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Compositional gatekeeping and nucleation inhibition in amorphous calcium carbonate: mechanisms beyond the classical framework

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Transient amorphous calcium carbonate (ACC) is central to carbonate formation in biogeochemical environments and modulates trace-element signatures that underpin carbonate proxy archives. Yet, classical models often fail to predict both foreign-ion/organic incorporation and the magnitude of nucleation suppression. Here, we scrutinize so-called prenucleation clusters: dynamic solute entities built from interconnected chains of carbonato–calcium units that have been discussed as proto-nucleation germs, although their mechanistic status remains debated. We adopt a chemical, mechanism-agnostic perspective and interpret them as supra-ionic coordination clusters that form spontaneously in solution rather than as a pseudo-phase.

Two recent, complementary studies—on organo-compound incorporation and on foreign-ion incorporation—converge on the same mechanistic control point and support cluster-governed pathways. In our first study [1], small acidic organic molecules interact with these clusters; when additives become structurally integrated into the supra-ionic species (via Ca coordination and partial carbonate replacement), they most strongly inhibit ACC nucleation and are the species found in significant amounts in ACC, consistent with cluster-derived precipitation. In our second study, earth-alkaline cations (Mg^{2+}, Sr^{2+}, Ba^{2+}) incorporate into supra-ionic clusters that act as compositional gatekeepers from which ACC forms by aggregation, yielding pronounced ion specificity in both nucleation interference and retention: progressive entropic nucleation inhibition for Ba with increasing Ba/Ca, retrograde inhibition-to-promotion for Sr depending on Sr/Ca, and distinctive Mg behavior involving multiple cluster populations, low distribution coefficients, and nucleation-coupled Mg release/expulsion.

Together, these results underline the limitations of classical concepts rooted in the Szilard postulate, bulk solubility/supersaturation considerations, and fixed-composition critical nuclei, and identify supra-ionic clusters as the key mechanistic level required to rationalize coupled foreign-component incorporation and nucleation inhibition in ACC.

[1] Duchstein et al. (2022), *Angew. Chemie Intern. Ed.* 61; e202208475. doi: 10.1002/anie.202208475

[2] Zhao et al. (2026), *Adv. Funct. Mater.* doi: 10.1002/adfm.202529192