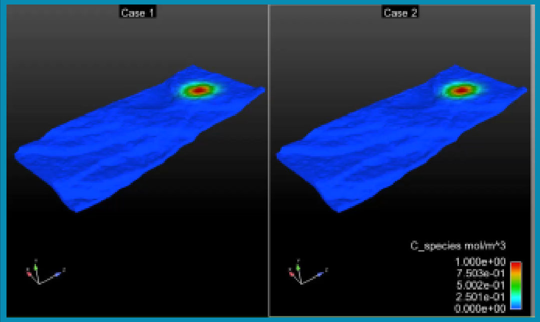
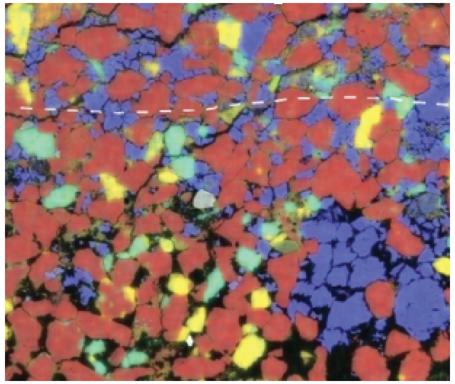
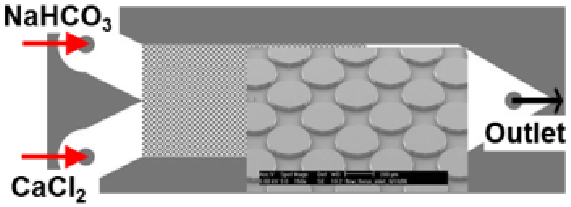
SAND2021-10062C

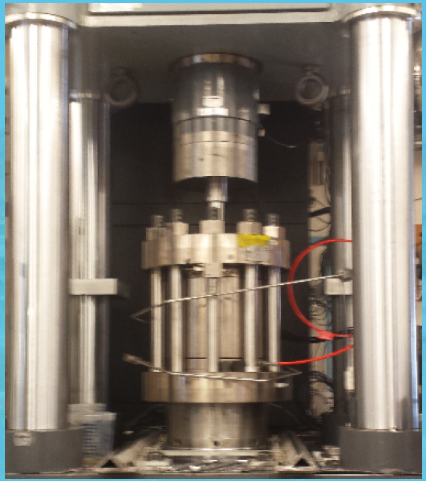
Sandia National Laboratories

The Combined Effects of Mg^{2+} and Sr^{2+} on Calcite Crystallization, Growth, and Incorporation Behavior









PRESENTED BY

Andrew Knight, Jacob Harvey, and Anastasia Ilgen

Sandia National Laboratories

August 2021, American Chemical Society Fall 2021 Meeting

U.S. DEPARTMENT OF ENERGY NNSA

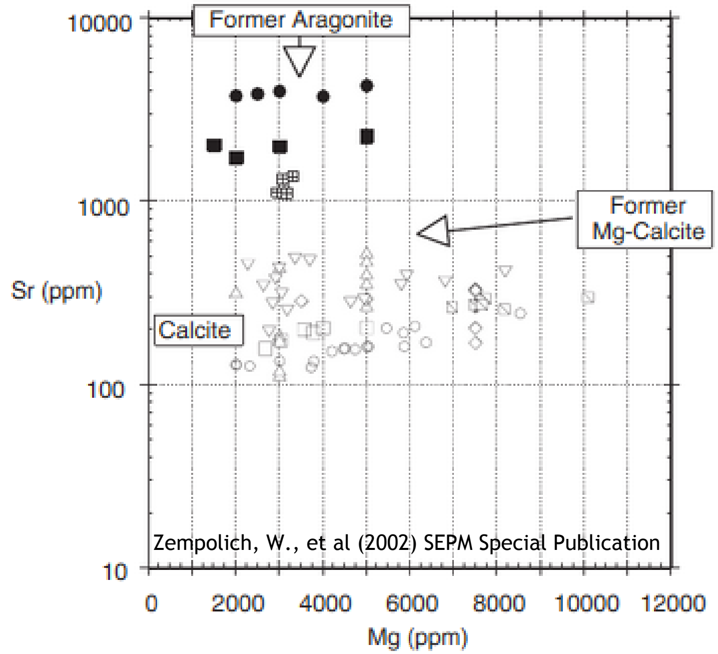
Elemental Incorporation and Isotope Fractionation

Quantifying elemental incorporation and stable isotopic fractionation in calcite can provide valuable information

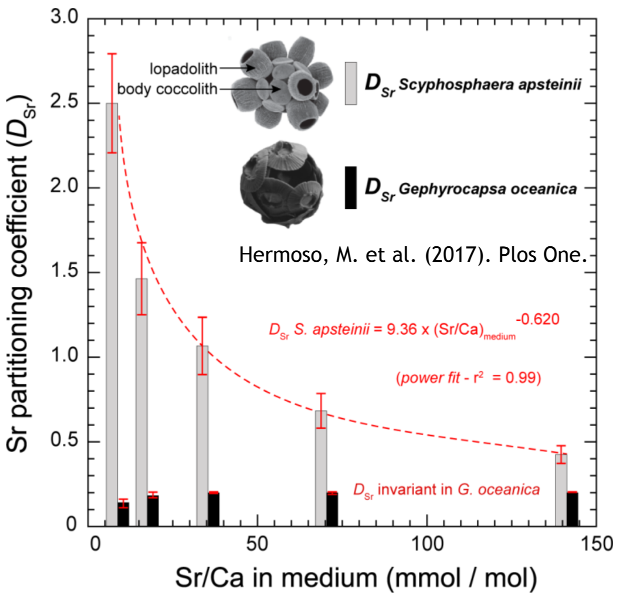
- Sr^{2+} is among the most commonly incorporated ions into calcite (second only to Mg^{2+})
  - D_{Sr} can be used as a marker for geological and biological processes
  - The presence of Mg has been shown to impact D_{Sr}

$$D_{Sr^{2+}} = \frac{\left(Sr^{2+}/Ca\right)_{Calcite}}{\left(Sr^{2+}/Ca\right)_{Aqueous}}$$

- Sr isotopic fractionation can be a tracer for calcite precipitation and dissolution events

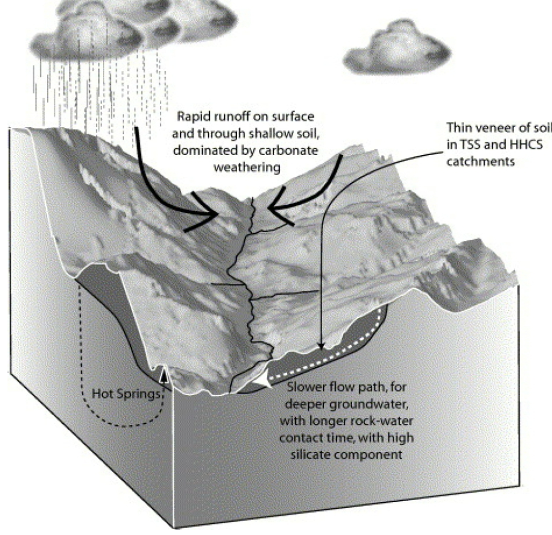


Sr and Mg composition in Ca-carbonate minerals



D_{Sr} versus the Sr/Ca ratio in the media shown with the specific types of coccolithophores

Tipper, E. et al (2006). Geochim. Cosmoschim. Acta

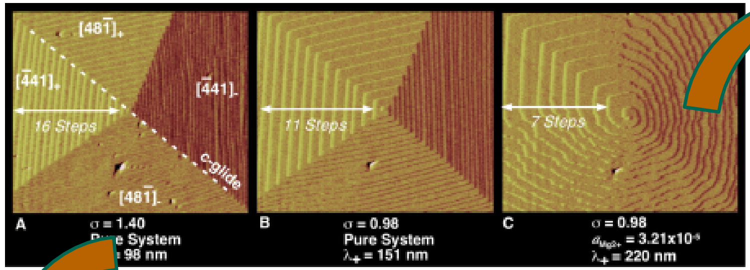


Seasonal $^{87}Sr/^{86}Sr$ ratios in the Marsyandi indicate greater carbonate dissolution relative to silicate at high runoff.

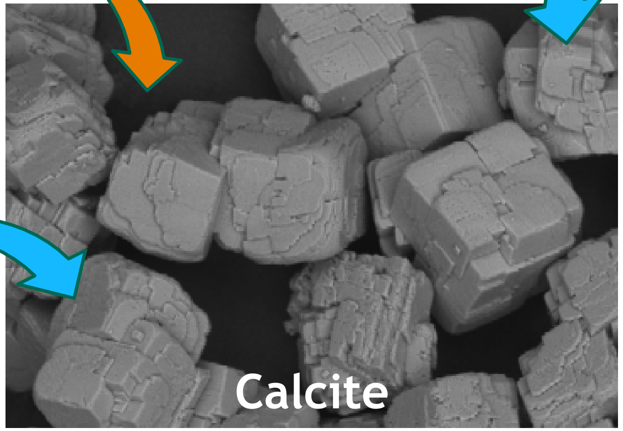
Precipitation Conditions Impact Calcite

The composition of the initial solution has an impact on the chemical and physical properties of calcite

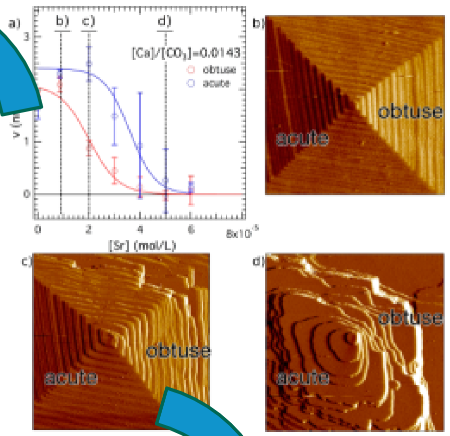
Davis, K.J. et al. (2000) Science



Mg impact on crystallization and growth



Bracco, J.N., et al. (2012) Crystal Growth & Design

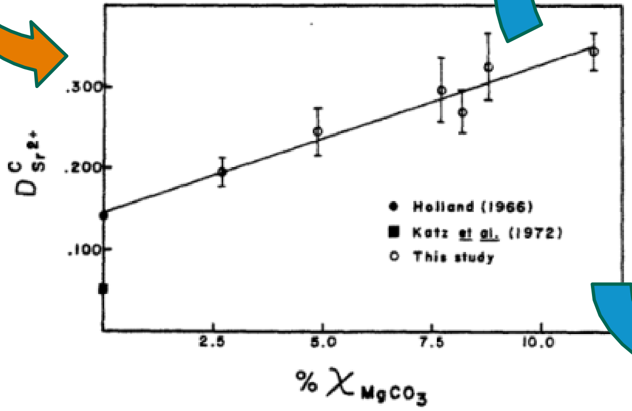


Sr impact on crystallization and growth

Mg impacts D_{Sr}

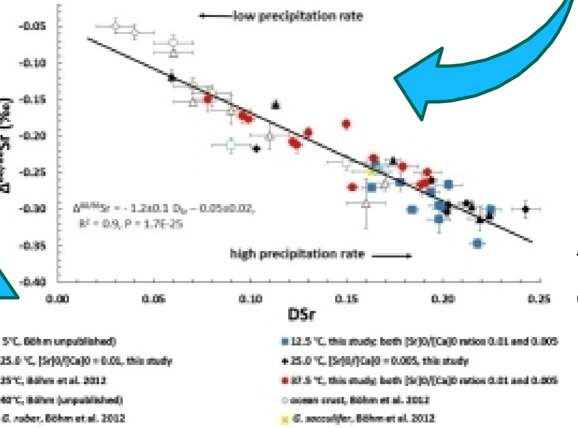
D_{Sr} impacts crystallization and growth

Sr isotope fractionation is related to D_{Sr}



Mucci et al (1983) Geochimica et Cosmochimica Acta

Sr isotope fractionation is related to D_{Sr} – which can be enhanced by Mg



AlKhatib, M. and Eisenhauser, A. (2017) Geochimica et Cosmochimica Acta

Calcite Crystallization

- Crystallization
  - Particle size, morphology, and lattice parameters
- Ion Incorporation of Sr^{2+} and/or Mg^{2+} into calcite
  - The role of Mg^{2+} on Sr^{2+} incorporation
  - Ion specific behavior
- Sr-isotopic fractionation

Calcite Precipitation and Crystal Growth

Studies have shown the impact of Sr^{2+} and Mg^{2+} (combined or together), but the collective impact on the chemical and physical properties requires specific attention.

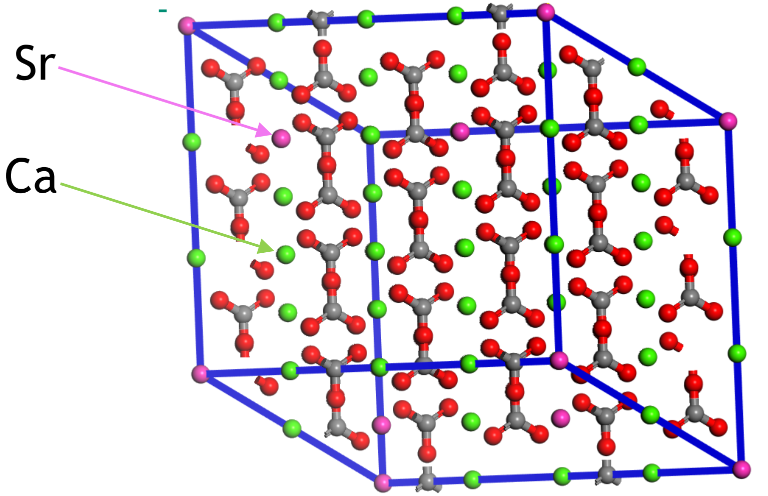
To better understand the intricate relationships between calcite precipitation conditions and resulting properties, calcite was analyzed in the presence of both Sr^{2+} and Mg^{2+} to demonstrate their respective and combined impact on calcite crystallization and composition

Experimental test matrix

Sample #	Sr:Ca mol%	Mg:Ca mol%	$\Omega_{calcite}$
1	0	0	4.15
2	0.1	0	4.15
3	1	0	4.14
4	5	0	4.14
5	0	5	4.14
6	0.1	5	4.14
7	1	5	4.13

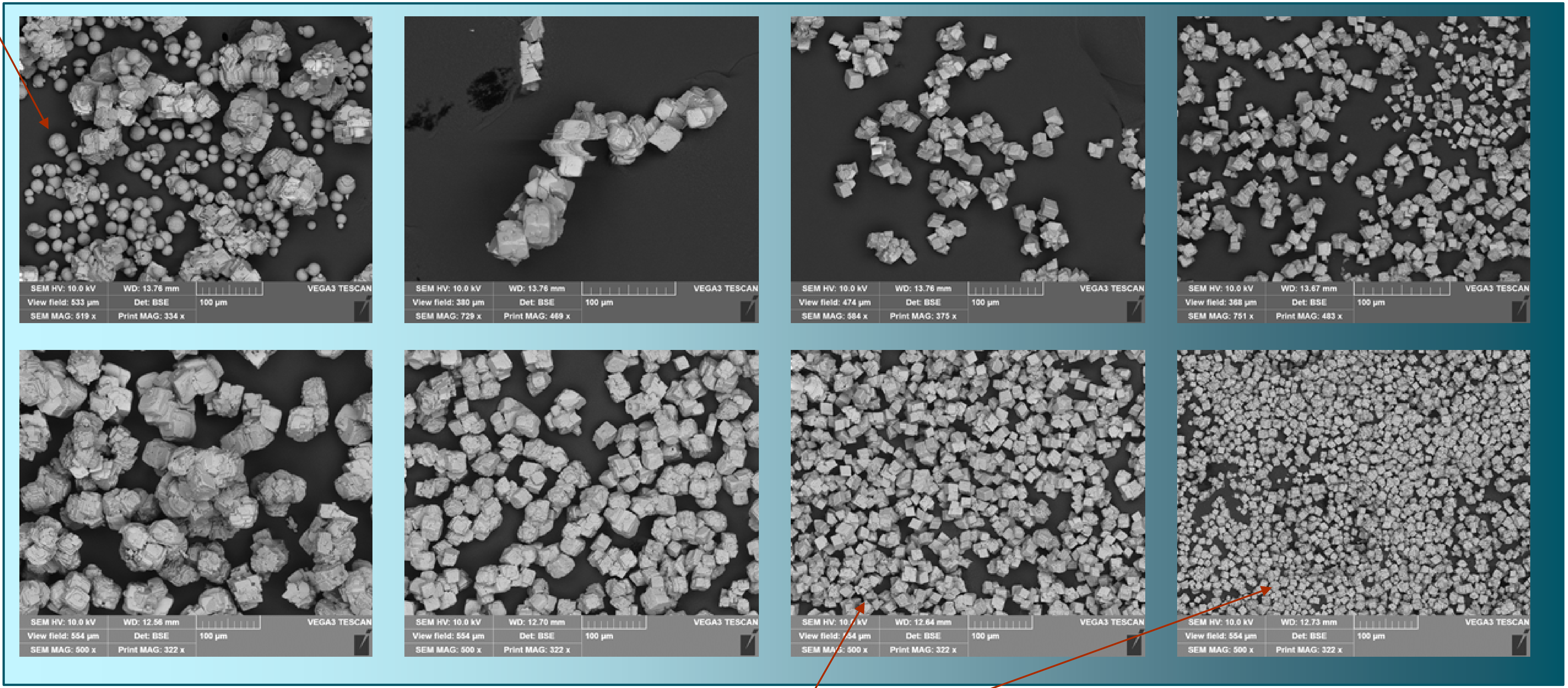
- **Experimentally:** Calcite was prepared directly by the double decomposition reaction of $NaHCO_3$ and $CaCl_2$ and relatively constant saturation index .
  - Known amounts of $SrCl_2$ and/or $MgCl_2$ were added to the solution prior to precipitation.
  - Sampled at 1 day, 4 days, 7 days, 10 days, 14 days, and 21 days
- **Computationally:** Molecular modeling work optimized calcite structures with known substitutions of Sr and/or Mg and calculated the impact on unit cell parameters

Example computational calcite structure containing Sr substitutions



Crystallization

$(Mg/Ca)_{initial} = 0$



Crystallization

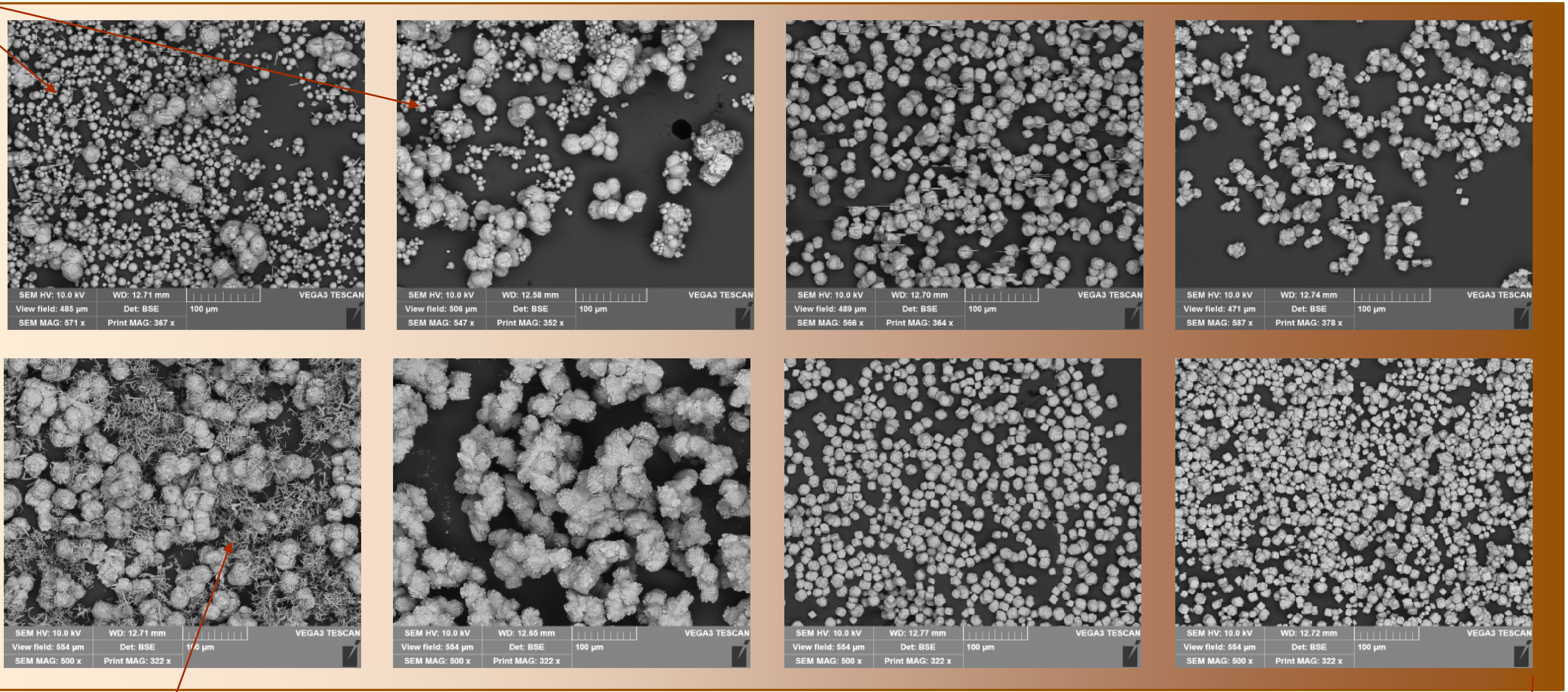
$(Mg/Ca)_{initial} = 5$

Vaterite or Aragonite observed

$(Sr/Ca)_{initial} = 0$ | $(Sr/Ca)_{initial} = 0.1$ | $(Sr/Ca)_{initial} = 1$ | $(Sr/Ca)_{initial} = 5$

1 day

21 days



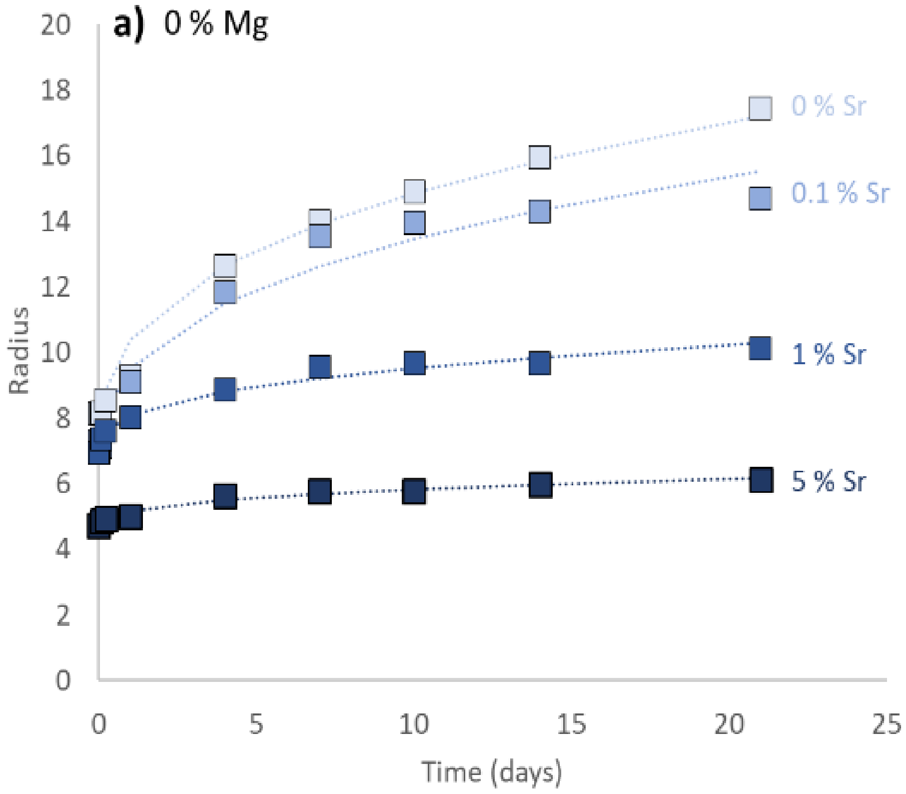
Needle Fiber Calcite observed

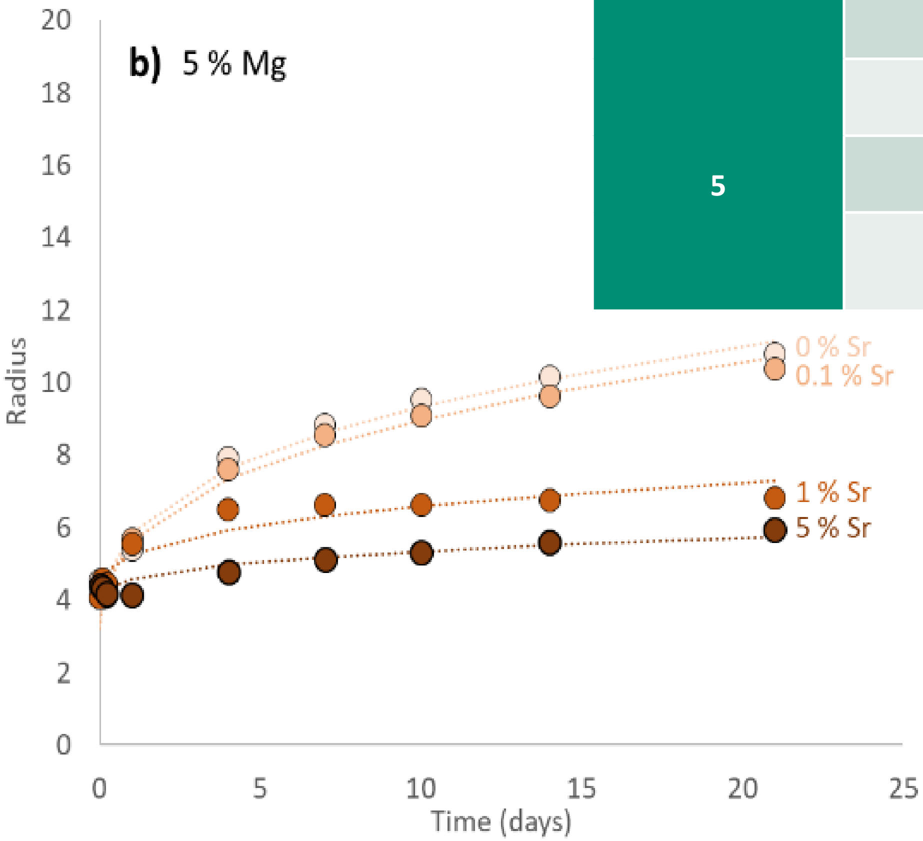
Irregular crystallization

Crystal Sizes

- Crystal sizes were estimated through image analysis and fit with the LSW Ostwald Ripening Equation[1]
- Sr^{2+} and Mg^{2+} inhibit calcite crystal growth

$(Mg:Ca)_{initial}$ (%)	$(Sr:Ca)_{initial}$ (%)	$\bar{R}(0)$	K(Q)
0	0	1.23	57.7
	0.1	1.22	39.3
	1	1.24	1.94
	5	1.19	0.185
5	0	1.12	27.0
	0.1	1.12	23.9
	1	1.17	1.54
	5	1.16	0.287





$$\bar{R}(t) = \sqrt[3]{\bar{R}^3(0) + K(Q)t}$$

$\bar{R}(0)$ is the average radius at the onset of coarsening

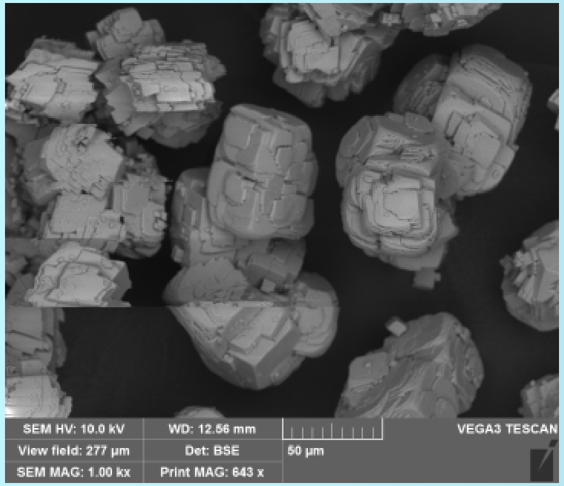
$\bar{R}(t)$ is the average radius at time = t,

K(Q) is a monotonically increasing function of Q.

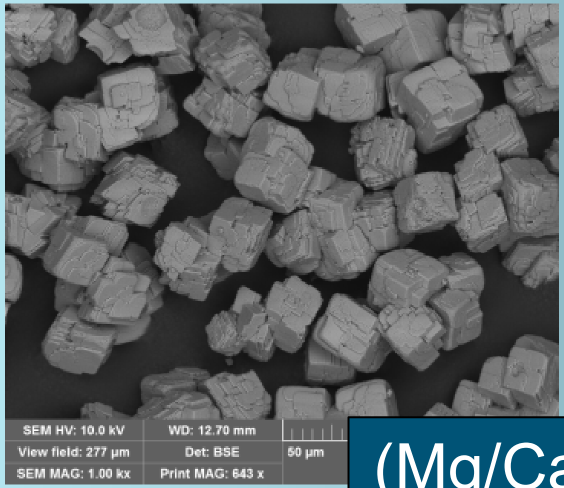
[1]Baldan, A.. (2002) Journal of Materials Science

Morphology - 21 Days

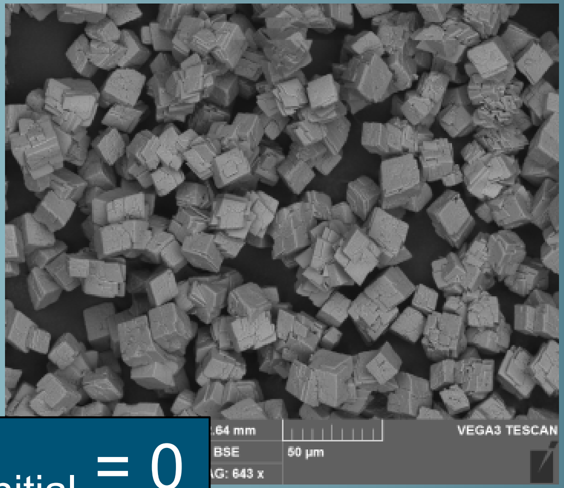
$(Sr/Ca)_{initial}$ = 0



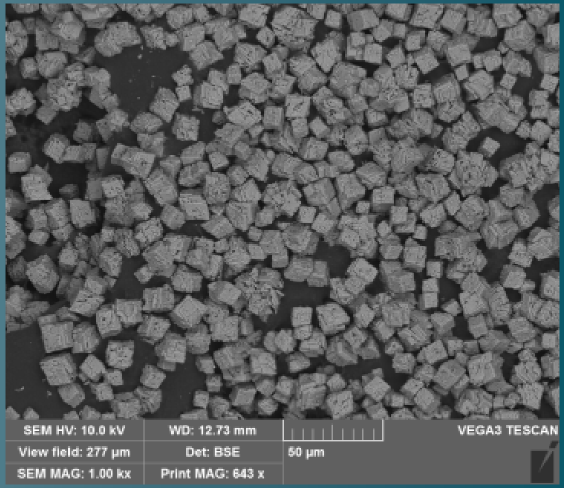
$(Sr/Ca)_{initial}$ = 0.1



$(Sr/Ca)_{initial}$ = 1

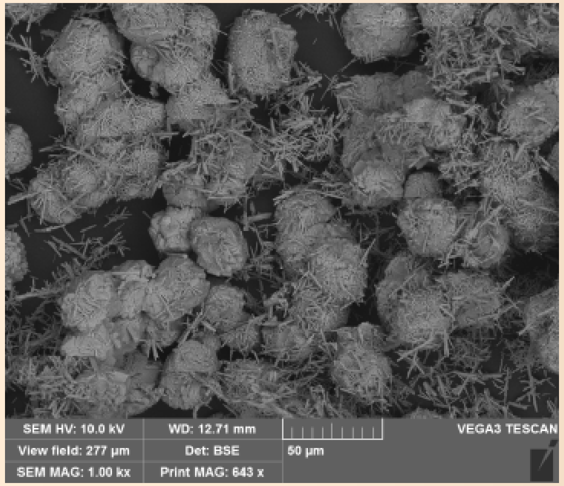


$(Sr/Ca)_{initial}$ = 5

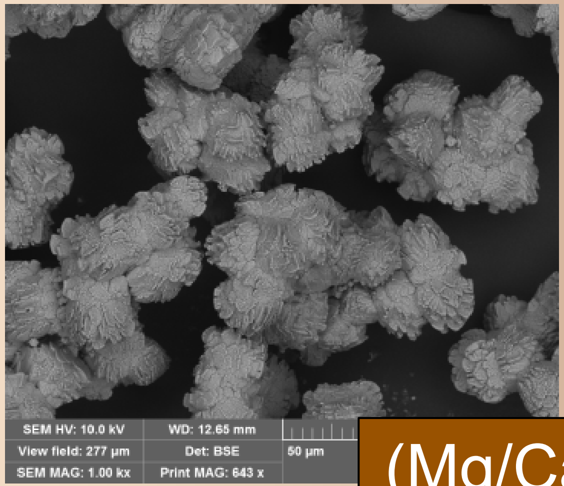


$(Mg/Ca)_{initial}$ = 0

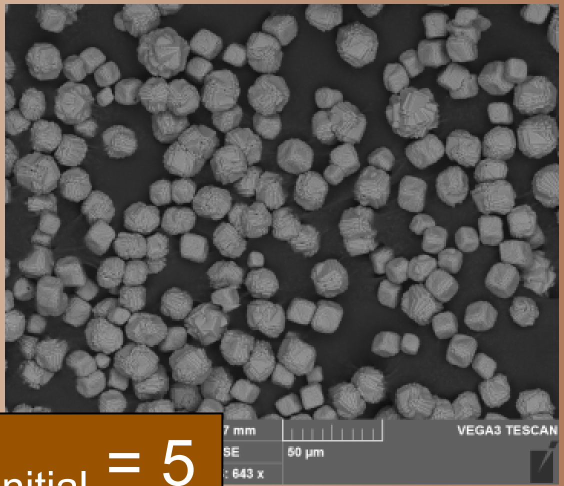
$(Sr/Ca)_{initial}$ = 0



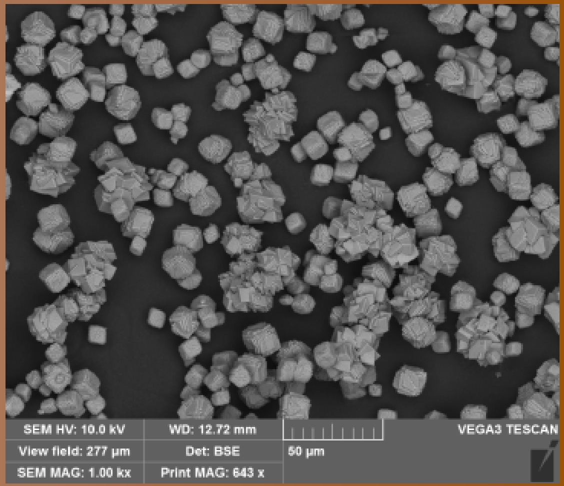
$(Sr/Ca)_{initial}$ = 0.1



$(Sr/Ca)_{initial}$ = 1



$(Sr/Ca)_{initial}$ = 5

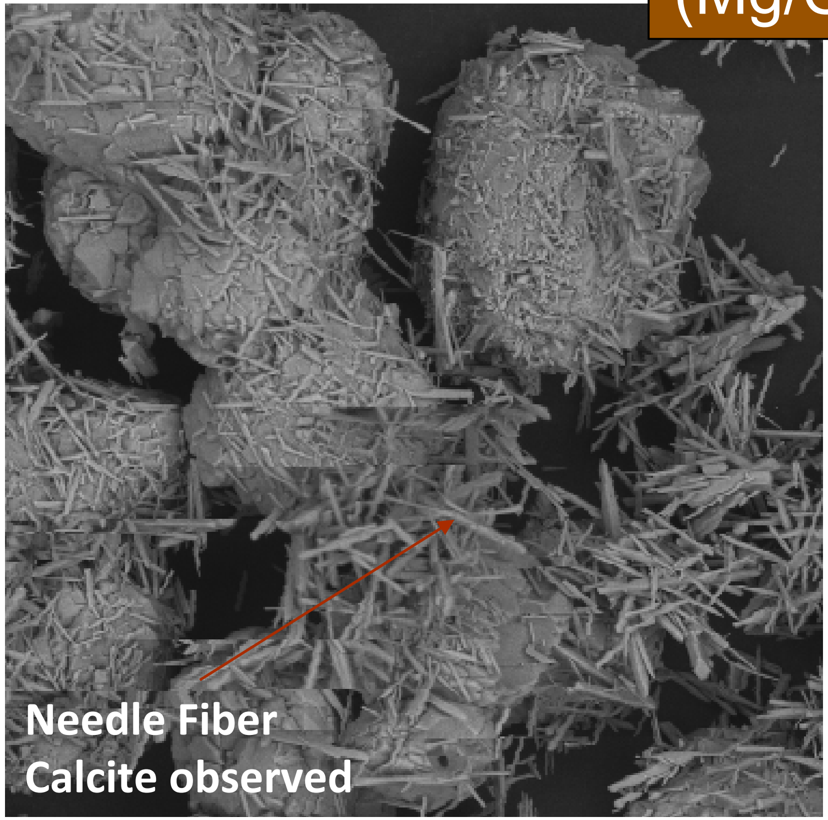


$(Mg/Ca)_{initial}$ = 5

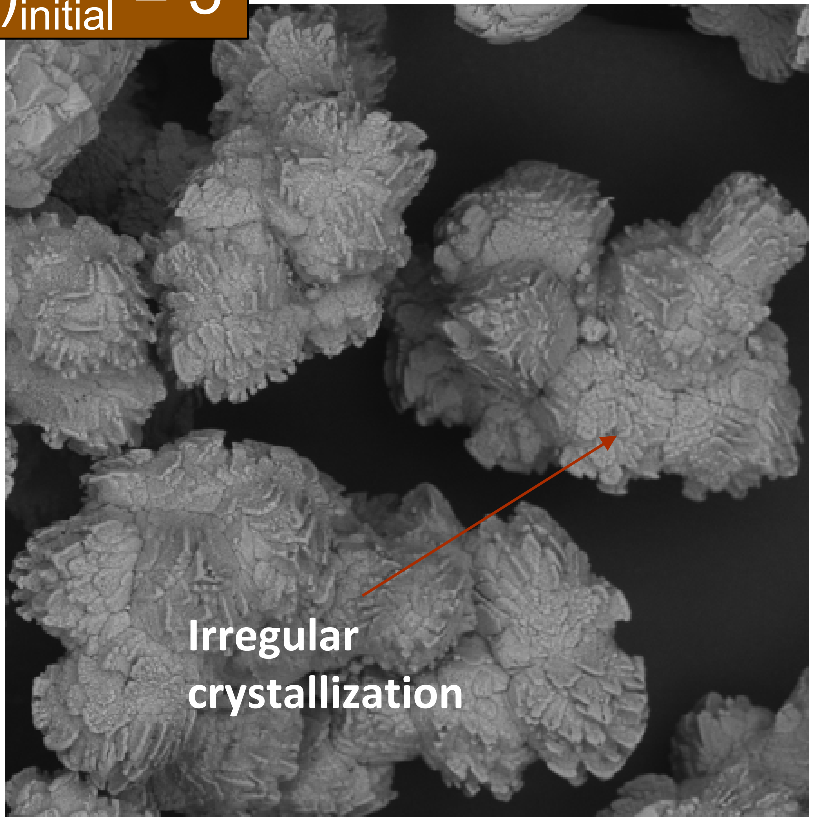
Phase Identification

- Non-calcite phases were only identified under short equilibrium times (e.g. 1 day)
  - Analyzed by XRD and SAED. Neither technique showed patterns of vaterite or aragonite (even on samples with abnormal morphologies) after 4 days

$(Mg/Ca)_{initial} = 5$

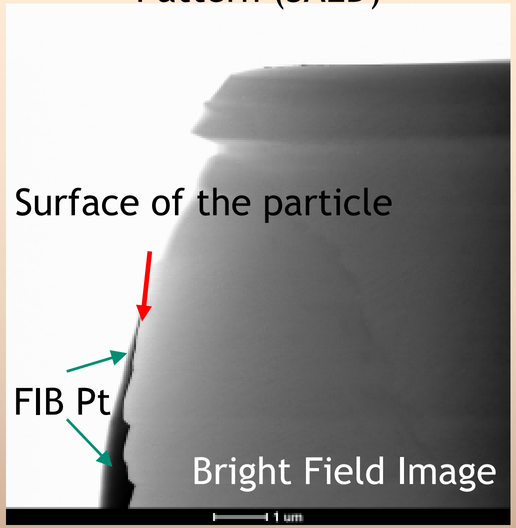


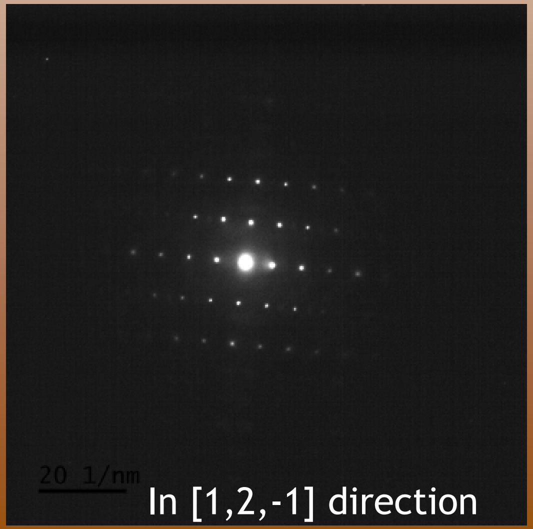
$(Sr/Ca)_{initial} = 0$



$(Sr/Ca)_{initial} =$

Selected Area Electron Diffraction Pattern (SAED)

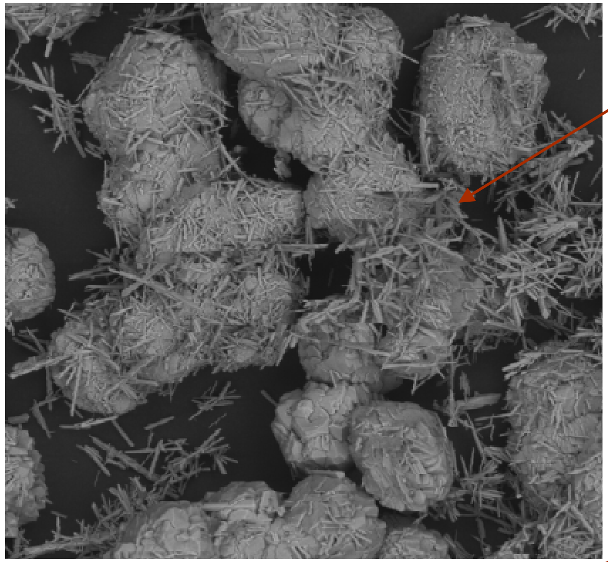




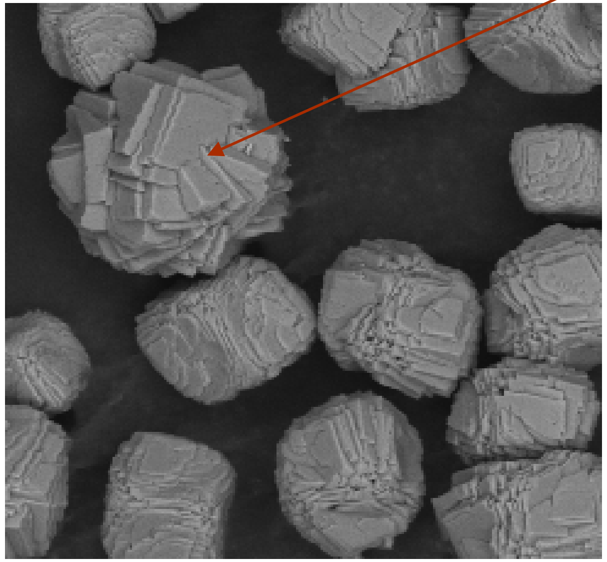
Morphology (21 Days)

$(Mg/Ca)_{initial} = 5$

$(Sr/Ca)_{initial} = 0$



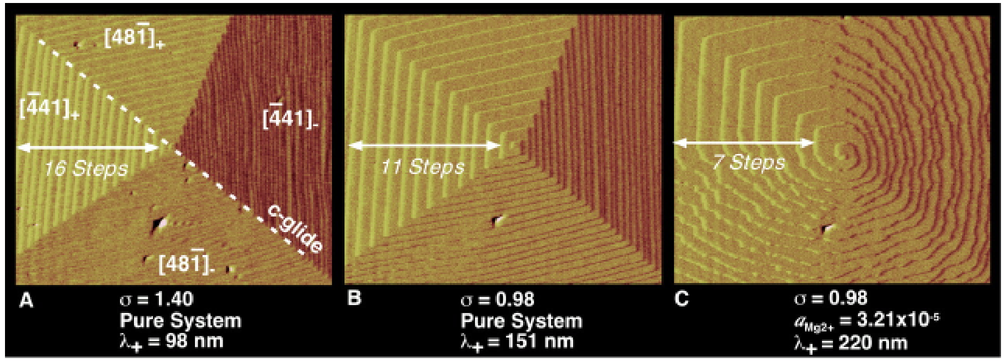
$(Sr/Ca)_{initial} = 5$



Needle fiber calcite has been shown to form from inorganic and biogenic sources with rapid precipitation rates. Mg^{2+} has recently been shown to play a role in the formation of needle fiber calcite[1,2].

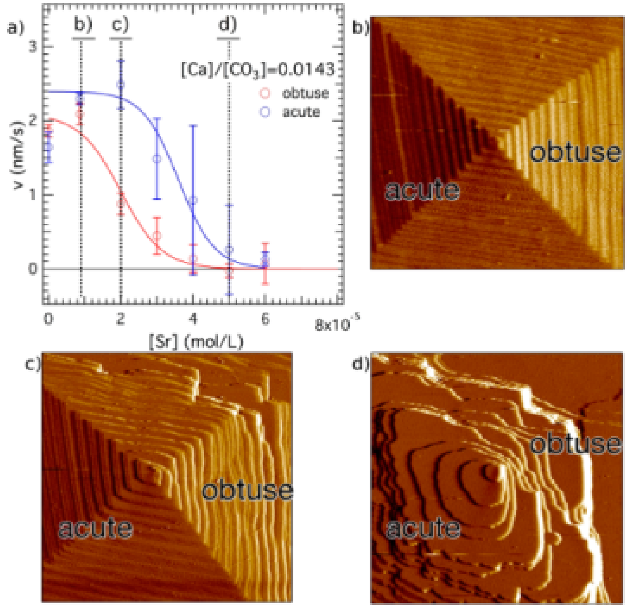
When $(Sr/Ca)_{initial}$ and $(Mg/Ca)_{initial} = 5$, spiral like aggregation occurs. This is likely caused by the fact that Mg preferentially binds to the acute angels and Sr to the obtuse.

Davis, K.J. et al. (2000) Science



Impact of Mg^{2+} alone

Bracco, J.N., et al. (2012) Crystal Growth & Design

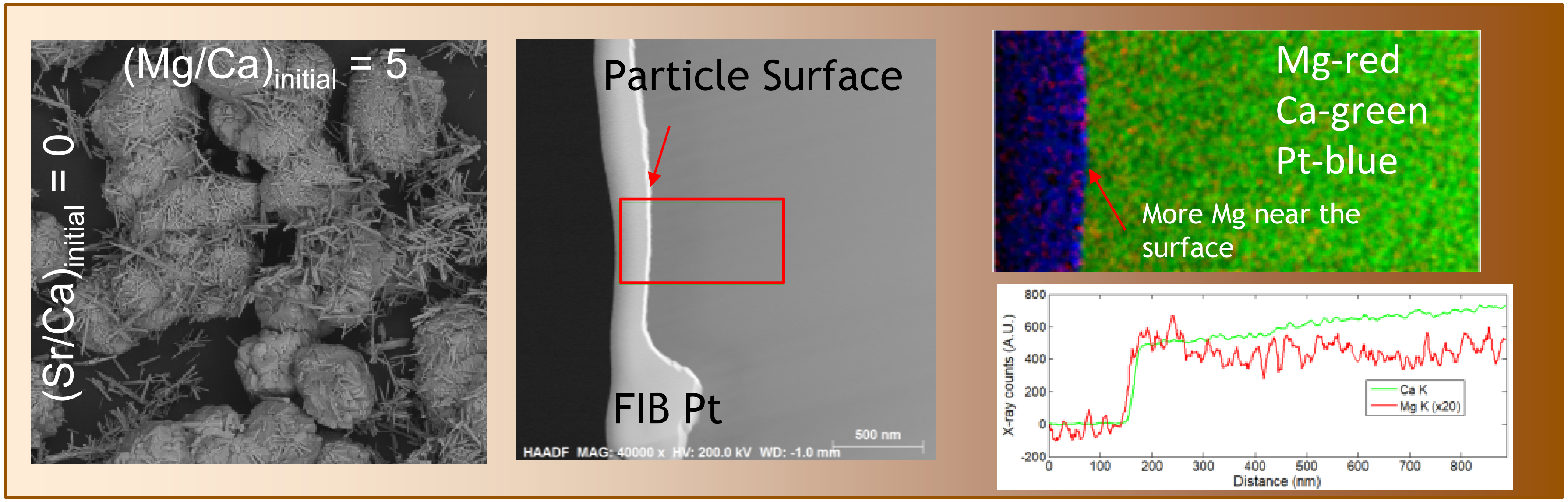


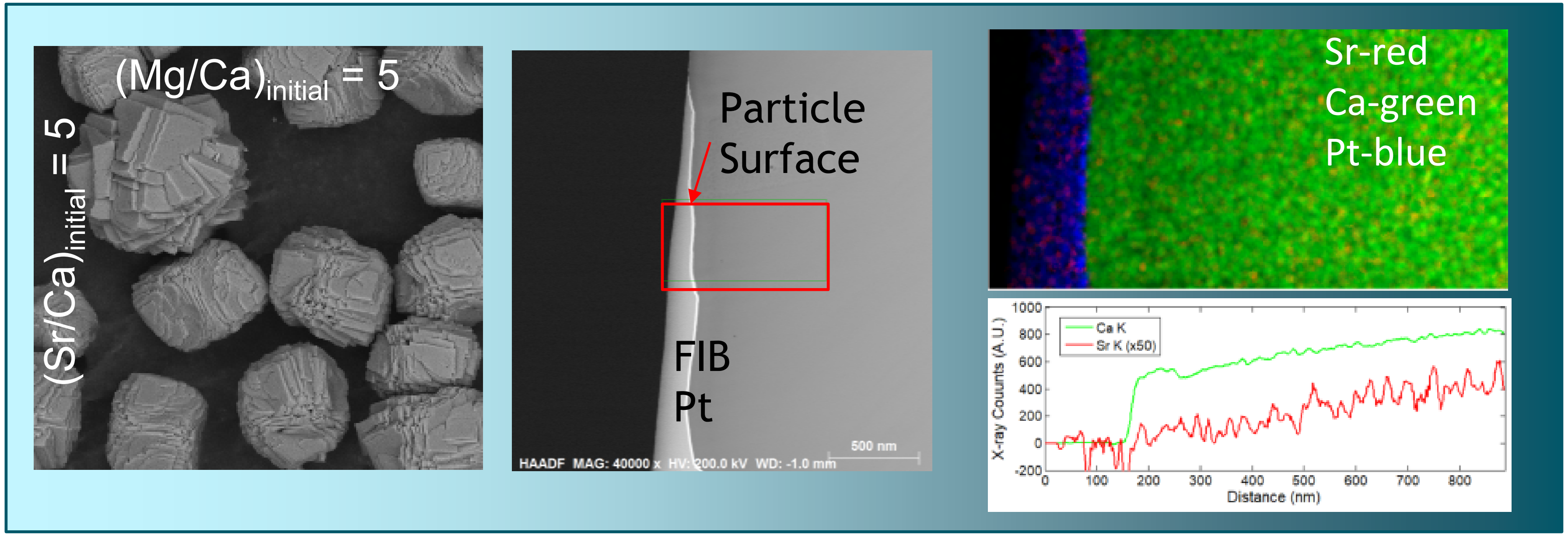
Impact of Sr^{2+} alone

[1]Olszta, M.J., et al., (2004) Chemistry of Materials
[2]Cañaveras, J. C. et al., (2006) The Science of Nature

Morphology (21 Days) –TEM/EDS

Mg^{2+} is a strongly hydrated cation and more readily forms outer sphere complexes with the surface





Kersit, S. et al (2004) JACS

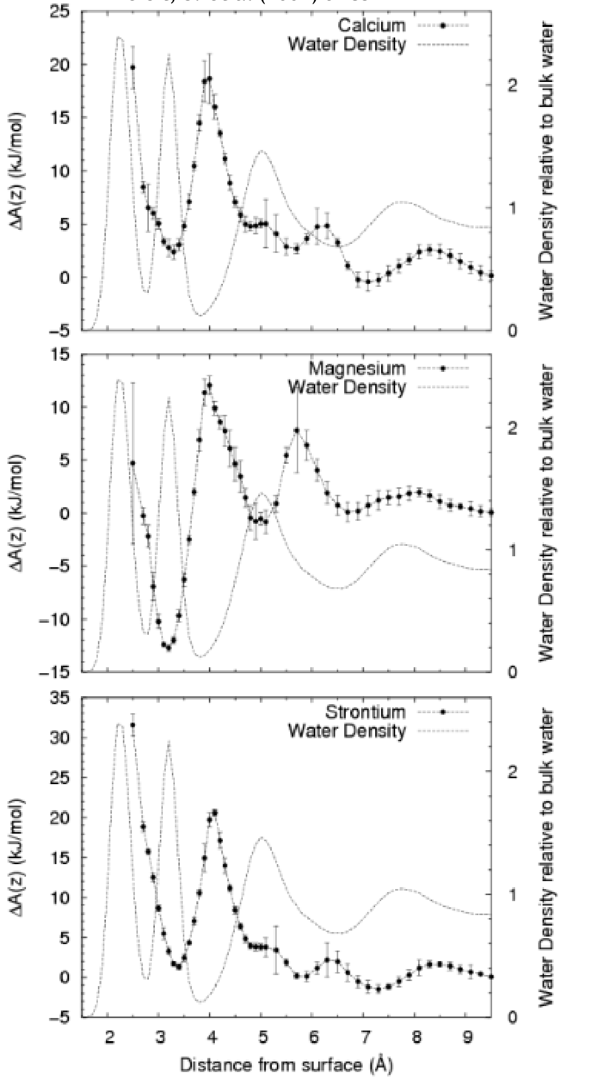
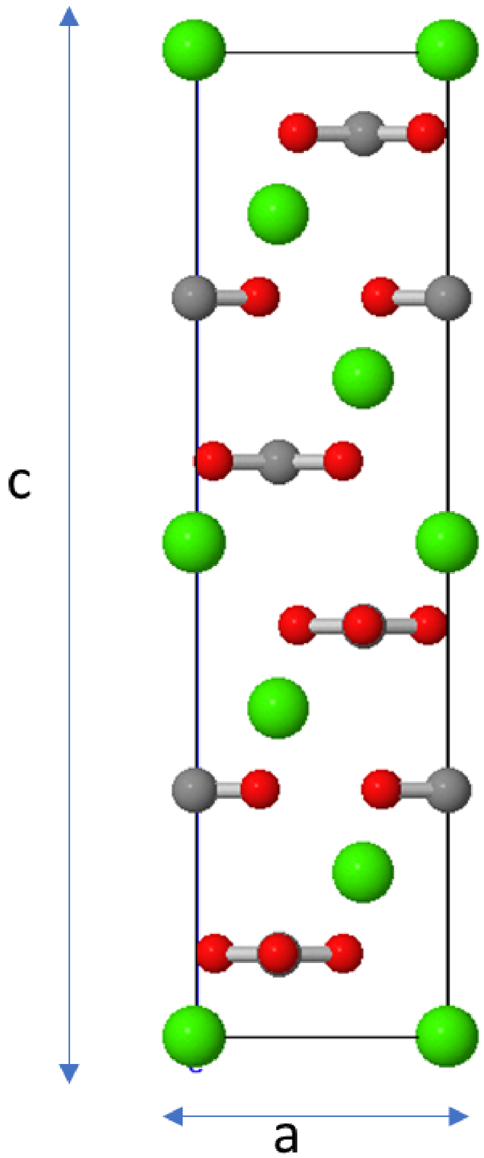


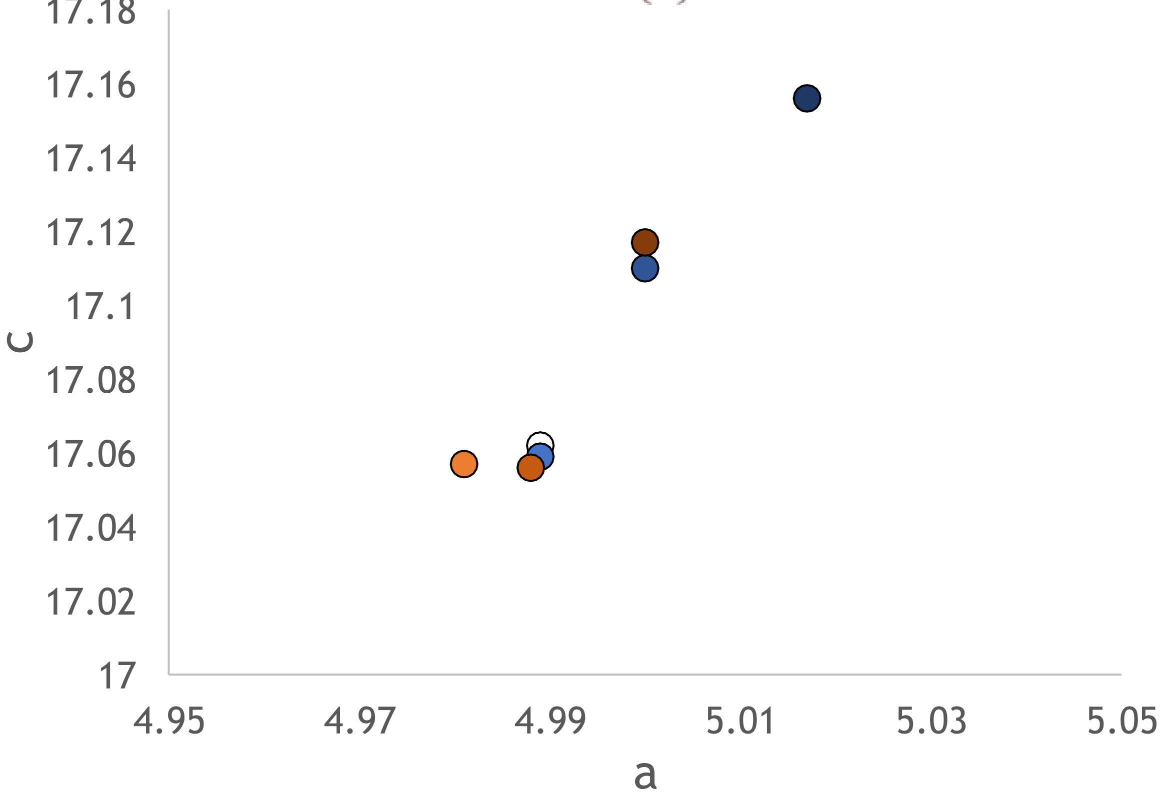
Figure 5. Calcium, magnesium, and strontium free energy profile as a function of distance from the surface.

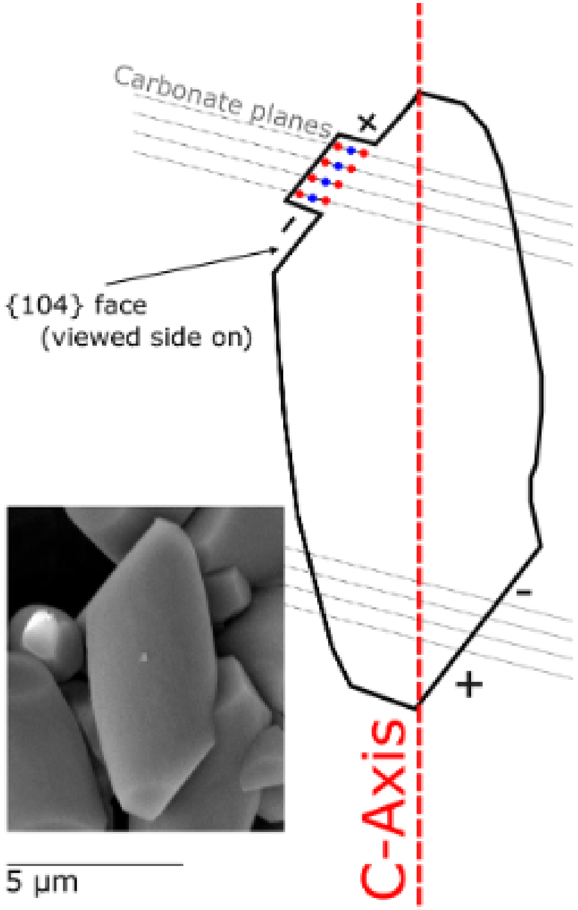
Unit Cell Parameters



With increased Sr^{2+}, the unit cell elongates in the c direction primarily. Mg^{2+} decreases the calcite unit cell in the a direction

$$unit\ cell\ volume\ (v) = a^2 c\ \sin 60°$$

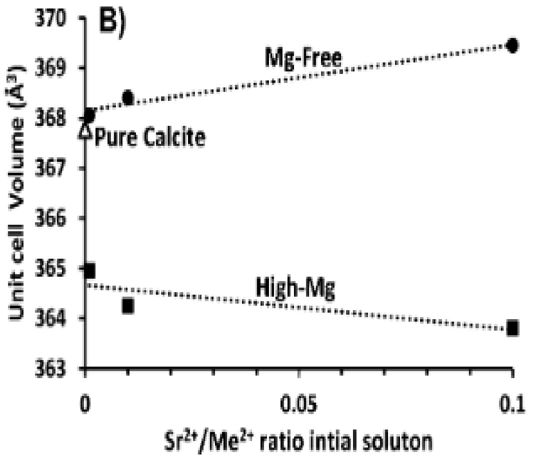




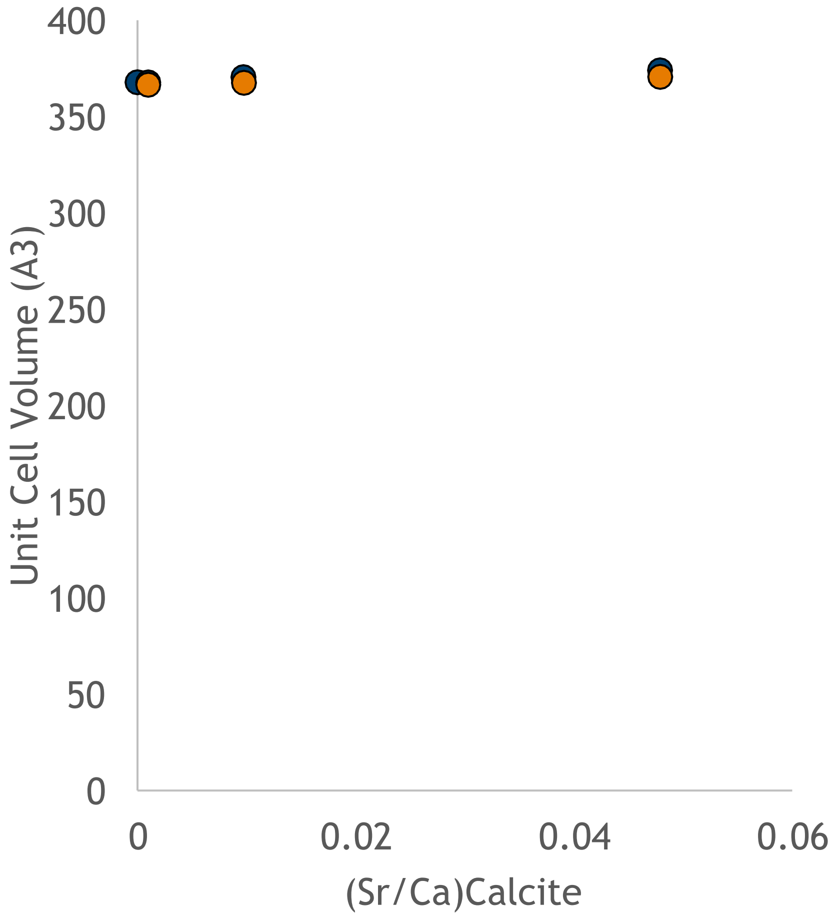
Hodkin, D. J. et al., (2018) Crystal Growth and Design

Unit Cell Parameters

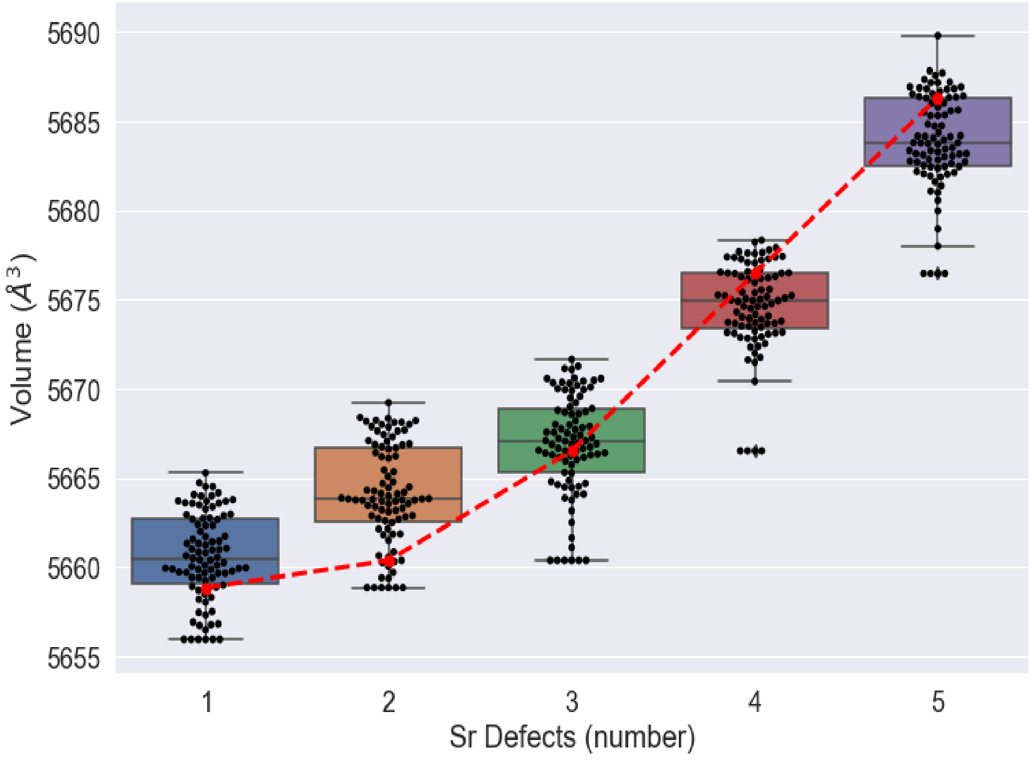
The unit cell expansion from Sr incorporation can be alleviated to some degree by the presence of Mg, leading to an increase in D_{Sr}



Littlewood, J. et al. (2014). Crystal Growth and Design

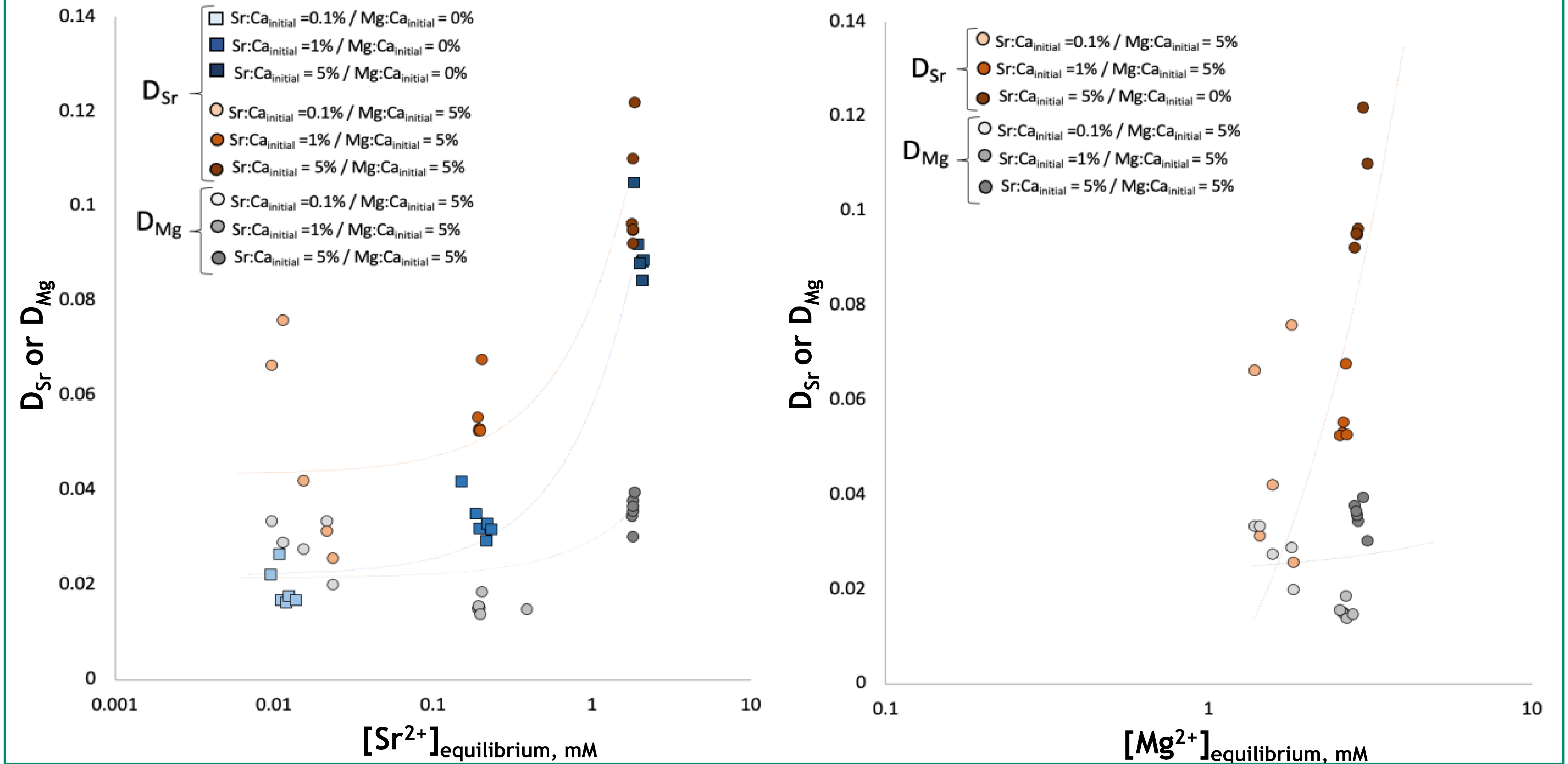


With 5 mol% Mg^{2+}, modeling efforts demonstrate the impact on unit cell volume of adding each additional Sr^{2+} ion to calcite.



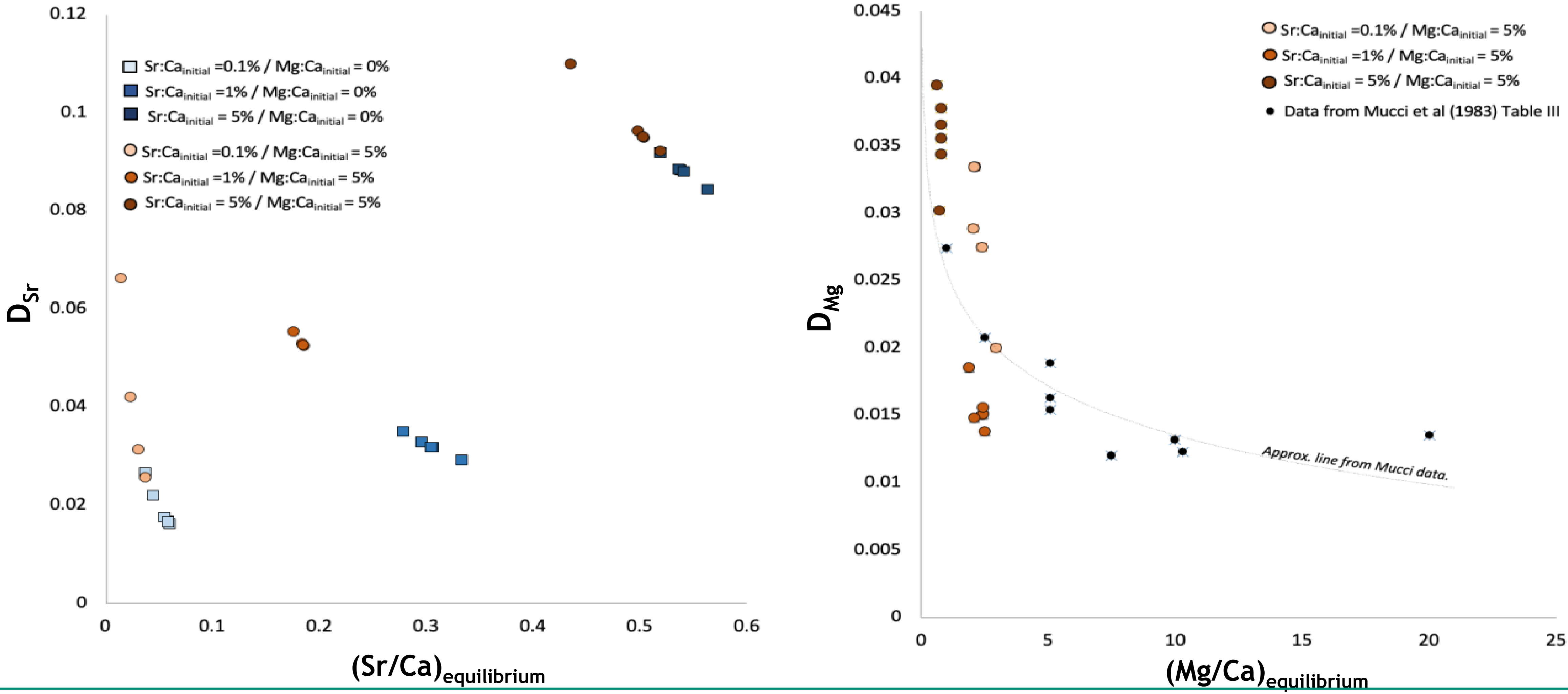
Incorporation of Sr^{2+} and Mg^{2+} into Calcite

D_{Sr} is generally larger than D_{Mg} and is dependent upon the $[Sr^{2+}]_{eq}$ and the $[Mg^{2+}]_{eq}$.
The presence of Mg^{2+} enhances the incorporation of Sr^{2+}.
D_{Mg} is relatively stable and unimpacted by Sr^{2+}



Incorporation of Sr^{2+} and Mg^{2+} into Calcite

D_{Sr} increases with increasing $(Sr/Ca)_{eq}$ ratio and enhanced by Mg^{2+}.
D_{Mg} decreases with greater $(Mg/Ca)_{eq}$
D_{Sr} versus particle radius reduces down to a single trend with Mg^{2+} is present or absent



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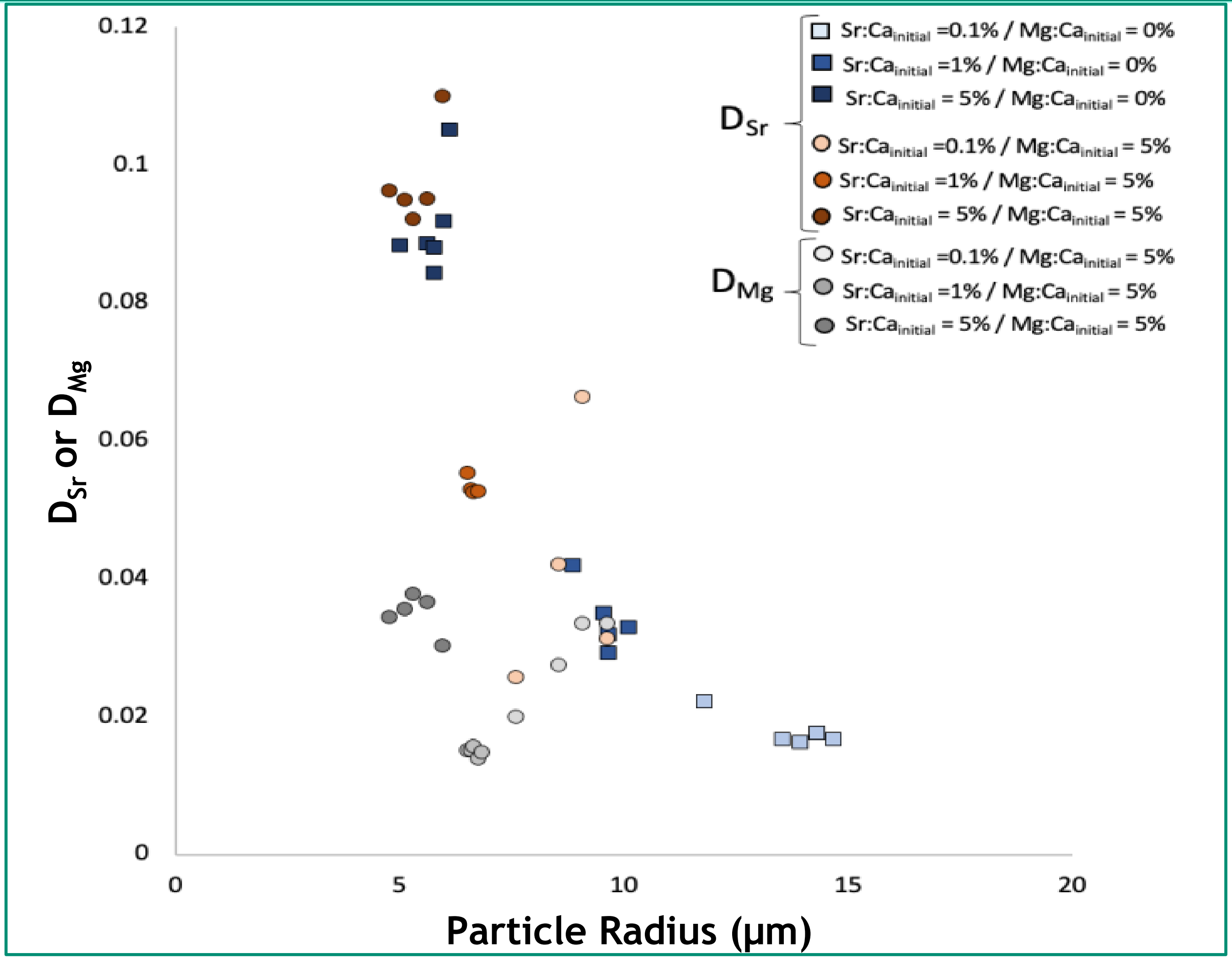
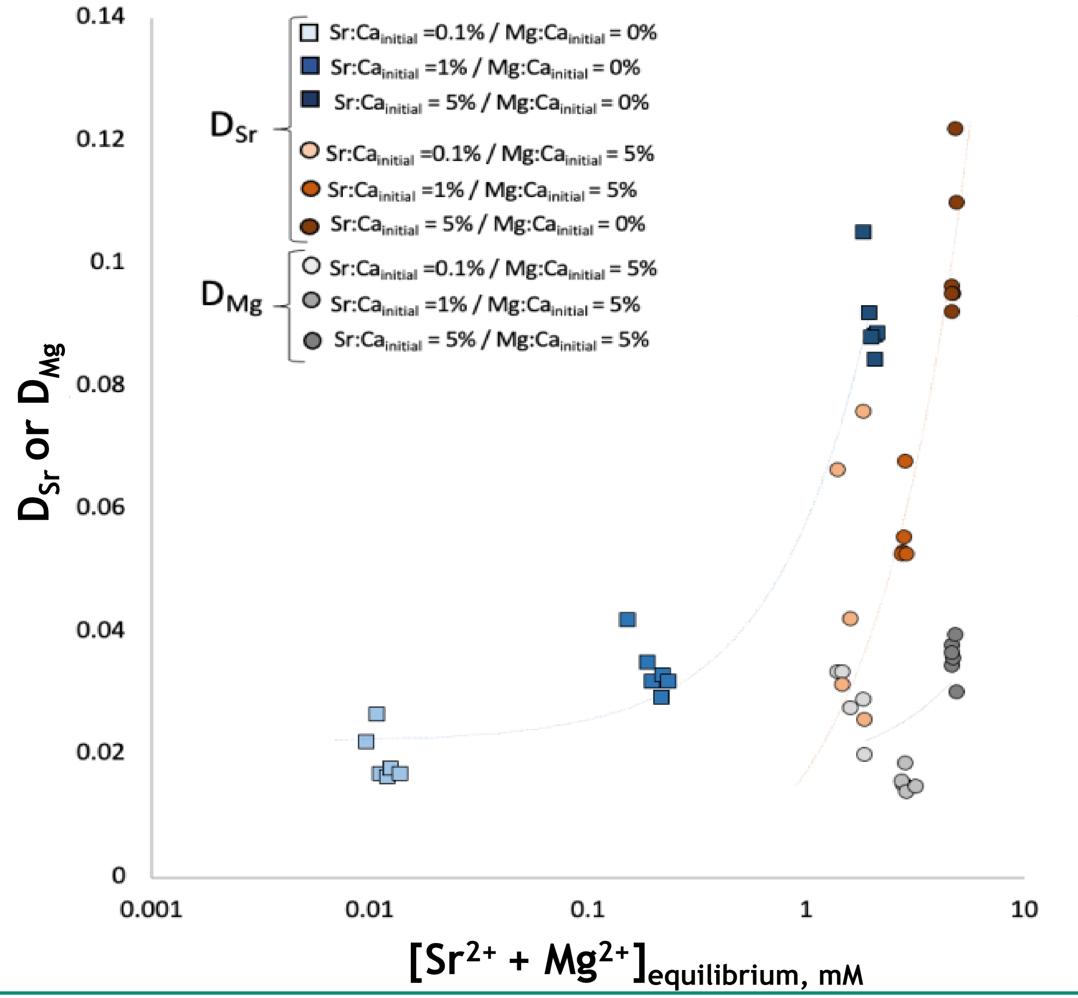
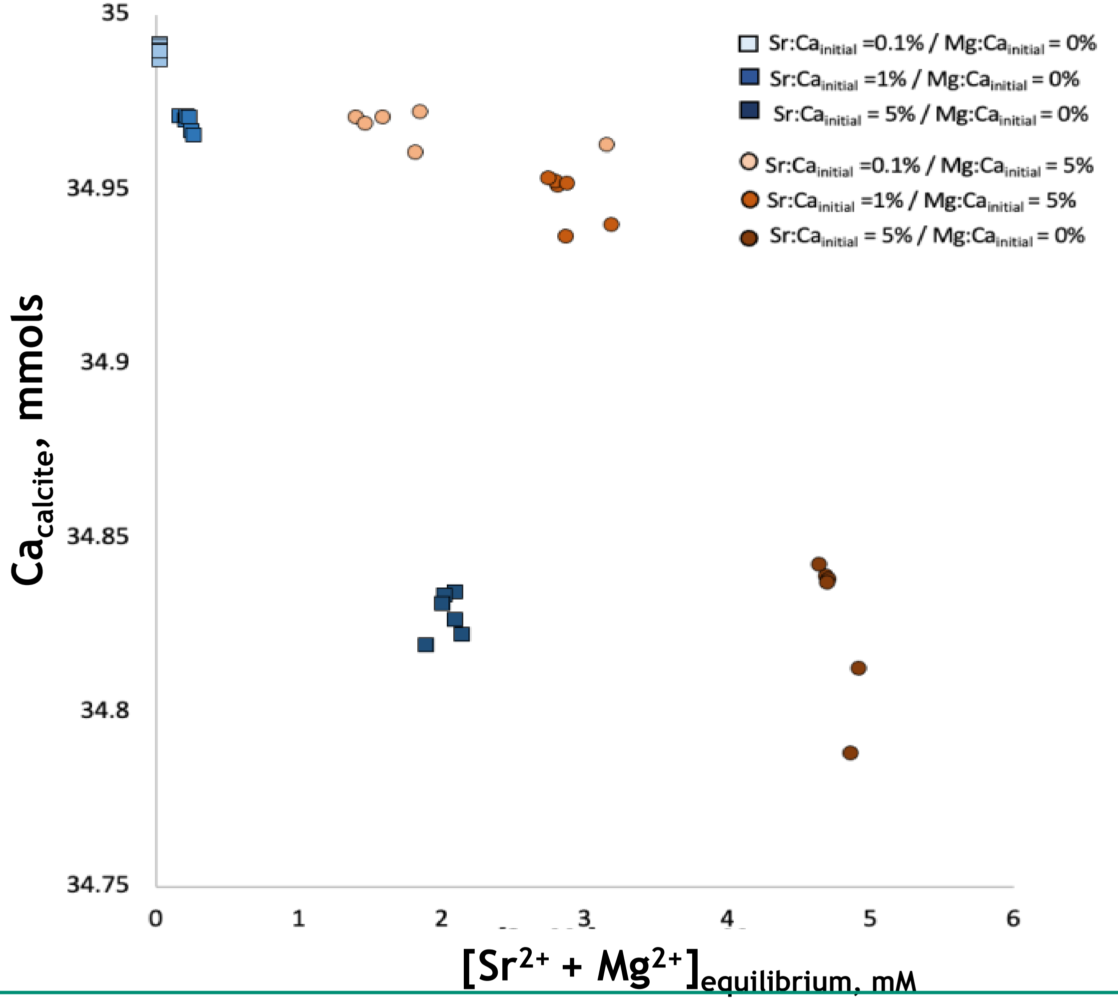


Incorporation of Sr^{2+} and Mg^{2+} into Calcite

Do Mg^{2+} and Sr^{2+} have ion specific impacts or simply the sum of total exogenous cations?

When $D_{Sr/Mg}$, $Ca_{calcite}$, and particle radius are plotted versus $[Sr+Mg]_{eq}$ two trend lines emerge signifying the impact of this ions are not additive.





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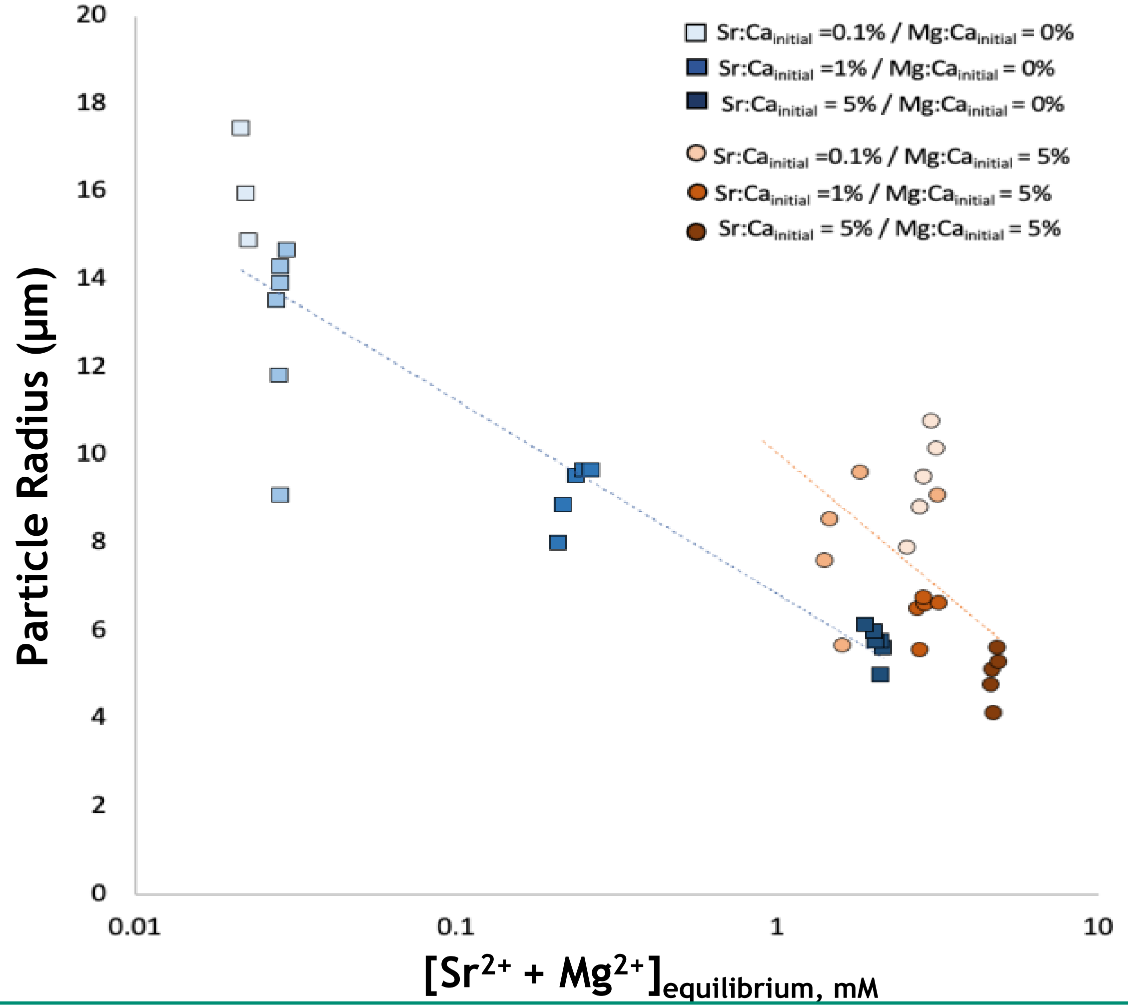
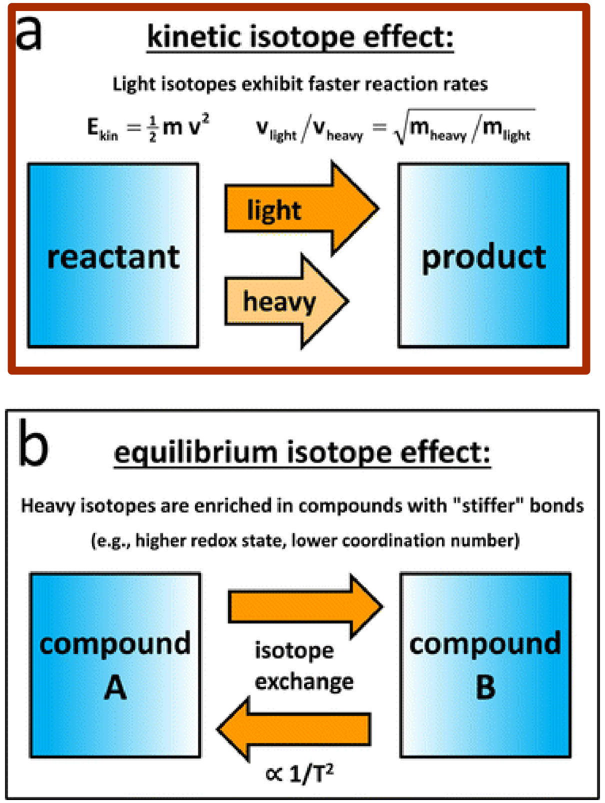
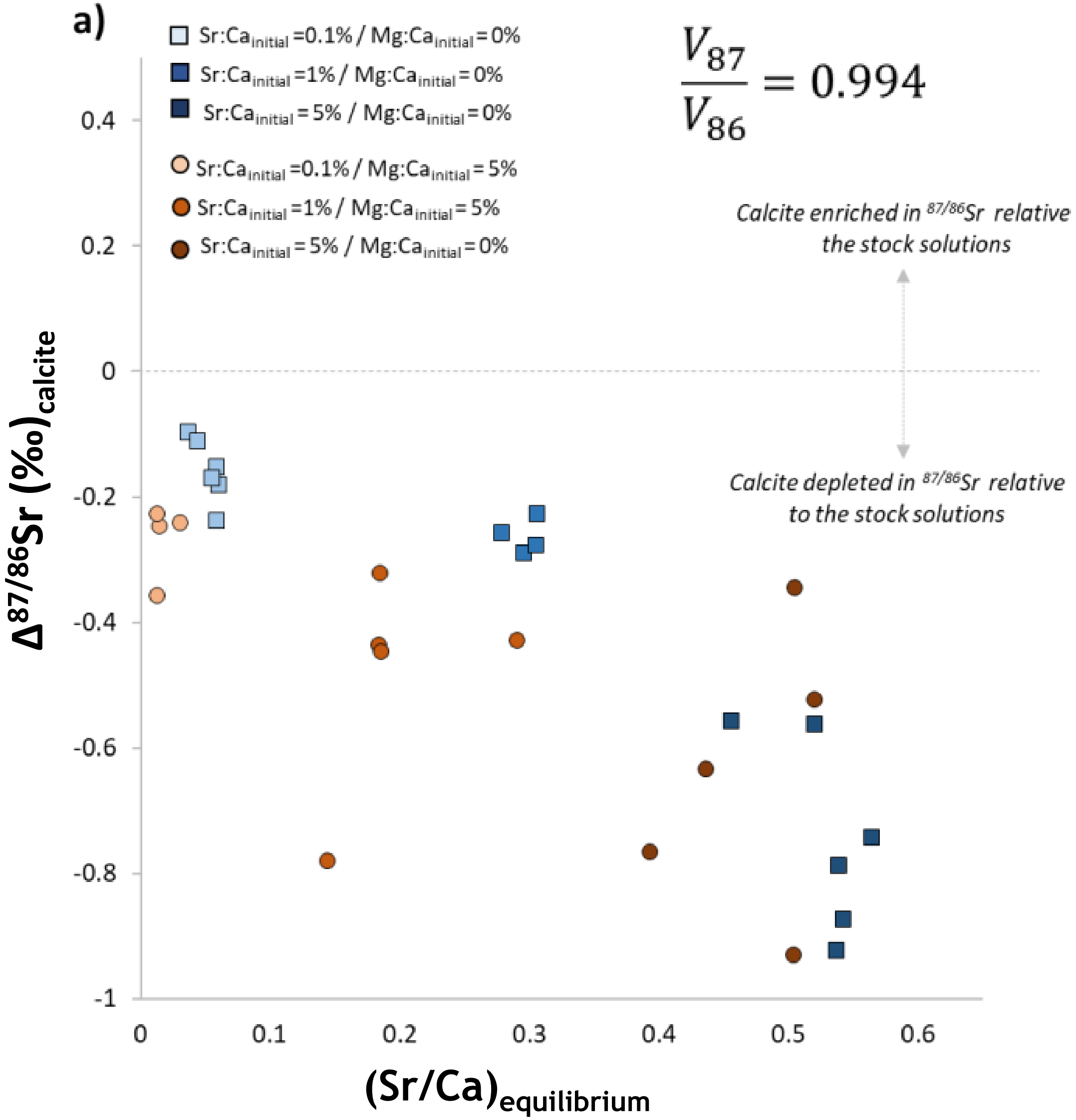


Sr Isotopic Fractionation

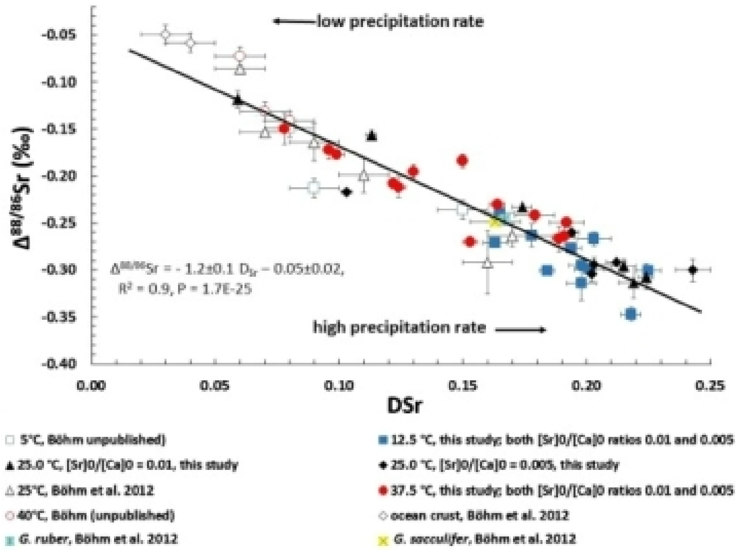
Fractionation signature suggests the kinetic Isotope effect is the dominant mechanism.
$\Delta^{87/86}Sr$ (‰)$_{calcite}$ is proportional to $(Sr/Ca)_{equilibrium}$



Wiederhold, J. (2014). Environ. Sci. & Tech.



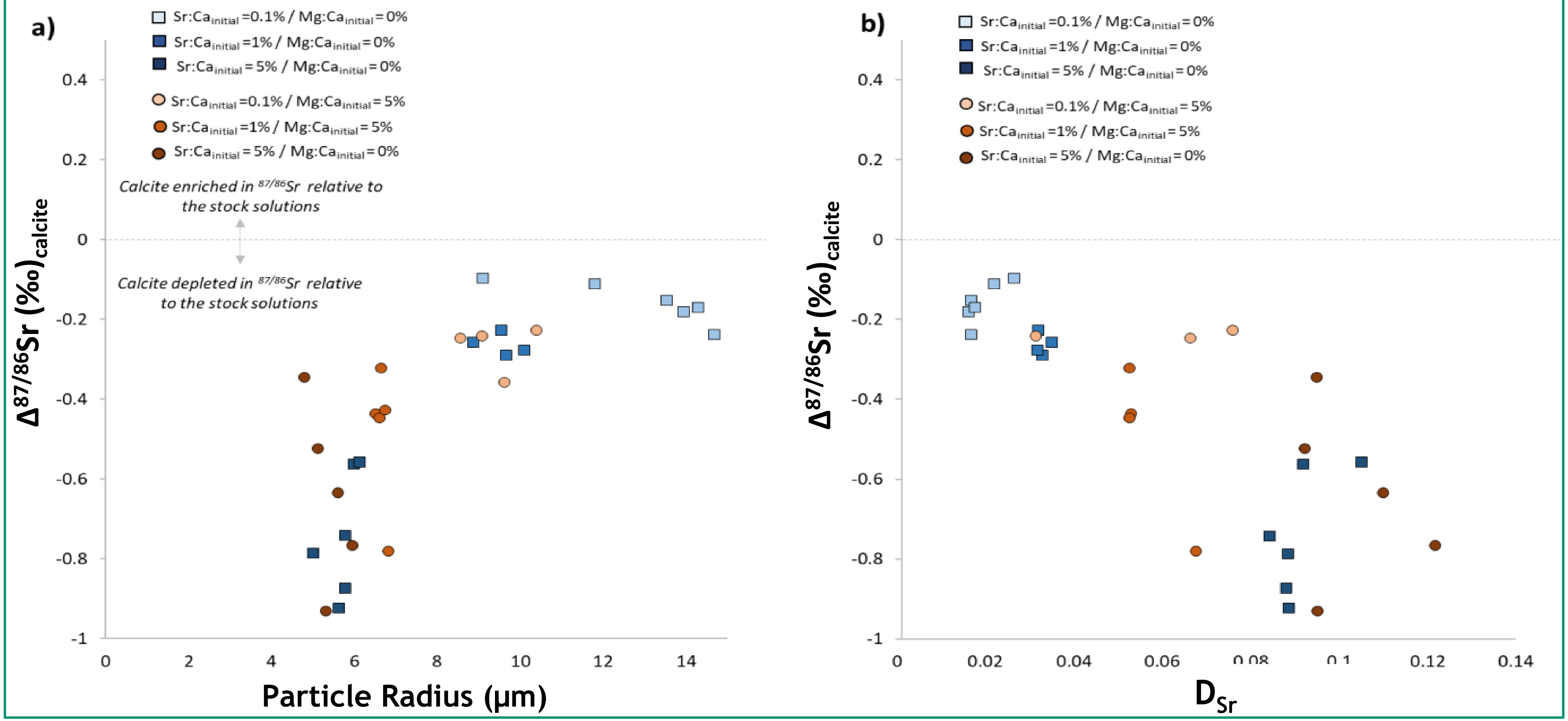
AlKhatib, M. and Eisenhauser, A. (2017) Geochimica et Cosmochimica Acta



Sr Isotopic Fractionation

Can $\Delta^{87/86}Sr$ (‰)$_{calcite}$ be estimated from crystal size or D_{Sr}?

$\Delta^{87/86}Sr$ (‰)$_{calcite}$ is dependent upon the average particle radius and the D_{Sr} and could be a potential indictor to the calcite formation conditions.



Conclusions and Future Work

Conclusions

- Sr^{2+} and Mg^{2+} inhibit calcite crystal growth, though their adsorption and incorporation mechanisms are different
  - Mg^{2+} is a strongly hydrating ion and tends to form surface complexes, which preferentially adsorbs to the acute edges of calcite. In contrast, Sr^{2+} more readily dehydrates and associates with the obtuse angled sides.
- Sr^{2+} incorporated into calcite increases the unit cell volume by elongation along the c axis. Mg^{2+} decreases the unit cell volume and may alleviate lattice strain allowing for more Sr^{2+} to be incorporated
- D_{Sr} increases with increasing Sr^{2+} and in the presence of Mg^{2+}; D_{Mg} decreases with increasing Mg^{2+} and relatively small impact from increasing Sr^{2+}
  - The incorporation of Mg and Sr appear to be ion specific and not just the sum of the total ion concentration.
- $^{87/86}Sr$ isotopic occurs during calcite precipitation and D_{Sr} and crystal size can be potential descriptors the extent of the fractionation.

Future Work

- Ongoing computation modeling efforts to evaluate the impact of Sr and Mg incorporation on the surface defect energy and the crystal lattice energy

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Questions?