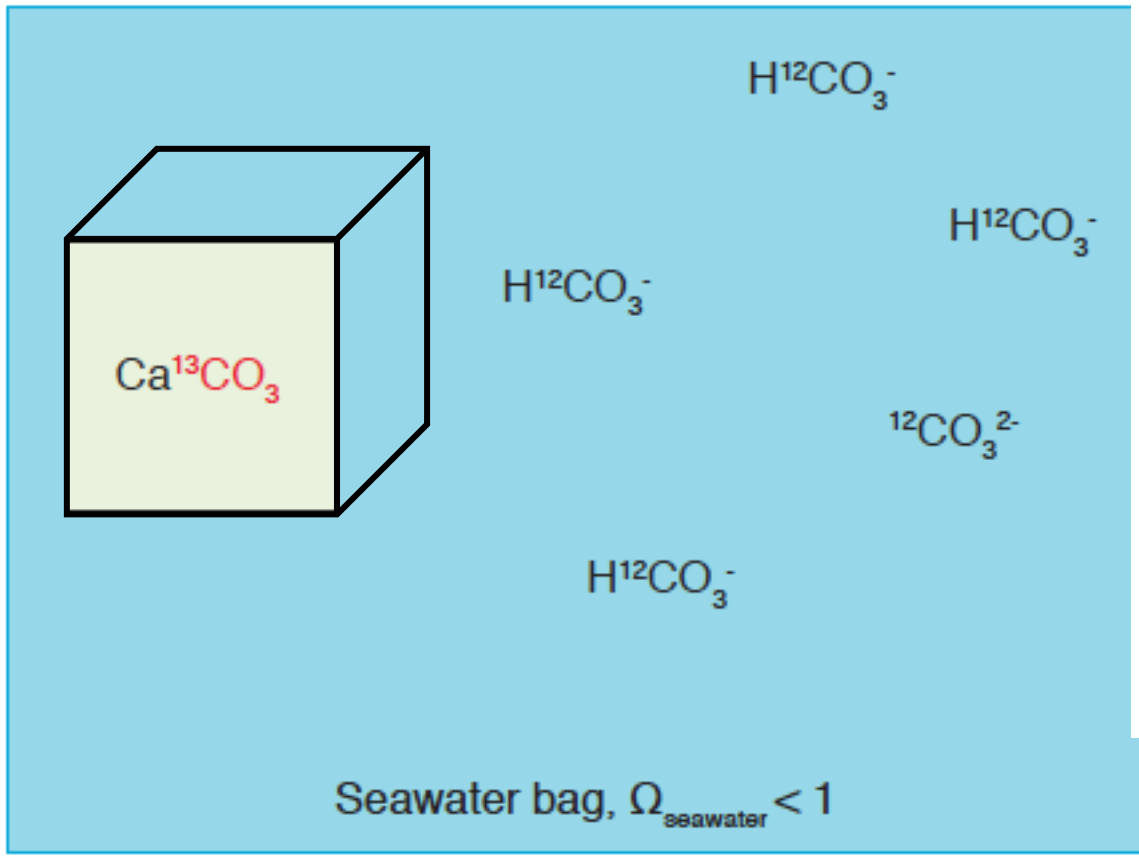
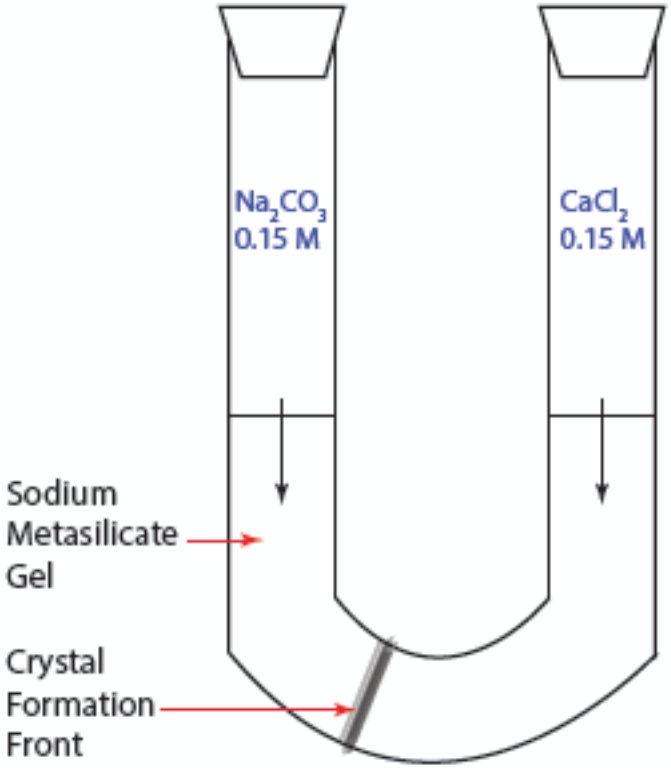
Ocean Acidification—Carbonate Dissolution Kinetics: Lab vs. Field

Will Berelson—USC
Jess Adkins—Caltech
Adam Subhas—Caltech
Nick Rollins—USC
Sijia Dong—USC
Jonathan Erez—Hebrew Univ.

Methodology

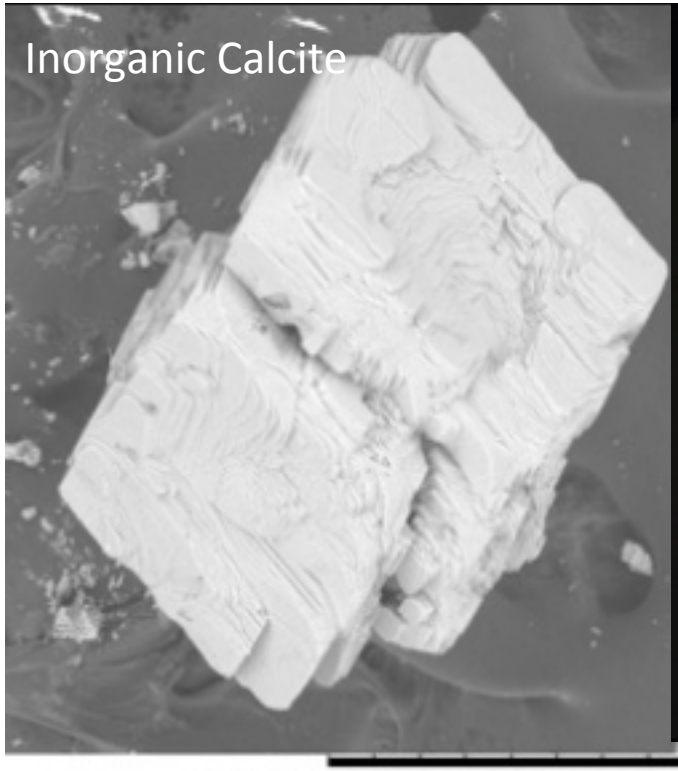


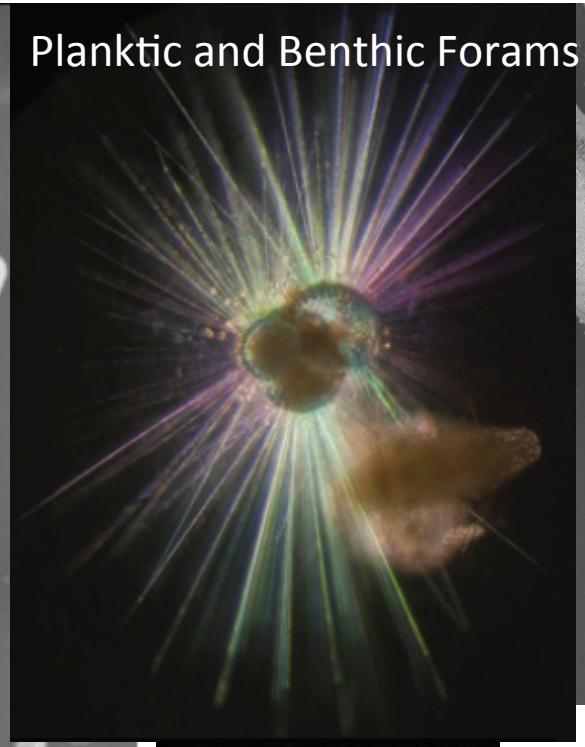


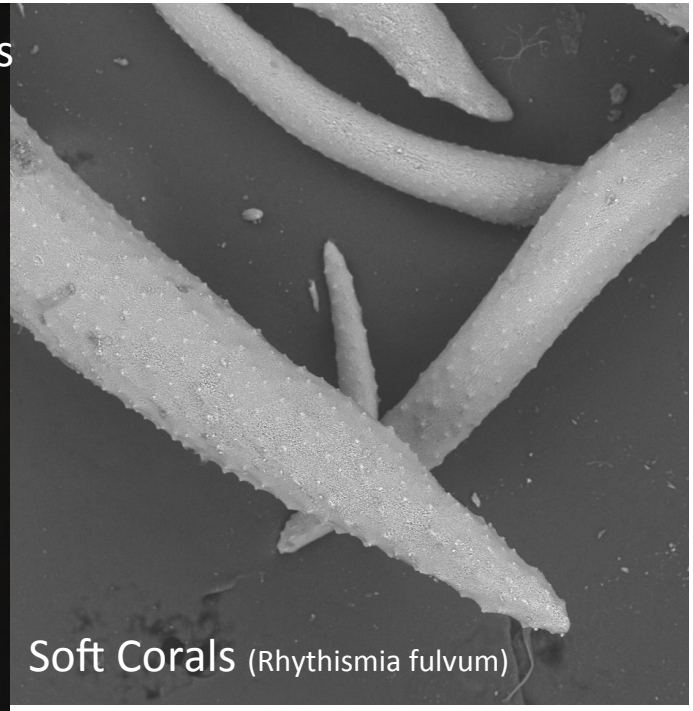
$DIC = [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}]$

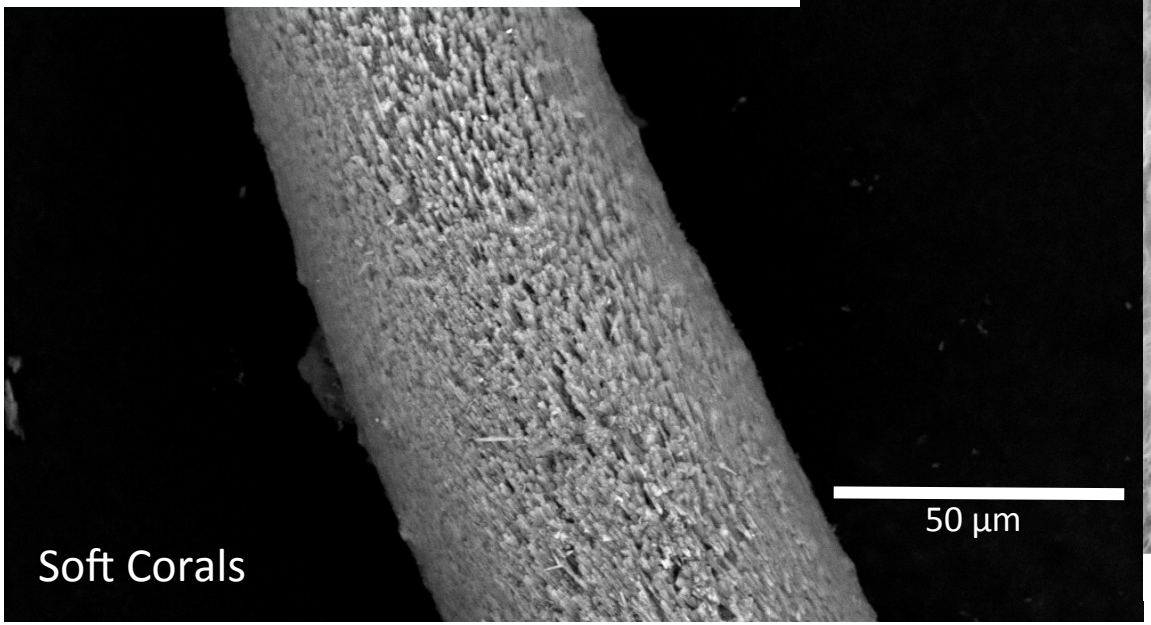
$Alk \approx [HCO_3^-] + 2[CO_3^{2-}]$

Isotope labeled calcite:
Store-bought (Aldrich) and home-made calcite

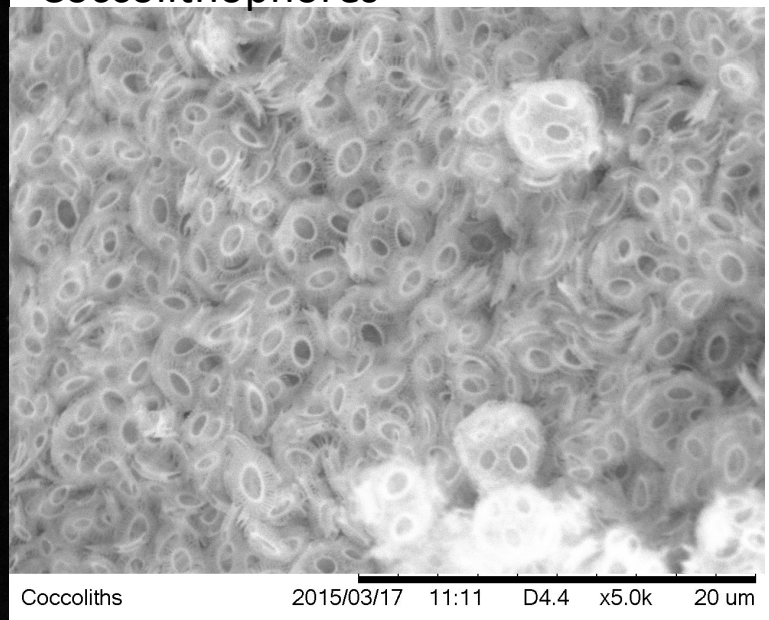


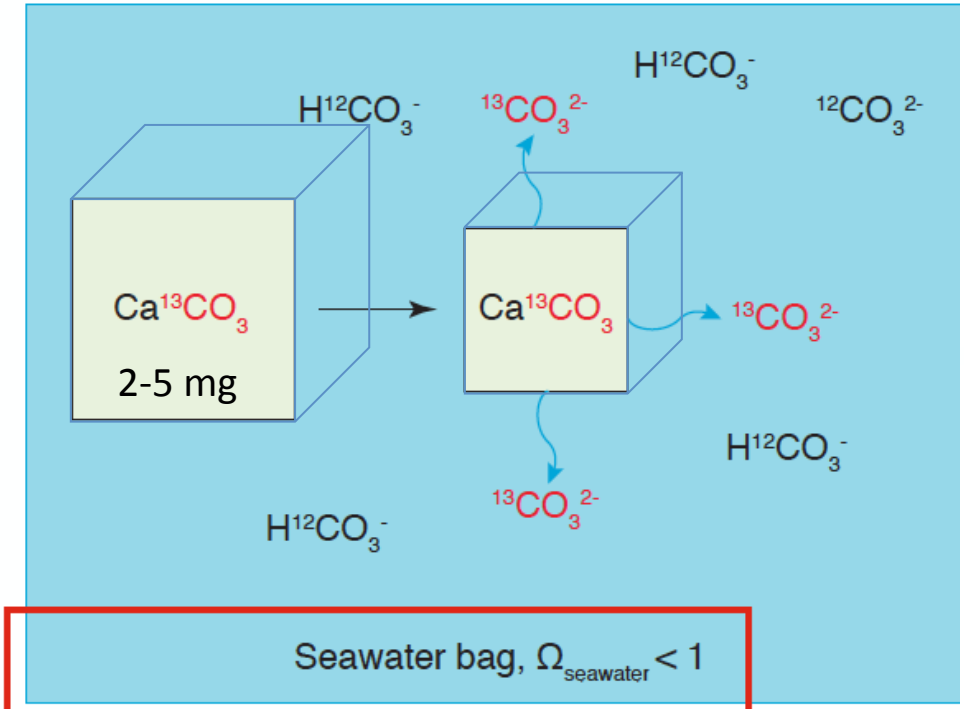






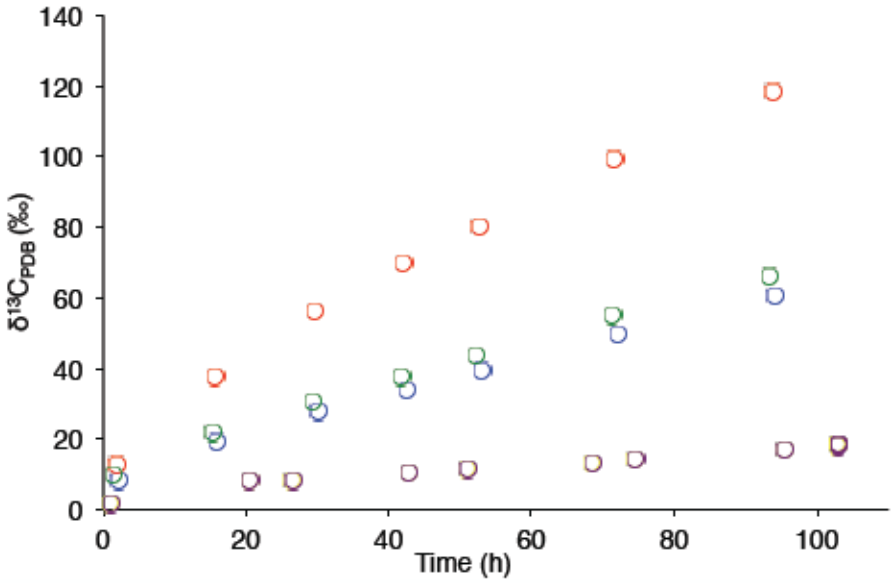
Coccolithophores

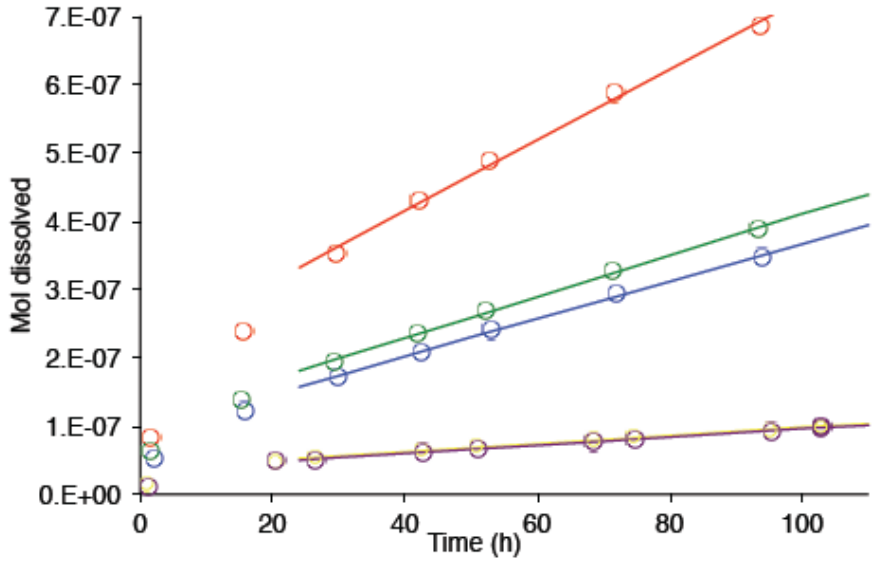




$DIC = [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}]$

$Alk \approx [HCO_3^-] + 2[CO_3^{2-}]$





Some Analytical Details:

TCO2 is measured on 3-7 ml of sea water, Alk on 16-20 ml. TCO2 prep per sample, 2 minutes, run per sample 10 minutes (TCO2 analyzed on Picarro CRDS).

Alk prep per sample, 2 minutes, run per sample 15 minutes.

Del ^{13}C measured on TCO2 is analyzed at same time as TCO2 (Picarro CRDS).

To date, have run >2000 TCO2's, del^{13}C's and >500 Alks.

Dickson water is our TCO2 and Alk Standard. We also make sub-standards from ocean water.

Continued:

Solid $CaCO_3$ calibrated to VPDB is used as a del ^{13}C standard.

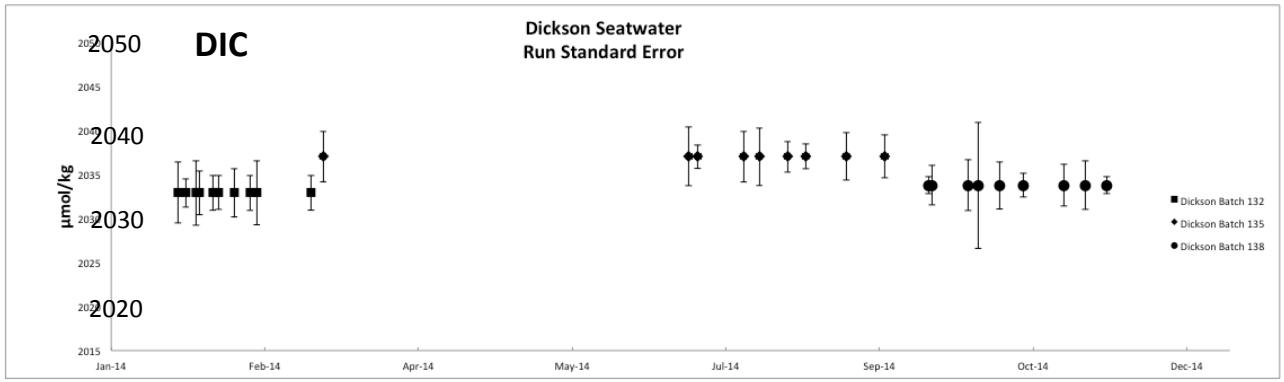
Picarro has been cross-calibrated with Mass Spec at Caltech.

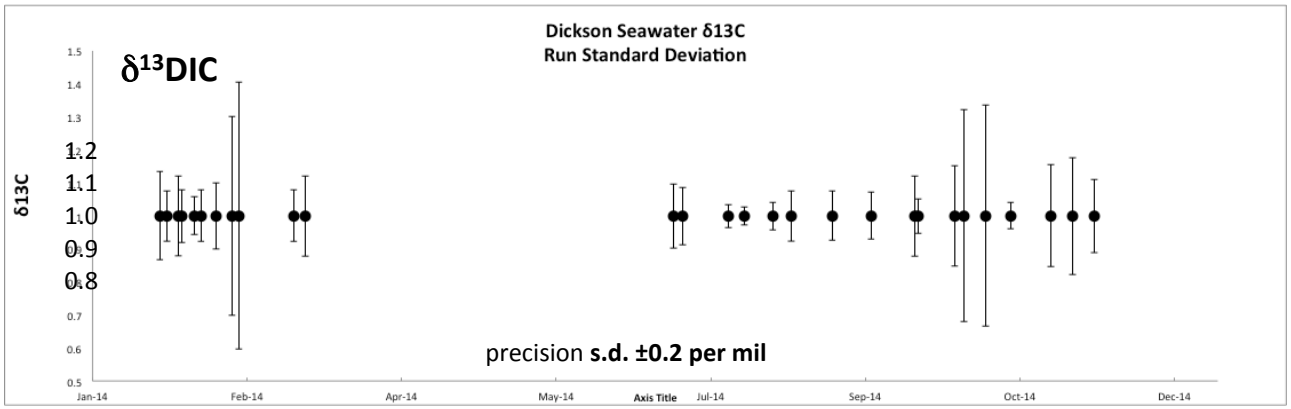
Picarro has been adapted with mass flow control valve, water vapor trap and other personalized data management to improve accuracy and precision

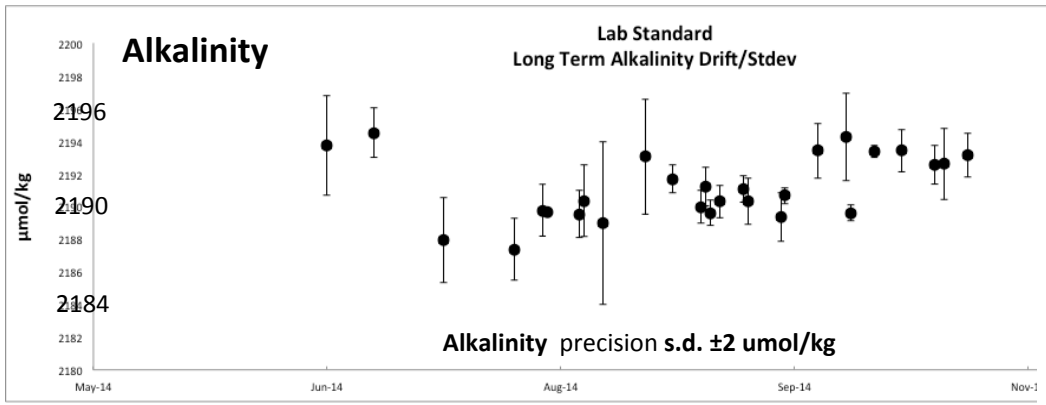
Experiments generally involve 300 ml water in Supelco bags, on shaker table, effect of shaking has been calibrated

We use bags made from interlayed Al foil and polyethylene (Supelco) for experiments.

We have found TCO2 and Alk blanks ABOUND, gas loss, gas gain, acid leaching, base leaching!!







Average errors in Ω are ~0.01-0.02 units

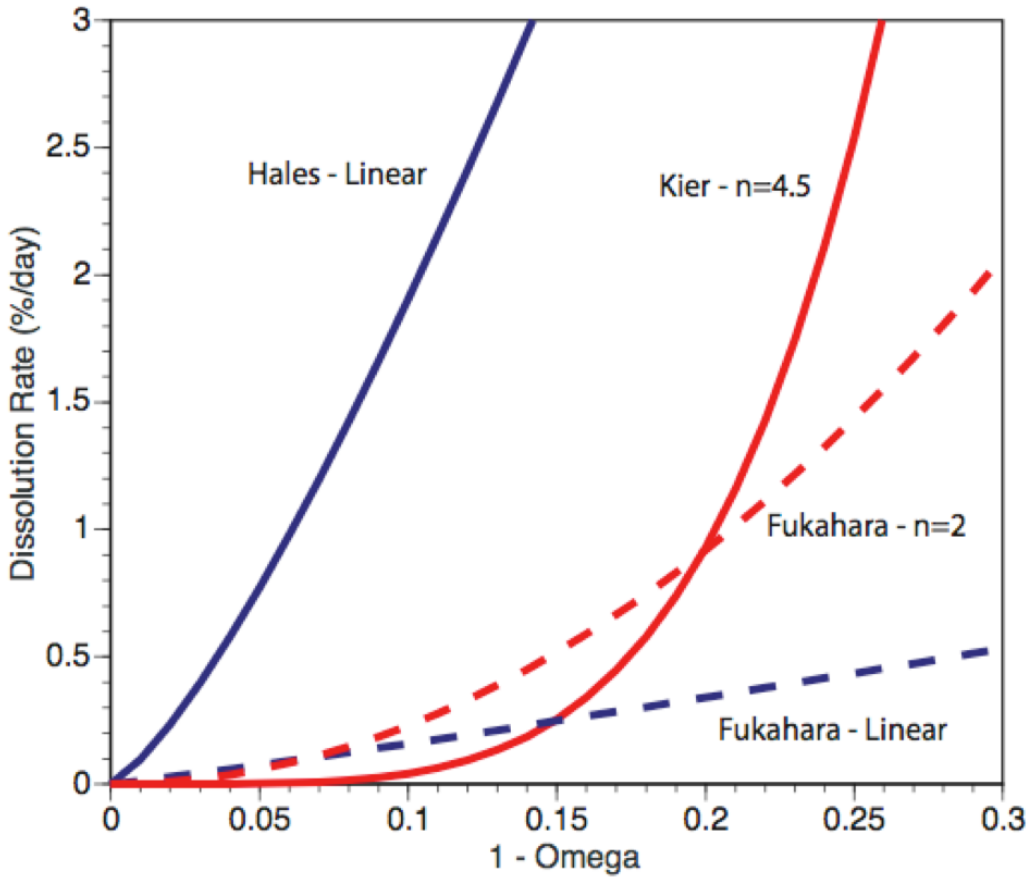
SW sample size: 7g DIC 16 g Alk	Alkalinity (µeq/kg)	DIC (µmol/kg)
Mean Value	~2100	~2000
Internal error	2.5	5.1
Intermediate error (1σ)	2.0	5.6
External error (1σ)	2.5	5.2
MSWD	0.7	1.0

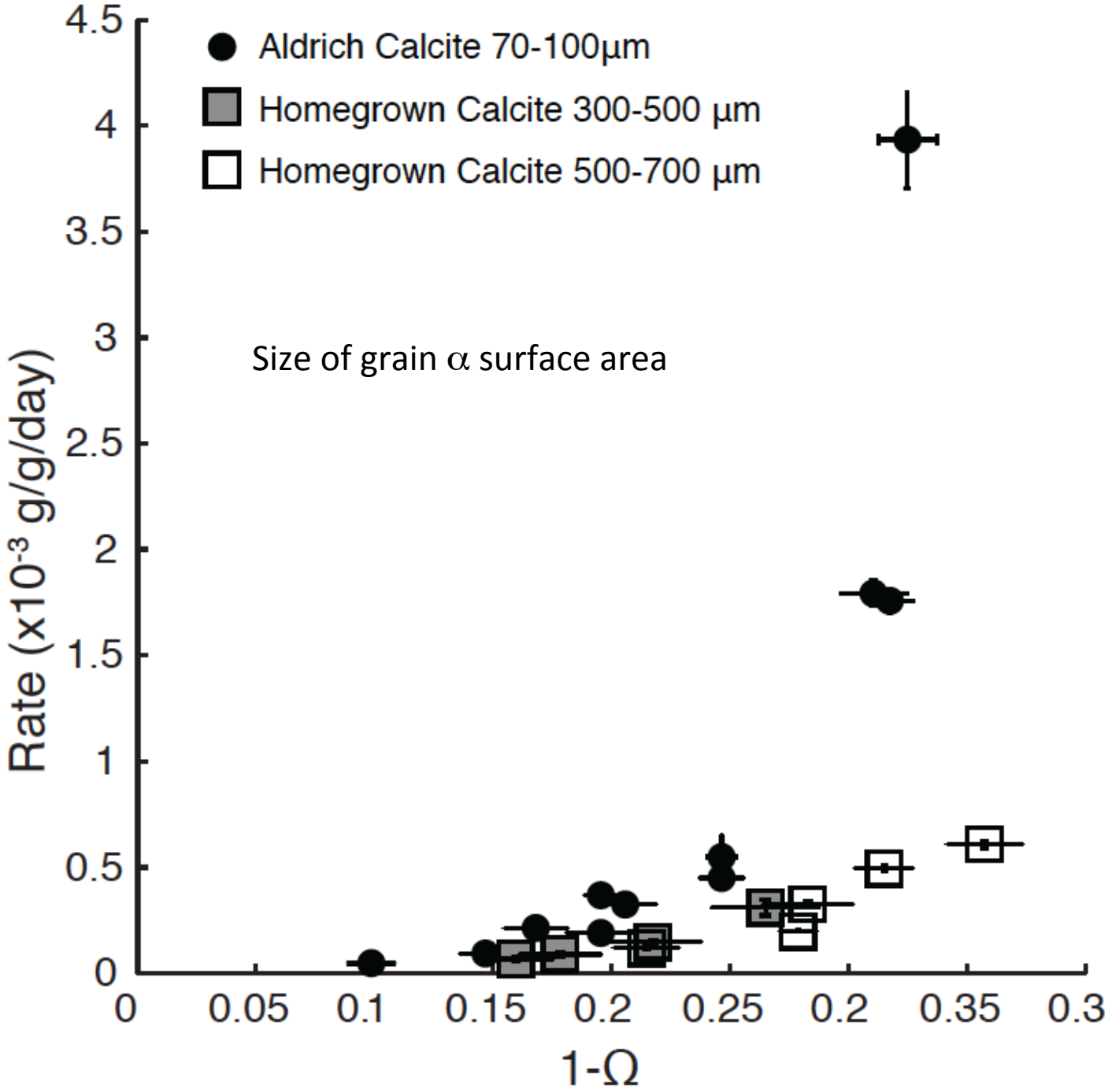
Using 100% labeled materials,

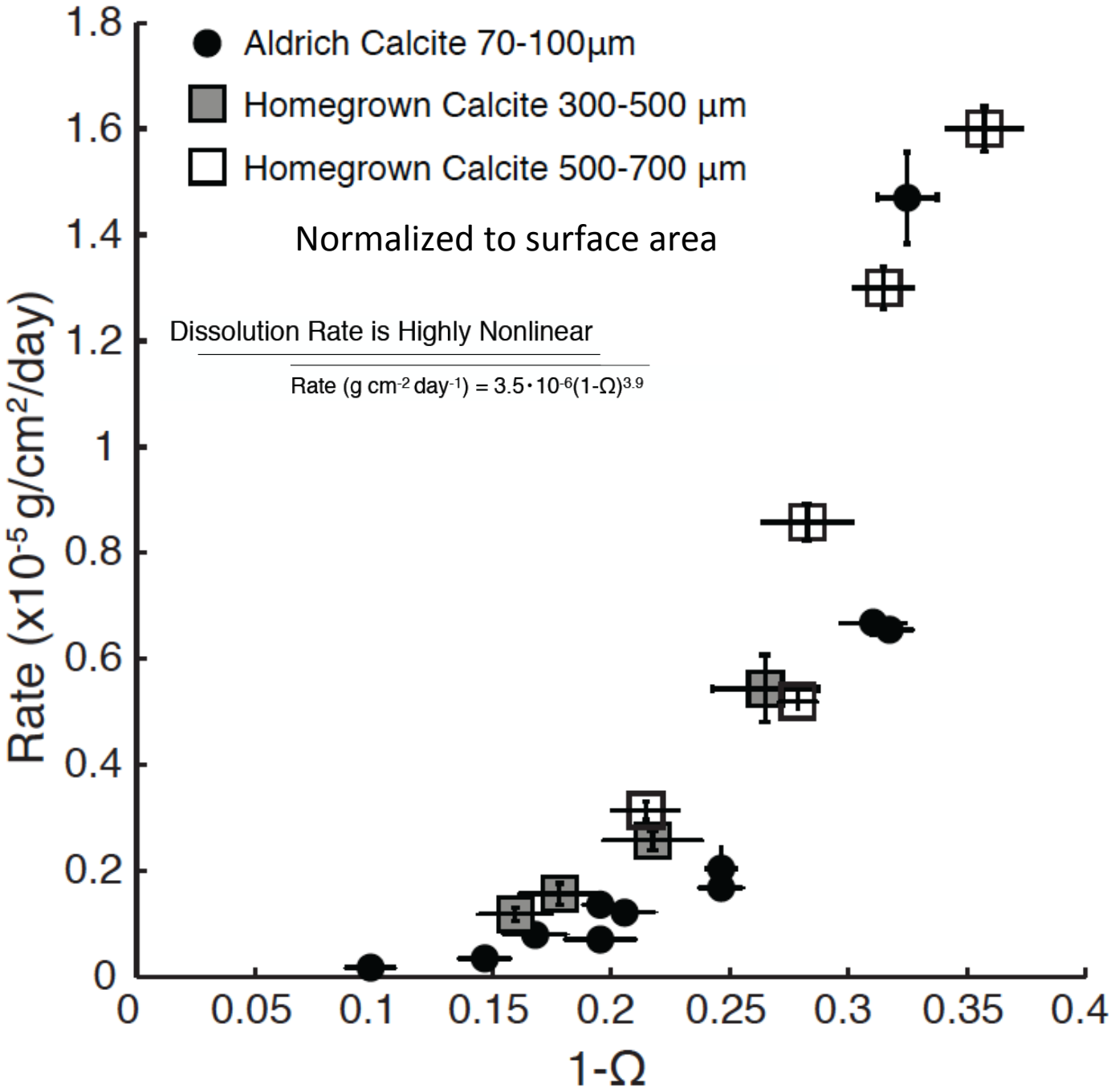
A 20‰ signal in $\delta^{13}C$ changes alkalinity by 1 µeq/kg!

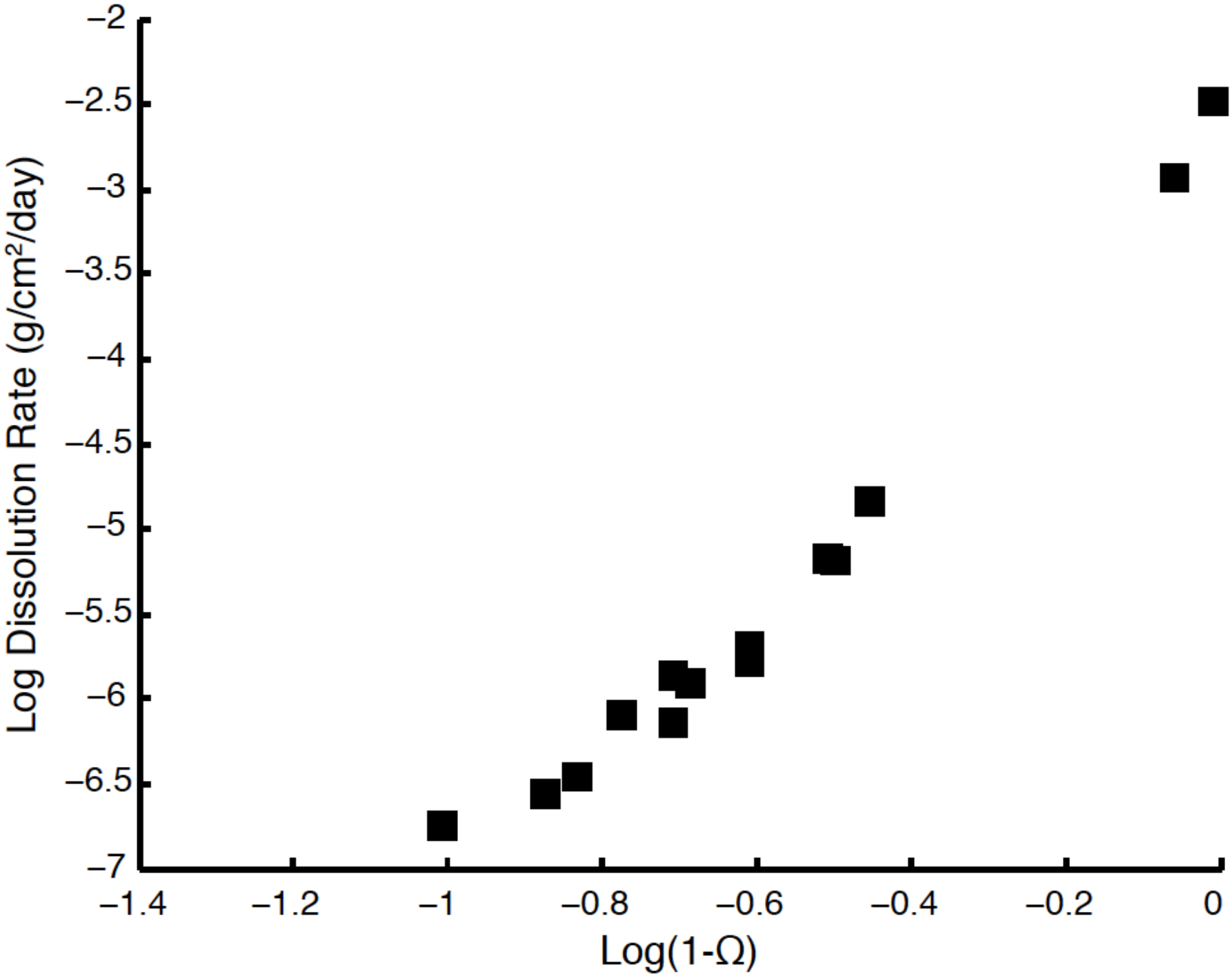
Average errors in Ω are ~0.01-0.02 units

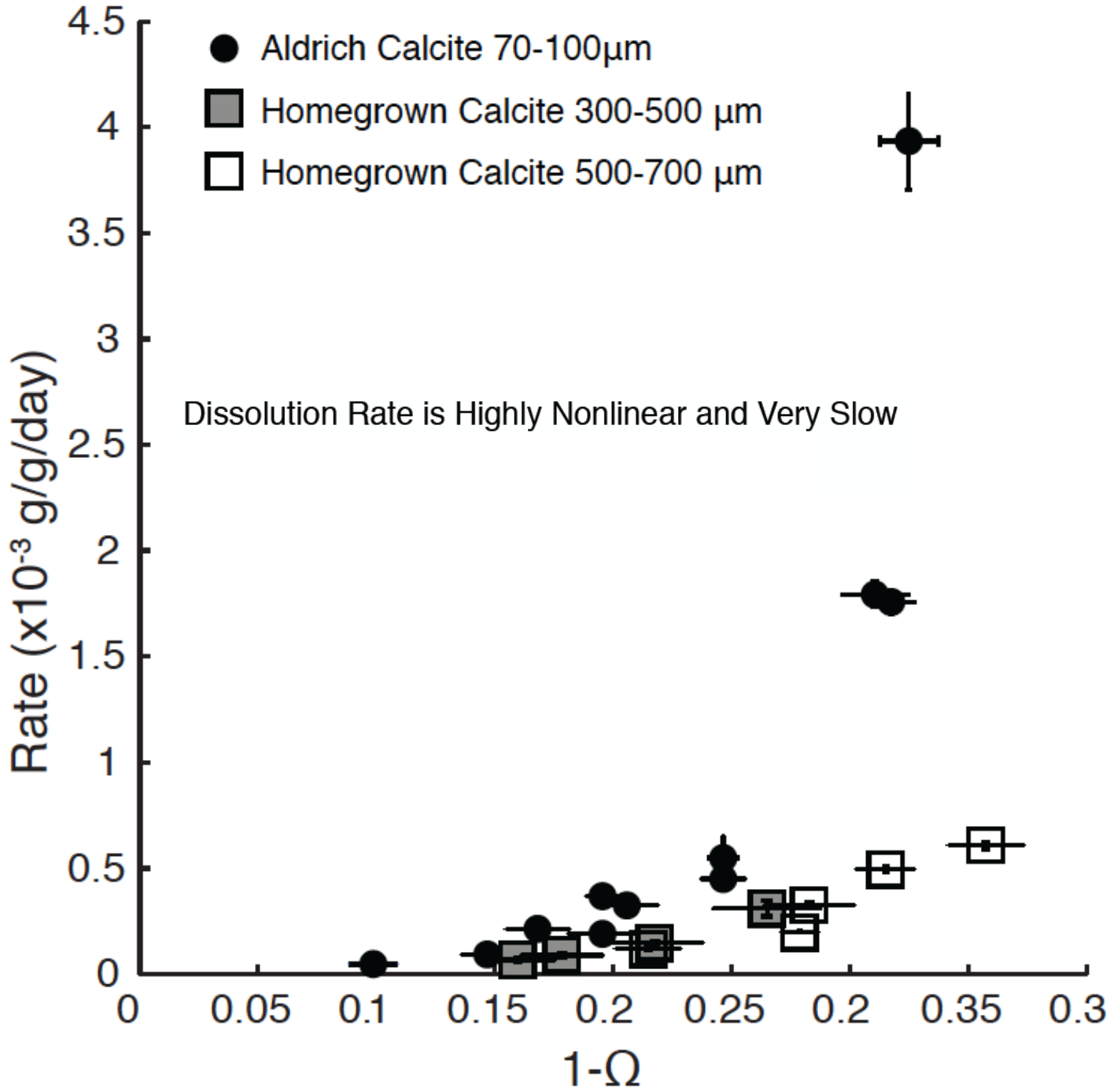
What is the correct formulation of dissolution as function of Omega???

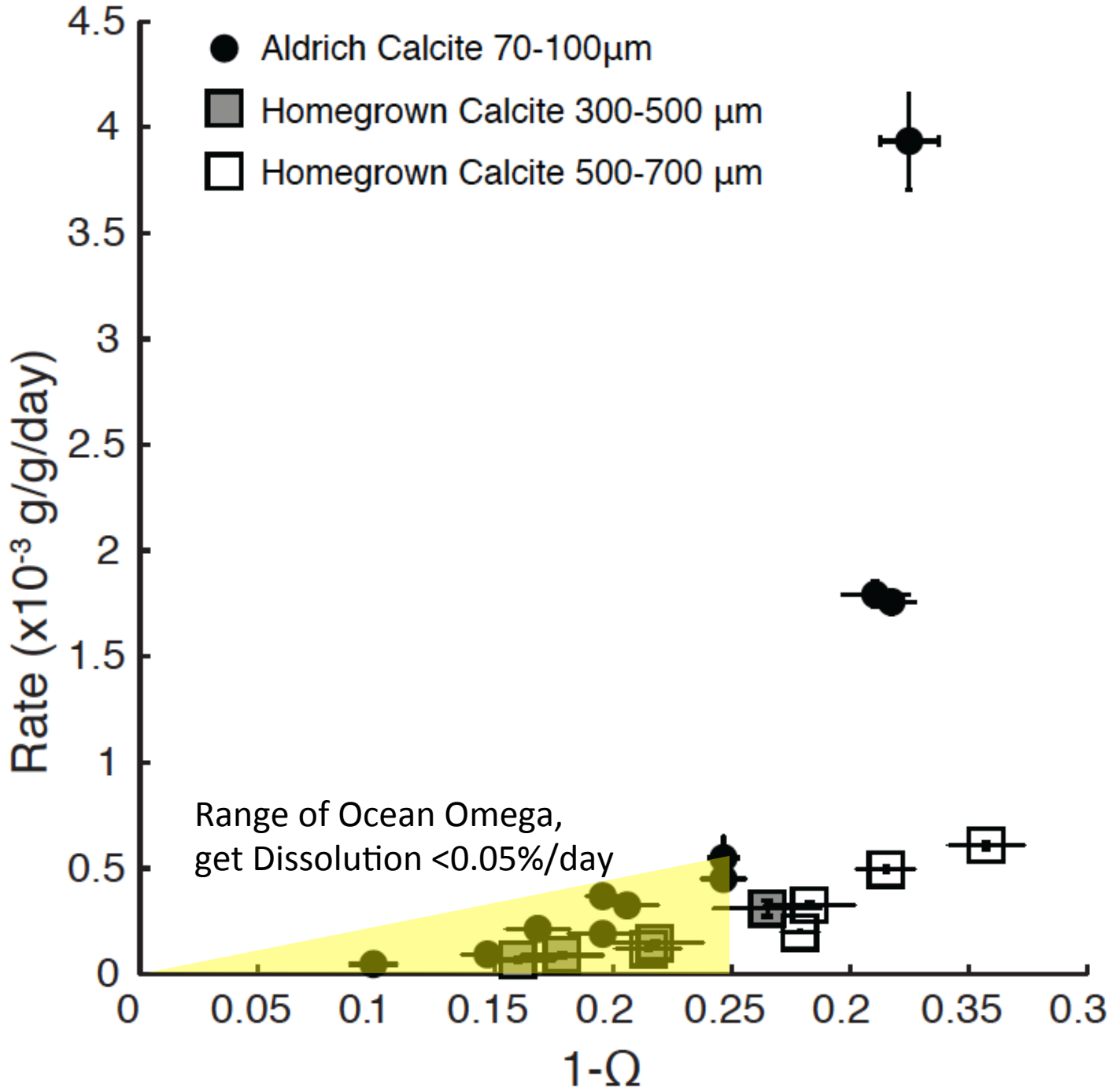



Aldrich Calcite 70-100µm
Homegrown Calcite 300-500 µm
Homegrown Calcite 500-700 µm
Size of grain α surface area
Rate (x10-3 g/g/day)
1-Ω
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
0
0.05
0.1
0.15
0.2
0.25
0.2
0.35
0.3

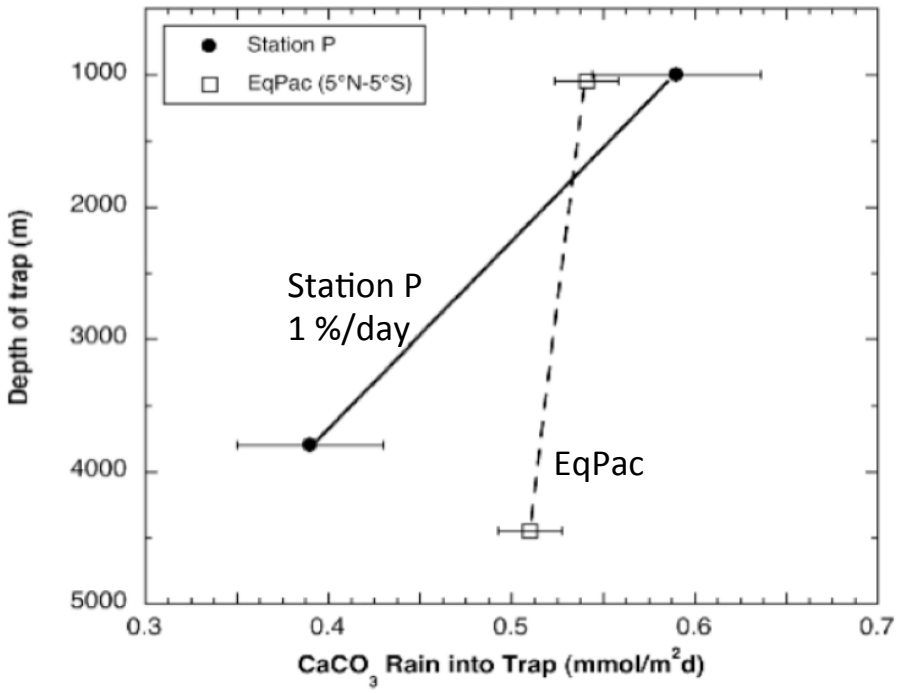

Aldrich Calcite 70-100µm
Homegrown Calcite 300-500 µm
Homegrown Calcite 500-700 µm
Normalized to surface area
Dissolution Rate is Highly Nonlinear
Rate (g cm-2 day-1) = 3.5·10-6(1-Ω)3.9
Rate (x10-5 g/cm2/day)
1-Ω
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
0.05
0.1
0.15
0.25
0.3
0.35

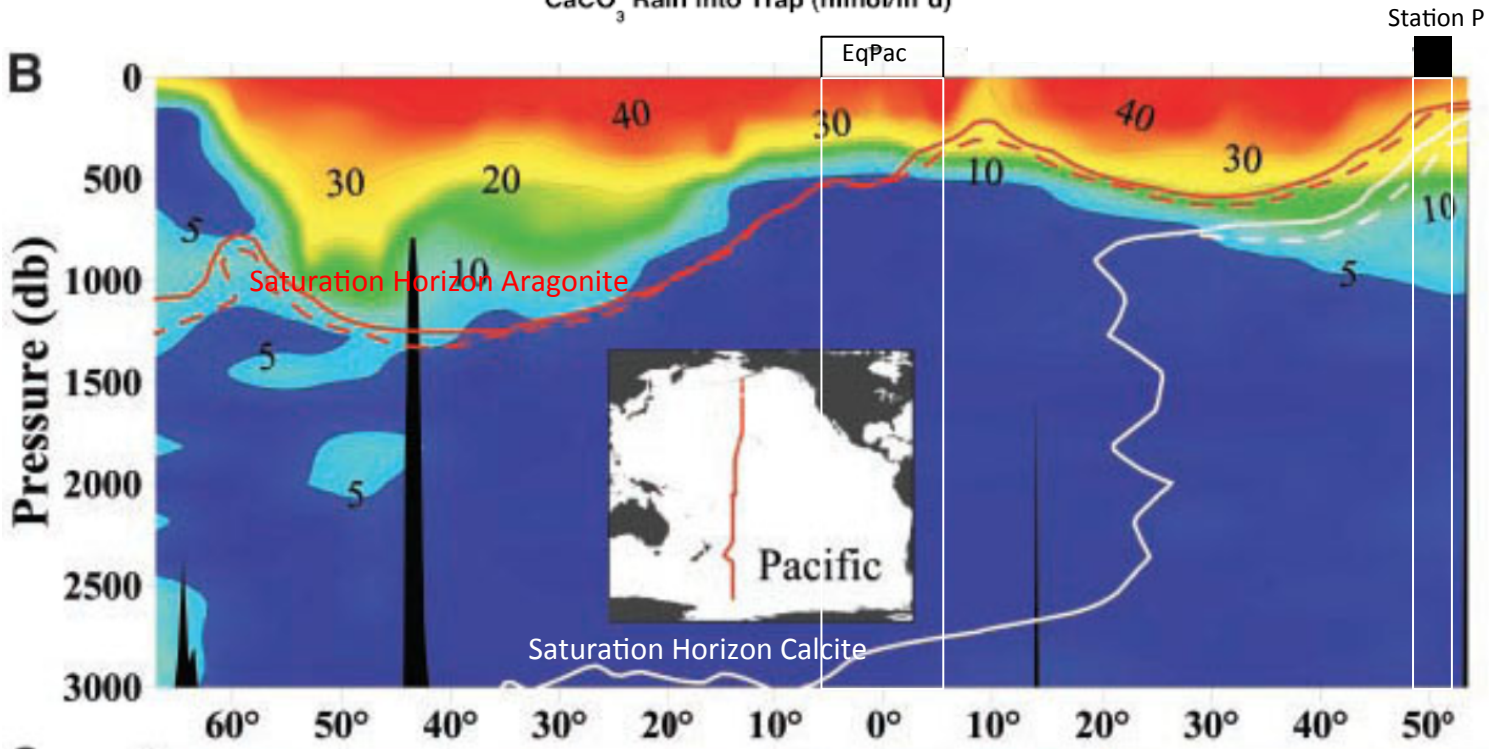

−2
−2.5
−3
−3.5
−4
−4.5
−5
−5.5
−6
−6.5
−7
Log Dissolution Rate (g/cm²/day)
−1.4
−1.2
−1
−0.8
−0.6
−0.4
−0.2
0
Log(1-Ω)


Aldrich Calcite 70-100µm
Homegrown Calcite 300-500 µm
Homegrown Calcite 500-700 µm
Dissolution Rate is Highly Nonlinear and Very Slow
Rate (x10-3 g/g/day)
1-Ω
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
0
0.05
0.1
0.15
0.2
0.25
0.2
0.35
0.3

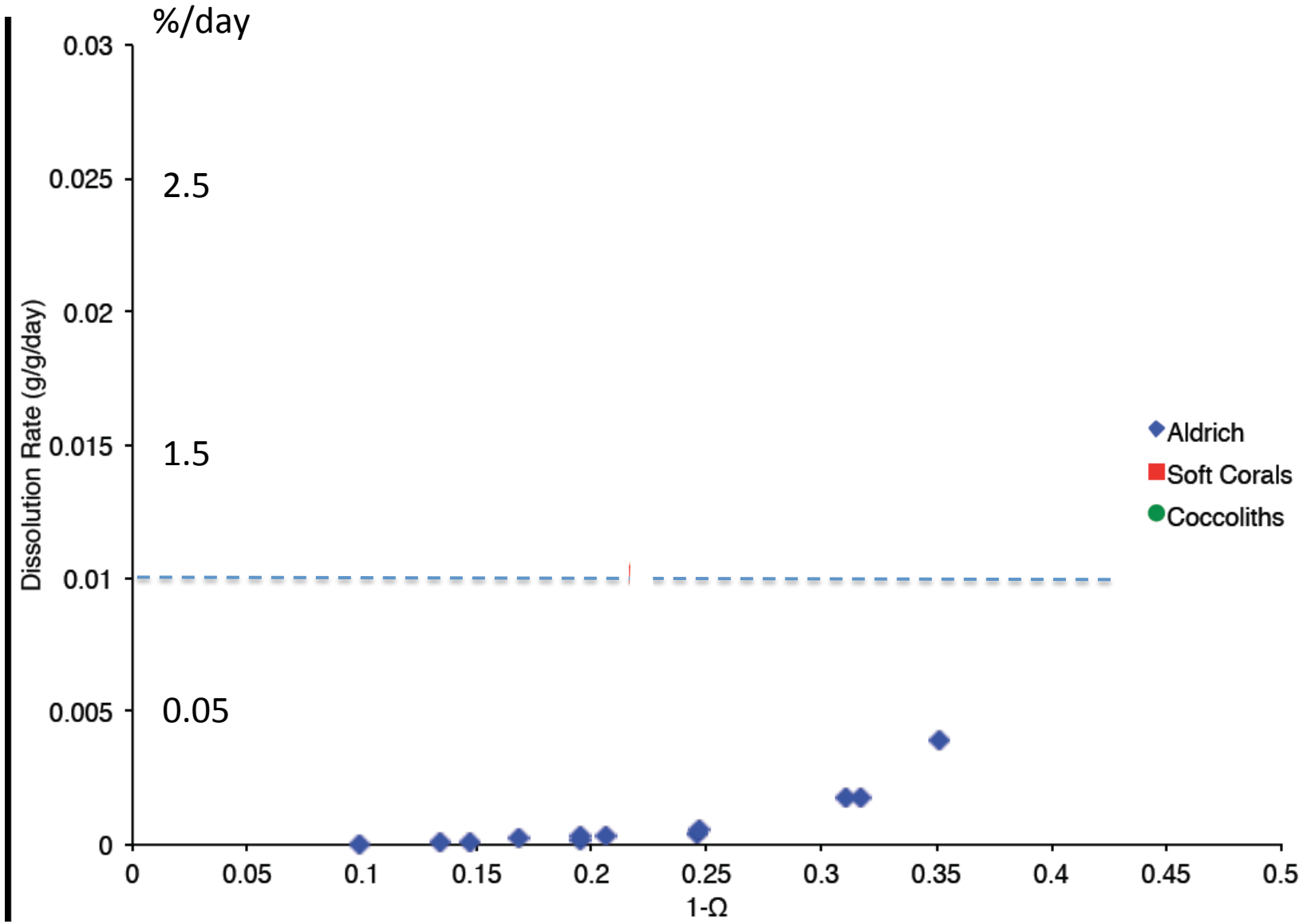

Aldrich Calcite 70-100µm
Homegrown Calcite 300-500 µm
Homegrown Calcite 500-700 µm
Range of Ocean Omega,
get Dissolution <0.05%/day
Rate (x10-3 g/g/day)
1-Ω
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
0
0.05
0.1
0.15
0.2
0.25
0.2
0.35
0.3

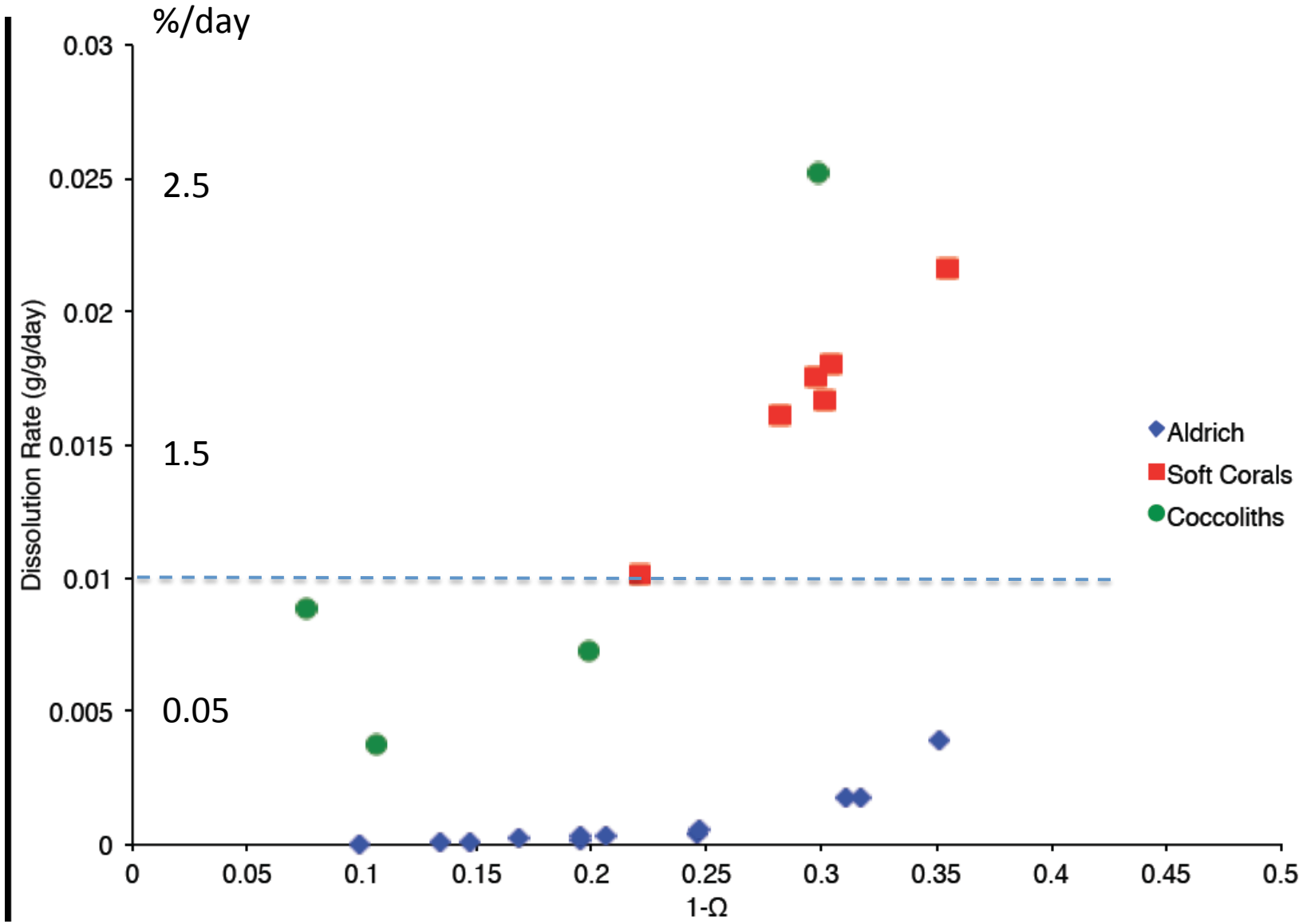
Field Data

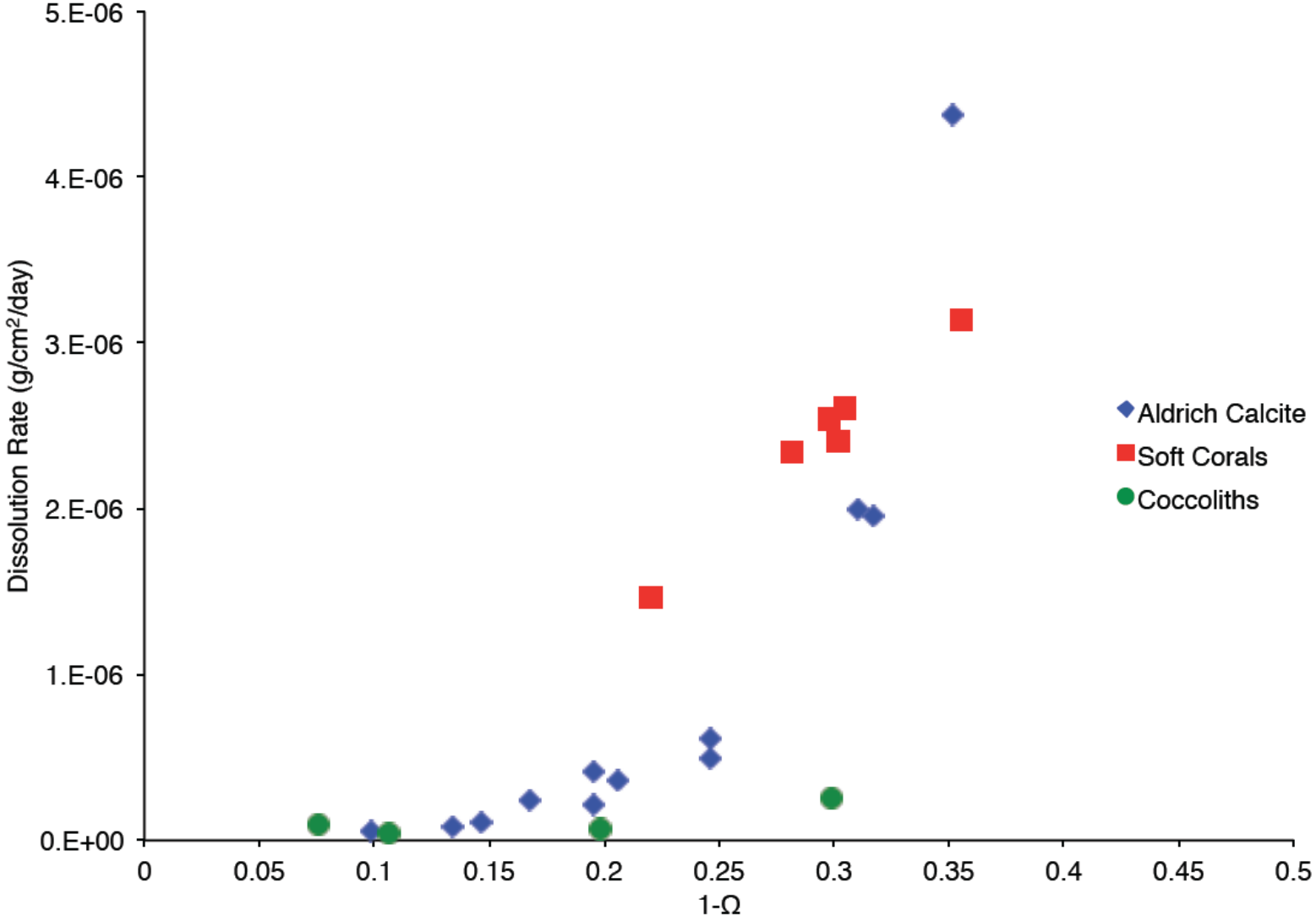




Feely et al.


%/day
0.03
0.025
0.02
0.015
0.01
0.005
0
2.5
1.5
0.05
Dissolution Rate (g/g/day)
0
0.05
0.1
0.15
0.2
0.25
0.3
0.35
0.4
0.45
0.5
1-Ω
Aldrich
Soft Corals
Coccoliths

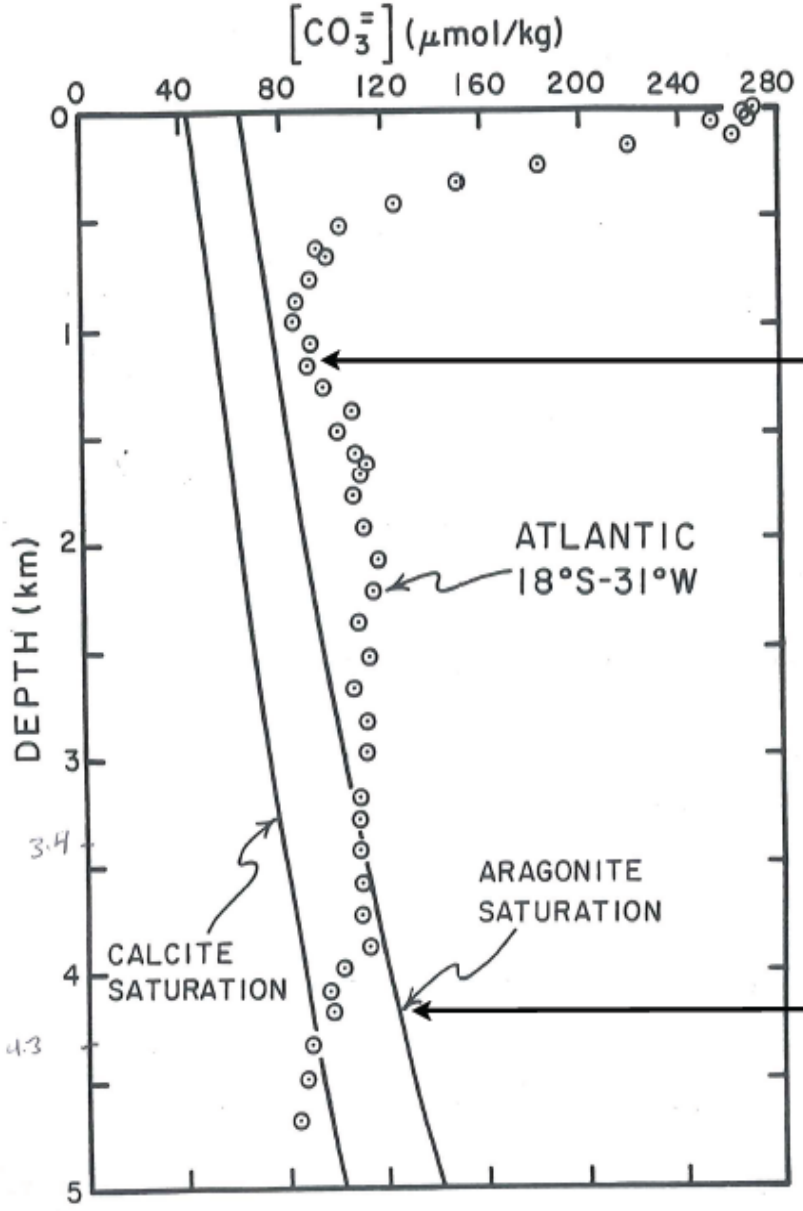

%/day
0.03
0.025
0.02
0.015
0.01
0.005
0
2.5
1.5
0.05
Dissolution Rate (g/g/day)
0
0.05
0.1
0.15
0.2
0.25
0.3
0.35
0.4
0.45
0.5
1-Ω
Aldrich
Soft Corals
Coccoliths


5.E-06
4.E-06
3.E-06
2.E-06
1.E-06
0.E+00
Dissolution Rate (g/cm²/day)
0
0.05
0.1
0.15
0.2
0.25
0.3
0.35
0.4
0.45
0.5
1-Ω
Aldrich Calcite
Soft Corals
Coccoliths

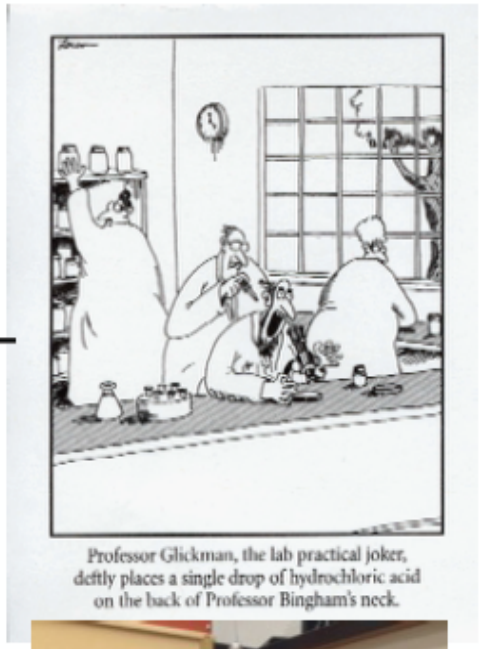
What other Relationships between Lab and Field that are critical to understanding carbonate dissolution??

-phosphate inhibition
-organic coatings

What role does pressure play in dissolution?



Broecker and Peng, 1982



Professor Glickman, the lab practical joker, deftly places a single drop of hydrochloric acid on the back of Professor Bingham's neck.

$$\Omega = \frac{[Ca^{2+}][CO_3^{2-}]}{K'_{sp}}$$

$$\Omega = \frac{[Ca^{2+}][CO_3^{2-}]}{K'_{sp}}$$

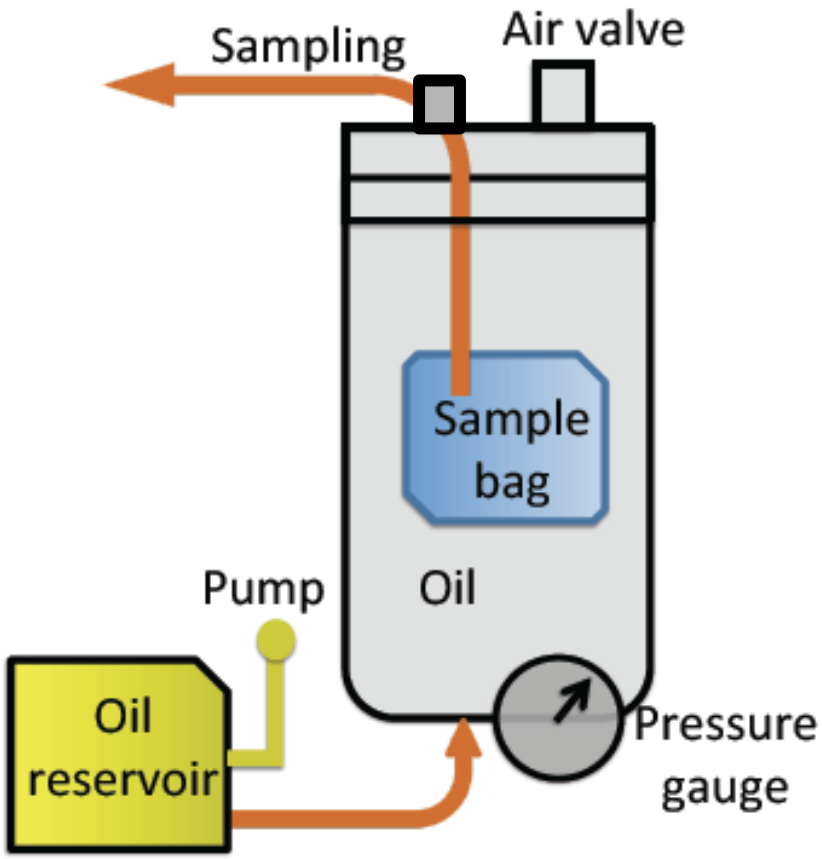


Fig.1 *Pressure chamber diagram*

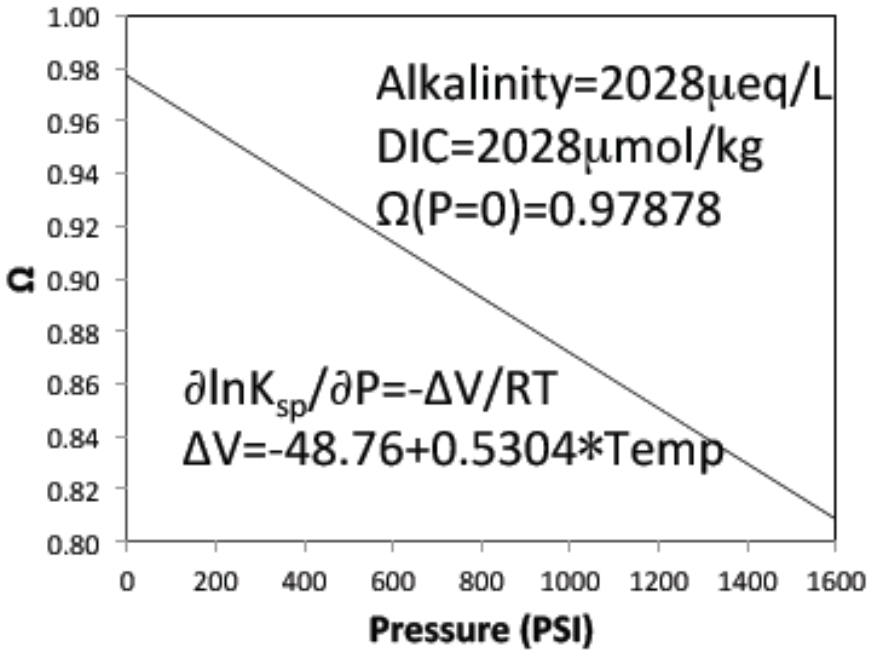


Fig.2 *Ω-pressure correlation (calculated by CO2SYS*

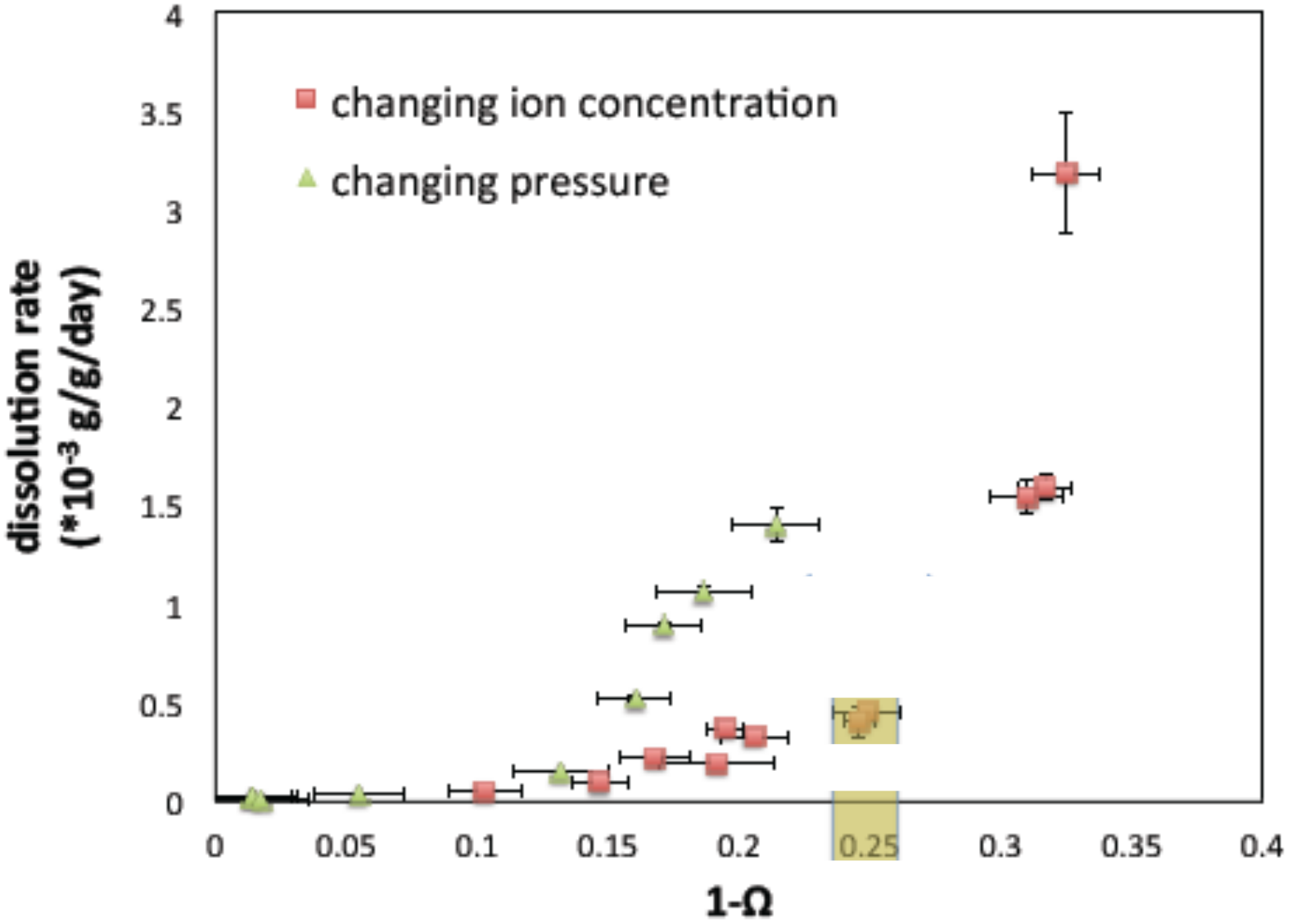


***Fig.4** Dissolution rate vs. undersaturation*

Variations in K_{sp}-pressure correlation expressions (empirical equations):

- $\partial \ln K_{sp}/\partial P = -\Delta V/RT$ (Millero and Berner, 1972; Duedall,1972)
- $\mathrm{Log}(K'^{P}_{sp}/K'^{1}_{sp}) = \Delta V(P-1)/2.303RT$ (Edmond and Gieskes, 1970)
- $RT\ln(K'^{P}_{sp}/K'^{1}_{sp}) = -\Delta V(P-1)+1/2\Delta K(P-1)^2$ (Ingle, 1975)
- $\mathrm{Ln}(K^{p}/K^{o}) = -(\Delta VP+0.5\Delta KP^2)/RT$ (Millero, 1979)

Table 2 *Apparent partial molal volume change for calcite dissolution*

Substance	T (°C)	ΔV (cm^3)	Author
Calcite	25	-34.4	Ingle (1975)
Calcite	25	-35.5	Ingle (1975)
Calcite	2	-42.3	Ingle (1975)
Calcite	2	-47.7	Ingle (1975)
Iceland spar	25	-35.5	Ingle (1975)
Oolites	2	-31.8	Ingle (1975)
Oolites	2	-33.1	Hawley and Pytkowicz (1969)
Oolites	22	-27.8	Hawley and Pytkowicz (1969)
Foraminifera	22	-30.7	Pytkowicz and Fowler (1967)
Calcite	25	-39.4	Millero and Berner (1969)
Calcite	20	-43.4	Duedall (1972)

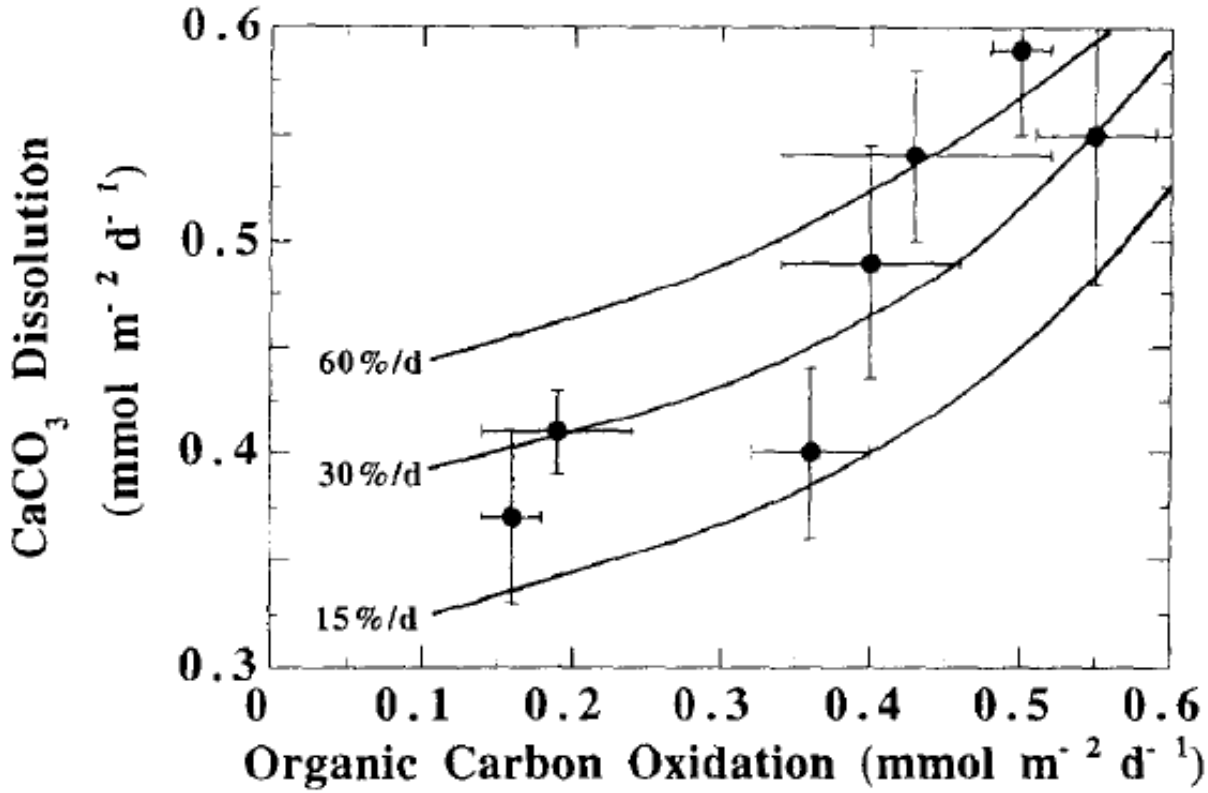
A revised ΔV from -37.6cm^3 to -41.1cm^3 would make the dissolution formulation equation agree.

-Pressure could contribute to enhanced dissolution in field

-Surface Area
-Different types of $CaCO_3$, mole fraction Mg

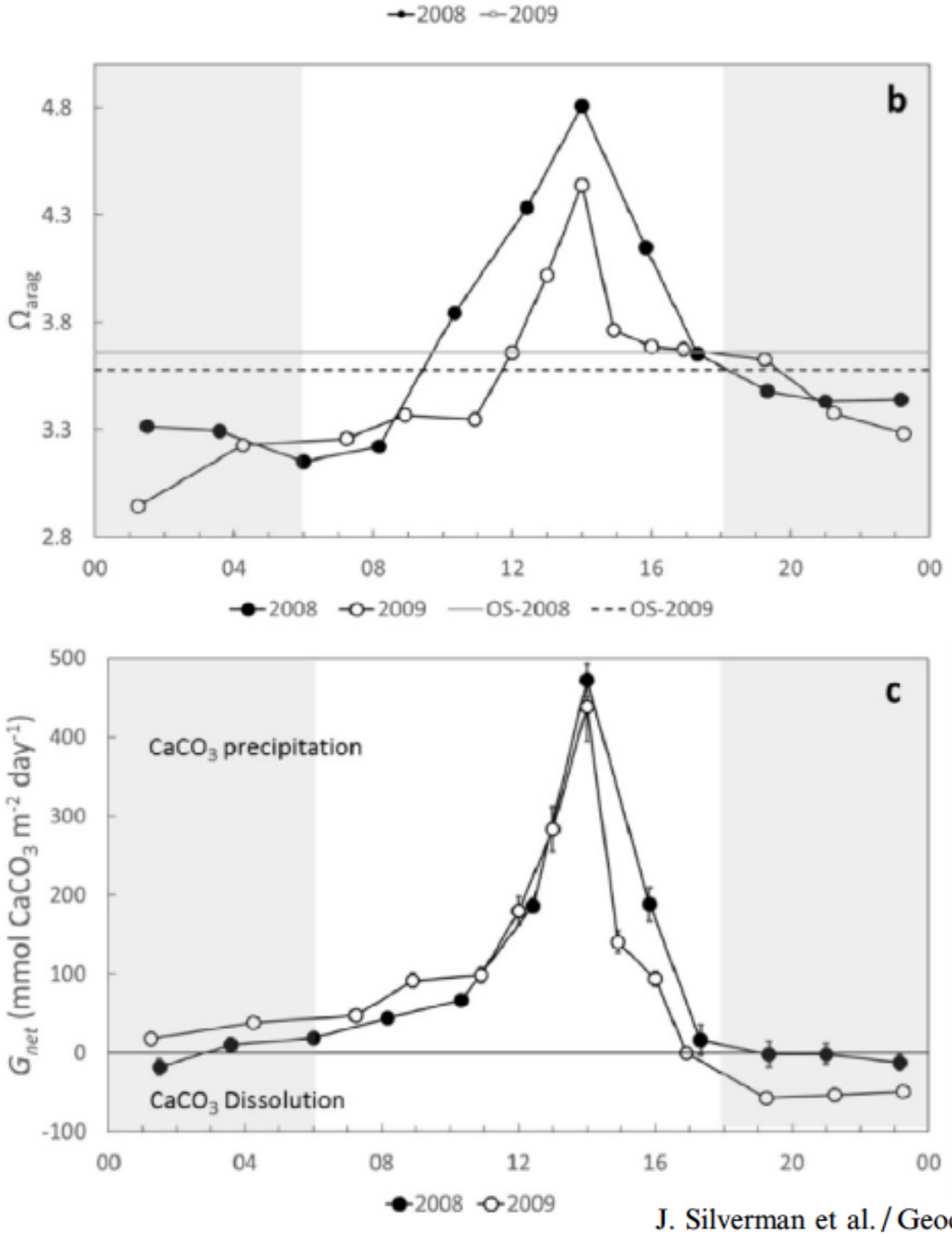
Take Home: no simple function will describe carbonate dissolution as function of omega

What else can field dissolution rates be attributed to?



Equatorial Pacific, sea floor, all sites same Omega ~ 0.8

Carbonate dissolution 'driven' by C_{org} oxidation



24 hours on a reef in Australia

Dissolution occurs at Omega >3

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Our Future Directions:

Field measurements of dissolution rate (novel Niskin apparatus)

Dissolution rate of more biogenics

Pressure effect

One of the big challenges we are facing is how to bridge our current understanding of $CaCO_3$ dissolution based on controlled laboratory experiments to natural systems. This will require a holistic approach combining laboratory, field and numerical modelling studies.

Bradley D. Eyre[1]*, Andreas J. Andersson[2] and Tyler Cyronak[1]

nature climate change
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Thanks