Electrochemical Acceleration of Chemical Weathering & Geoengineering

Kurt Zenz House

KITP Climate Physics Conference

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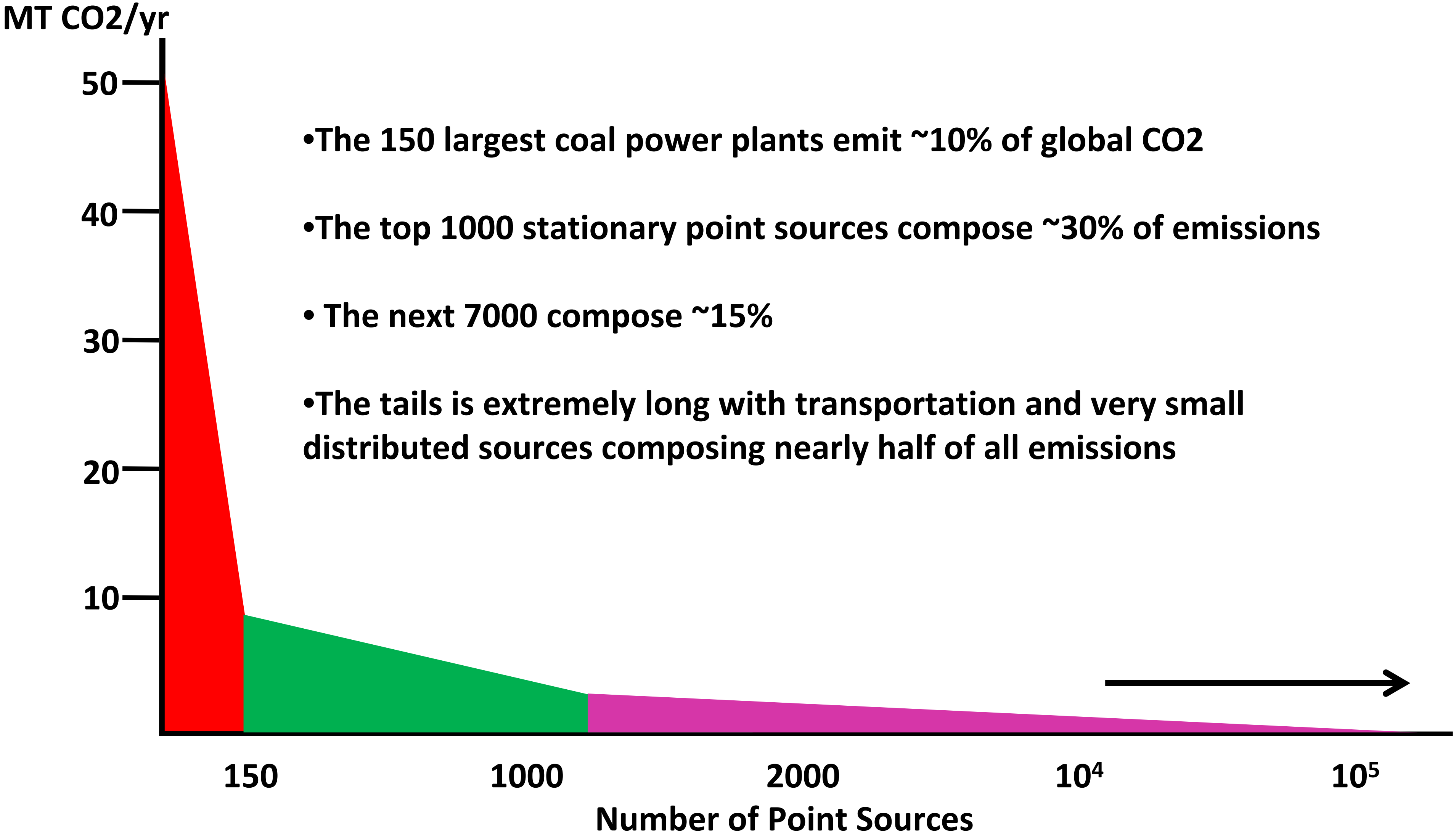
The extremely skewed distribution of point sources indicates the potential need for multiple strategies



- The 150 largest coal power plants emit ~10% of global CO2
- The top 1000 stationary point sources compose ~30% of emissions
- The next 7000 compose ~15%
- The tails is extremely long with transportation and very small distributed sources composing nearly half of all emissions

Source: Alliance Bernstein

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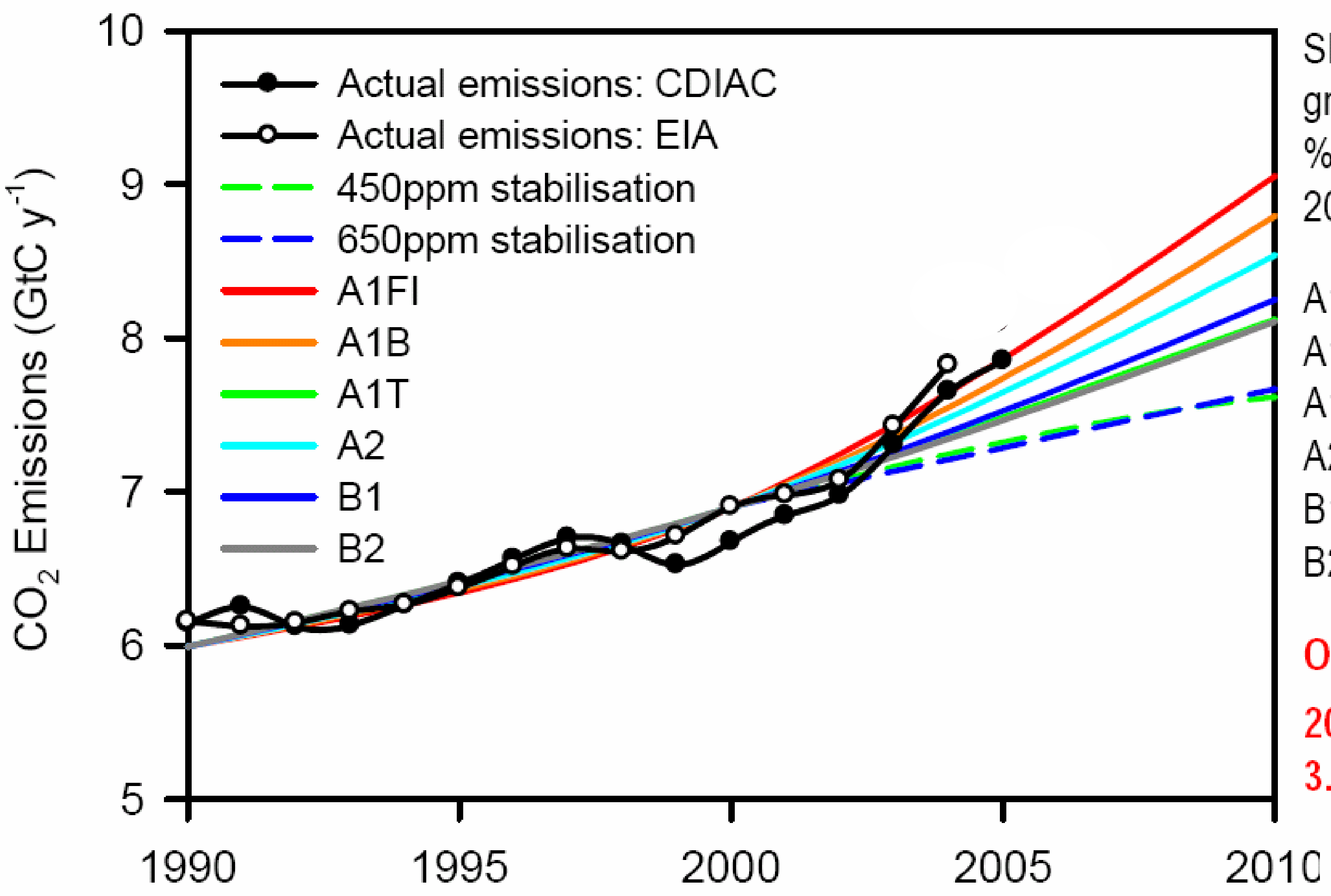
Agenda

- Accelerating atmospheric CO_2 concentration
- The Taxonomy of climate change abatement technology
- The details of electrochemical weathering

“The emissions growth rate since 2000 was greater than for the most fossil-fuel intensive of the IPCC emissions scenarios developed in the late 1990s”

- Raupach et al, PNAS (2007)



SRES (2000)
growth rates in
% y^{-1} for
2000-2010:

A1B: 2.42
A1FI: 2.71
A1T: 1.63
A2: 2.13
B1: 1.79
B2: 1.61

Observed
2000-2006
3.3%

Raupach et al, PNAS (2007)

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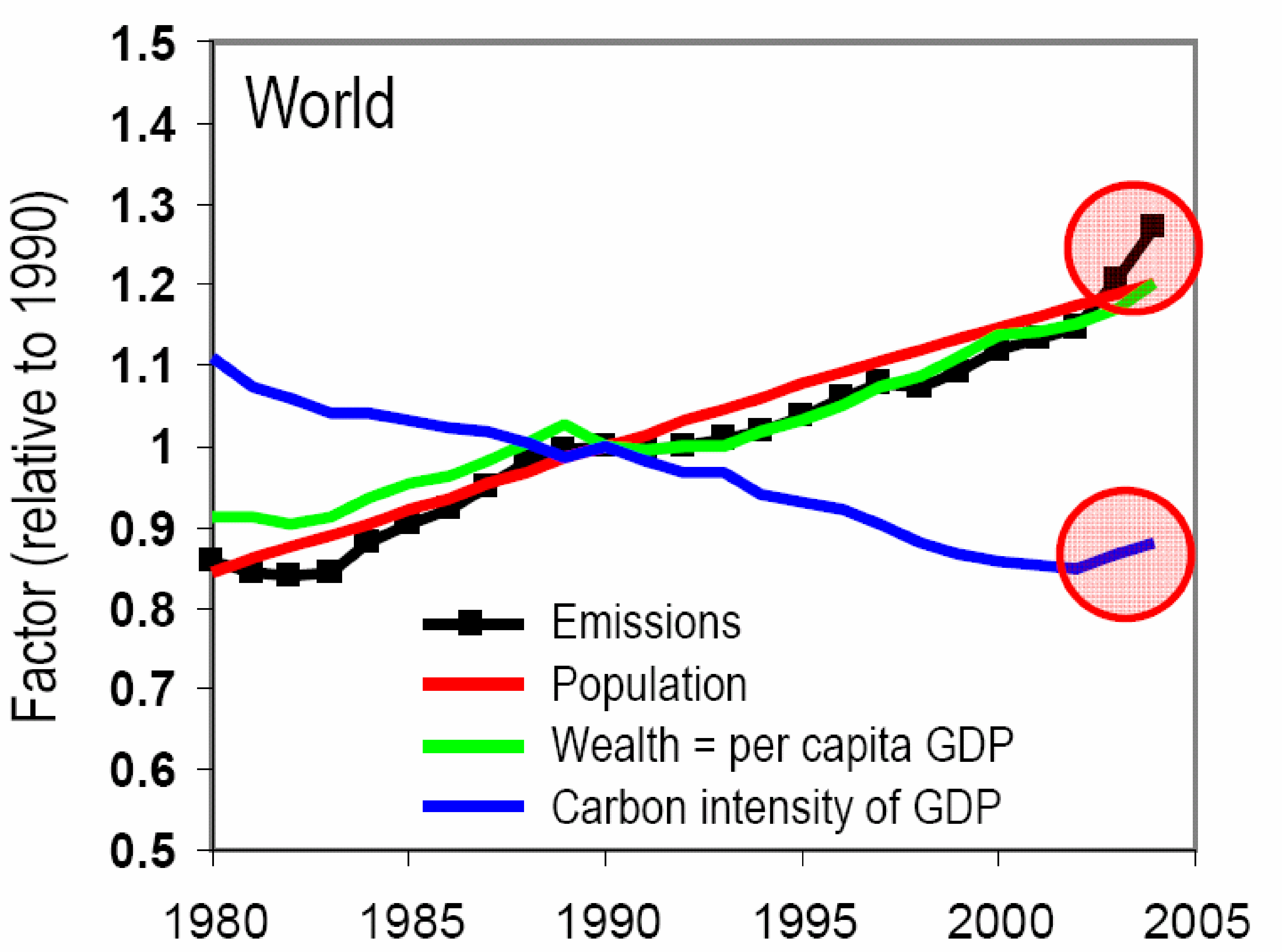
The biggest surprise has been a reversal of the long-time trend in carbon intensity (kgC/$GDP)



Raupach et al, PNAS (2007)

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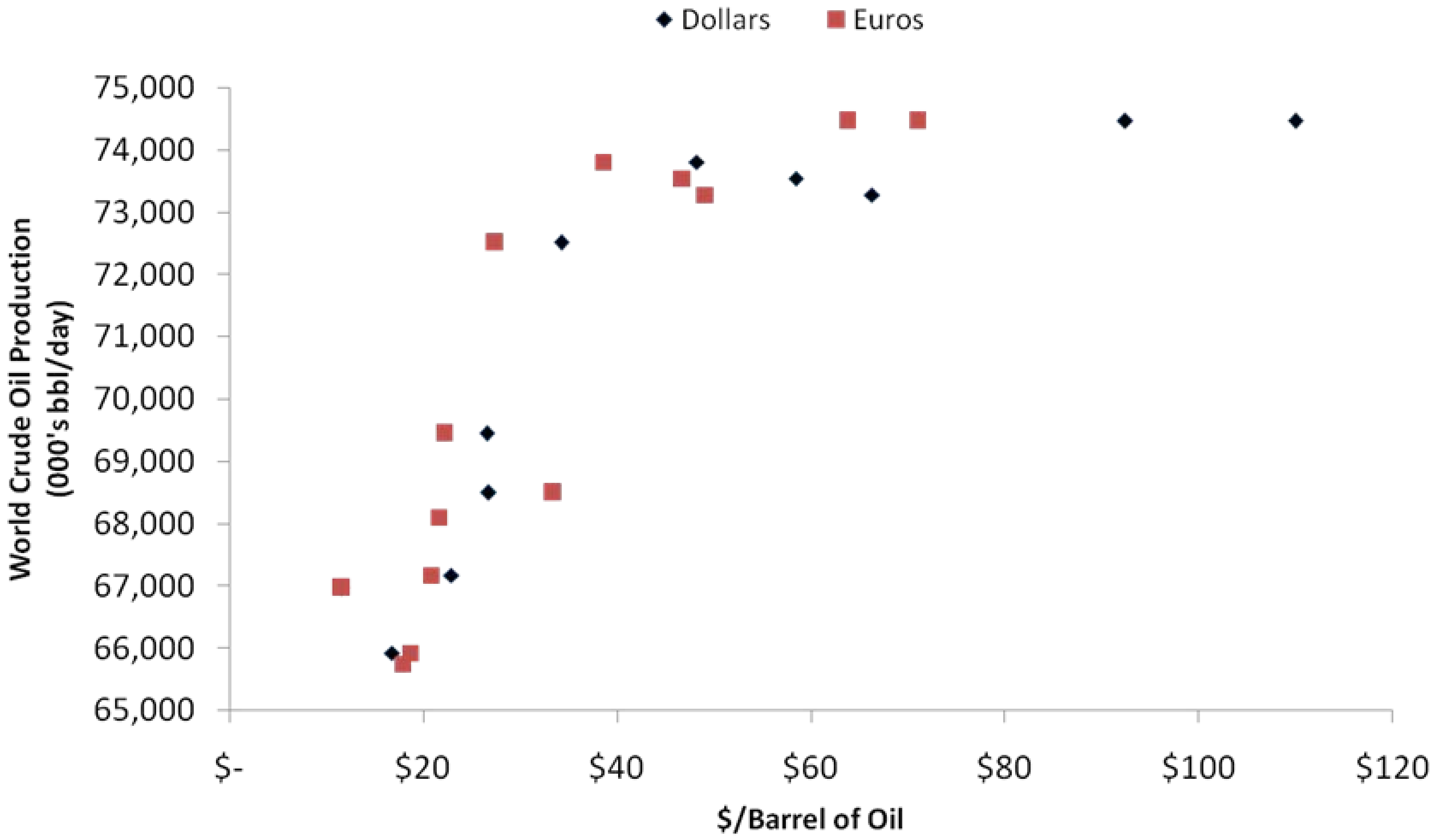
The oil supply curve suggests that supply is have trouble keeping up with demand



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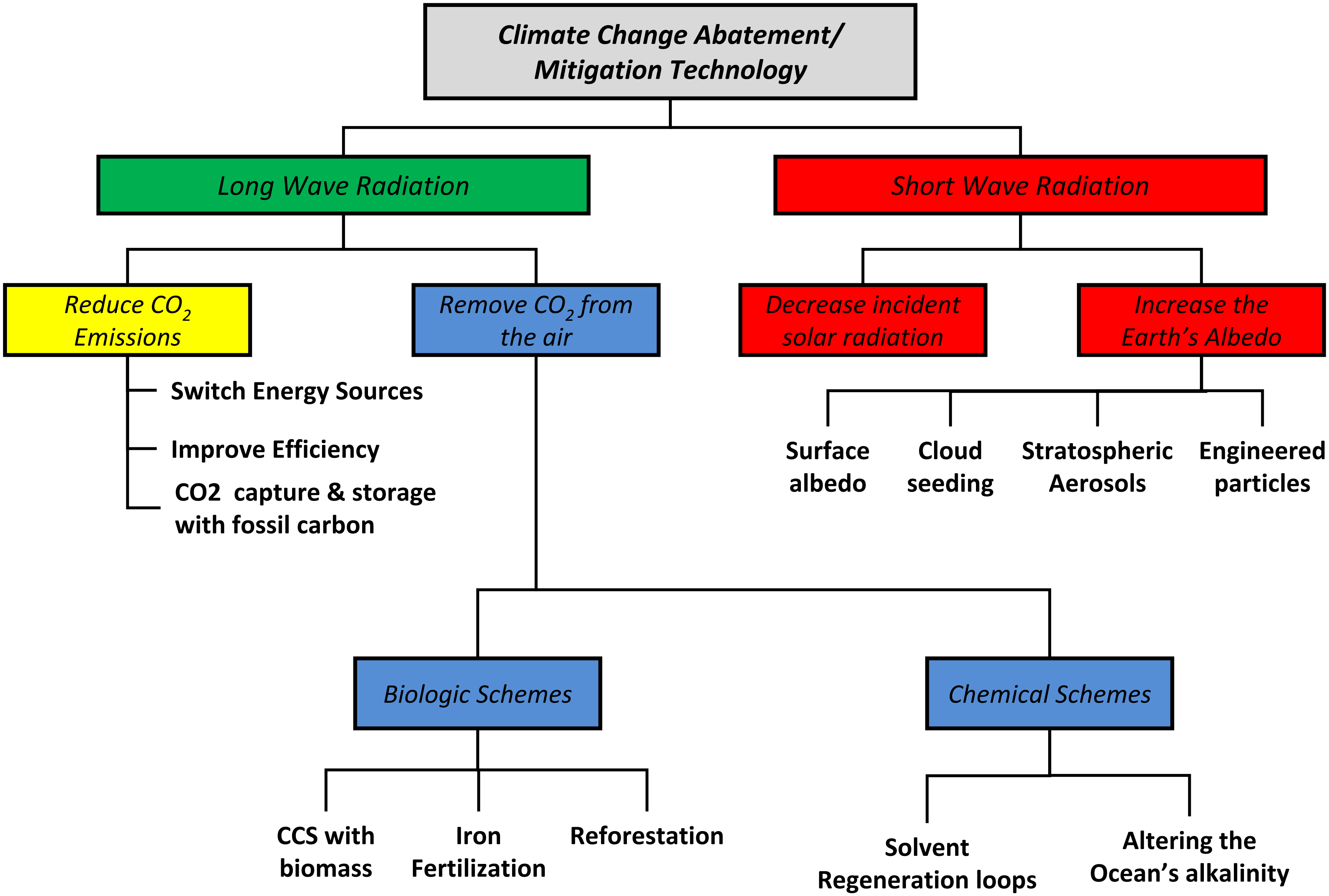

- *Climate Change Abatement/ Mitigation Technology*
  - *Long Wave Radiation*
    - *Reduce CO_2 Emissions*
      - **Switch Energy Sources**
      - **Improve Efficiency**
      - **CO2 capture & storage with fossil carbon**
    - *Remove CO_2 from the air*
      - *Biologic Schemes*
        - **CCS with biomass**
        - **Iron Fertilization**
        - **Reforestation**
      - *Chemical Schemes*
        - **Solvent Regeneration loops**
        - **Altering the Ocean's alkalinity**
  - *Short Wave Radiation*
    - *Decrease incident solar radiation*
    - *Increase the Earth's Albedo*
      - **Surface albedo**
      - **Cloud seeding**
      - **Stratospheric Aerosols**
      - **Engineered particles**

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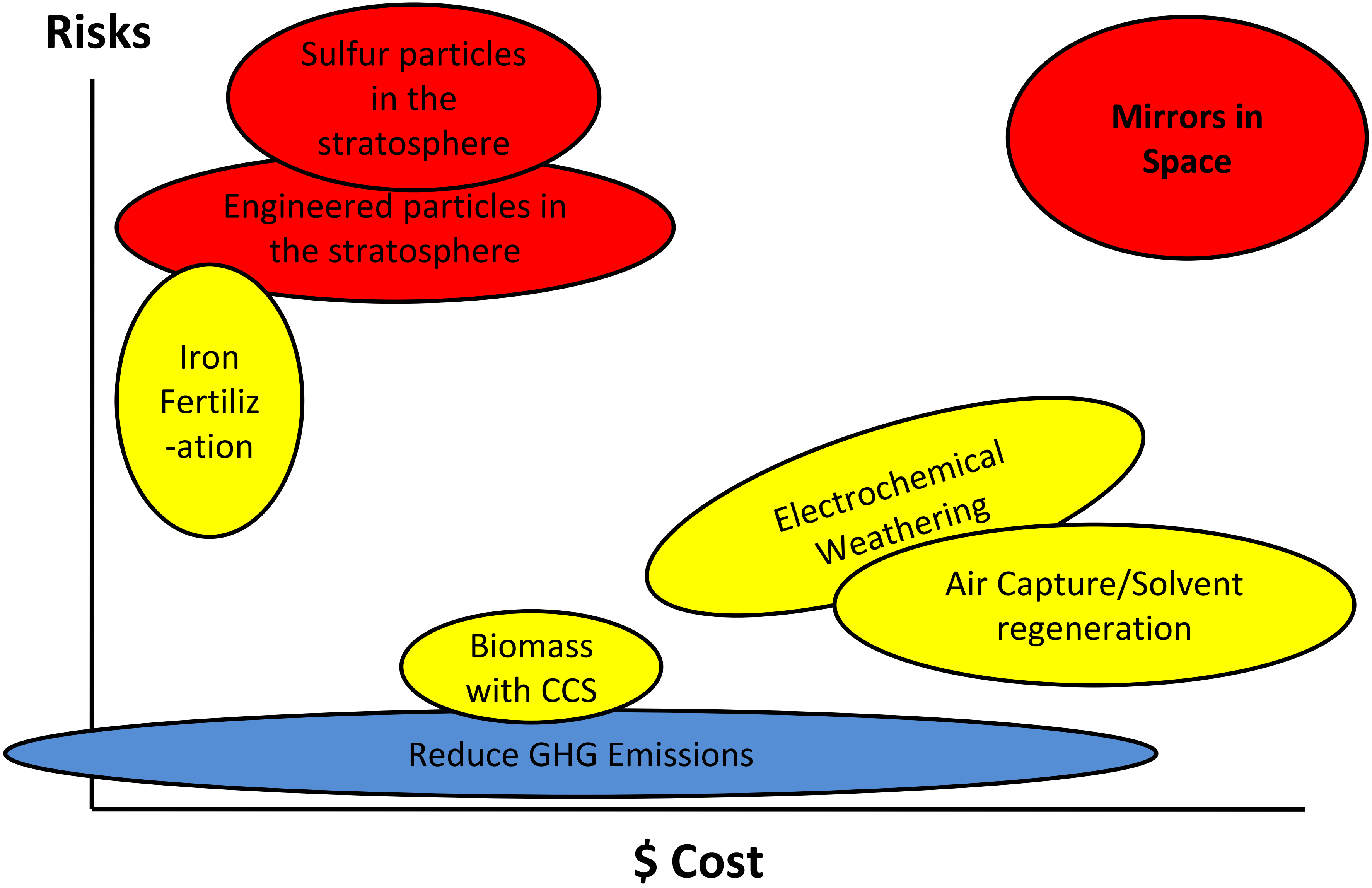
The sensibility of these various schemes can be visualized in risk-cost space



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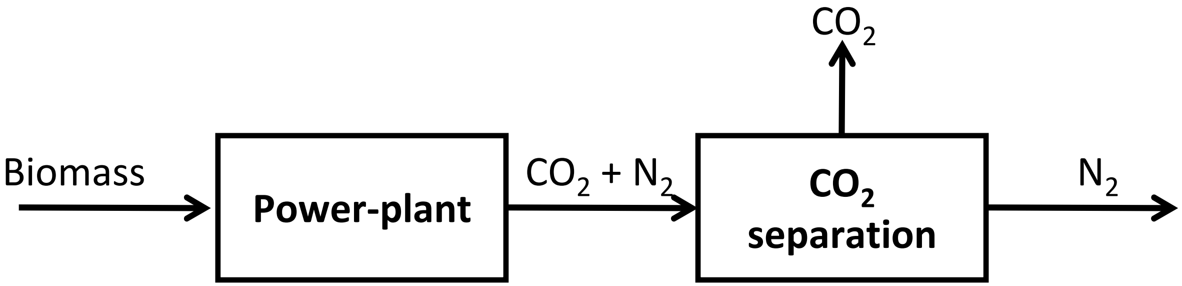
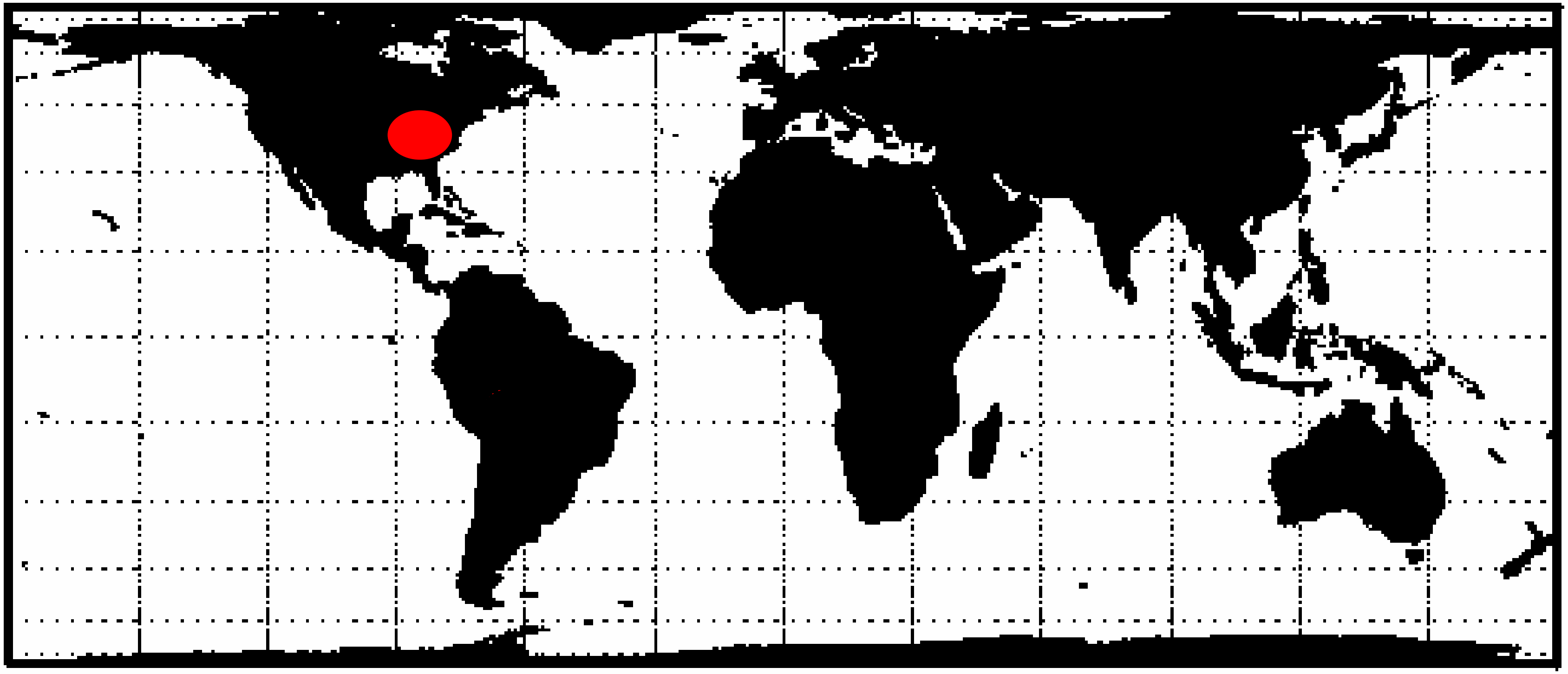
The cheapest way to remove CO2 from the air is to combust appropriately harvested biomass and capture and store the CO_2



Biomass → **Power-plant** → $CO_2 + N_2$ → **CO_2 separation** → N_2

CO_2 separation → CO_2



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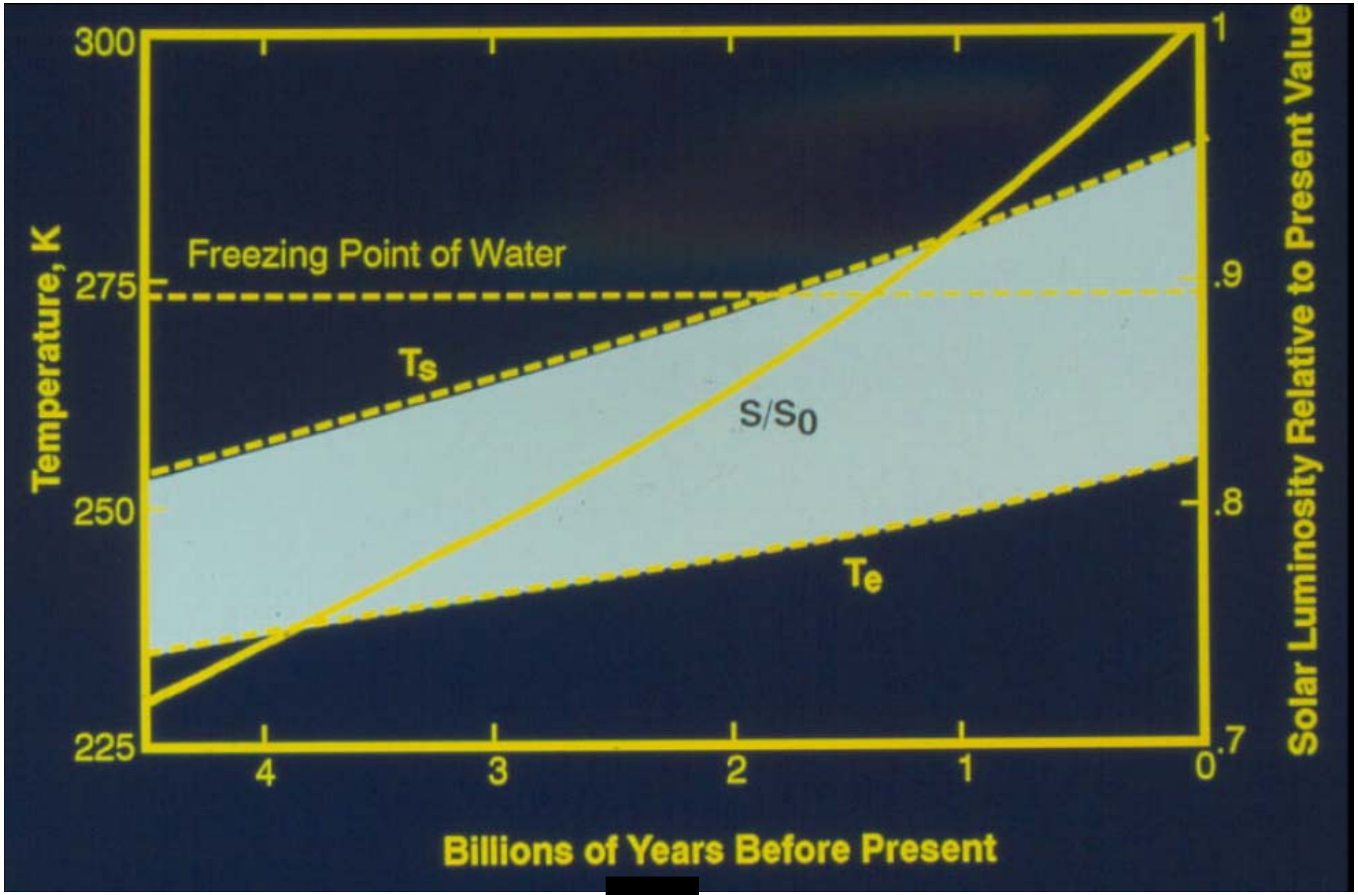
Chemical weathering is the Earth’s thermostat



$$CaSiO_3 + CO_2 \longrightarrow CaCO_3 + SiO_2$$

$$MgSiO_3 + CO_2 \longrightarrow MgCO_3 + SiO_2$$

Can chemical weathering be accelerated?

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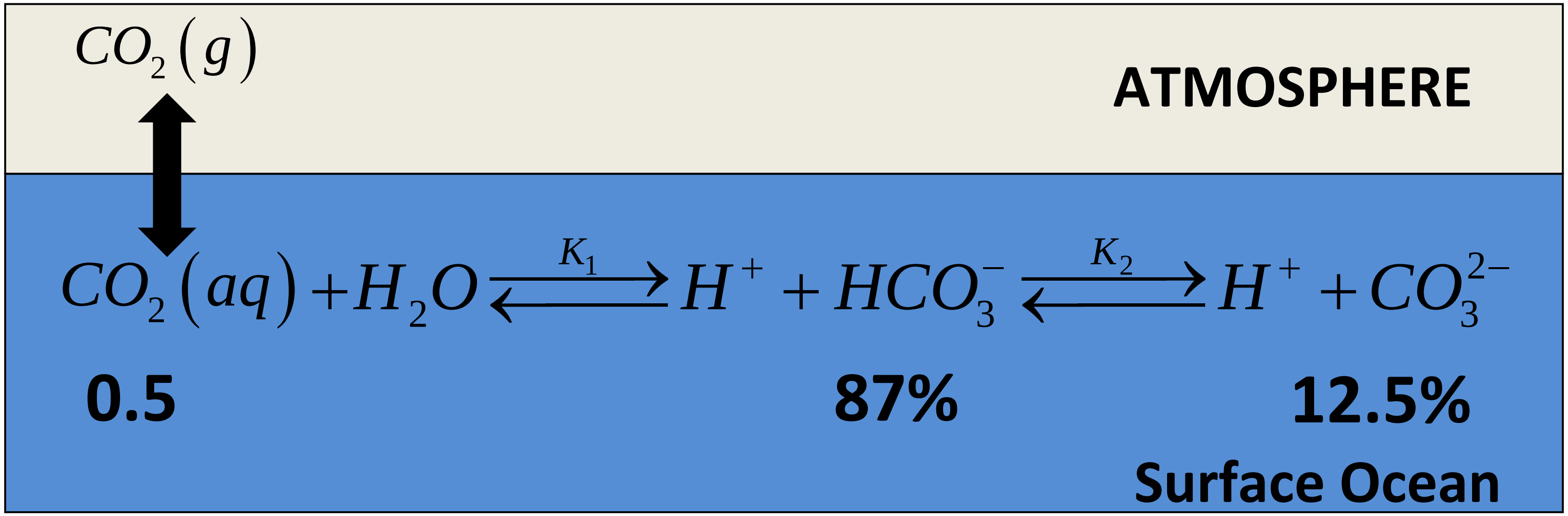
The partitioning of carbon between the atmosphere and the oceans is controlled in part by the ocean’s alkalinity



$CO_2(g)$

ATMOSPHERE

$$CO_2(aq) + H_2O \underset{}{\overset{K_1}{\rightleftarrows}} H^+ + HCO_3^- \underset{}{\overset{K_2}{\rightleftarrows}} H^+ + CO_3^{2-}$$

0.5 **87%** **12.5%**

Surface Ocean

The ocean has a surplus of conservative positive charge

$$Alkalinity = \left[Na^+\right] + 2\left[Mg^{2+}\right] + 2\left[Ca^{2+}\right] + \left[K^+\right] + \ldots - \left[Cl^-\right] - 2\left[SO_4^{2-}\right] - \ldots$$

…which is primarily balanced by the carbonate system

$$Alkalinity = \left[HCO_3^-\right] + 2\left[CO_3^{2-}\right] + \ldots$$

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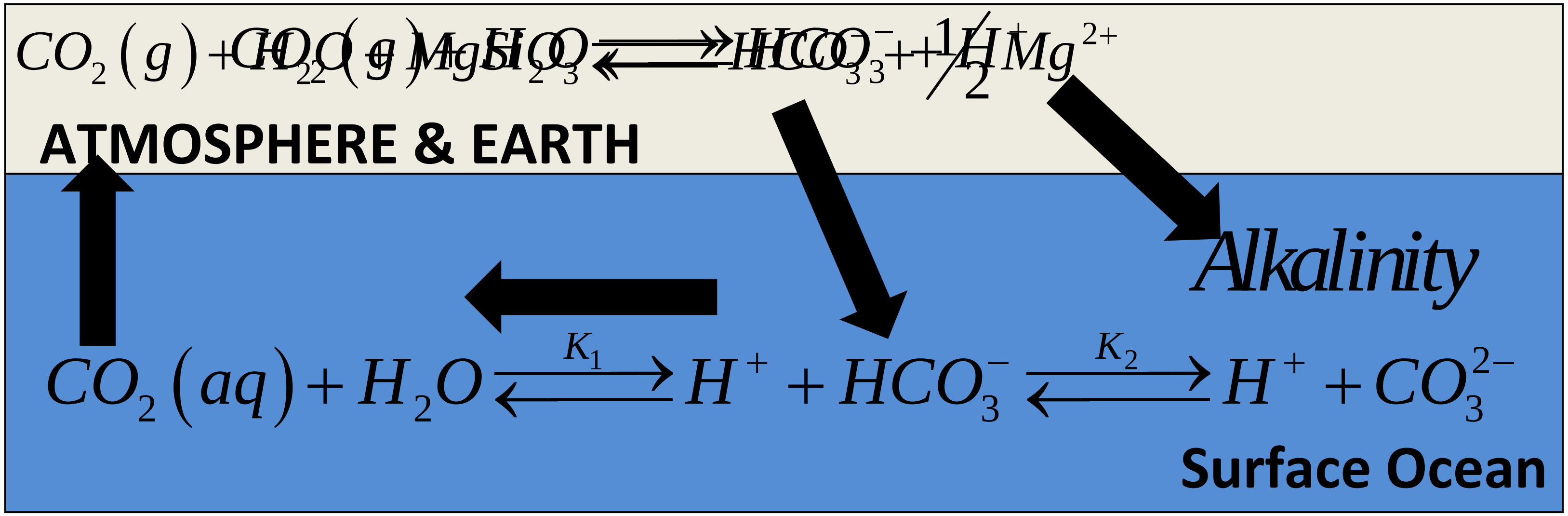
On long time scales, nature will solve global warming on its own (in multiple ways)



$CO_2(g) + H_2O \rightleftharpoons HCO_3^- + H^+$

$CO_2(g) + MgSiO_3 + H_2O \rightleftharpoons HCO_3^- + \frac{1}{2}Mg^{2+}$

ATMOSPHERE & EARTH

Alkalinity

$$CO_2(aq) + H_2O \underset{}{\overset{K_1}{\rightleftharpoons}} H^+ + HCO_3^- \overset{K_2}{\rightleftharpoons} H^+ + CO_3^{2-}$$

Surface Ocean

Droplet A reacts with $MgSiO_3$

- Adds $2HCO_3^-$ + Mg^{2+} to ocean
- The increase in Alkalinity shifts the partitioning toward HCO_3^-
- Most of the additional HCO_3^- remains as such

Droplet B falls directly into ocean

- Adds HCO_3^- + H^+
- $[H^+]$ goes up; pH goes down
- Shifts dissolved inorganic carbon partitioning toward $CO_2(aq)$

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If alkalinity can be added to the ocean at industrial rates, then the ocean will take up atmospheric CO_2

$$Alkalinity = \left[Na^{+}\right] + 2\left[Mg^{2+}\right] + 2\left[Ca^{2+}\right] + \left[K^{+}\right] + \ldots - \left[Cl^{-}\right] - 2\left[SO_4^{2-}\right] - \ldots$$

Various scholars have considered ways to increase the ocean's alkalinity by dissolving carbonates into the ocean (e.g., Broecker, Caldeira)

So I thought, perhaps we can remove *conservative* negative charge in order to increase the ocean's alkalinity

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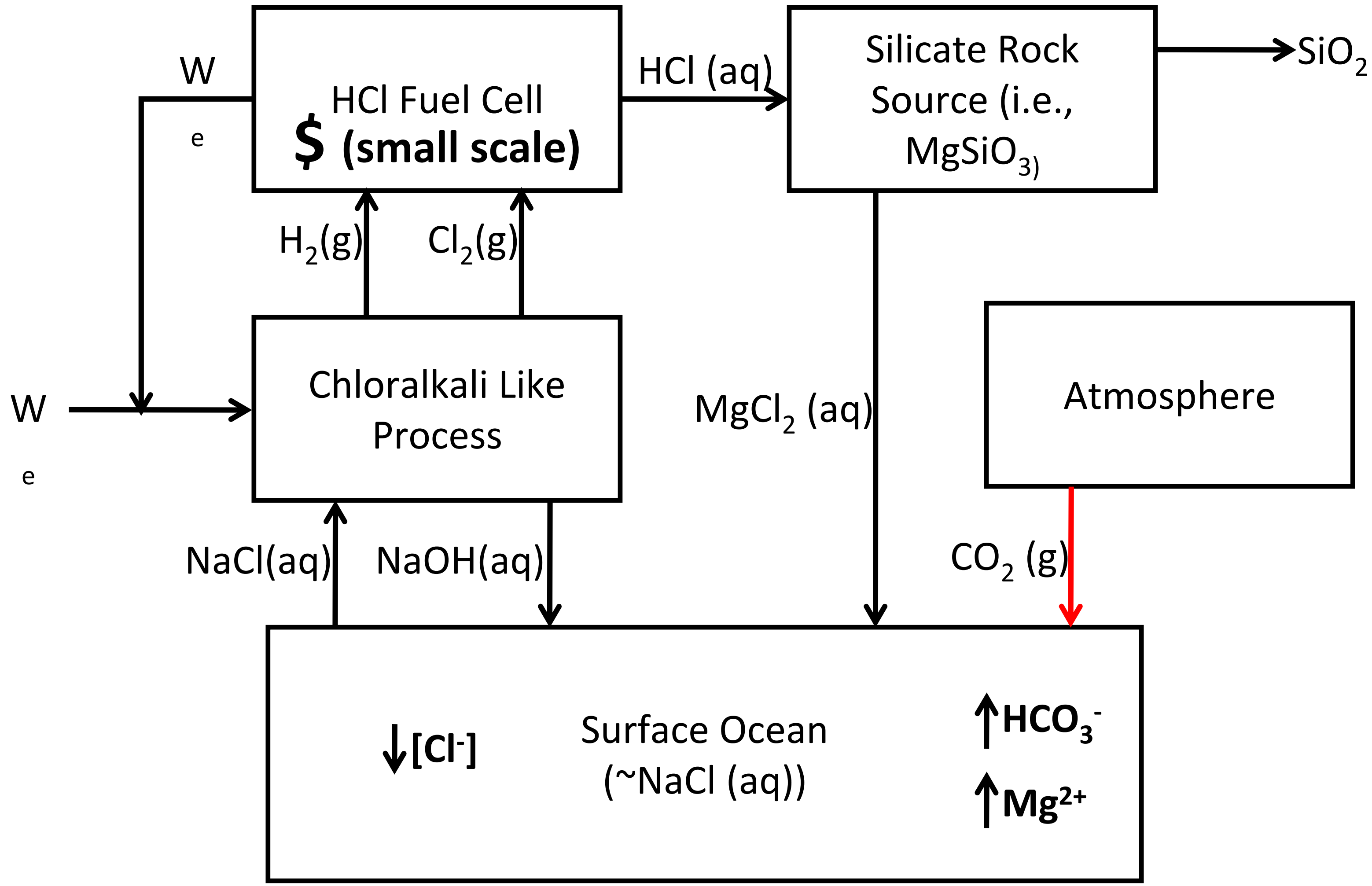
More detailed block diagram (version 1)



W

e

HCl Fuel Cell

$ **(small scale)**

HCl (aq)

Silicate Rock Source (i.e., $MgSiO_3$)

SiO_2

$H_2(g)$

$Cl_2(g)$

W

e

Chloralkali Like Process

$MgCl_2$ (aq)

Atmosphere

NaCl(aq)

NaOH(aq)

CO_2 (g)

↓$[Cl^-]$

Surface Ocean (~NaCl (aq))

↑HCO_3^-

↑Mg^{2+}

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Chemical steps (version 1)

Step 1: electrolysis

$\Delta G_1 = +212$ kJ/(mol NaOH)

$$2NaCl(aq) + 2H_2O(l) \longrightarrow 2NaOH(aq) + Cl_2(g) + H_2(g)$$

Step 2: HCl Fuel Cell

$\Delta G_2 = -131$ kJ/(mol HCl)

$$Cl_2(g) + H_2(g) \longrightarrow 2HCl(aq)$$

Step 3: Rock Dissolution

$\Delta H_3 = -58$ kJ/(mol HCl)

$$2HCl(aq) + MgSiO_3(s) \longrightarrow MgCl_2(aq) + SiO_2(s) + H_2O$$

Step 4: CO_2 capture, storage

$\Delta H_4 = -70$ kJ/(mol NaOH)

$$2CO_2(g) + 2NaOH(aq) \longrightarrow 2NaHCO_3(aq)$$

Overall Process:

$\Delta G = -4$ kJ/(mol NaOH)

$$\boxed{MgSiO_3(s) + H_2O(l) + 2CO_2(g) \longrightarrow Mg^{2+} + SiO_2(s) + 2HCO_3^-}$$

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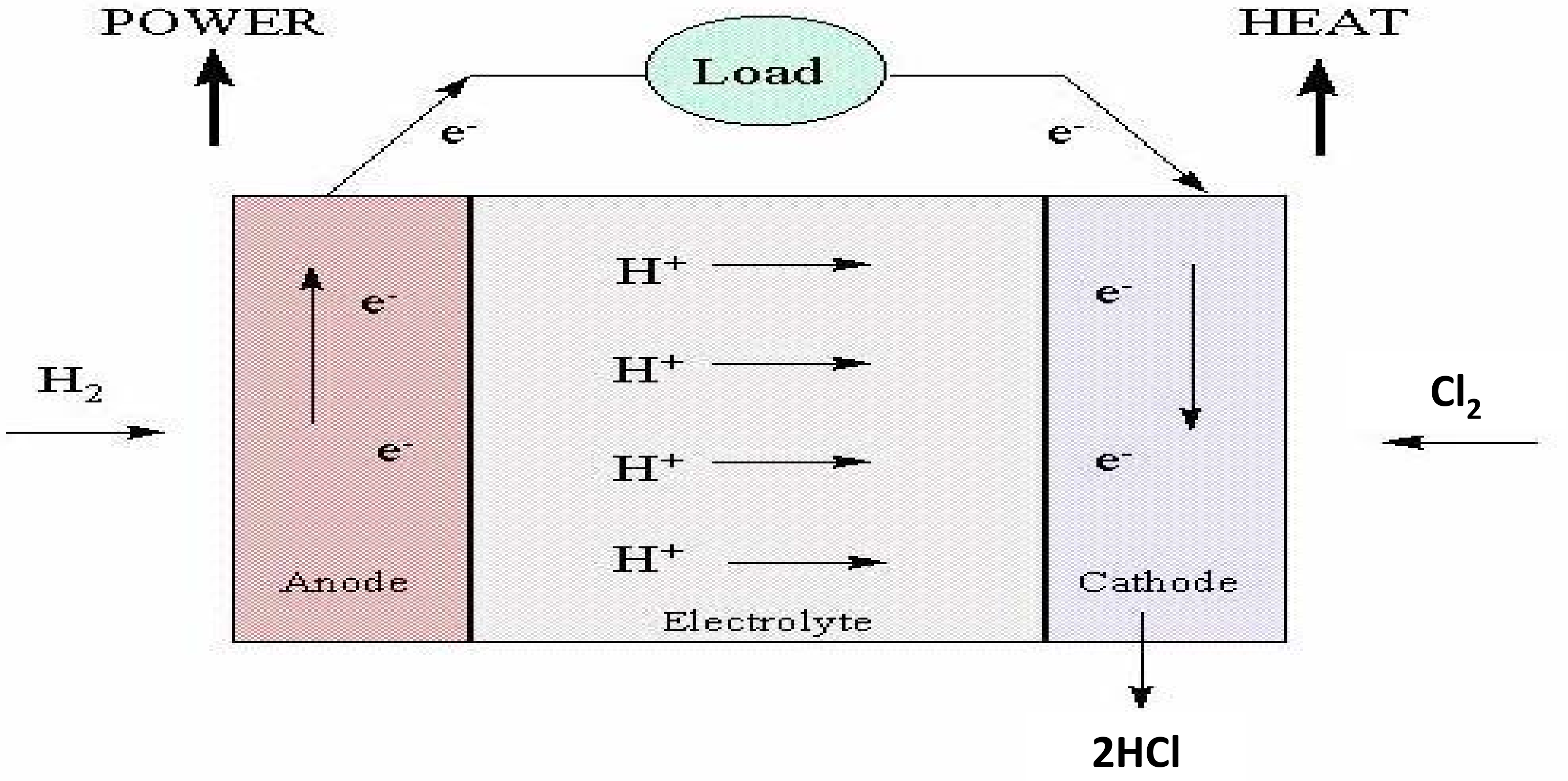
It turns out that halogen-fuel cells have great potential for grid scale energy storage

DUAL USE POTENTIAL for HCl Fuel Cell

- CO_2 sequestration
- Peak shaving / load leveling



Jason Rugolo (2 yr Harvard GS)

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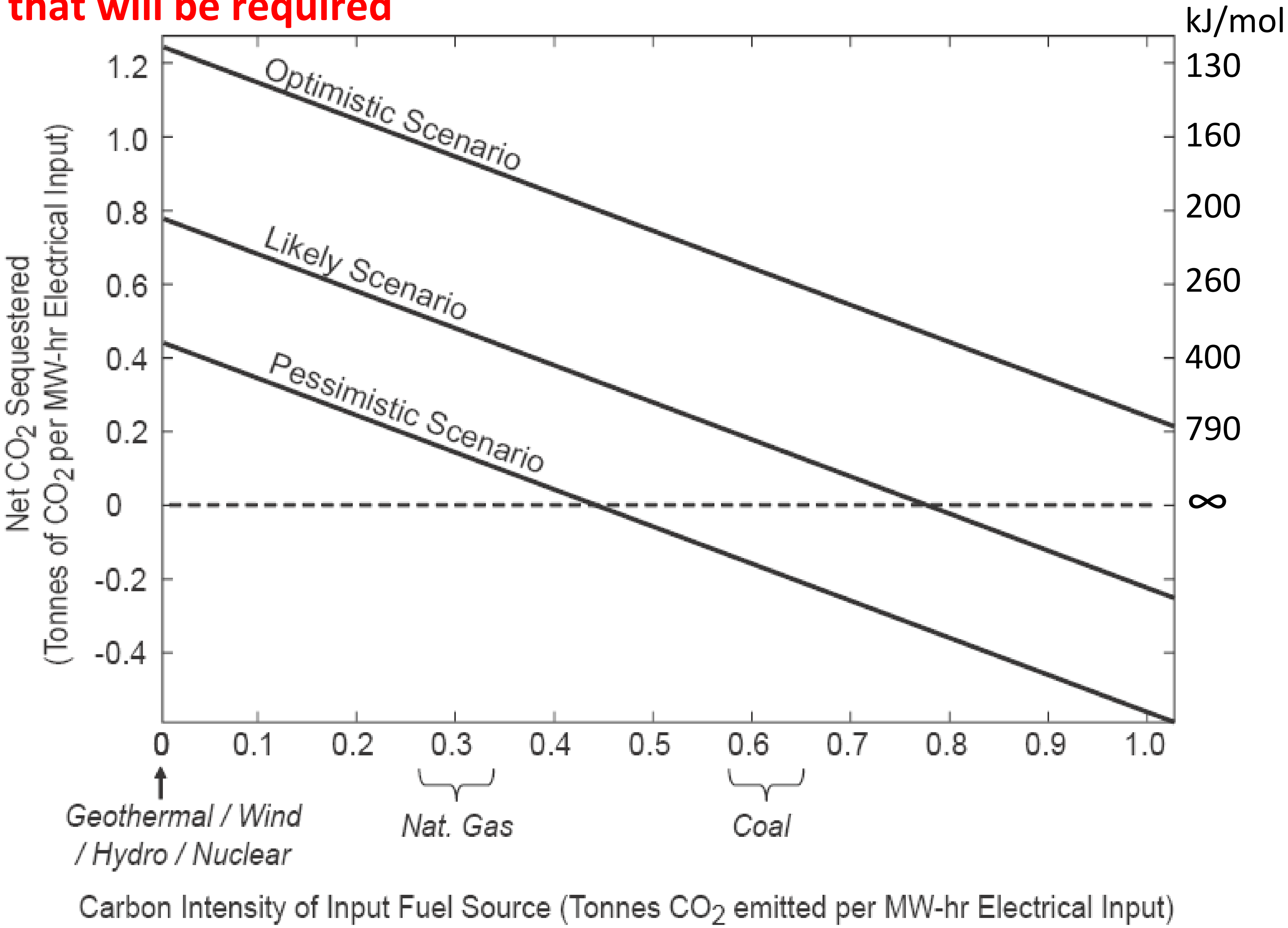
The net reaction is spontaneous, but a range of scenarios bounds the work that will be required



House et al, ES&T (2007)

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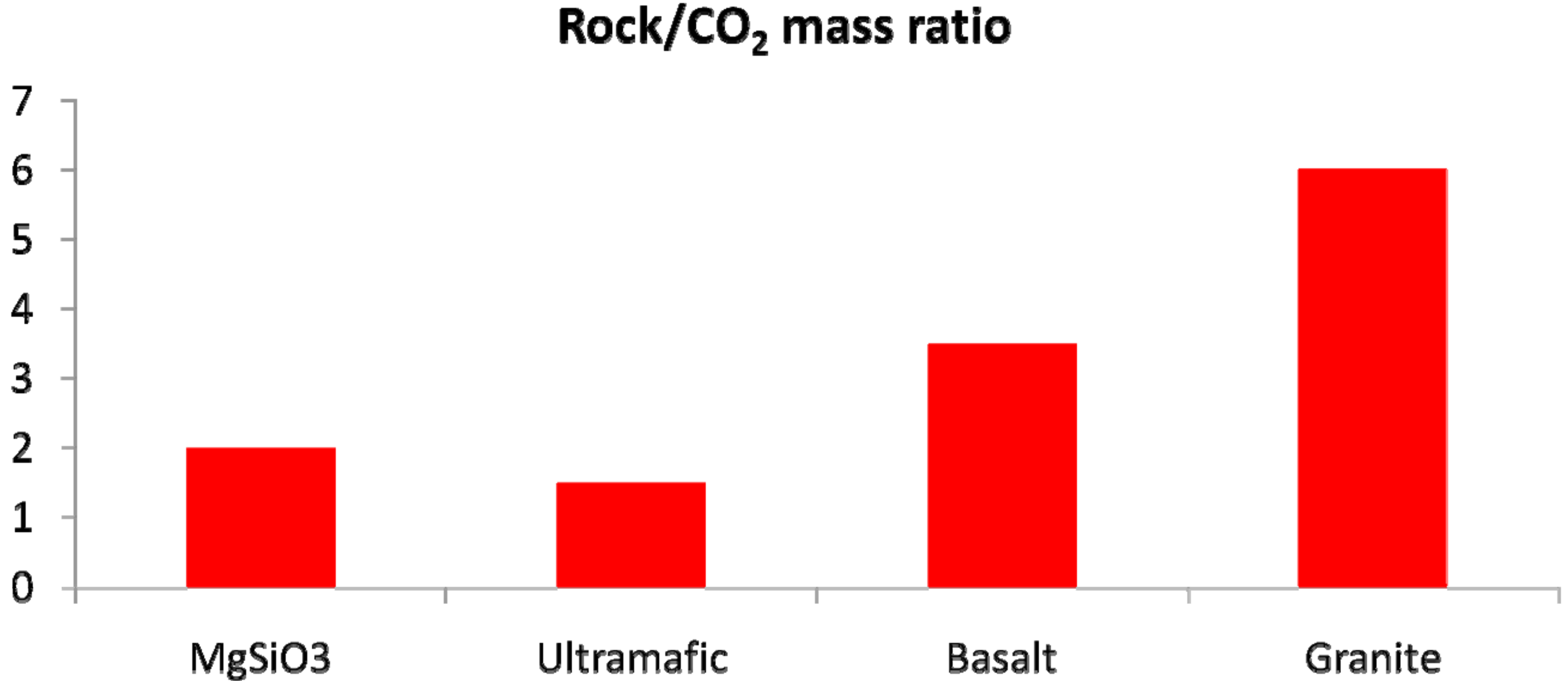
Rock type matters



Furthermore, secondary reactions can limit the alkalinity generated pure unit mass of the rock. For example:

$$FeS_2 + 2H^- + 2Cl^- + H_2O + {}^{5}\!/_{2}\,O_2 \longrightarrow FeCl_2 + 2HSO_3^- + 2H^+$$

$$FeCl_2 + 2H_2O \longrightarrow Fe\left(OH\right)_2 + 2H^- + 2Cl^-$$

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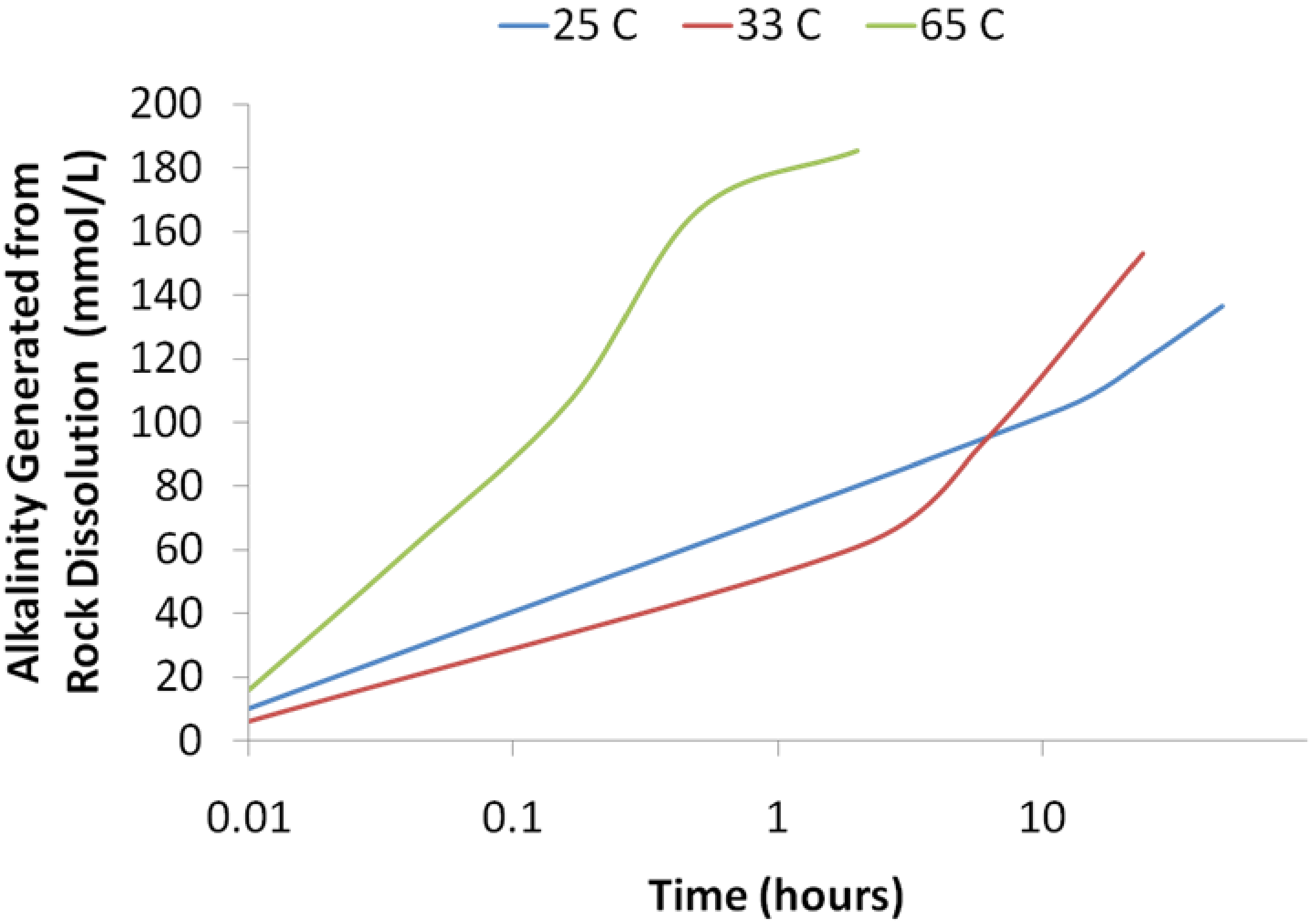
Dissolution reaction kinetics are highly temperature dependent



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Enhanced $CaCO_3$ precipitation is the ultimate fate of the additional alkalinity and carbon

$$MgSiO_3(s) + H_2O(l) + 2CO_2(g) \longrightarrow Mg^{2+} + SiO_2(s) + 2HCO_3^-$$

$$2HCO_3^- + Ca^{2+} \longrightarrow CaCO_3 + CO_2 + H_2O$$

If the dissolution products are returned to the ocean, $CaCO_3$ is certain to precipitate quickly due to the increase in local alkalinity

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Another way to think about this the creation of artificial soda-lakes

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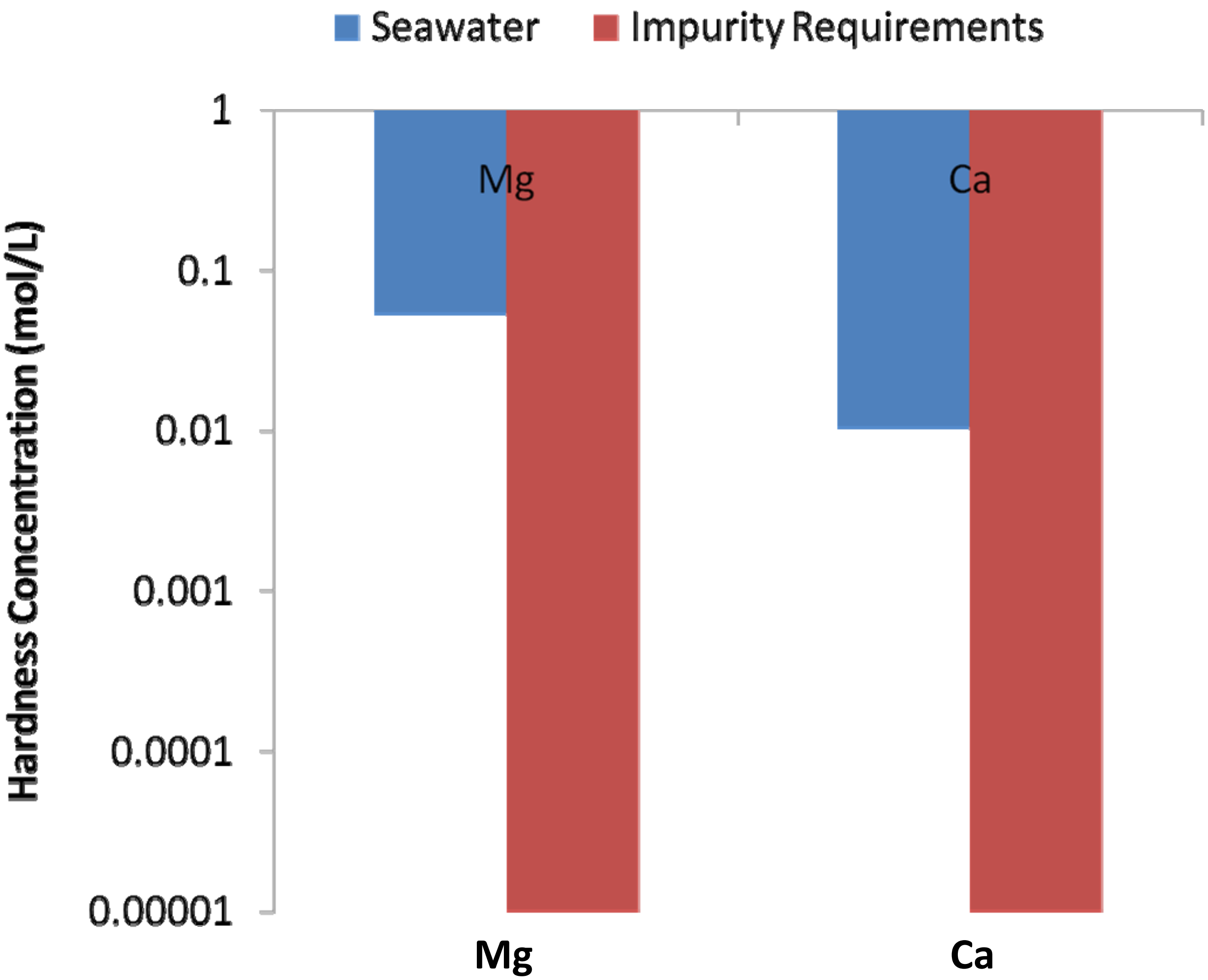
The purity requirements pose a serious engineering challenge



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Offsetting 1 GtC/yr with electrochemical weathering is a serious task

- To offset 1 GtC, ~10^{14} moles of HCl would have to be produced and neutralized each year
    1. Volumetric flow rate of seawater equal to 6000 m^3/sec
    2. Volumetric flow rate of artificial brine from mined halite of 600 m^3/s

- If basalt were used for neutralization, then 10 Gt would be required annually

- Our kinetic experiments indicate the rock dissolution would require ~10^7 m^3 of reaction volume (1500 Olympic swimming pools)

- The global weathering rate would be x10

- Local alkalinity hot spots would form and potentially cause severe damage to marine biota

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Benefits of electrochemical weathering

- Permanency of storage to do thermodynamics and kinetics of marine chemistry
- Simultaneously manage the oceans and the atmosphere → particularly ocean pH
- Could be run off stranded power
- 1 large plant (~50 m^3/sec) would offset ~5,000,000 cars

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Conclusions

- Despite global awareness and the Kyoto treaty, CO_2 emissions have outpaced our most pessimistic forecast

- A wide variety of schemes—other than decreasing CO_2 emissions—have been proposed to deal with climate change

- Of these, biomass with CO_2 capture & storage will work, but is limited in scale to about 1 GtC/year

- We can accelerate weathering with electrochemistry, but it will be expensive and the rock requirements will severely limit its scale