

Nucleation of Metastable Aragonite CaCO_3 in Seawater

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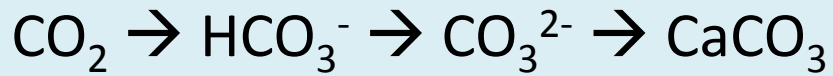
Faraday Discussions Slides

March 31st, 2015

Sun, Wenhao, et al. "Nucleation of metastable aragonite CaCO_3 in seawater."
Proceedings of the National Academy of Sciences 112.11 (2015): 3199-3204.

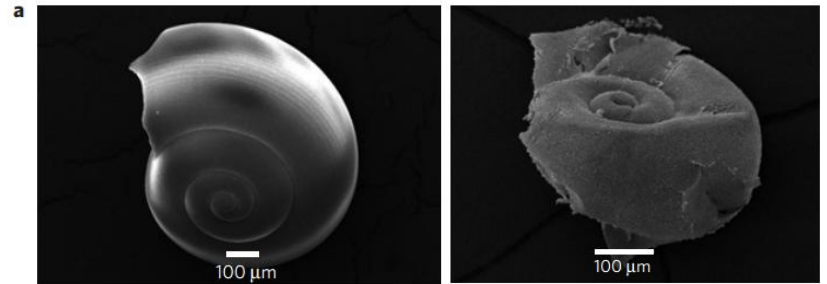
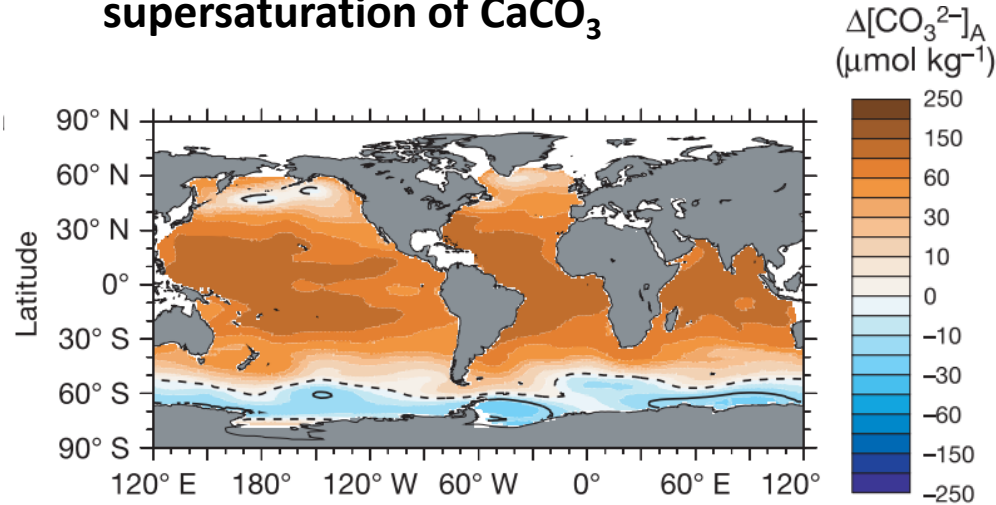
Calcium Carbonate Formation in Marine Environments

The largest global scale CO₂ sink



Atmospheric CO₂ deposits into the ocean, forming the shells of corals, pteropods, and molluscs.

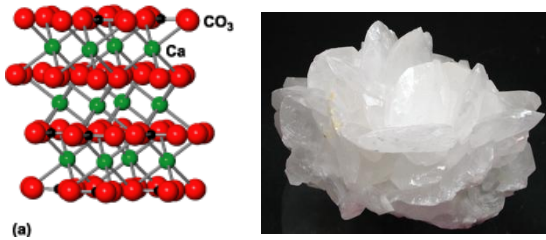
Increasing ocean acidification reduces supersaturation of CaCO₃



Healthy Shellfish

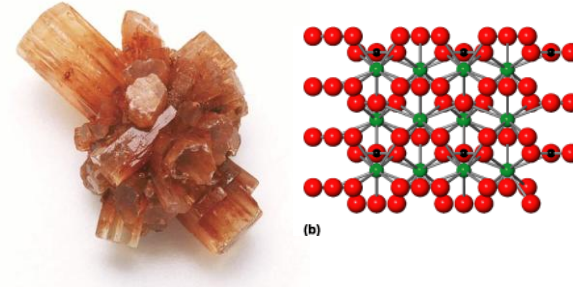
From Antarctica

Calcite



Equilibrium Phase

Aragonite

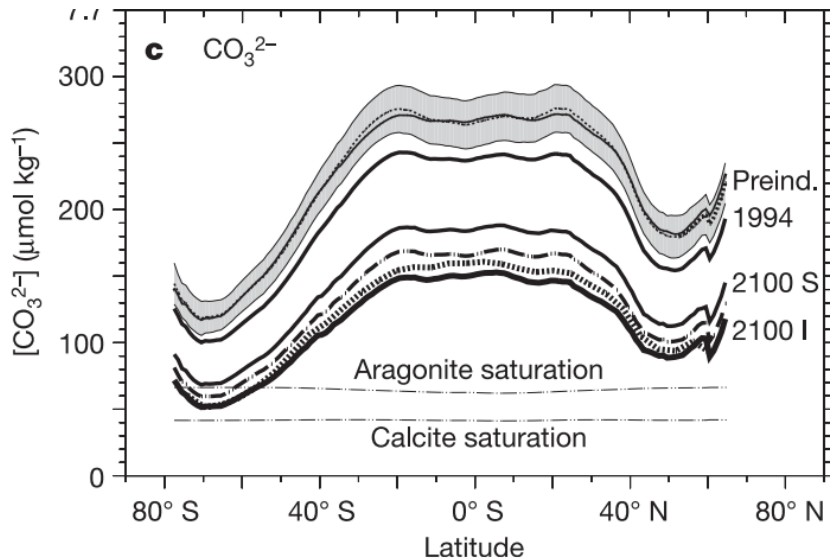


Precipitated phase in Seawater
(Metastable by 2.5 meV/atom)

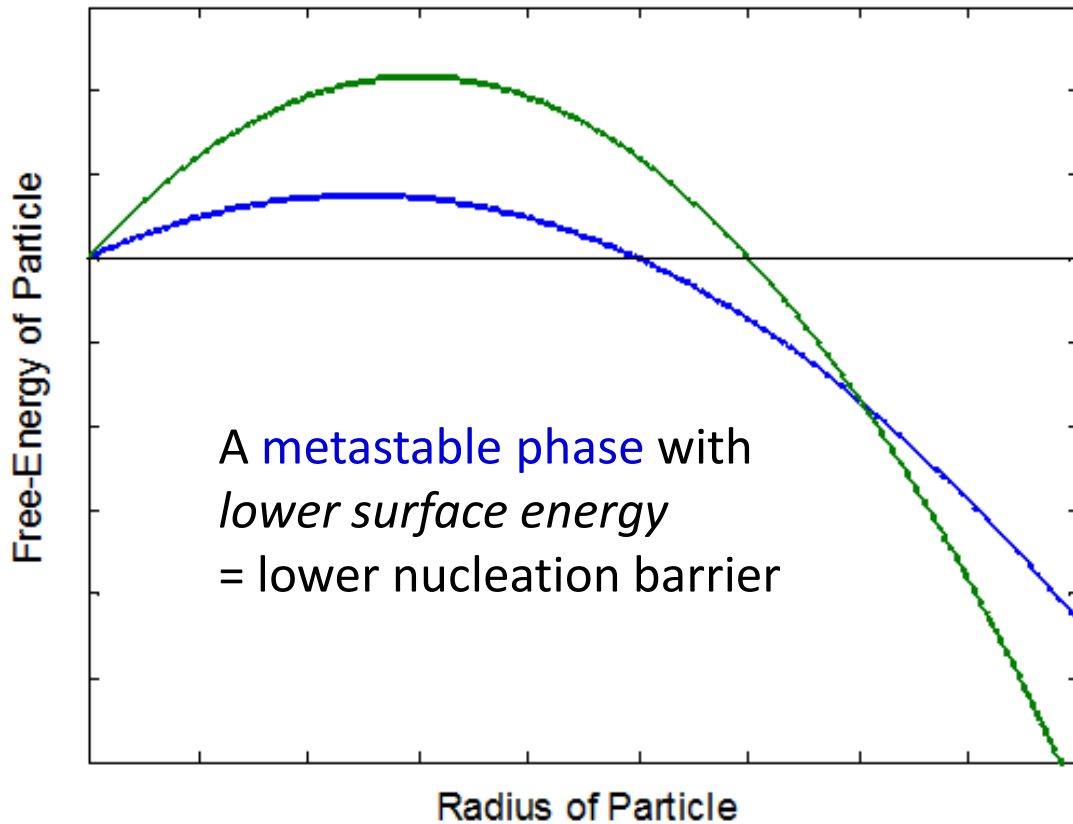
Metastable aragonite is 50% more soluble than calcite.

Biom mineralized aragonite (Corals, Molluscs, Pteropods) more vulnerable to ocean acidification

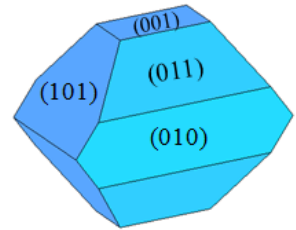
What are the solution conditions that promote the kinetic preference for Aragonite?



Two Phases in Competitive Nucleation



- Surface energy calculations from HT surfaces work



- Bulk Thermodynamic driving forces from Pourbaix formalism

$$\Delta G_{Bulk} = \mu_{solid} - \mu_{ions}$$

↑
DFT

↑
Referenced
(Pourbaix)

$$J \sim \exp\left(\frac{-\Delta G_c}{k_B T}\right) \quad \Delta G_c \propto \frac{\gamma^3}{(\Delta G_{Bulk})^2}$$

Calculate steady-state nucleation rates!

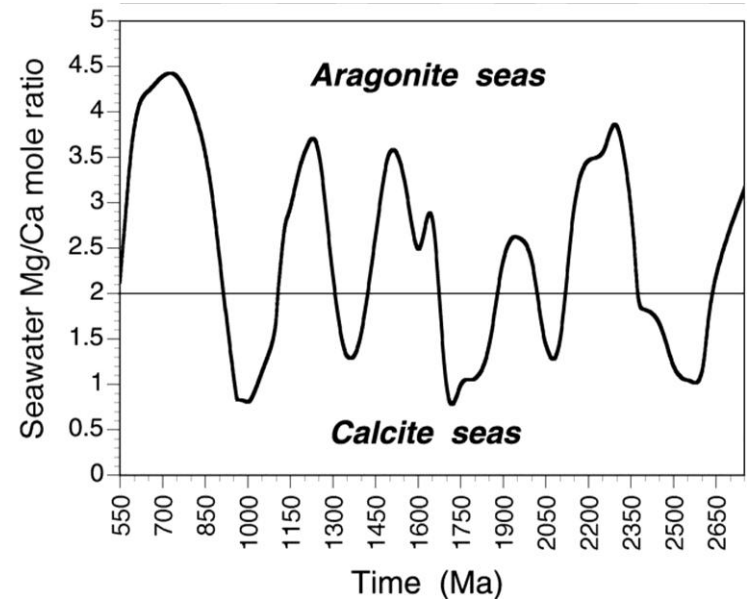
The role of aqueous Mg^{2+} in inhibiting calcite nucleation

Observations:

When **solution Mg/Ca > 2**,
Aragonite is preferred over **Calcite**.

In seawater (**Mg/Ca = 5.2**), Calcite
incorporates $\sim 7\%$ Mg^{2+} in solid solution

Aragonite precipitation not affected by Mg/Ca



$$\Delta G_c \propto \frac{\gamma^3}{(\Delta G_{Bulk})^2}$$

Does Mg^{2+} affect:
Mg-calcite surface energy?
or
Mg-calcite solubility?

BULK MINERAL-SOLUTION EXCHANGE THERMODYNAMICS



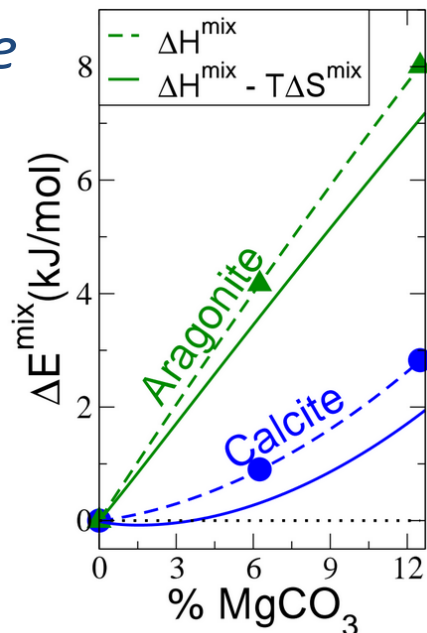
$$\Delta G_{\text{Ca}_{1-x}\text{Mg}_x\text{CO}_3} = \underbrace{\Delta H_{\text{Ca}_{1-x}\text{Mg}_x\text{CO}_3}^{\text{mix}}}_{\text{DFT calculated solid-solution formation enthalpy}} - \underbrace{T\Delta S_{\text{Ca}_{1-x}\text{Mg}_x\text{CO}_3}^{\text{mix}}}_{\text{Mixing Entropy Of Ideal Solution}} + \underbrace{xRT \ln \left(\left(\frac{K_{sp}^{\text{MgCO}_3}}{K_{sp}^{\text{CaCO}_3}} \right) \left(\frac{a_{\text{Ca}^{2+}}}{a_{\text{Mg}^{2+}}} \right) \right)}_{\text{Chemical potential of ion Mg/Ca exchange with solution}}$$

DFT calculated
solid-solution
formation enthalpy

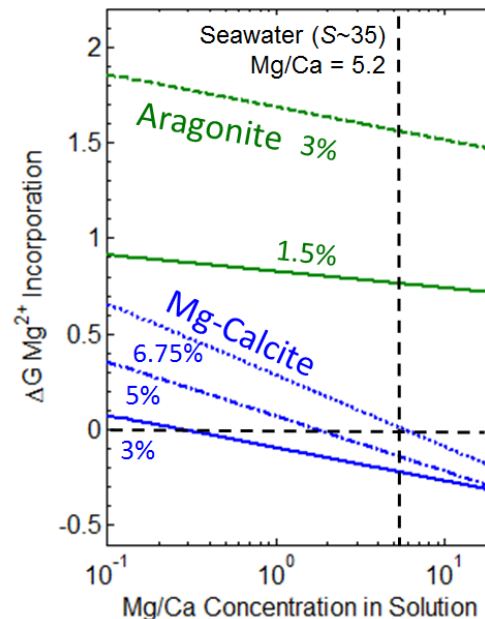
Mixing Entropy
Of Ideal Solution

Chemical potential of ion
Mg/Ca exchange with solution

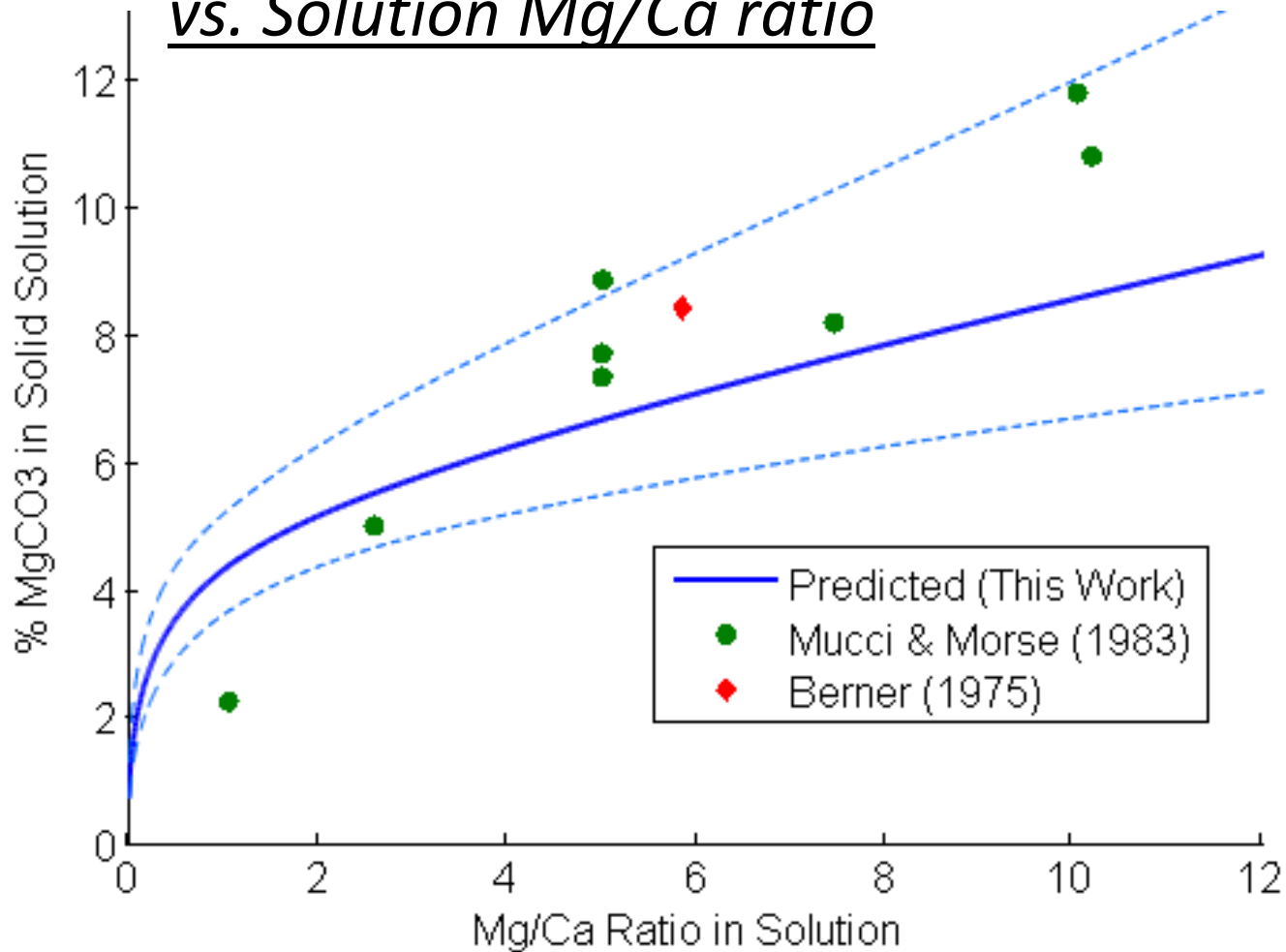
*Solid-state
mixing*



*Solution-Mineral
Exchange*



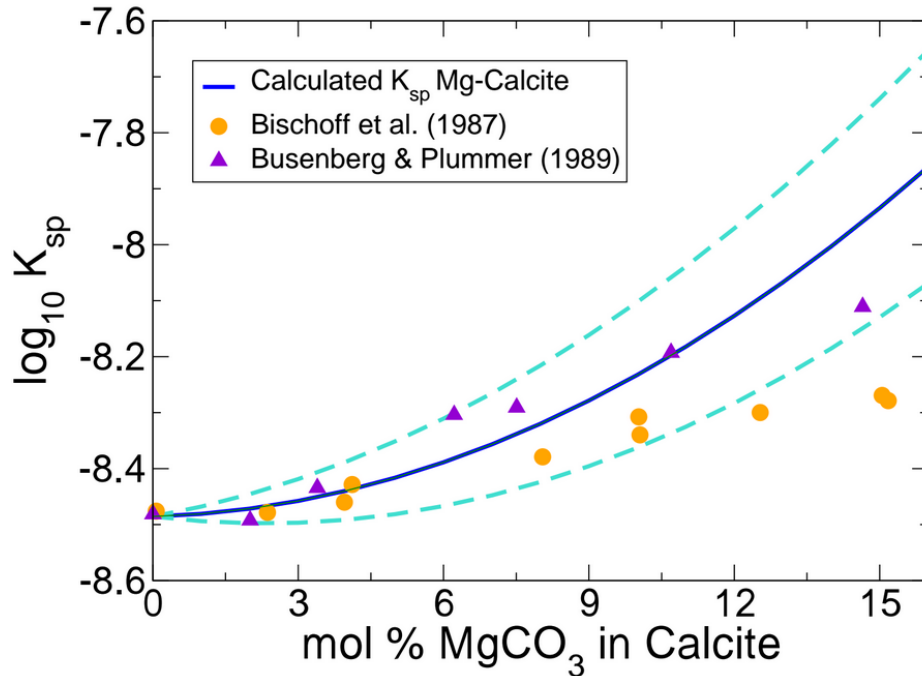
Equilibrium Mg^{2+} concentration in Calcite
vs. Solution Mg/Ca ratio



High enthalpy of Mg^{2+} incorporation into Aragonite can not be stabilized by any Mg/Ca ratio. (Empirically known, *theoretically confirmed*)

Mg-CALCITE SOLUBILITY

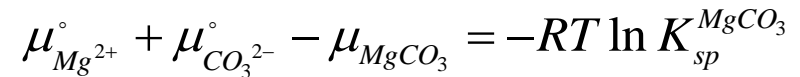
$$-RT \ln K_{sp}^{Ca_{1-x}Mg_xCO_3} = (1-x)\mu_{Ca^{2+}}^\circ + x\mu_{Mg^{2+}}^\circ + \mu_{CO_3^{2-}}^\circ - \mu_{Ca_{1-x}Mg_xCO_3}$$



DFT



Expt.

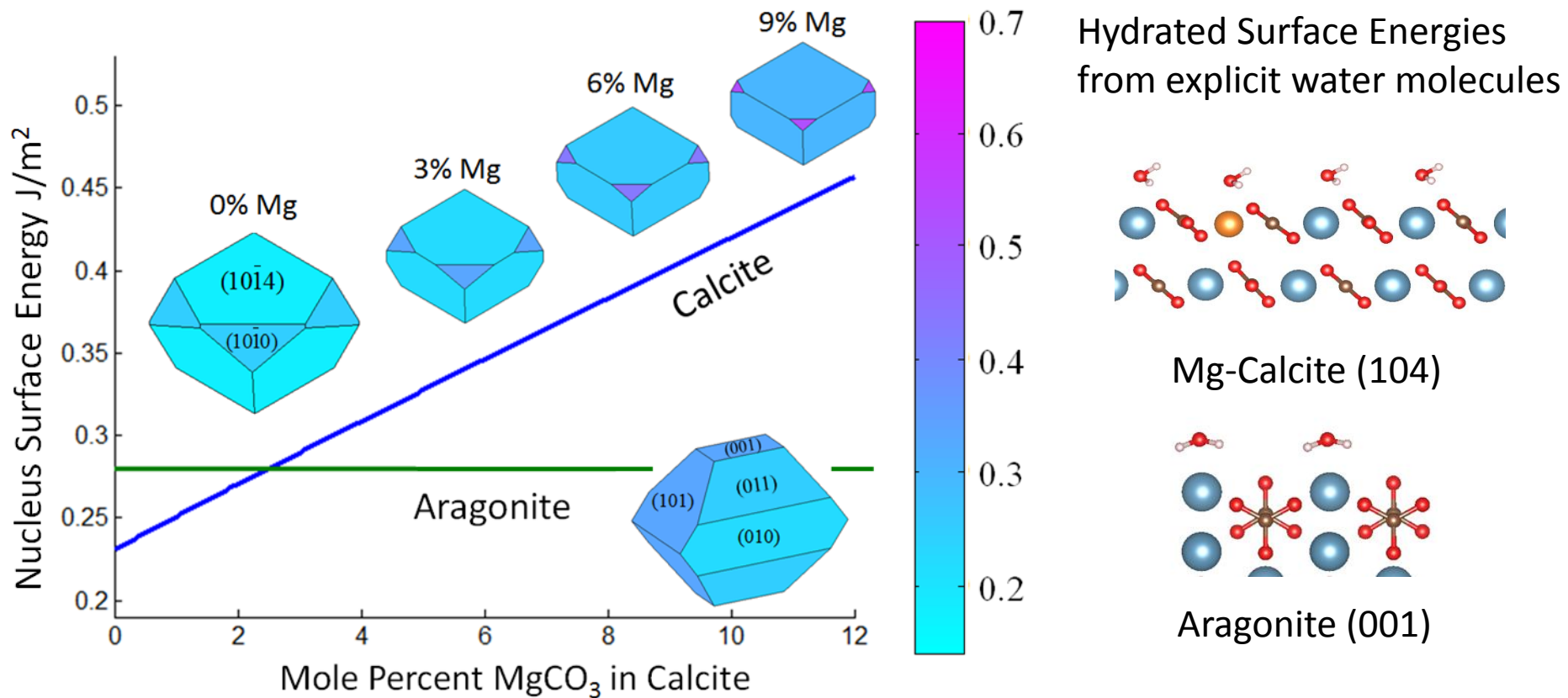


Referenced

We predict a 30% increase of increase of Mg-calcite solubility from $10^{-8.48}$ to $10^{-8.36}$ at ~7% MgCO₃, in close agreement with experiment.

This corresponds to only 0.3 RT/mol reduction in bulk driving force. Typical nucleation driving forces are an order of magnitude higher.

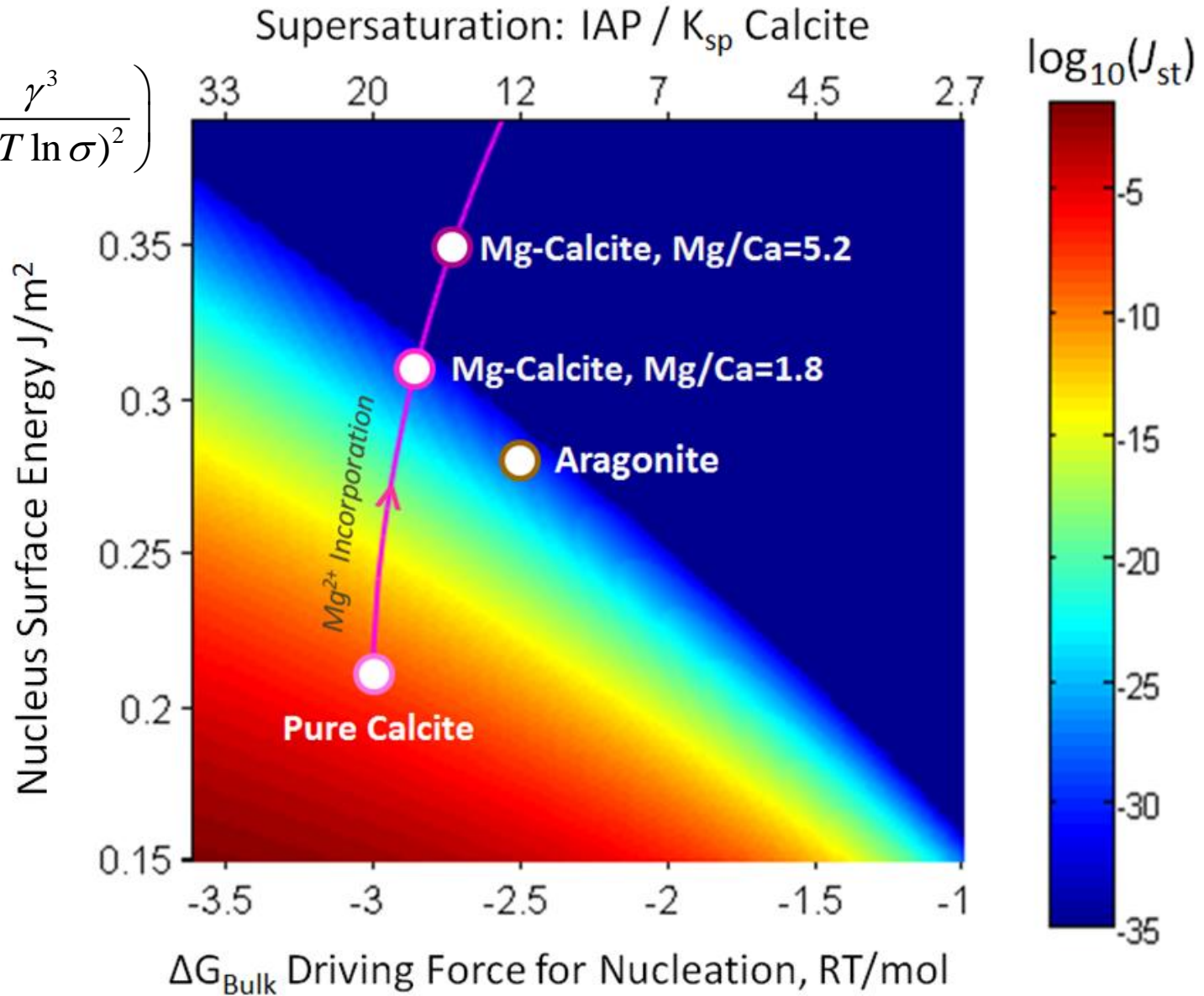
Surface energy of calcite increases with $MgCO_3$ in solid-solution

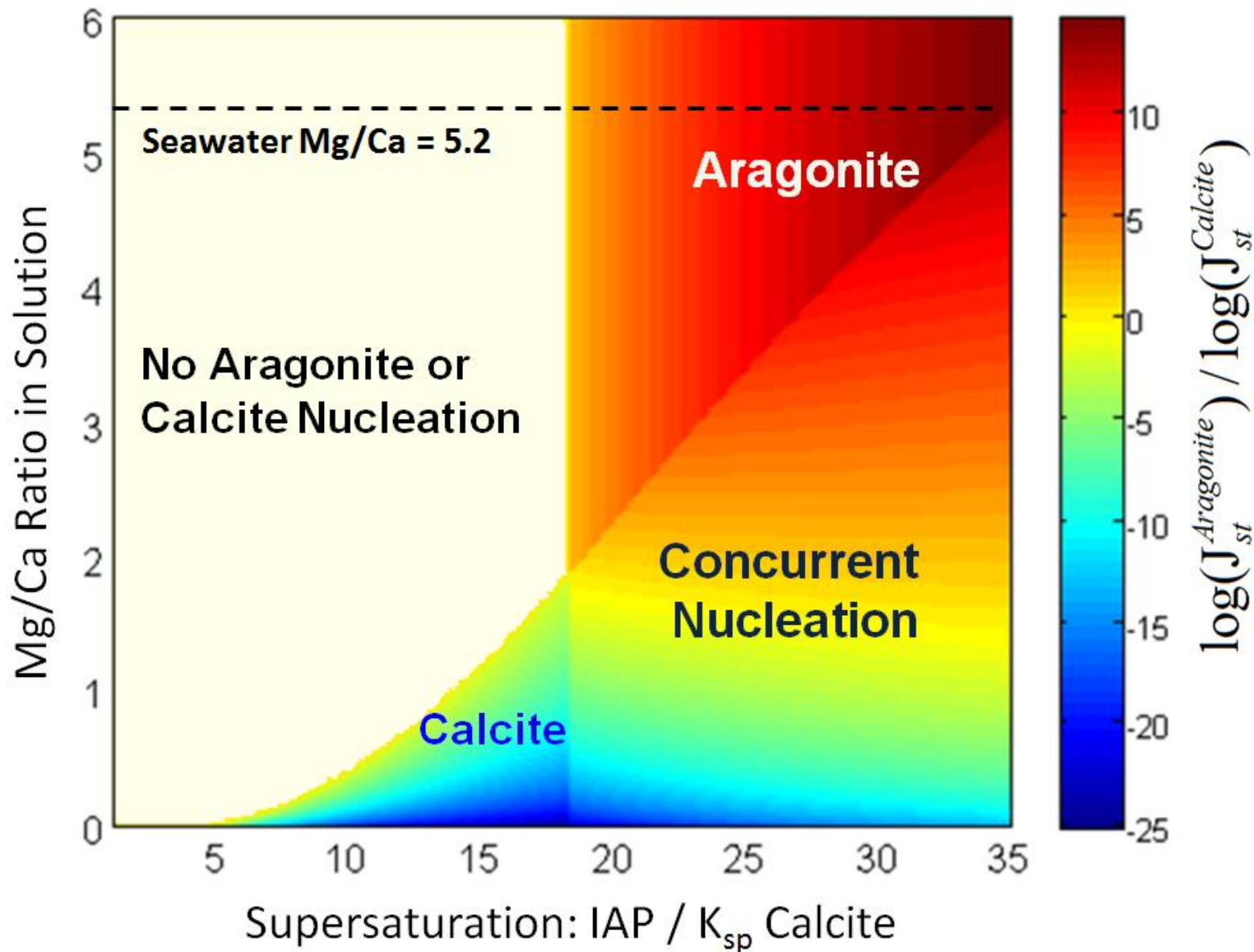


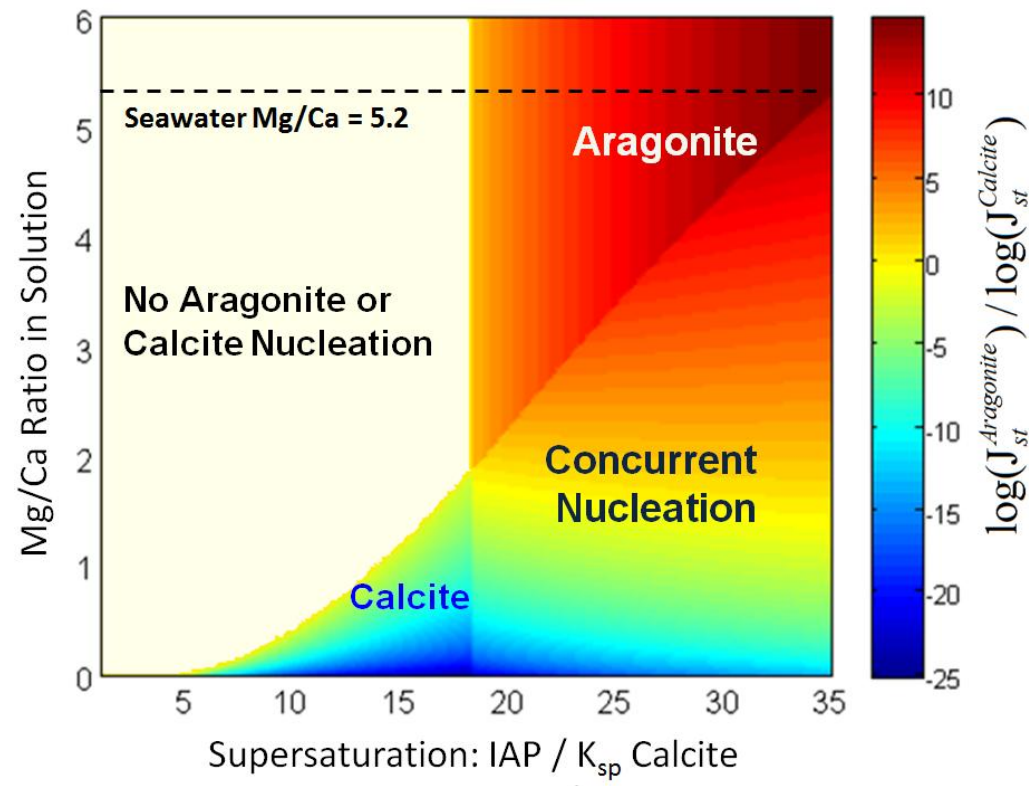
γ_{Calcite} from 0.2 $J/m^2 \rightarrow$ 0.35 J/m^2 at seawater Mg/Ca ratios

Steady-State Nucleation Rates (J_{st}) of Aragonite and Mg-Calcite

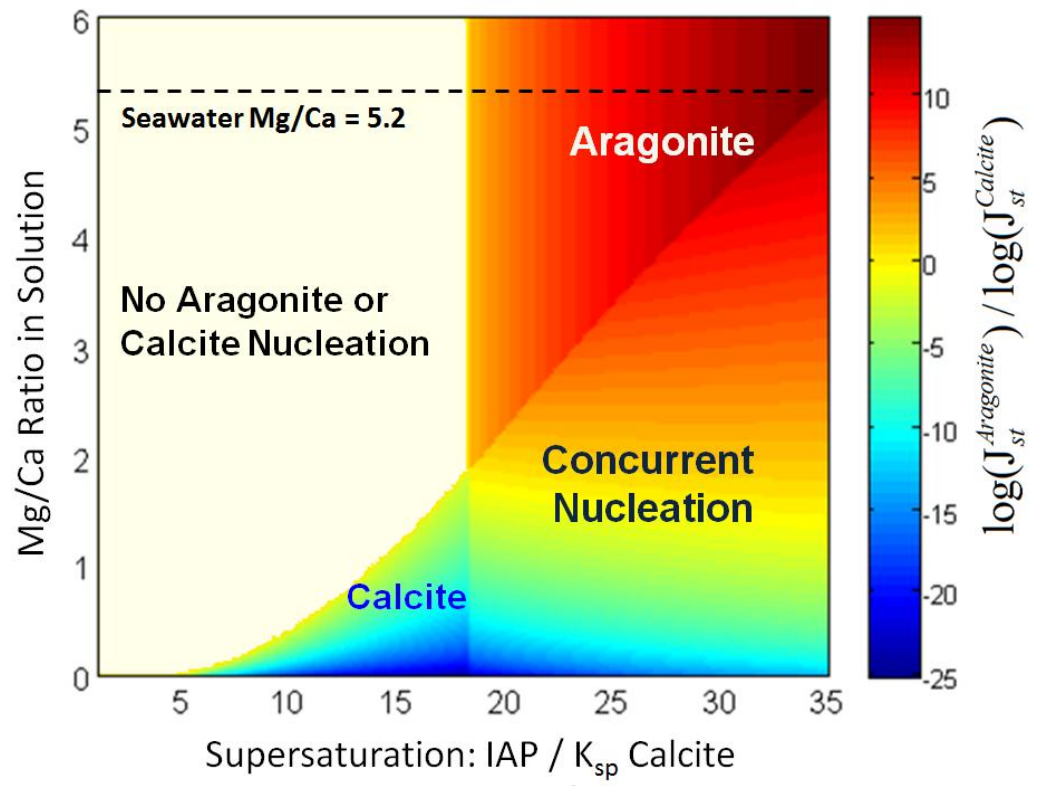
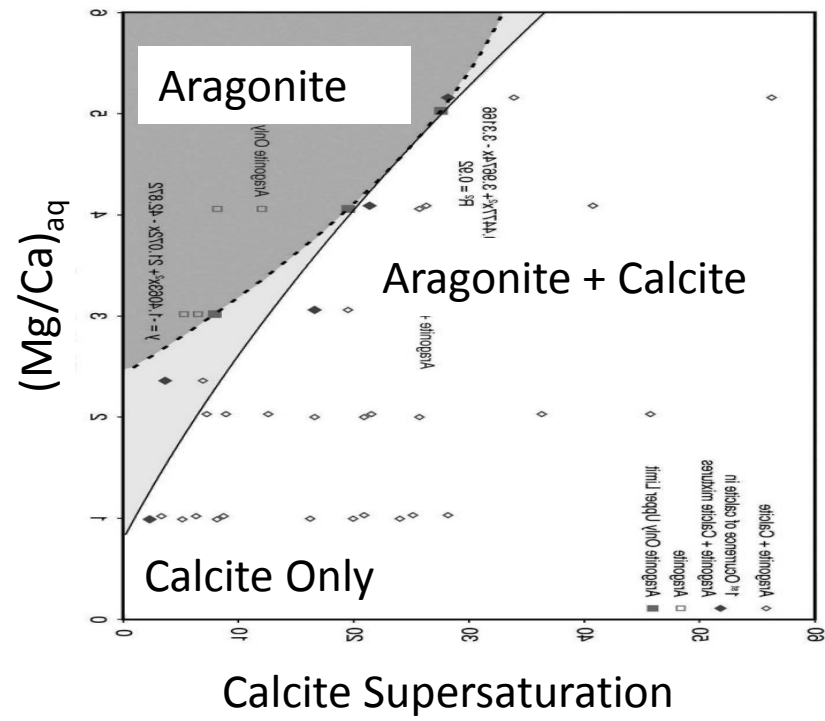
$$J \sim \exp\left(\frac{\gamma^3}{(RT \ln \sigma)^2}\right)$$







*Choudens-Sanchez and Gonzales (2009)



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