How mild dissolution can actually promote bulk crystal growth
The case of dolomite $CaMg(CO_3)_2$

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ABSTRACT

Dolomite, $CaMg(CO_3)_2$, is a geologically-abundant sedimentary mineral that cannot be precipitated in the laboratory at ambient conditions—not even under highly-supersaturated solutions. Known as the 'Dolomite Problem', this apparent contradiction represents a longstanding mystery in both geochemistry and crystal growth theory. Although bulk-ordered dolomite is thermodynamically stable, here we use atomistic simulations to show that during crystal growth, the entropy of Ca/Mg disordering overwhelms the enthalpy of cation ordering. This leads to the deposition of a disordered dolomite surface layer that inhibits further bulk crystal growth. Dissolution-reprecipitation gradually orders disordered dolomite—but intriguingly, we predict that this ordering process can be dramatically accelerated by iterative periods of undersaturation, which preferentially dissolves disordered surface regions and makes way for increased cation order during reprecipitation. To validate this mechanism, we perform 994 supersaturation cycles inside an *in situ* liquid-cell TEM, directly observing 30 nm of bulk dolomite crystal growth. Our theory rationalizes why modern dolomite is primarily found in environments with natural salinity fluctuations and further reveals a counterintuitive insight that growth of defect-free crystals can be promoted by deliberate periods of mild dissolution.