School of Earth and Ocean Sciences
Ysgol Gwyddorau'r Ddaear a'r Môr

An Accelerated Weathering of Limestone reactor

Dr. Phil Renforth

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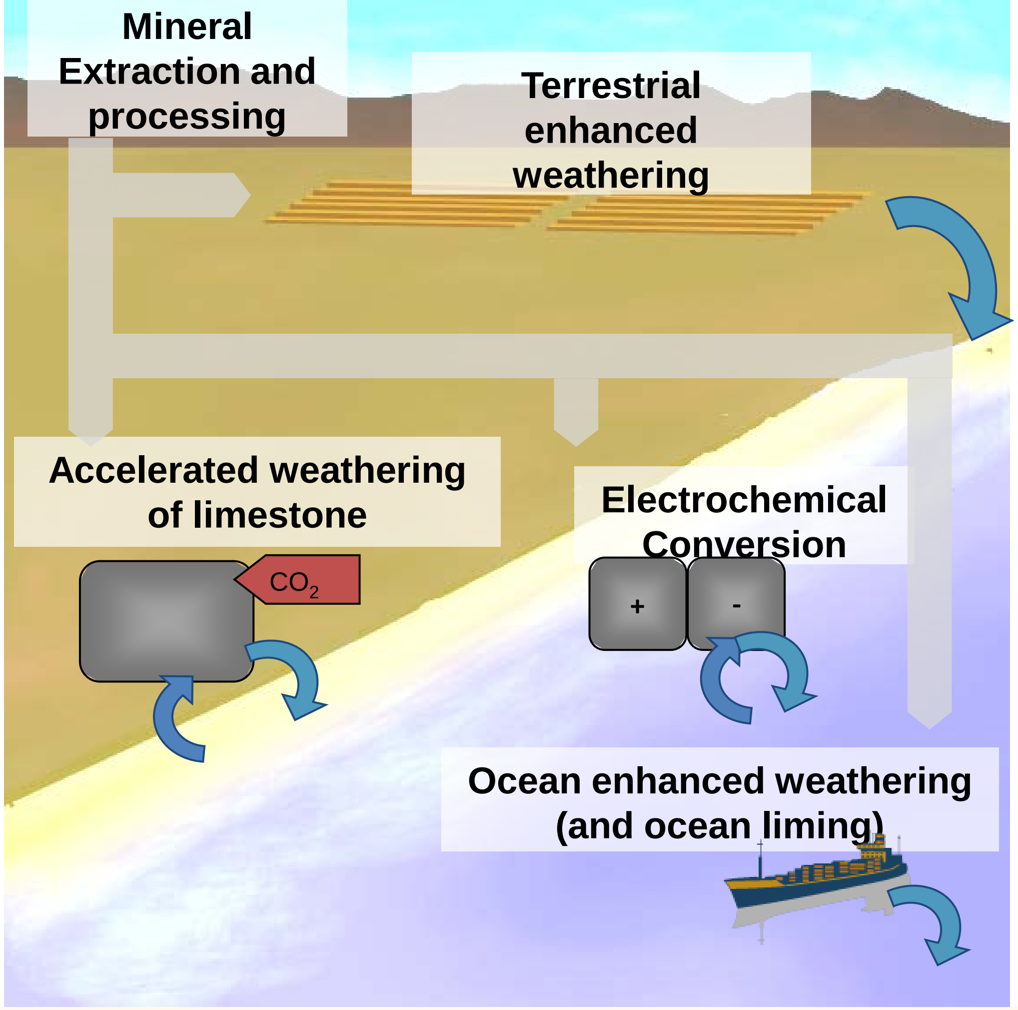
Alternative CCS technologies meeting (Oxford, UK) 26th June 2014

The potential of ocean alkalinity



- Global potential of carbon storage as alkalinity not fully understood.
- Large volumes of carbon may be stored. (~ 000's $GtCO_2$)

Paquay and Zeebe, 2013
Ilyina et al., 2013

Ocean alkalinity carbon storage questions

- What is the environmental impact of a large scale AWL industry?

- How stable is the carbon reservoir?

AWL as a reactor

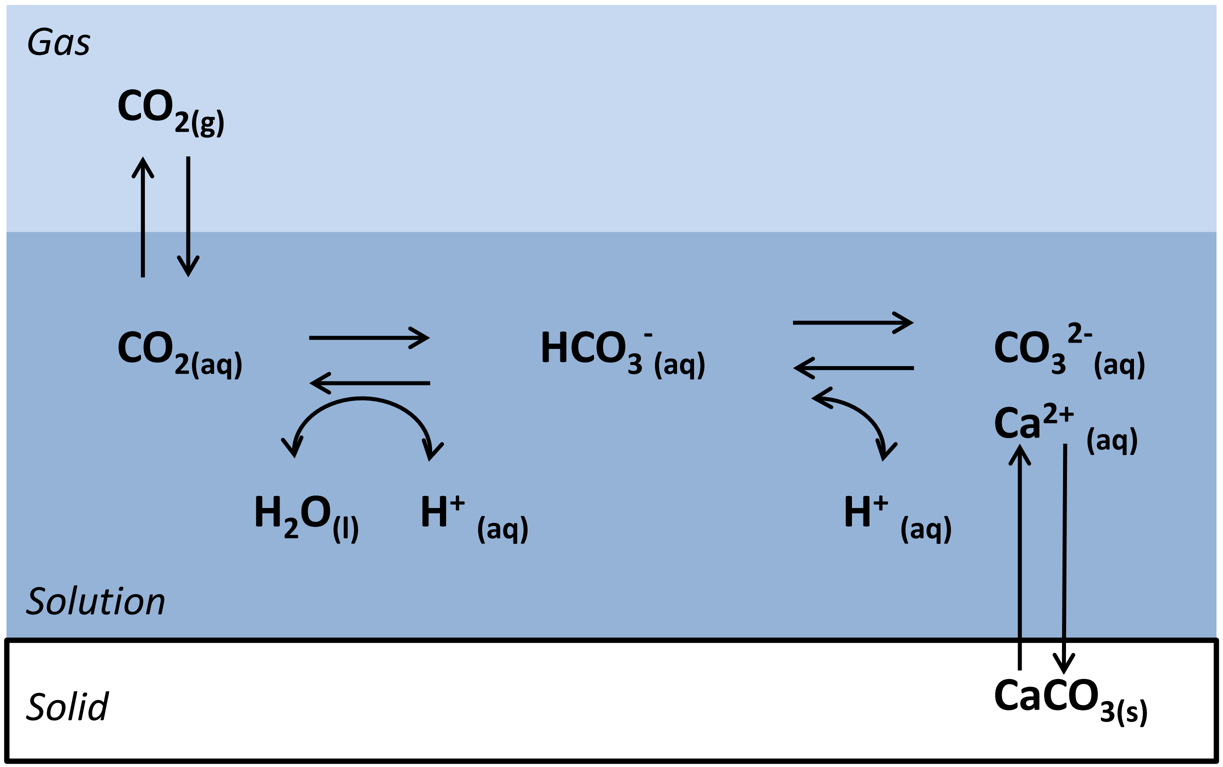
poor carbonate mineral solubility =

Large mass ratio of seawater to CO_2 ('000s)

- Pumping is likely to be one of the primary energy consuming activities
- Minimise/or be limited by, vertical displacement of water
- Lack of control
- Probably a large reactor

AWL - Reactions

$CaCO_{3(s)} + H_2O_{(l)} + CO_{2(g)} \longrightarrow Ca^{2+}_{(aq)} + 2HCO3^{-}_{(aq)}$



Other species (% of total dissolved carbon species):

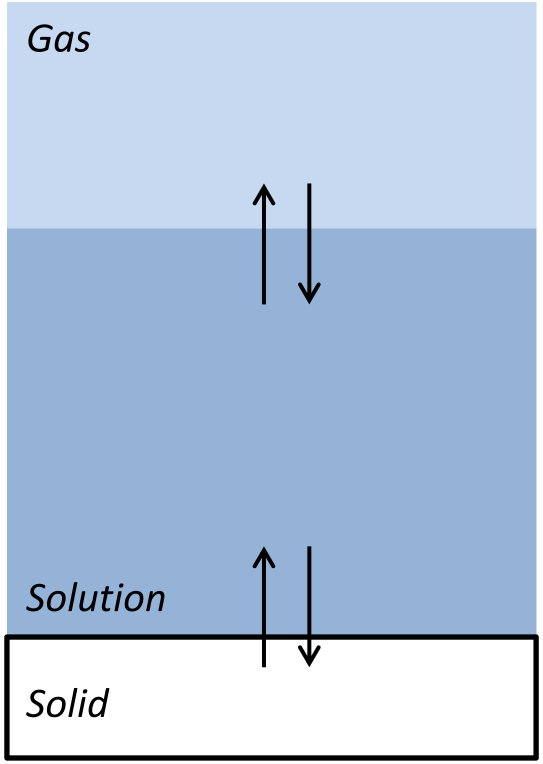
$MgHCO_3^{+}{}_{(aq)}$	(11%)
$NaHCO_{3\,(aq)}$	(8%)
$CaHCO_3^{+}{}_{(aq)}$	(2%)
$MgCO_{3\,(aq)}$	(0.6%)
$NaCO_3^{-}{}_{(aq)}$	(0.3%)
$CO_3^{2-}{}_{(aq)}$	(0.3%)

High ionic strength of seawater

Y_{Ca2+}	0.26
Y_{HCO3-}	0.68
Y_{CO32-}	0.21

Approach

PHREEQC modelling



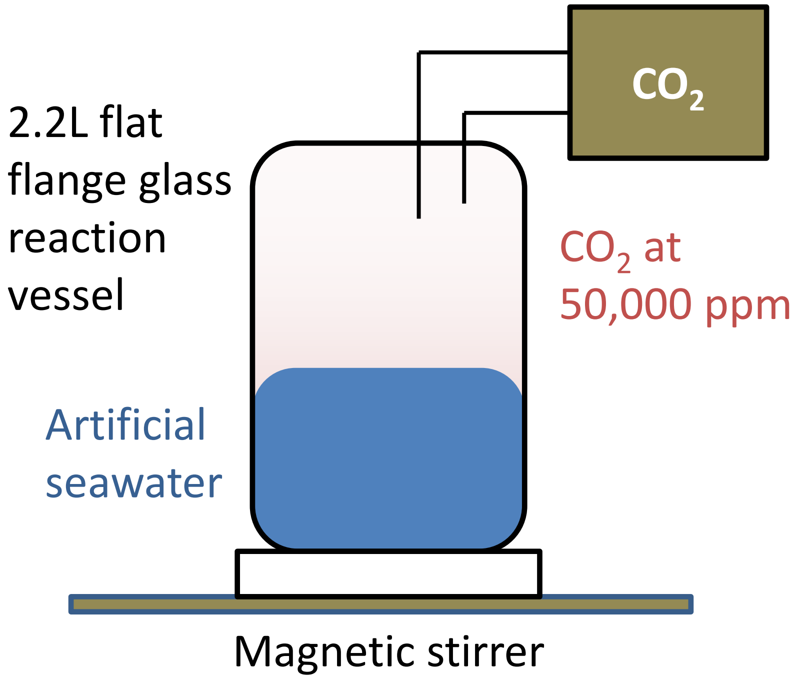
Input: partial P, Volume, Temp,

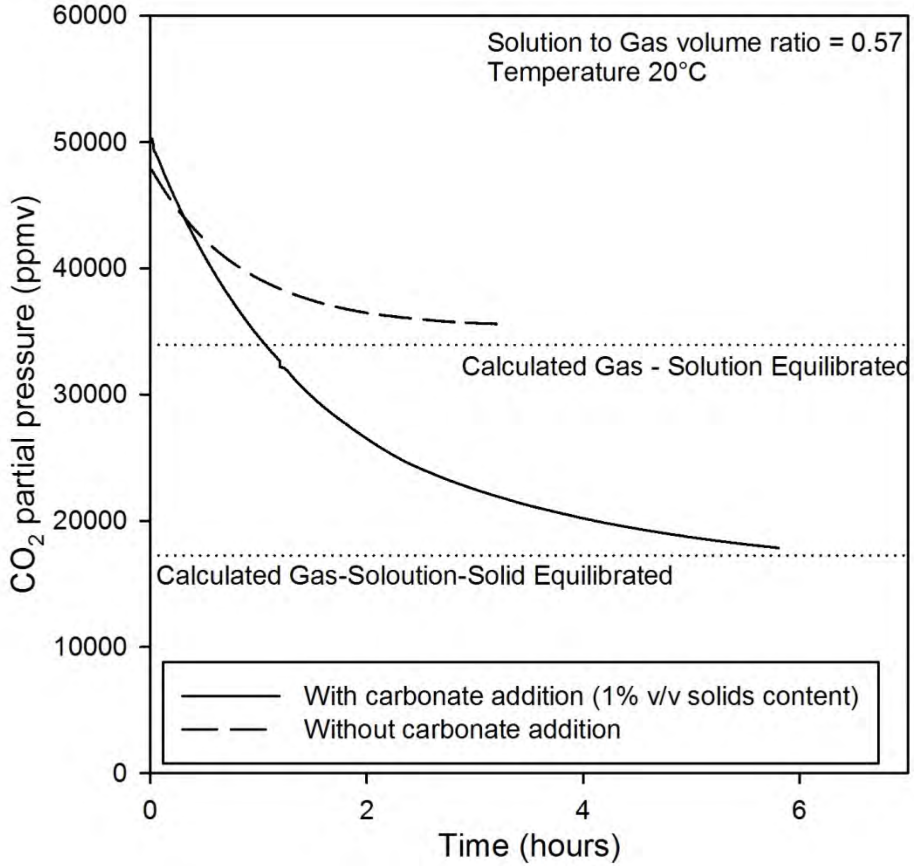
Input: Initial seawater chemistry, Volume, Temp,

Input: mineral, moles to dissolve and/or saturation state

Batch experiments

Experimental





Limestone: The great Oolitie formation,
Crushed and dry sieved to between 500 – 1000µm
Sonicated in dionised water to remove microfines

Kinetic Modelling

Gas mass transfer

$$CO_{2(g)} \xleftrightarrow{k_1} CO_{2(aq)}$$

$$r_1 = \frac{D_{CO_2} \cdot k_1}{z}([CO_2]_{(gas)} - [CO_2]_{(sol)})$$

CO_2 hydration

$$CO_{2(aq)} + H_2O_{(l)} \xleftrightarrow{k_2} HCO^-_{3\,(aq)} + H^+_{(aq)}$$

$$r_2 = k_2[CO_2] - k_2'[HCO_3^-][H^+]$$

Limestone dissolution

$$CaCO_{3(s)} \xleftrightarrow{k_3} Ca^{2+}_{(aq)} + CO^{2-}_{3(aq)}$$

$$r_3 = k_3\left(1 - \frac{[Ca^{2+}][CO_3^{2-}]}{k_{sp}}\right)$$

Considerable existing work deriving $k_1, k_2, k_3, k_{sp}, D_{CO2}$ (T,S).

Rates r_1 and r_3 multiplied by interfacial area normalised to solution volume.

Boundary layer z assumed ~ 60µm (Bolin 1960; Jähne 2012)

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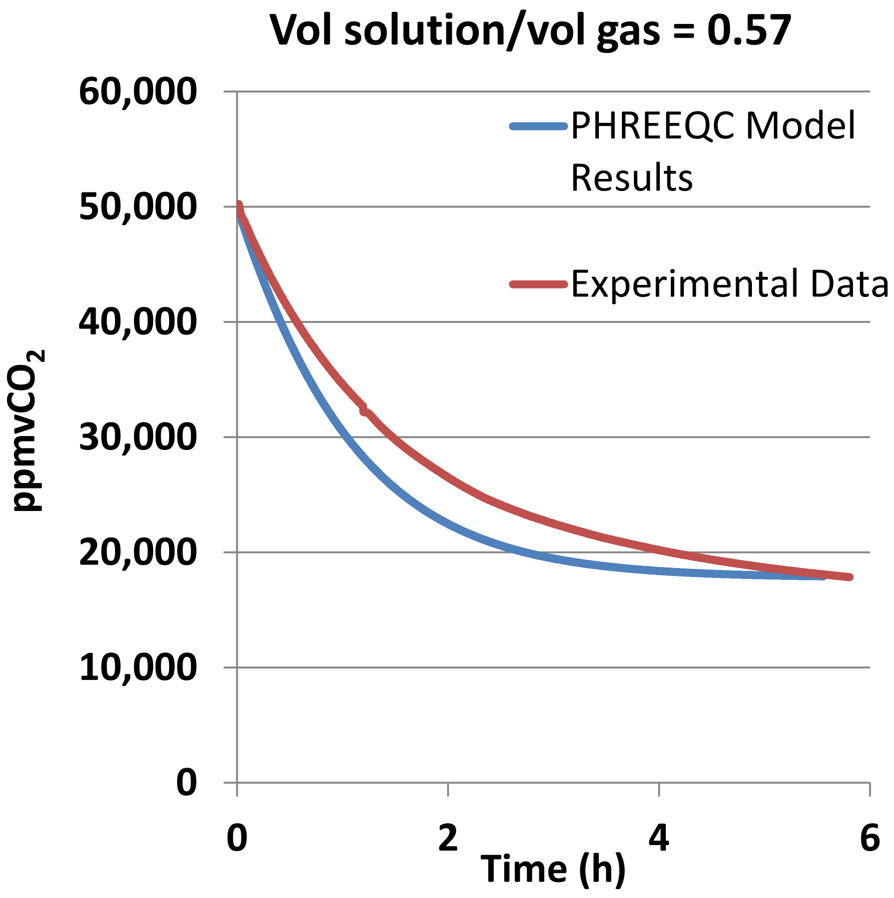
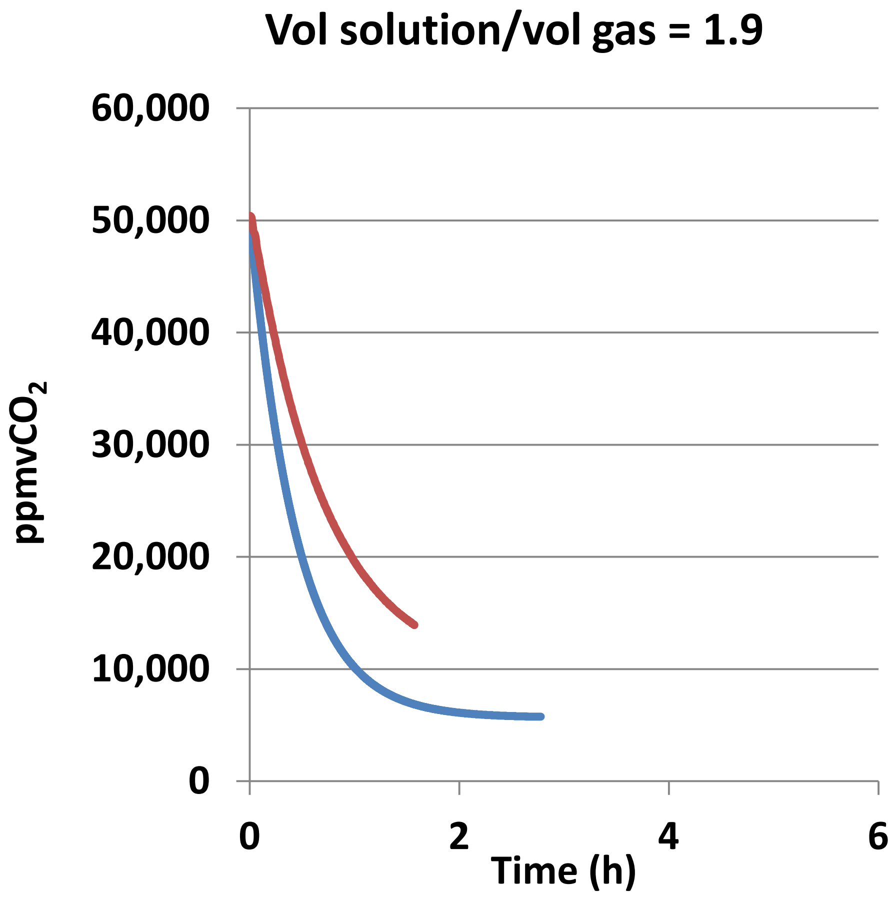
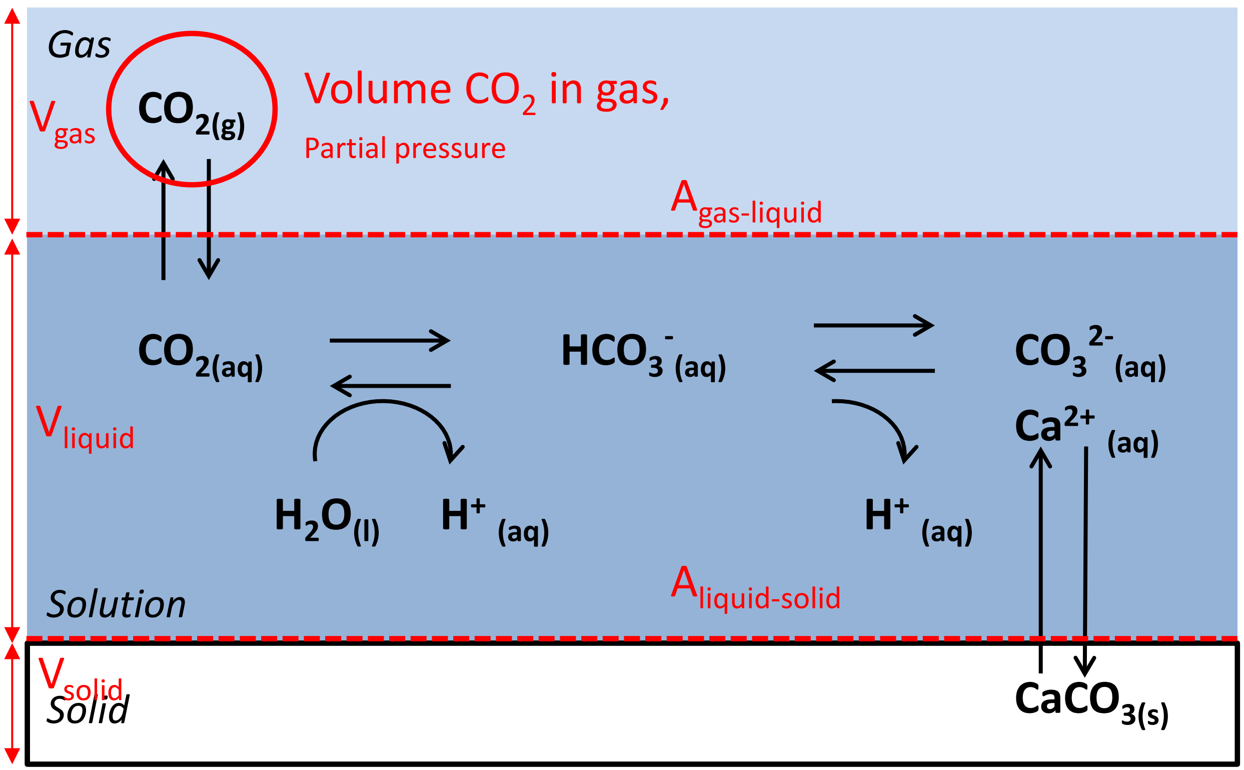
Results comparison





AWL – Reactions Control

$CaCO_{3(s)} + H_2O_{(l)} + CO_{2(g)} \longrightarrow Ca^{2+}_{(aq)} + 2HCO3^{-}_{(aq)}$



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Integrated model

Initial cond.

pCO_2, F_{CO2}, T…

PHREEQC Reactor model

Outcomes

Residency time

Reactor volume

Cursory reactor design

Energy requirements

Solid material handling

Surface area creation (comminution),
Short distance material transport,
Stacking, Dewatering,
Fuel

Gas blowing and compression

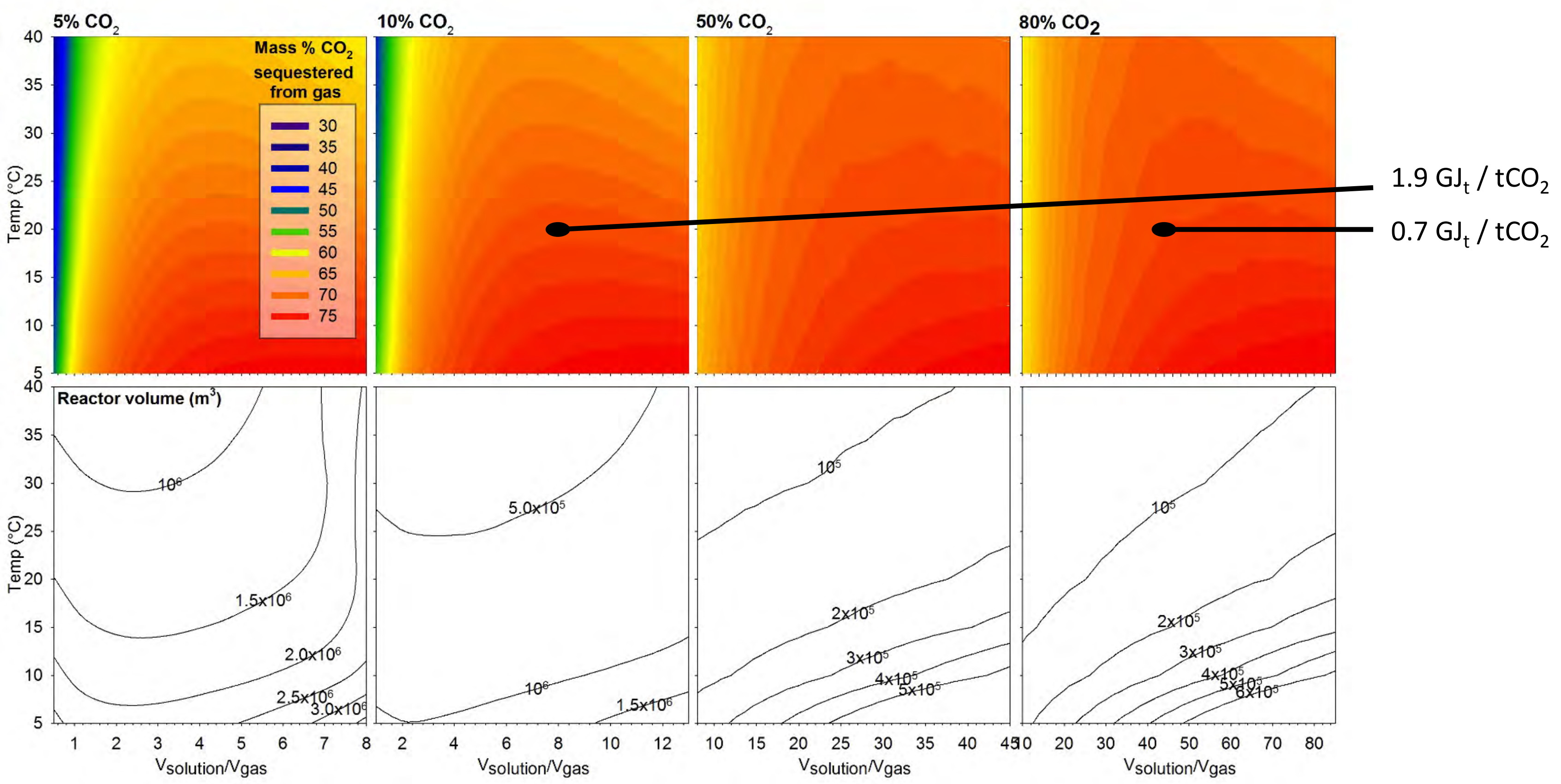
Fun (water depth, interfacial area, recirculation)
~0.5 bar overpressure

Seawater movement/ pumping

Fun (velocity head, frictional losses)
Fun (residency time, reactor dimensions,
Static mixing, material)

Normalised as total thermal to net carbon sequestered
GJ_t / tCO_2

Sensitivity analysis



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Conclusions and future work

- Large reactor (10^5-10^6 m^3 per million tonne CO_2 p.a.)

- Higher CO_2 capture in colder waters, but larger reactor volume

- Potential relative benefits of gas separation

- Counter-flow for volume reduction?

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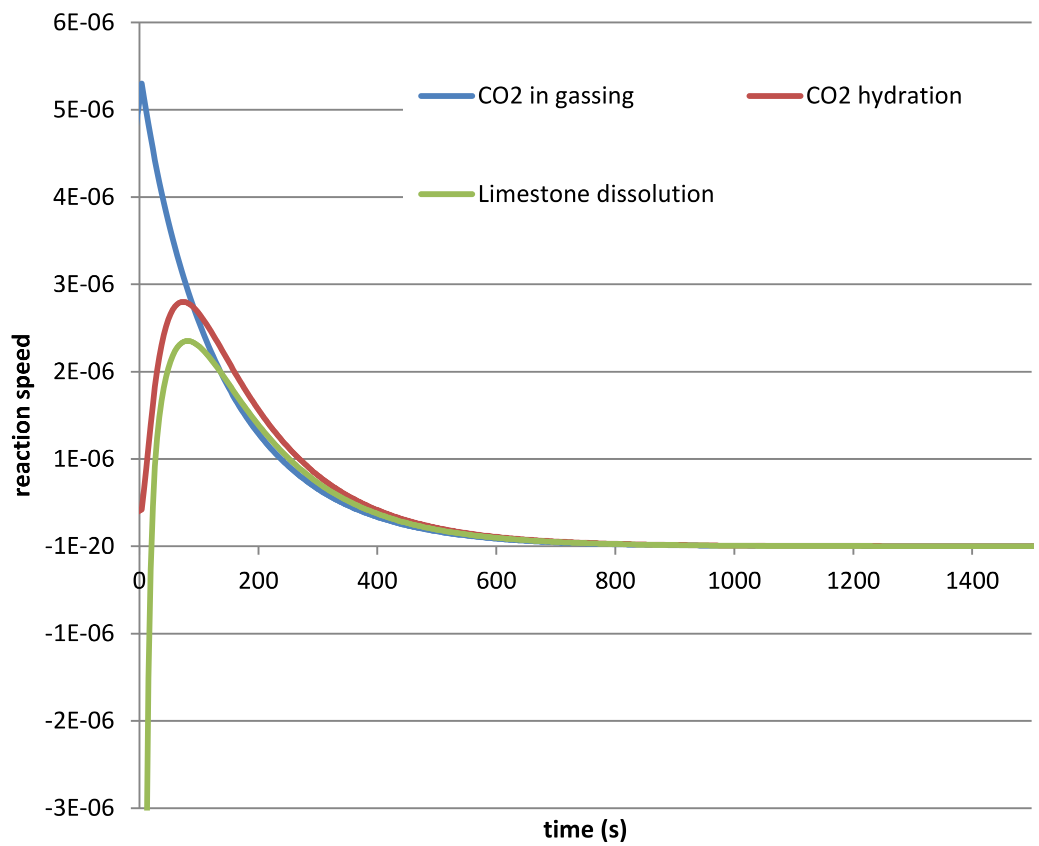
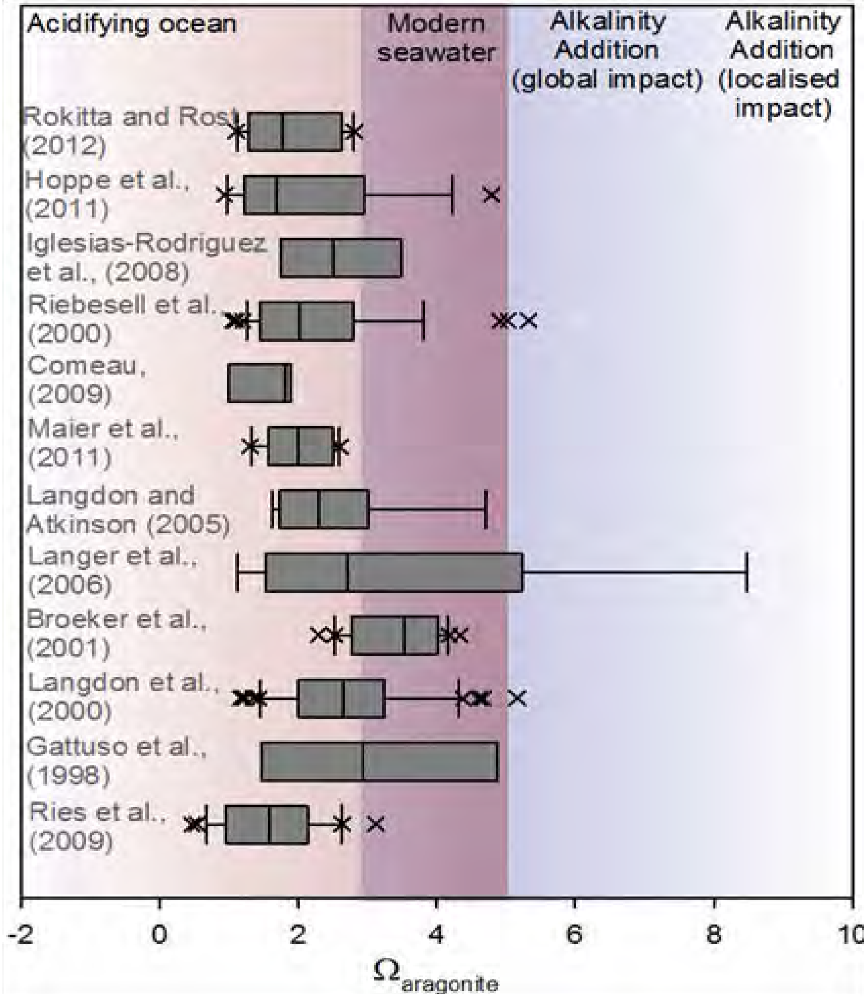
Thanks to: Prof. Richard Darton and Tim Kruger (Oxford)


CO2 in gassing
CO2 hydration
Limestone dissolution
reaction speed
6E-06
5E-06
4E-06
3E-06
2E-06
1E-06
-1E-20
-1E-06
-2E-06
-3E-06
0
200
400
600
800
1000
1200
1400
time (s)



Example spread of existing research on biological response to changes in the carbonate system.