

PS Acceleration of Calcite Deposition Imposed by Organic Substrate of Self-Assembled Monolayers*

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Abstract

Underground deposition of calcium carbonate (CaCO_3) withdrawing atmospheric CO_2 is a crucial topic for carbon sequestration. Plenty of evidence has proved that microbes and organic matters are able to speed up carbonate deposition rate up to a couple of order of magnitudes. In the past decade, to reproduce the controls of organic molecules on carbonate mineralization, simpler self-assembled monolayers (SAMs) terminated by carboxylic groups have been heavily used as model templates for CaCO_3 crystallization.

COOH-terminated 16-mercaptohexadecanoic acid (MHA) monolayer is the most representative SAM. It strongly favors nucleation of calcite on the non-natural (012) oriented faces (Aizenberg et al., 1999; Whitesides et al., 1994). However, the kinetic and thermodynamic controls imposed by MHA are poorly understood. The reduction of formation energy of calcite by MHA has not been addressed. In this study, we cultivate calcite at MHA surfaces on Au (111) faces, and quantify the interfacial energy associated with template-directed calcite on MHA by measuring the dependence of the nucleation rate on supersaturation.

The results reveal that (1) the MHA SAM significantly reduces the surface energy created during calcite nucleation from at least 97 mJ/m^2 for homogenous nucleation in solution to about 46 mJ/m^2 , which confirm the strong capacity of MHA of promoting CaCO_3 deposition; and (2) amorphous calcium carbonate begins to appear when the supersaturation with respect to that phase is only 0.02, suggesting that the pathway of nucleation is not determined by the free energy barrier, but rather the kinetic factors.

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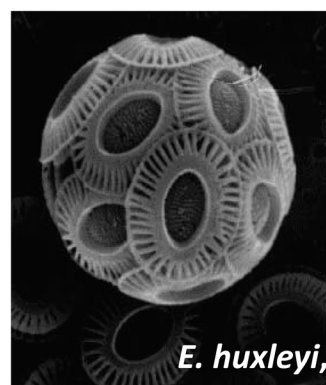
Introduction

Carbonate biomineralization is so pervasive it impacts sea water chemistry on a global scale



Life cycle w/in surface ocean (G. Gorick)

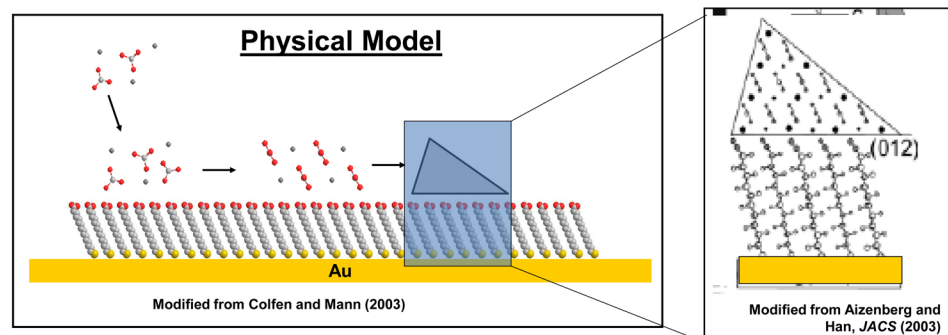
- Significant factor in regulating climate
- Crucial topic to CO₂ sequestration
- Major contributor to carbon reservoir



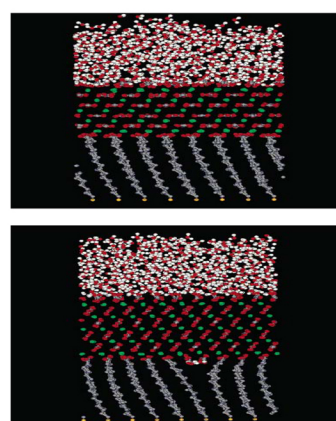
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Experiments and Results



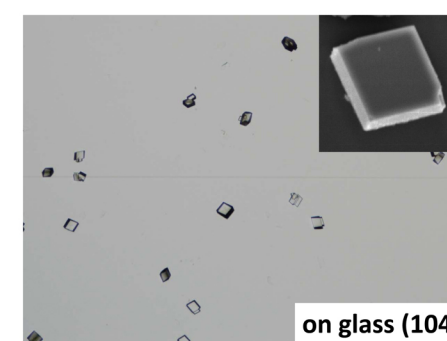
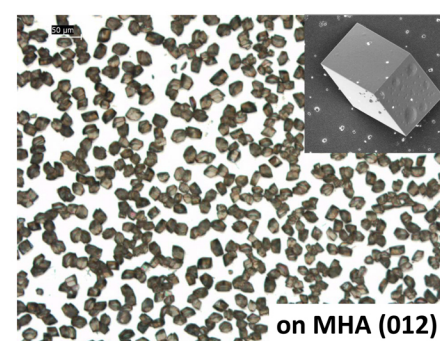
Schematic representations depicting the orientated precipitation of calcite on carboxylic groups of SAMs



	(0001)			(0112)		
	γ_{cm} (J m ⁻²)	m	$f(m)$	γ_{cm} (J m ⁻²)	m	$f(m)$
even (MHA)	0.081	-0.62	0.90	0.074	-0.57	0.88
odd (MPA)	0.086	-0.66	0.92	0.095	-0.73	0.95

Left: simulations of oriented calcite on MHA. Above: interfacial Energy of the (001) and (012) faces with MPA and MHA, calculated by molecular dynamics simulations (Dorothy M. Duffy et al, J. Phys. Chem. (2005))

1. Increased precipitation density and controlled orientation of calcite nucleation on SAM substrates

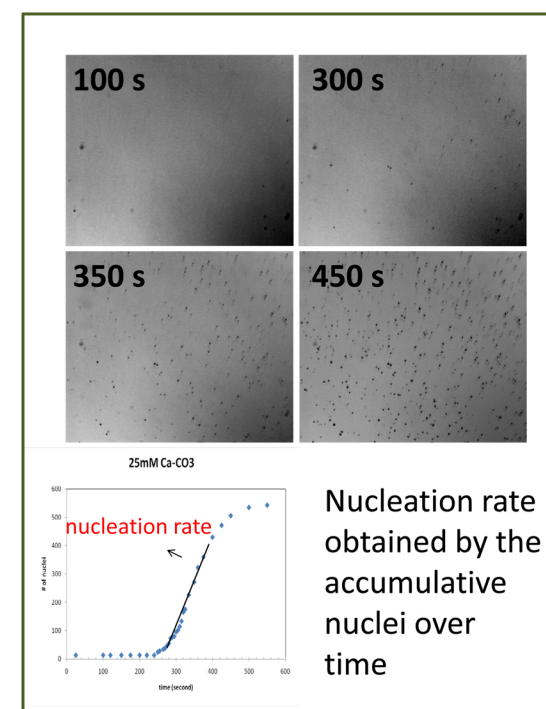


2. Calculate surface energies of calcite on SAMs by experiments:

Dependence of the nucleation rate on supersaturation(σ) and interfacial energy (α):

$$J_n = A \exp \left(-B \frac{\alpha'^3}{\sigma^2} \right); \quad \frac{1}{\sigma'^2} = - \frac{(\ln J_n - \ln A)}{B \alpha'^3}$$

where A and B are constants



Saturation States of Calcite and ACC in Each Run

	saturation state* - calcite**	saturation state* - ACC**
10mM	1.523	-0.564
18mM	1.841	-0.246
20mM	1.897	-0.19
21mM	1.922	-0.165
22.5mM	1.958	-0.129
24mM	1.992	-0.095
25mM	2.013	-0.074
30mM	2.108	0.021

*saturation state (σ) = $\log \left(\frac{a(Ca^{2+})a(CO_3^{2-})}{K_{sp}} \right)$

** the value of $10^{-8.48}$ and $10^{-6.393}$ are used as solubility product of calcite and ACC (Breckvic and Nielsen, 1989)

Nucleation rate obtained by the accumulative nuclei over time

Key questions

- Is precipitation speeded up?
- Is surface energy minimized?
- Kinetics vs. thermodynamics?

Self-assembled monolayers (SAMs) have been heavily used as model organic substrates for CaCO₃ deposition

Our study analyzes the control of two SAMs on calcite precipitation: mercaptohexadecanoic acid (**MHA**) and Mercaptoundecanoic acid (**MUA**)

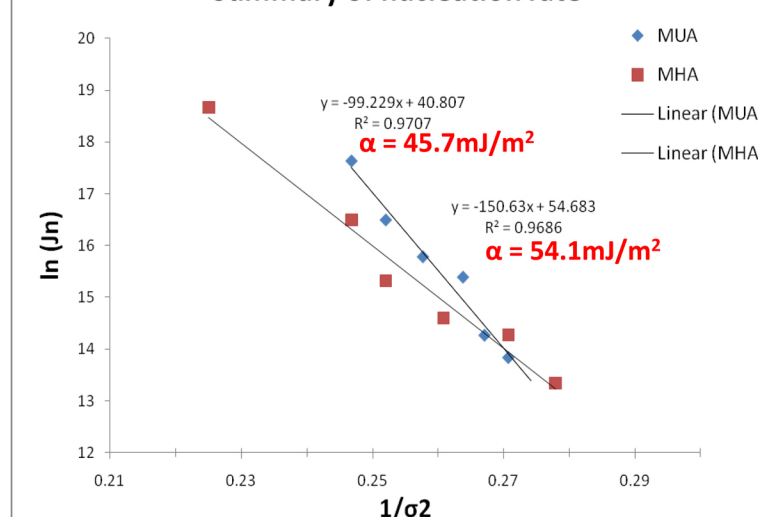
Conclusions

- MHA and MUA greatly promote the calcite precipitation and induce calcite to nucleate on non-natural planes (012) & (013).
- The organic template MHA and MUA significantly reduce the surface energy created during calcite nucleation from 97 mJ/m² to about 46 and 54 mJ/m² respectively

Acknowledgement

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Summary of nucleation rate



Interfacial energy (α) is estimated by the slope of the trendline