

The Fate of Agricultural Lime: Implications for Carbon Accounting

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Why are we interested in this topic?

The 1996 IPCC Greenhouse Gas Inventory Reference Manual assumes that all agriculture carbon goes to the atmosphere. Clearly this is an oversimplification – we want to know whether or not it is significantly so.

An interdisciplinary project

Agriculture

Soil physics

Soil chemistry

Hydrology

Aquatic / ocean chemistry

Biogeochemistry

Marine ecology

Cellular biology

What is aglime?

Aglime is mostly crushed limestone (CaCO_3) and sometimes a bit of crushed dolomite ($\text{MgCa}(\text{CO}_3)_2$). Crushed limestone has other uses, but we call it aglime when we spread it over crops.



Why do we spread aglime on crops?

Two reasons:

- 1) To increase the pH of acidic soil.
- 2) To provide calcium and magnesium to crops.

The first reason – raising pH – is more important.

Relative yields at various pH levels

	pH 4.7	pH 5.0	pH 5.7	pH 6.8	pH 7.5
Corn	34%	73%	83%	100%	85%
Soybeans	65%	79%	80%	100%	93%
Wheat	68%	76%	89%	100%	85%
Oats	77%	93%	99%	98%	100%
Barley	0%	23%	80%	95%	100%
Sweet clover	0%	2%	49%	89%	100%

A & L Mid West Agricultural Laboratories, Inc. Omaha, Nebraska

How much aglime do we apply each year in the United States?

According to the US Geological Survey (and their advice for interpreting incomplete data), we apply $19.9 \pm .6$ teragrams of aglime each year. That's the same as:

$2.39 \pm .07$ Tg C, or

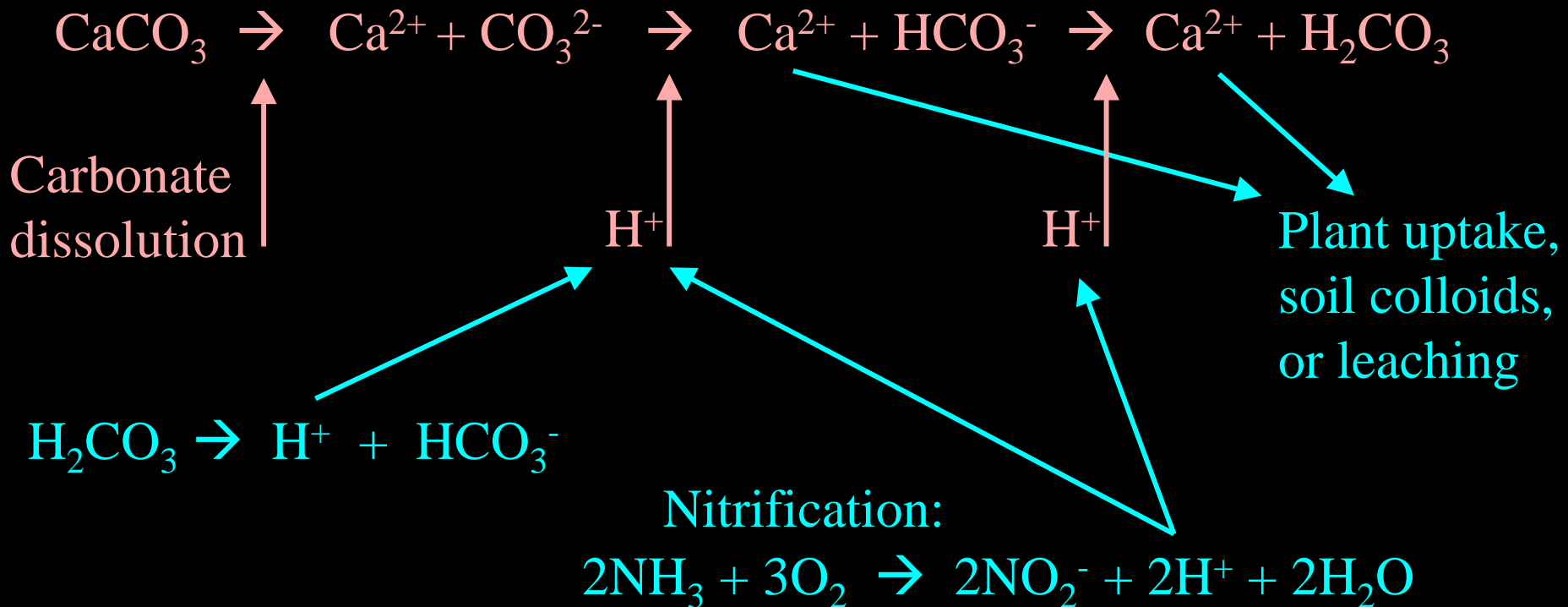
$8.8 \pm .3$ Tg CO₂ equivalent. That's a small fraction of total US CO₂ emission, but a large fraction of CO₂ flux changes associated with changing agricultural practice. Lime use could decrease with shifts to no-till agriculture or increase with increasing N fertilization, and we need to know how such changes affect C budgets (Steve Hamilton, unpublished).

Inorganic carbon compounds:

CaCO_3	Calcium carbonate, calcite, aragonite, limestone, aglime, lime
$\text{MgCa}(\text{CO}_3)_2$	Dolomite, aglime, lime
H_2CO_3	Carbonic acid
HCO_3^-	Bicarbonate ion
CO_3^{2-}	Carbonate ion

How does aglime work to increase pH?

Harder question than you'd hope. Reaction equations can be misleading. Different things can happen, but the important part is in pink:



Keep in mind: $H_2CO_3 \leftrightarrow H_2O + CO_2$,
based on partial pressure of CO_2 .

Do we know what happens to the carbon in aglime?

The IPCC says: “When added to acid soil [liming] compounds release CO_2 in the bicarbonate equilibrium reaction.”

But as pointed out by Steve Hamilton (unpublished), CO_2 is only released when the carbonate ion bonds with two H^+ to form H_2CO_3 . If we stop at HCO_3^- , as we would if the H^+ came from H_2CO_3 in the first place, we would actually take up a mole of atmospheric carbon.

Such a reaction would not cause an increase in soil pH. But soils can be highly buffered, so there's no reason to think that the dominant reaction need be one that raises pH.

What substances are leaching from the soil?

Ca²⁺: We need to know the proportion of applied Ca²⁺ that leaches:

- 1) With respect to the amount of solid aglime dissolved, and
- 2) From soils that have been repeatedly limed over many years, to account for long-term changes in cation exchange capacity with agricultural practices (including liming itself).

To our knowledge, no existing studies of Ca²⁺ leaching after liming meet both these criteria, because they're interested in different questions than we are. Existing studies may suggest that anywhere from 10% to 50% of the applied Ca²⁺ leaches (Dierolf *et al.* 1997, Blette and Newton 1996).

Of course, even with consistent methodology, Ca²⁺ leaching should vary a great deal with precipitation and soil type.

Where does the rest of the applied Ca^{2+} go?

It must go to one of three places:

- 1) The harvested crop. . . and then, perhaps, the biosphere.
- 2) Soil clay particles. . . this does happen, but surely it can't accumulate forever.
- 3) Leaching.

What substances are leaching from the soil?

HCO_3^- : Bicarbonate concentration is difficult to measure directly, and few studies have looked at proportion of bicarbonate leaching under any conditions, much less the conditions we're interested in.

But we don't fully understand which ion -- HCO_3^- or Ca^{2+} -- we should be more concerned with. In theory, they need not leach equally ($2\text{HCO}_3^- + \text{Ca}^{2+}$); other ions could complete the charge balance.

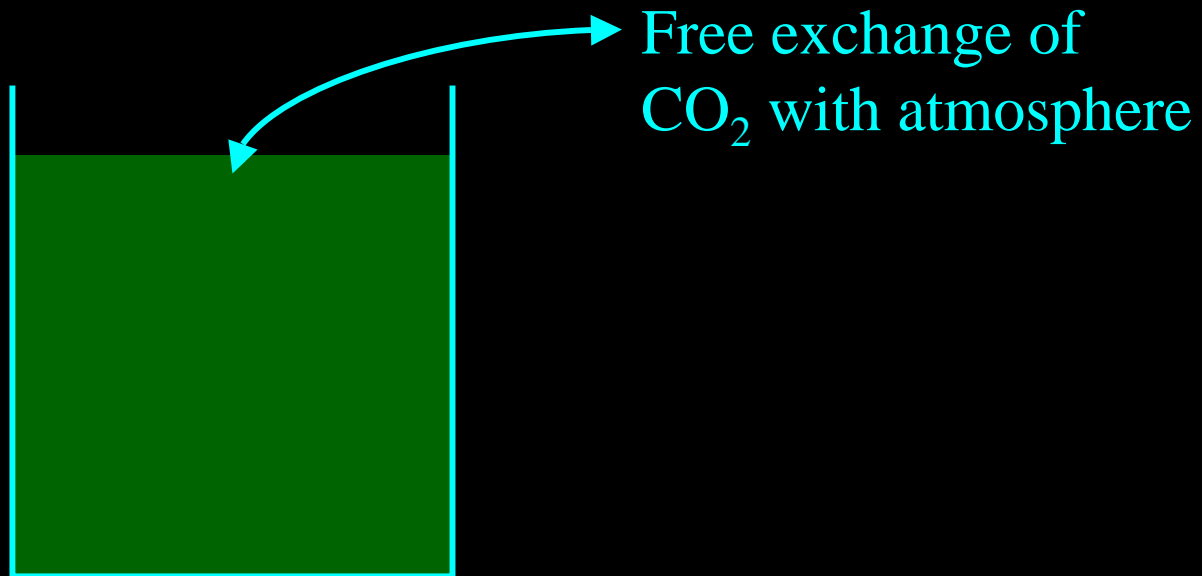
In a pure water-lime- CO_2 system, we would want to focus on the Ca^{2+} , since we know in the ocean we'd end up with $2\text{HCO}_3^- + \text{Ca}^{2+}$, no matter the amount of HCO_3^- leaching from the soil.

But other compounds, like ammonia, are responsible for the reacidification that requires repeated liming. If NO_3^- were leached along with the Ca^{2+} , for example, we may not end up with $2\text{HCO}_3^- + \text{Ca}^{2+}$ in the ocean.

What happens to the carbon in a glime?

We don't know. I'll tell you our best guess, but first we'll look at some theory.

Say we have a bucket of water open to a given P_{CO_2} and containing nothing but water, inorganic carbon, and calcium. We can calculate the concentration of every species just by knowing how much calcium we have.



Solving for carbonate distribution in an open system that's unsaturated with CaCO_3

Unknown quantities:

- 1) $[\text{CO}_3^{2-}]$
- 2) $[\text{HCO}_3^-]$
- 3) $[\text{H}_2\text{CO}_3]$
- 4) $[\text{H}^+]$
- 5) $[\text{OH}^-]$

From
Garrels and
Christ, 1965

Equations:

- 1) $[\text{H}^+][\text{OH}^-] = 10^{-14.0}$
- 2) $\frac{[\text{H}_2\text{CO}_3]}{P_{\text{CO}_2}} = 10^{-1.47}$
- 3) $\frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = 10^{-6.4}$
- 4) $\frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} = 10^{-10.3}$
- 5) $2[\text{Ca}^{2+}] + [\text{H}^+] = 2[\text{CO}_3^{2-}] + [\text{HCO}_3^-] + [\text{OH}^-]$

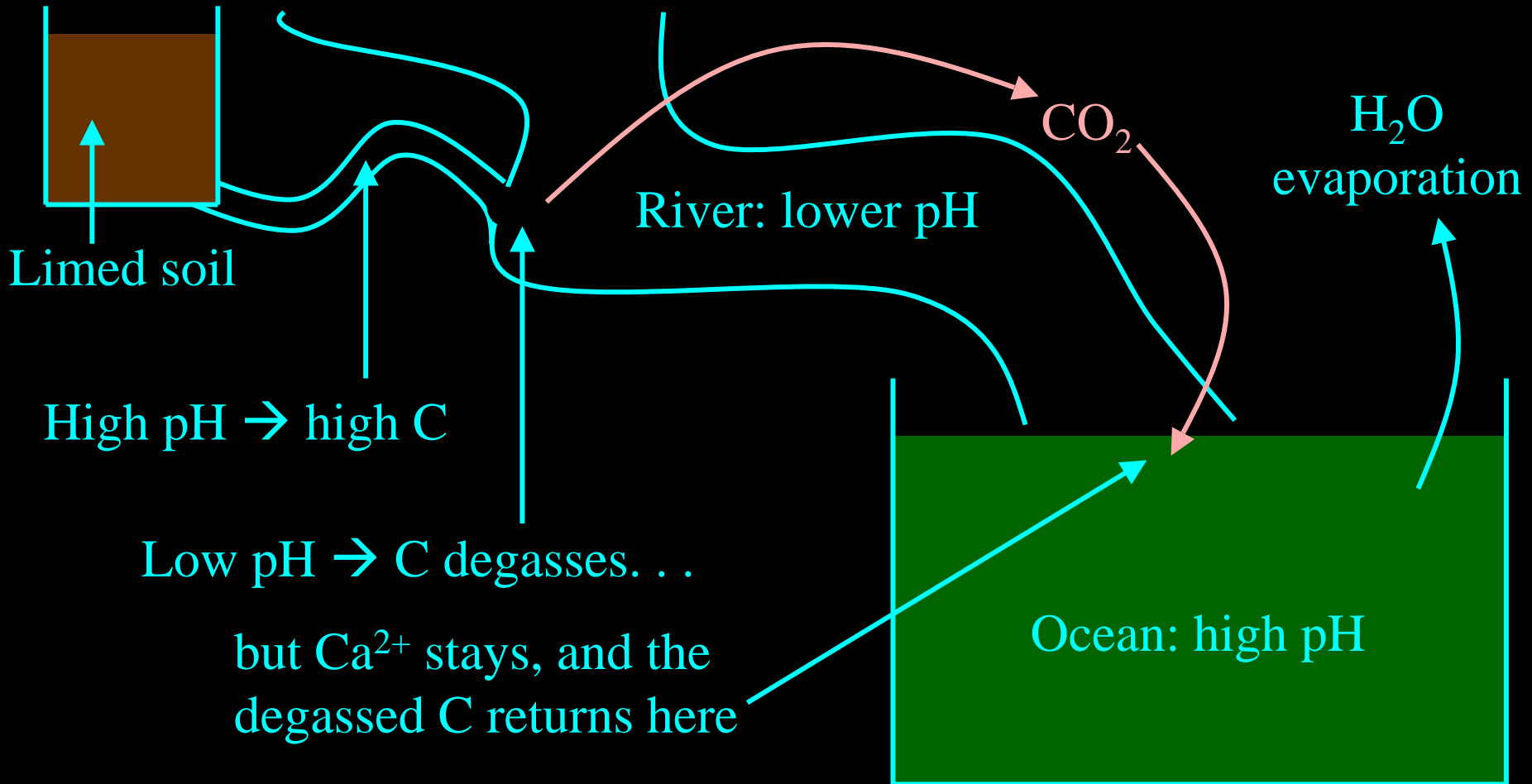
Known quantities:

$[\text{Ca}^{2+}]$

P_{CO_2}

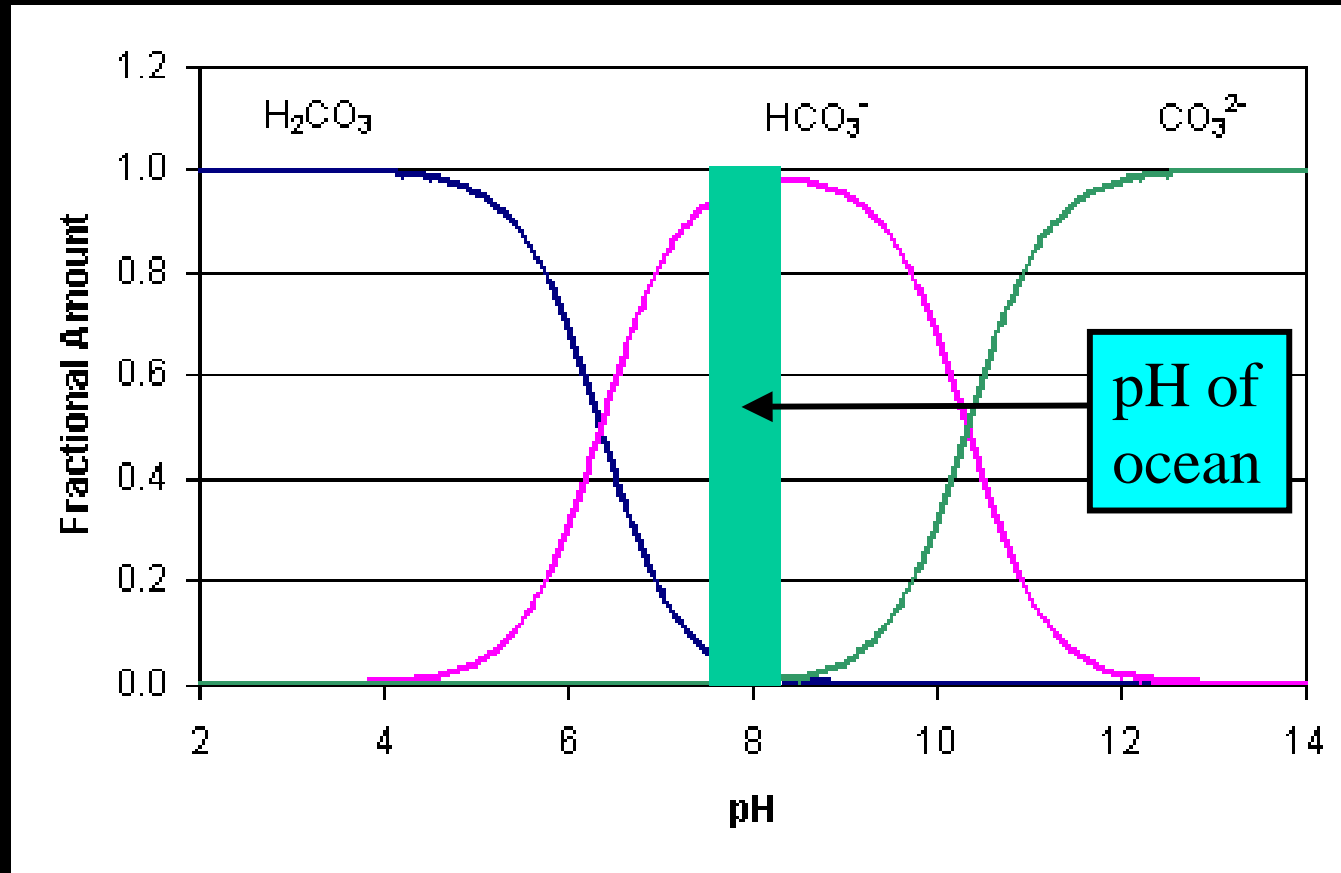
What do these equations tell us?

Except for calcite precipitation along the way, all we need to know about is what's coming out of the limed soil and what the environment of the ocean is. We can ignore the rivers in between.



In the ocean

Almost all dissolved inorganic carbon (DIC) in the ocean exists as bicarbonate, HCO_3^- .



DIC distribution curves from Prof. Stephen Bialkowski's website at Utah State, <http://www.chem.usu.edu/faculty/sbialkow/>

What will happen to the bicarbonate?

But it may not stay bicarbonate. Two other things could happen:

Moles of the aglime C sequestered per mole of Ca^{2+} leached, under simplistic assumptions about leaching:

It chemically precipitates by
 $\text{Ca}^{2+} + 2\text{HCO}_3^- \rightarrow \text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O}$

→ One

It stays as bicarbonate.

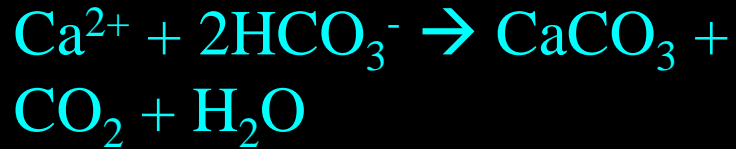
→ Two

It enters the ocean's biological C cycle.

→ Between one and two

What will happen to the bicarbonate?

It chemically precipitates by



The ocean is already supersaturated without chemical precipitation, and Ken Caldeira and Greg Rau (2000) imply that they think it can freely become more so.

It stays as bicarbonate.



If the above point is right, and biocalcifiers are not substrate-limited, it could stay as bicarbonate.

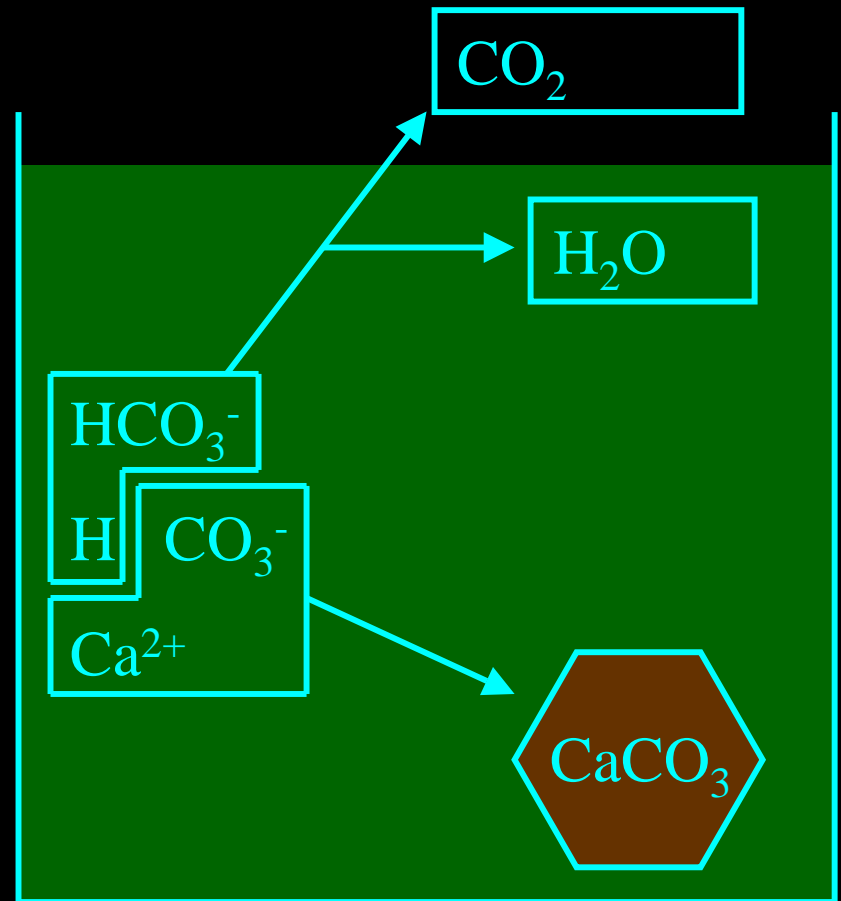
It enters the ocean's biological C cycle.



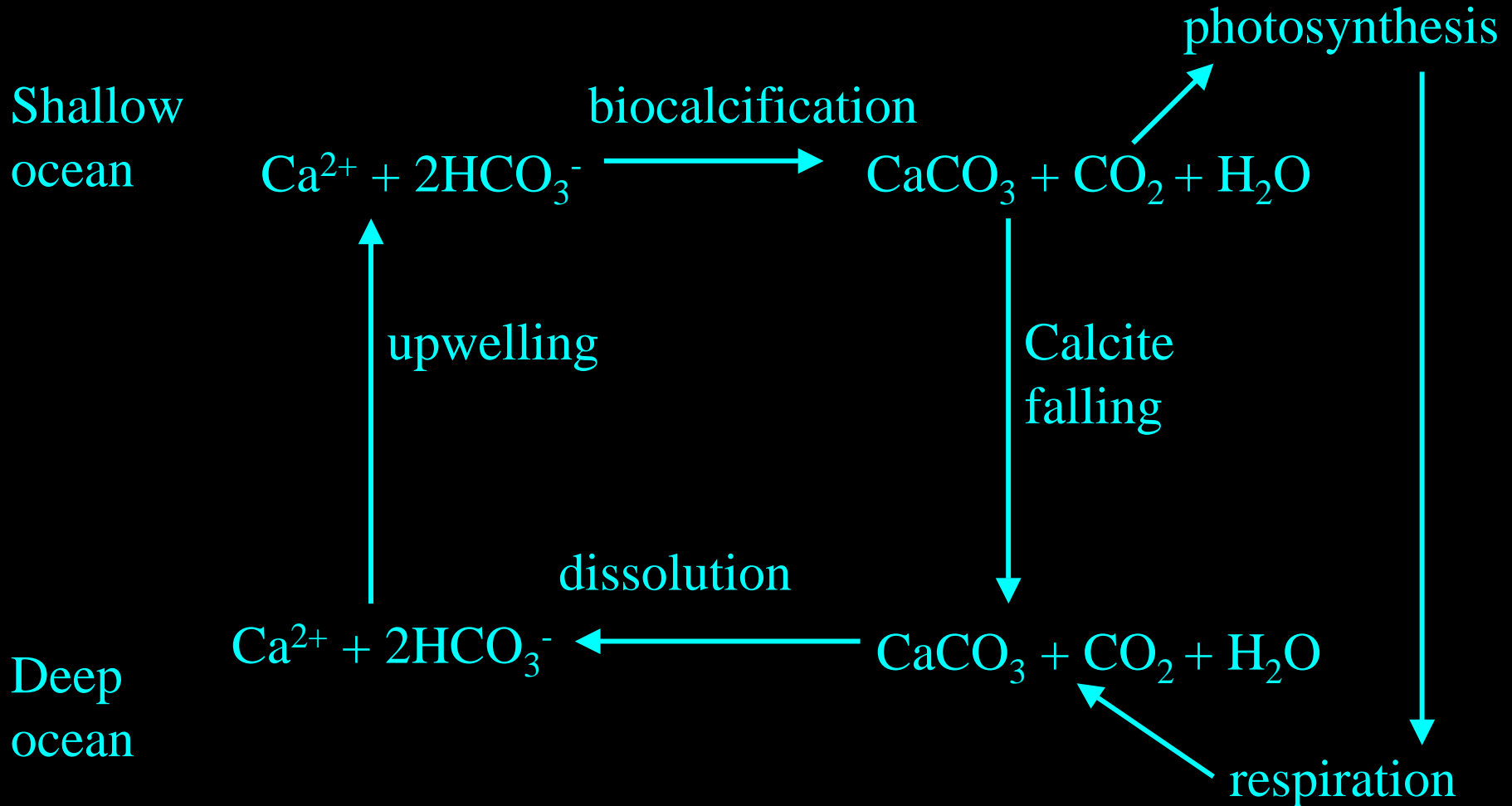
But if biocalcifiers are substrate-limited, as suggested by Berry *et al.* (2002), it could enter the bio-C-cycle.

Adding Ca^{2+} to water beyond CaCO_3 saturation

pH and DIC species distribution are determined when a system is in equilibrium with CaCO_3 and P_{CO_2} . So additional Ca^{2+} and HCO_3^- must react in ways that don't change pH or DIC distribution, meaning half of the additional C must precipitate as CaCO_3 and the other half must degas as CO_2 .



The normal ocean carbonate cycle



Conclusions

Determining the proportion of aglime carbon that enters the atmosphere as carbon dioxide requires knowing precipitation, soil type, and the correct answers to the theoretical questions outlined in this presentation. Here are two extreme scenarios:

- 1) 10% calcium leaching, chemical calcite precipitation in the ocean: 90% of the aglime carbon enters the atmosphere.
- 2) 50% calcium leaching, bicarbonate stays in the ocean: 0% of the aglime carbon enters the atmosphere.

Even if the answers to the theoretical questions turn out to be simple, we still have plenty left to determine experimentally.

Future research

We need experiments designed explicitly to determine the fate of aglime carbon. We would need such experiments even if the theoretical solution to the problem were clearer.

Future experiments should:

- Measure flux from agricultural soils that have been treated with lime repeatedly over many years.
- Attempt to determine flux for all inorganic carbon species and major soil ions.
- Examine rate of solid carbonate precipitation in streams and rivers downstream from limed agricultural watersheds.
- Explore possible changes in biocalcification and chemical CaCO_3 in response to increases in coastal DIC and Ca^{2+} concentration.

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