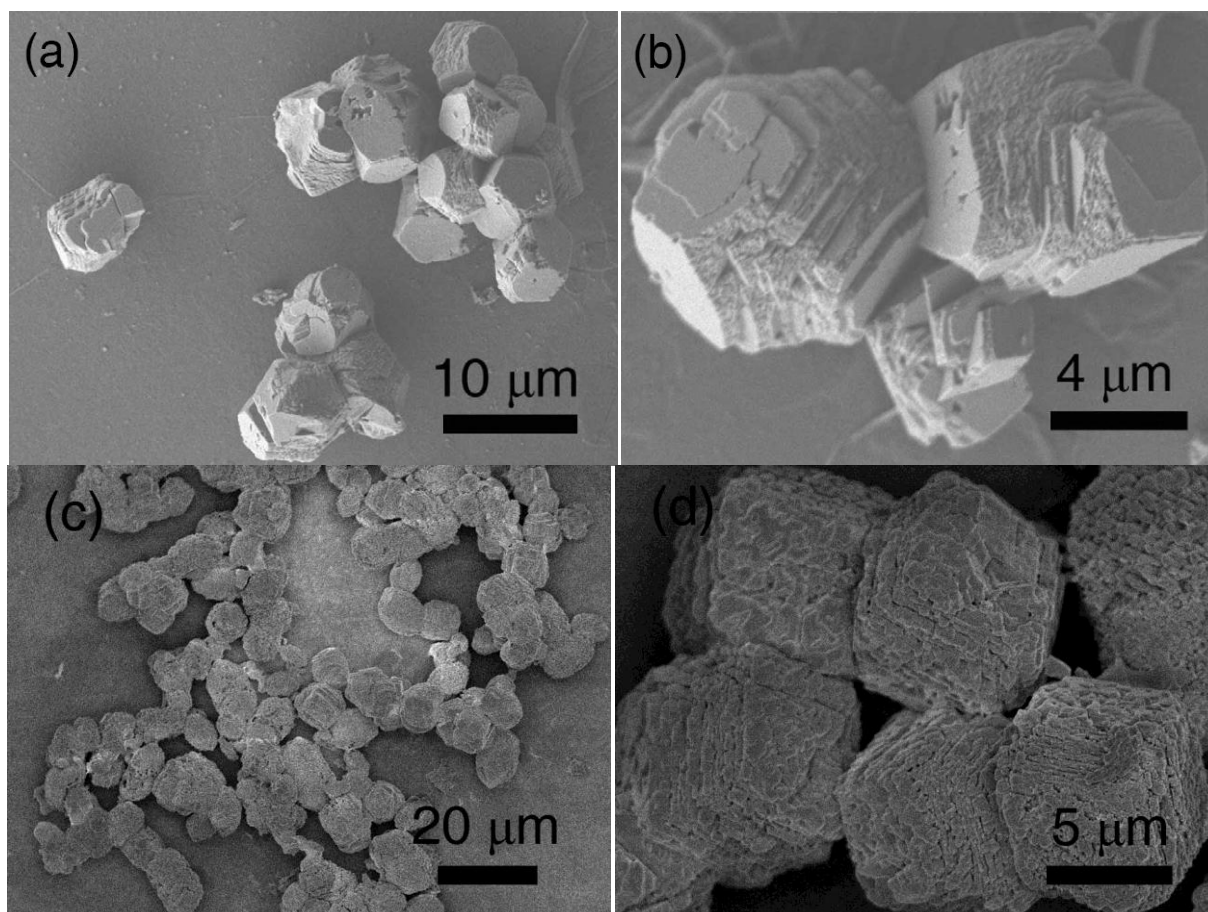


Fig. S5. SEM images of anhydrous calcite crystals collected from a NaCl incubation system in the presence of 200.0 mM acetylacetone for 24 h: (a, b), at 60°C; (c, d), at 30°C.

Polyhedral structures of calcite were obtained, possessing an average size of $7.6 \pm 0.1 \mu\text{m}$, shown in the panels (a) and (b) of *Fig.S5*. The panels (c) and (d) of *Fig.S5* show the rhombohedral superstructures of calcite obtained at 30°C, which has been discussed in the main part of submission and used as a control to emphasize temperature contribution. At 60°C the manifest crystal faces are relatively smooth and there is obvious stepwise surface for some crystallites.

High-resolution SEM observation shows that the polyhedral calcite crystallites, obtained at 60°C, are seemingly the hierarchical superstructures composed of small building blocks. This indicates that the higher incubation temperature accelerates the transformation of MHC to smaller anhydrous calcite nanoparticles and therefore facilitates the fusion of tiny building blocks to form a more compact surface of calcite superstructures.

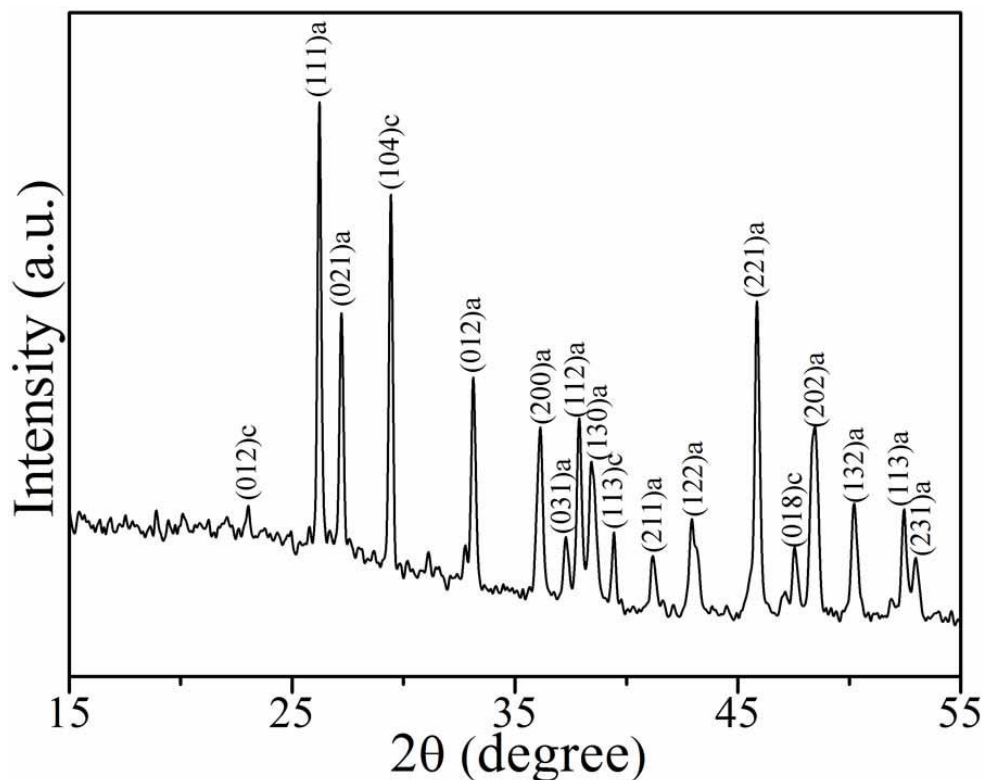


Fig. S6. XRD patterns of anhydrous CaCO₃ crystals collected from a NaCl incubation system in the presence of NaOH for pH adjustment (pH~12.0) at 60°C for 24 h. The subscripts *c* and *a* denote the crystal phases of rhombohedral calcite and orthorhombic aragonite, respectively.

Interestingly, both anhydrous aragonite and anhydrous calcite were obtained. By estimation using the Rao's equation (J. Crystal Growth 2003, 250: 516-524.), the weight fraction of aragonite, in the crystalline mixture of aragonite and calcite, is higher than 50 wt%.

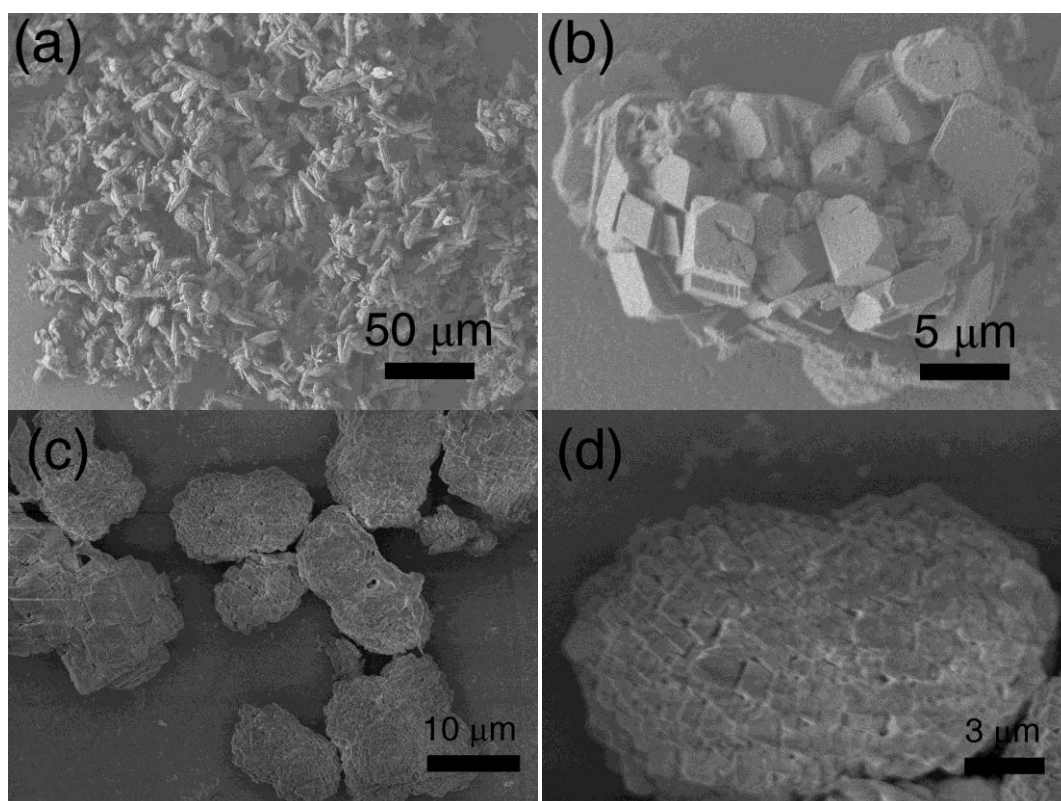


Fig. S7. SEM images of anhydrous CaCO_3 crystals collected from a NaCl aqueous system in the presence of NaOH for pH adjustment (pH~12.0) for 24 h: (a, b), at 60°C; (c, d), at 30°C.

At 60°C the presence of NaOH (pH~12.0) induces the transformation of MHC dumbbell-like superstructures to the crystalline mixture of anhydrous aragonite and calcite: the major rod-like aragonite (panel (a) of *Fig.S7*) and the minor rhombohedral calcite (panel (b) of *Fig.S7*).

At 30°C the presence of NaOH (pH~12.0) can modify the normal phase transformation of crystalline MHC to anhydrous aragonite, resulting in dumbbell-like structures composed of tiny calcite rhombohedrons.

By comparison, the higher incubation temperature (60°C) accelerates the dissolution (or increase the solubility) of crystalline MHC dumbbells, which facilitates transformation of MHC to aragonite prior to the complete consumption of released Mg^{2+} ions.