

The National Academies of
SCIENCES • ENGINEERING • MEDICINE

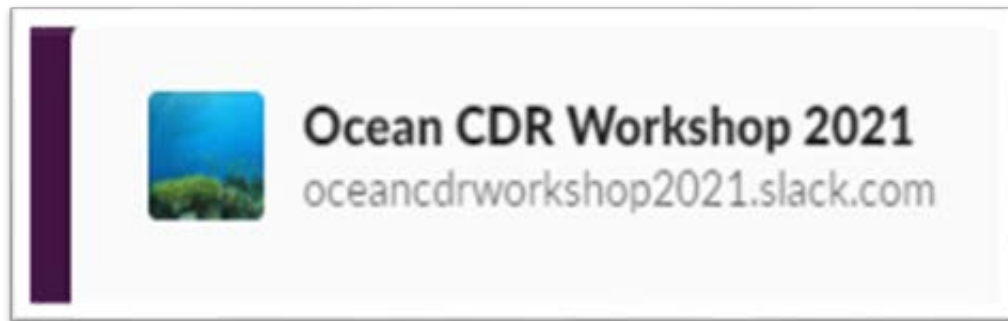
A RESEARCH STRATEGY FOR OCEAN CARBON DIOXIDE REMOVAL AND SEQUESTRATION

We will start at 1pm EST

**Workshop Series Part 2: Technological and
Natural Approaches to OAE and CO₂ removal
January 27, 2021**

Virtual Logistics

- Committee members and panelists, please use the raise hand function or submit questions through the chat
- If you are watching the webinar, submit questions or comment through Q&A
- Slack Channel is open for communications and resource sharing.



- Presentations and recording will be posted on our project website: <https://www.nationalacademies.org/our-work/a-research-strategy-for-ocean-carbon-dioxide-removal-and-sequestration>

Background

- NASEM Consensus Study
- Sponsored by the ClimateWorks Foundation
- Exploring 6 Ocean-based CDR Strategies:
 - Identify the most urgent unanswered scientific and technical questions needed to: assess the benefits, risks, and sustainable scale potential CDR approaches
 - Define the essential components of a research and development program and specific steps that would be required to answer these questions;
 - Estimate the costs and potential environmental impacts of such a research and development program to the extent possible in the timeframe of the study.
 - Recommend ways to implement such a research and development program that could be used by public or private organizations.

Workshop Series

- **January 19, 2021** - Part 1: Setting the Stage
- **January 27, 2021** - Part 2: Technological and Natural Approaches to Ocean Alkalinity Enhancement and CO₂ removal
- **February 2, 2021** - Part 3: Ecosystem Recovery and Seaweed Cultivation
- **February 25, 2021** - Part 4: Nutrient Fertilization and Artificial Upwelling and Downwelling

The Committee

Scott Doney (Chair)

Ken Buesseler

Jane Flegal

Debora Iglesias-Rodriguez

Kate Moran

Andreas Oschlies

Phil Renforth

Joe Roman

Gaurav Sant

David Siegel

Romany Webb

Angelicque White

University of Virginia

Woods Hole Oceanographic Institution

William and Flora Hewlett Foundation

UC Santa Barbara

Ocean Networks Canada

GEOMAR

Heriot-Watt University

University of Vermont

UC Los Angeles

UC Santa Barbara

Columbia Law School

University of Hawai'i

Agenda

1:00pm	Welcome
1:05pm	Technological Approaches to Increase Alkalinity and Remove CO ₂
2:45pm	BREAK
3:00pm	Natural Approaches to Alkalinity Enhancement
4:45pm	Validation & Monitoring and Environmental Risk
5:30pm	Adjourn

Opportunities and challenges to ocean alkalinity enhancement and to electrochemical CDR approaches

Ken Caldeira*
Senior Scientist (Emeritus)
Carnegie Institution for Science

*Temporarily serving as Senior Advisor (Climate Science) to Gates Ventures, LLC, soon to transfer to a related non-profit entity.

XXXI. *On the Influence of Carbonic Acid in the Air upon the Temperature of the Ground.* By Prof. SVANTE ARRHENIUS *.

The carbon dioxide problem can be thought of as an acid-base problem.

Acids and bases react to form salts.

THE
LONDON, EDINBURGH, AND DUBLIN
PHILOSOPHICAL MAGAZINE
AND
JOURNAL OF SCIENCE.

[FIFTH SERIES.]

APRIL 1896.

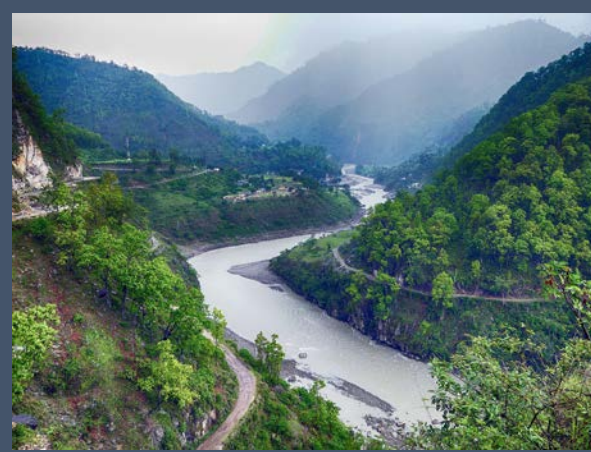
XXXI. *On the Influence of Carbonic Acid in the Air upon the Temperature of the Ground.* By Prof. SVANTE ARRHENIUS *.

I. *Introduction : Observations of Langley on Atmospheric Absorption.*

A GREAT deal has been written on the influence of the absorption of the atmosphere upon the climate.



CO_2 is a weak acid and reacts with bases to form carbonate salts, such as limestone, characterized as CaCO_3 .



By A. J. T. Johnsingh, WWF-India and NCF - Own work, CC BY-SA 4.0, <https://commons.wikimedia.org/w/index.php?curid=52917072>

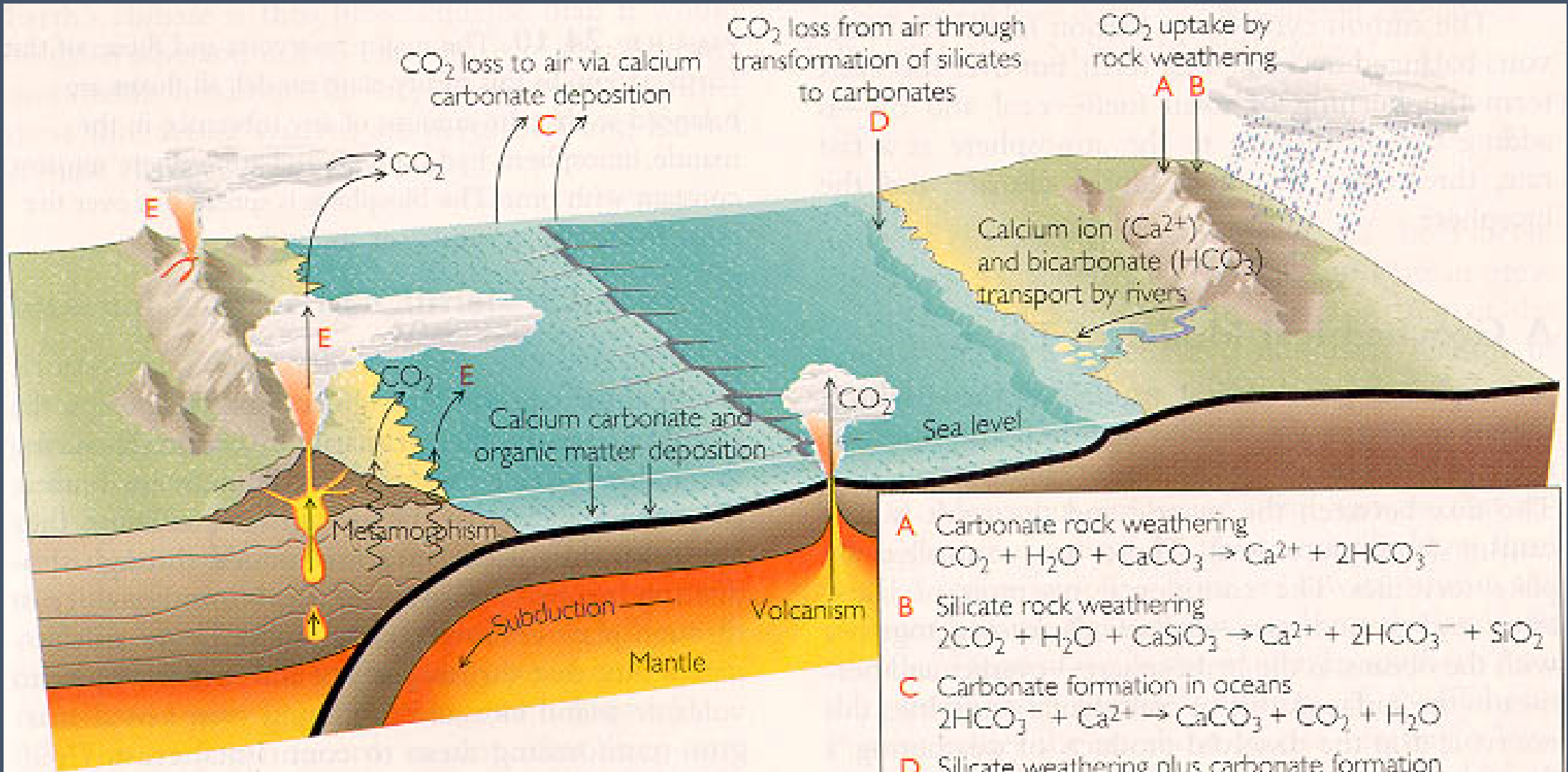
An alkali is a base that dissolves in water.

In water, bases (alkalinity) neutralize carbon acidity, and tend to draw in additional CO_2 from the atmosphere.

With added alkalinity, most of the negative charge on the anion from the carbonic acid ion is balanced by the cation from the base instead of a hydrogen ion.



Photo: Ken Caldeira



Sources, Reservoirs, and Fluxes of Carbon in the Earth System. Letters indicate the prevalent chemical reactions.

- A** Carbonate rock weathering

$$\text{CO}_2 + \text{H}_2\text{O} + \text{CaCO}_3 \rightarrow \text{Ca}^{2+} + 2\text{HCO}_3^-$$
- B** Silicate rock weathering

$$2\text{CO}_2 + \text{H}_2\text{O} + \text{CaSiO}_3 \rightarrow \text{Ca}^{2+} + 2\text{HCO}_3^- + \text{SiO}_2$$
- C** Carbonate formation in oceans

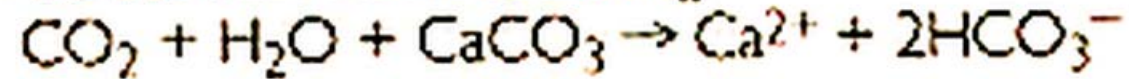
$$2\text{HCO}_3^- + \text{Ca}^{2+} \rightarrow \text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O}$$
- D** Silicate weathering plus carbonate formation (reactions B + C)

$$\text{CO}_2 + \text{CaSiO}_3 \rightarrow \text{CaCO}_3 + \text{SiO}_2$$
- E** Metamorphic/magmatic breakdown of carbonate

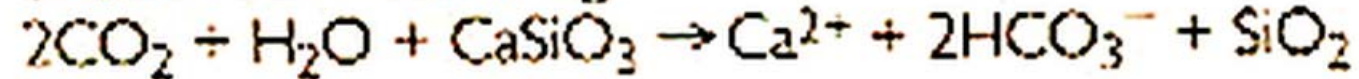
$$\text{CaCO}_3 + \text{SiO}_2 \rightarrow \text{CaSiO}_3 + \text{CO}_2$$

Schematic weathering and carbonate formation reactions

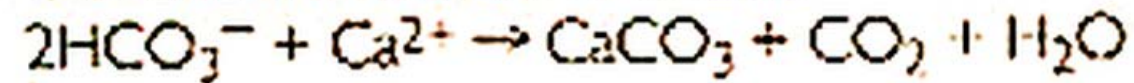
A Carbonate rock weathering



B Silicate rock weathering



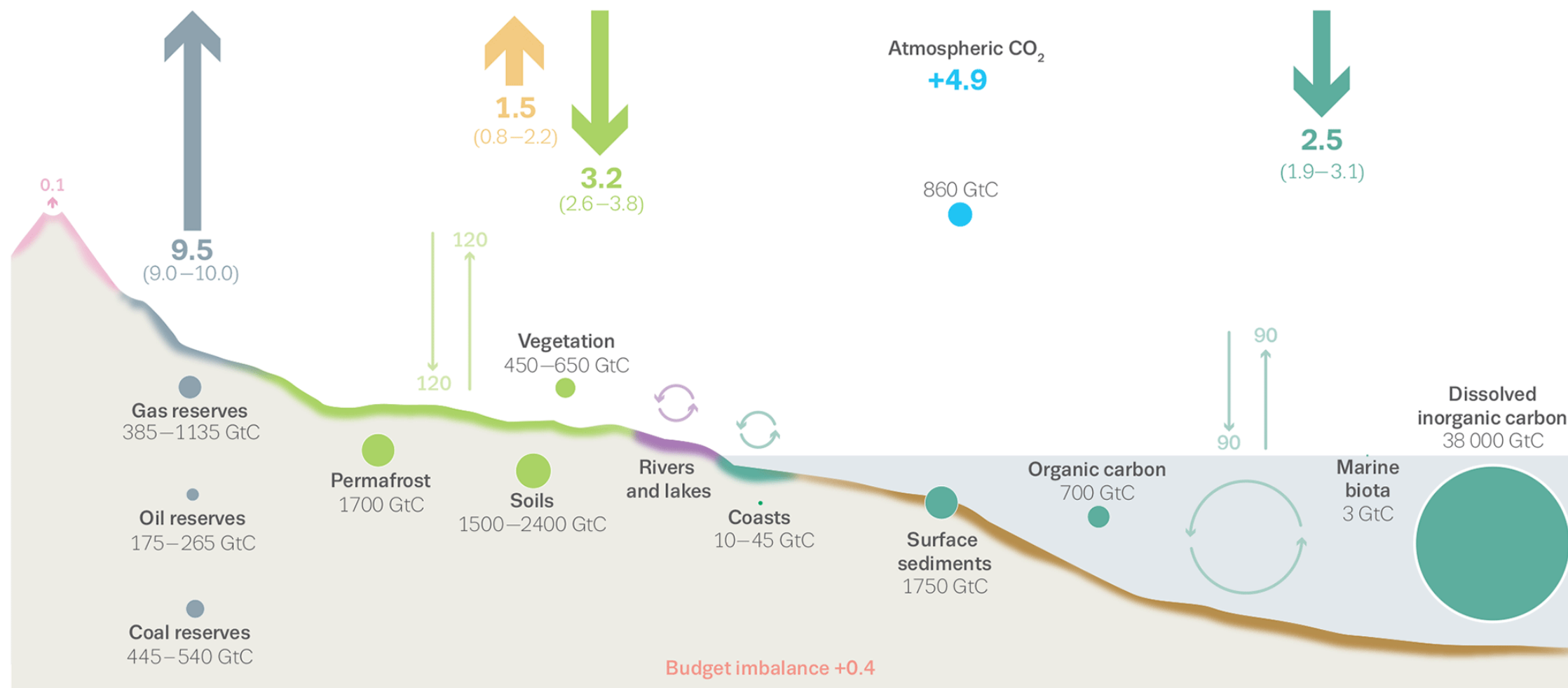
C Carbonate formation in oceans



Rock weathering adds alkalinity (cations) to the ocean.

Carbonate mineral formation removes alkalinity from the ocean.

The global carbon cycle



Anthropogenic fluxes 2009–2018 average GtC per year



Fossil CO₂ E_{FF}



Land use change E_{LUC}



Land uptake S_{LAND}



Ocean uptake S_{OCEAN}



Atmospheric increase G_{ATM}



Budget imbalance B_{IM}



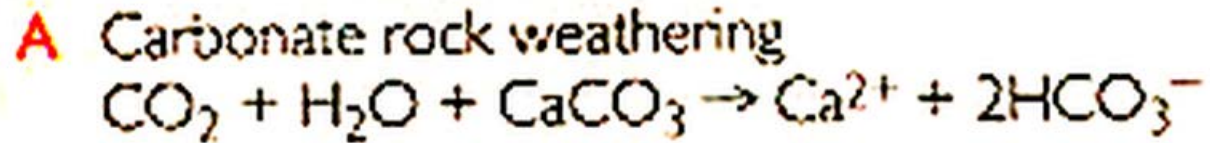
Carbon cycling GtC per year



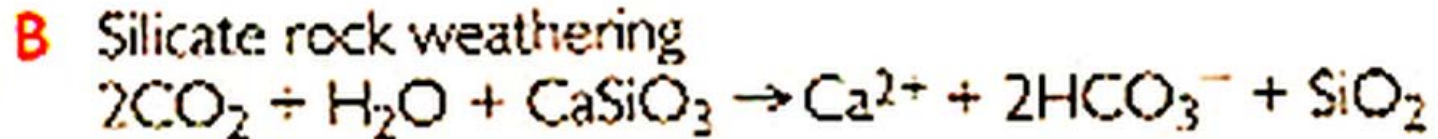
Stocks GtC

Fossil-fuel CO₂ emissions are approximately 10^{13} kgC yr⁻¹,
– about 3 kg C per person per day, inequitably distributed.

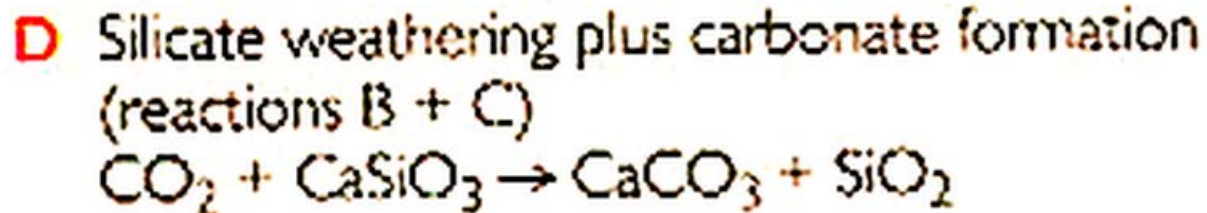
There are no big multipliers in chemistry.



3 kg C means 25 kg CaCO_3 per day, if it remains dissolved in the ocean.



3 kg C means 14.5 kg CaSiO_3 per day, it remains dissolved in the ocean.



3 kg C means 29 kg CaSiO_3 per day, if it reprecipitates as CaCO_3 .

Could enough base be added to the ocean to neutralize a meaningful amount of carbonic acid in a way that would have net overall benefit (cost, impacts, etc)?

Renforth and Henderson (2017)

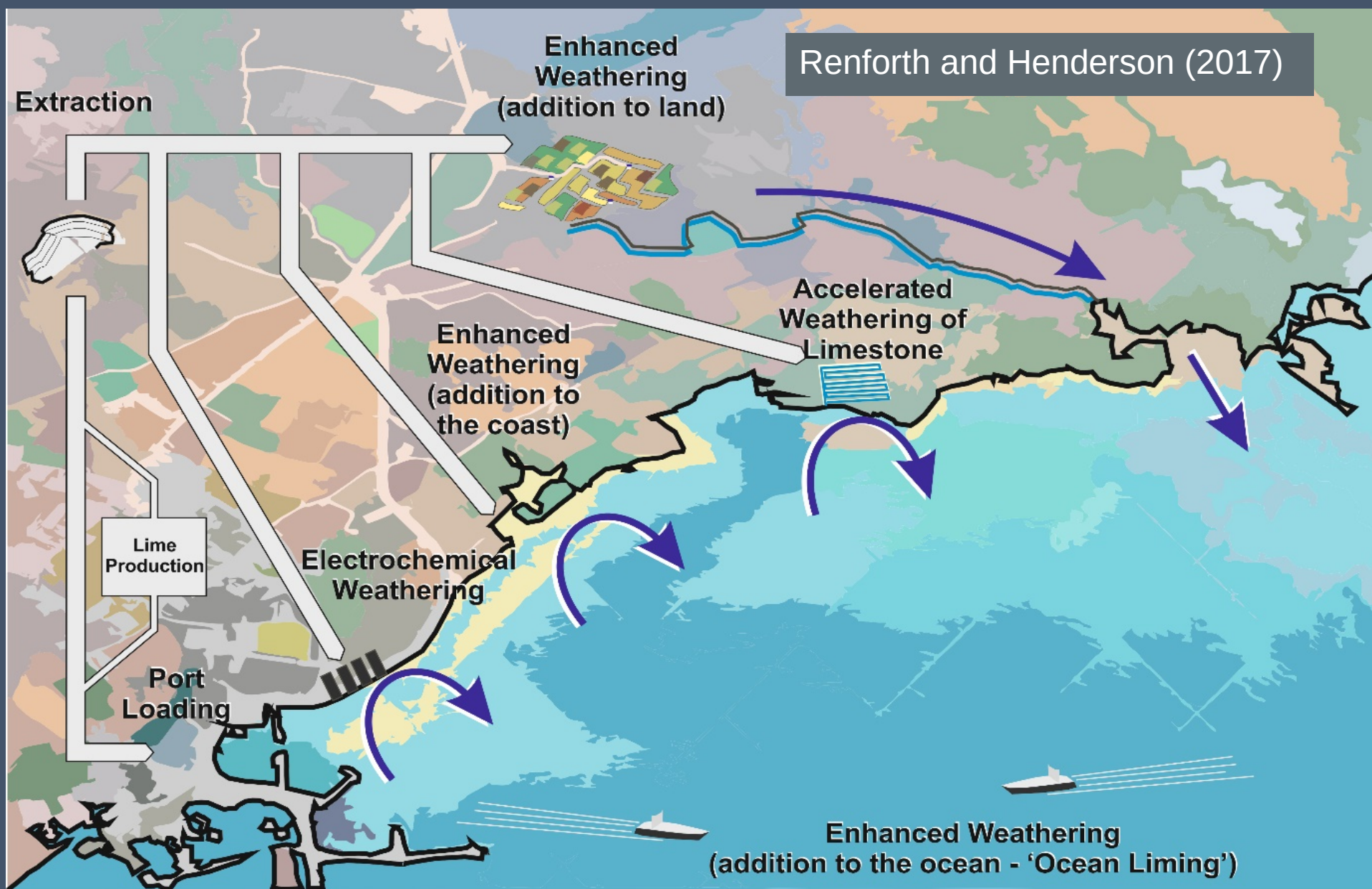


Table 3. Comparison of Electrical and Thermal Energy Requirements and Financial Costs of Ocean Alkalinity Carbon Storage Technologies^a

Technology	GJ tCO ₂ ^{-1b}		US\$ tCO ₂ ^{-1b}
	Electricity	Thermal	
Ocean liming (Oxy-fuel flash calciner: limestone)	1.3	4.8	126
Ocean liming (Endex CFC: limestone)	-0.1	5.5	100
Ocean liming (Oxy-fuel flash calciner dolomite)	0.7	3.2	95
Ocean liming (Endex CFC: dolomite)	-0.1	4.2	72
Ocean liming (Solar calciner: limestone)	0.4	0.6 ^c	159
Electrochemical weathering (Mg-Silicate)	5 ^d		86–154
Electrochemical weathering (CaCO ₃)	5 ^d		14–190
Electrochemical weathering (NaOH production)	3–18		–
Direct carbonate addition to upwelling regions	<0.1	3.6	–
Mineral carbonation/ocean liming	2.2	5.0	
Accelerated weathering of limestone			10–40
Enhanced weathering	0.1–8.4	0.8–4.2	20–600
Direct air capture	7.5–10		100–1000

Renforth and Henderson (2017) Reviews of Geophysics

At \$100/tCO₂ and 40 GtCO₂/yr, global abatement would cost about \$4 trillion/yr.
This is about 5% of global GDP.

A few closing observations (1)

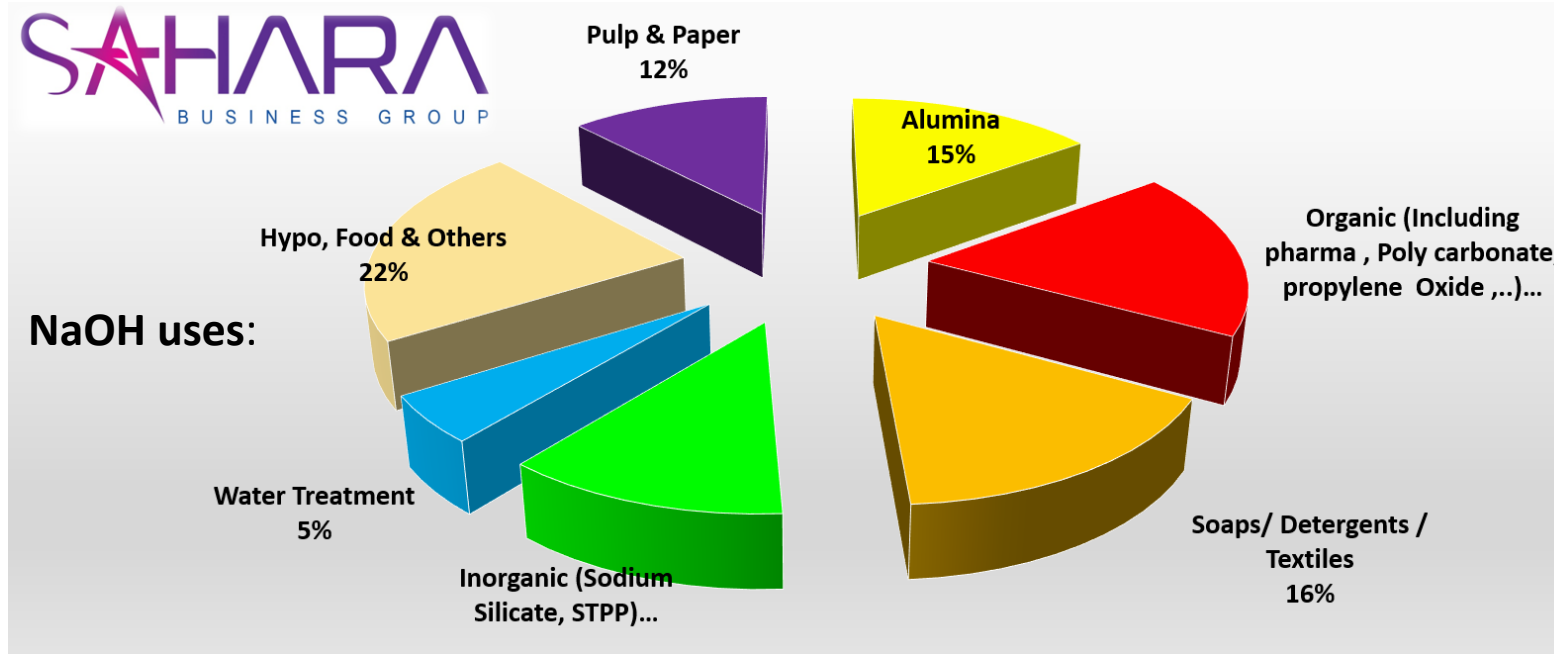
- Ocean alkalinity addition proposals face a variety of social challenges:
 - Whether justified or not, there is social resistance to using the oceans as a repository for our waste CO₂.
 - There is likely to be social resistance to large scale up of mining, although mining-related jobs could be welcome in some areas.
 - It can be challenging to motivate people to create a large capital intensive industry that does not confer commensurate direct local benefits.

A few closing observations (2)

- If we rule out the end members of:
 - All anthropogenic CO₂ should be neutralized by alkalinity addition, and
 - No anthropogenic CO₂ should ever be neutralized by alkalinity addition.
- We are left with the question of under what circumstances might each ocean alkalinity enhancement proposal be the best application of resources aimed at protecting our atmosphere or oceans?
 - What would we need to know to answer that question?

Electrolytic production of “alkalinity” (NaOH) is a mature technology

Global annual caustic soda production (chlor-alkali process) is 75 million tons (2015; projected 100 Mt by 2024). 100Mt/yr NaOH $\approx$ 100 Mt CDR/yr potential (assuming zero-emissions NaOH production).



<https://saharabizz.com/global-application-and-capacity-of-caustic-soda/>

But adding NaOH to the ocean has only been done once →

The Ken Caldeira team's clever NaOH + tracer addition to a coral reef demonstrated antacid effects and restoration of coral calcification, but CDR not measured(?) (Albright et al. 2016)

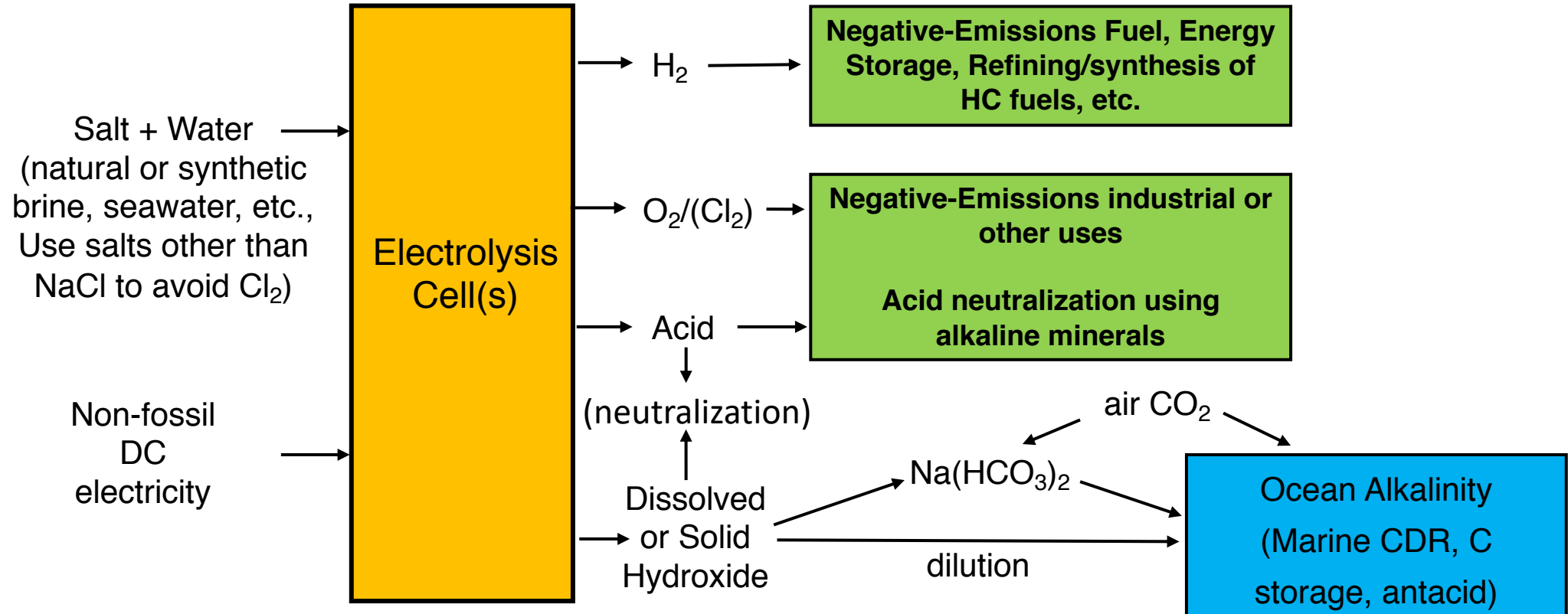


<https://www.nature.com/news/landmark-experiment-confirms-ocean-acidification-s-toll-on-great-barrier-reef-1.19410>

Electrolytic Schemes to Produce Ocean Alkalinity and Other Products and Services

INPUTS:

OUTPUTS/USES:



Theoretically as much as 40kg CO₂ removed/kg H₂ produced, assuming zero-emissions energy input, etc.

Preliminary Energy and \$\$ Cost

Example reactions: $3\text{H}_2\text{O} + \text{Na}_2\text{SO}_4 + V_{\text{dc}} \rightarrow 2\text{NaOH} + \text{H}_2\text{SO}_4 + \text{H}_2 + 0.5\text{O}_2$ $\Delta G = 540 \text{ kJ/mol H}_2$ (1)

$2\text{NaOH} + 1.9\text{CO}_2 \rightarrow 1.8\text{NaHCO}_{3(\text{aq})} + 0.1\text{Na}_2\text{CO}_{3(\text{aq})} + 0.1\text{H}_2\text{O (in SW)}$ (2)

Energy requirement

Assuming 50% energy efficiency: Gross Energy Required = $3.7\text{MWh}_e/\text{t NaOH} = 3.4\text{MWh}_e/\text{t CO}_2$ removed

HOWEVER, subtracting energy content of the H_2 produced, Net Energy Required = $2.7\text{MWh}_e/\text{t CO}_2$ removed

Previous estimates: $1\text{--}2\text{MWh}_e/\text{t CO}_2$ (House et al 2007); $1\text{--}1.3\text{MWh}_e/\text{t CO}_2$ (Rau et al. 2018)

Compared to: DAC = $0.6\text{MWh}_e/\text{t CO}_2 + 1.5\text{MWh}(\text{heat})/\text{t CO}_2 = 2.1\text{MWh}/\text{t CO}_2$. (Keith et al. 2018)

BECCS = $1\text{MWh}(\text{mostly heat using MEA capture; Bui et al. 2017})$

Economics Assuming: i) $3.4\text{MWh}_e/\text{t CO}_2$ removed ii) $\$0.02/\text{kWh}$ renewable electricity, iii) total $\$/\text{tCO}_2$ removed = $2 \times \$$ electricity/ t CO_2 , iv) $\$$ value of $\text{H}_2 = \$2/\text{kg}$, and v) $\$$ value of $\text{O}_2 = \$40/\text{t}$, then:

Gross cost = $\$136/\text{t CO}_2$ removed

Revenues = $\$45/\text{t CO}_2$ (for H_2) + $\$7/\text{t CO}_2$ (for O_2) = $-\$52/\text{t CO}_2$ removed

net cost = $\$84/\text{t CO}_2$ Likely range = $\$50\text{--}\$100/\text{t CO}_2$

Compare/contrast: DAC = $>\$100/\text{t CO}_2$ (Keith et al. 2018)

BECCS = $\$67\text{--}\$99/\text{t CO}_2$ (NASEM, 2019)

***So electrolytic alkalinity production is no energy bargain,
but value of co-products significantly reduces net CDR cost***

Electrolytic OAE:

Benefits/advantages

- 1) Fewer contaminants and faster CO₂ reactivity than OAE via alkaline minerals.
- 2) Negative-emissions: i) H₂ production (fuel, energy transport and storage), and ii) other products (O₂/Cl₂, acid). Compare/contrast BECCS.
- 2) Potentially high global capacity with marine siting flexibility, including offshore, esp if NaCl can be used.
- 4) Synergies with existing existing off-shore platforms (off-shore wind, OTEC, etc.) and with existing water discharges to the ocean e.g., wastewater, powerplant cooling water, etc.)

Disadvantages, Concerns, Issues

- 1) Energy intensive.
- 2) Requires C crediting in the range of \$50-\$100/t CO₂ to be cost-effective. Presently available credits = \$200-400/t CO₂ (Calif. and Germany).
- 3) Concentrated hydroxide will require rapid dilution/reaction to avoid seawater chemistry/biology impacts.
- 4) Difficulties in measuring/monitoring downstream chemical and biological impacts (and benefits), including verifying CDR.

R&D Needs

- 1) Design and test optimum electrochem designs and hydroxide release/dilution strategies at lab to pilot scales.
- 2) Determine optimum: sites, CDR potential, markets and economics.
- 3) Explore safe use of cheap, globally abundant NaCl as electrolyte.
- 4) Develop cost-effective methods of measuring/monitoring CDR and environmental benefits/impacts.
- 5) R&D Investment: Need \$30M/yr x 10 yrs → 1st full-scale plant?

References (with annotation):

Albright, R. et al. 2016. Reversal of ocean acidification enhances net coral reef calcification. *Nature* 531 (7594): 362–65. <https://doi.org/10.1038/nature17155>. (First test of NaOH addition to the ocean (coral reef), in the context of OA reduction.)

Bui, M. et al. 2017. Bio-Energy with CCS (BECCS) performance evaluation: Efficiency enhancement and emissions reduction. *Applied Energy* 195: 289–302. (BECCS energy analysis)

House, K.Z., C.H. House, D.P. Schrag, and M.J. Aziz. 2007. Electrochemical Acceleration of Chemical Weathering as an Energetically Feasible Approach to Mitigating Anthropogenic Climate Change. *Environmental Science & Technology* 41 (24): 8464–70. <https://doi.org/10.1021/es0701816>. (First electrogeochemical CDR concept. Adaptation of the chlor-alkali process for ocean alkalinity production and enhanced silicate weathering.)

Keith, D.W. et al. 2018. A process for capturing CO₂ from the atmosphere. *Joule* 2 (8): 1573–1594. [doi:10.1016/j.joule.2018.05.006](https://doi.org/10.1016/j.joule.2018.05.006). (detailed DAC example)

National Academies of Sciences, Engineering, and Medicine. 2019. *Negative Emissions Technologies and Reliable Sequestration: A Research Agenda*. Washington, DC: The National Academies Press. [doi:10.17226/25259](https://doi.org/10.17226/25259) (Review of BECCS and DAC.)

Rau, G. H. 2008. Electrochemical Splitting of Calcium Carbonate to Increase Solution Alkalinity: Implications for Mitigation of Carbon Dioxide and Ocean Acidity. *Environmental Science & Technology* 42 (23): 8935–40. <https://doi.org/10.1021/es800366q>. (First lab-scale use of CaCO₃ mineral in an electrogeochemical CDR scheme.)

Rau, G. H., S.A. Carroll, W.L. Bourcier, M.J. Singleton, M.M. Smith, and R.D. Aines. 2013. Direct electrolytic dissolution of silicate minerals for air CO₂ mitigation and carbon-negative H₂ production. *Proceedings of the National Academy of Sciences* 110 (25): 10095–100. <https://doi.org/10.1073/pnas.1222358110>. (First lab-scale use of silicate minerals within an electrochemical cell to demonstrate CDR potential)

Rau, G.H., H. D. Willauer, and Z.J. Ren. 2018. The global potential for converting renewable electricity to negative-CO₂-emissions hydrogen. *Nature Climate Change* 8 (7): 621–25. <https://doi.org/10.1038/s41558-018-0203-0>. (Evaluated global potential for electrogeochemical CDR.)



OCEAN CAPTURE

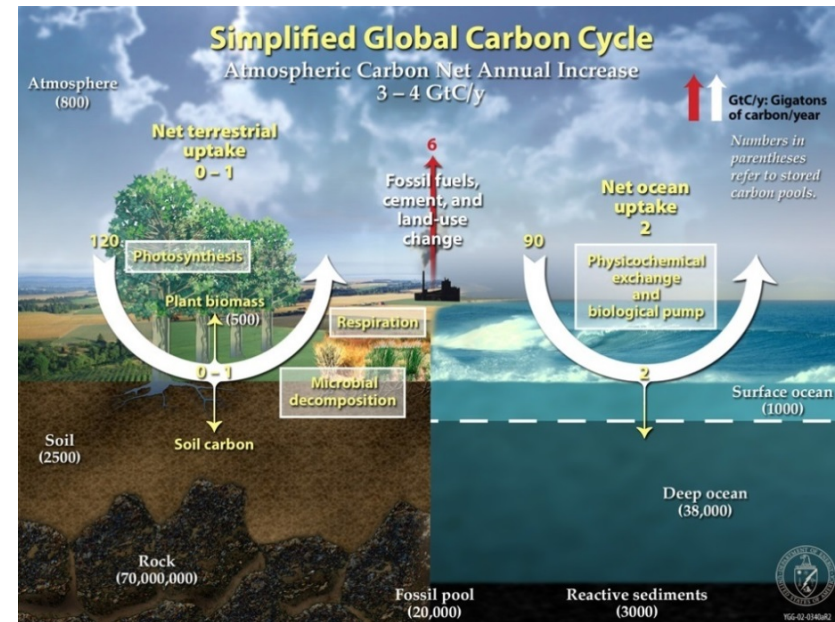
NASEM Ocean CDR Workshop: OAE and CO₂
removal January 27, 2021

Materials Science & Technology Division
U.S. Naval Research Laboratory, Washington DC

January 2021

Why capture CO₂ from Seawater?

- Renewable supply of CO₂ and H₂ feedstocks in Navy marine and littoral environments ~72% of the globe.
- CO₂ is 140 times more concentrated in seawater than air on a (w/v) basis (100 mg/L seawater vs 0.77 mg/L air).
- CO₂ from seawater is 1/3 (100 mg/L) the concentration of CO₂ found in stack gas from coal fire power plants (296 mg/L).
- Additional electrolysis equipment for production of H₂ is required if CO₂ is capture from air.



Genomics: GTL Roadmap, U.S. Department of Energy Office of Science, August 2005

NRL Work in Carbon Capture



US 2005/0232833A1

(19) **United States**

(12) **Patent Application Publication** (10) Pub. No.: US 2005/0232833 A1
Hardy et al. (43) Pub. Date: Oct. 20, 2005

(54) **PROCESS FOR PRODUCING SYNTHETIC
LIQUID HYDROCARBON FUELS**

Publication Classification

(76) Inventors: Dennis R. Hardy, Alexandria, VA
(US); Timothy Coffey, McLean, VA
(US)

(51) Int. Cl.⁷ B01J 8/04; C07C 27/06
(52) U.S. Cl. 422/188; 518/726

Correspondence Address:
NAVAL RESEARCH LABORATORY
ASSOCIATE COUNSEL (PATENTS)
CODE 1008.2
4555 OVERLOOK AVENUE, S.W.
WASHINGTON, DC 20375-5320 (US)

(57) **ABSTRACT**

(21) Appl. No.: 11/108,149

(22) Filed: Apr. 12, 2005

Related U.S. Application Data

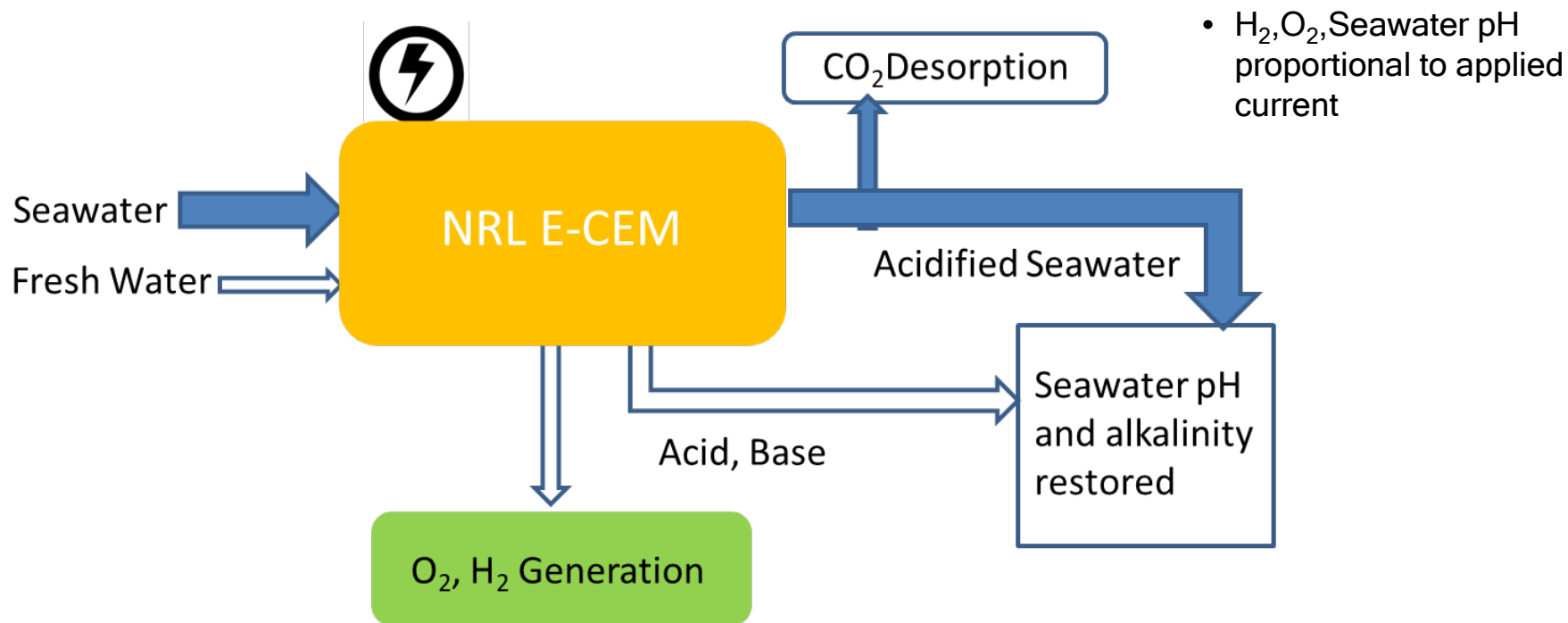
(60) Provisional application No. 60/562,410, filed on Apr.
15, 2004.

A process for producing synthetic hydrocarbons that reacts carbon dioxide, obtained from seawater of air, and hydrogen obtained from water, with a catalyst in a chemical process such as reverse water gas shift combined with Fischer Tropsch synthesis. The hydrogen is produced by nuclear reactor electricity, nuclear waste heat conversion, ocean thermal energy conversion, or any other source that is fossil fuel-free, such as wind or wave energy. The process can be either land based or sea based.

- NRL has been working in this space since 2000 with Dr. Dennis R. Hardy and Dr. Timothy Coffey as the lead scientist
- NRL's object is to make fuel on demand for the Navy
- I started work in this field in 2006

- Capturing large quantities of carbon dioxide and hydrogen quickly and efficiently.
- Achieving high catalytic conversion efficiencies and selectivities of carbon dioxide plus hydrogen to designer fuel.
- Keeping both the extraction module and the fuel production plant footprints to a reasonable size and weight.

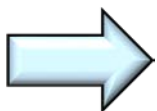
NRL Carbon Capture



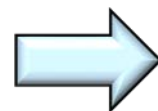
1. PN US 7,420,004, B2; Hardy, D. R. and Coffey, T. "Process and System for Producing Synthetic Liquid Hydrocarbon Fuels."
2. PN US 8,313,557; H. D. Willauer, D. R. Hardy, M. K. Lewis, E. C. Ndubizu, F. W. Williams; "Recovery of [CO₂]_T From Seawater/Aqueous Bicarbonate Systems Using a Multi-Layer Gas Permeable Membrane." November 20, 2012.
3. PN US 8,663,365; H. D. Willauer, J. Barile, LCDR F. DiMascio, D. R. Hardy, F. W. Williams; "Method for the continuous of carbon dioxide from acidified seawater," March 4, 2014.
4. PN US 9,303,323; LT Felice DiMascio, Dr Dennis R. Hardy, Dr Heather D. Willauer, CAPT M Kathleen Lewis and Dr Frederick W. Williams; "An Electrochemical Method To Acidify Seawater and Recover CO₂ Simultaneously with Hydrogen Gas from Alkaline Water Sources Such as Seawater," April 5, 2016.
5. PN US 9,719,178; CDR Felice DiMascio, Heather D. Willauer, Dennis R. Hardy, Frederick W. Williams, and M. Kathleen Lewis; "Electrochemical Module Configuration for the Continuous Acidification of Alkaline Water Sources such as Seawater and Recovery of CO₂ with Continuous Hydrogen Production," August 1, 2017.

NRL Technologies Developed In Parallel

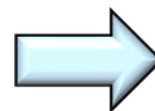
Electrolytic cation exchange module (E-CEM), 110 mL seawater (TRL 3)



Scaling and integrating E-CEM to process 0.5 gpm seawater



E-CEM 4, 0.5 gpm seawater



Scaling E-CEM, 25 gpm (TRL 7)



CO₂ and H₂ Capture Process

2009 to 2019

Laboratory scale production of hydrocarbons (TRL 3)



Flight using fuel from CO₂ and H₂



Commercial scale testing of NRL catalyst systems (TRL 6)



NRL Fuel Synthesis Skid (TRL 7)



<https://www.youtube.com/watch?v=lavz7AnKI8I>

Fuel Synthesis Process

2011 to 2019

Specific Challenges in OC

Research Objectives

Environmental effects on the ocean and marine life

- Large scale studies supported by modeling to understand reaction kinetics and ocean re-equilibration utilizing different electrochemical methods.
- Reaction kinetics and equilibration will lead to understanding of how to engineer the process for the best environmental outcome.

DoD Obstacles

Cost, Power, Size

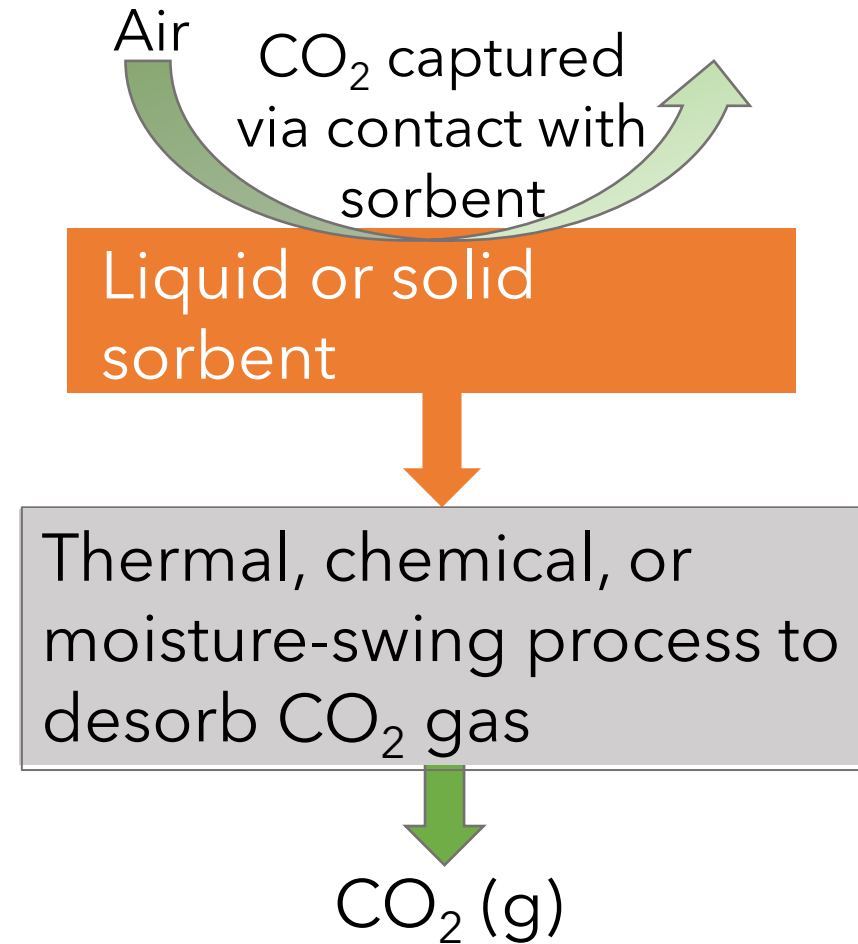
- JP5 \$2.40/gallon and F76 \$2.39/gallon
- Fully Burden cost \$5.66 and \$5.65
- Size and cost of power source



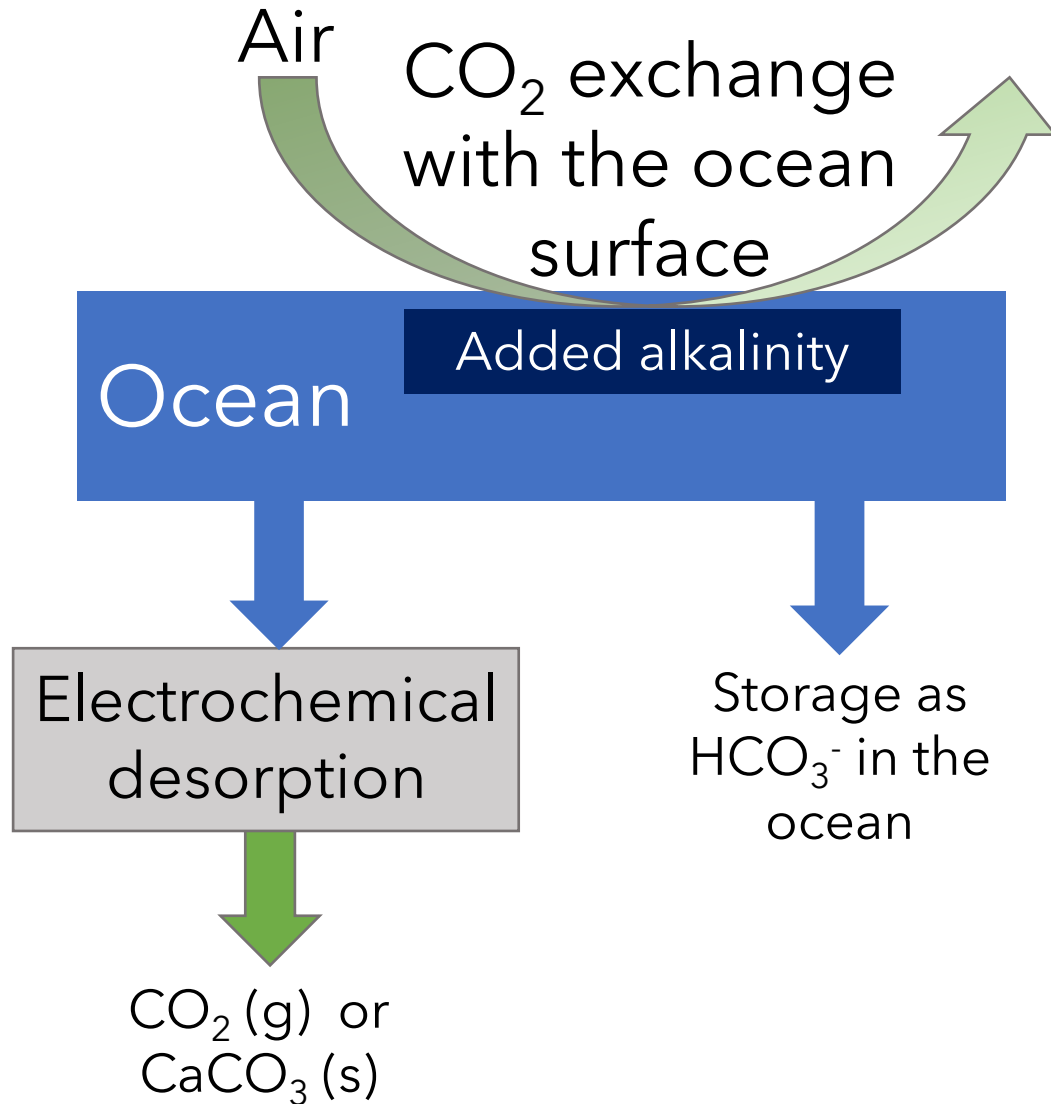
Electrochemical Ocean CDR: Current Status and Future Opportunities

Matthew Eisaman (Stony Brook University)

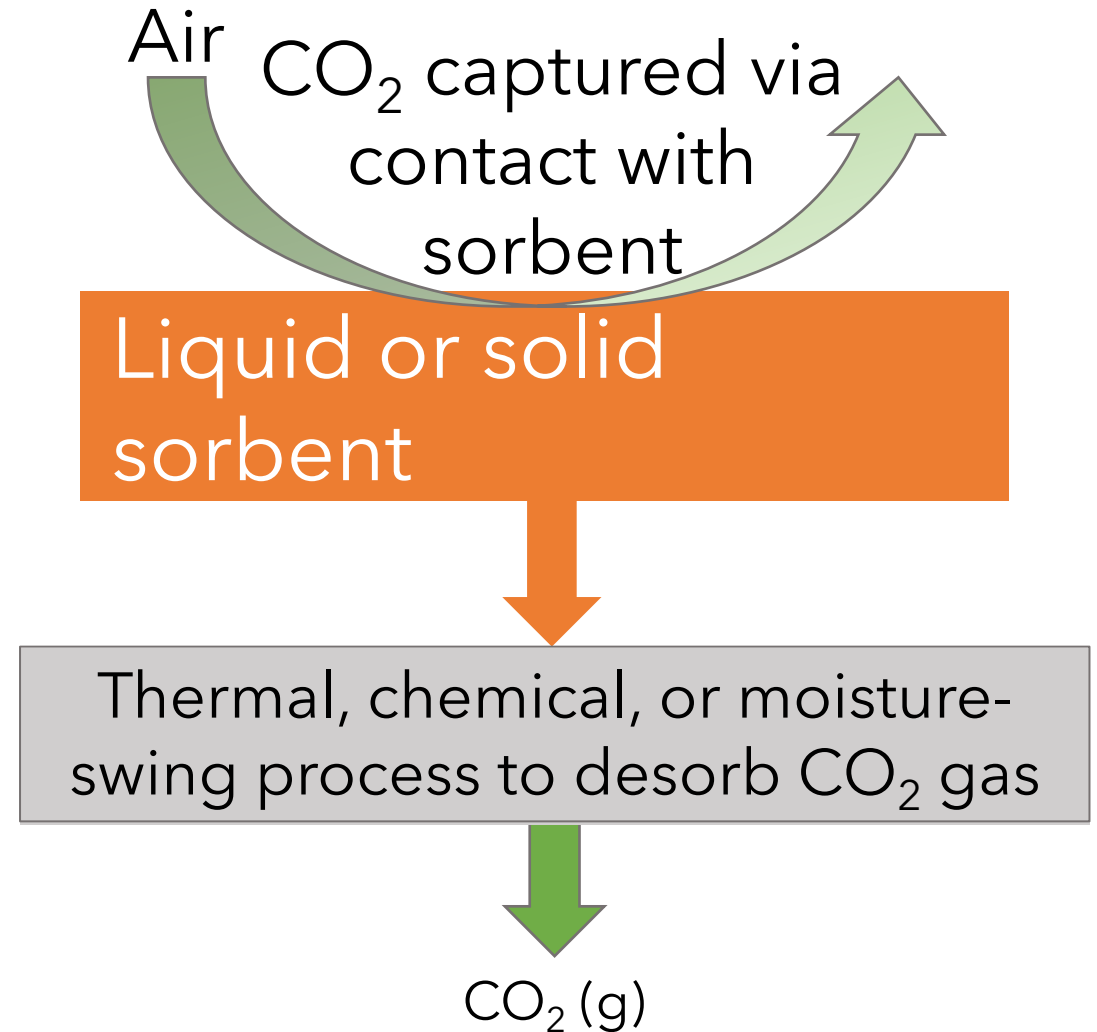
Direct Air Capture (DAC)



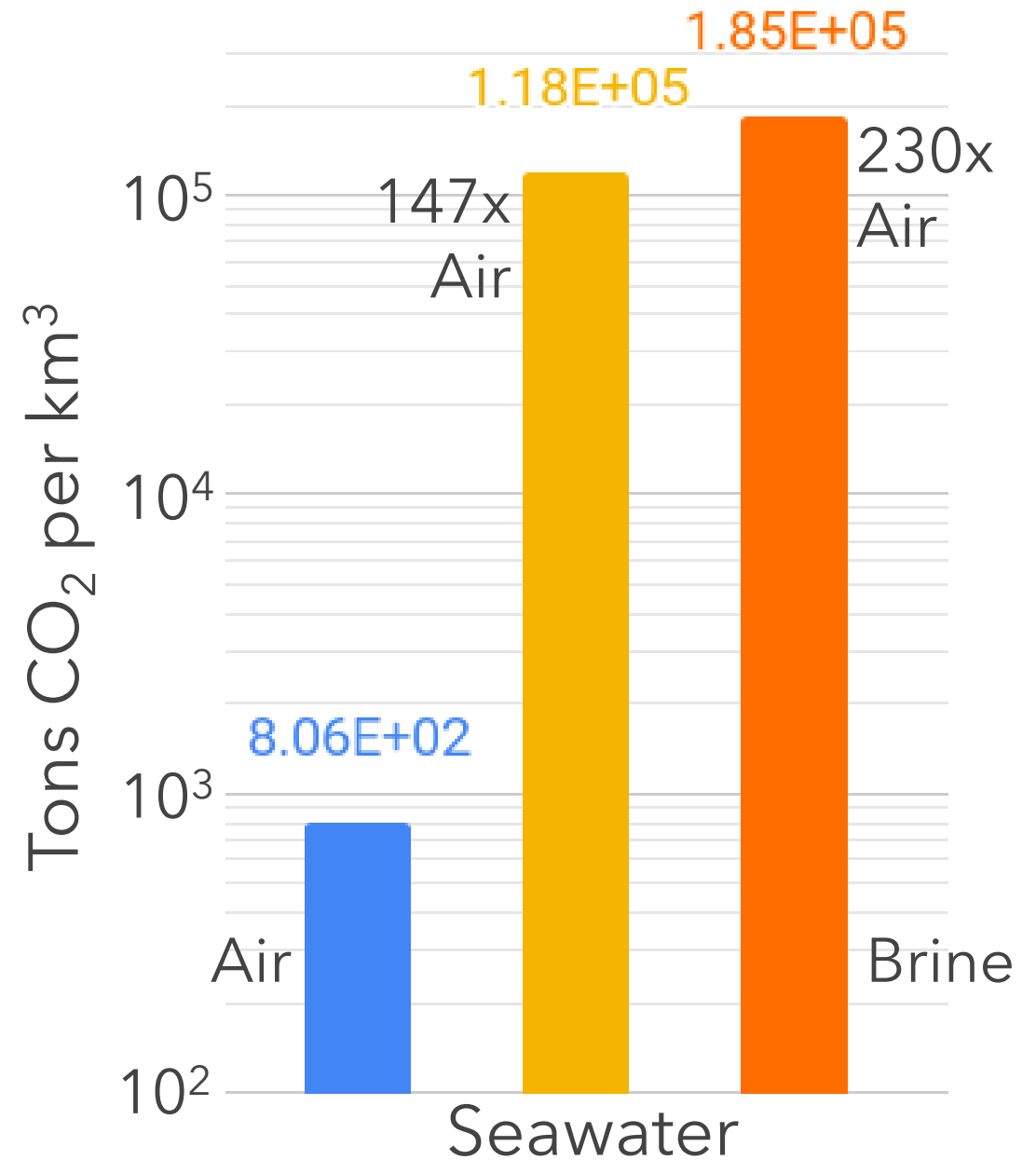
Direct Ocean Capture (DOC)



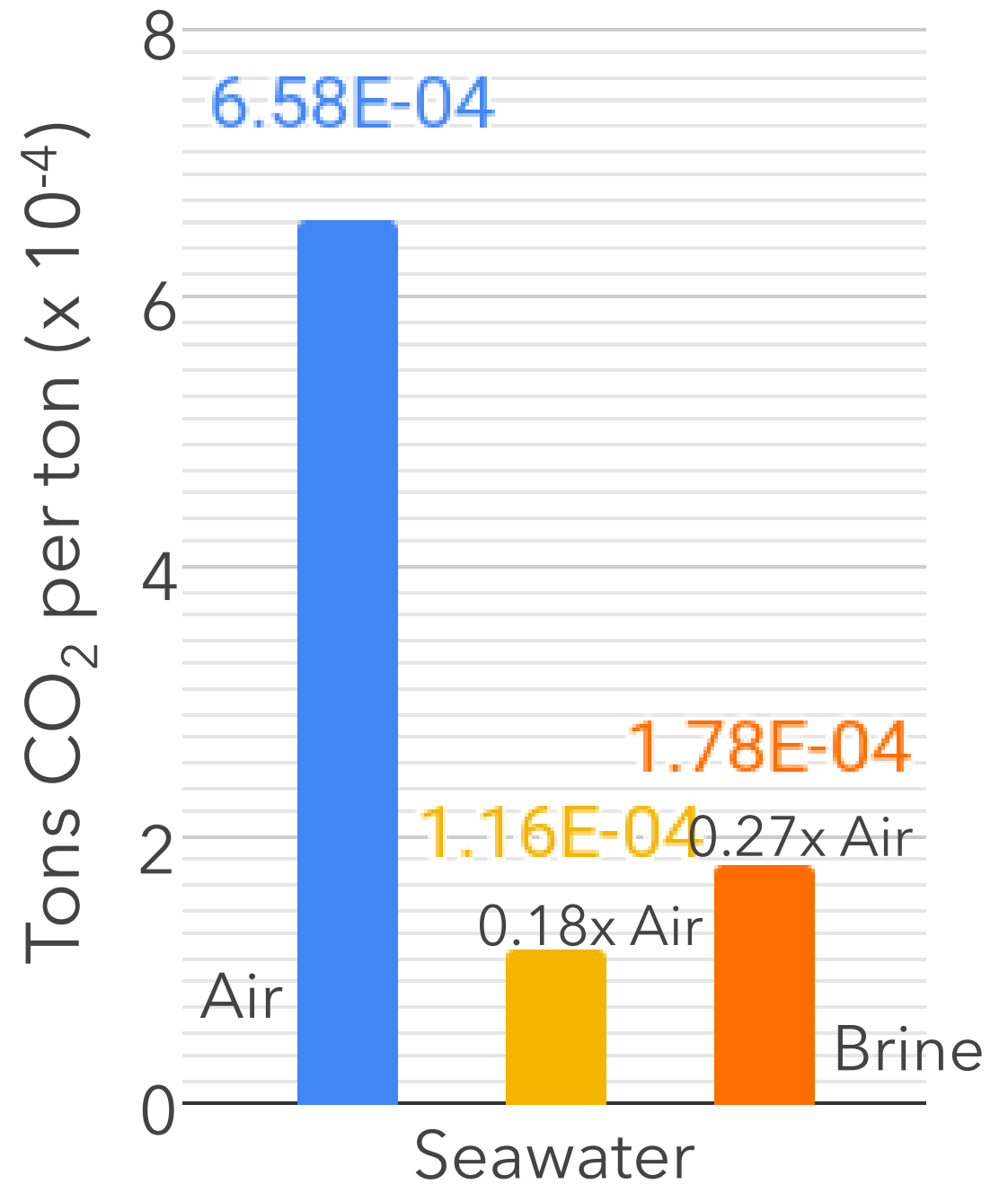
Direct Air Capture (DAC)



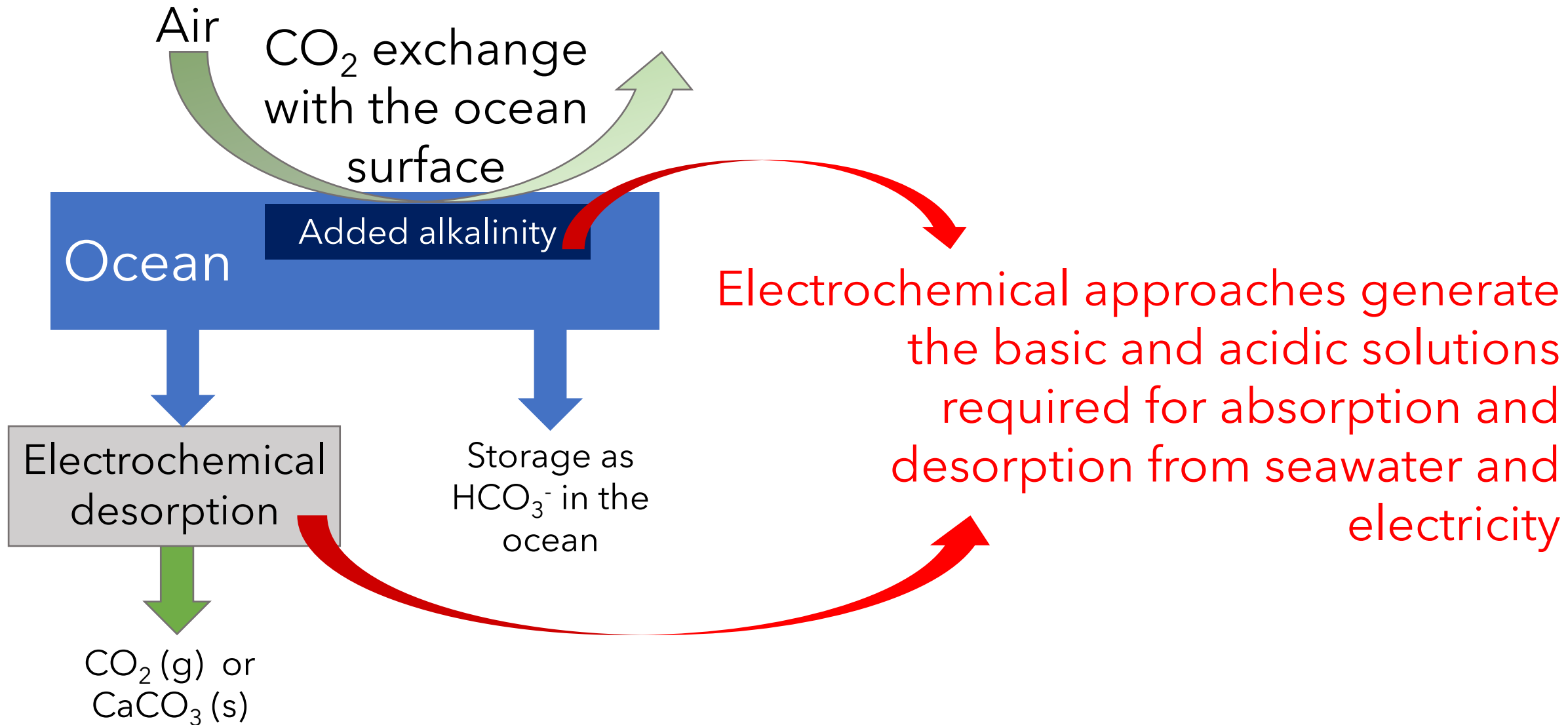
CO₂ is much more concentrated in seawater (147x) and brine (230x) than air, *per unit volume*



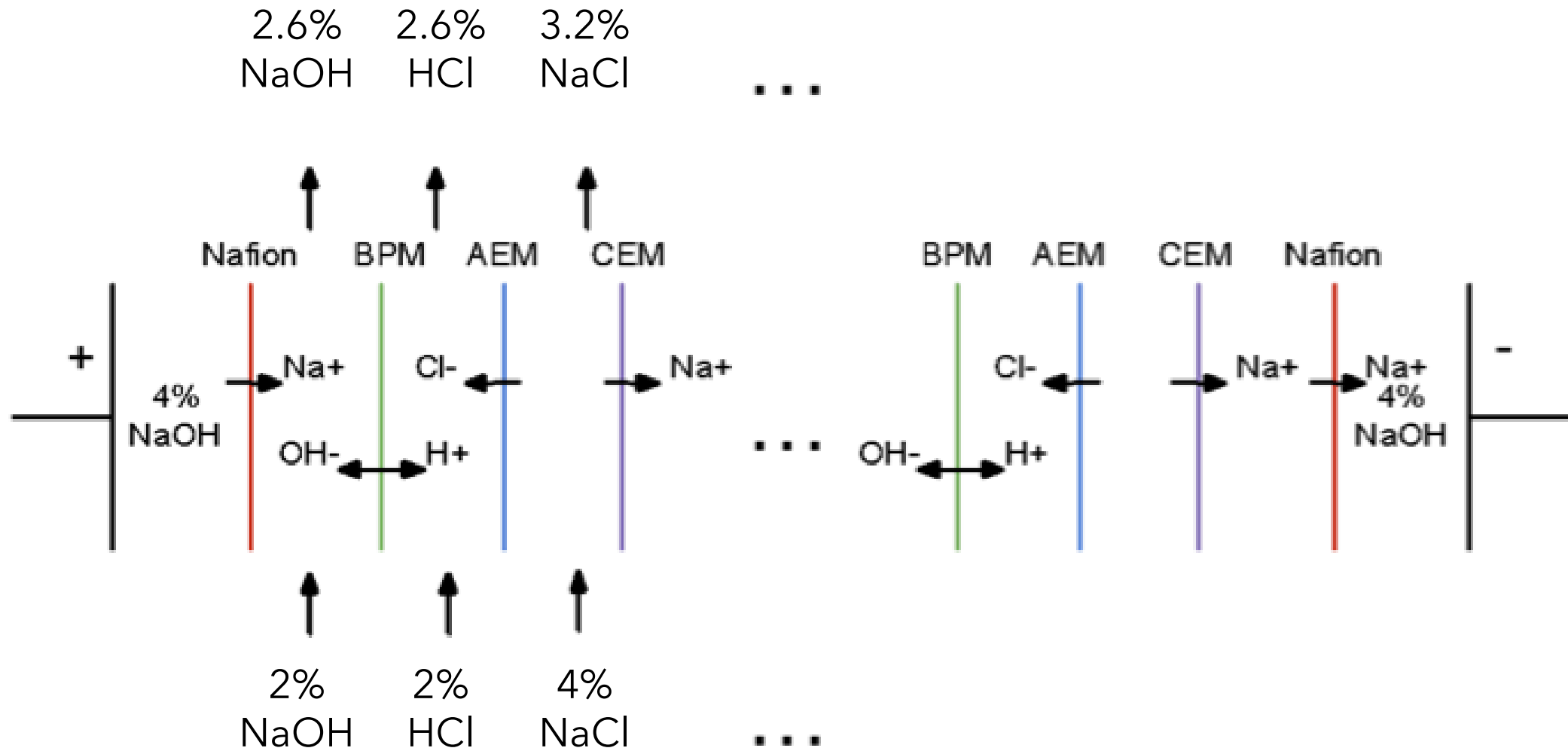
But CO₂ is less concentrated in seawater (~5x) and brine (~4x) than air, *per unit mass*



Direct Ocean Capture (DOC)



Electrodialysis: Acid & base from salt using ion-exchange membranes



Acidic
pH 4.5

More H^+
(acidic)

Ocean
pH 8.1

More OH^-
(basic)

Basic
pH 9.3

Dissolved
 CO_2



Seawater composition

NaCl to make acid (HCl) and base (NaOH)

Dissolved Inorganic Carbon (DIC) =
 $[\text{CO}_2(\text{g})] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$

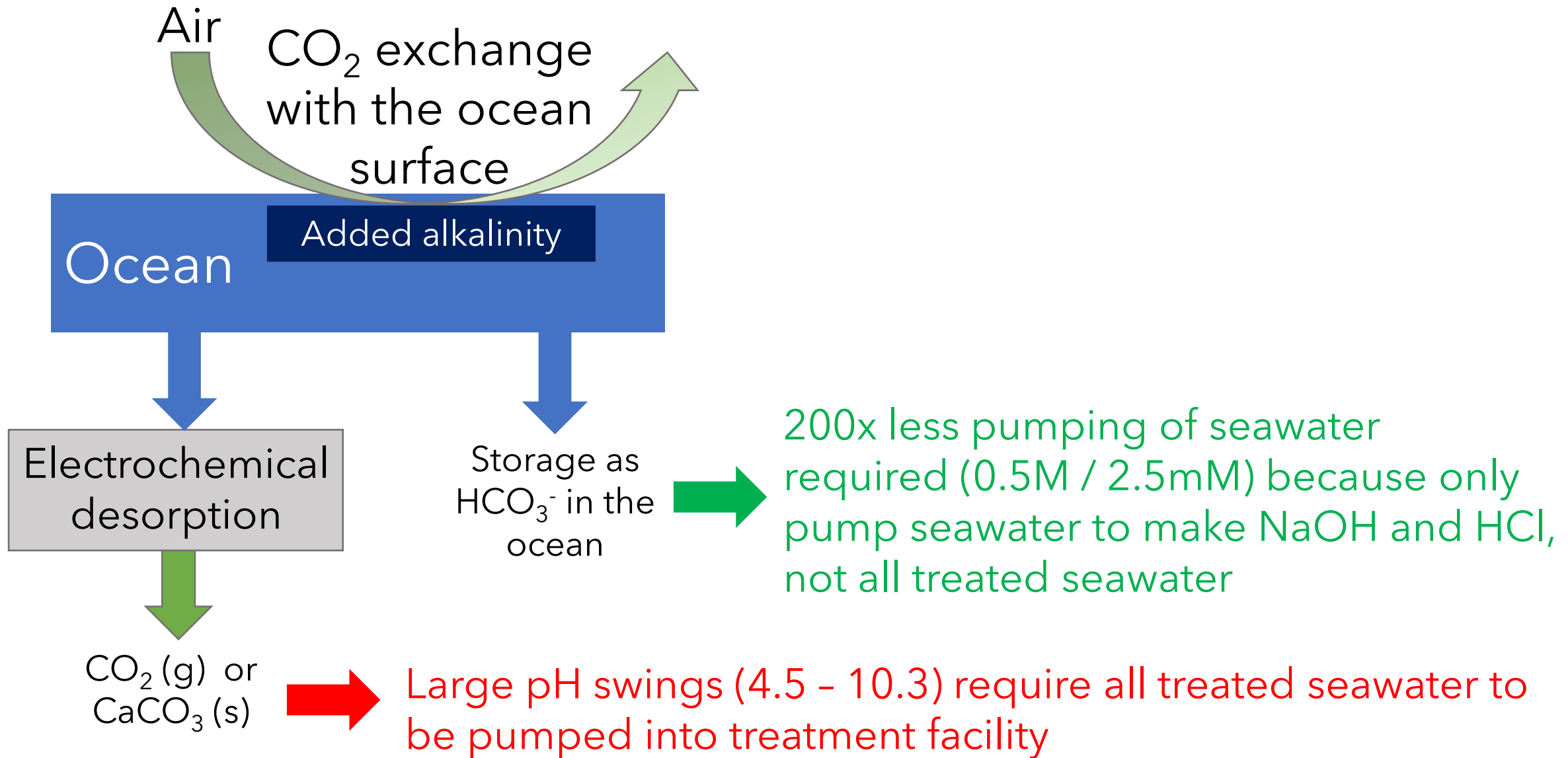
$$\frac{\text{Volume seawater used to make acid/base}}{\text{Total volume of treated seawater}} \approx \frac{1}{200}$$

Composition of normal seawater* and world average river water† (mmole/kg)

Component	Seawater	River water
Na ⁺	468.04	0.274
K ⁺	10.00	0.059
Mg ⁺⁺	53.27	0.169
Ca ⁺⁺	10.33	0.375
Sr ⁺⁺	0.10	
Cl ⁻	545.88	0.220
SO ₄ ⁼	28.20	0.117
Br ⁻	0.83	
F ⁻	0.07	0.0053
HCO ₃ ⁻ (+CO ₂ + CO ₃ ⁼)	2.2–2.5 [†]	0.957
B(OH) ₃ + B(OH) ₄ ⁻	0.43	
Si(OH) ₄ + SiO(OH) ₃ ⁻	0.001–0.1 [†]	0.218
H ₂ PO ₄ ⁻ + HPO ₄ ⁼ + PO ₄ ⁼	0.0001–0.005 [†]	
NO ₃ ⁻	0.0001–0.05	0.017
pH	(7.4 to 8.3)	(6.0 to 8.5)
Ionic strength	700	2.09

Butler, *Carbon Dioxide Equilibria and their Applications*

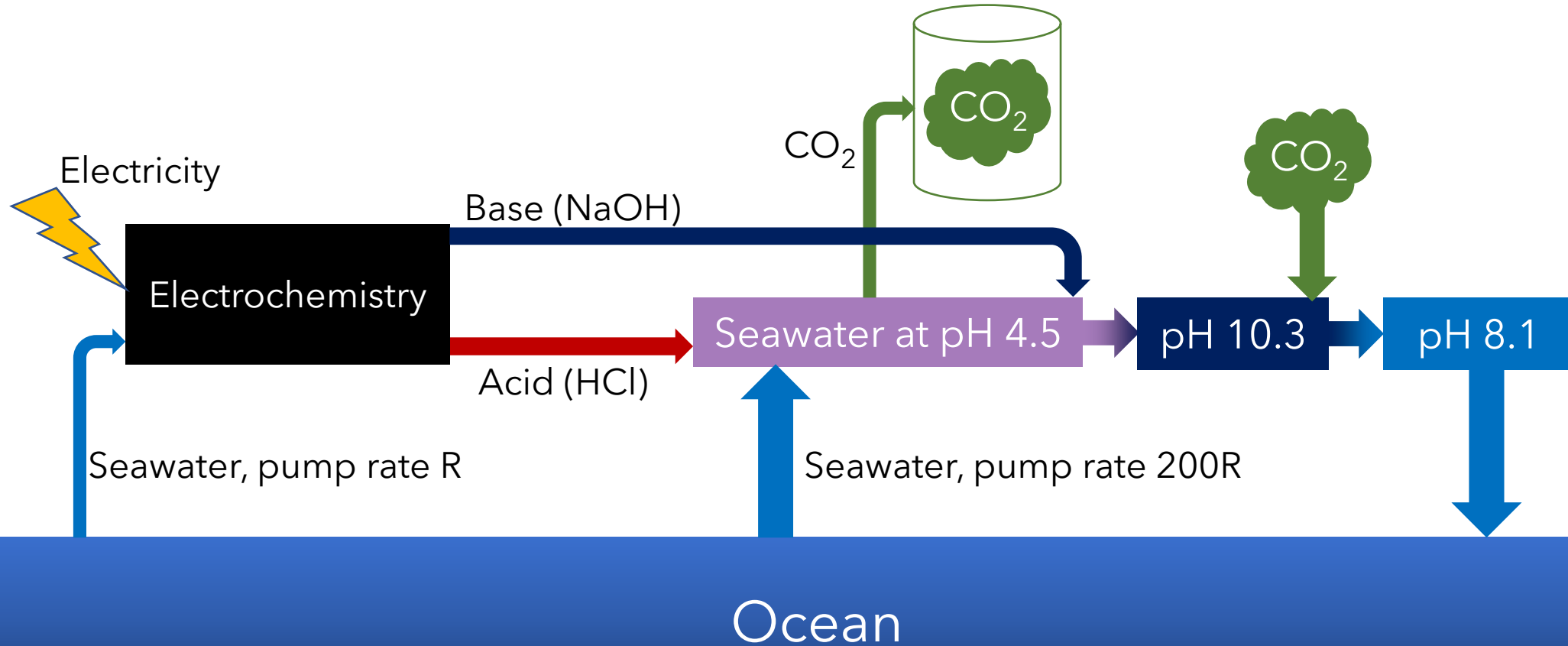
Direct Ocean Capture (DOC)



Lab system: 1,000 gallons of seawater per day

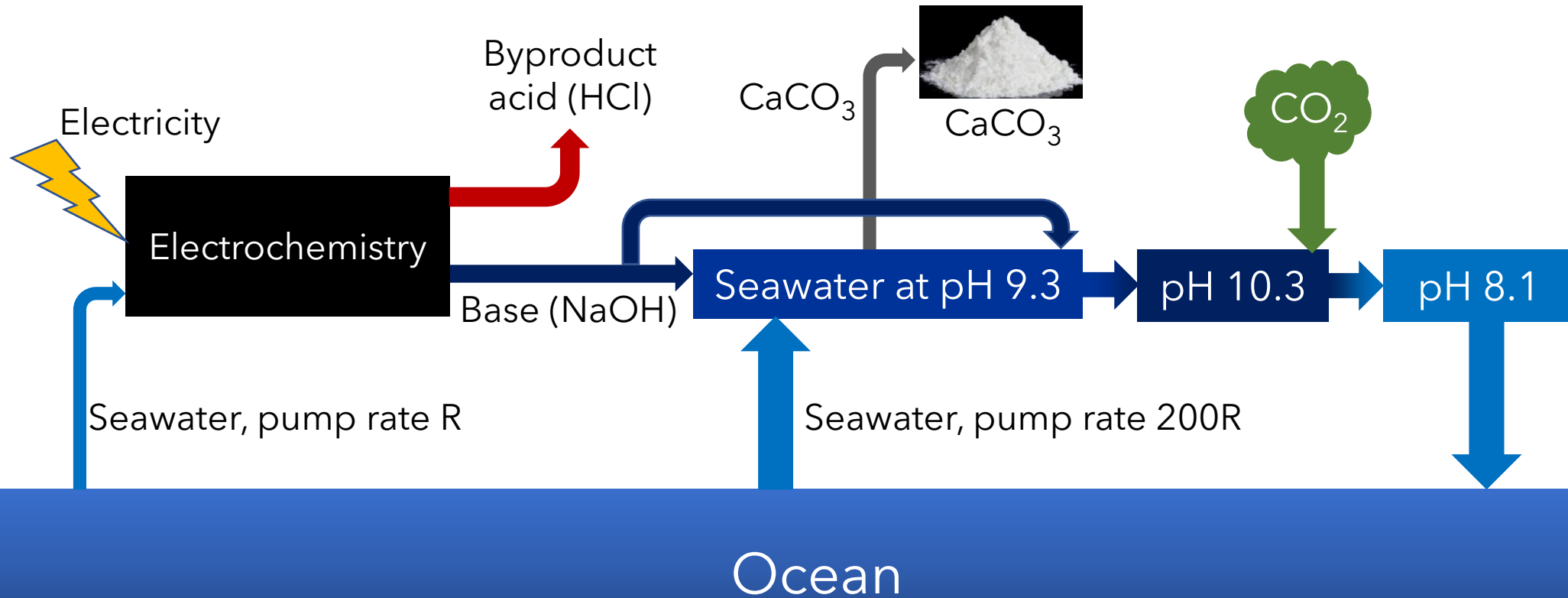


Process 1: Store atmospheric CO₂ as extracted CO₂ gas



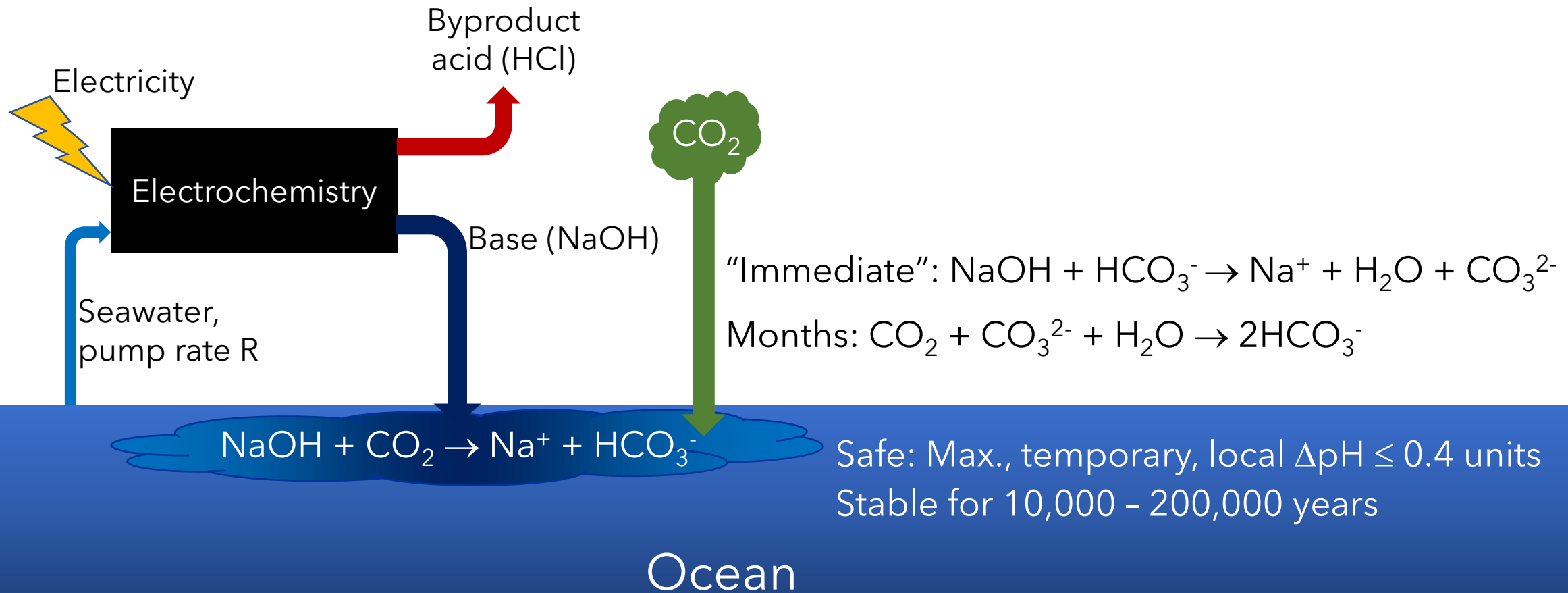
Cost: $\geq \$430/\text{t}(\text{CO}_2)$

Process 2: Store atmospheric CO₂ as extracted solid CaCO₃



Cost: $\geq \$370/\text{t}(\text{CO}_2)$

Process 3: Store atmospheric CO₂ as HCO₃⁻ in the ocean



Cost: $\leq \$100/\text{t}(\text{CO}_2)$

Most critical questions and research areas to address

1. **Social License and Environmental Safety:** Lab tests transitioning to field tests demonstrating the ability of these processes to operate in the ocean without harm to marine life
2. **Standards and verification:** Standardized methods developed and tested for sensors to monitor carbon sequestration
3. **Pilot plant demonstration and techno-economics:** Build and operate pilot plants co-located with synergistic industries (aquaculture, desalination facilities, etc.) and assess techno-economics
4. **Modeling:** Development of high-resolution oceanographic models of these processes to optimize siting and predict region effects on seawater chemistry

References (papers)

1. Matthew D. Eisaman, [Negative Emissions Technologies: The Tradeoffs of Air-Capture Economics](https://doi.org/10.1016/j.joule.2020.02.007), Joule, **4**, 516-520 (2020), <https://doi.org/10.1016/j.joule.2020.02.007>.
2. Matthew D. Eisaman, Jessy L.B. Rivest, Stephen D. Karnitz, Charles-François de Lannoy, Arun Jose, Richard W. DeVaul, Kathy Hannun, [Indirect ocean capture of atmospheric CO₂: Part II. Understanding the cost of negative emissions](https://doi.org/10.1016/j.ijggc.2018.02.020), Int. J. Greenh. Gas Control, **70**, 254-261 (2018), <https://doi.org/10.1016/j.ijggc.2018.02.020>.
3. Charles-Francois de Lannoy, Matthew D. Eisaman, Arun Jose, Stephen D. Karnitz, Richard W. DeVaul, Kathy Hannun, and Jessy L.B. Rivest, [Indirect ocean capture of atmospheric CO₂: Part I. Prototype of a negative emissions technology](https://doi.org/10.1016/j.ijggc.2017.10.007), Int. J. Greenh. Gas Cont., **70**, 243-253 (2018), <https://doi.org/10.1016/j.ijggc.2017.10.007>.
4. Matthew D. Eisaman, Keshav Parajuly, Alexander Tuganov, Craig Eldershaw, Norine Chang, and Karl A. Littau, [CO₂ extraction from seawater using bipolar membrane electrodialysis](#), Energy & Environmental Science, **5**, 7346-7352 (2012).
5. R. J. Pearson, M. D. Eisaman, J.W.G. Turner, P.P. Edwards, Z. Jiang, V. L. Kuznetsov, K. A. Littau, L. di Marco, and S. R. G. Taylor, [Invited Paper: Energy Storage Via Carbon-Neutral Fuels Made From CO₂, Water, and Renewable Energy](#), Proceedings of the IEEE, **100**, 440 - 460 (2012).
6. M. D. Eisaman, L. Alvarado, D. Larner, P. Wang, and K. A. Littau, [CO₂ concentration using high-pressure bipolar membrane electrodialysis](#), Energy & Environmental Science, **4**, 4031 - 4037 (2011).
7. M. D. Eisaman, L. Alvarado, D. Larner, P. Wang, B. Garg, and K. A. Littau, [CO₂ concentration using bipolar membrane electrodialysis](#), Energy & Environmental Science, **4**, 1319 - 1328 (2011).

References (patents)

1. M. D. Eisaman, inventor; 2015 Dec. 16, Recycle loop for reduced scaling in bipolar membrane electrodialysis, [US Patent 9,937,471](#). (April 10, 2018).
2. M.D. Eisaman, inventor; 2015 Jun. 11, Energy efficient method for stripping CO₂ from seawater, [US Patent 9,914,644](#). (Mar. 13, 2018).
3. M. D. Eisaman, inventor; 2016 May 26, Fuel synthesis from an aqueous solution, [US Patent 9,914,683](#). (March 13, 2018).
4. M. D. Eisaman, and K. E. Cooper, inventors; 2016 May 26, Hydrocarbon extraction through carbon dioxide production and injection into a hydrocarbon well, [US Patent 9,915,136](#) (March 13, 2018).
5. M. D. Eisaman, S. D. Karnitz, and J. L. B. Rivest, inventors; 2016 July 7, Method for efficient CO₂ degasiification, [US Patent 9,873,650](#) (Jan. 23, 2018).
6. M. D. Eisaman, inventor; 2016 May 26, Building materials from an aqueous solution, [US Patent 9,862,643](#) (Jan. 9, 2018).
7. M. D. Eisaman and K. A. Littau, inventors; 2011 July 6, Electrodialytic separation of CO₂ gas from seawater, [US patent 9,586,181](#) (2017, March 7).
8. M. D. Eisaman, K. A. Littau, and D. Larner, inventors; 2010 Dec. 15, High-pressure electrodialysis device, [US patent 8,784,632](#) (2014, July 22).
9. M. D. Eisaman and K. A. Littau, inventors; 2010 Dec. 15, Electrodialytic separation of gas from aqueous carbonate and bicarbonate solutions, [US patent 8,778,156](#) (2014, July 15).
10. M. D. Eisaman and K. A. Littau, inventors; 2012 June 29, Electrodialytic separation of gas from seawater, [European patent EP2543427B1](#) (2015, Nov. 4).

Advanced technologies to enable giga-ton scale engineered carbon dioxide removal from ocean water

David M. Babson, Ph.D. | Email: David.Babson@hq.doe.gov
Program Director
Advanced Research Projects Agency – Energy

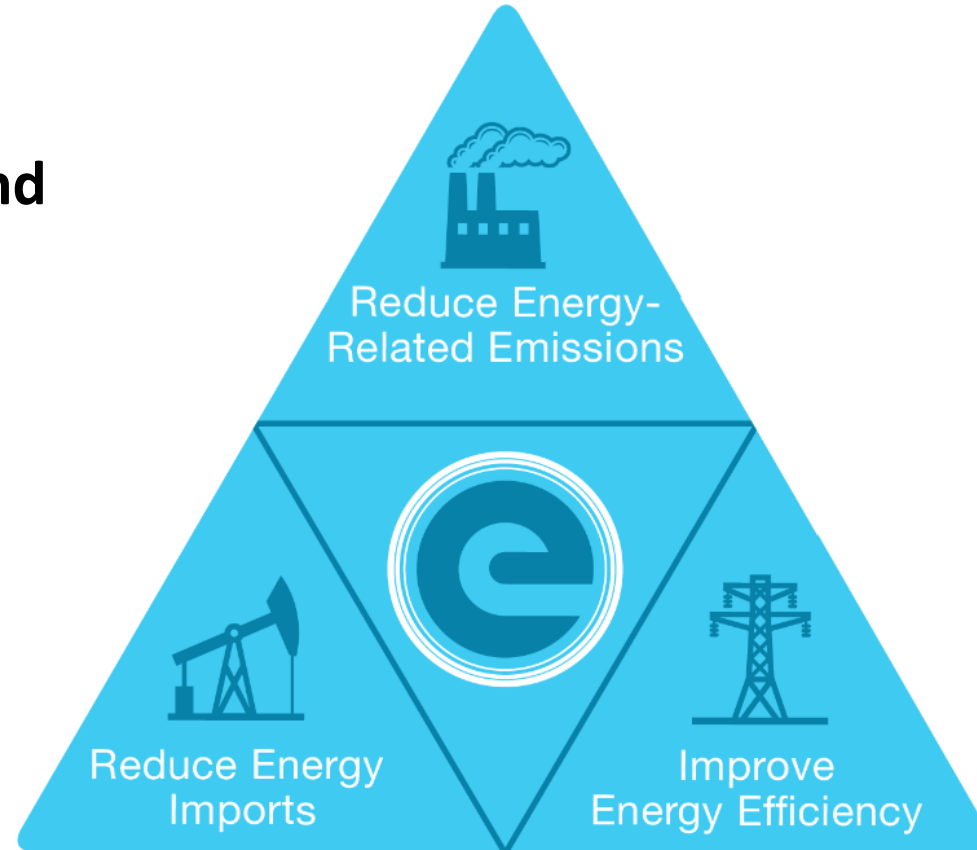
NASEM Ocean CDR – Panel
January 27, 2021

Who is ARPA-E?

Advanced Research Projects Agency - Energy

Mission

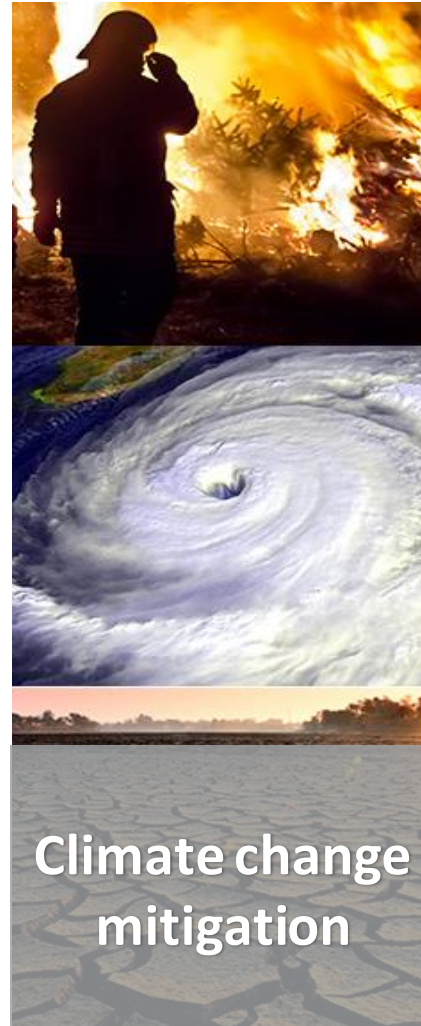
Overcome long-term and high-risk technological barriers in the development of transformative technologies ...



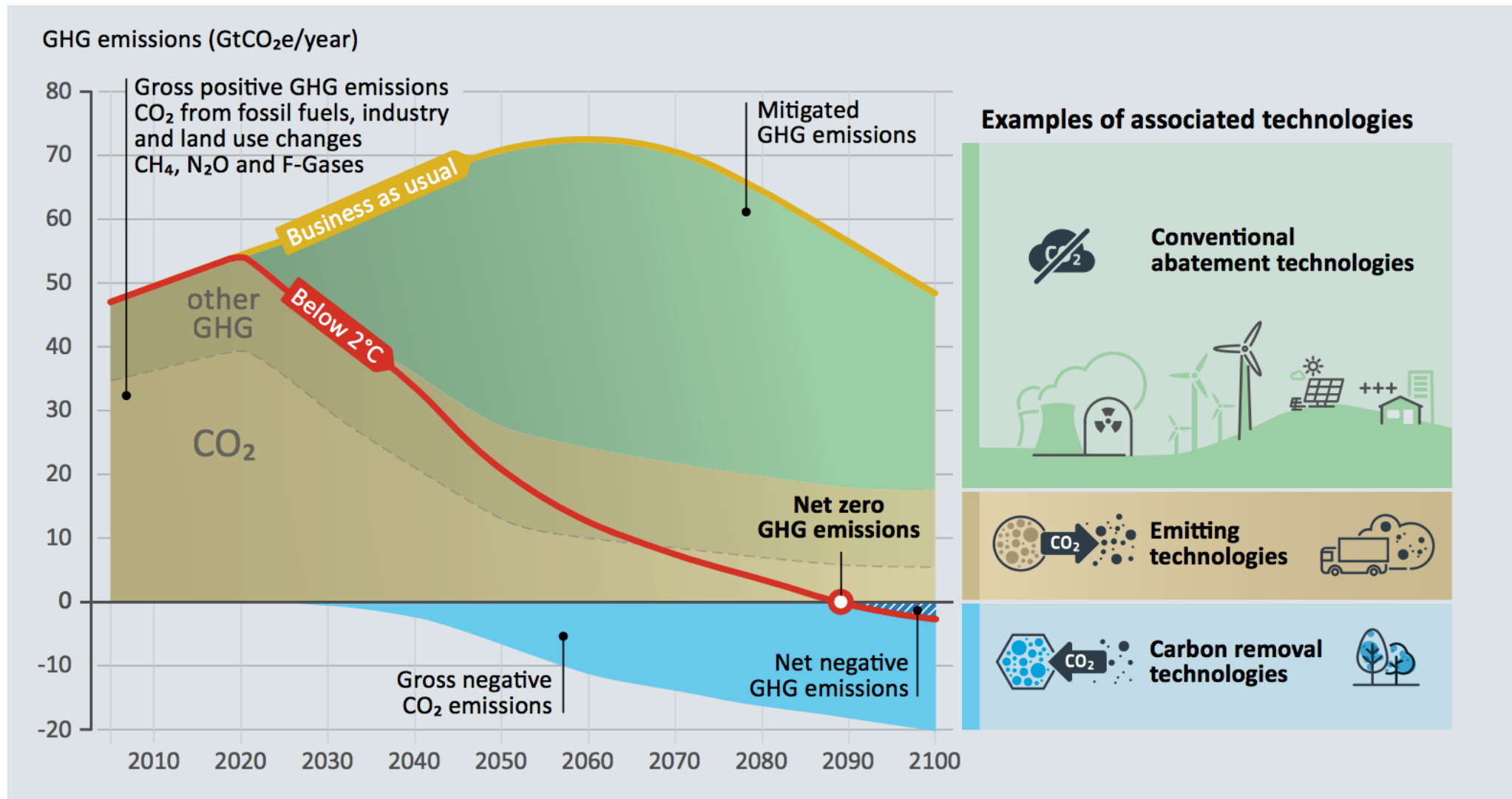
... that ensure U.S. national security, technology leadership, and economic prosperity



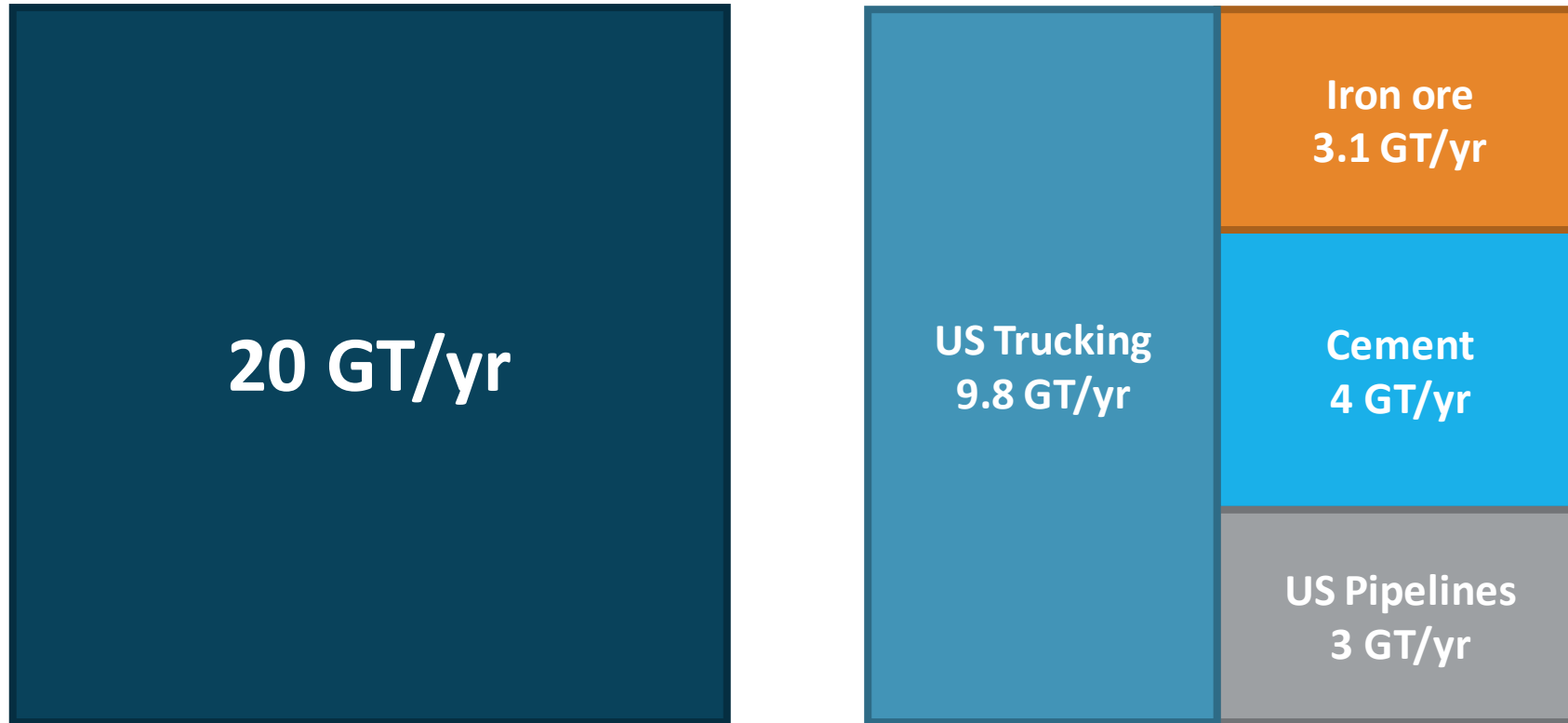
Who are we and what solutions are we working to offer?



The context for new ideas that interest me – All paths to 2° C go through zero



Just how much is 20 gigatons?



Biological Solutions



Coastal Blue Carbon and
Aquatic Systems



Forest and Land
Management

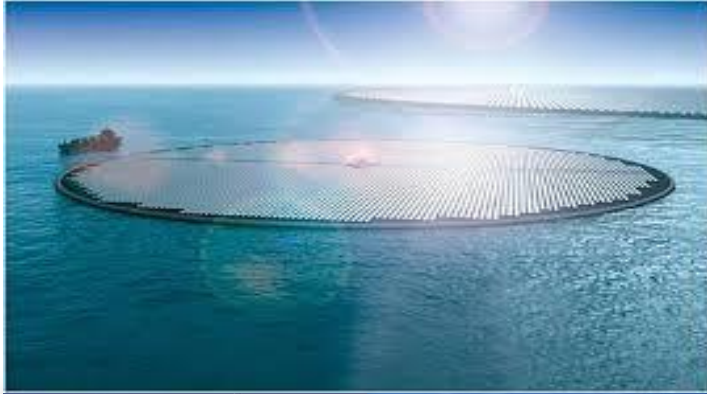


Soil Carbon
Sequestration

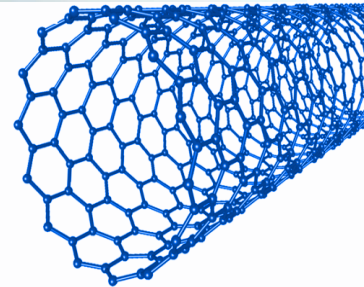


Soil Amendments &
Nutrient Management

Engineered Solutions



Direct Air/Ocean Capture



Conversion and Use



Enhanced Weathering and Mineralization

Hybrid Solutions



Bioenergy with carbon capture and storage

BECCS



Construction and Buildings



Biochar

CDR – diverse and broadly distributed industry



Why Direct Ocean Capture of CO₂?

- ▶ Directly reverse ocean acidification
- ▶ High concentration of DIC in water
- ▶ High volumetric concentration of dissolved inorganic carbon (relative to air)
- ▶ And from an scientific and technical standpoint it is ripe for substantially more investigation and innovation



Why pursue engineered systems?

- ▶ Modularity to achieve GT-scales through modular deployment
- ▶ Engineered to produce pure CO₂ offering:
 - Direct mitigation of CO₂
 - Both CO utilization and CO storage opportunities
- ▶ Avoid by-products that can create waste issues or ancillary environmental harms
- ▶ Hybridization with existing water treatment systems and water piping networks improves economics (desalination plants, once-through cooling, municipal water treatment)
- ▶ Co-location with other ocean-pumping industries (e.g., desalination, power plant cooling, material extraction) can improve economics



Current DOC portfolio

Development of An Off-Shore, Stand-Alone System for Efficient CO₂ Removal from Oceanwater



- Develop a low-overpotential electrodialyzer
- Develop membrane contactor to facilitate unprecedented rapid removal of CO₂

Hydrolytic Softening of Ocean Water for Carbon Dioxide Removal



- Develop hydrolytic softening thermochemical cycle for decarbonating (i.e., softening) ocean water
- Demonstrate regenerative brine hydrolysis for continuous sustainable system operation

Electrochemically Modulated CO₂ Removal From Ocean Waters



- Demonstrate proton cycling via applied voltage to drive CO₂ removal from seawater feed
- Develop novel aerophilic surfaces trap and remove CO₂ bubbles as they form in a single stream, with no reagents and no chemical byproducts

Looking forward to the panel discussion!

Contact me

David M. Babson, Ph.D.

Program Director | Advanced Research Projects Agency - Energy

U.S. Department of Energy

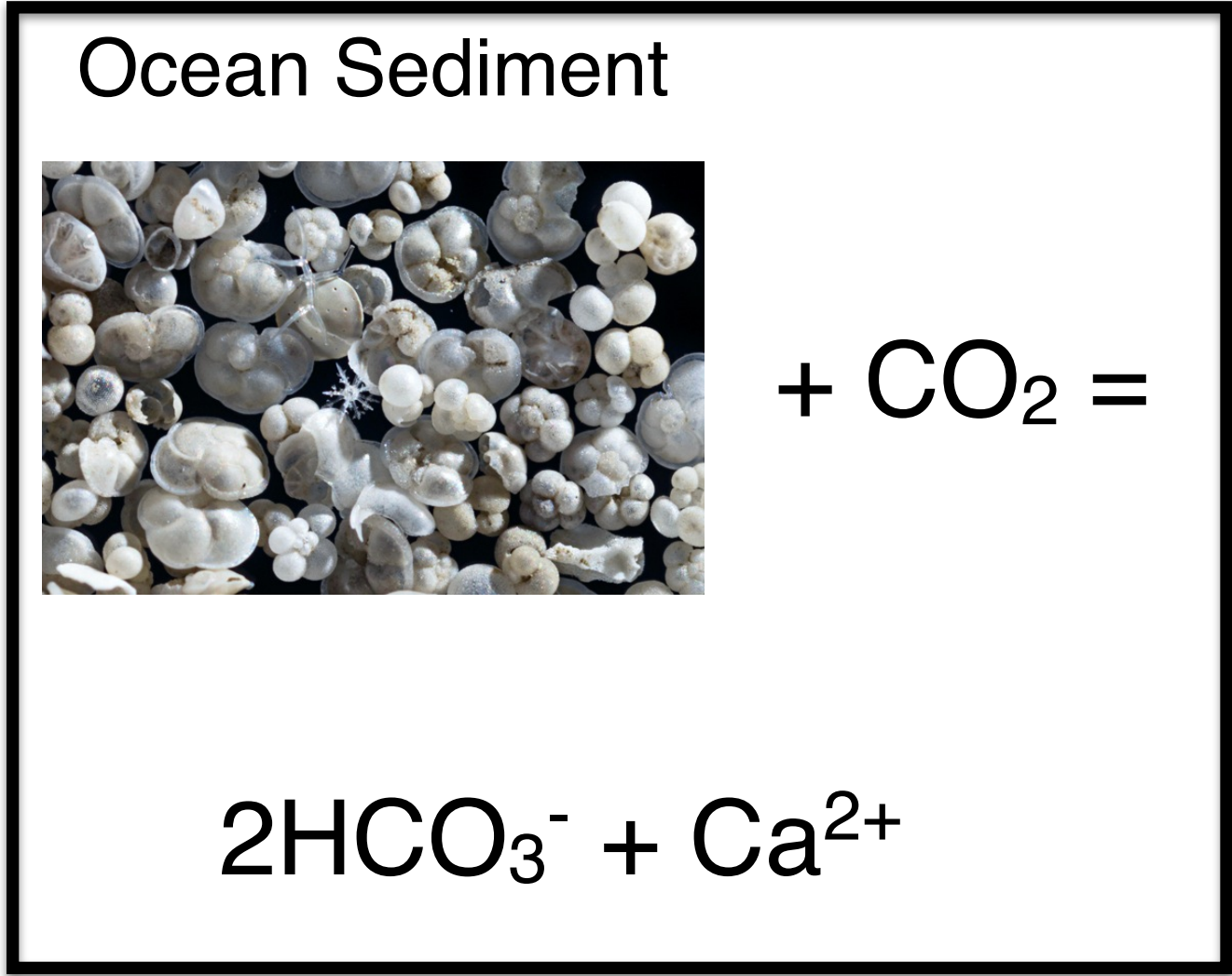
o. 202-586-6907 | David.Babson@hq.doe.gov

Follow me

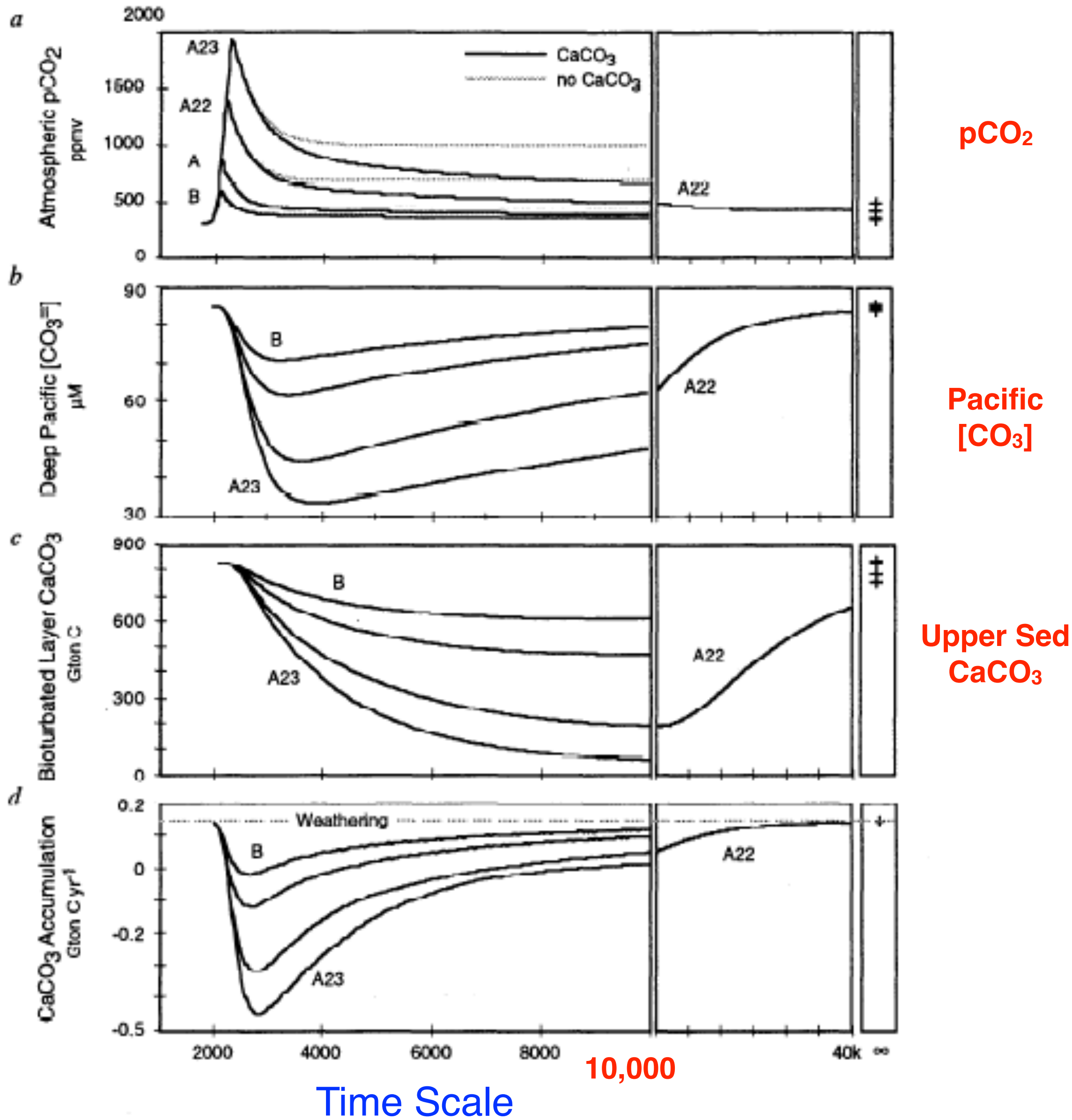
Twitter: @realDavidBabson

CO₂ Reaction with CaCO₃ is Permanent Sequestration

The ocean and atmosphere will respond to excess CO₂ emissions by reacting it with CaCO₃ sediments in the deep ocean. That is, the shells of dead plankton will buffer the CO₂ addition.



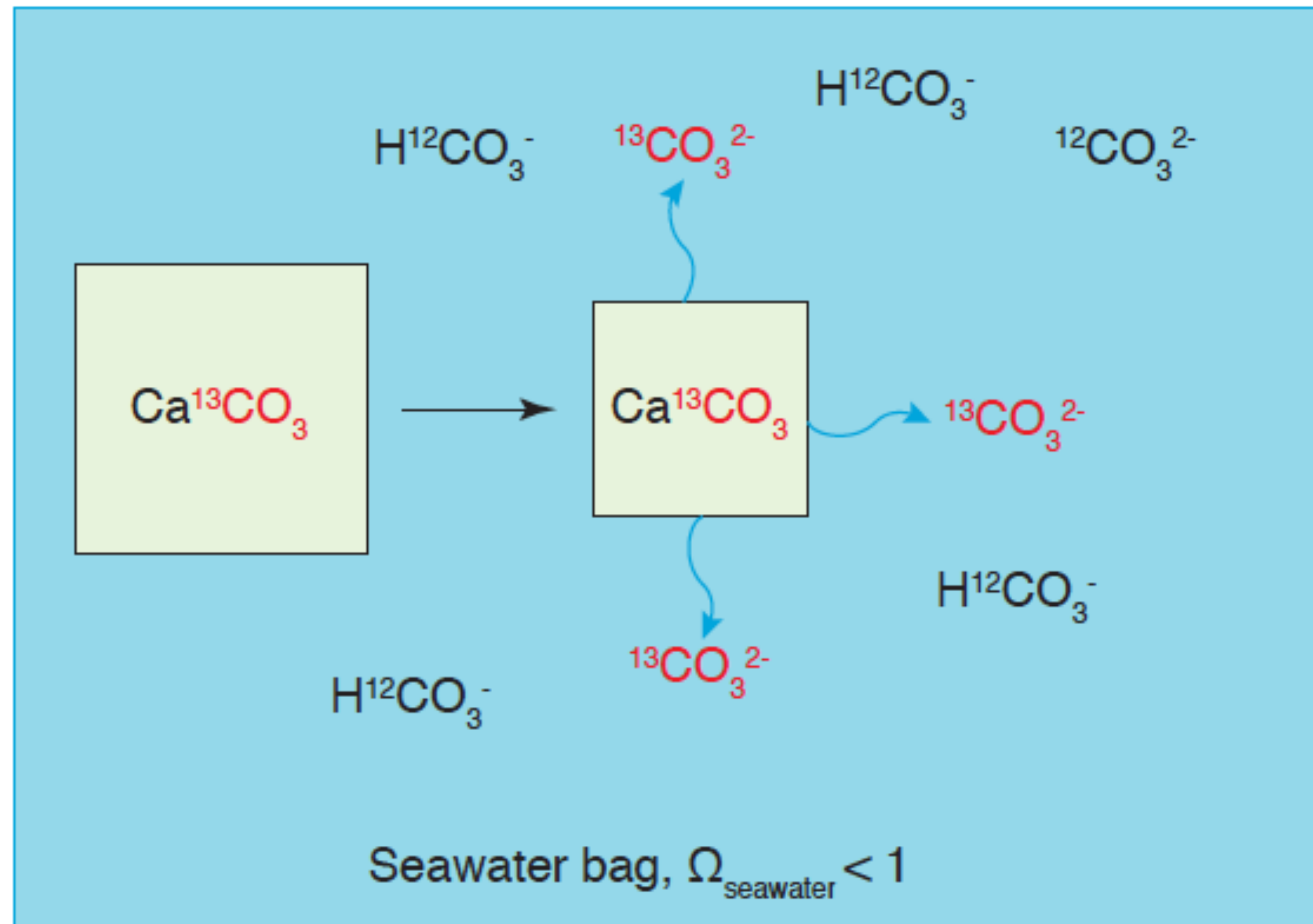
This happens in the deep ocean because the saturation state for CaCO₃ (Omega, Ω) is pressure dependent



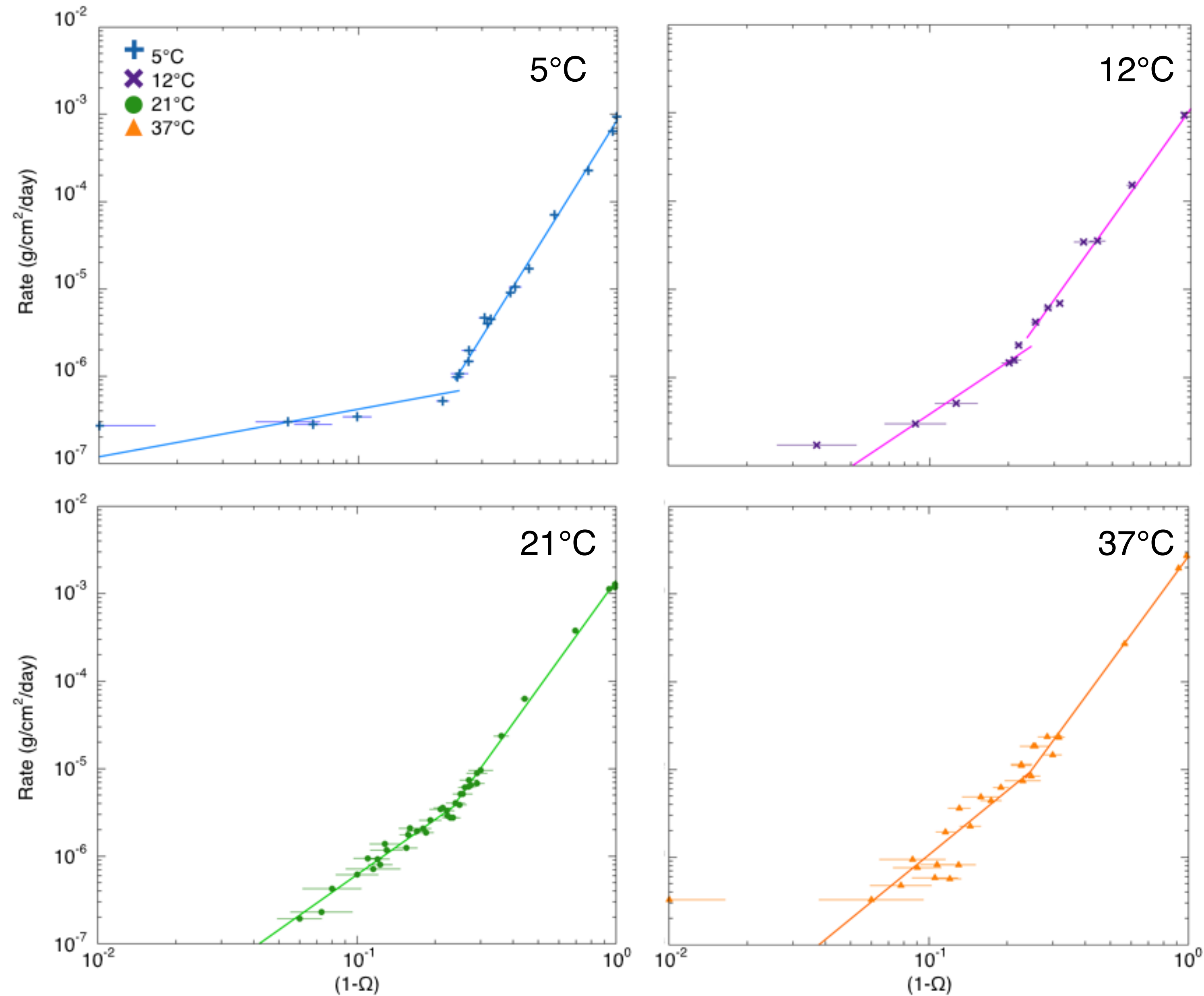
Four Basic Approaches to the Accelerated Weathering of Limestone (AWL)

	Fresh Water ($\Omega \ll 1$)	Seawater ($\Omega \sim 3$)
Ambient CO ₂	Backyard Streams (highly distributed)	NEED CATALYST (and ~ 5x CO ₂ Concentration)
Flue Gas CO ₂	Coupled Power Plants and Wastewater Treatment	Point sources on the coast or in the ocean (power plants, ships, etc.)

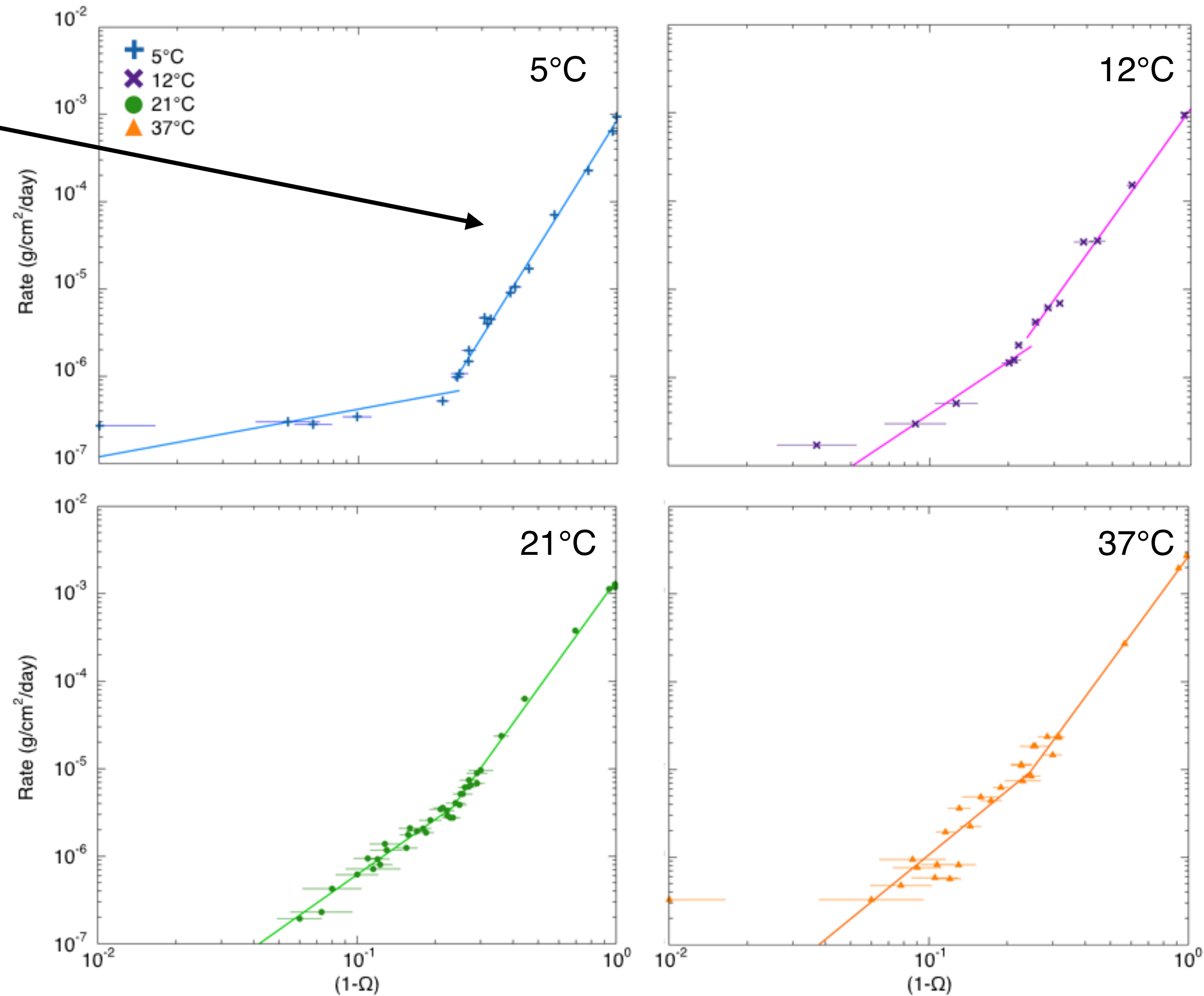
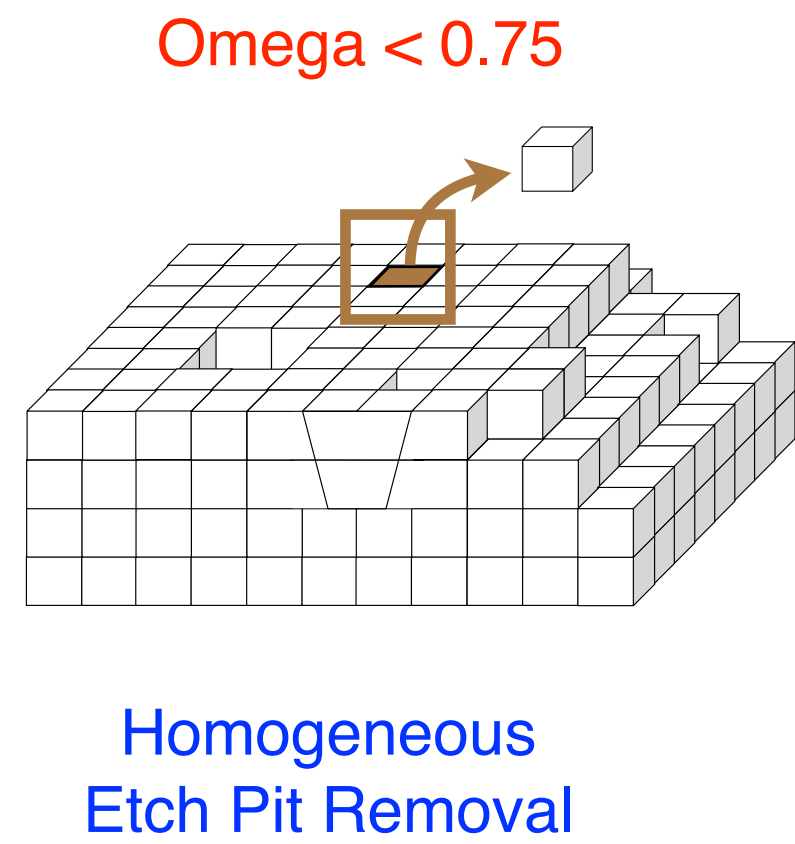
In the lab, and at sea, our new method is 20-200x more sensitive



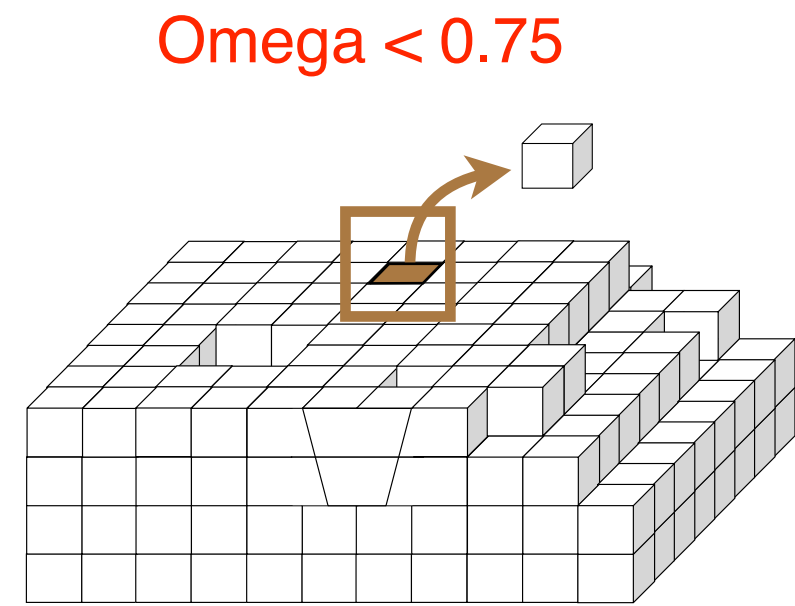
There are Distinct Breaks in Slope that Give Rise to the ‘Curvature’ in Other Rate Laws



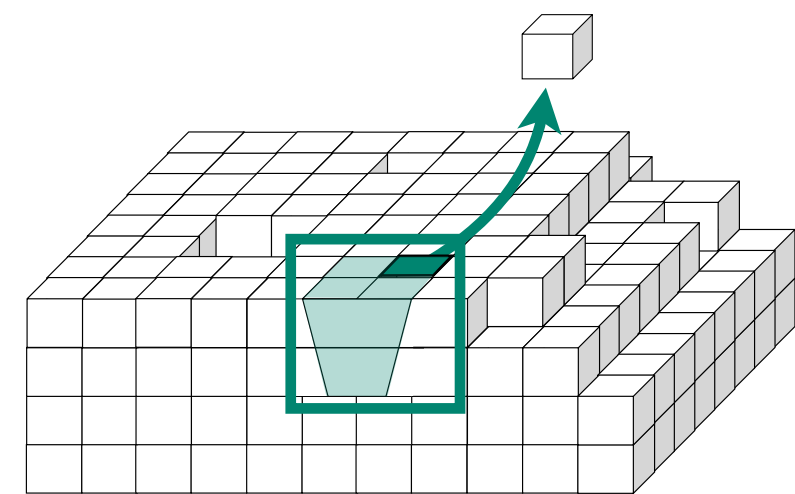
There are Distinct Breaks in Slope that Give Rise to the ‘Curvature’ in Other Rate Laws



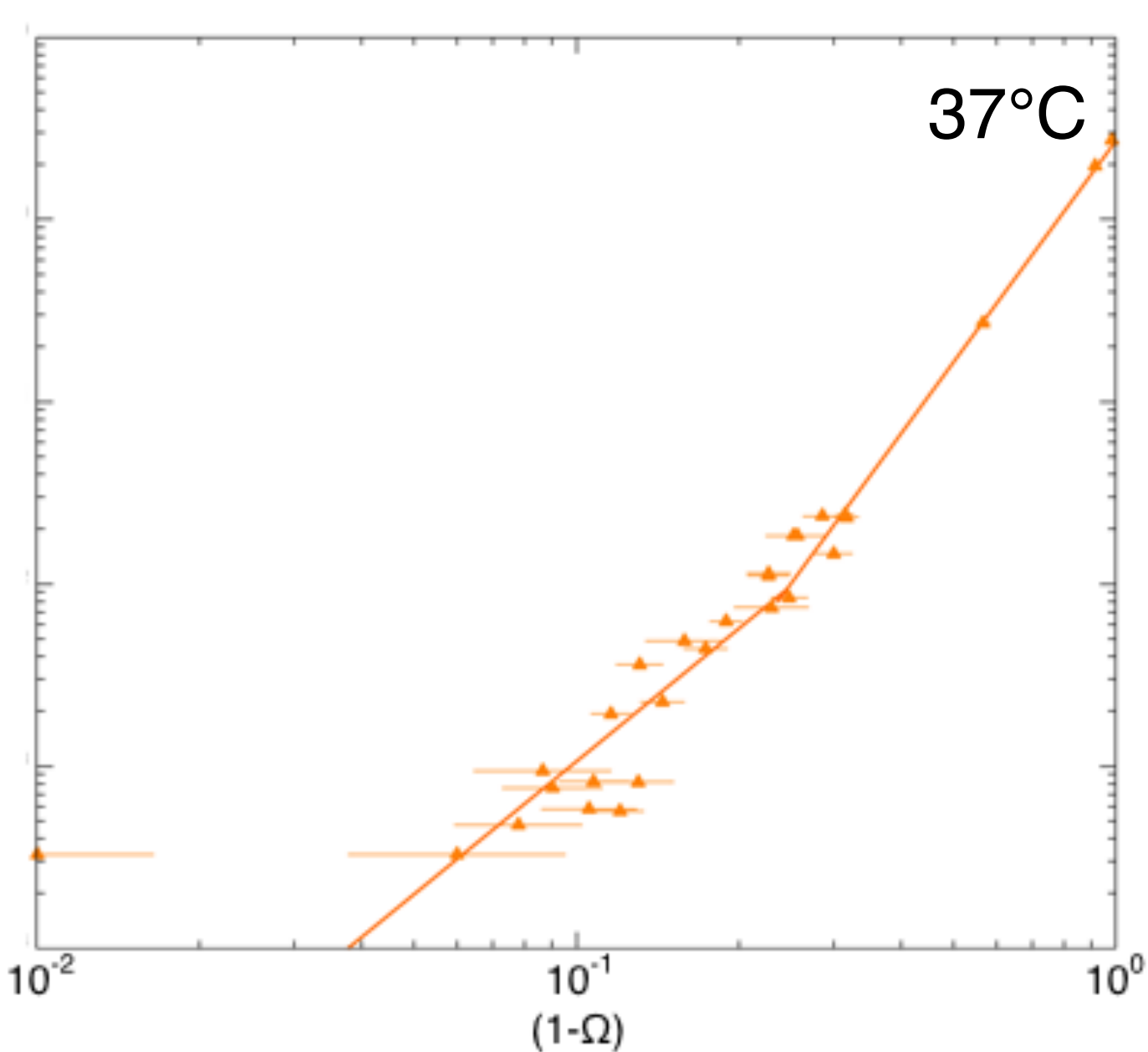
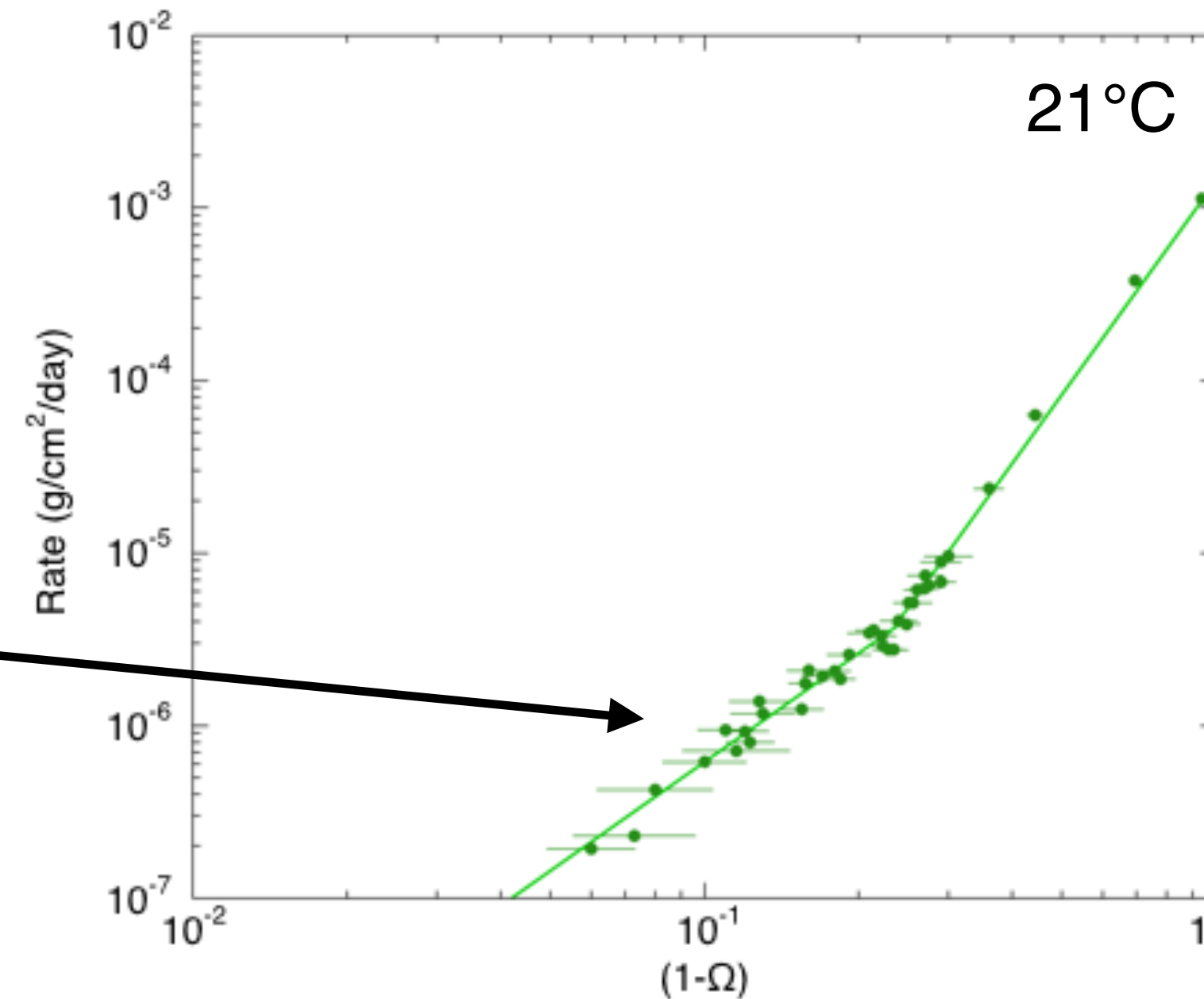
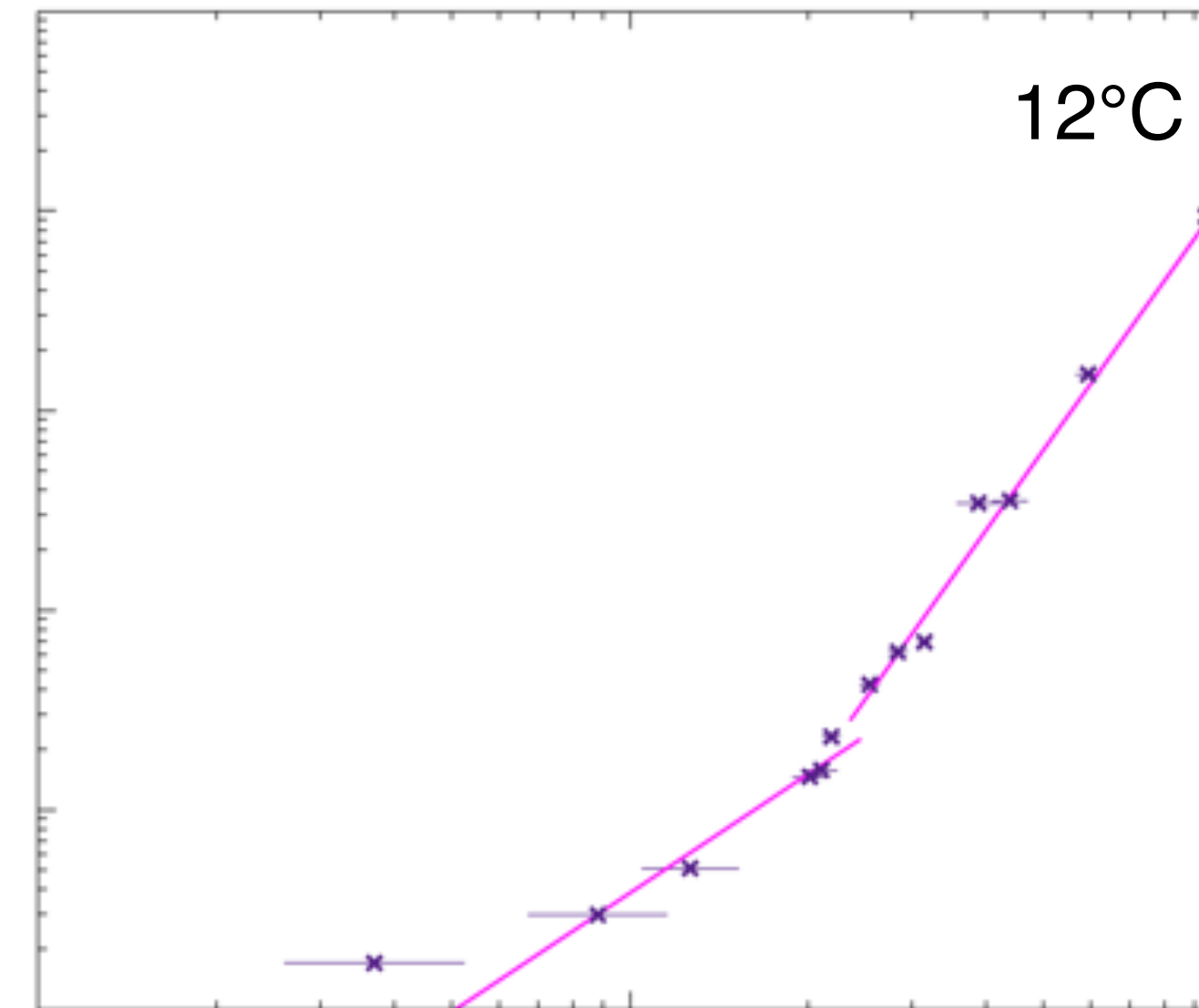
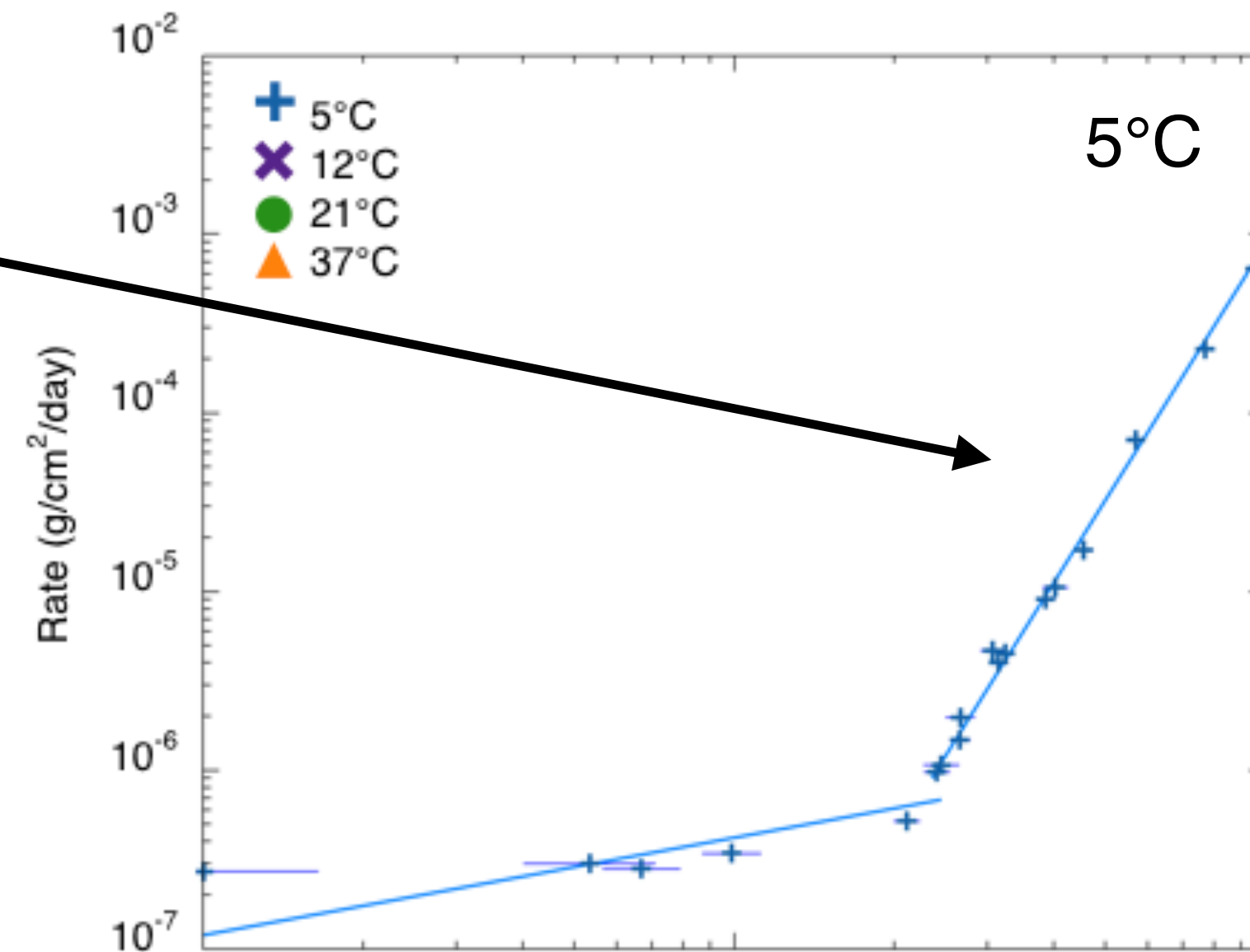
There are Distinct Breaks in Slope that Give Rise to the ‘Curvature’ in Other Rate Laws



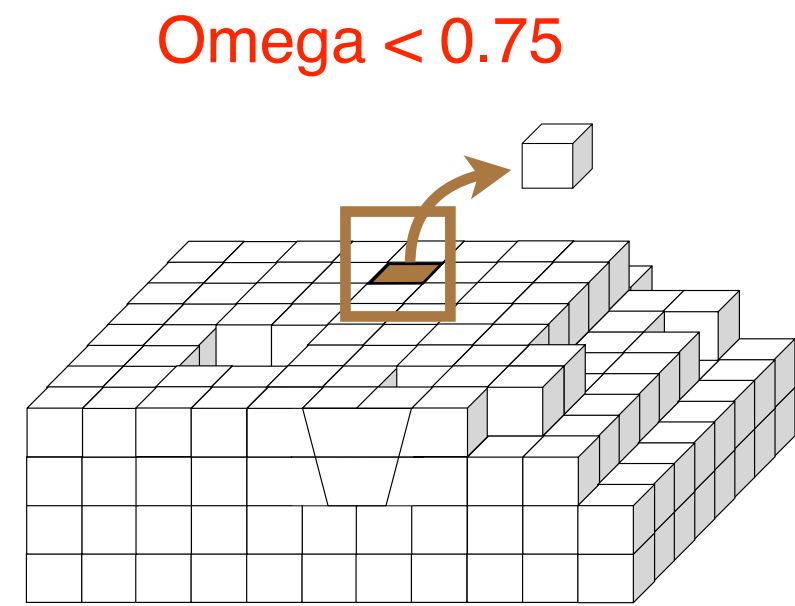
Homogeneous
Etch Pit Removal



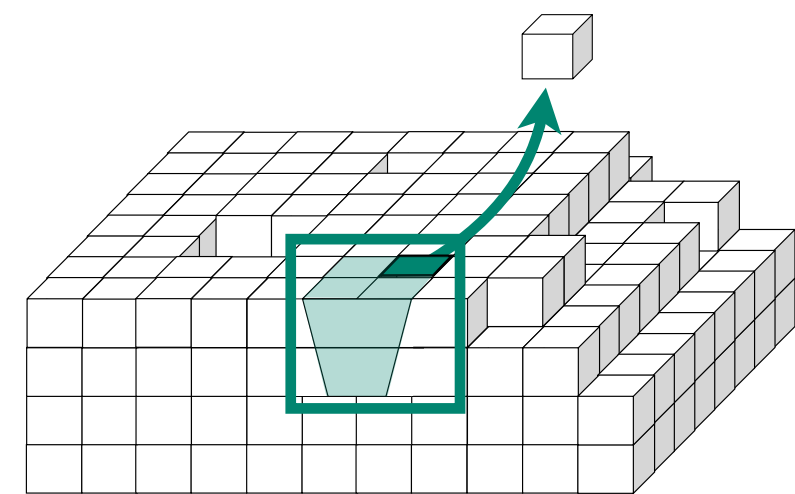
Defect Assisted
Etch Pit Removal



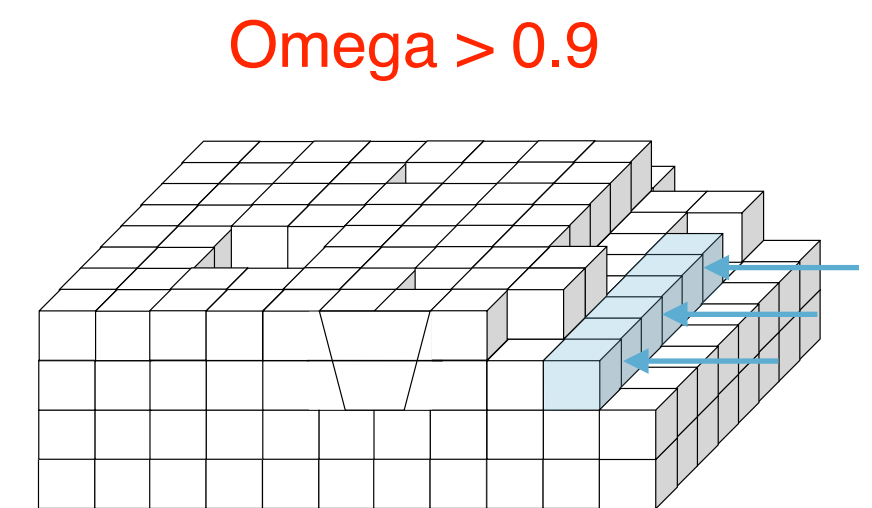
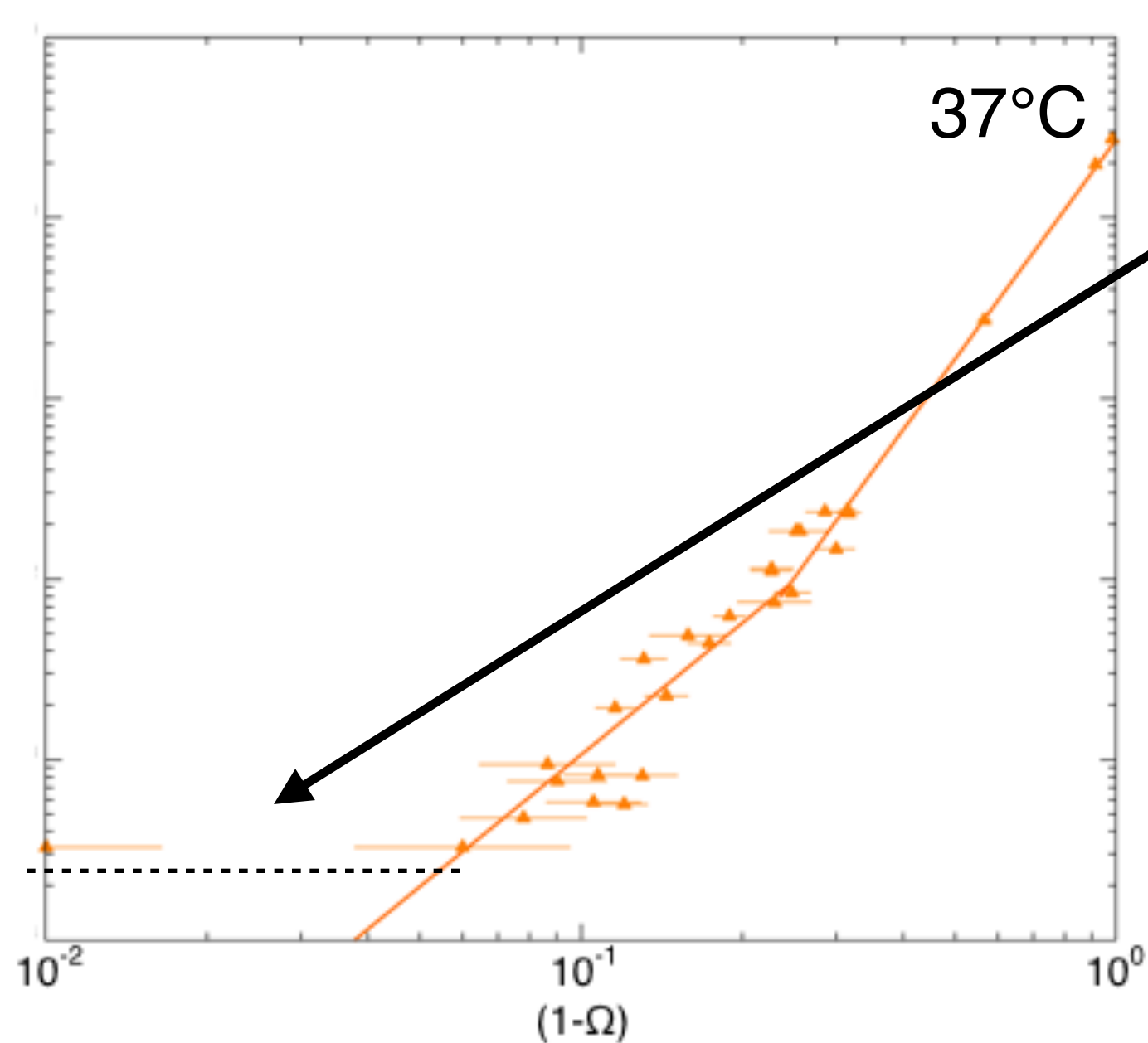
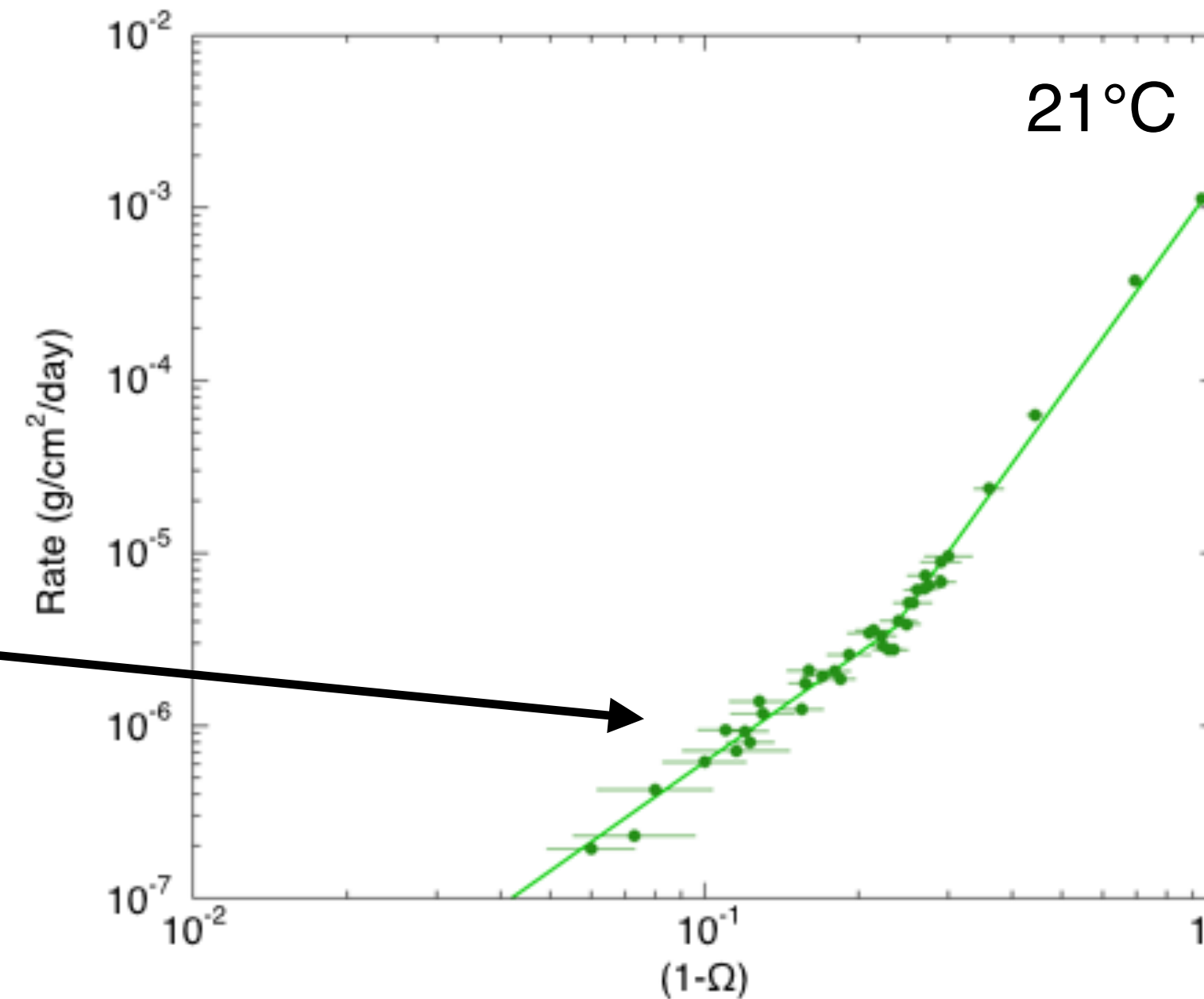
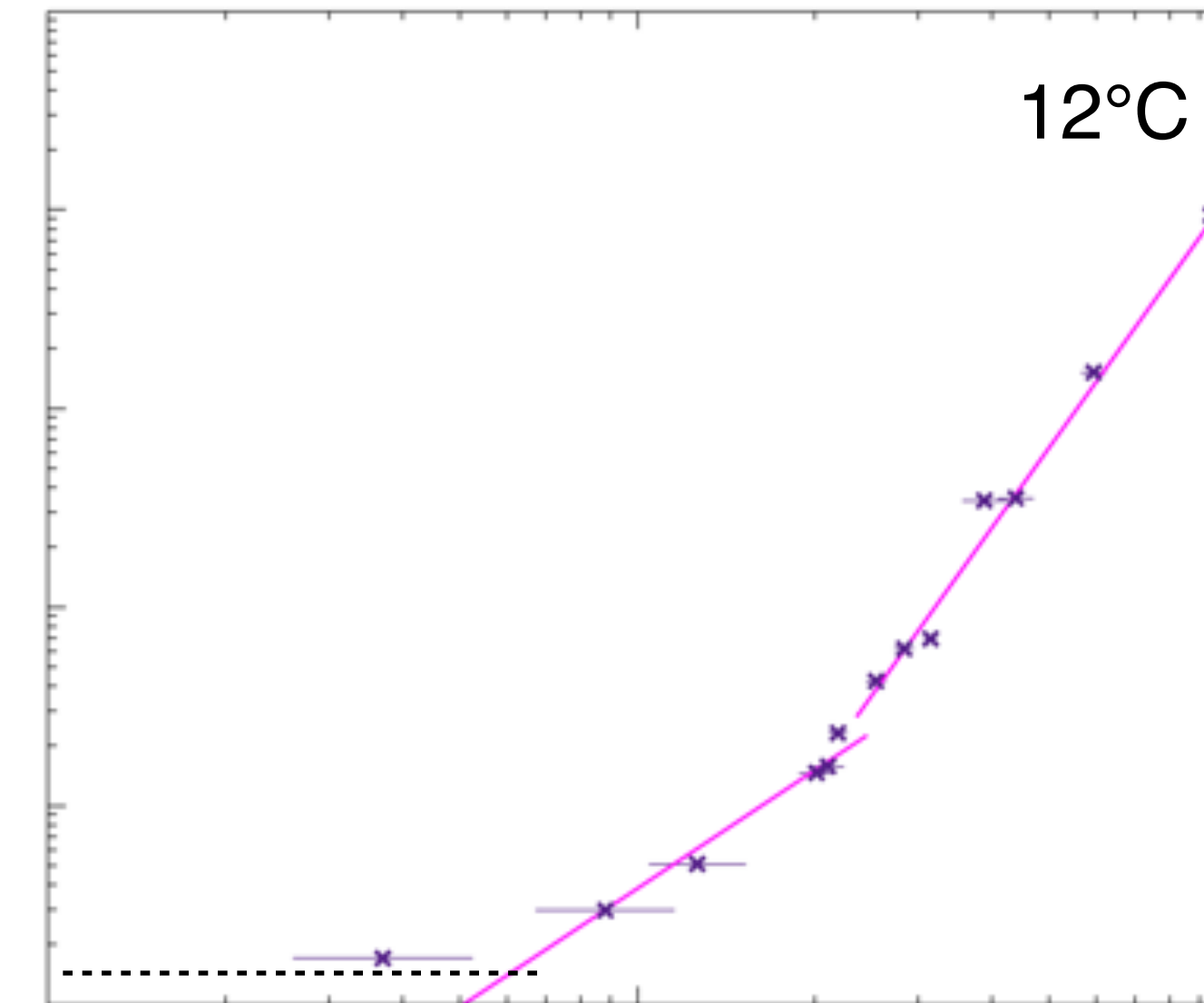
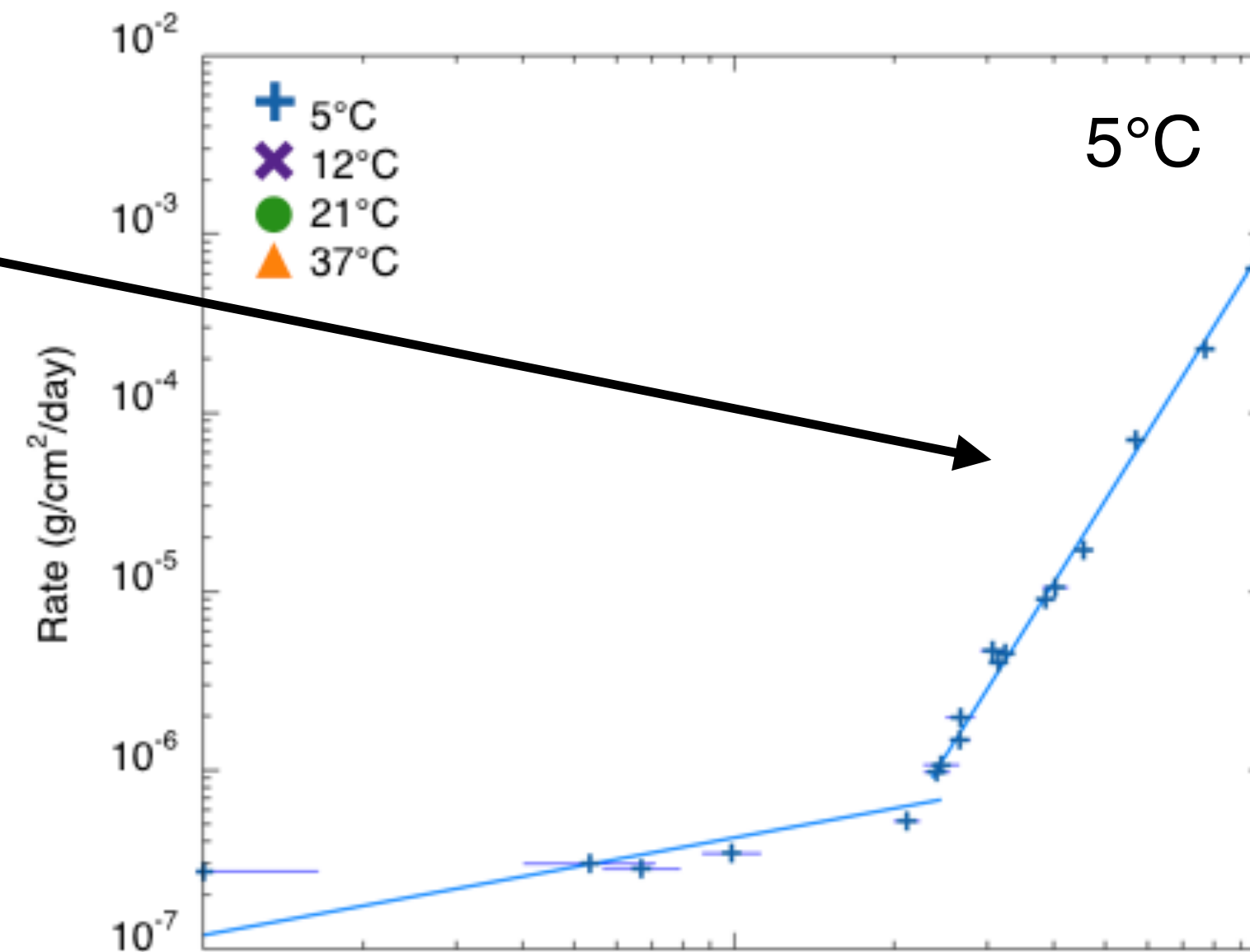
There are Distinct Breaks in Slope that Give Rise to the ‘Curvature’ in Other Rate Laws



Homogeneous
Etch Pit Removal

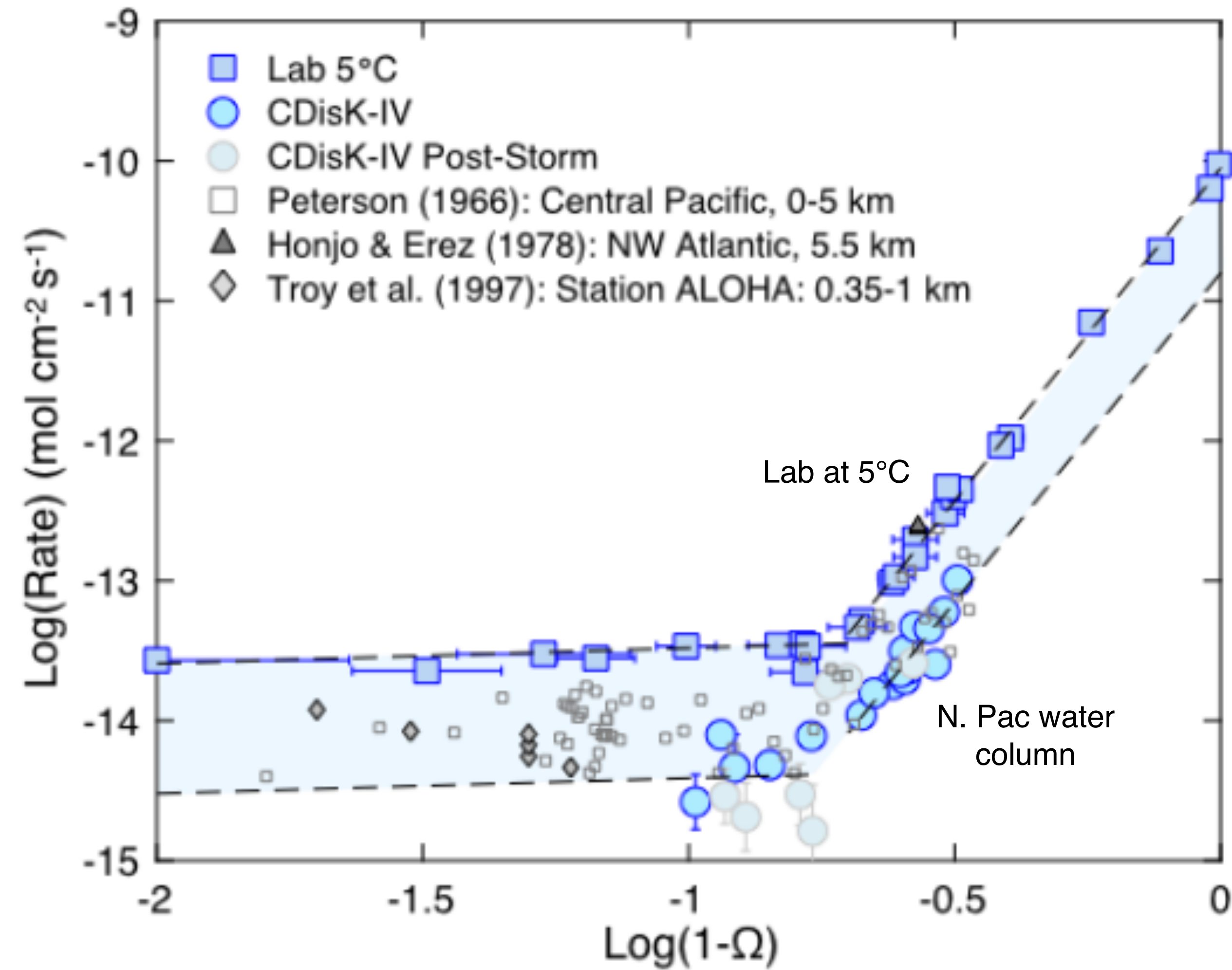


Defect Assisted
Etch Pit Removal

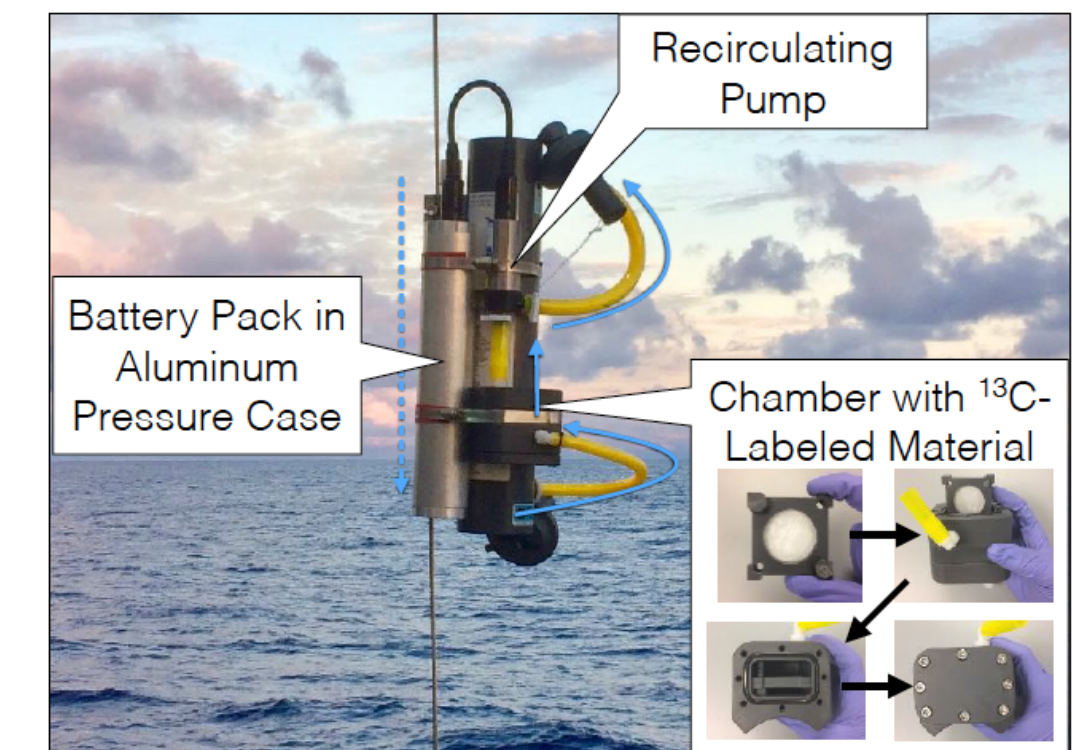
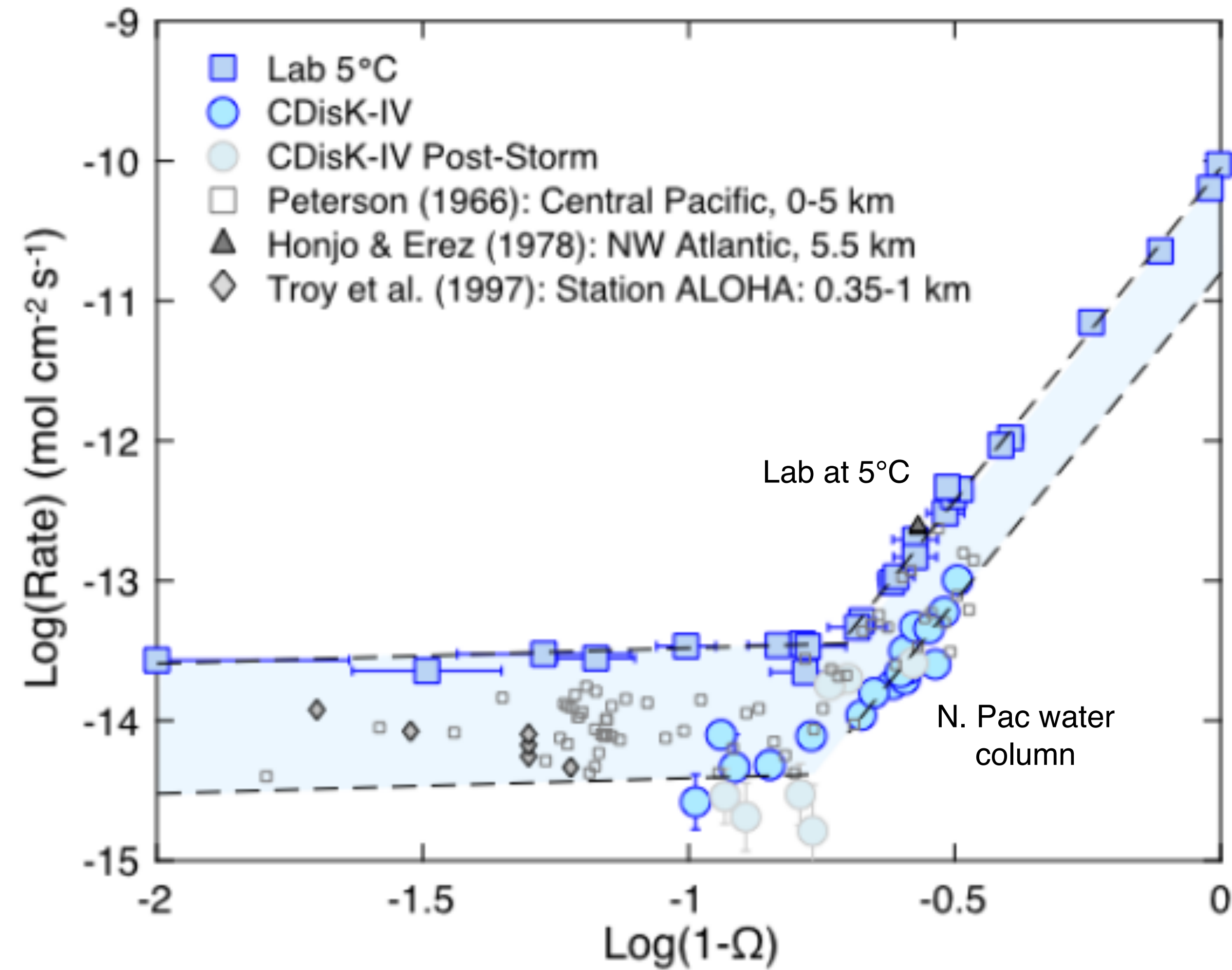


Step Edge Retreat

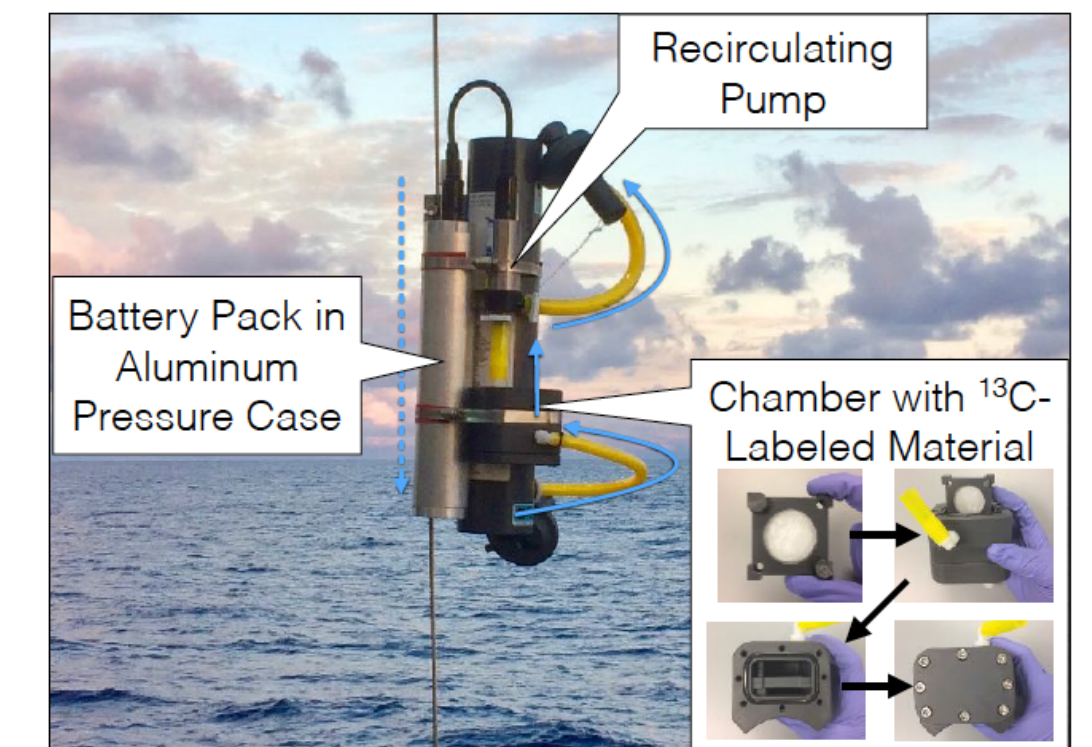
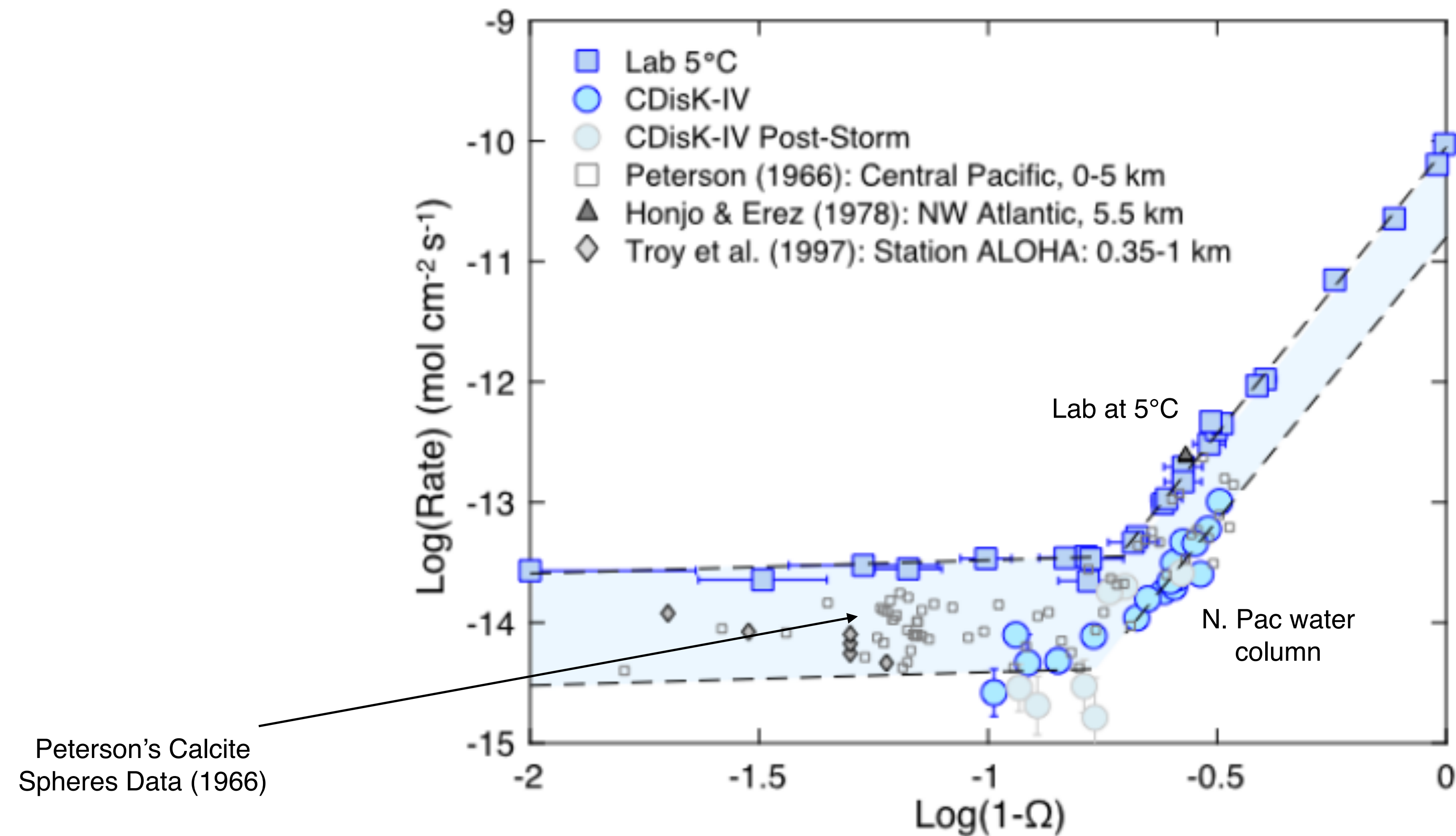
The Real Water Column has the Same Rate Law as Our Lab Data



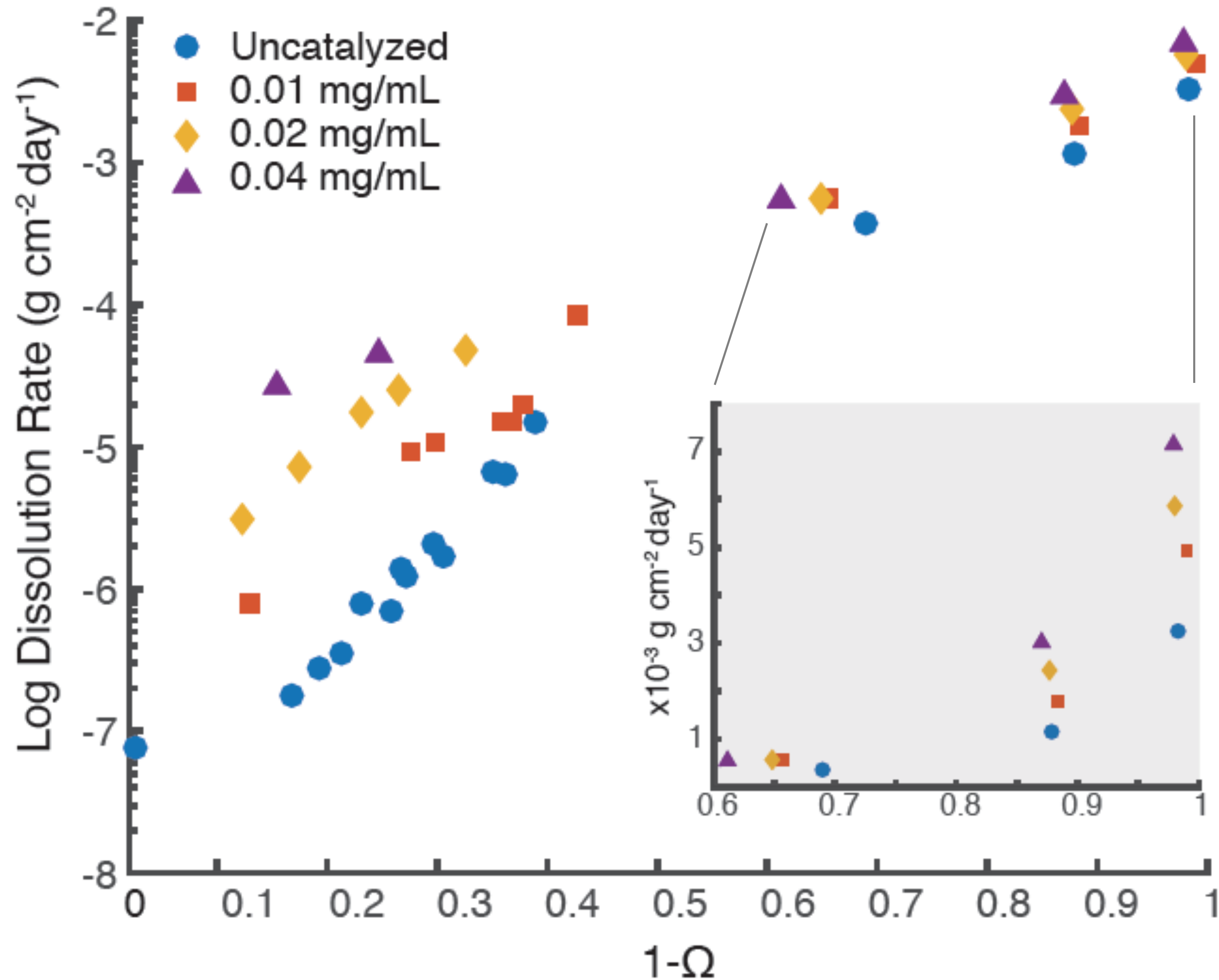
The Real Water Column has the Same Rate Law as Our Lab Data



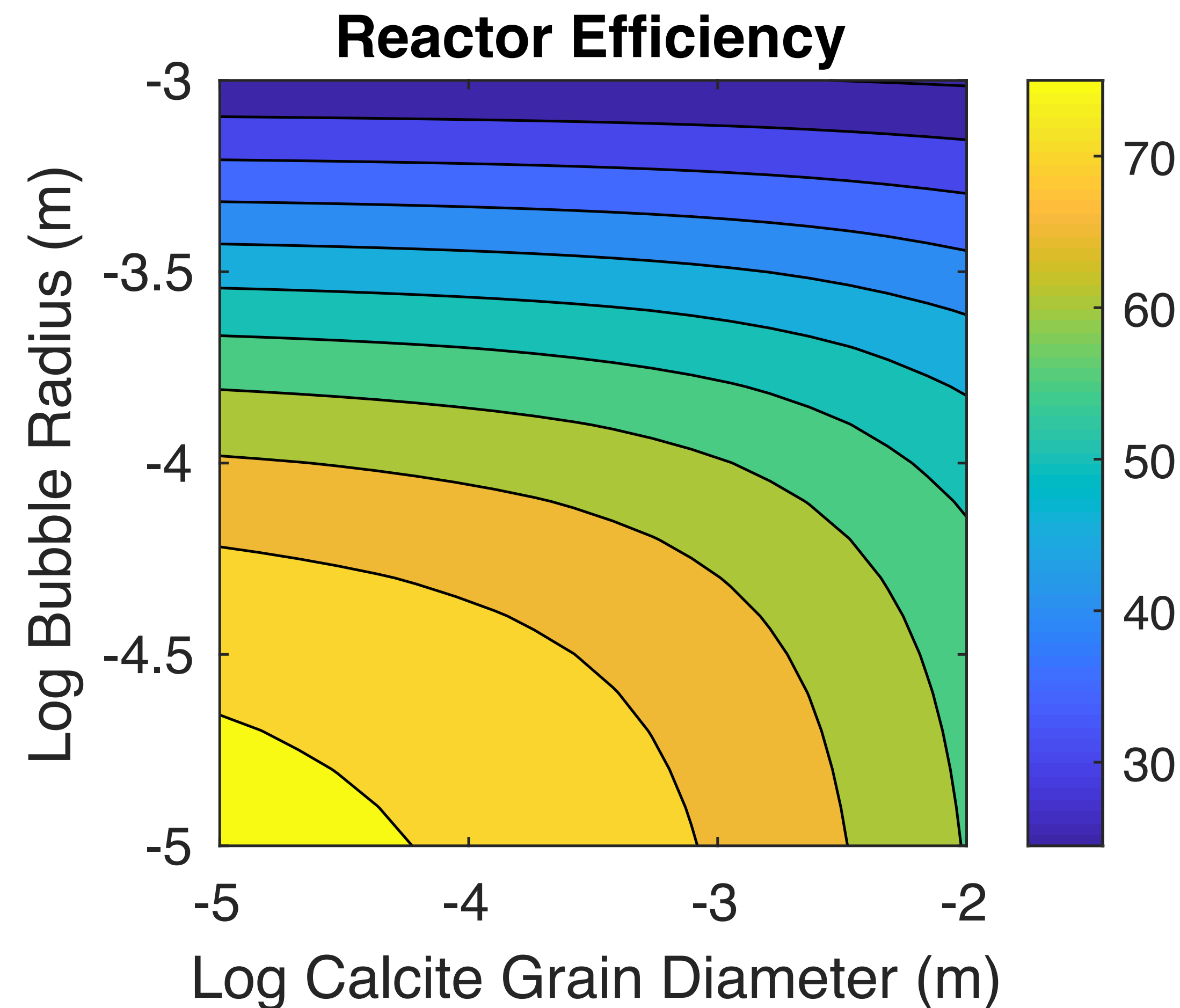
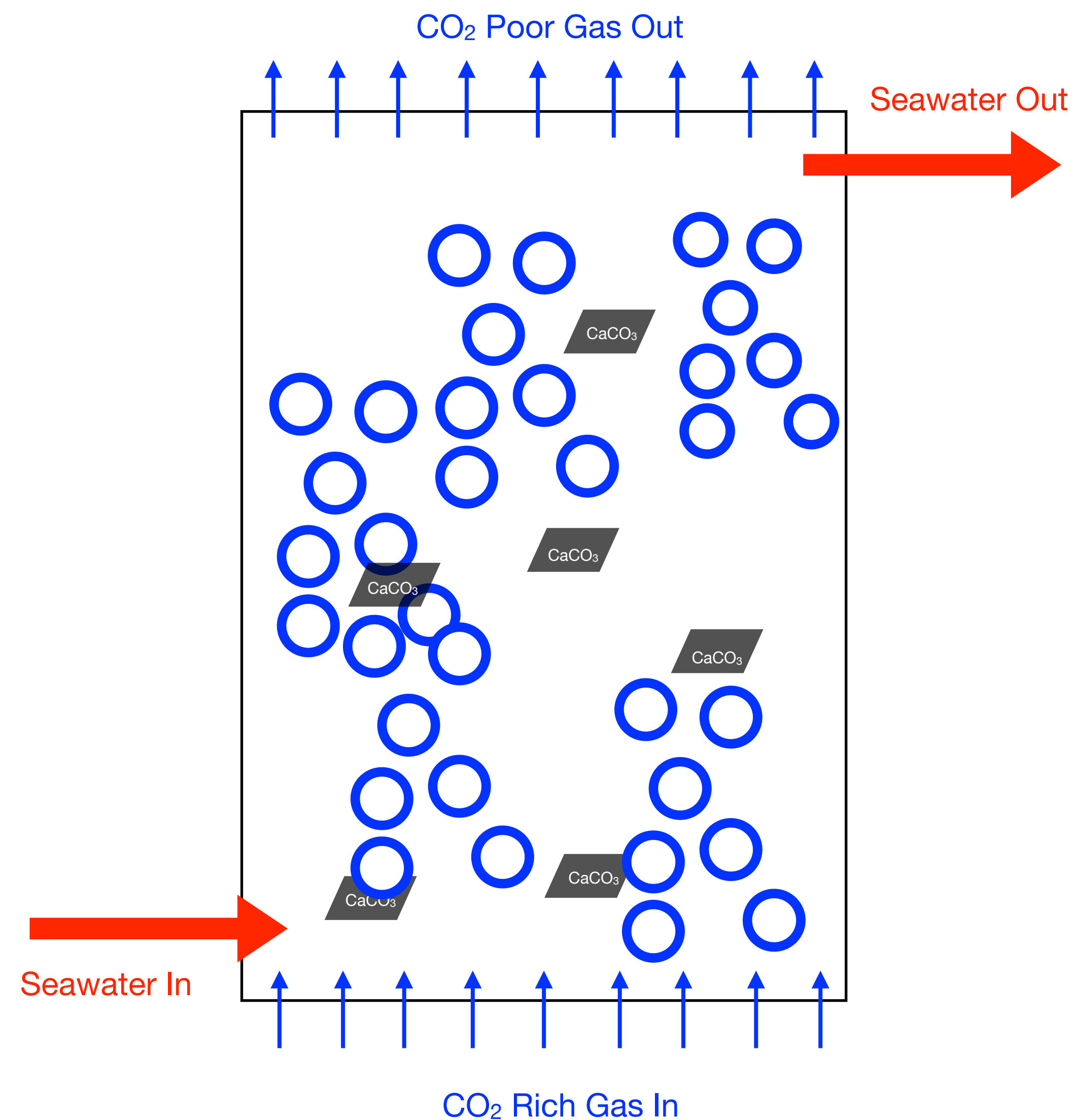
The Real Water Column has the Same Rate Law as Our Lab Data



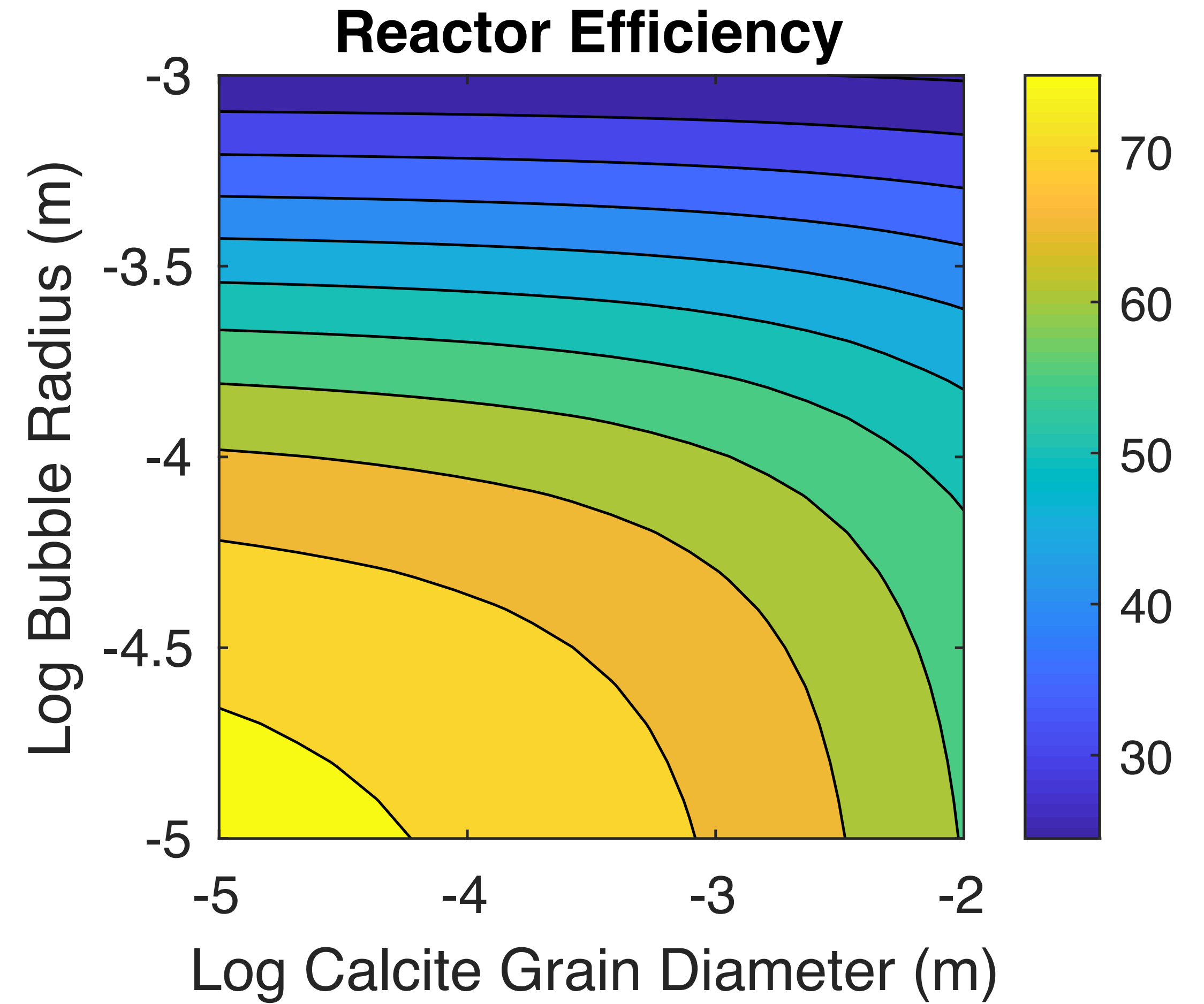
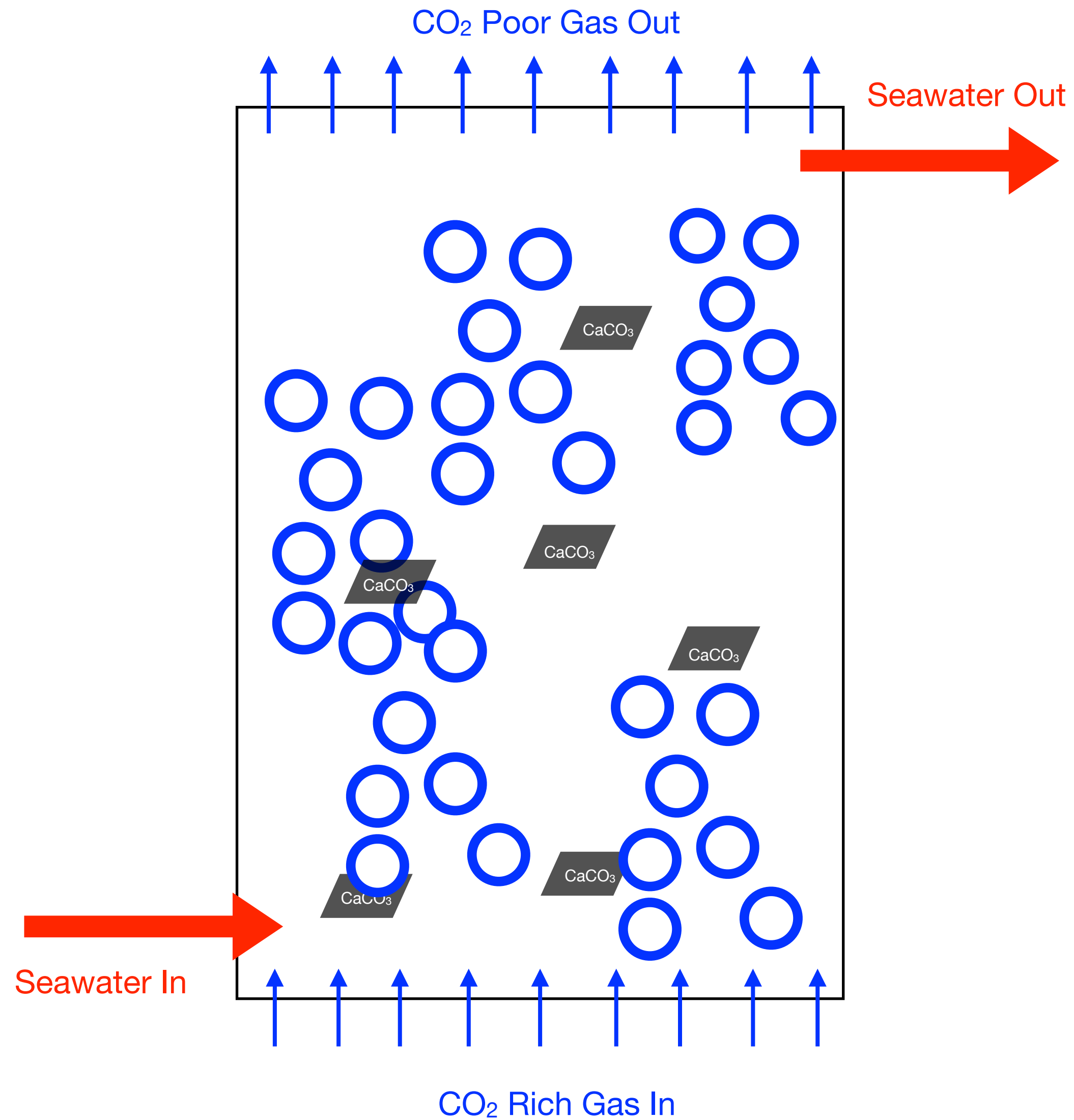
It is Possible to Find Catalysts for CaCO_3 Dissolution Too



We Have Made Reactors with 5% CO₂ Input...



We Have Made Reactors with 5% CO₂ Input...



...But What About the Output Once in the Environment?



LOW CARBON
VENTURES

Operating and Scale-Up Considerations of Chlor-Alkali Technology for Ocean CDR

NASEM Ocean CDR Workshop
Dr. Robert L. Zeller, VP Technology

www.oxylowcarbon.com
January 27, 2021

Ocean CDR via Electrolysis

Baseline to the existing Chlor-Alkali Industry

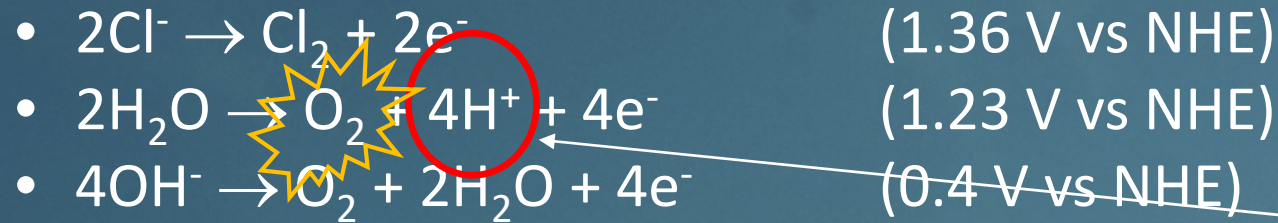
- OxyChem is a leading Chloro-Vinyls manufacturing company
 - Chlor-Alkali roots started in 1906 in Niagara Falls, NY
 - Salt and Water, Power and People: A Short History of Hooker Electrochemical Company by Bjarne Klaussen, Robert E. Thomas, and R. Lindley Murray (1955)
 - Vinyl roots started with its discovery by BF Goodrich
 - A man of ideas: the biography of Dr. Waldo Lonsbury Semon, inventor of plasticized polyvinyl chloride by Elizabeth Smith (1993)
- Total US Capacity of NaOH/KOH at ~13 million tons per year*
 - Corresponds to ~6.5 million metric tons CO₂ per year as Na₂CO₃
 - Corresponds to ~30 million metric tons of additional carbonate available from bicarbonate
- Existing alkali supply useful to derisk technology development
 - Need a “willingness to pay”
 - Historically cyclical with ranges from ~\$200 to over ~\$1000 per dry ton NaOH

*Reference: The Chlorine Institute, *Pamphlet 10, North American Chlor-Alkali Industry Plants and Production Data Report for 2019* (Dec 2020)
www.chlorineinstitute.org

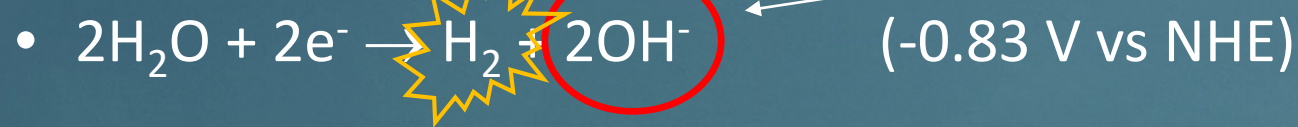
Chlor-Alkali Basics

Reactions

- Anode Reactions



- Primary Cathode Reaction



- Overall Reaction for NaCl Feed



A separator is needed between the anode compartment and cathode compartment

Chlor-Alkali Considerations

Planning for Ocean CDR

- Sea water can be used as a feedstock in traditional chlor-alkali technology
 - Requires concentration (from ~3.5% to near saturation or ~25%)
 - Brine purification essential
 - Impurity levels of ppm to ppb levels required (technology specific, diaphragm less stringent vs membrane)
 - TOC removal needed to avoid halogenated hydrocarbon by-products
 - Concentration and purity necessary for high current density operation for CAPEX efficiency
 - Co-location opportunity with desalination plants (i.e., concentrated reject brine typically at 7 wt%)
- Chlorine management is a key for plant siting
 - Chlorine is designated a Highly Hazardous Chemical (HHC) and is a Toxic Inhalation Hazard (TIH)
 - Major chlorine uses include water treatment, medicines, vinyls, polyurethanes, epoxy-resins, Teflon[®], Neoprene[®], TiO₂, refrigerants, foam blowing agents, and muriatic acid (wet HCl)
 - Chlorine drying, compression, purification, and liquefaction is capital intensive
 - Chlorine rail transport increasingly expensive and regulated

Chlor-Alkali Considerations

Closed Loop Chlorine Management for Ocean CDR

- Production of HCl (muriatic acid) via a managed thermal reaction of Cl_2 and H_2 is well known (called a HCl synthesis unit or HCl “burner”)
 - H_2 / Cl_2 fuel cell concepts studied for decades but not commercialized due to significant materials and technical challenges
- House (2007) proposed using muriatic acid to digest a land-based silicate rock source (e.g., MgSiO_3) to produce MgCl_2 and SiO_2^* , and recycle back to the ocean
 - Alternative to olivine weathering concepts of using waves and particle attrition
- Chlor-Alkali plants are capital intensive and highly integrated - intermittent operation leads to poor economics and process safety issues
 - Reliable 24/7/365 power key
 - Current C/A power sources include emissions-free power such as hydropower and nuclear; low carbon power such as natural gas combined cycle cogeneration; note grid continues to “green” with renewables

*Reference: House et al., *Electrochemical Acceleration of Chemical Weathering as an Energetically Feasible Approach to Mitigating Anthropogenic Climate Change*, Environmental Science & Technology, **41**, 24 8464-8470 (2007)

Chlor-Alkali Key Take-Aways

Application to Ocean CDR

- Brine quality (concentration and purity) key for efficient and safe operation
- Managing chlorine co-product most challenging and a key to success
- Reliable 24/7/365 power important for reliable and safe operation
- Brine/sea water electrolysis without a separator is futile for ocean CDR and potentially dangerous



LOW CARBON

V E N T U R E S

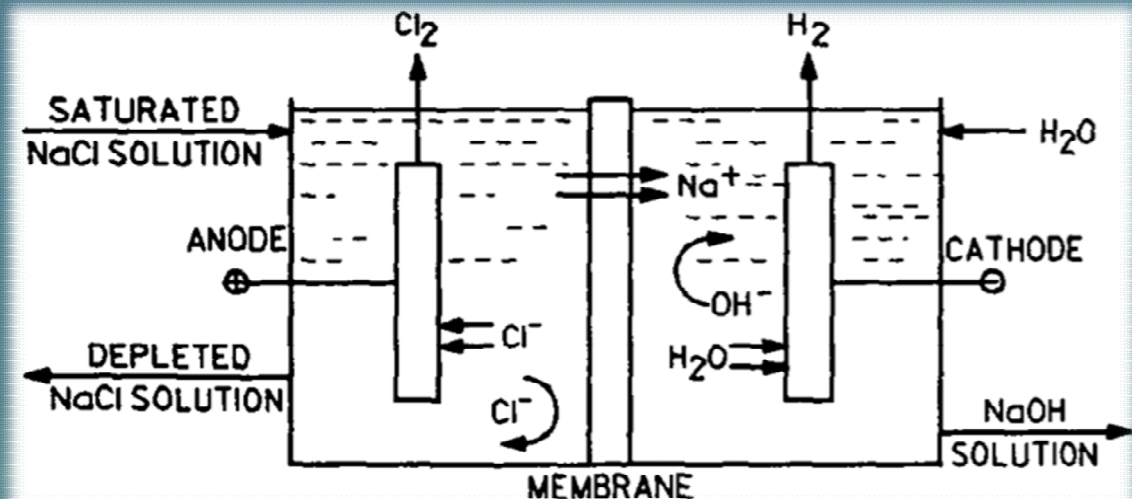
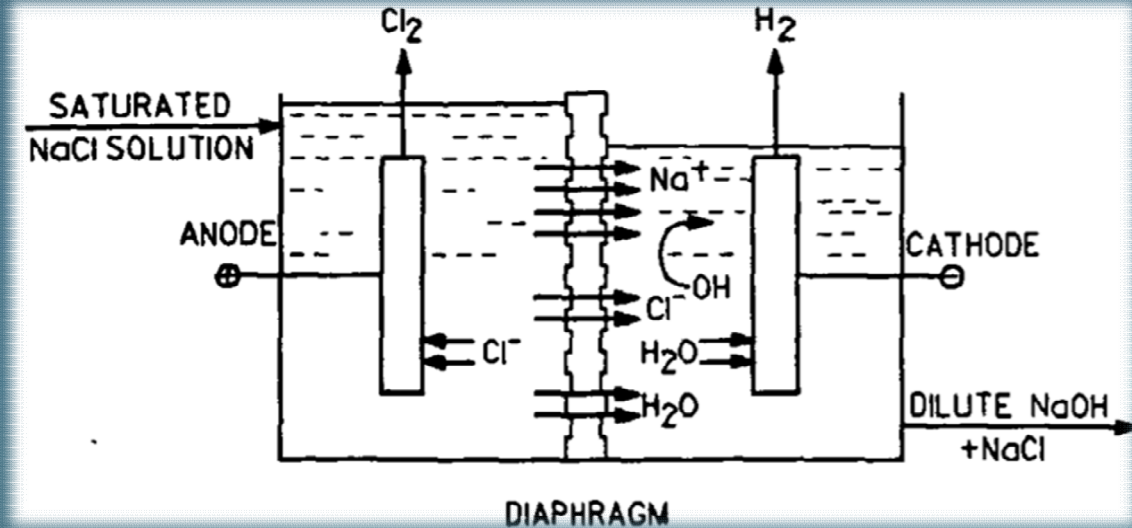
Building the World's Largest Direct Air Capture Plant

Learn more at
www.oxylowcarbon.com
www.1pointfive.com

Chlor-Alkali Basics

Technology Options

- Two chlor-alkali technologies operating today
 - Separators: Diaphragm and Membrane
 - Diaphragm likely best choice for Ocean CDR
- Cell performance tied to feed brine quality
 - Start with nearly saturated brine
 - Solution-mined or solid (mined/solar)
 - Primary Brine Treatment (precipitation of Ca/Mg/Fe to ppm levels)
 - Secondary Brine Treatment (Ion Exchange to ppb levels)
 - Purer brine equals higher current density equals lower CAPEX



Clarke's Three Laws

The Hope for Ocean CDR

British science fiction writer Arthur C. Clarke formulated three adages known as Clarke's Three Laws

1. When a distinguished but elderly scientist states that something is possible, he is almost certainly right. When he states that something is impossible, he is very probably wrong.
2. The only way of discovering the limits of the possible is to venture a little way past them into the impossible.
3. Any sufficiently advanced technology is indistinguishable from magic.

Some thoughts on novel CDR

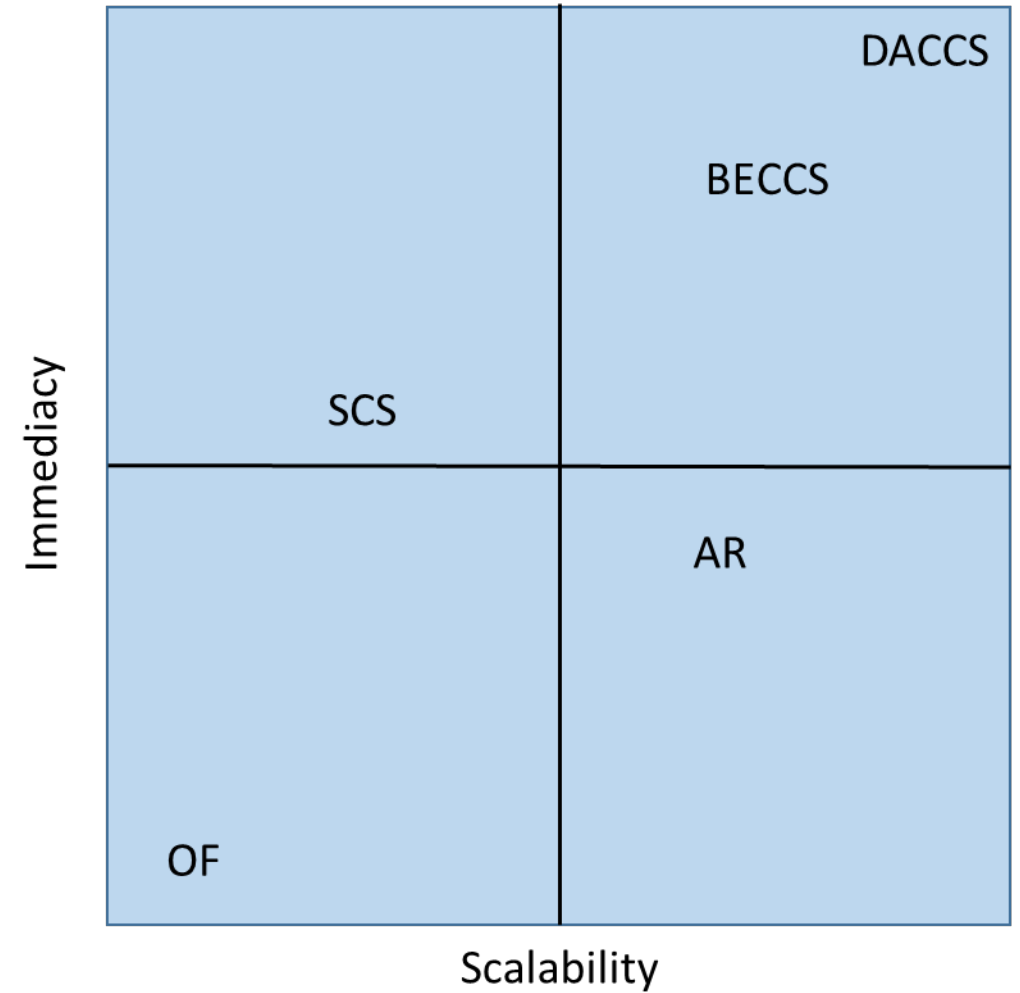
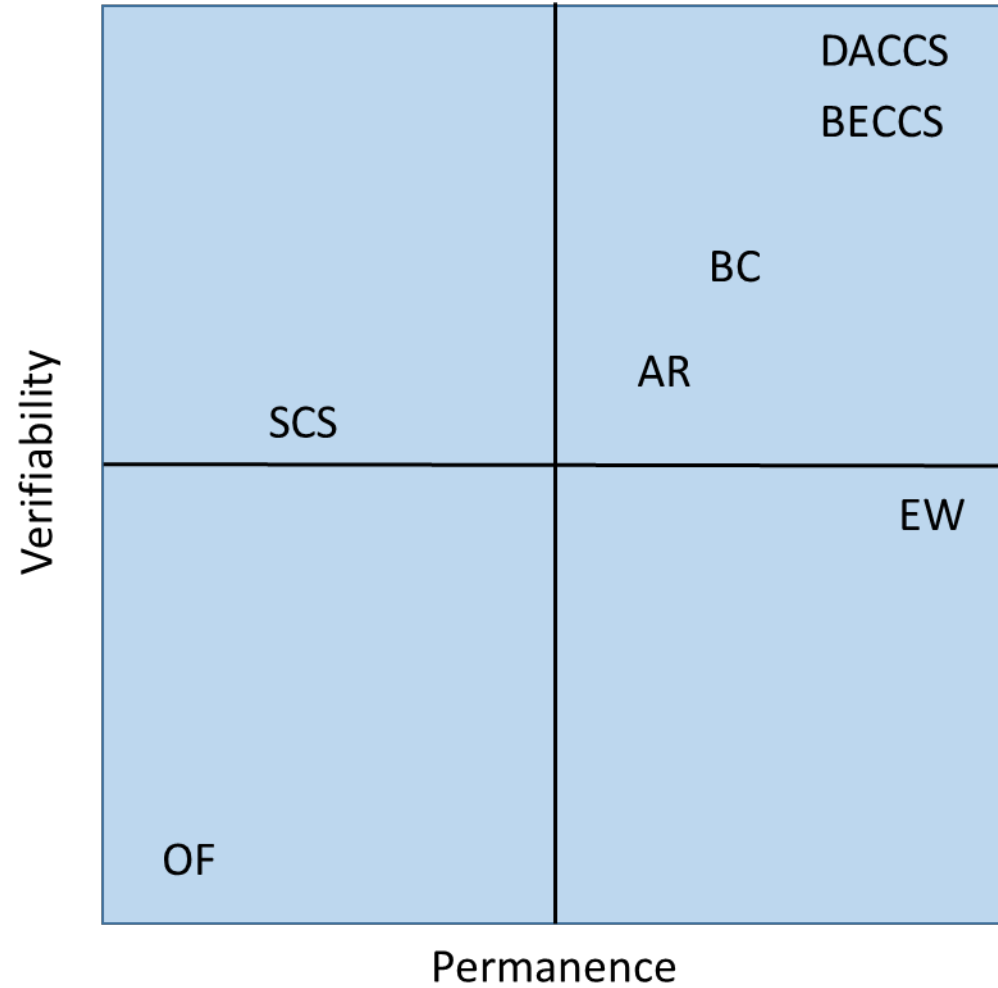
Niall Mac Dowell

Imperial College London

niall@imperial.ac.uk

@niallmacdowell

Lenses to consider when evaluating GGR options



Key principles of credible GGRs – all links to MRV

1. Permanence
2. Verifiability
3. Scalability
4. Immediacy
5. Auditability
6. Broader environmental impacts
7. Accountability

BREAK

We will resume at 3:00pm EST



10KV 10.7KX 1U 1321

Large-scale ocean alkalization

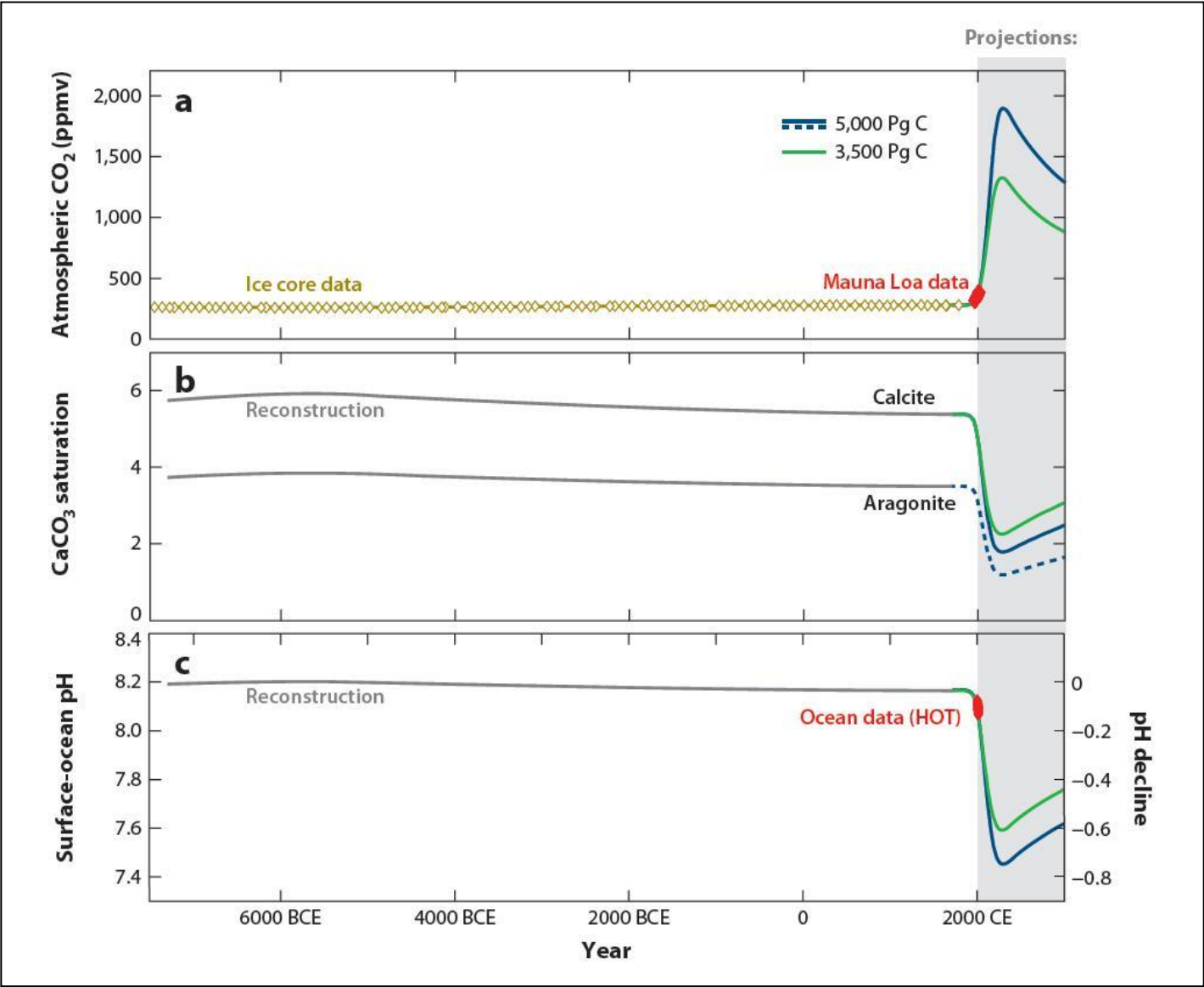
Richard E. Zeebe

SOEST, Hawaii



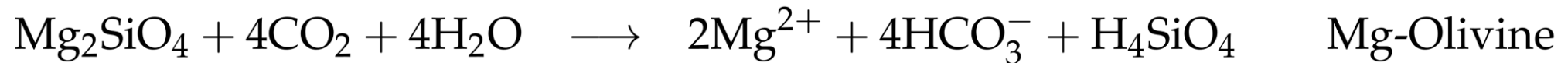
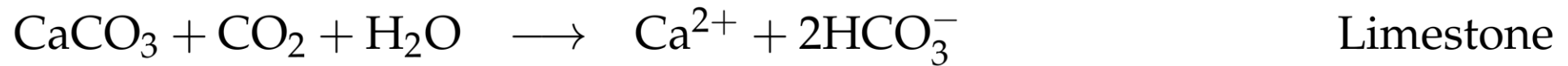
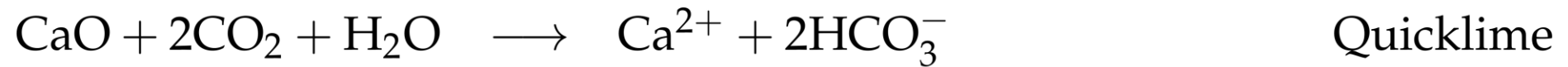
Image credits: B. Rost, HJ Spero, V. Fabry

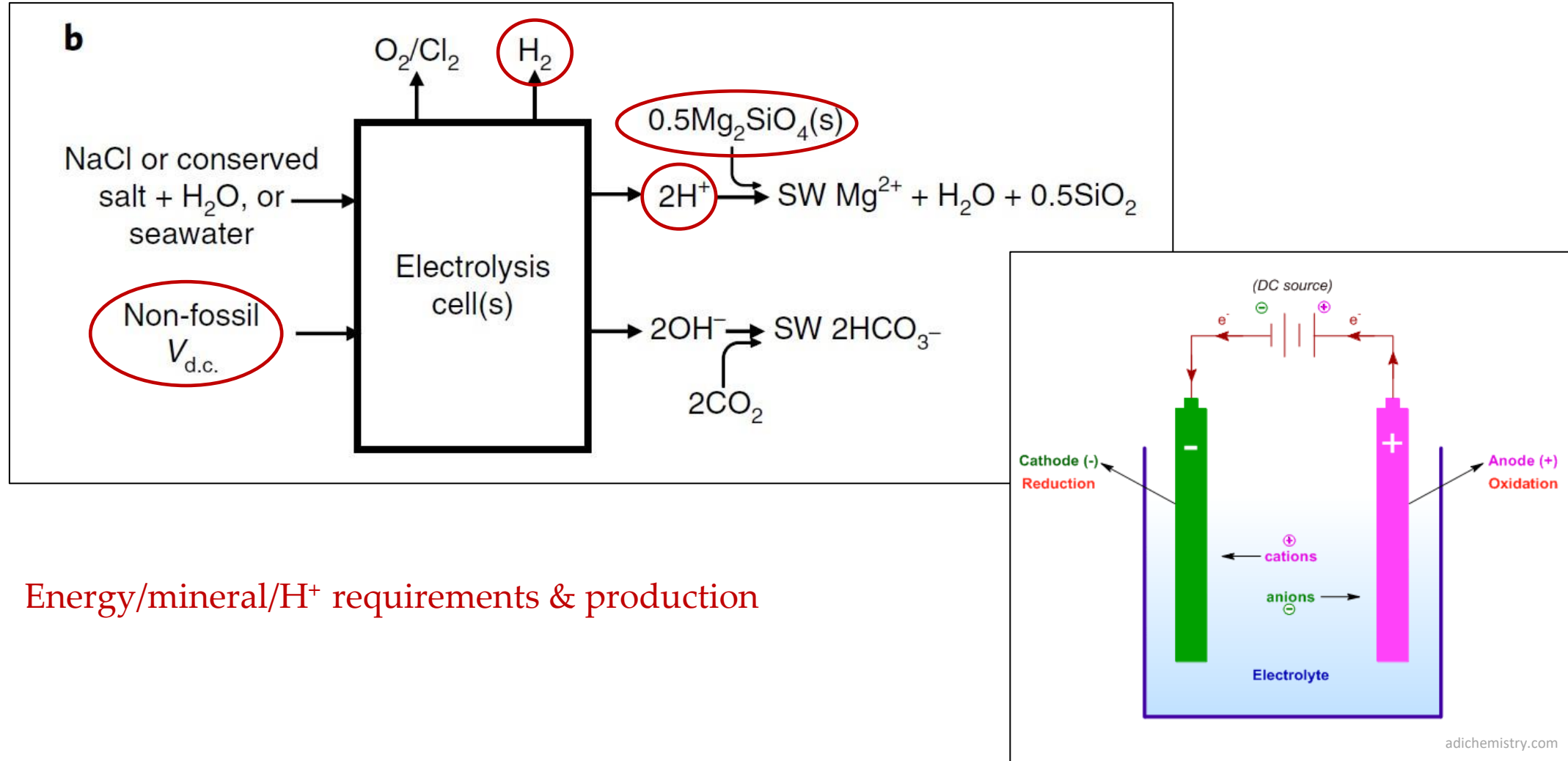
Zeebe (Ann. Rev., 2012)



Scale of operation controlled by mole-to-mole ratio

(mineral element : C sequestered = 1 : x , x order of magnitude 1).



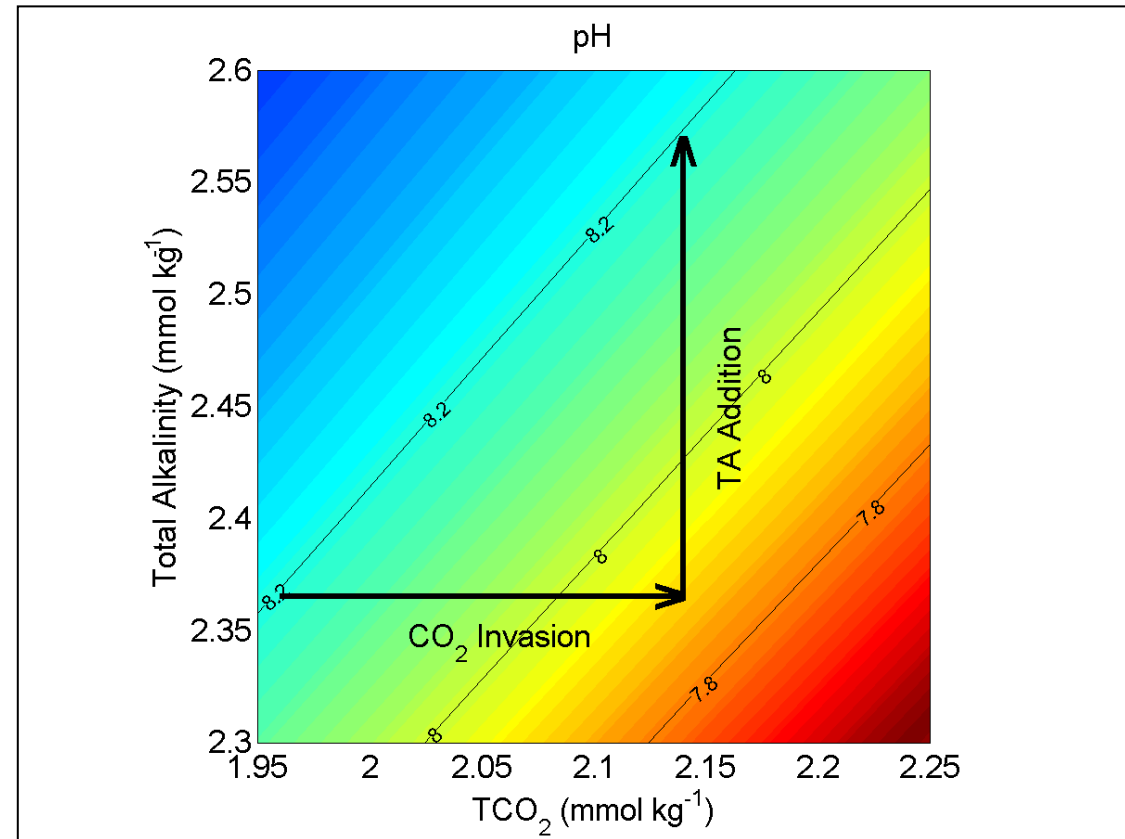


Energy/mineral/H⁺ requirements & production

→ Stabilize $p\text{CO}_2$, restore pH

- **Important: Evaluation**

- Basic research (geochemistry, biology, ...)
- Large-scale projections
- Technological, economic feasibility
- Ecological impacts
- Public acceptability
- etc.



Zeebe & Wolf-Gladrow (2001)

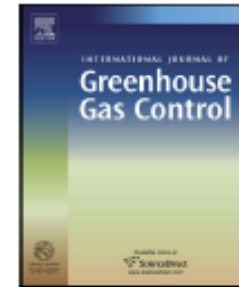
International Journal of Greenhouse Gas Control 17 (2013) 183–188



Contents lists available at SciVerse ScienceDirect

International Journal of Greenhouse Gas Control

journal homepage: www.elsevier.com/locate/ijggc



Assessing possible consequences of ocean liming on ocean pH, atmospheric CO₂ concentration and associated costs

François S. Paquay*, Richard E. Zeebe

Department of Oceanography, University of Hawaii at Manoa, 1000 Pope Road, Marine Science Building (MSB) 205, Honolulu, HI 96822, USA



Liming penalties → carbon capture, solar thermal production, etc.

Geosci. Model Dev., 5, 149–166, 2012
www.geosci-model-dev.net/5/149/2012/
doi:10.5194/gmd-5-149-2012
© Author(s) 2012. CC Attribution 3.0 License.

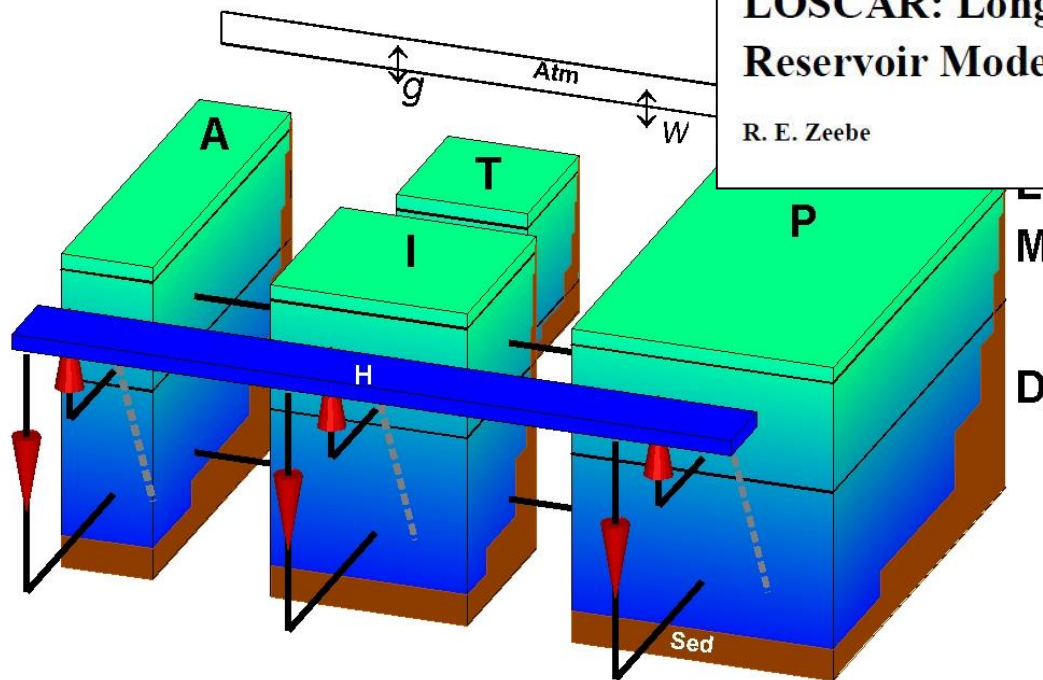


Geoscientific
Model Development

loscar.model@gmail.com

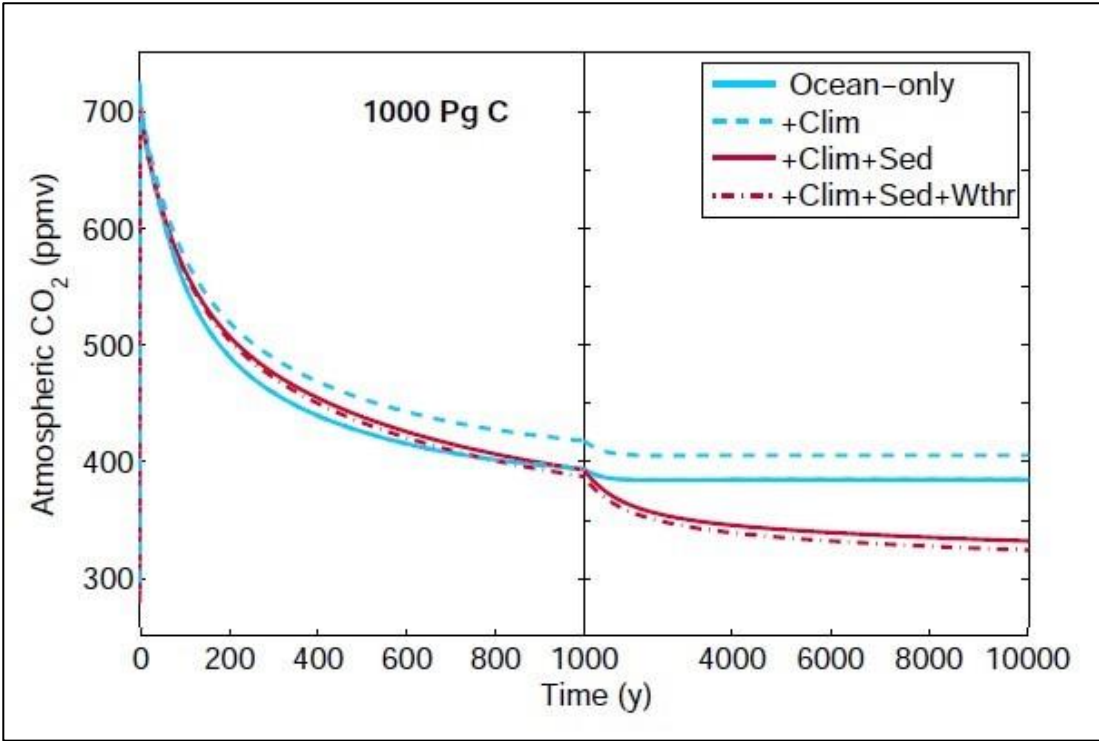
LOSCAR: Long-term Ocean-atmosphere-Sediment Carbon cycle Reservoir Model v2.0.4

R. E. Zeebe



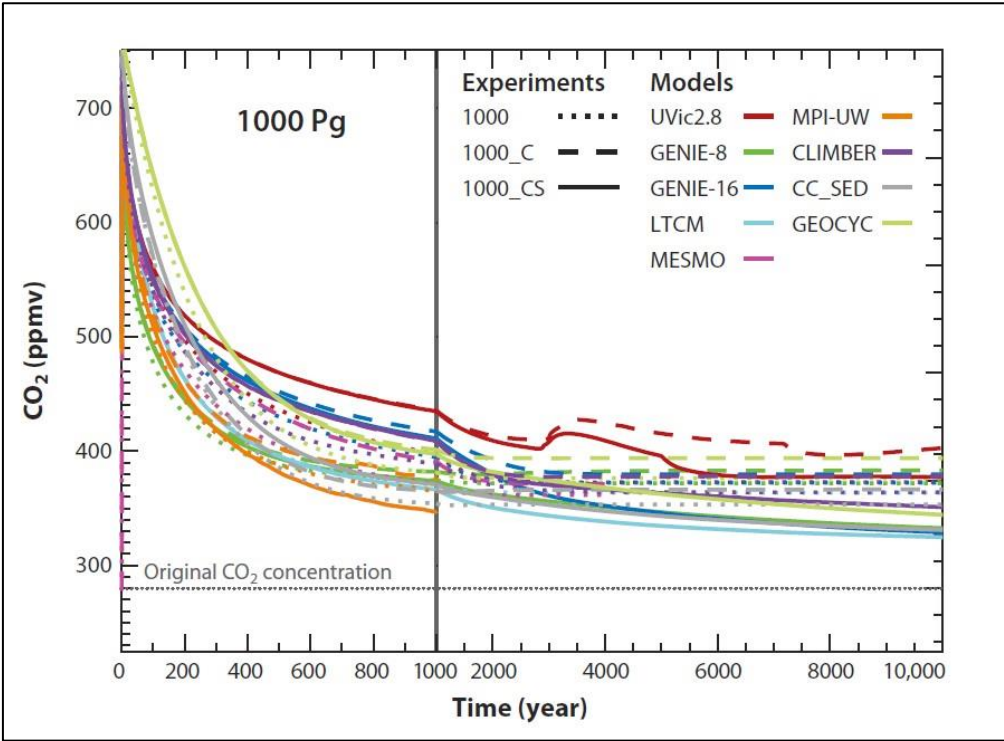
Zeebe et al. (2008, 2009); ...; Zeebe (GMD, 2011)

LOSCAR

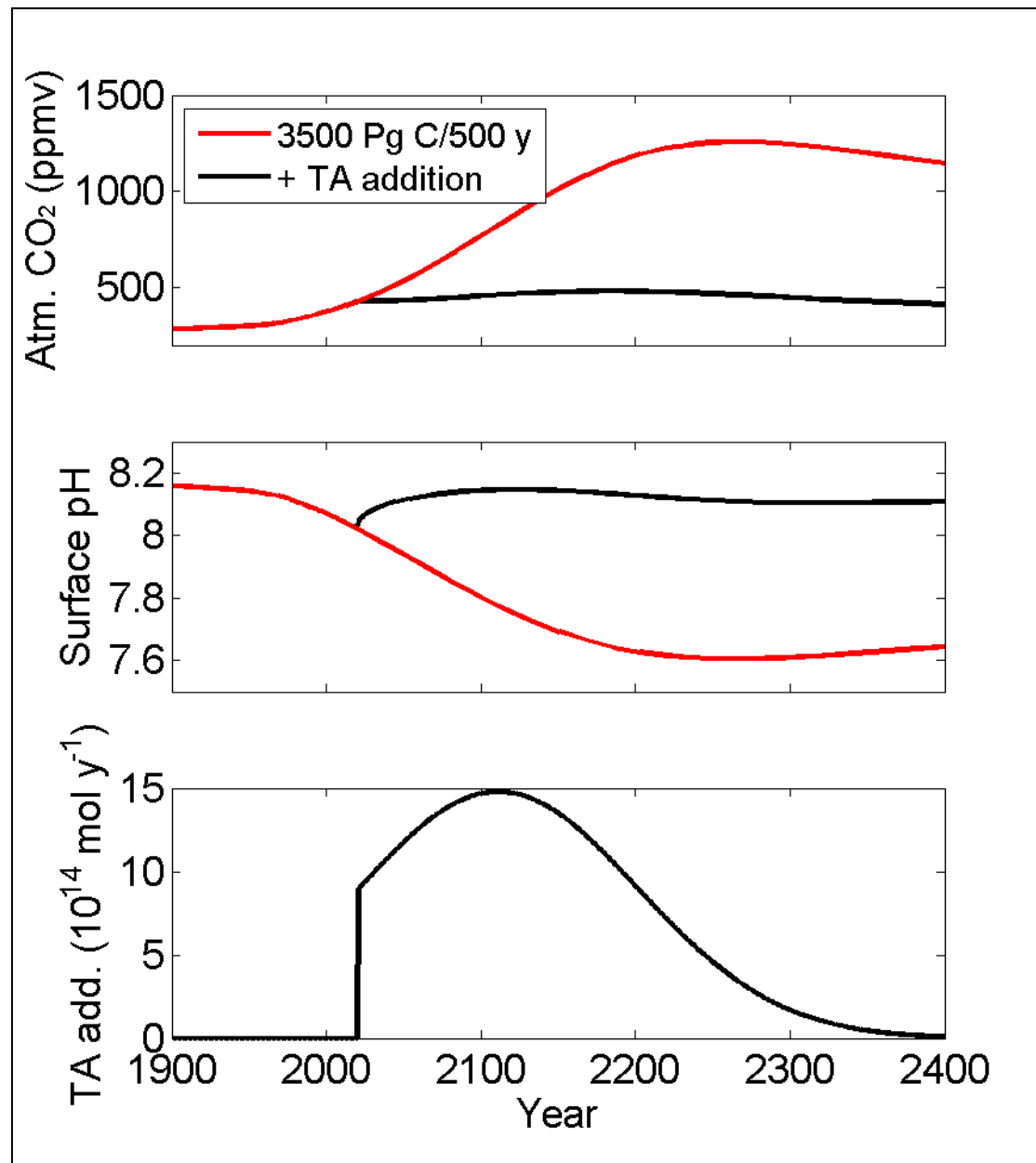


Zeebe (GMD, 2011)

EMICs & GCMs



Archer et al. (2009)

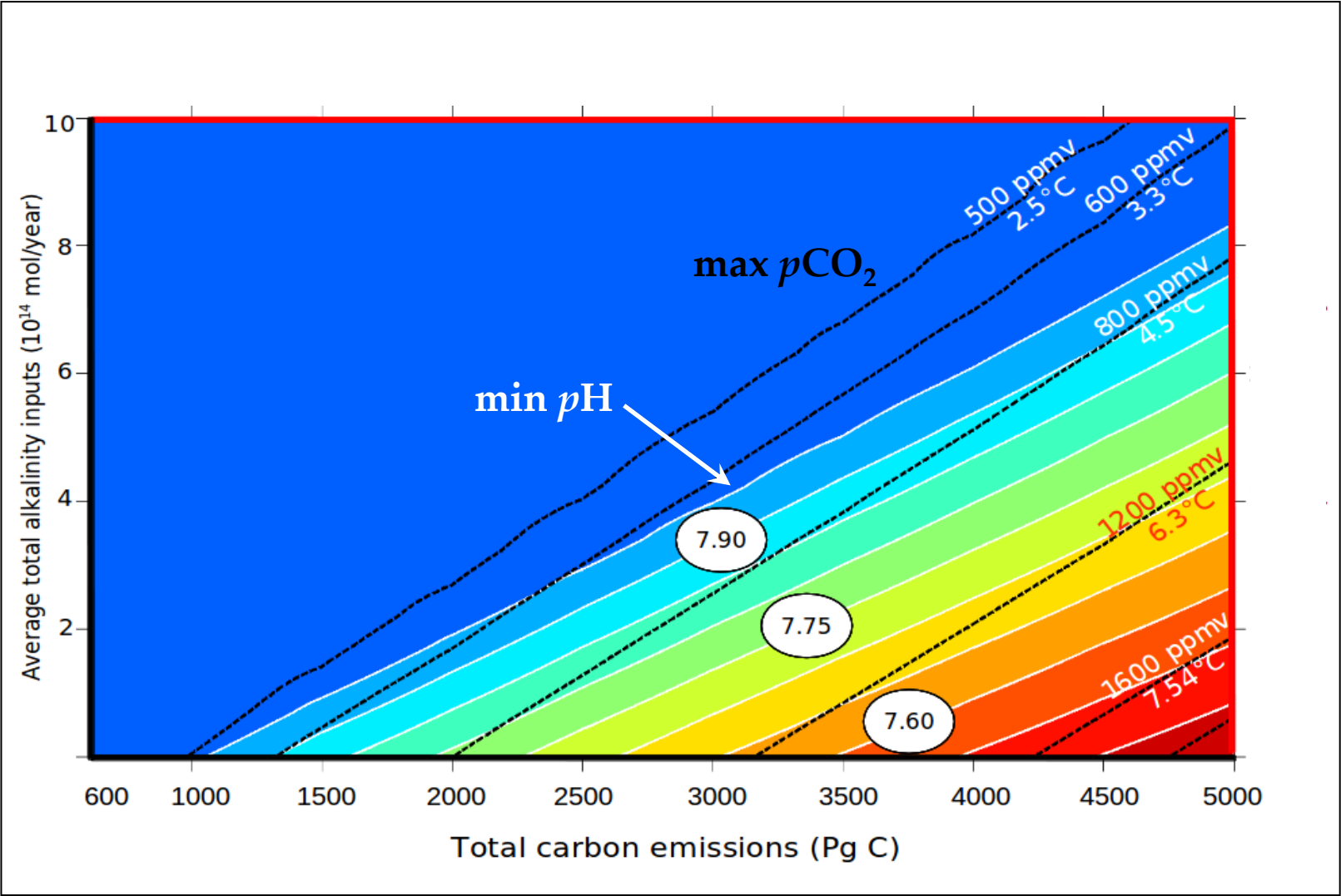


Paquay & Zeebe (2013)

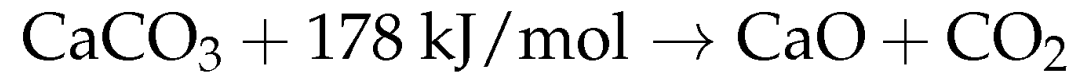
Average required lime production ($\frac{1}{2}\text{TA}$) $\simeq 3.7 \times 10^{14} \text{ mol y}^{-1}$



30 Gibraltar "Limestone"-Rocks annually.



Paquay & Zeebe (2013)

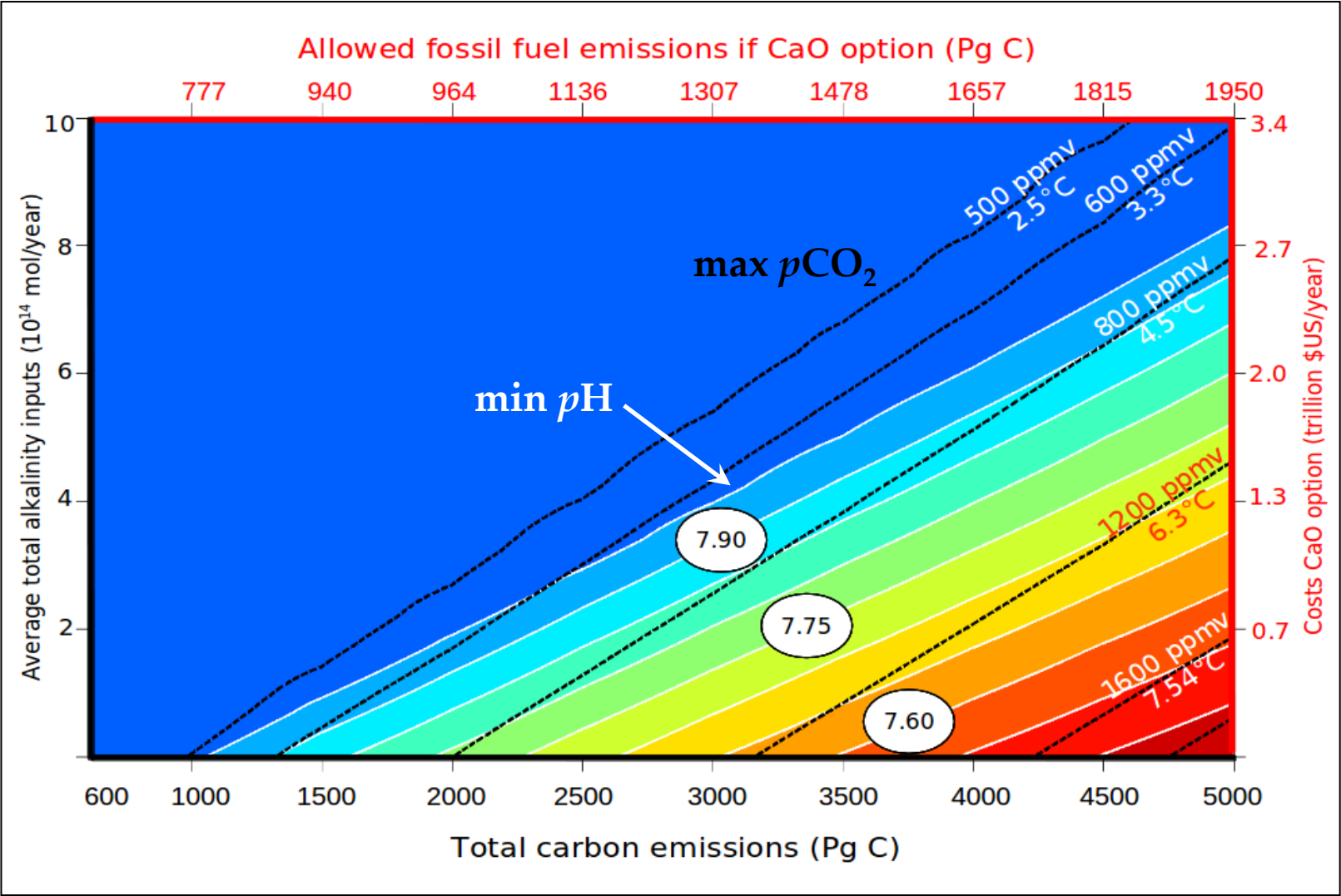


Energy

Emissions



Paquay & Zeebe (2013)



103-144 \$US
per ton CO₂

Table 3. Comparison of Electrical and Thermal Energy Requirements and Financial Costs of Ocean Alkalinity Carbon Storage Technologies^a

Technology	GJ tCO ₂ ^{-1b}		US\$ tCO ₂ ^{-1b}
	Electricity	Thermal	
Ocean liming (Oxy-fuel flash calciner: limestone)	1.3	4.8	126
Ocean liming (Endex CFC: limestone)	-0.1	5.5	100
Ocean liming (Oxy-fuel flash calciner dolomite)	0.7	3.2	95
Ocean liming (Endex CFC: dolomite)	-0.1	4.2	72
Ocean liming (Solar calciner: limestone)	0.4	0.6 ^c	159
Electrochemical weathering (Mg-Silicate)	5 ^d		86–154
Electrochemical weathering (CaCO ₃)	5 ^d		14–190
Electrochemical weathering (NaOH production)	3–18		–
Direct carbonate addition to upwelling regions	<0.1	3.6	–
Mineral carbonation/ocean liming	2.2	5.0	
Accelerated weathering of limestone			10–40
Enhanced weathering	0.1–8.4	0.8–4.2	20–600
Direct air capture	7.5–10		100–1000
Typical cost of “conventional” CCS	6.7		30–100
Energy cost of decommissioning coal	3	10	

^a[Renforth et al., 2013; Renforth and Kruger, 2013 and references therein].^bPer net ton of carbon dioxide sequestered.^cAdditional thermal requirements from fossil fuels.^dPer ton of CO₂ extracted rather than net sequestration.

Examples:

...

Harvey (2008)

Henderson et al. (2008)

Paquay & Zeebe (2013)

Ilyina et al. (2013)

Koehler et al. (2013)

Keller et al. (2014)

Hauck et al. (2016)

Feng et al. (2016)

Ferrer & Ilyina et al. (2016)

Feng et al. (2017)

Keller et al. (2018)

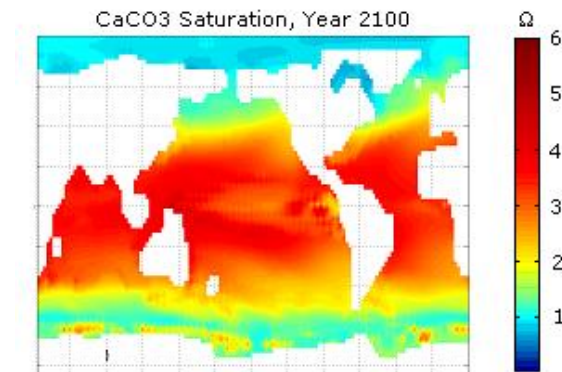
Lenton et al. (2018)

Ferrer et al. (2018)

Koehler (2020)

...

- Most remain theoretical (omit feasibility).
- Carbon Dioxide Removal Model Intercomparison Project uses large TA input of $0.14 \text{ Pmol TA/y} \approx 5 \text{ Pg/y}$ Ca(OH)_2 or Mg_2SiO_4 .
- However, very few mention technological and/or economic feasibility.
- Koehler (2020): “The amount of material necessary for a complete sequestration of all anthropogenic emissions is huge.”



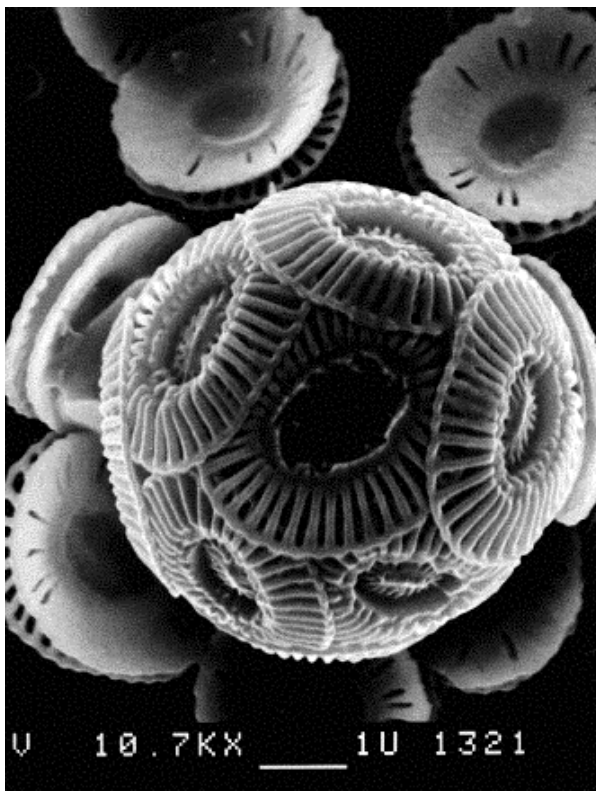


Image credits: B. Rost, HJ Spero, V. Fabry

Biogeochemical Impacts & Research Funding

Commercial sea urchin control:

“Quicklime [] has been used to control starfish in oyster beds and sea urchins in commercially harvested kelp beds. It releases heat when combined with water and kills echinoderms by causing epidermal lesions that permit bacteria to enter the coelomic fluid.” (Bernstein and Welsford, 1982).



Takumi Sasaki

100% mortality in *Crangon septemspinosa* (sand shrimp) after 96h in treatments with $\text{Ca}(\text{OH})_2$ concentrations >500 mg/L = 6.8 mmol/L, pH > 9.5 (Locke et al., 2009).

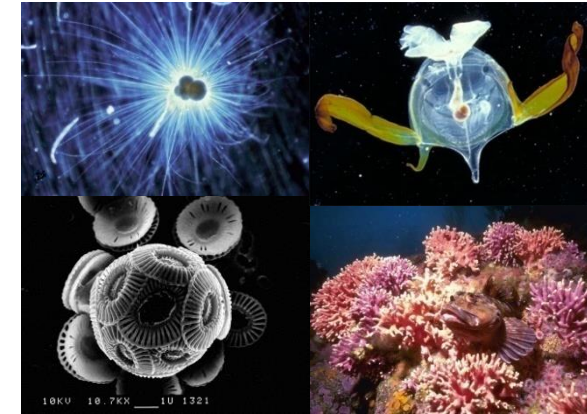


Slight respiratory alkalosis and hyperkalemia in *Carcinus maenas* (shore crab) after 6h in treatments with $\text{Ca}(\text{OH})_2$ concentrations 0.54 mmol/L, pH = 8.77 (Cripps et al., 2013).



Corals, calc. red algae, etc. (see Albright et al, 2016; Gim et al., 2018; Gore et al., 2019, ...).

- **Biogeochemical assessment would have to include comprehensive organism studies**
- **TA, TCO₂ ONLY!**
Likely beneficial to calcifiers (no impurities, etc.)
- **Major mineral elements: Ca, Mg, Fe, Si**
Lime, limestone: modest increase in Ca (global, but local?).
Olivine: Fe, Si effects on biogeochemistry?
- **Minor elements**
Impurities, trace metals, etc.: Fe, Ni, Cd, ...
- **Quicklime**
Temperature, pH?



Feasibility/Geochemical/Paleo assessment

- Technological, economic feasibility. Public acceptability.
- Suitability of different minerals:
Dissolution rates, reaction kinetics, particle size, etc.
- Paleoanalogs: high pH /saturation state effects on organisms?
(alkalinity inappropriate)
- etc.



Subject Proposal Notification, Date **Tuesday**, May 21

Title: Effects of carbonate chemistry and calcium ions on the boron partitioning between aqueous solution and inorganic calcium carbonate

Richard –

Just a quick note to let you know unofficially that **we are recommending that your pending proposal be funded.**

Subject Proposal Notification, Date **Monday**, Dec 19

Title: **Assessing impacts and feasibility of alkalinity addition to surface seawater for mitigating future changes in ocean chemistry and climate**

Dear Dr. Zeebe:

I regret to inform you that ... is **unable to support your proposal referenced above.**

Ocean Alkalinity Enhancement:
Current state of knowledge and potential role of philanthropy

Table 2: : Priority areas of engagement for philanthropy – Ocean Alkalinity Enhancement

	Fit for philanthropy		
	Low Fit	Medium Fit	High Fit
\$>20 Million	Large-scale demonstration pilots to validate effectiveness at scale	Technology development to lower cost to < \$50 per net ton removed	
\$5-20 Million		Medium-scale experiments including offshore mesocosms	Public Education Assess market incentives and pathways of OAE Assess policy Levers that enable OAE at scale
\$0-5 Million		NAS Study on OAE Establish international network of experts to exchange and coordinate research/technology Promote ocean CDR research outside of U.S. (UK, Japan, EU)	Improve understanding of OAE's ecological impact (through lab/mesocosm and modeling) Build community of practitioners including universities, NGOs, and public institutions Improved techno-economic analysis Public outreach and engagement to ensure social licensing and public funding

Ocean alkalinity enhancement – what can be learned from ocean acidification research

Ulf Riebesell

GEOMAR Helmholtz Center for Ocean Research Kiel, Germany



OCEANS
FROM THE DEEP SEA
TO THE ATMOSPHERE

OAE – what can be learned from OA

- ecological fitness can be more relevant than physiological performance
- indirect effects are more common than direct effects
- high impact surprises are likely to happen

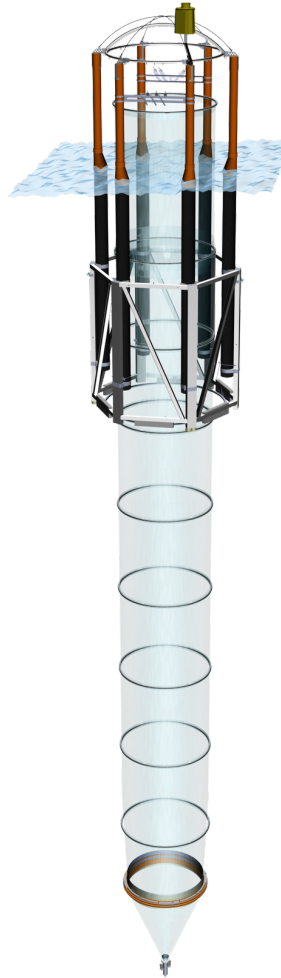
OAE – what can be learned from OA

Ecological fitness more relevant than physiological performance



Emiliania huxleyi

Riebesell et al. (2017)



↑ 50% reduced production of "cooling agent" dimethylsulfide (DMS)

↑
E. huxleyi bloom failure at $p\text{CO}_2 > 500 \mu\text{atm}$
↓

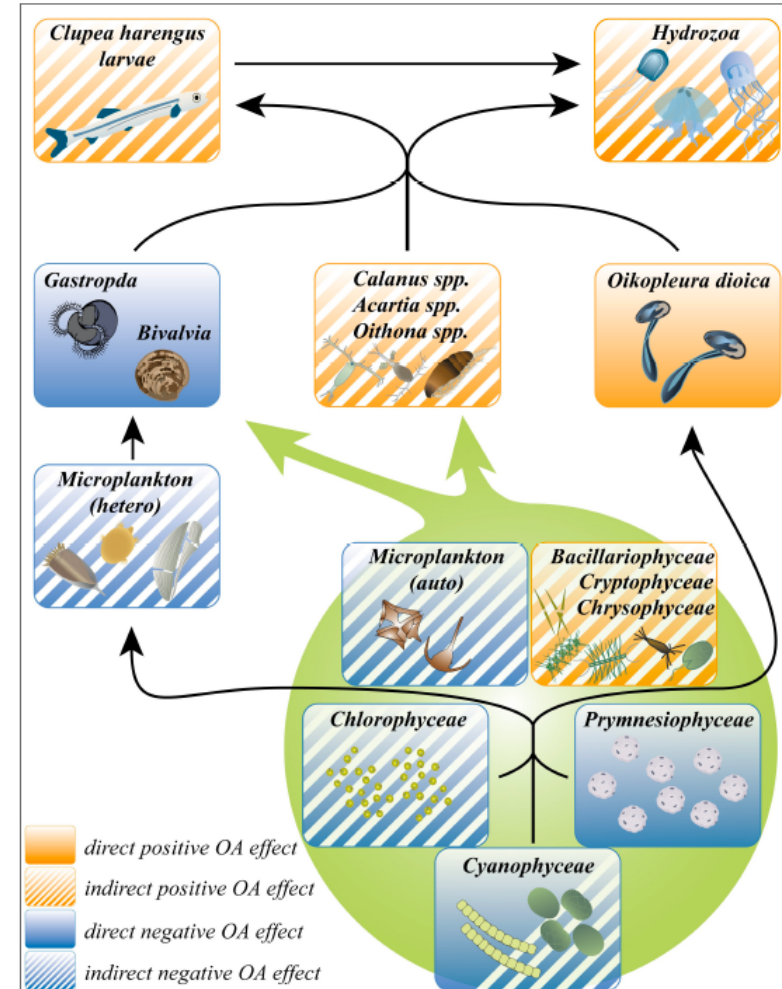
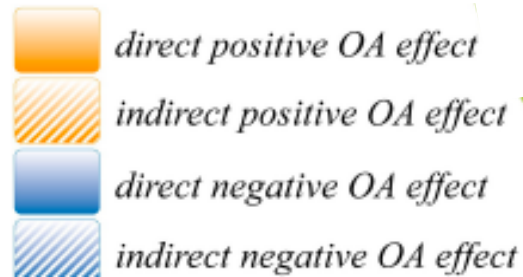
↓ 80% reduced CaCO_3 ballast
25% reduced org. matter flux

➤ positive climate system feedbacks

OAE – what can be learned from OA

Spisla et al. (2021)

Indirect effects more common than direct effects



OAE – what can be learned from OA

High impact surprises likely to happen

nature
climate change

LETTERS

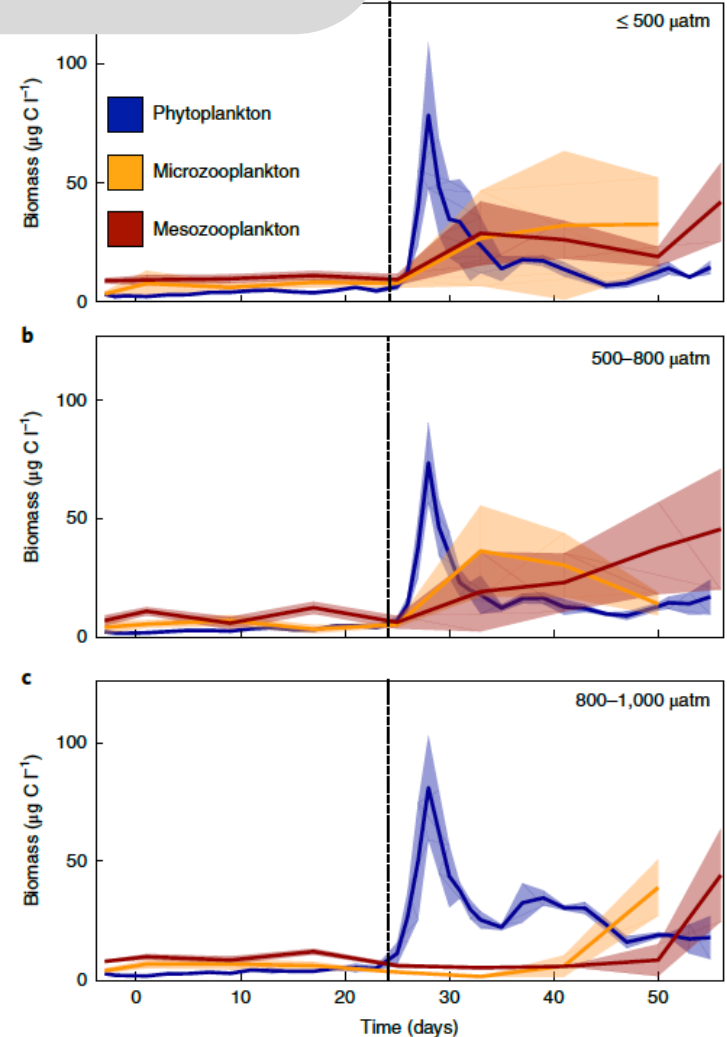
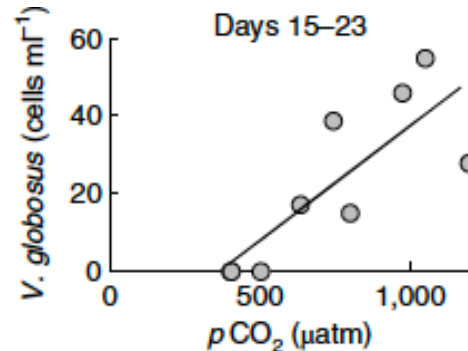
<https://doi.org/10.1038/s41558-018-0344-1>

Toxic algal bloom induced by ocean acidification disrupts the pelagic food web

Ulf Riebesell^{1*}, Nicole Aberle-Malzahn², Eric P. Achterberg¹, María Algueró-Muñiz³, Santiago Alvarez-Fernandez³, Javier Aristegui⁴, Lennart T. Bach¹, Maarten Boersma³, Tim Boxhammer¹, Wanchun Guan⁵, Mathias Haunost¹, Henriette G. Horn³, Carolin R. Löscher⁶, Andrea Ludwig¹, Carsten Spisla¹, Michael Sswat¹, Paul Stange¹ and Jan Taucher¹



Vicicitus globosus



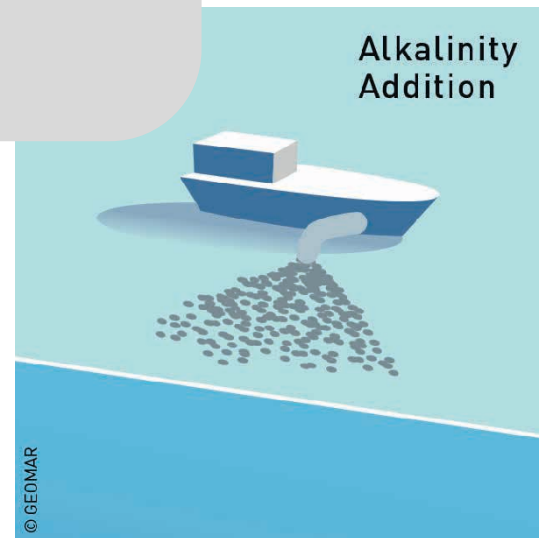
OAE – take home message

Recommendation

- OAE research to start at community level
- Where OAE impacts appear, do targeted experiments to unravel the underlying mechanisms

OAE – realistic levels to test

CO₂-equilibrated vs. non-equilibrated



OAE with limestone (CaCO₃)

Control

ΔTA=2400

non-equilibrated

ΔTA=2400

CO₂-equilibrated

TA	DIC	pH	pCO ₂	HCO ₃ ⁻	CO ₃ ²⁻	Ω _{Ca}	Ω _{Ar}
2400	2136	8,06	400,2	1928,9	194,1	4,7	3,1
4800	3336	8,81	77,6	2121,8	1211,7	29,4	19,0
4800	4067	8,31	400,0	3437,7	616,7	15,0	9,7

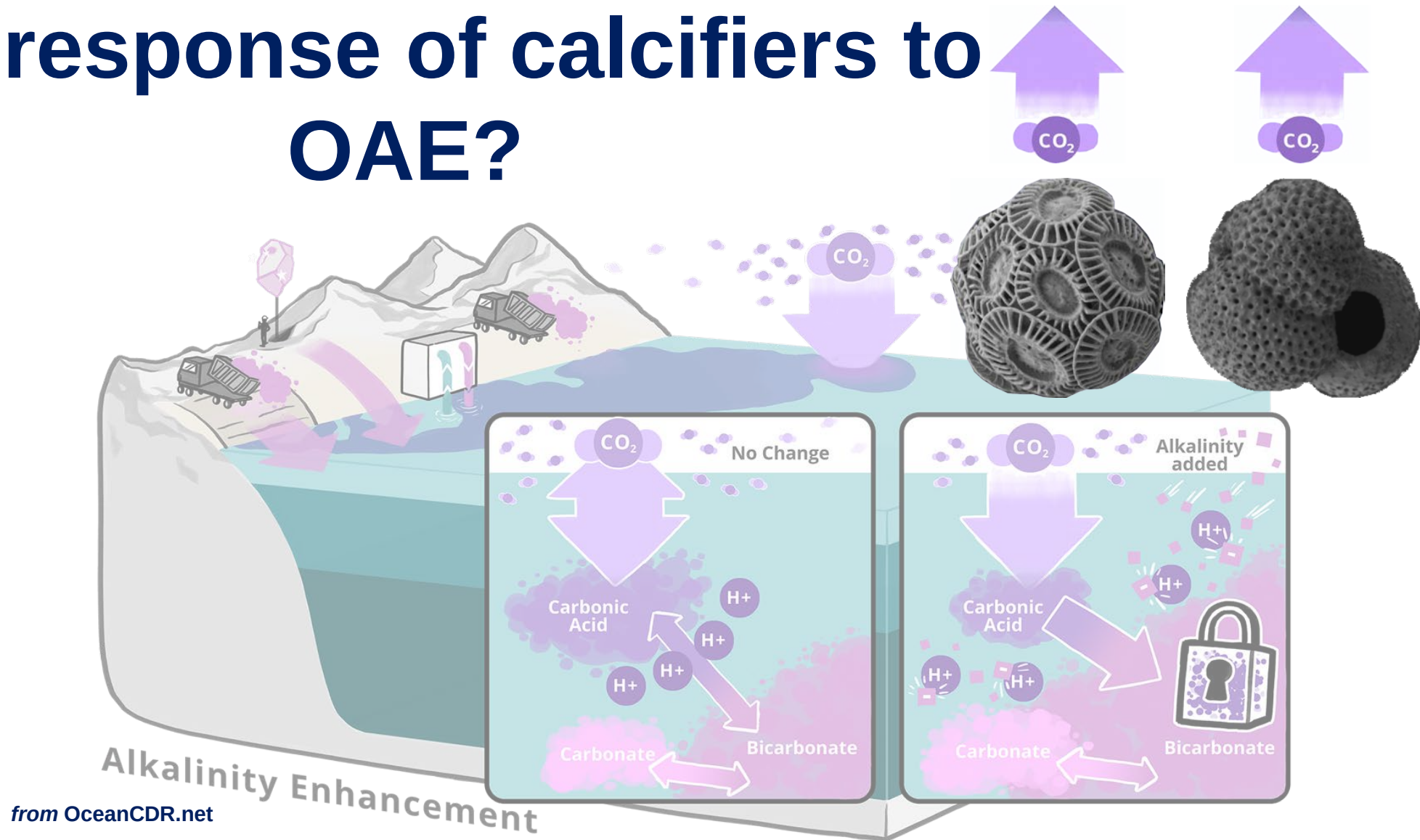
S=33, T=20°C

If CO₂-equilibrated proves harmful → showstopper for OAE

References

- Riebesell, U., Bach, L. T., Bellerby, R. G. J., Bermudez, R., Boxhammer, T., Czerny, J., Larsen, A., Ludwig, A., Schulz, K. G. (2017) Ocean acidification impairs competitive fitness of a predominant pelagic calcifier. *Nature Geoscience* 10, 19-24, doi:10.1038/ngeo2854
- Riebesell, U., Aberle-Malzahn, N., Achterberg, E. P., Alguero-Muniz, M., Alvarez-Fernandez, S., Aristegui, J., Bach L. T., Boersma, M., Boxhammer, T., Guan, W., Haunost, M., Horn, H. G., Löscher, C. R., Ludwig, A., Spisla, C., Sswat, M., Stange, P., Taucher, J. (2018) Toxic algal bloom induced by ocean acidification disrupts the pelagic food. *Nature Climate Change* 8, 1082-1086
- Spisla C., Taucher J., Bach L.T., Haunost M., Boxhammer T., King A.L., Jenkins B.D., Wallace J.R., Ludwig A., Meyer J., Stange P., Minutolo F., Lohbeck K.T., Nauendorf A., Kalter V., Lischka S., Sswat M., Dörner I., Ismar-Rebitz S.M.H., Aberle N., Yong J.C., Bouquet J.-M., Lechtenbörger A.K., Kohnert P., Krudewig M., Riebesell U. (2021) Extreme levels of ocean acidification restructure the plankton community and biogeochemistry of a temperate coastal ecosystem: A mesocosm study. *Frontiers in Marine Science* 7, 611157, doi: 10.3389/fmars.2020.611157

The response of calcifiers to OAE?



Sophie Gill, Jonathan Erez, Gideon Henderson, Ros Rickaby

Experimental design

Treatment	Total Alkalinity ($\mu\text{mol/kg}$)
<i>SOW (control)</i>	<i>2400-2600</i>
<i>SOW + NaHCO₃</i>	<i>3000</i>
	<i>3500</i>
	4000
<i>SOW + Na₂CO₃ + CaCl₂</i>	<i>3000</i>
	<i>3500</i>
	4000

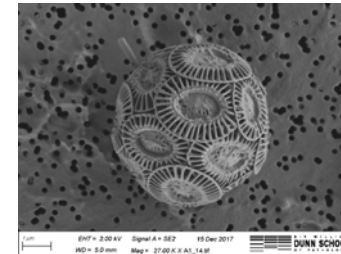
Foraminifera



Globigerinella siphonifera
Globigerinoides ruber

Credit: PAGES

Coccolithophores



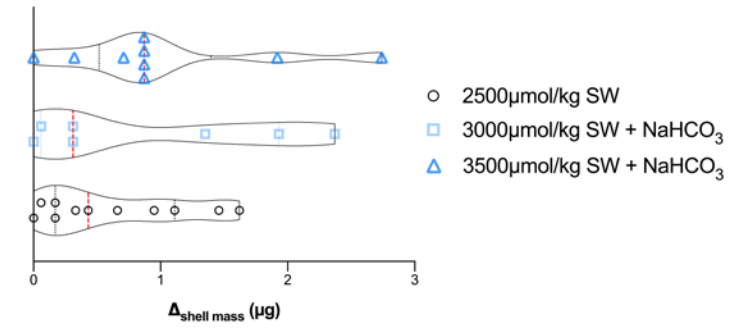
Emiliania huxleyi
Coccolithus braarudii

Carbonate chemistry

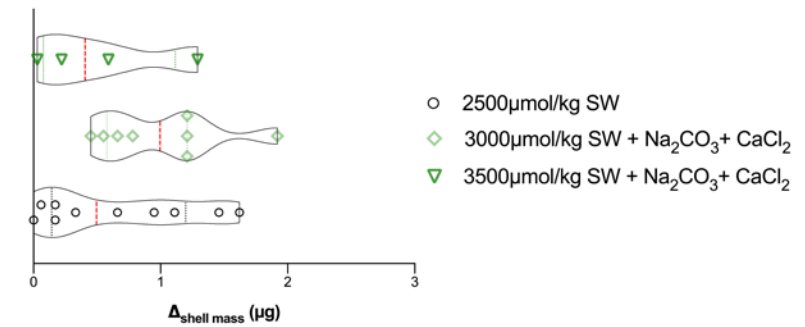
treatment	Total Alkalinity, TA ($\mu\text{mol/kg}$)	Dissolved Inorganic Carbon, DIC ($\mu\text{mol/kg}$)	pH	pCO_2 (μatm)	HCO_3^- ($\mu\text{mol/kg}$)	CO_3^{2-} ($\mu\text{mol/kg}$)	CO_2 ($\mu\text{mol/kg}$)	ΩCaCO_3	Ca concentration (mM/L)
SW (control)	2461	2078	8.072	367	1801	266	10.1	6.1	10.3
SW + NaHCO_3	2926	2349	8.237	268	1925	417	7.4	9.5	10.3
	3393	2658	8.320	242	2101	550	6.6	12.6	10.3
SW + Na_2CO_3 + CaCl_2	2941	2338	8.263	249	1895	435	6.8	10.0	10.6
	3355	2635	8.312	245	2091	538	6.7	12.3	10.8

G. ruber

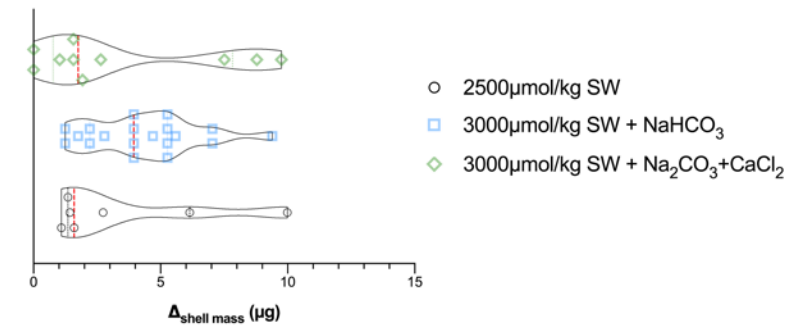
(a)

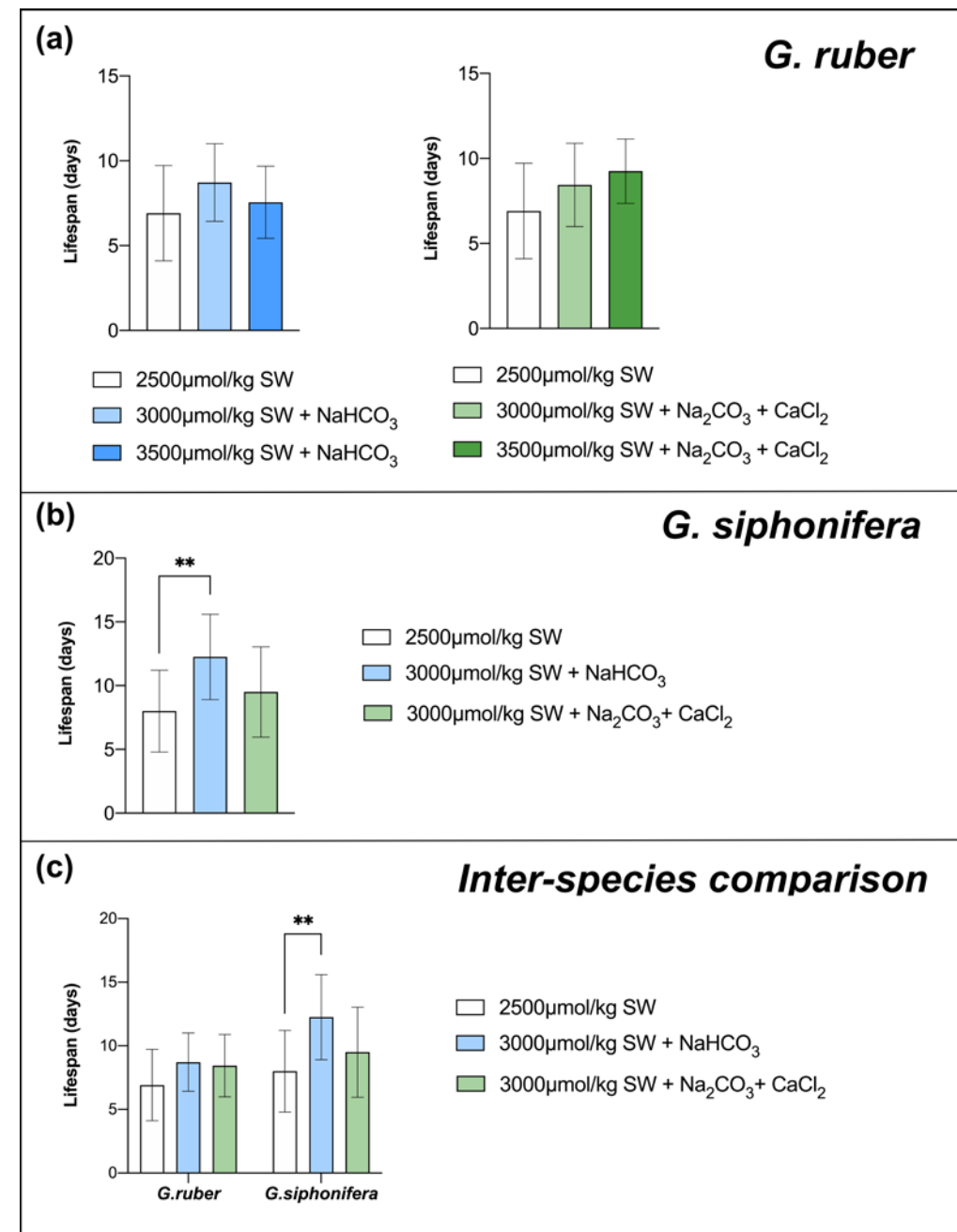
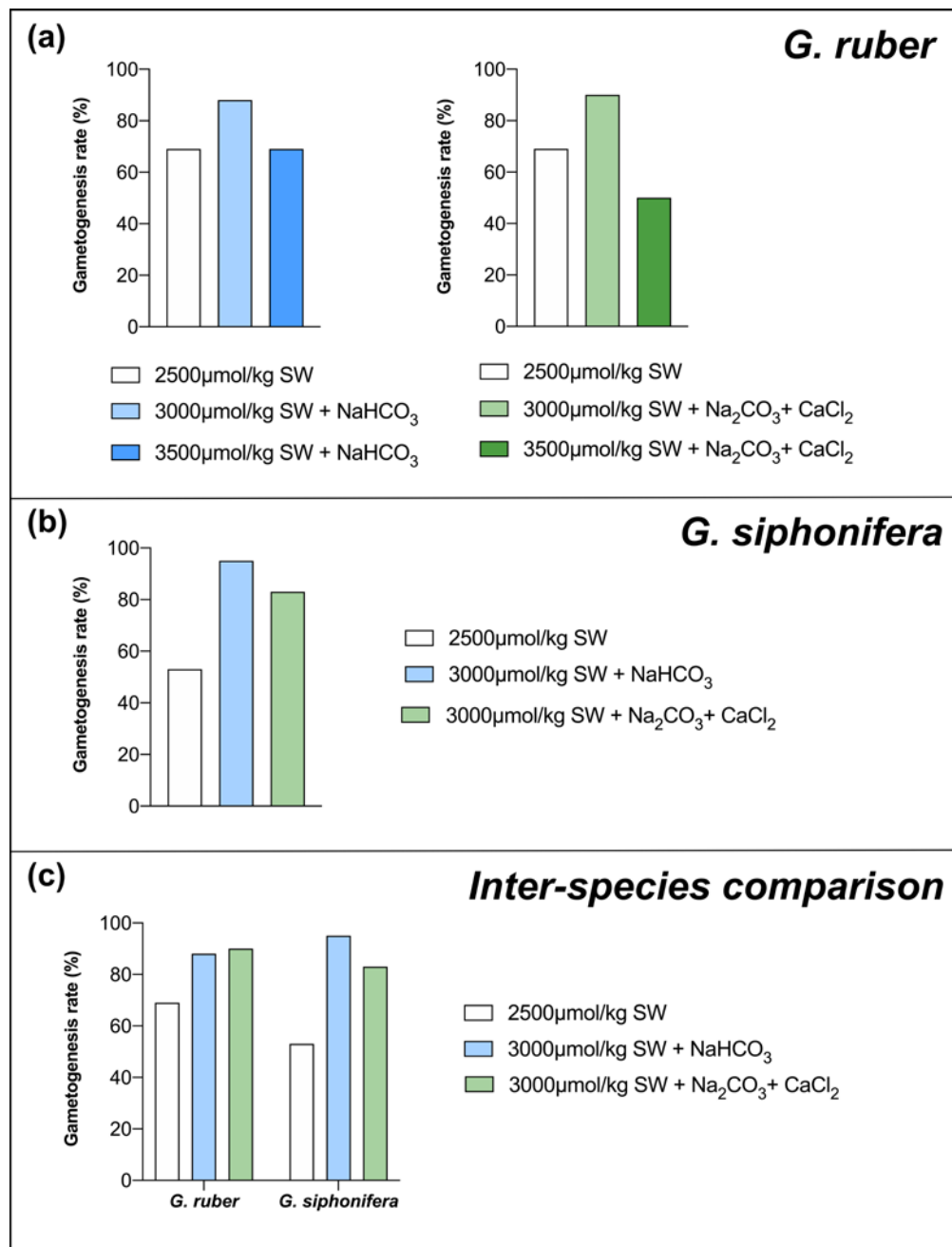


(b)

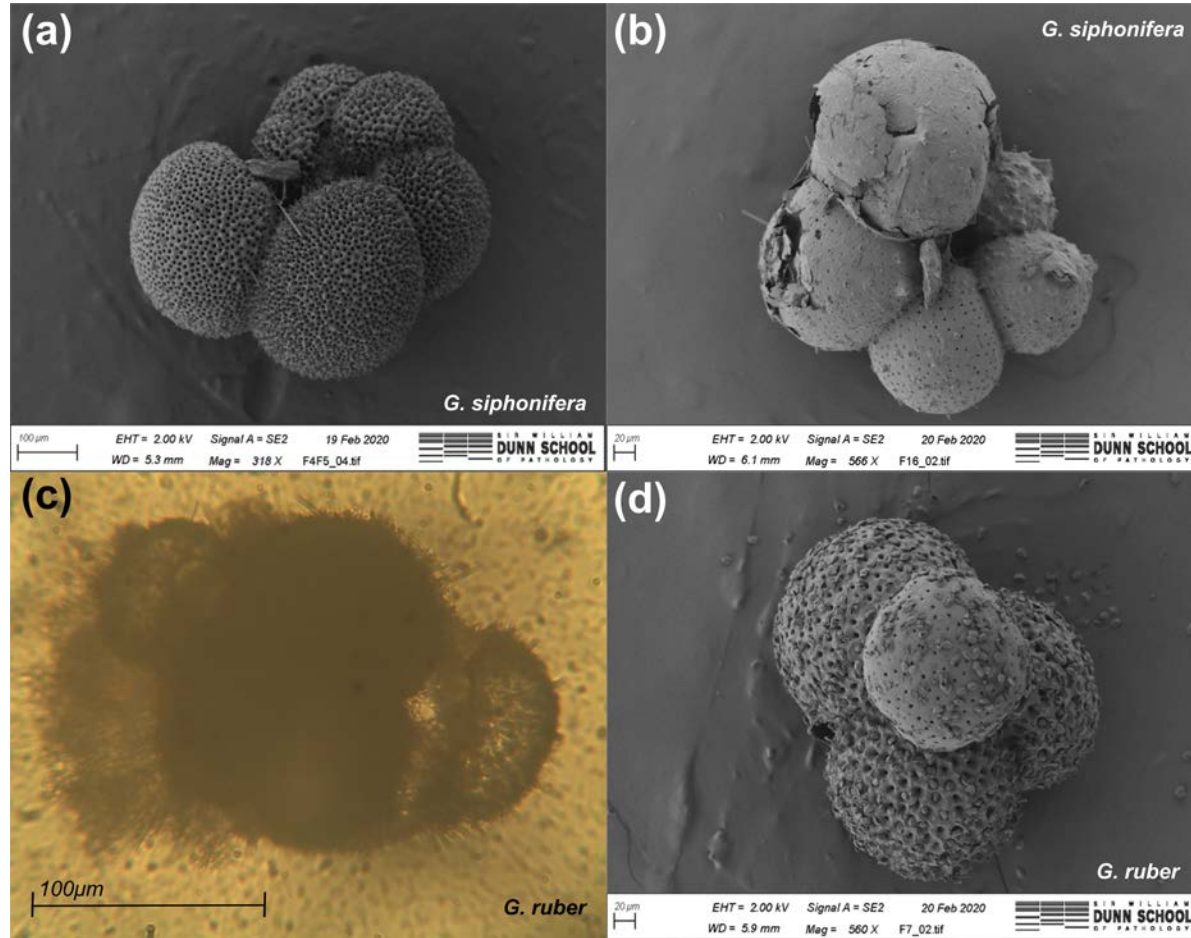


G. siphonifera

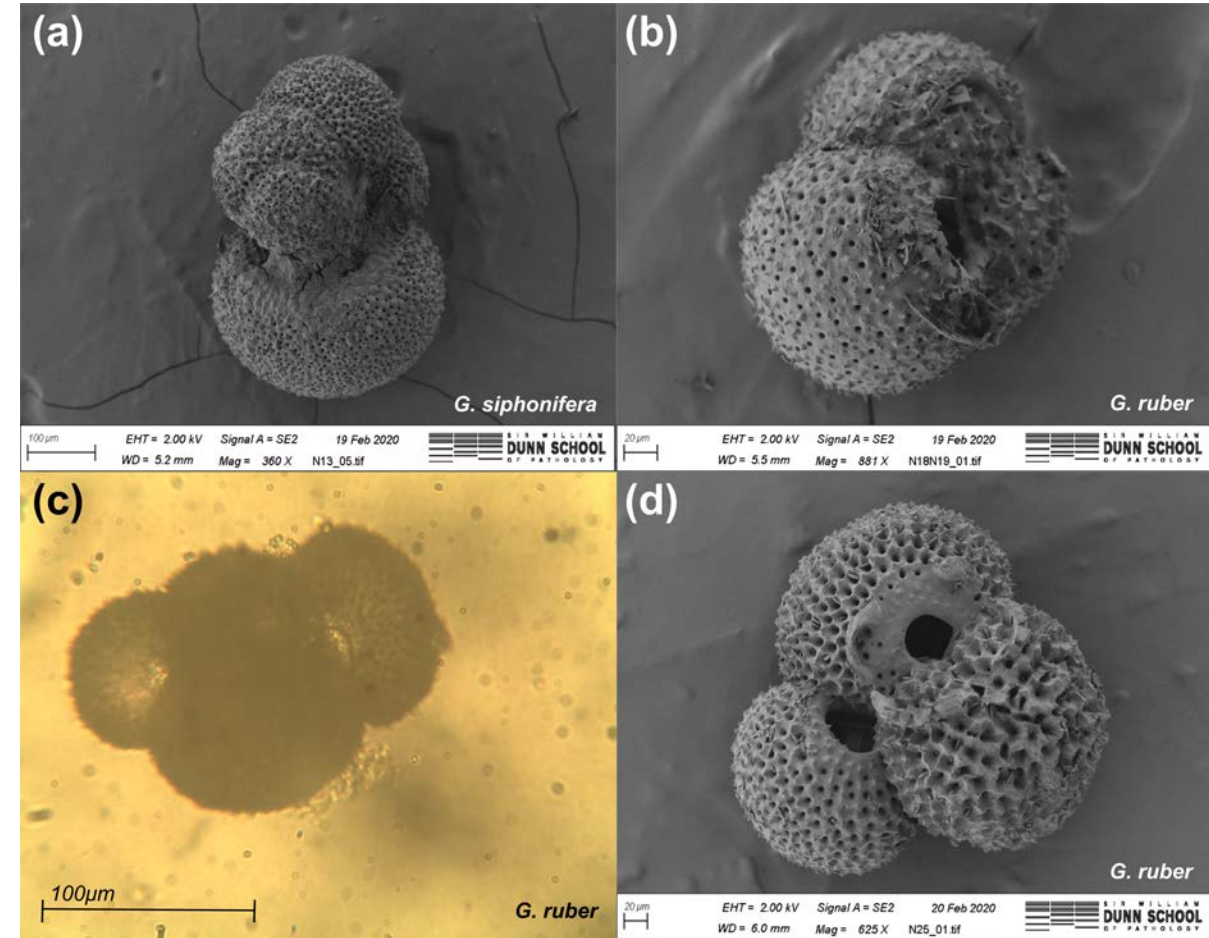


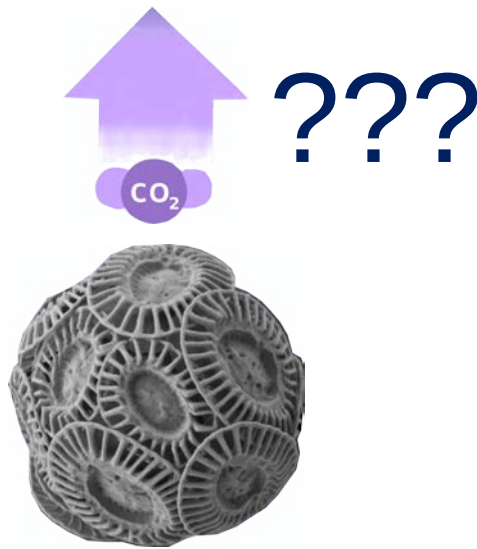


~3000 μ mol/kg SW + NaHCO₃



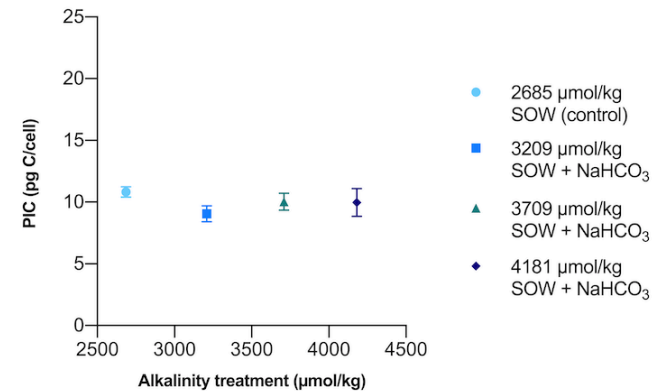
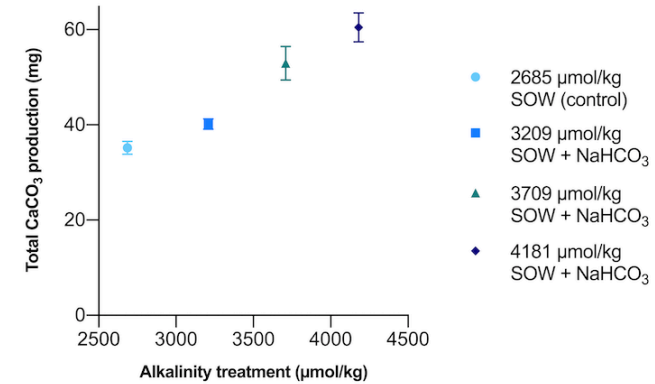
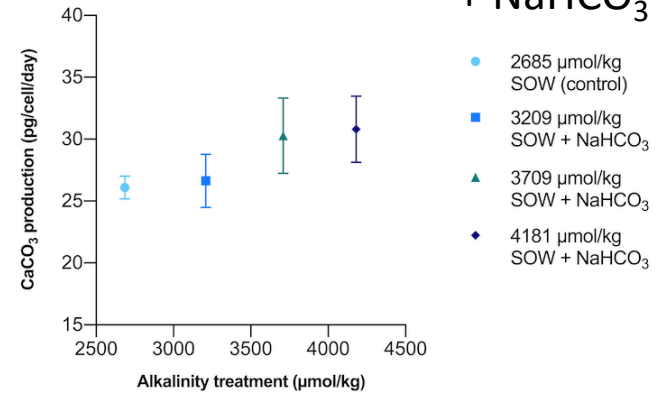
~3000 μ mol/kg SW + Na₂CO₃ + CaCl₂





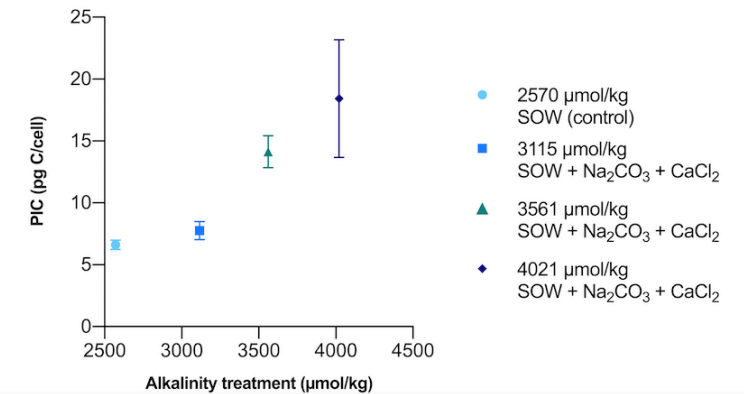
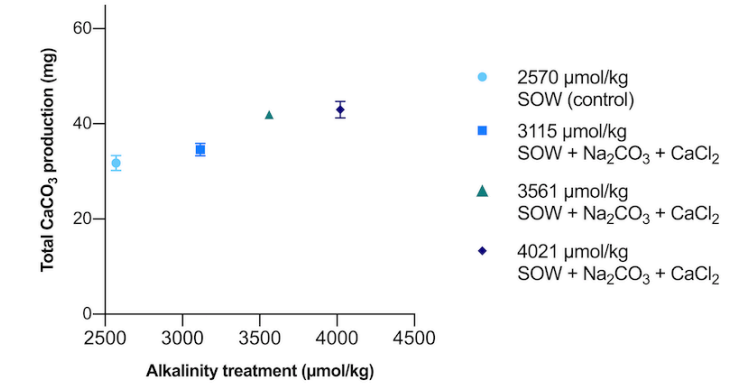
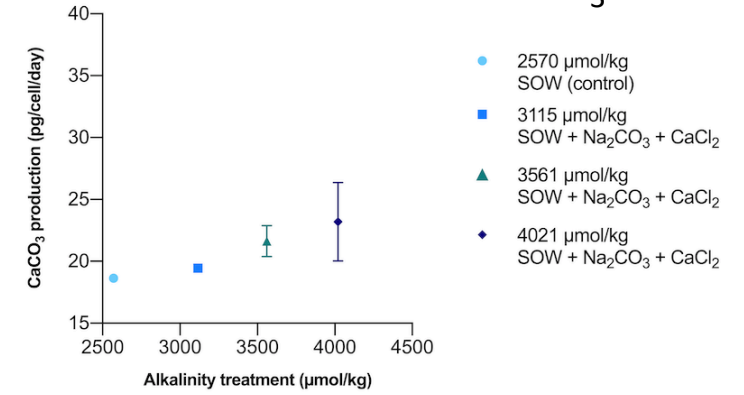
(A) Pathway 1

+ NaHCO₃



(B) Pathway 2

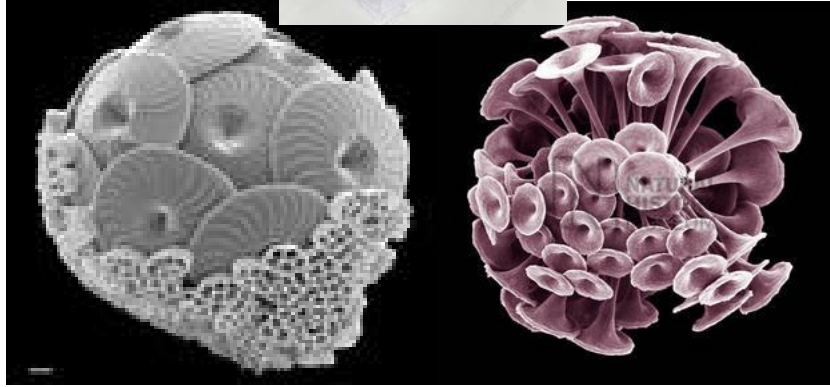
+ NaCO₃ + Ca



Conclusions

- Preliminary culture data suggest that enhanced alkalinity does impact the calcification process in foraminifera
- The observation of longer periods of time to gametogenesis could lead to greater calcification rates of a foraminifera population
- Very preliminary culture data suggest enhanced alkalinity does increase calcification in coccolithophores
- BUT Enhancing alkalinity may predispose the ocean towards greater CO₂ limitation of phytoplankton

Calcification

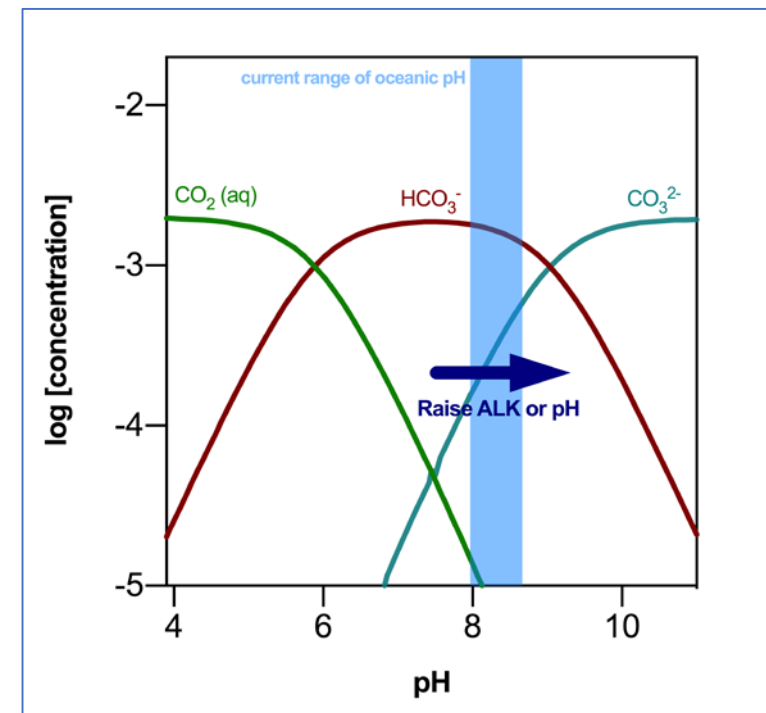
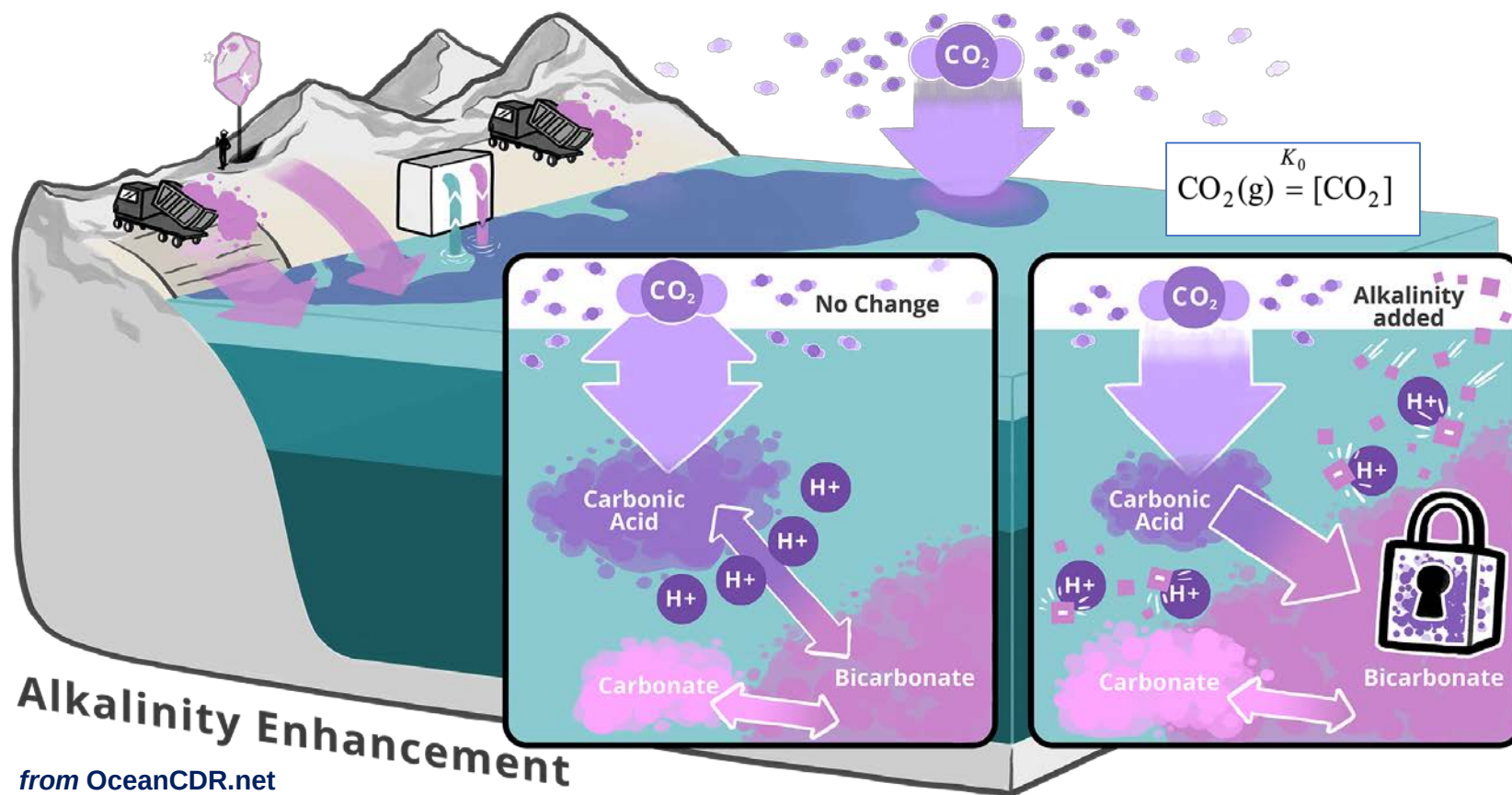


Weathering



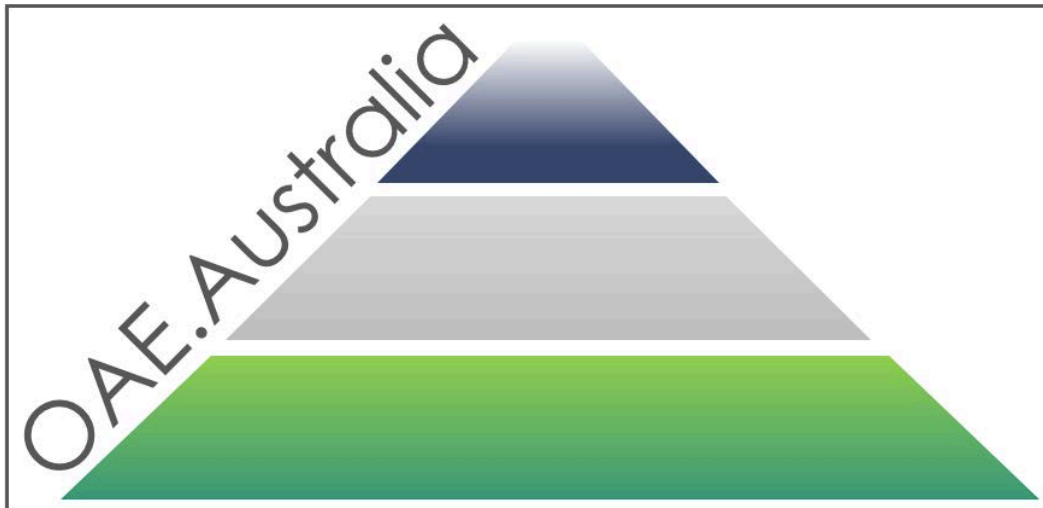
Views of the Earth, Copyright © 2006 by Christoph Hormann <http://earth.imagico.de/>

- i. Dissolution of silicate with products stored in the ocean (uptake of two moles of CO_2)
- ii. Dissolution of silicate resulting in precipitation of carbonate (net uptake of 1 mole CO_2)
- iii. Dissolution of carbonate with products stored in the ocean (uptake of 1 mole CO_2)



modified from Heinze et al. (2015)

Ocean Alkalinity Enhancement (OAE): Hidden knowledge and learning from natural analogues



Australian Research Council Future Fellowship project

Lennart Bach



Biological impacts - What we (don't) know



Goal: NAS wants to assess the biological impacts of OAE

Problem: Contextual knowledge is low

“Hidden” knowledge on OAE is high

Transforming hidden into contextual knowledge



“*White or green ocean hypothesis*”

(Bach et al., 2019, Frontiers in Climate)



CaO

“carbonates”

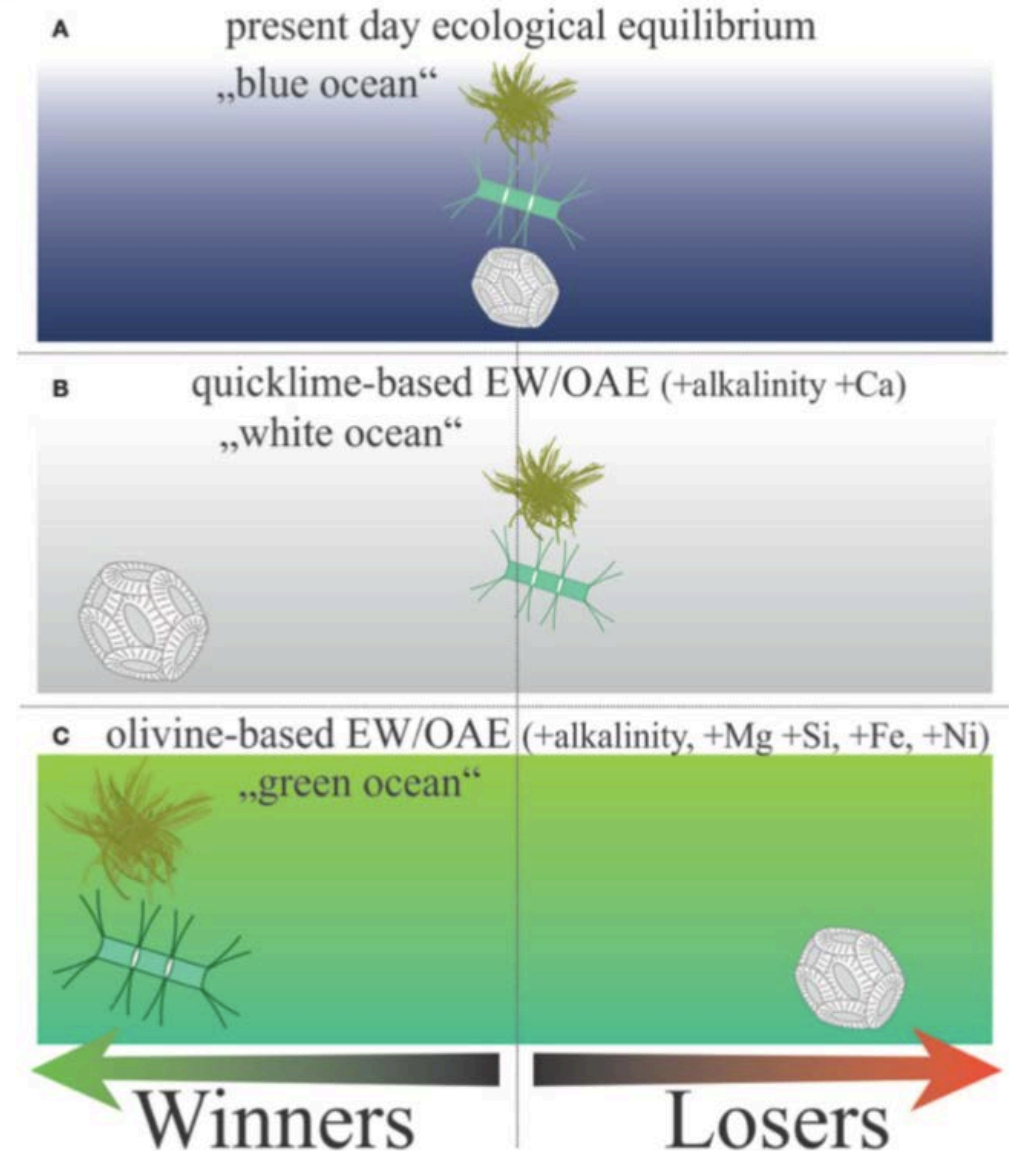
+ alkalinity, +Ca



Mg₂SiO₄

“silicates”

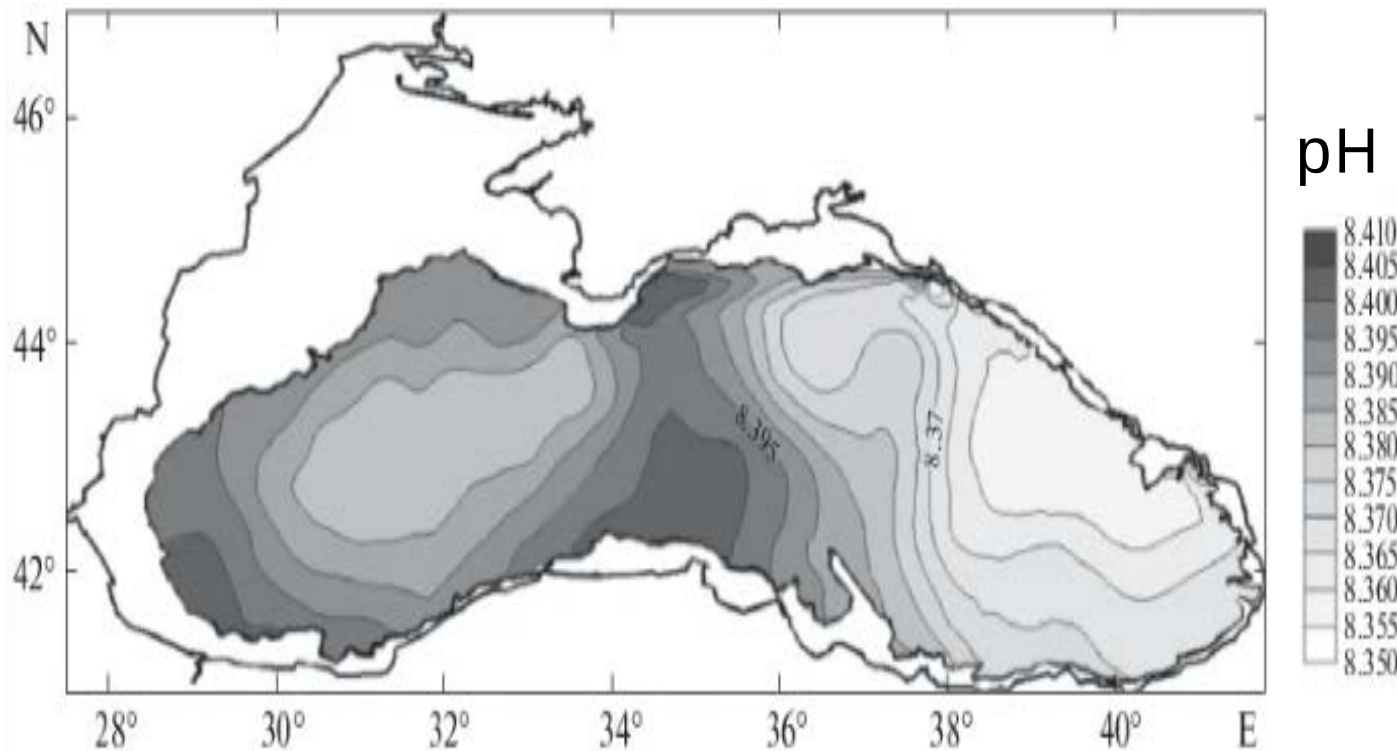
+ alkalinity, +Mg, +Si, +Fe, +Ni



The Black Sea: a natural OAE analogue?

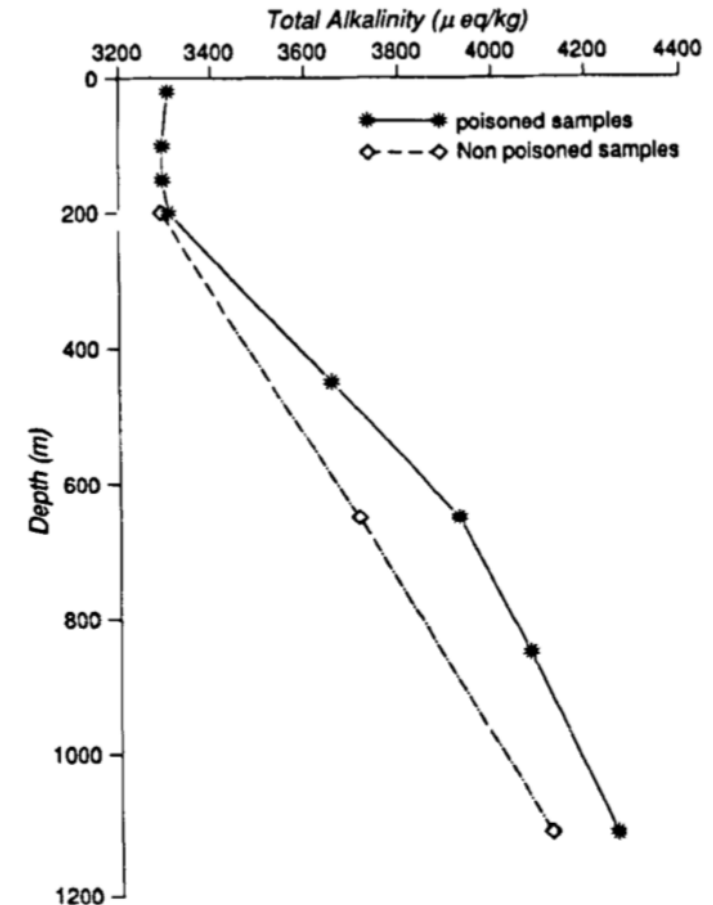


surface pH ~8.3-8.4



Polonsky and Grebneva, 2019, Doklady Earth Sciences

surface alkalinity ~3300 $\mu\text{mol/kg}$



Goyet et al., 1991, Marine Chemistry

The Black Sea: a natural OAE analogue?



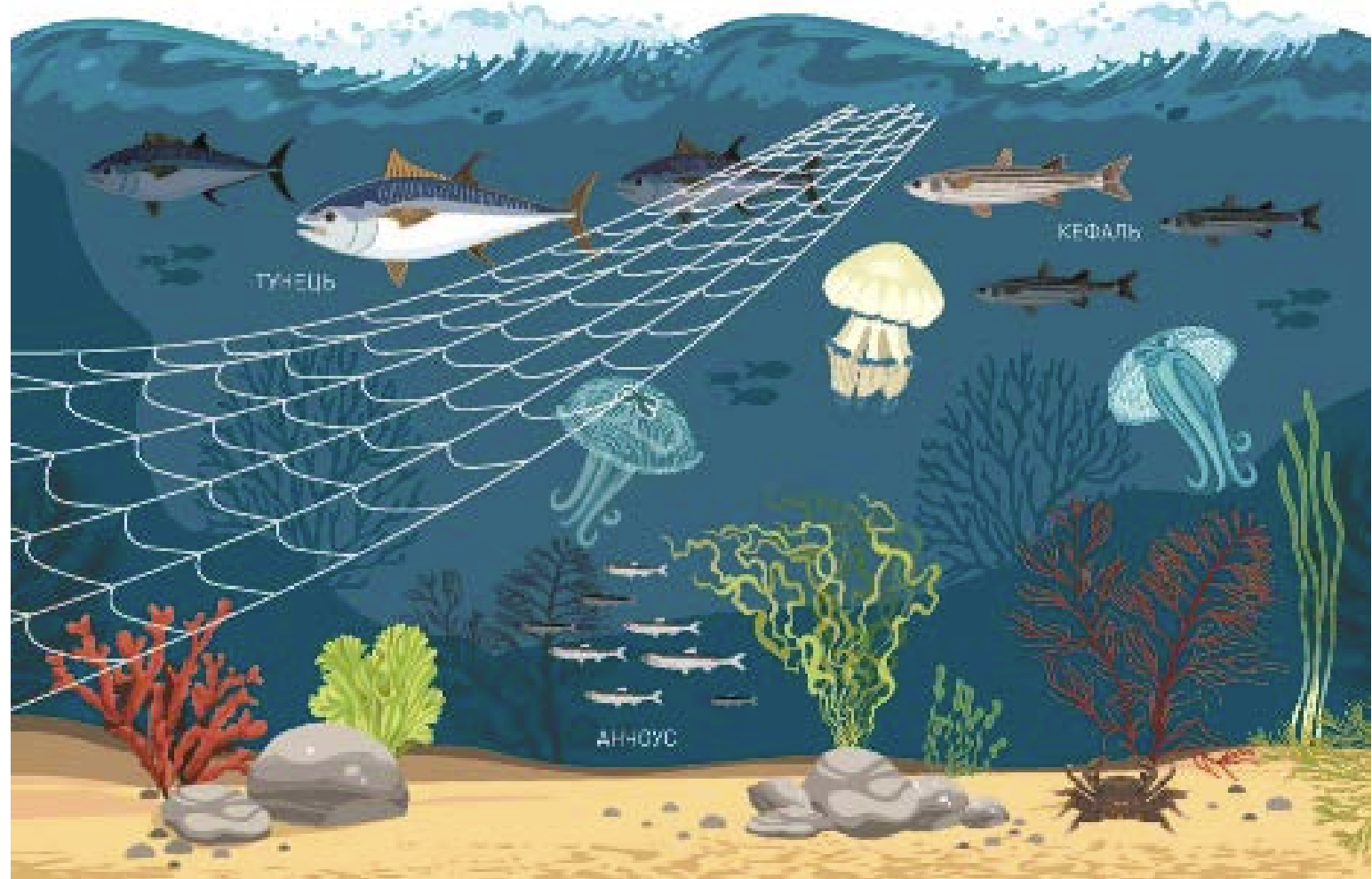
1st insight

Black Sea in its non-polluted state is a “healthy” sea.

~200 fish species

~390,000 tonnes fish/year
(FAO)

➡ High Alkalinity does not
impede marine life.



The Black Sea: a natural OAE analogue?



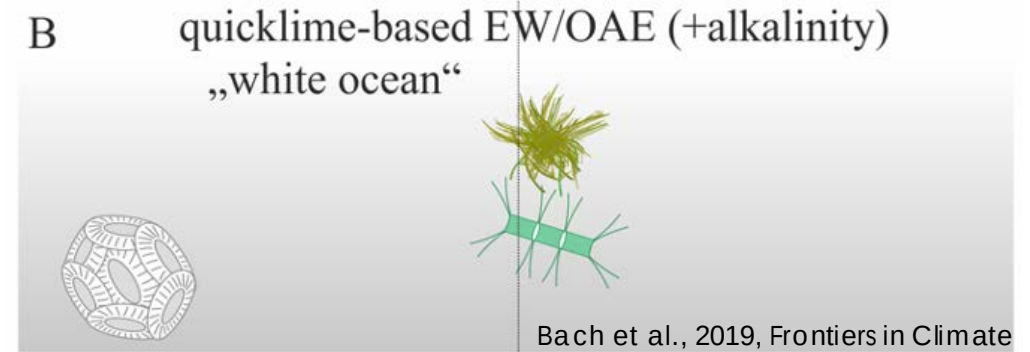
2nd insight

3rd approach in addition to modelling
and experimentation

NASA, Modis Aqua, 29 May 2017

<https://www.eurekalert.org/multimedia/pub/167144.php>

Black Sea – the “white ocean”?



© Associated Press Photo

<https://www.dailymail.co.uk/sciencetech/article-4606810/Microscopic-organisms-turn-Istanbul-shores-turquoise.html>

Lessons from Ocean Alkalinity Enhancement on Smaller Scales



George G. Waldbusser and
Mark Green, Burke Hales, Iria Gimenez



Why Smaller Scale?

The global issue clearly mandates scalability, smaller scale trials allow:

- 1) Feasibility and limitations (unintended consequences...)
- 2) Assuage concern(s) from policy makers and other stakeholders
- 3) Identify opportunities for outsized impacts (ROI)

Three Successful Alkalinity Enhancement Examples

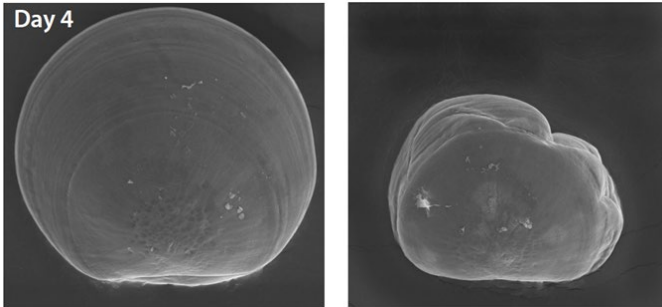
System	Efficacy
Aquaculture Facilities	Excellent, widely used
Intertidal Sediments	Can work well, technical guidance needed
Oyster Reef Restoration	Potential for embayment scale impacts

Example #1: Alkalinity Enhancement of Aquaculture Facilities.



Impacts of Coastal Acidification
on the **Pacific Northwest
Shellfish Industry**
and Adaptation Strategies
Implemented in Response

Barton et al. 2012, 2015



Hatchery Failures plagued industry 2007-
Monitoring connected upwelling and losses
Implemented water buffering
First just small larvae
Now entire hatchery
Single most effective strategy (OAE)
Largely in practice across industry

Industry uses a pH target to obtain a Ω_{ar} of ~ 4
 Na_2CO_3 is alkalinity enhancing agent of choice (NaOH and NaHCO_3 not as effective)

Upsides

Many of these facilities run seawater 24/7
Co-Production of food and OAE injection site...

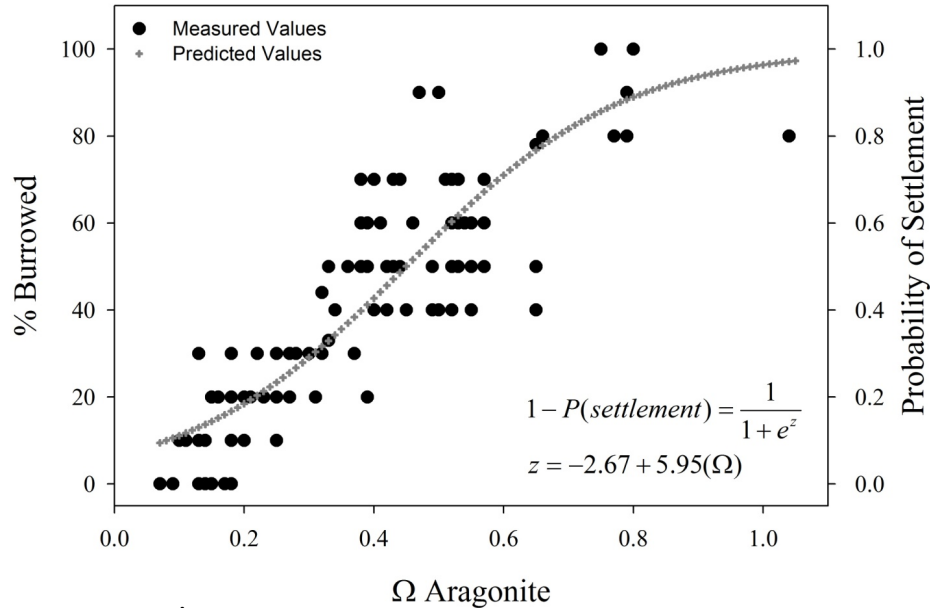
Issues

Limited scope/scale (industry financial incentives?)
Concerns with other trace elements in mined materials

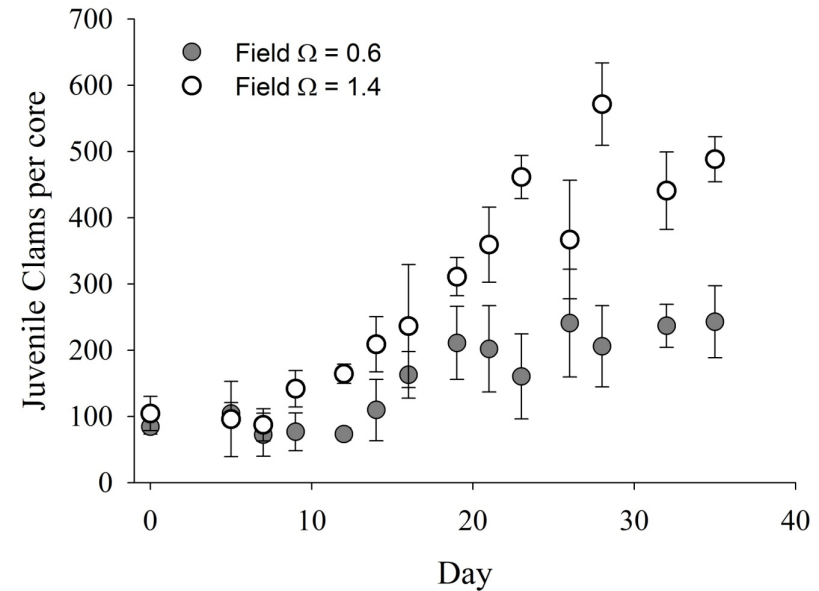
Example #2: Alkalinity Enhancement of Intertidal Sediments



In Laboratory



In Field Experiment



Green et al. 2013

- Field trials with ground clam shell (aragonite)
- Marine sediments a source of natural CO_2 , (i.e. carbonate counter pump)
- ~ 1 megatonne of shell per year removed (UNICEF harvest data, not aquaculture)
- Reaction/Transport dynamics important
- Formation of shell is alkalinity uptake (degree depends on a)... at best an offset...
- Other minerals could work, trials underway with Dolomite, Calcite, and Olivine.

Example #2a: Alkalinity Enhancement of Intertidal Sediments

“this doesn’t work...”

ClimateWorks Funded Project (Waldbusser, Gimenez, Green, Mahrt, Meile)

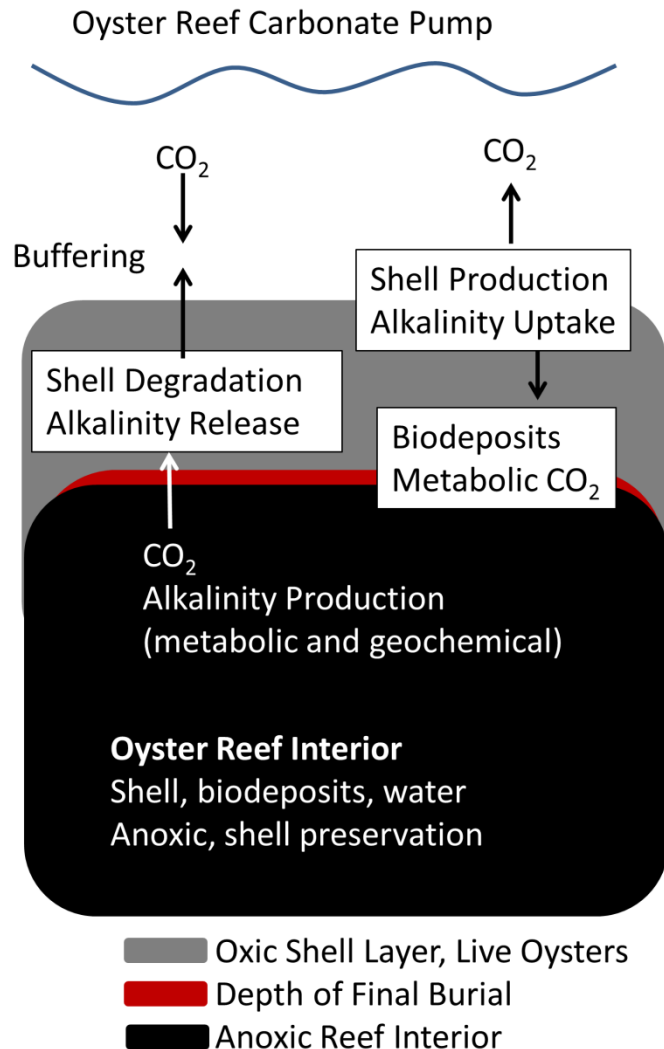
Assess mineral types, size, surface area across sediment types

Measure chemical effects in lab and field, as well as long-term changes to communities

Develop biogeochemical model and ‘applications’ tool for stakeholders to amend aquaculture plots



Example #3: Alkalinity Enhancement of via Restoring Alkalinity ‘Rich’ Habitats.



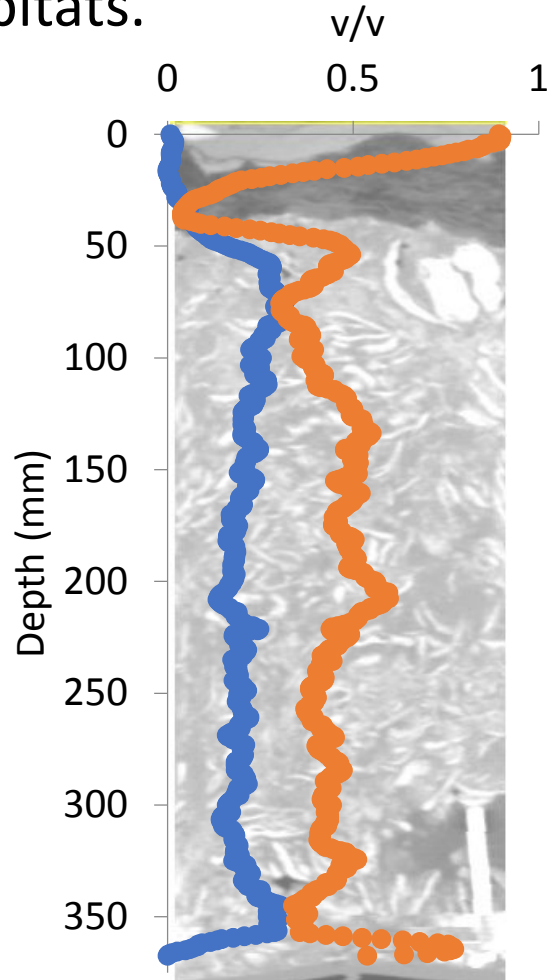
Waldbusser et al. 2013

System	Alkalinity flux (mmol m ² d ⁻¹)
Coastal Arctic (Svalbard harbor) Mud-fine sand. ~2.5% Org C	12 - 42
Coastal and shelf sediments	0.5-3.0
Intertidal sand flats ~ 0.23% Org C (Netherlands)	33
Florida Keys Coral Reefs	1.8 - 400
Shallow carbonate sediments (Mediterranean NW)	0-36
Seagrass beds in carbonate sands	0-50
Restored Oyster Reef	68-212

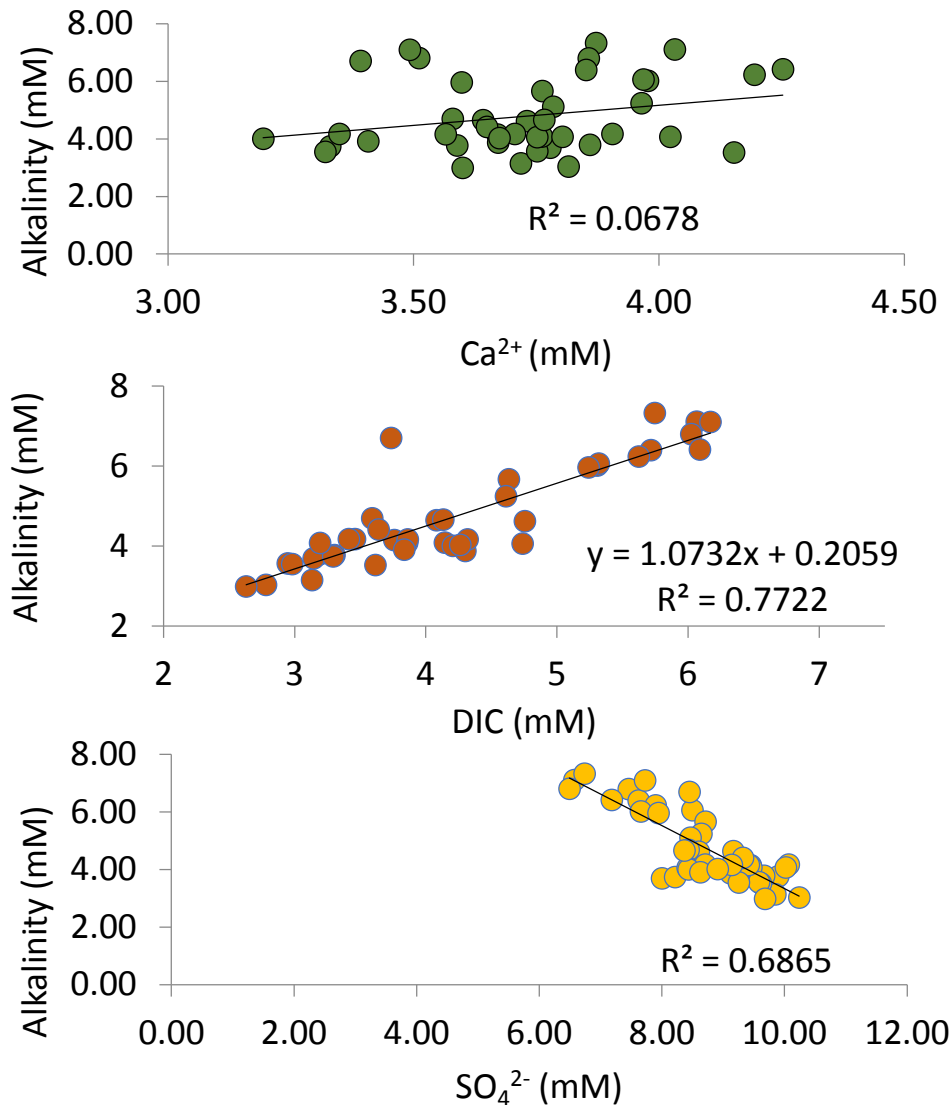
Refs: Gazeau et al. 2014, Hu and Cai 2011, Krummins et al. 2013, Gustafsson et al. 2014 , Rao et al. 2014, Lisle et al. 2014, Rassmann et al. 2018, Burdige et al. 2008

Gimenez et al. (in prep)

Example #3: Alkalinity Enhancement of via Restoring Alkalinity 'Rich' Habitats.



System generates more alkalinity than can be explained by shell alone...

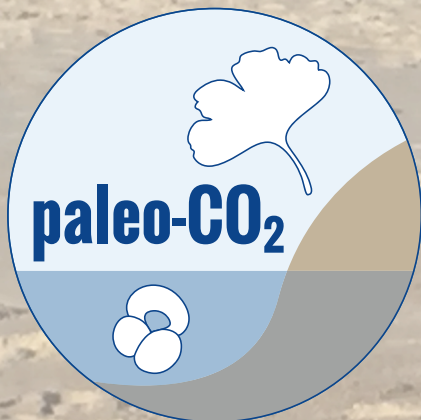


Related References:

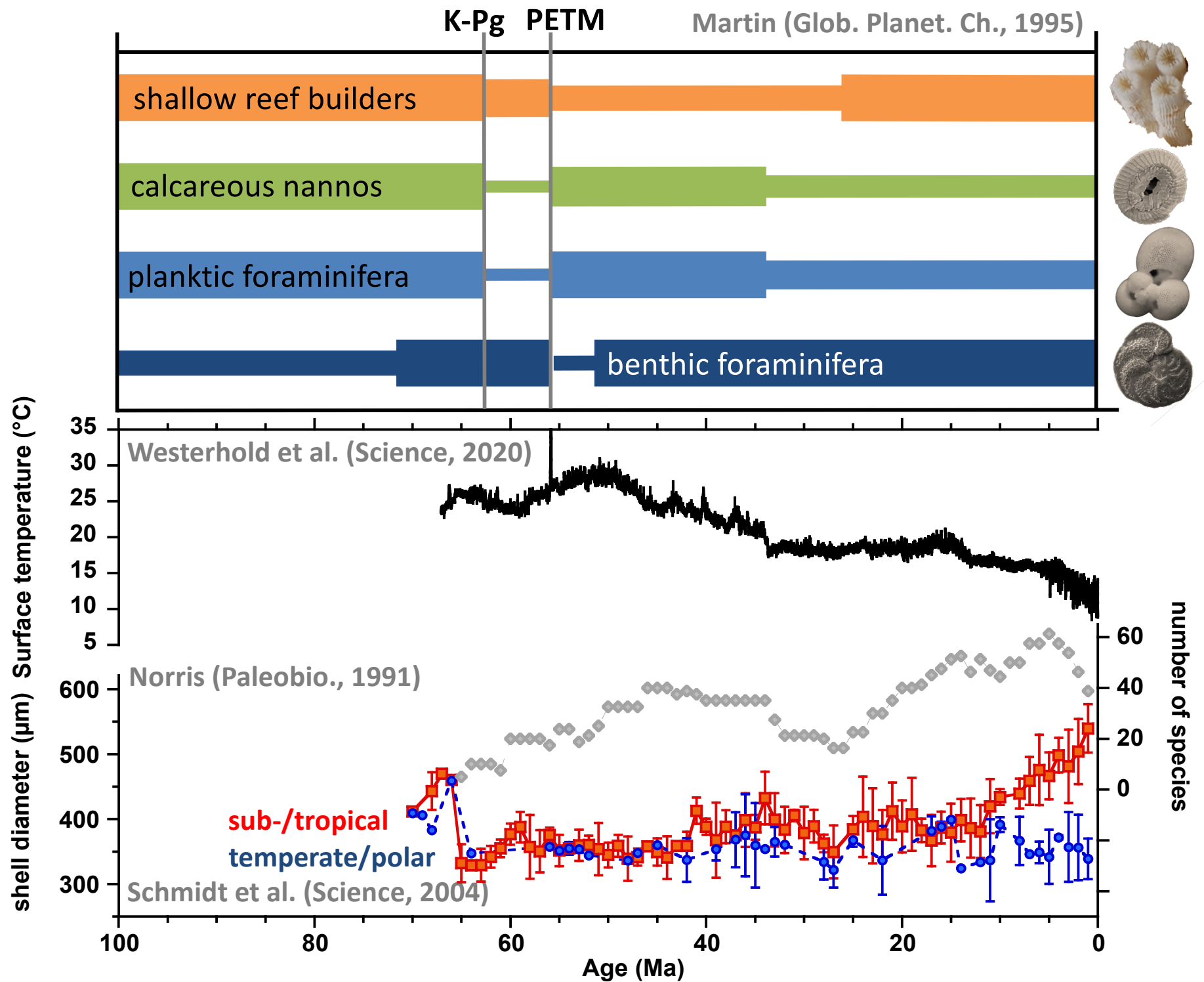
- Barton, A., B. Hales, G. G. Waldbusser, C. Langdon, and R. A. Feely. 2012. The Pacific oyster, *Crassostrea gigas*, shows negative correlation to naturally elevated carbon dioxide levels: Implications for near-term ocean acidification effects. *Limnol. Oceanogr.* **57**: 698-710.
- Barton, A. and others 2015. Impacts of Coastal Acidification on the Pacific Northwest Shellfish Industry and Adaptation Strategies Implemented in Response. *Oceanography* **28**: 146-159.
- Gimenez, I. 2018. Ocean Acidification Impacts on Bivalves at Multiple Organizational Levels: From Individual Larvae to Bivalve Aggregations Habitats. PhD Dissertation, Oregon State University
- Green, M. A., G. G. Waldbusser, S. L. Reilly, K. Emerson, and S. O'Donnell. 2009. Death by dissolution: Sediment saturation state as a mortality factor for juvenile bivalves. *Limnol. Oceanogr.* **54**: 1037-1047.
- Green, M. A., G. G. Waldbusser, L. Hubazc, E. Cathcart, and J. Hall. 2013. Carbonate Mineral Saturation State as the Recruitment Cue for Settling Bivalves in Marine Muds. *Estuaries Coasts* **36**: 18-27.
- Waldbusser, G. G., E. N. Powell, and R. Mann. 2013. Ecosystem effects of shell aggregations and cycling in coastal waters: an example of Chesapeake Bay oyster reefs. *Ecology* **94**: 895-903.

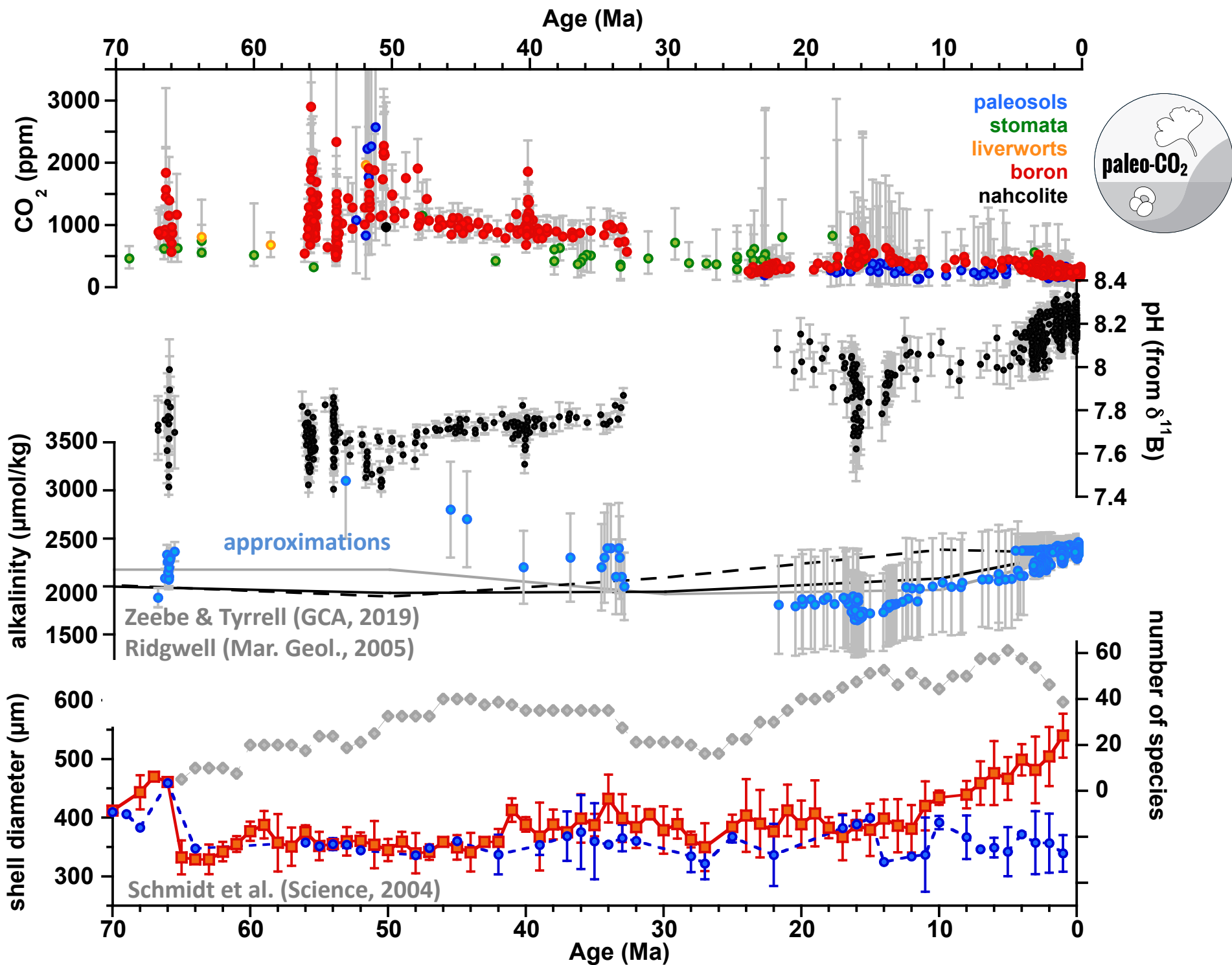
Bärbel Hönisch

hoenisch@ldeo.columbia.edu



Lamont-Doherty Earth Observatory
COLUMBIA UNIVERSITY | EARTH INSTITUTE





Questions

To better quantify past marine carbonate chemistry, we need a reliable proxy for alkalinity or DIC.

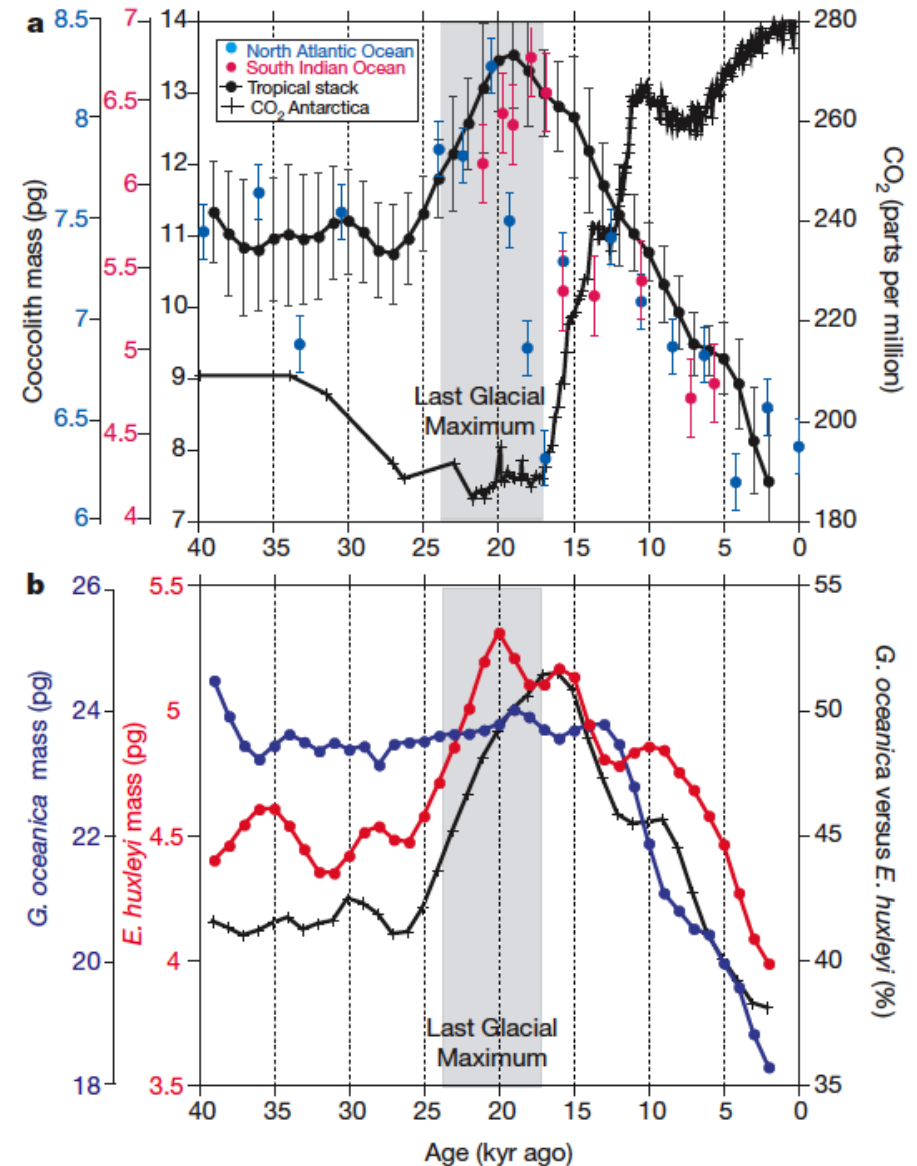
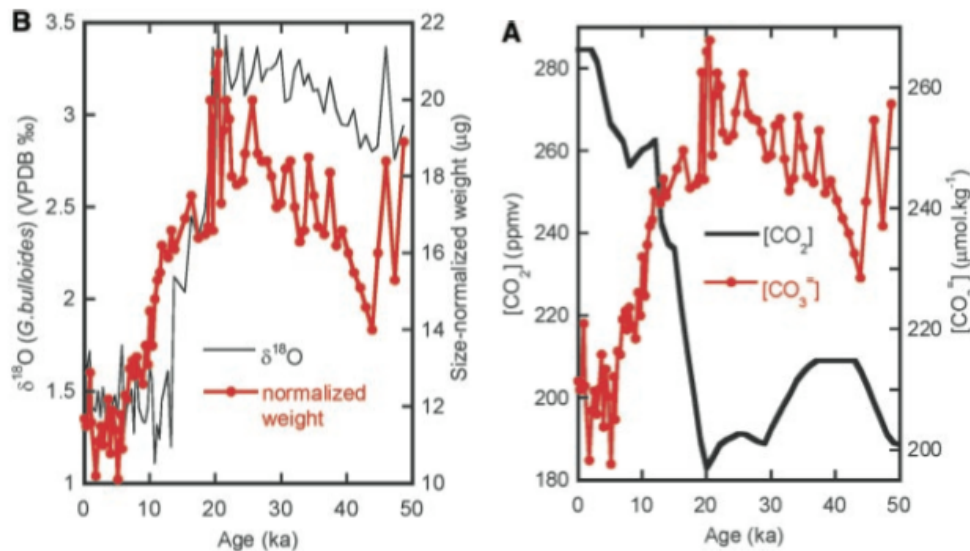
What is the importance of alkalinity versus other environmental parameters on marine calcifier productivity and marine life as a whole?

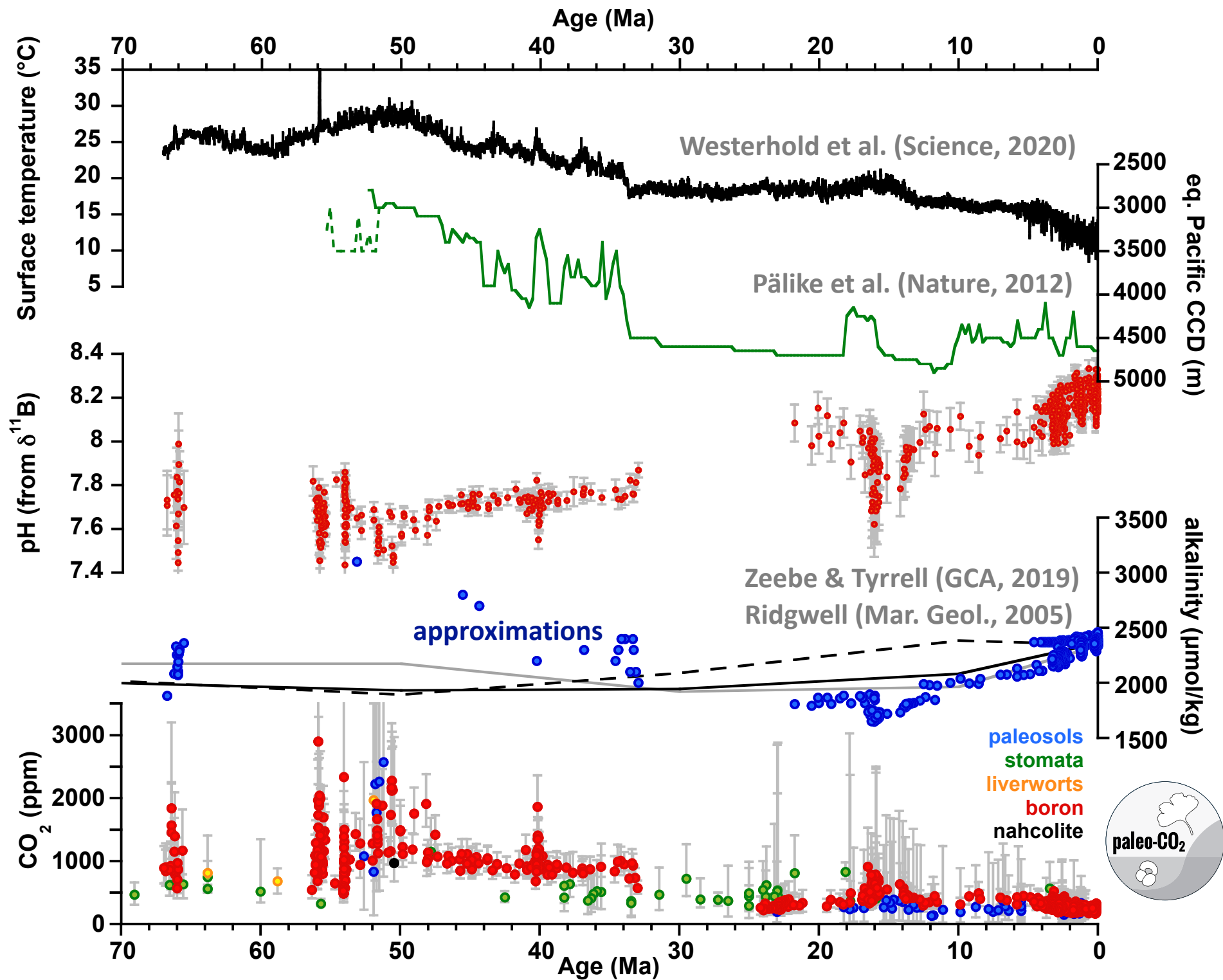
Sensitivity of coccolithophores to carbonate chemistry and ocean acidification (Nature, 2011)

L. Beaufort¹, I. Probert², T. de Garidel-Thoron¹, E. M. Bendif², D. Ruiz-Pino³, N. Metz^{1,3}, C. Goyet⁴, N. Buchet¹, P. Coupel³, M. Grelaud^{1,†}, B. Rost⁵, R. E. M. Rickaby⁶ & C. de Vargas²

Foraminiferal Calcification Response to Glacial-Interglacial Changes in Atmospheric CO₂

Stephen Barker* and Henry Elderfield (Science, 2002)





References

<https://paleo-co2.org>

Martin, R.E. (1995) Cyclic and secular variation in microfossil biomineralization: clues to the biogeochemical evolution of Phanerozoic oceans. *Glob. Planet. Change* 11, 1-23.

Schmidt et al. (2004) Abiotic forcing of plankton evolution in the Cenozoic. *Science* 303, 207-210.

see also: Schmidt et al. (2006) Biogeography and evolution of body size in marine plankton. *Earth-Sci. Rev.* 78, 239-266.

Zeebe, R.E. and Tyrrell, T. (2019) History of carbonate ion concentration over the last 100 million years II: Revised calculations and new data. *GCA* 257, 373-392.

Ridgwell, A. and Zeebe, R.E. (2005) The role of the global carbonate cycle in the regulation and evolution of the Earth system. *EPSL* 234, 299-315.

Barker, S. and Elderfield, H. (2002) Foraminiferal calcification response to glacial-interglacial changes in atmospheric CO₂. *Science* 297, 833-836.

Beaufort et al. (2011) Sensitivity of coccolithophores to carbonate chemistry and ocean acidification. *Nature* 476, 80-83.

Li-proxy for DIC? pH?

Roberts et al. (2018) Lithium isotopic composition of benthic foraminifera: A new proxy for paleo-pH reconstruction. *GCA* 236, 336-350.

Vigier et al. (2015) Lithium isotopes in foraminifera shells as a novel proxy for the ocean dissolved inorganic carbon (DIC). *Comptes Rendus Geoscience* 347, 43-51.

Allen et al. (2016) Trace element proxies for surface ocean conditions: A synthesis of culture calibrations with planktic foraminifera. *GCA* 193, 197-221.

Ecological lessons from the past?

Andy Ridgwell

University of California – Riverside



Condamine et al. [2013]

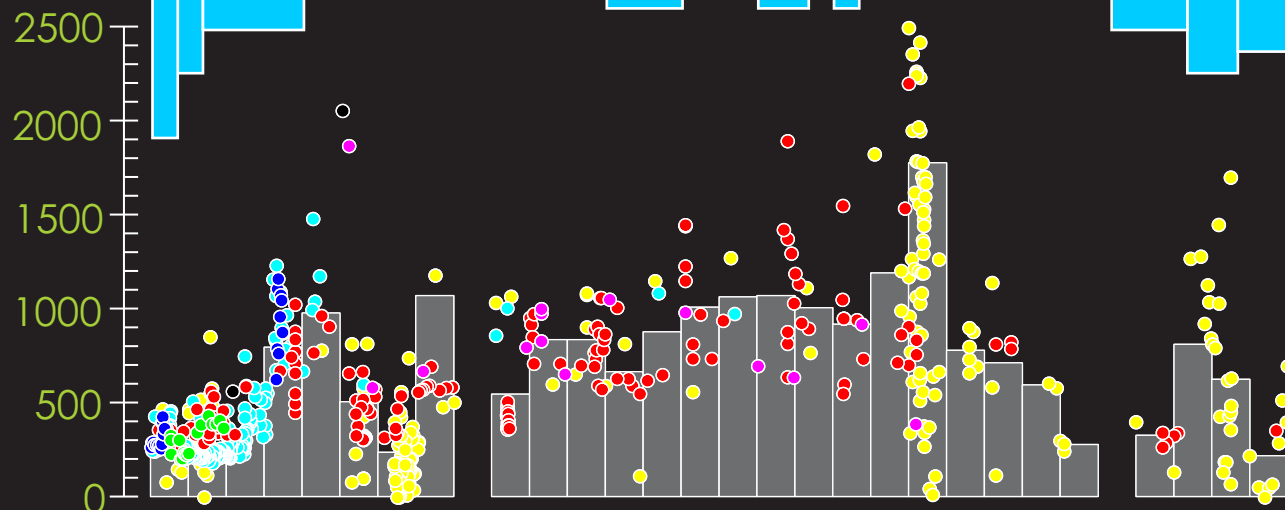
Extinction rate



Occurrence of ice ages (relative intensity)

From: Crowell [1999]

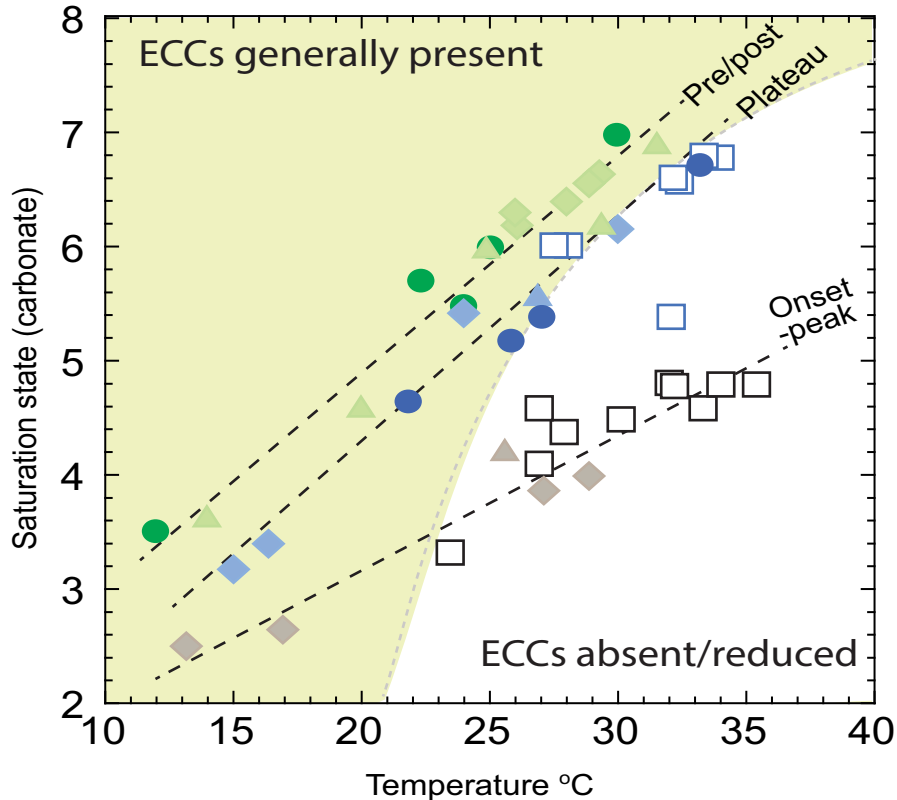
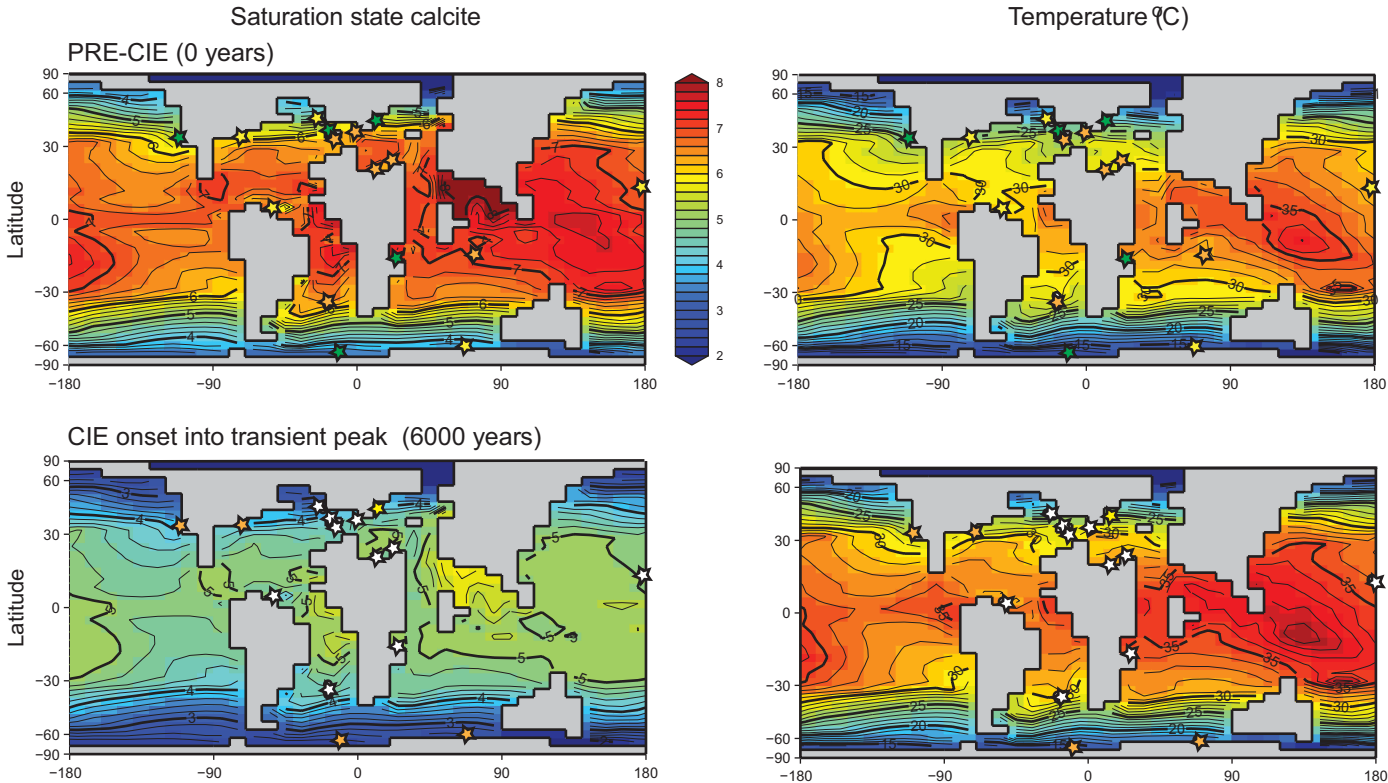
Atmospheric CO₂ (ppm)



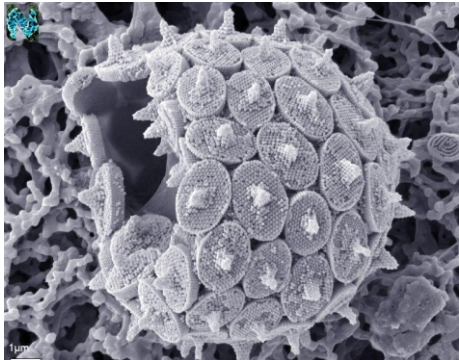
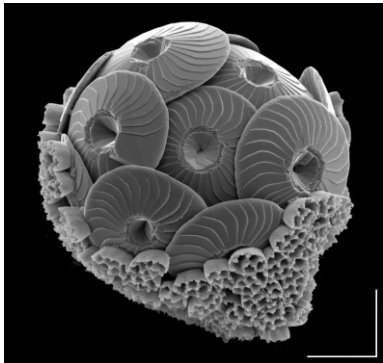
From: Hönisch et al. [2012]

Ocean warming, not acidification, controlled coccolithophore response during past greenhouse climate change

[Gibbs et al., 2015] (Geology)

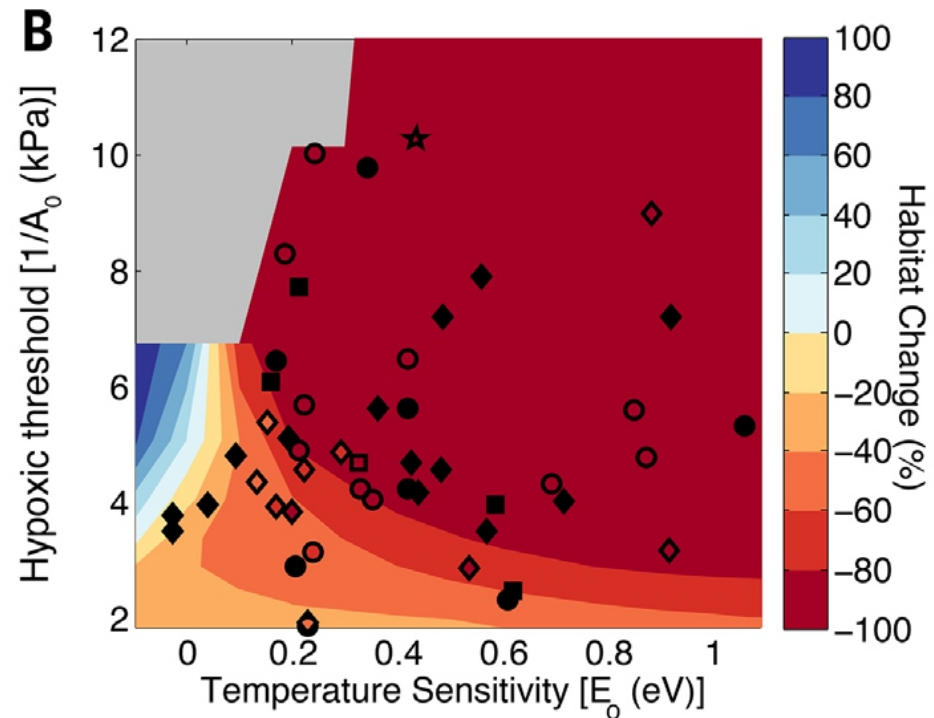
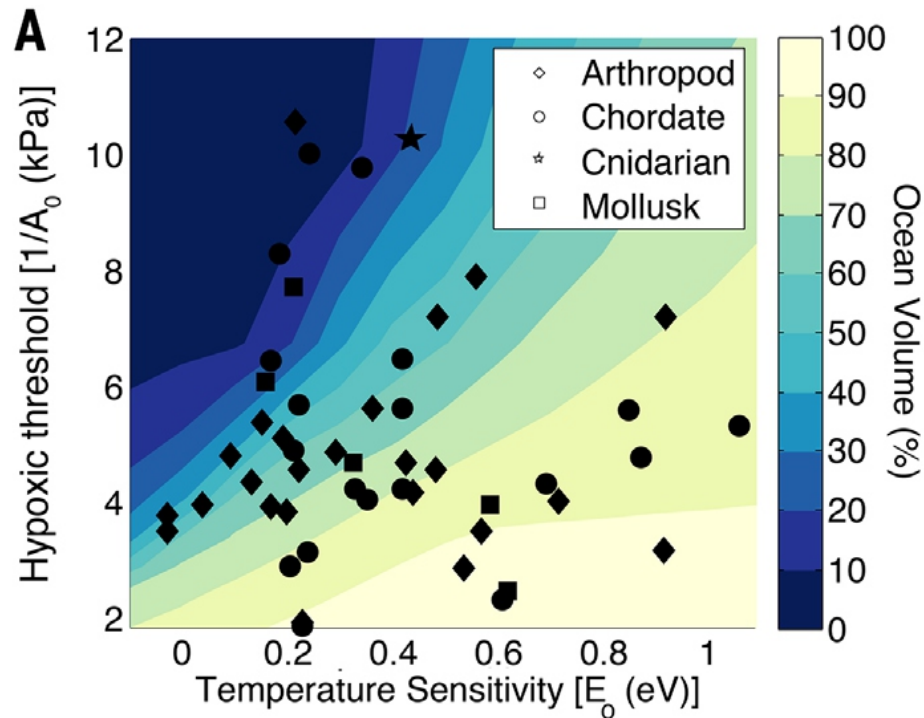
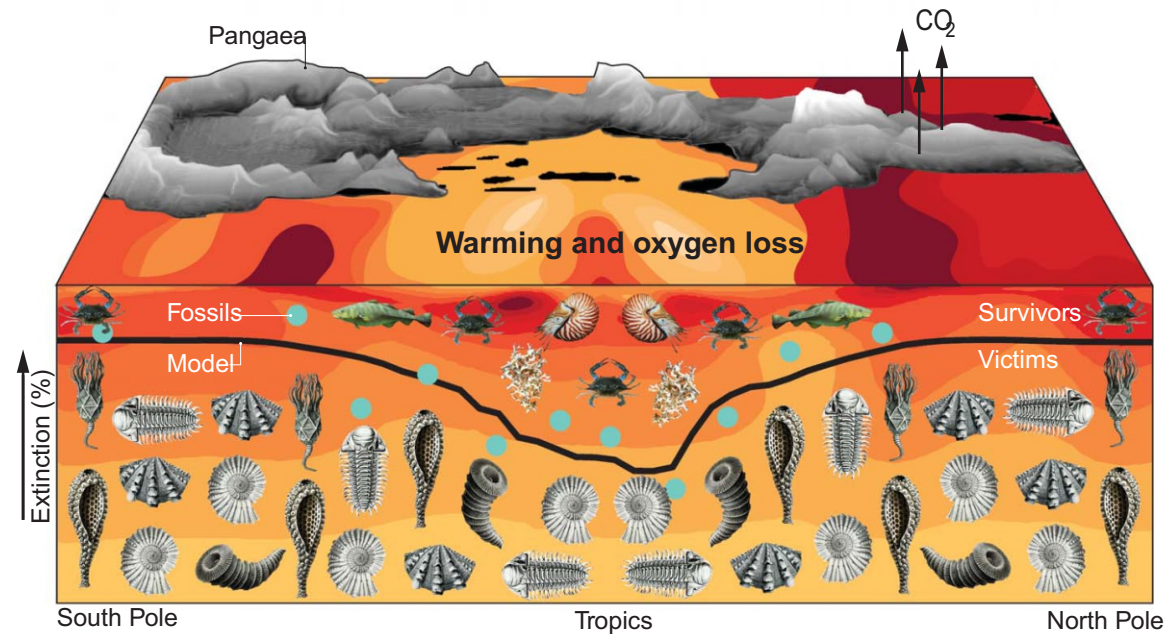


- Pre/post
- Onset-peak
- Plateau
- ECCs absent
- only *Z. bijugatus* present
- ECCs present but rare
- ECCs abundant

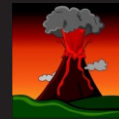


Temperature-dependent hypoxia explains biogeography and severity of end-Permian marine mass extinction

[Penn et al., 2018] (Science)



Where (when in geological time) is there a elevated-pCO₂ + elevated surface ocean carbonate saturation analogue?



Condamine et al. [2013]

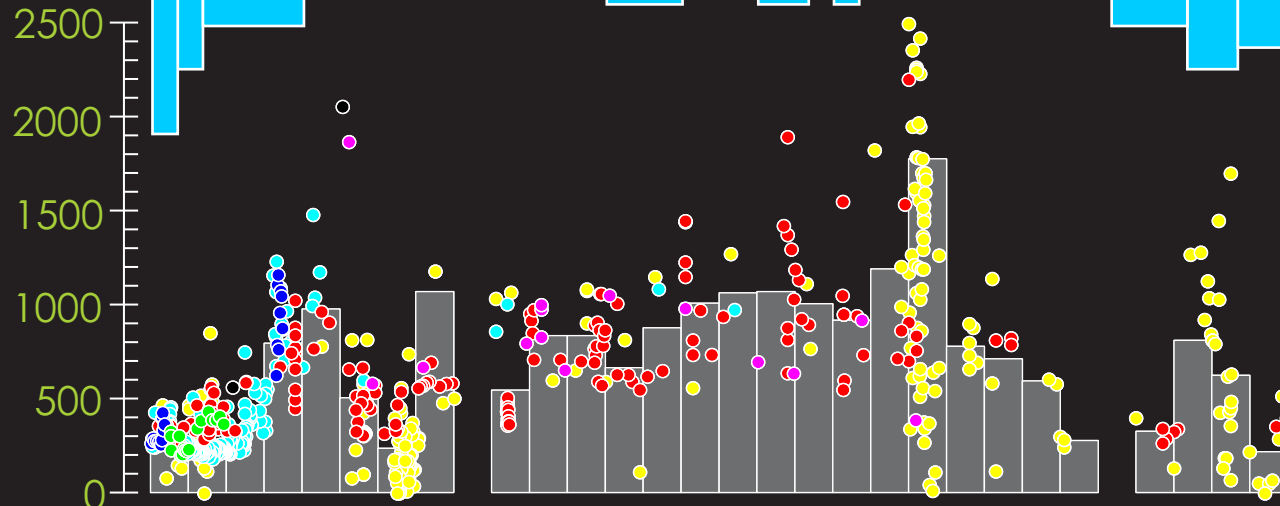
Extinction rate



Occurrence of ice ages (relative intensity)

From: Crowell [1999]

Atmospheric CO₂ (ppm)



N Pg K J Tr P Time (Ma)

From: Hönlisch et al. [2012]

From: Hönisch et al. [2012]

Mean ocean

surface $\Omega_{\text{(calcite)}}$

Atmospheric CO_2 (ppm)

mMg/Ca

Cretaceous

From: Ridgwell [2005] (Marine Geology)

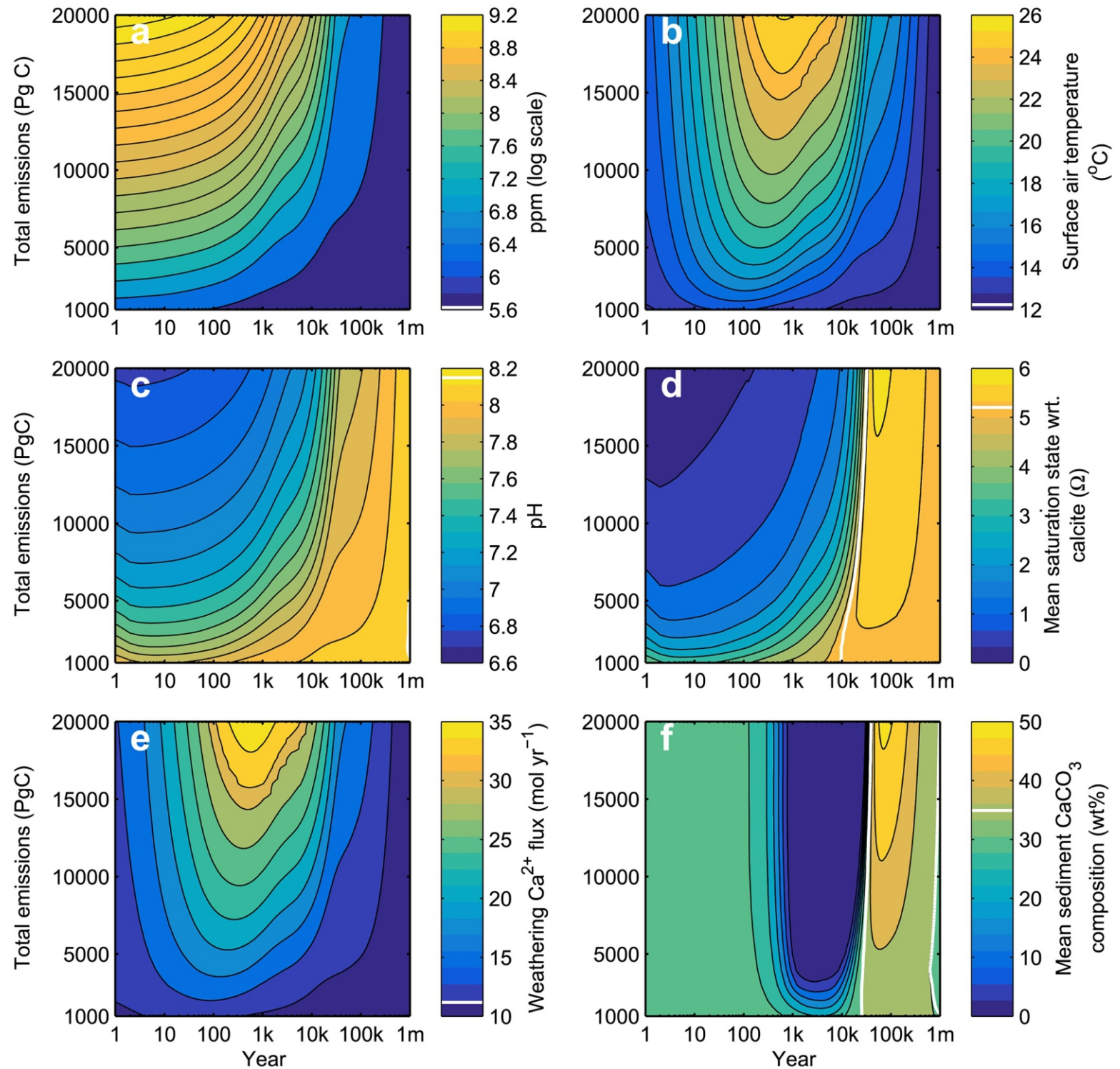
$[\text{Ca}^{2+}]$ (mmol kg^{-1})

N Pg K J Tr P Time (Ma)



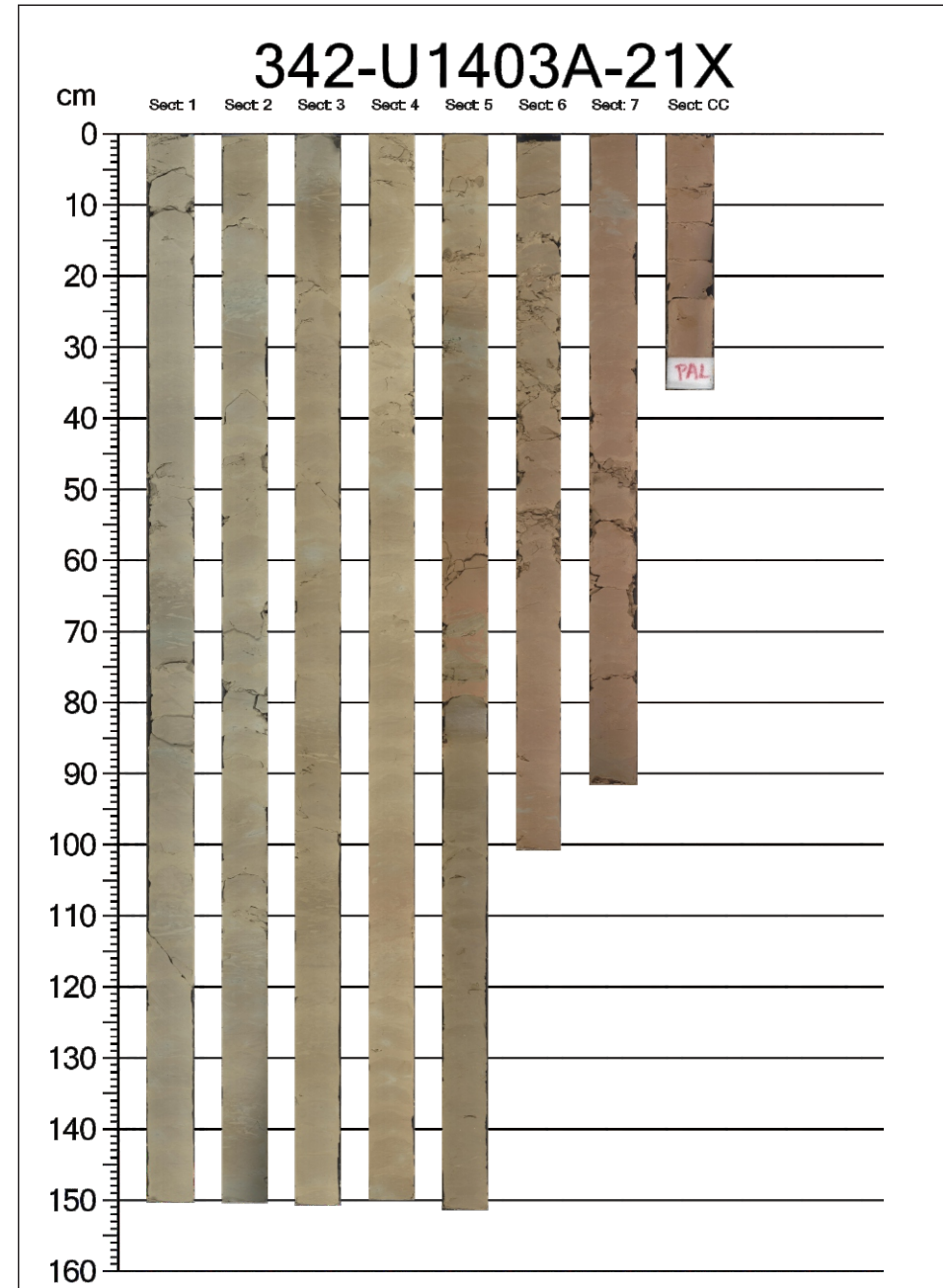
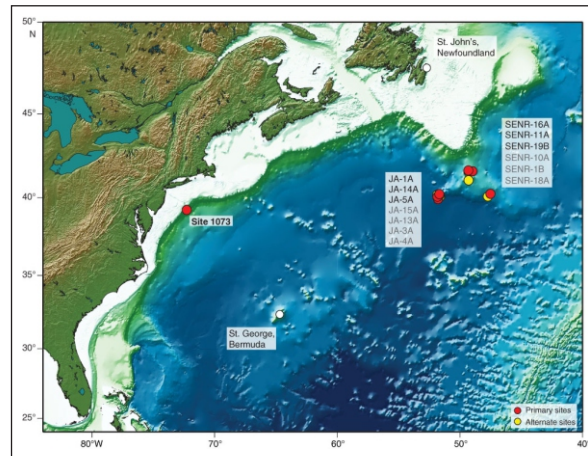
An impulse response function for the “long tail” of excess atmospheric CO₂ in an Earth system model

[Lord et al., 2015] (*Global Biogeochemical Cycles*)



An abyssal carbonate compensation depth overshoot in the aftermath of the Palaeocene–Eocene Thermal Maximum

[Penman et al., 2016] (*Nature Geoscience*)



Ecological lessons from the past – challenges

1. Even transient recovery 'over-shoots' in ocean carbonate saturation in the aftermath of massive CO₂ release events are slow (>100 kyr) compared to anthropogenic change and intervention.

This leaves the question of whether in the past, organisms adapted/evolved to changing ocean geochemical conditions.

2. Past (in the last ca. 200 Myr) intervals (whether steady state or transient) of enhanced surface ocean saturation were characterised by relatively small (<20%??) increases in saturation that occurred relatively uniformly over the ocean surface.

In contrast, ship-track based ocean chemistry manipulations may result in much more extreme and highly spatially heterogeneous changes in saturation.

3. Focus on reconstructing past changes in environment and ecology have focussed on analogue conditions to our unmitigated future (and peak pCO₂ and minima in pH and saturation).

A Research Strategy for Ocean Carbon Dioxide Removal and Sequestration

Validation & Monitoring and Environmental Risk

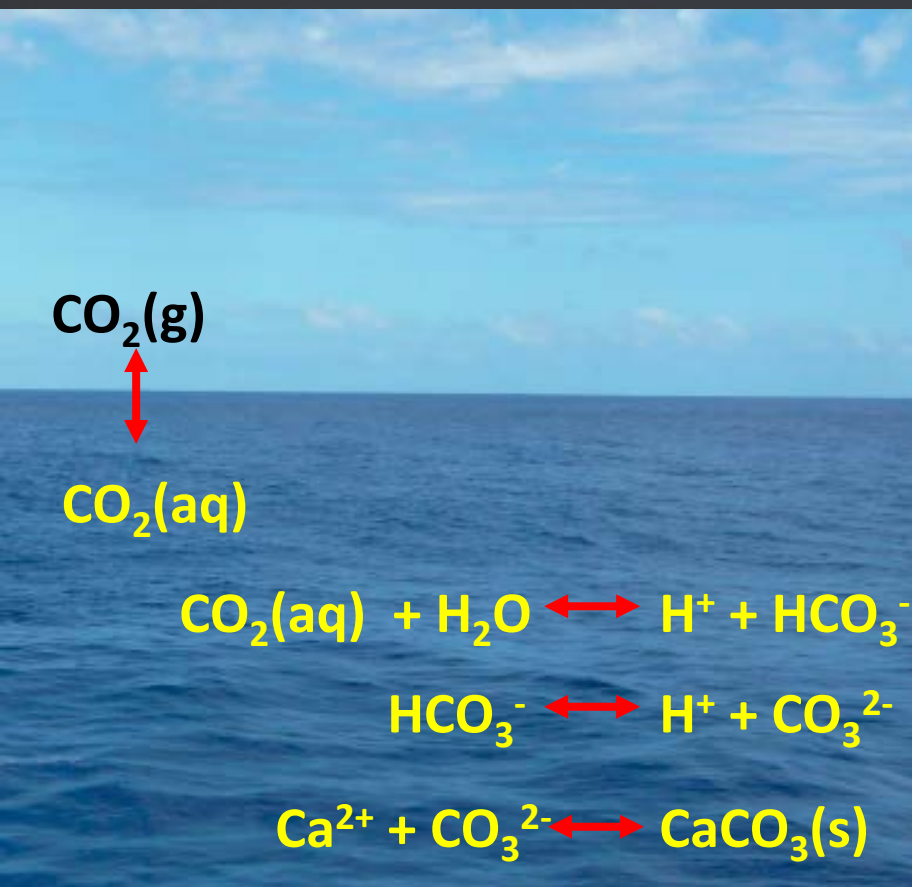
January 27, 2021

Available and emerging technologies for
monitoring marine inorganic carbon

Dr. Ellen Briggs
embriggs@hawaii.edu

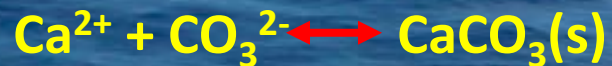


Carbon Variables



$\text{CO}_2(\text{g})$

$\text{CO}_2(\text{aq})$



pH

pCO_2

Dissolved Inorganic Carbon (C_T)

Total Alkalinity (A_T)

Repeat Hydrography (Benchtop Analyses): Climate Quality Data



Gold standard methods:

pH: Spectrophotometry

pCO₂: Gas chromatograph or
infrared CO₂ detector

C_T: Extraction of CO₂ by acidifying
seawater, coulometric titration

A_T: Acid-base titration

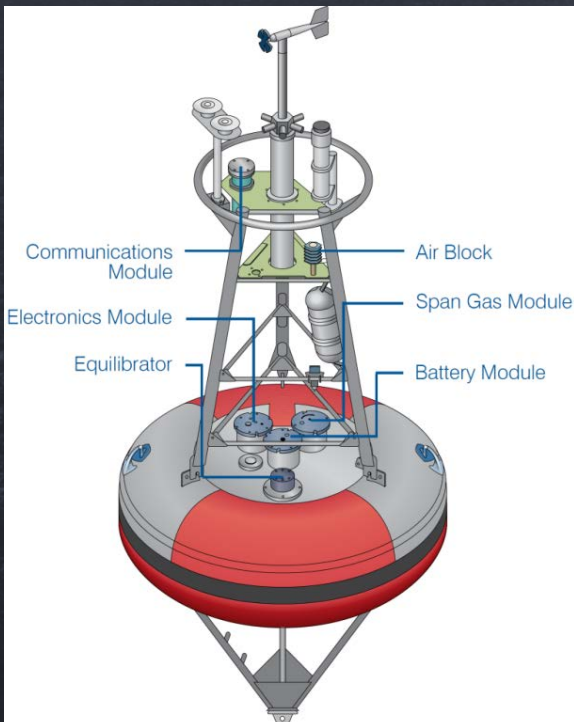
*Often limited to benchtop (not possible to miniaturize, power demands, reagents, moving parts, etc.)

In situ CO₂ measurements

Autonomous sensors for pCO₂ and pH are commercially available. Prototype C_T and A_T sensors have been developed but are not widely available.

Nearly all CO₂ sensors have been restricted to moored platforms due to high power requirements and slow response time.

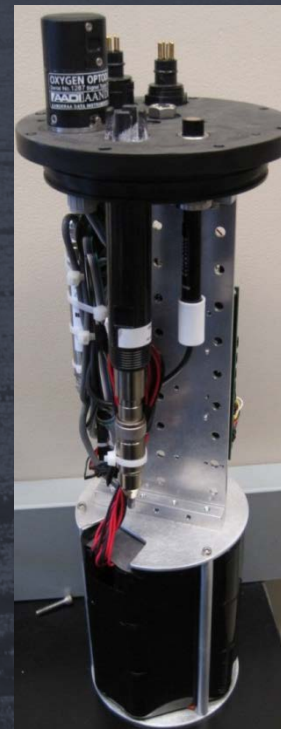
MBARI/PMEL/Battelle
pCO₂



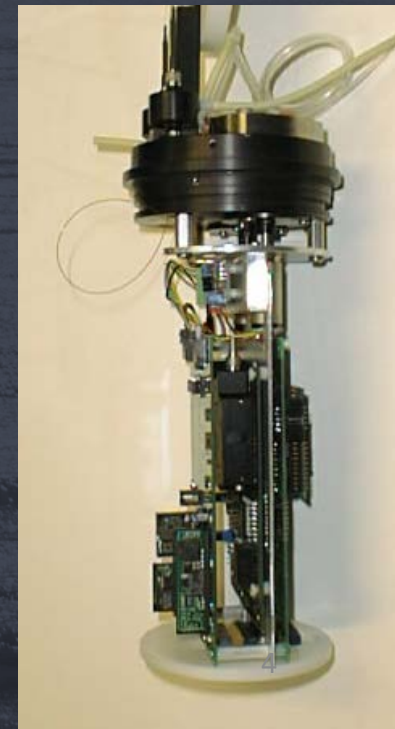
Sunburst Sensors
SAMI



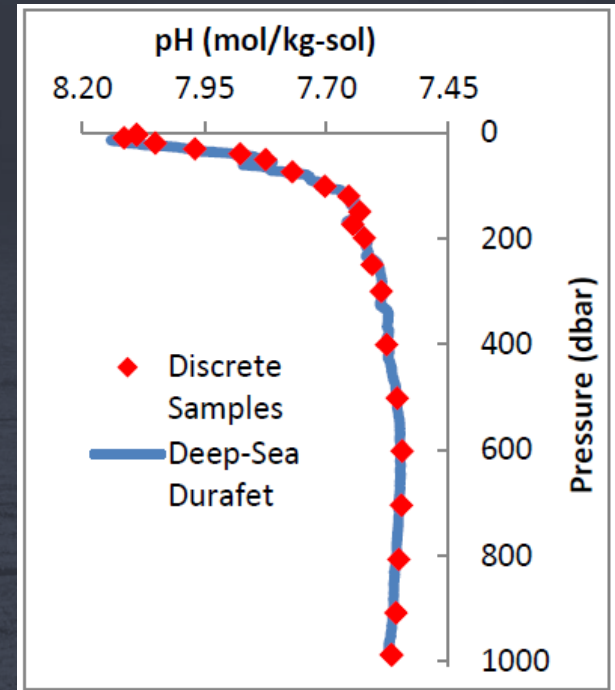
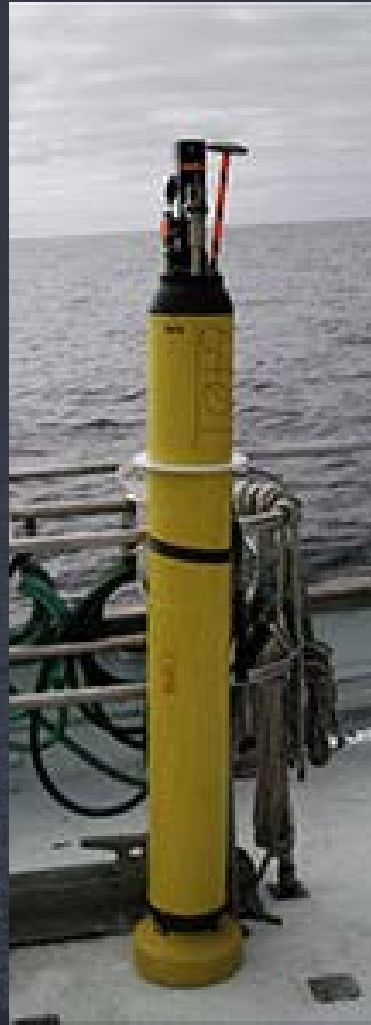
Scripps
SeapHOx



USF
S.E.A.S.



Ion Sensitive Field Effect Transistor: Solid State pH Sensor



Johnson, Kenneth S., et al. "Deep-Sea DuraFET: A pressure tolerant pH sensor designed for global sensor networks." *Analytical chemistry* 88.6 (2016): 3249-3256.

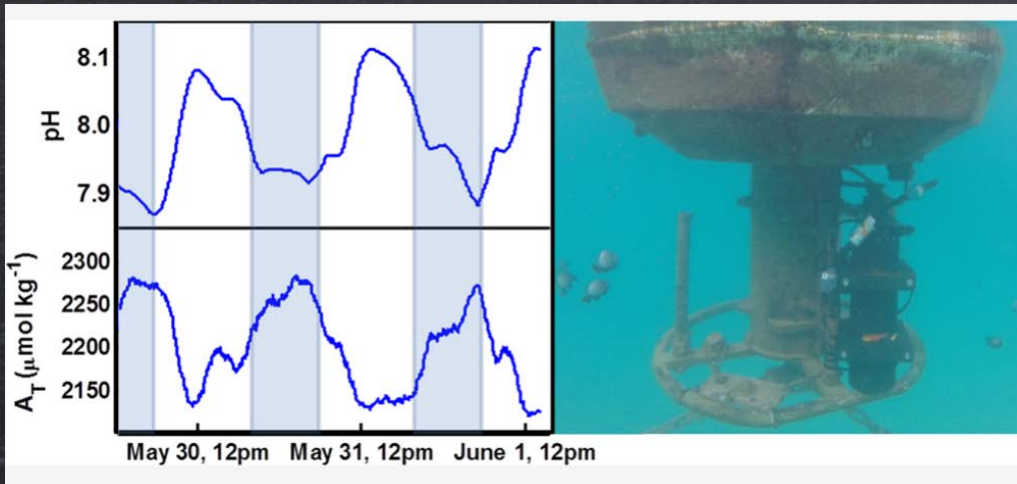
Dual pH-A_T Sensor



Integration of coulometric actuator device with ISFET:

- Titration takes seconds
- No volume/gravimetric concerns
- No reagents
- No moving parts
- nL sample
- All on one chip

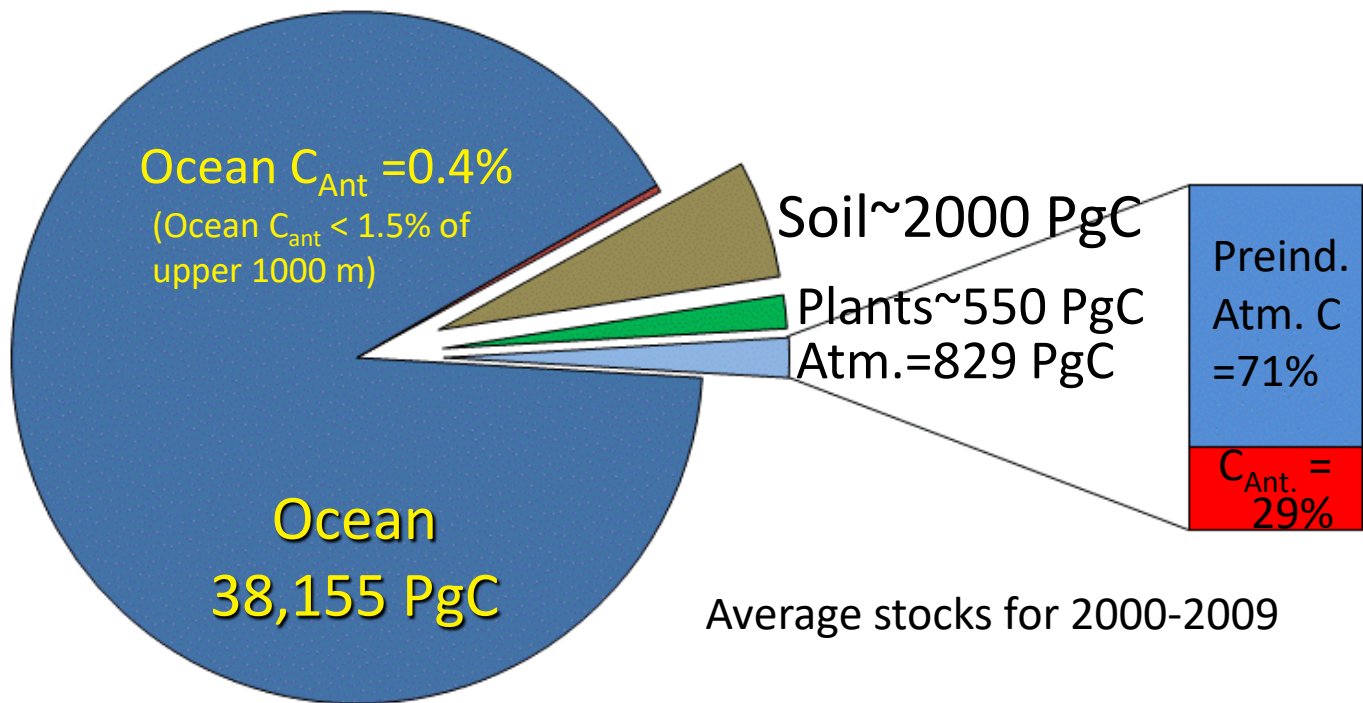
***Ideal for *in situ* monitoring!**



Questions I leave you with:

- What spatiotemporal scales required to validate and quantify carbon storage in the ocean and impacts on natural biogeochemical cycles and ecosystems?
- What degree of accuracy and precision will be required?
- Can we monitor on several smaller local scales (\$\$) or do we need a global scale effort (\$\$\$\$\$\$)?
- Which 2 of the 4 carbon parameters do we measure/prioritize? Or is there a better tracing approach (isotopes)?
- What new or emerging sensor or platform technologies do we need to invest time and resources in?

Christopher Sabine, Oceanography Professor and SOEST
Associate Dean for Research, University of Hawaii at Manoa



- Ocean contains ~90% of carbon in this 4 component system
- anthropogenic component is difficult to detect in the ocean

Ships are essential for observing the ocean, but they are expensive, require a lot of resources to mount a cruise, and have limited durability

NATIONAL RESEARCH COUNCIL

OF THE NATIONAL ACADEMIES

Ocean Studies Board

Division of Earth and Life Studies

“A suggested weighting is to initially and immediately reduce ... the UNOLS fleet by 5%.”

Autonomous platforms are a perfect complement to a CDR validation and monitoring effort



SEA CHANGE

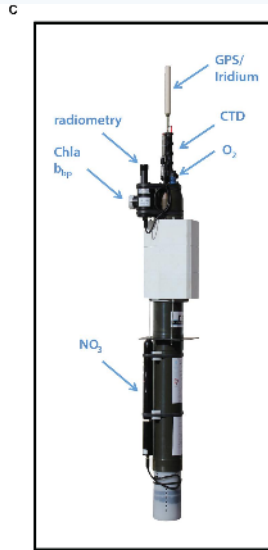
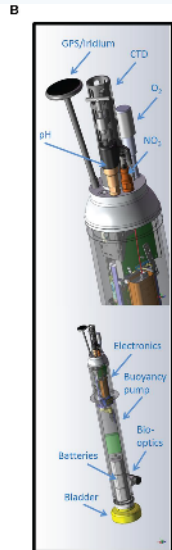
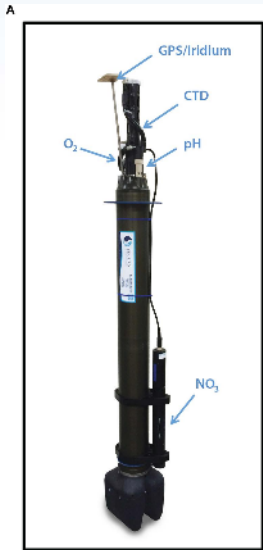
2015-2025
Decadal Survey
of Ocean Sciences

NATIONAL RESEARCH COUNCIL
OF THE NATIONAL ACADEMIES

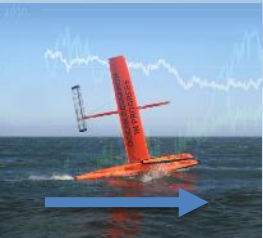
Many Varieties of Autonomous Surface Vehicles



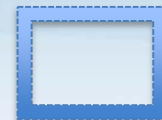
Many Varieties of Autonomous Subsurface Vehicles



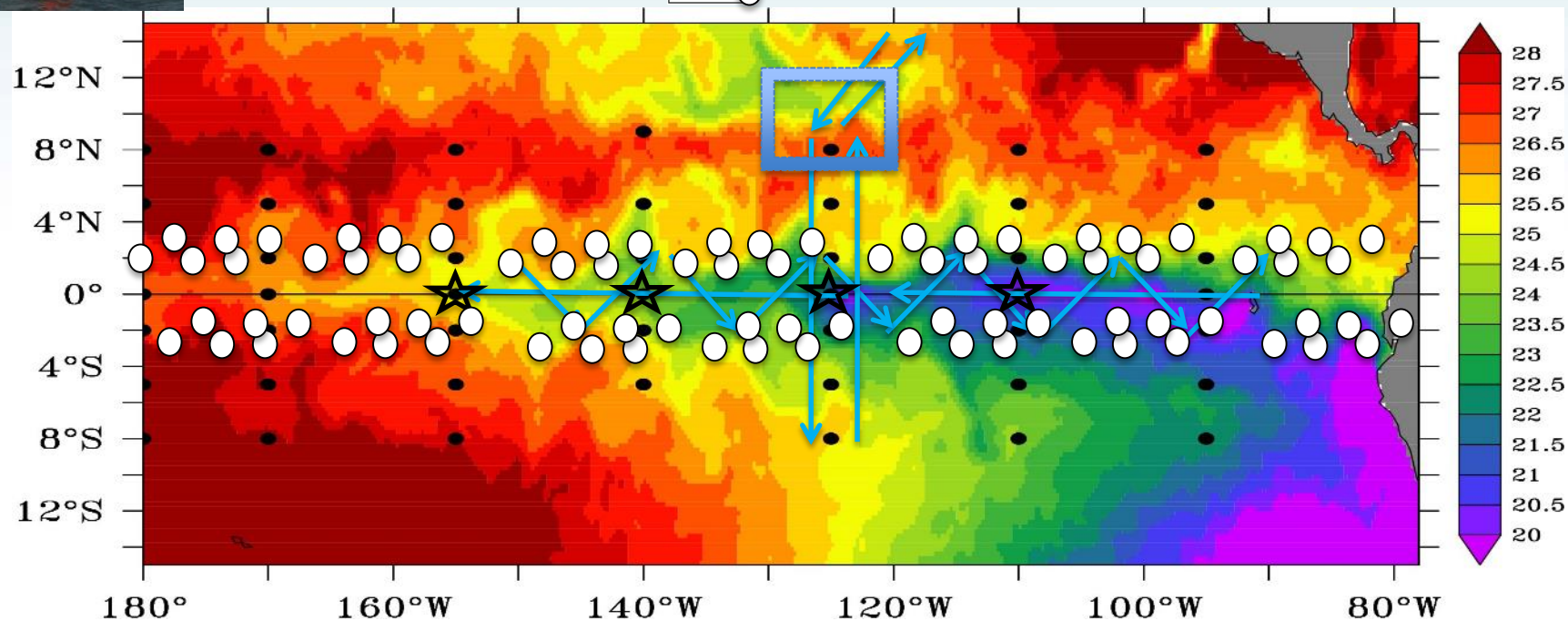
Autonomous Platforms as Low-Cost Alternatives for Observing the Planetary Boundary Layer and Surface Biogeochemistry in TPOS



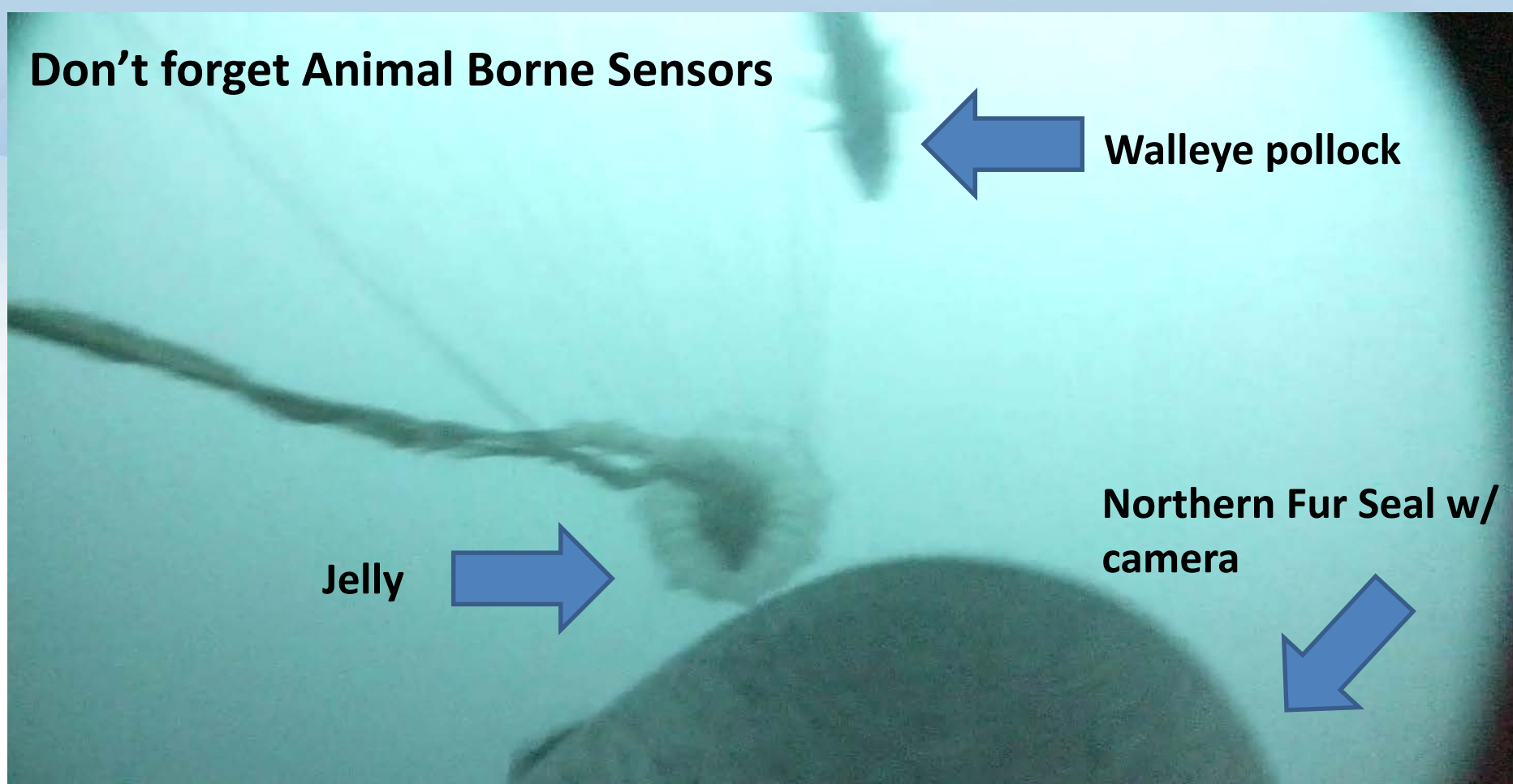
TAO buoy with CO₂
flux sensors



SPURS II
Intense Observation



Don't forget Animal Borne Sensors



Find the video and more information at:

<https://pmel.noaa.gov/itae/follow-saildrone-2017> (Northern Fur Seals equipped with CATS tags in the Bering Sea)

Questions to Consider:

- What are the potential ecological impacts from the CDR work that need to be monitored?
- Do we need to continue monitoring after the CDR experiment is over? How Long?
- Over what area do we need to monitor? Consider potential “down-stream” effects
- To what resolution do we need to measure (spatial and temporal)?

Technological and Natural Approaches to Ocean Alkalinity Enhancement and CO₂ Removal *Validation & Monitoring and Environmental Risk*

Prof. Andrew G. Dickson
UC San Diego



Validation & Monitoring

Validation & Monitoring

What is really needed?

Validation & Monitoring

What is really needed? And why?

Validation & Monitoring

What is really needed? And why?

Monitoring is the systematic and routine collection of data during project implementation for the purpose of establishing whether an intervention is moving towards the set objectives or project goals.

Validation & Monitoring

What is really needed? And why?

Monitoring is the systematic and routine collection of data during project implementation for the purpose of establishing whether an intervention is moving towards the set objectives or project goals.

Validation & Monitoring

What is really needed? And why?

Monitoring is the systematic and routine collection of data during project implementation for the purpose of establishing whether an intervention is moving towards the set objectives or project goals.

Validation & Monitoring

What is really needed? And why?

Monitoring is the systematic and routine collection of data during project implementation for the purpose of establishing whether an intervention is moving towards the set objectives or project goals.

Validation is the action of checking or proving the validity or accuracy of something; here that the set objectives or project goals have been achieved.

Validation & Monitoring

What is really needed? And why?

Monitoring is the systematic and routine collection of data during project implementation for the purpose of establishing whether an intervention is moving towards the set objectives or project goals.

Validation is the action of checking or proving the validity or accuracy of something; here that the set objectives or project goals have been achieved.

Validation & Monitoring

What is really needed? And why?

Monitoring is the systematic and routine collection of data during project implementation for the purpose of establishing whether an intervention is moving towards the set objectives or project goals.

Validation is the action of checking or proving the validity or accuracy of something; here that the set objectives or project goals have been achieved.

Fitness for purpose: the property of data produced by a measurement process that enables a user of the data to make technically correct decisions for a stated purpose.

Validation & Monitoring

What is really needed? And why?

Monitoring is the systematic and routine collection of data during project implementation for the purpose of establishing whether an intervention is moving towards the set objectives or project goals.

Validation is the action of checking or proving the validity or accuracy of something; here that the set objectives or project goals have been achieved.

Fitness for purpose: the property of data produced by a measurement process that enables a user of the data to make technically correct decisions for a stated purpose.

Validation & Monitoring

What is really needed? And why?

Monitoring is the systematic and routine collection of data during project implementation for the purpose of establishing whether an intervention is moving towards the set objectives or project goals.

Validation is the action of checking or proving the validity or accuracy of something; here that the set objectives or project goals have been achieved.

Fitness for purpose: the property of data produced by a measurement process that enables a user of the data to make technically correct decisions for a stated purpose.

Fitness for purpose therefore refers to the need to assess the magnitude of the uncertainty associated with measurement data in relation to the needs of the application.

Validation & Monitoring

What is really needed? And why?

Monitoring is the systematic and routine collection of data during project implementation for the purpose of establishing whether an intervention is moving towards the set objectives or project goals.

Validation is the action of checking or proving the validity or accuracy of something; here that the set objectives or project goals have been achieved.

Fitness for purpose: the property of data produced by a measurement process that enables a user of the data to make technically correct decisions for a stated purpose.

Fitness for purpose therefore refers to the need to assess the magnitude of the uncertainty associated with measurement data in relation to the needs of the application.

Validation & Monitoring

Validation & Monitoring

How to plan for these tasks

Validation & Monitoring

How to plan for these tasks

1. *Need to clearly articulate the set objectives of the experiment / process.*

Validation & Monitoring

How to plan for these tasks

- 1. Need to clearly articulate the set objectives of the experiment / process.*
- 2. Need to decide what measurements need to be made to monitor these effectively.*

Validation & Monitoring

How to plan for these tasks

1. *Need to clearly articulate the set objectives of the experiment / process.*
2. *Need to decide what measurements need to be made to monitor these effectively.*
Recall that characterizing changes in the state of the ocean CO₂ system needs S, T, & **two** CO₂ parameters.

Validation & Monitoring

How to plan for these tasks

- 1. Need to clearly articulate the set objectives of the experiment / process.*
- 2. Need to decide what measurements need to be made to monitor these effectively.*
Recall that characterizing changes in the state of the ocean CO₂ system needs S, T, & **two** CO₂ parameters.
- 3. Need measurements made with a small enough uncertainty to enable effective validation and monitoring.*

Validation & Monitoring

How to plan for these tasks

1. *Need to clearly articulate the set objectives of the experiment / process.*
2. *Need to decide what measurements need to be made to monitor these effectively.*
Recall that characterizing changes in the state of the ocean CO₂ system needs S, T, & **two** CO₂ parameters.
3. *Need measurements made with a small enough uncertainty to enable effective validation and monitoring.*
This condition is tightly linked to #1 and #2 above.

Validation & Monitoring

How to plan for these tasks

1. *Need to clearly articulate the set objectives of the experiment / process.*
2. *Need to decide what measurements need to be made to monitor these effectively.*
Recall that characterizing changes in the state of the ocean CO₂ system needs S, T, & **two** CO₂ parameters.
3. *Need measurements made with a small enough uncertainty to enable effective validation and monitoring.*
This condition is tightly linked to #1 and #2 above.
4. *Need to consider how frequently measurements need to be made and how they need to be distributed geographically.*

Validation & Monitoring

How to plan for these tasks

1. *Need to clearly articulate the set objectives of the experiment / process.*
2. *Need to decide what measurements need to be made to monitor these effectively.*
Recall that characterizing changes in the state of the ocean CO₂ system needs S, T, & **two** CO₂ parameters.
3. *Need measurements made with a small enough uncertainty to enable effective validation and monitoring.*
This condition is tightly linked to #1 and #2 above.
4. *Need to consider how frequently measurements need to be made and how they need to be distributed geographically.*
Does this imply the use of autonomous instrumentation?

Validation & Monitoring

How to plan for these tasks

1. *Need to clearly articulate the set objectives of the experiment / process.*
2. *Need to decide what measurements need to be made to monitor these effectively.*
Recall that characterizing changes in the state of the ocean CO₂ system needs S, T, & **two** CO₂ parameters.
3. *Need measurements made with a small enough uncertainty to enable effective validation and monitoring.*
This condition is tightly linked to #1 and #2 above.
4. *Need to consider how frequently measurements need to be made and how they need to be distributed geographically.*
Does this imply the use of autonomous instrumentation?
Do such instruments have the necessary measurement uncertainty?

Validation & Monitoring

How to plan for these tasks

Validation & Monitoring

How to plan for these tasks

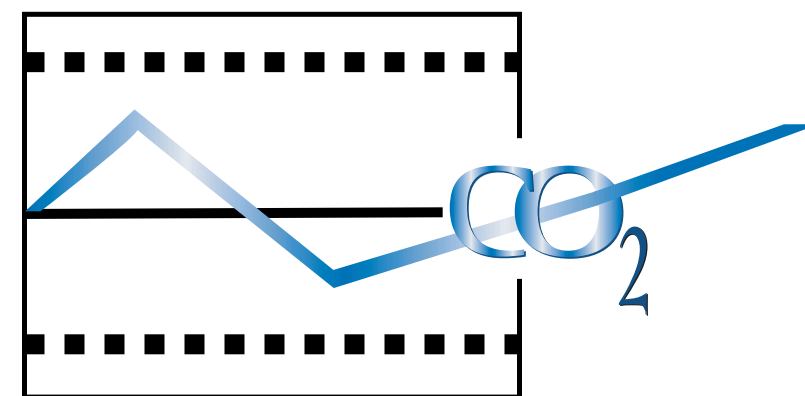
- 5. If validation is desirable for a legal purpose, then — of course — a suitable quality assurance plan is needed for each of the measurements made.*

Validation & Monitoring

How to plan for these tasks

5. *If validation is desirable for a legal purpose, then — of course — a suitable quality assurance plan is needed for each of the measurements made.*

The above discussion, although focussed on assessing the ocean CO₂ changes concomitant on ocean-based carbon dioxide removal and sequestration will need (I feel) a similar sequence of activities to monitor and validate accompanying studies of environmental risk.



A CaCO₃ Patch Experiment

“ChalkEx” 2001 and 2003

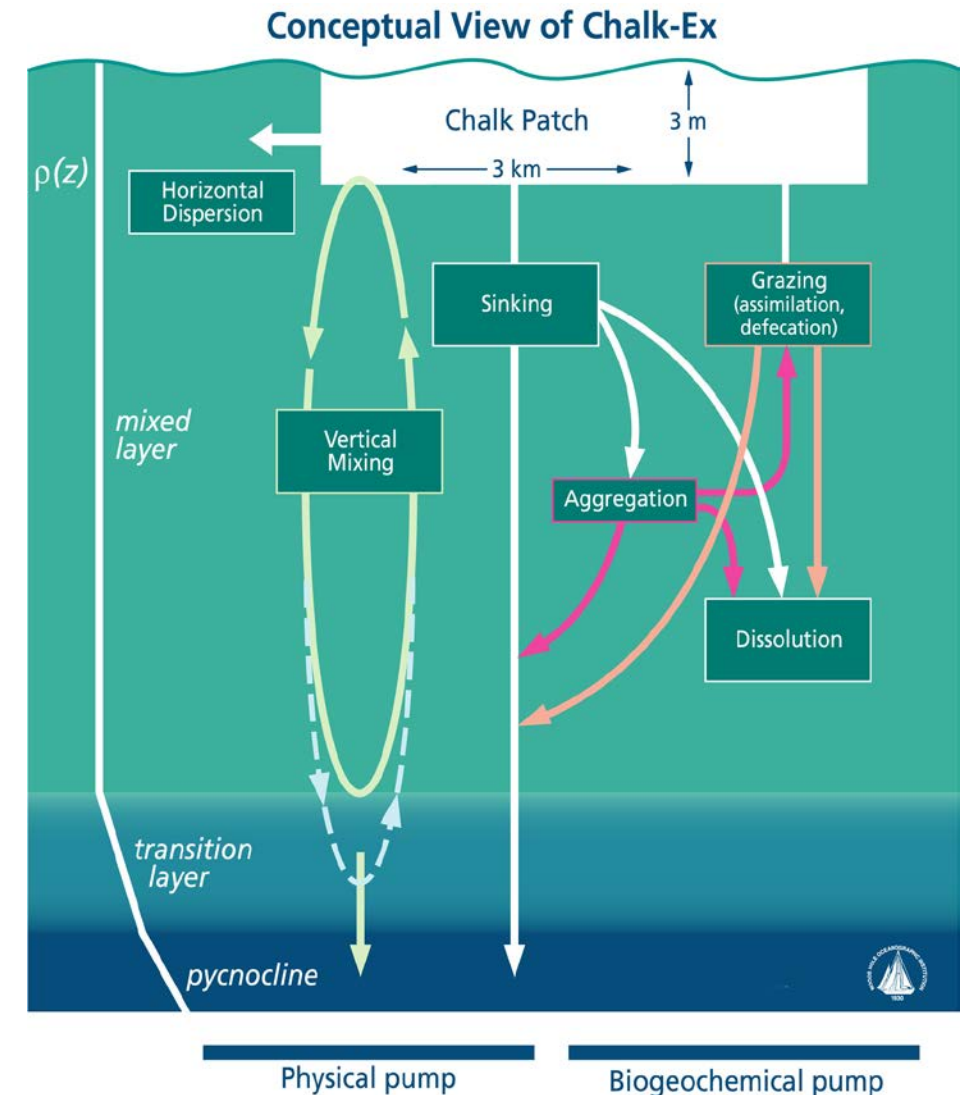
Conceived by : Dr Barney Balch, Bigelow Lab

Described in: Balch et al., 2009

doi:10.1029/2008JC004902

Motivation

- Fate of coccolithophore blooms
- Competing processes:
 - Production
 - Vertical mixing, horizontal dispersion
 - Aggregation, grazing, sinking
- Assessing a complex system
 - Control production in mixed layer
 - Quantify losses by observation
 - Use Lagrangian reference frame



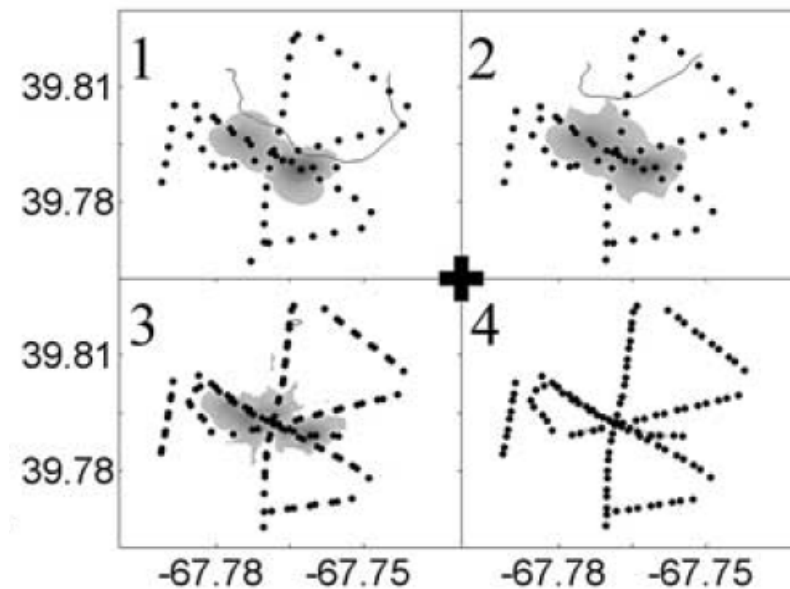
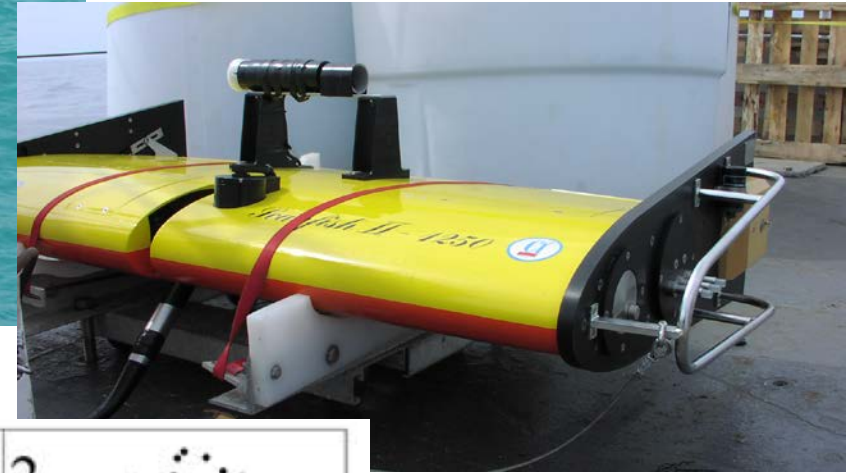
Approach

- Known production
 - Ground cretaceous chalk
 - 13,000 kg per patch
 - 10 micron size
- Create a patch
 - Dilute in 500 gal tanks
 - Disperse at the fantail
 - Steam a spiral



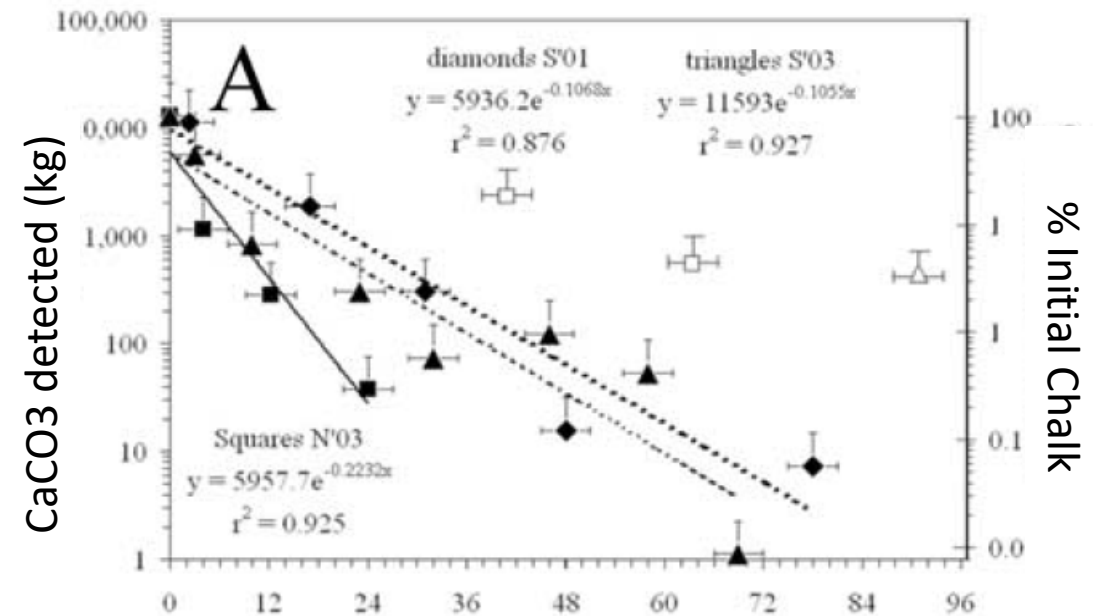
Approach

- Measure the patch
 - Lagrangian drifter
 - Towed-undulating vehicle
 - Detect optically
 - Map in layers
- Compute the chalk budget
 - Production known
 - Estimate loss terms



Results

- Exponential decline in detected mass
 - <10% accounted for after 24 hr
 - Undetectable after 72 hr
- Physical processes dominated
 - Dispersion and subduction
 - Eddy diffusivity 500-1000 m²/s
 - Thin layers at mixed-layer base
- Sustained Cocco. blooms?
 - Require exponential production



Implications and Questions

- Sampling and detection are difficult
 - Could not resolve a small patch (km-scale) with fast sampling (7.5 kt)
 - Rapid drop in concentration; high sensitivity needed
- Creation of a mega-patch raises some questions
 - Impact on primary production?
 - Shoal the euphotic zone to a few meters
 - Water column food web disruption?
 - Supply non-nutritious particles to grazers
 - Benthic ecosystem impacts?
 - Supply sinking particles to the sea floor