Does Precambrian carbonate $\delta^{13}C$ directly record fluctuations in the oxidative state of the biosphere?

- This is not relevant at all.
- Too late – this was only new 15 years ago.
- There are potentially important implications.
  But only 3 people in the World are going to care.
- Maybe.
- Yes.
- Meh.

forget about it
drink beer
be happy

keep going

meh

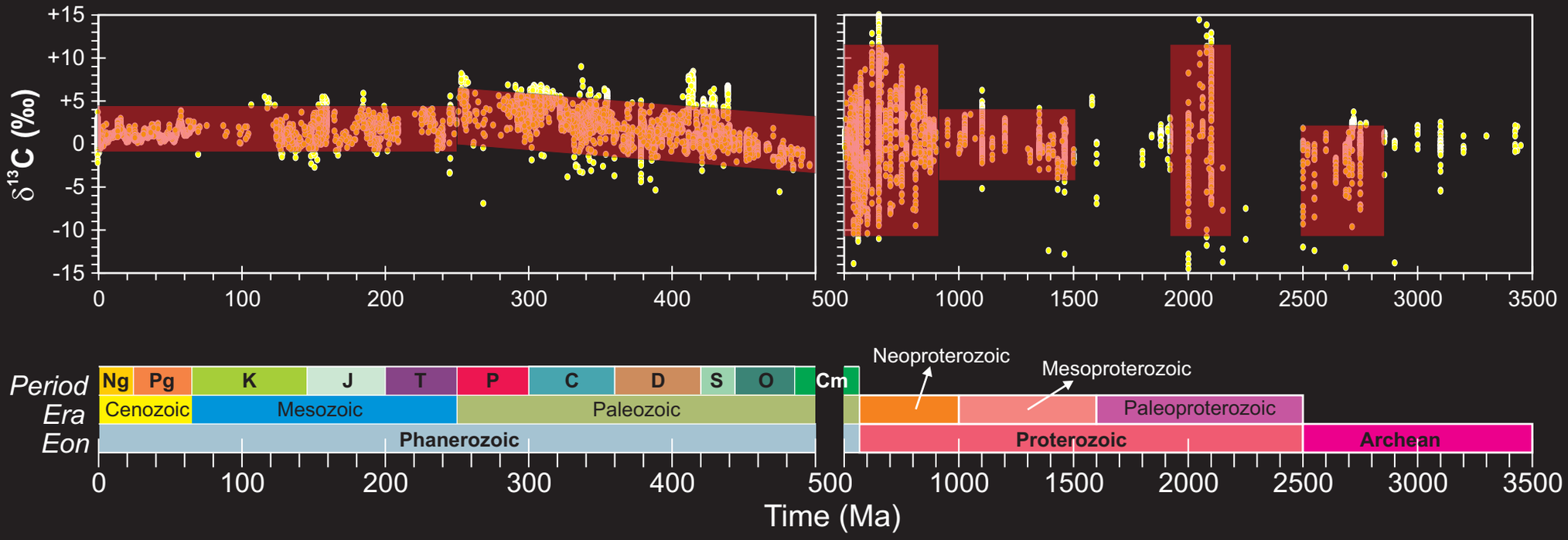




Carbonate $\delta^{13}C$ variability through time

what exactly does it (temporal changes in $\delta^{13}C$) mean?

Ridgwell and Arndt [2014]



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Re-partitioning of carbon between surficial reservoirs (cf. LGM)?

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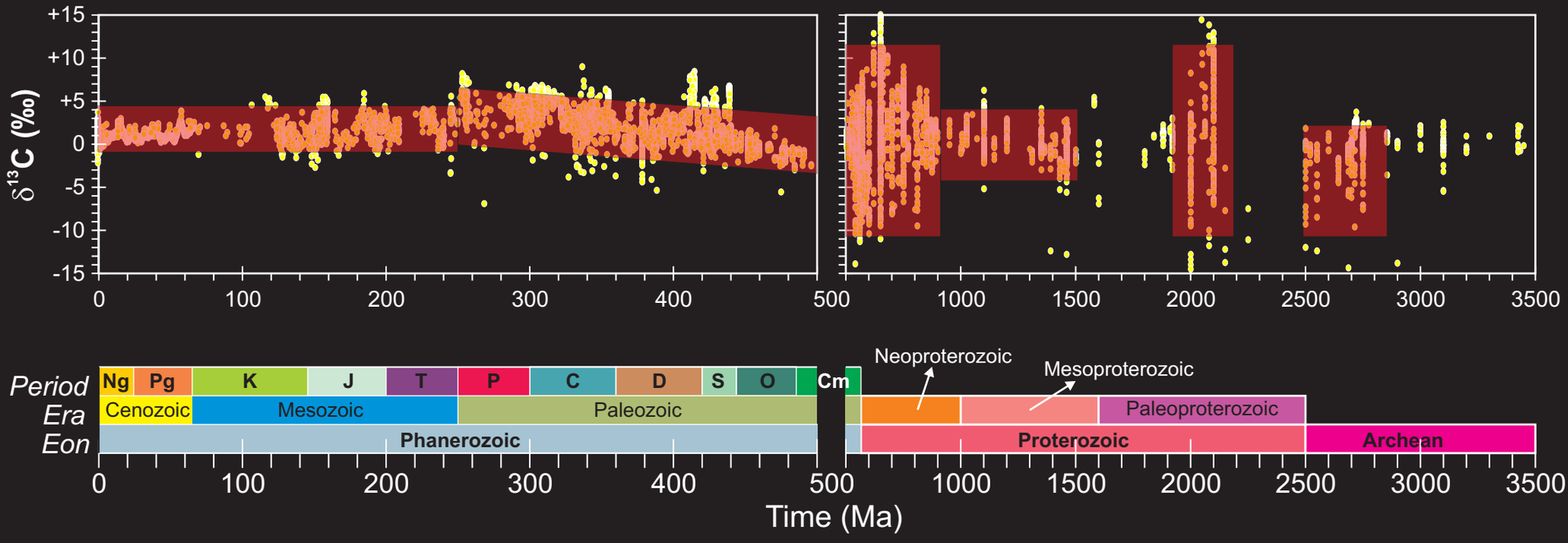

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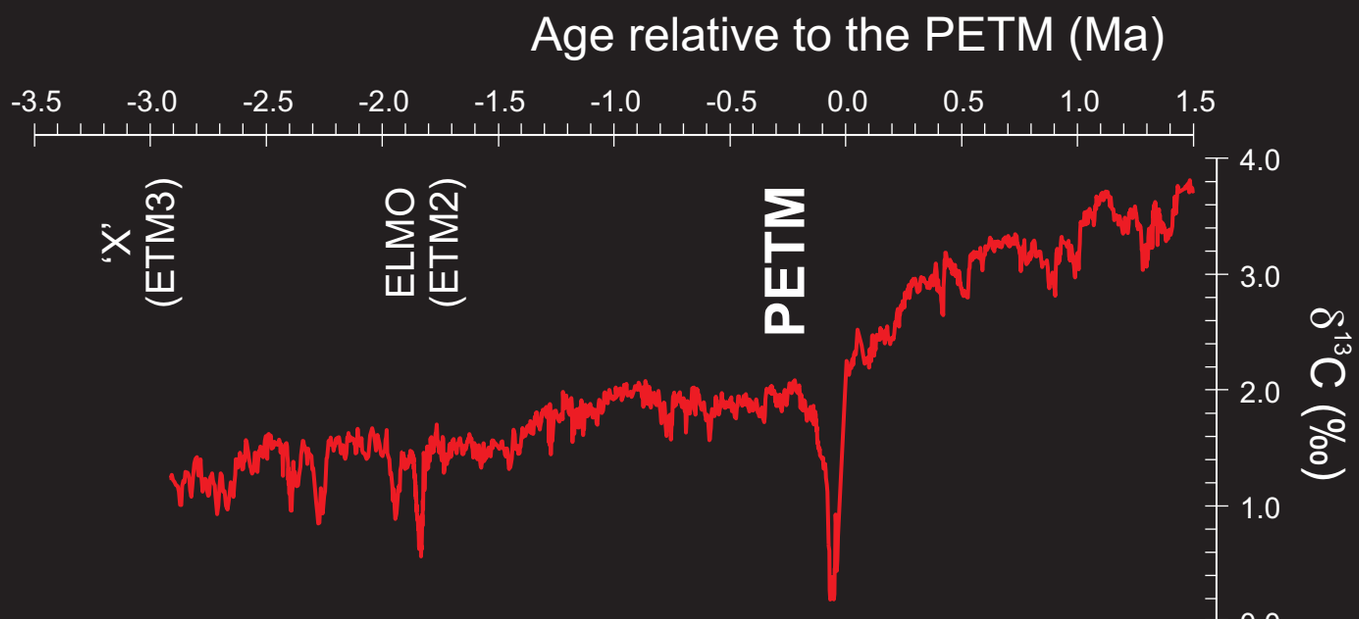

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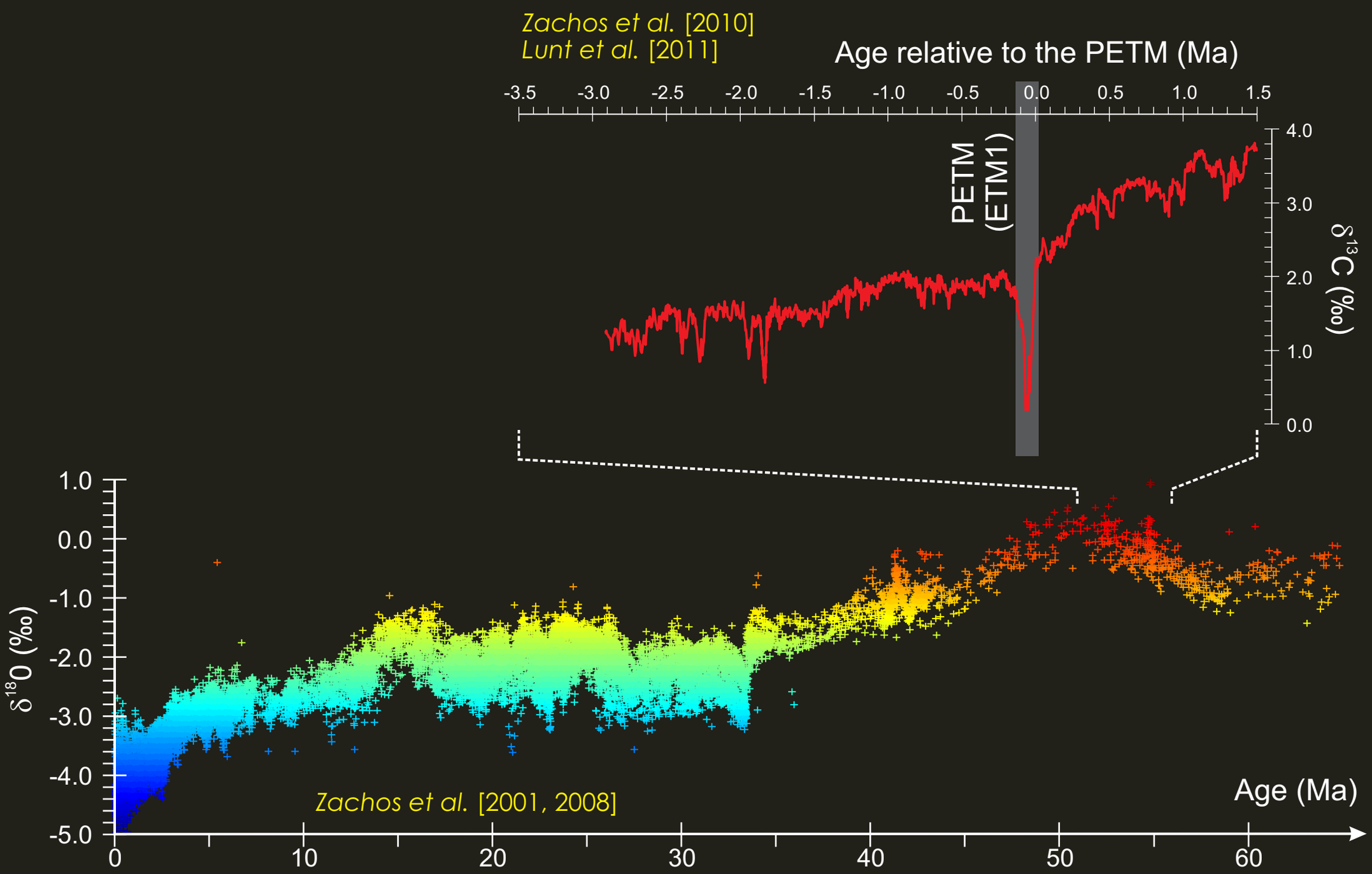

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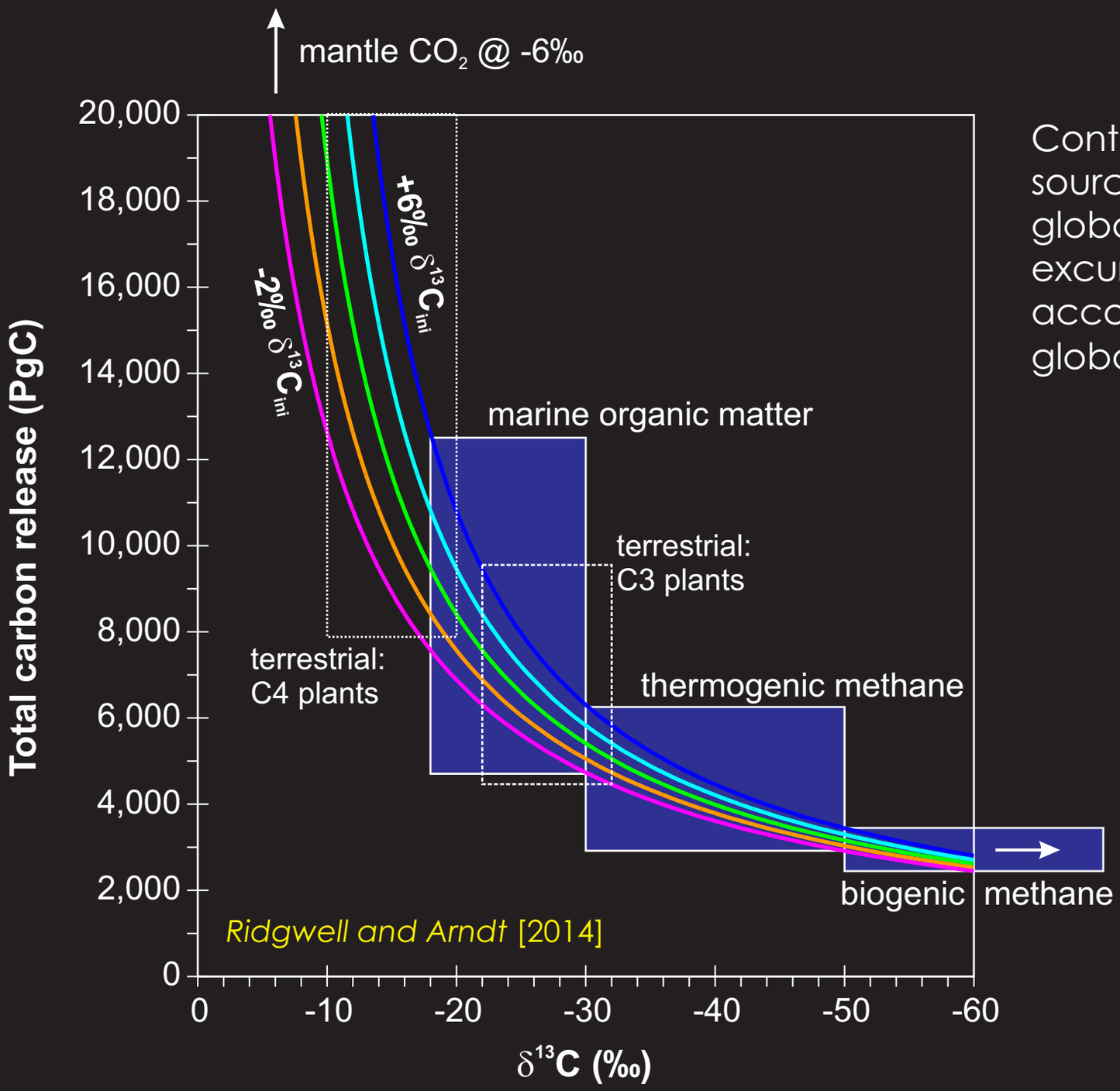
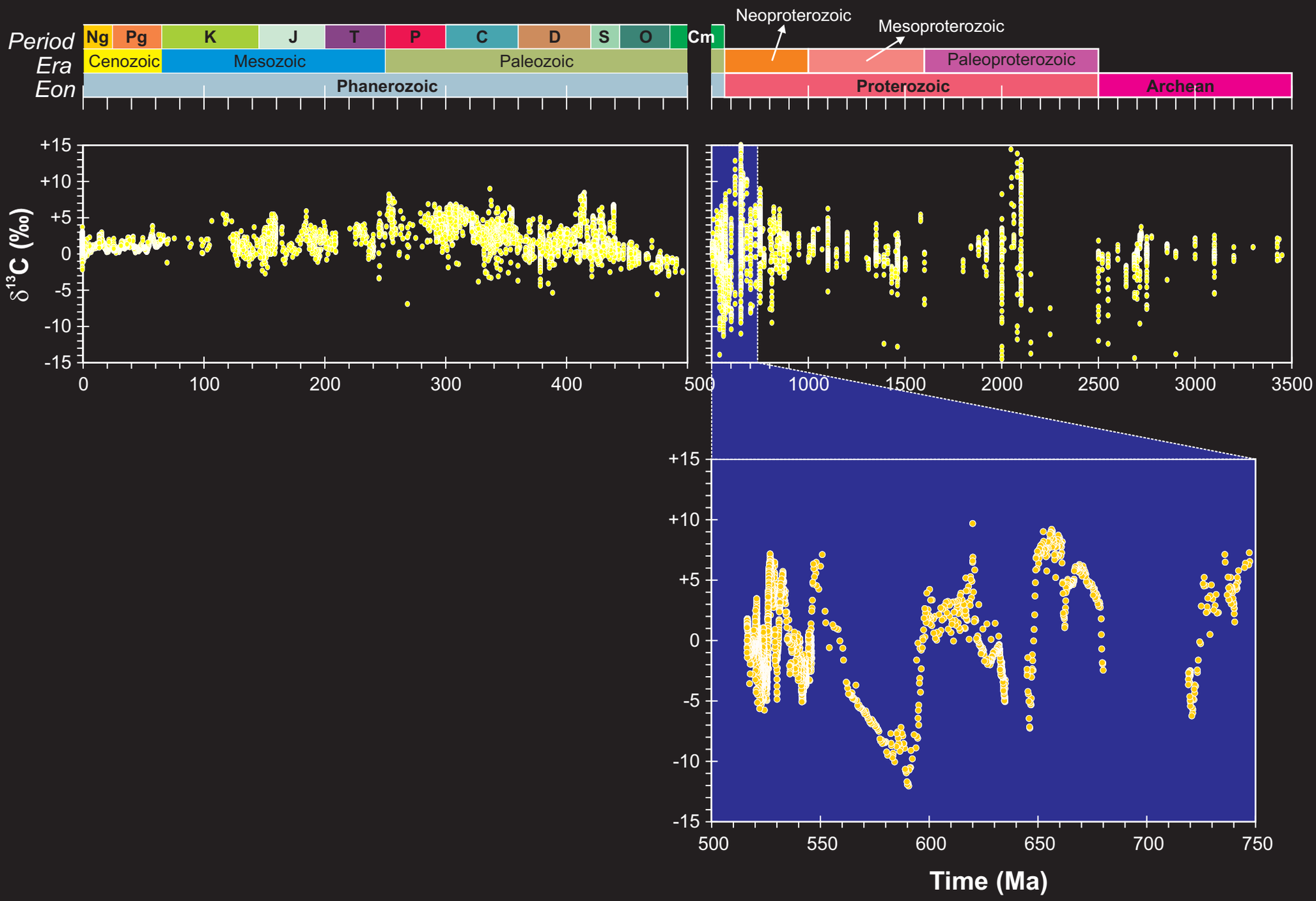


Contours of carbon release vs. source isotopic signature for a global -4‰ carbon isotopic excursion. Contours differ according to the initial mean global $\delta^{13}C$.

Carbonate $\delta^{13}C$ variability through time



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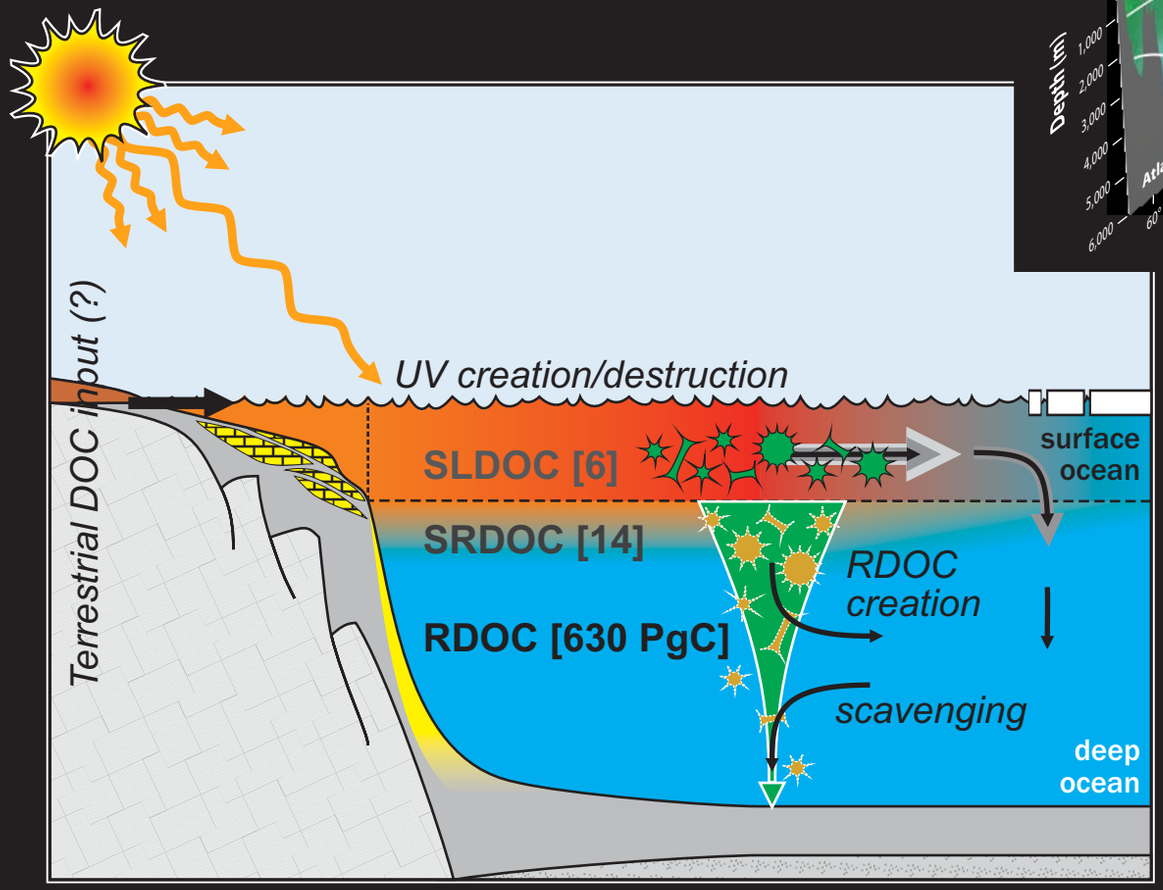

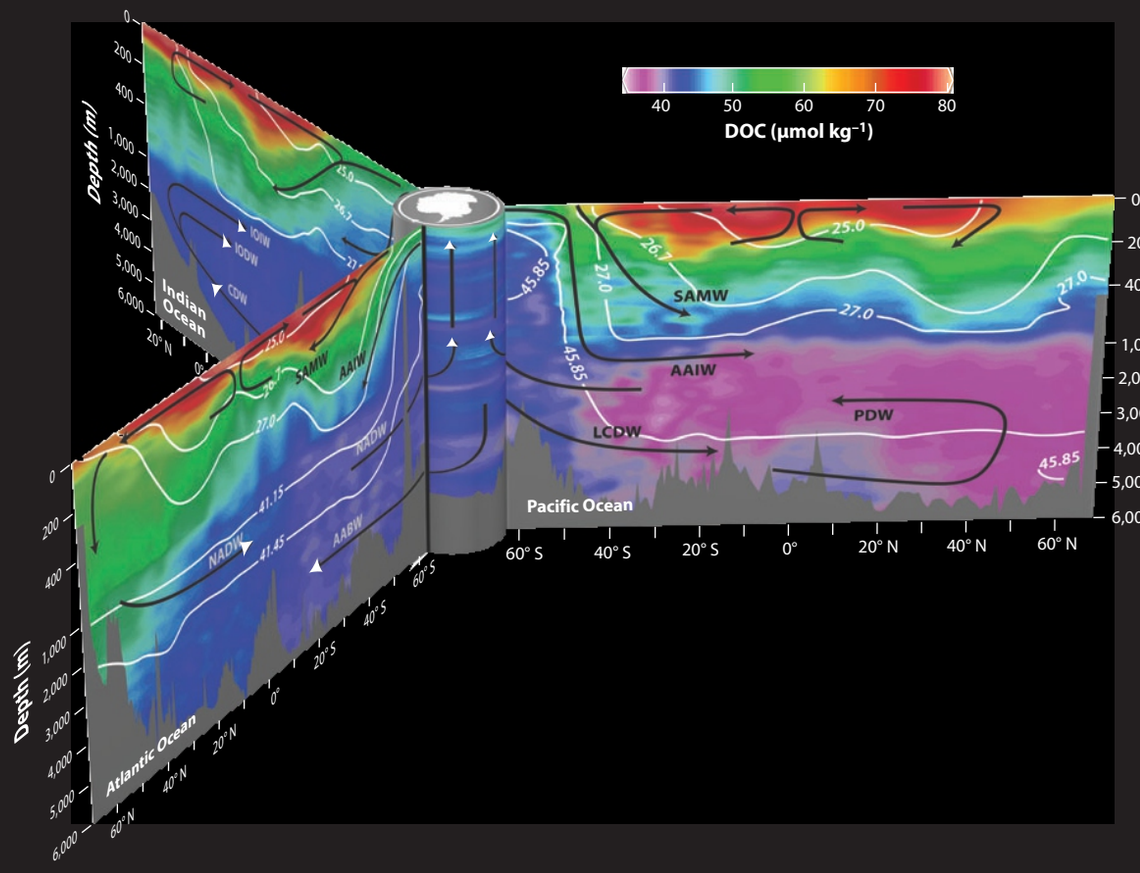

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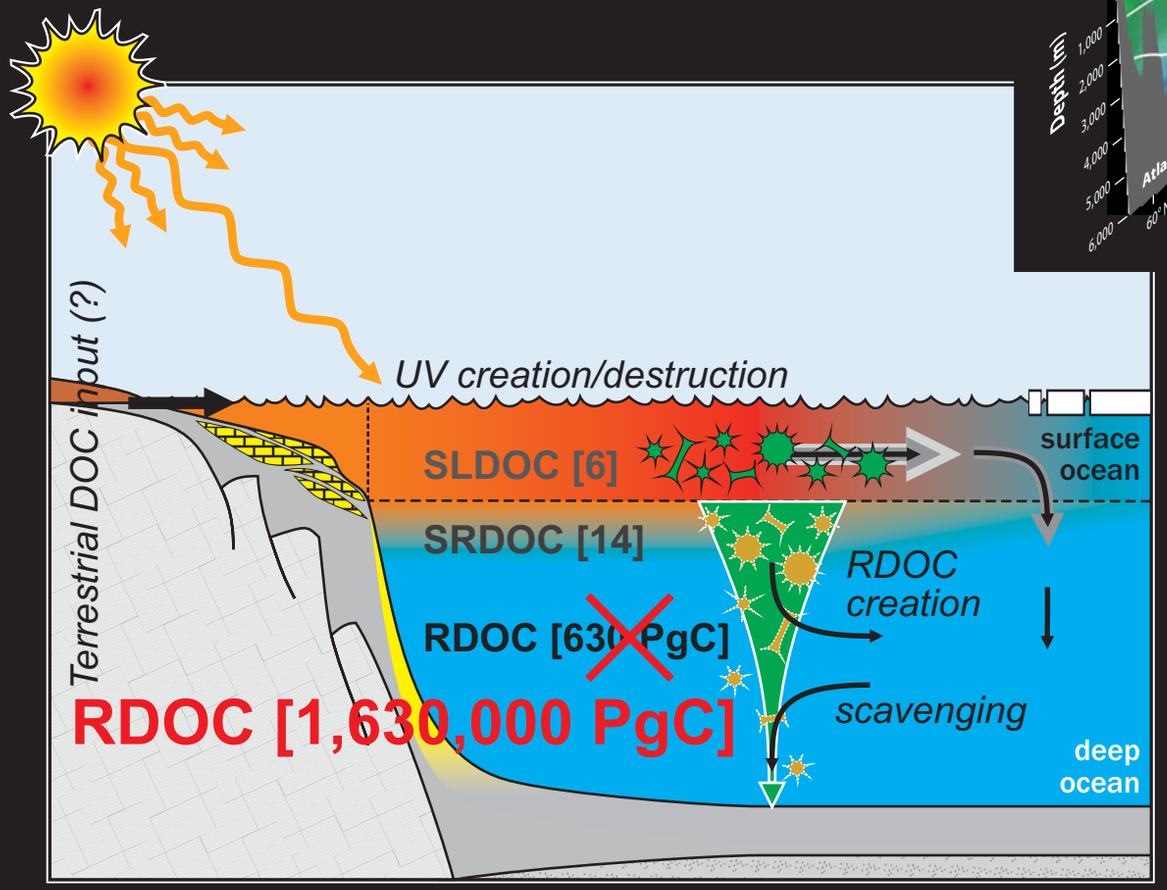

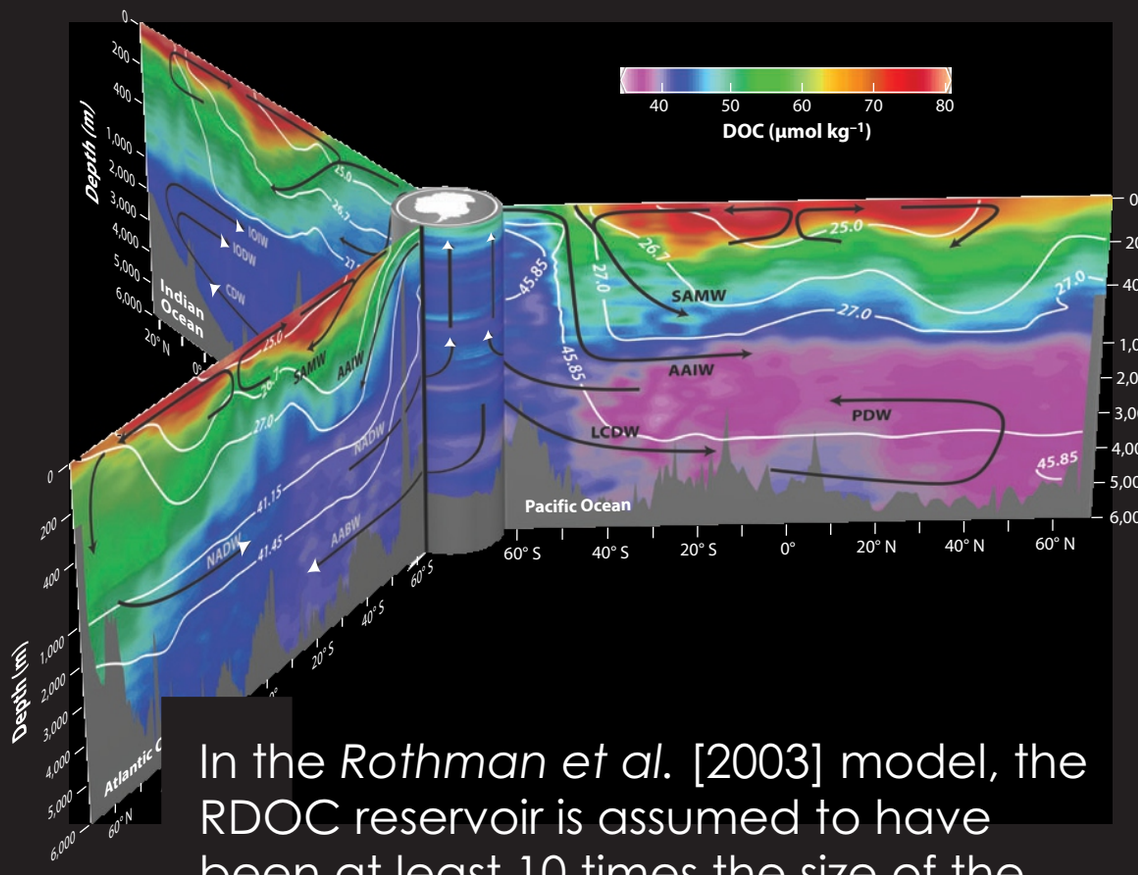

In the *Rothman et al.* [2003] model, the RDOC reservoir is assumed to have been at least 10 times the size of the inorganic (ocean DIC + atmospheric pCO_2) reservoir. For a modern DIC + pCO2 reservoir of 39,000 PgC, this mean 390,000 PgC of DOC – more than 500 times larger than modern).

(For a higher late Precambrian DIC reservoir, the minimum DOC reservoir becomes 1.6×10^6 PgC, equivalent to concentration of a little over 1000 mgC per L of seawater and becoming the third most dominant dissolved species in the ocean after Cl^-.)

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One can write (*Kump and Arthur* [1999], *Chem. Geol.*):

$$F_{Corg} / (F_{Corg} + F_{CaCO3}) = \text{C burial ratio}$$

$$(\delta^{13}C_{obs} - \delta^{13}C_{input}) / (\delta^{13}C_{CaCO3} - \delta^{13}C_{Corg})$$

observed (recorded) carbonate $\delta^{13}C$

-5.0

25.0

Carbonate $\delta^{13}C$ variability through time

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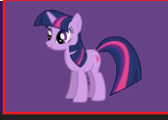

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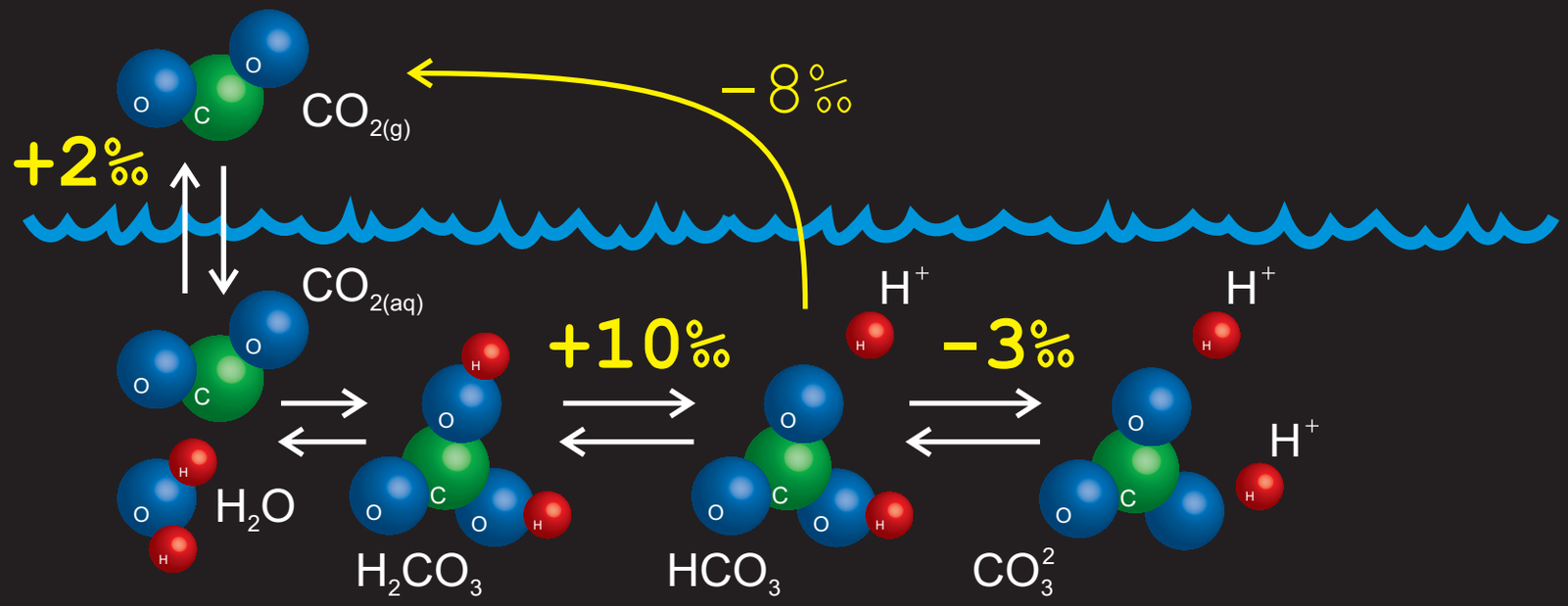
pH-driven re-partitioning of the where the isotopic composition of the mean surficial reservoir is held
(and what carbonate samples)

Also see: *Higgins and Schrag* [2003]

A new paleo Pokémon appears – The pH control on carbonate $\delta^{13}C$



Adapted from: *Barker and Ridgwell* [2012]

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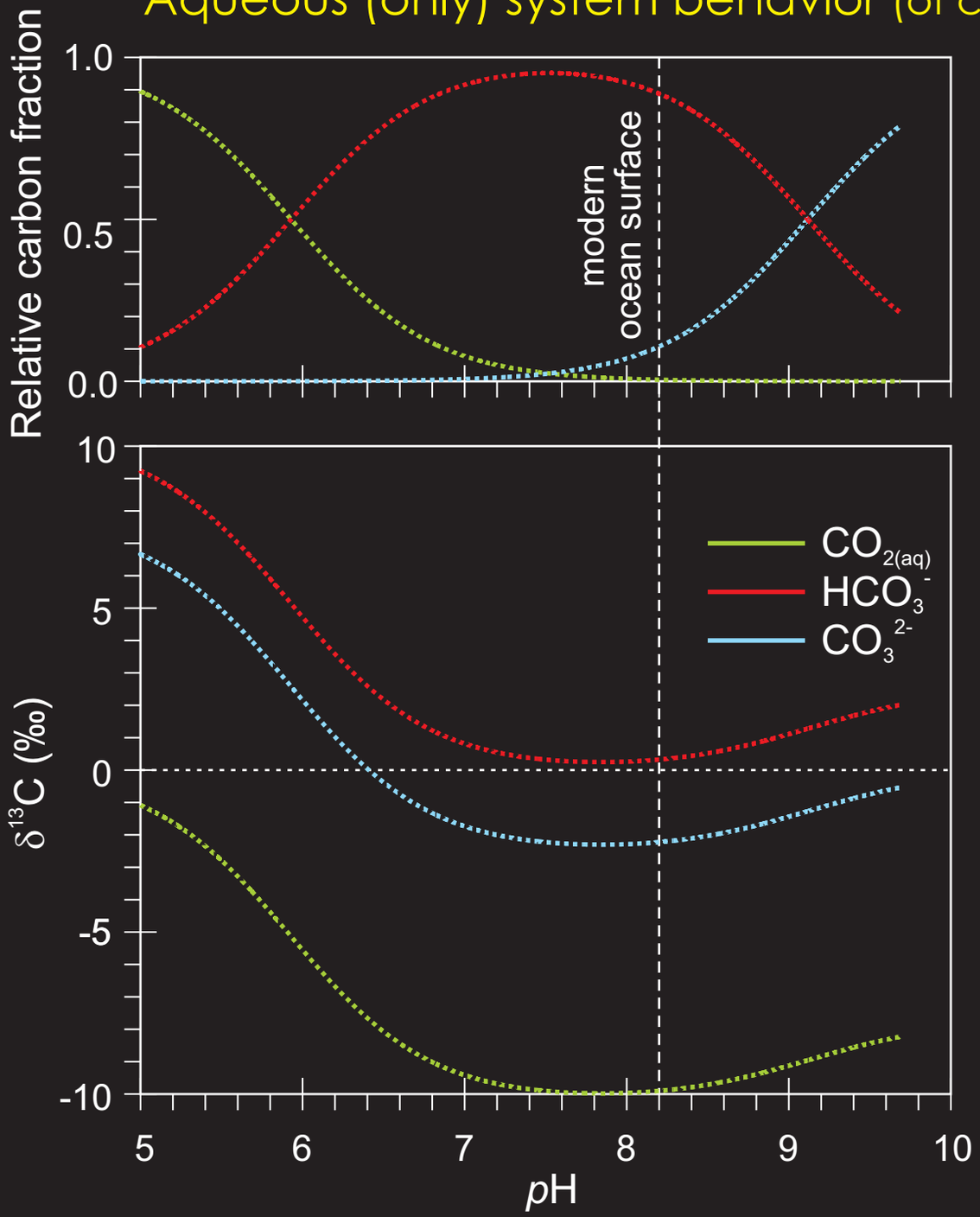
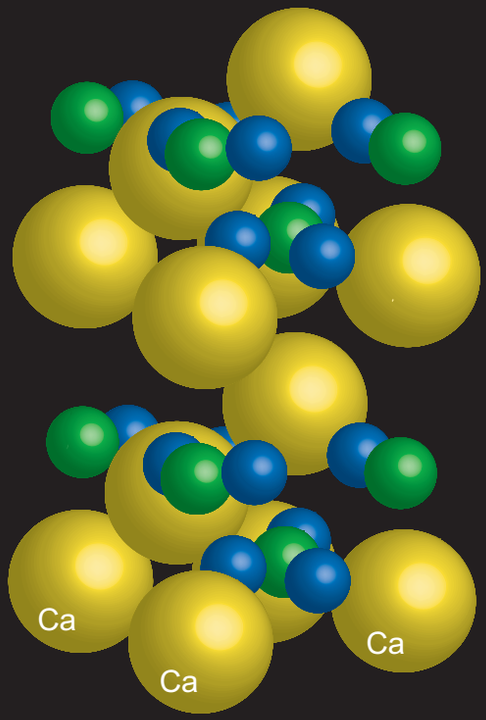
Aqueous (only) system behavior (of carbon partitioning between reservoirs)





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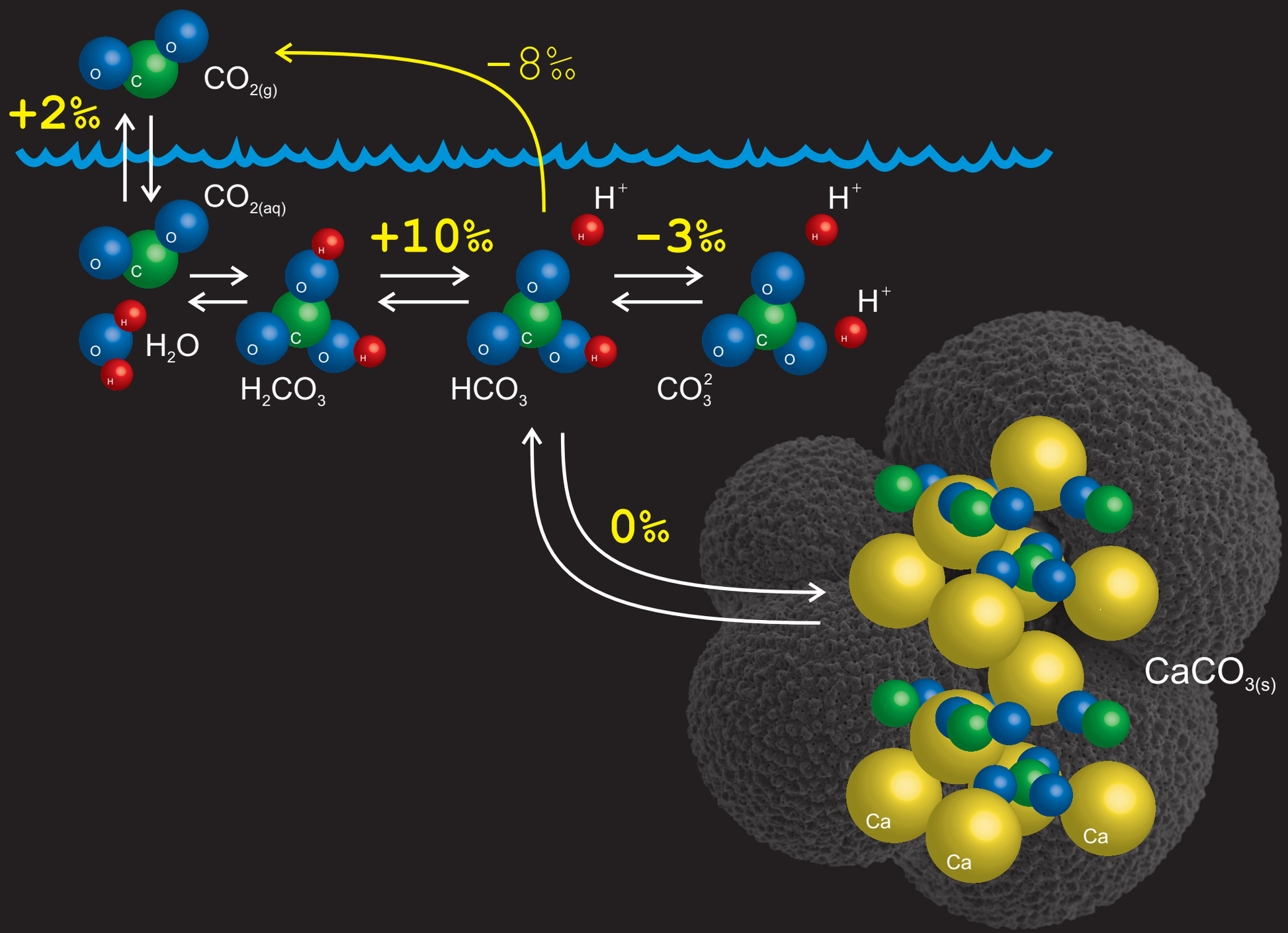

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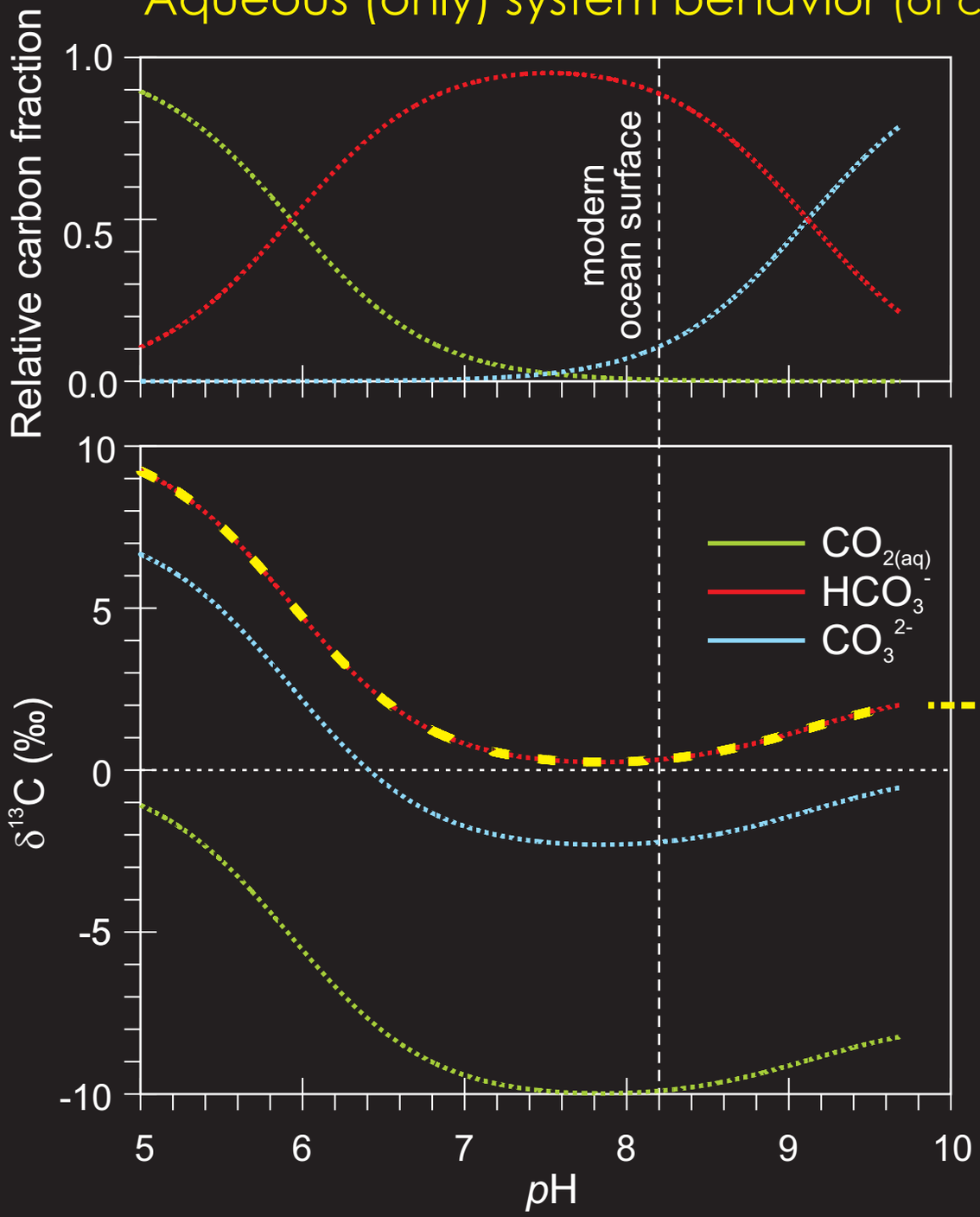

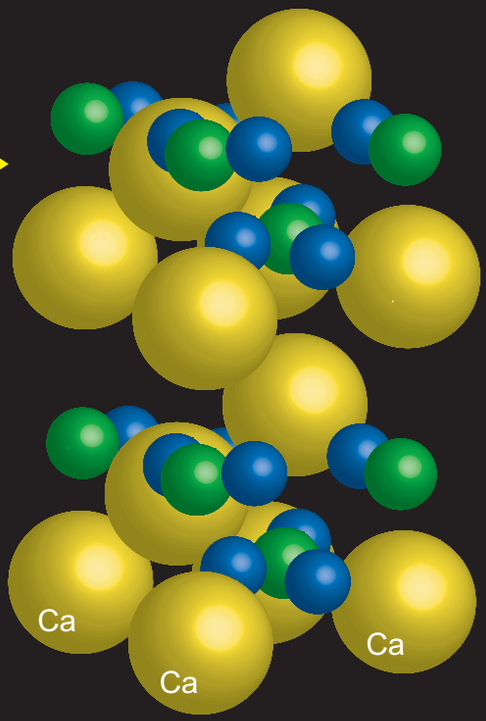

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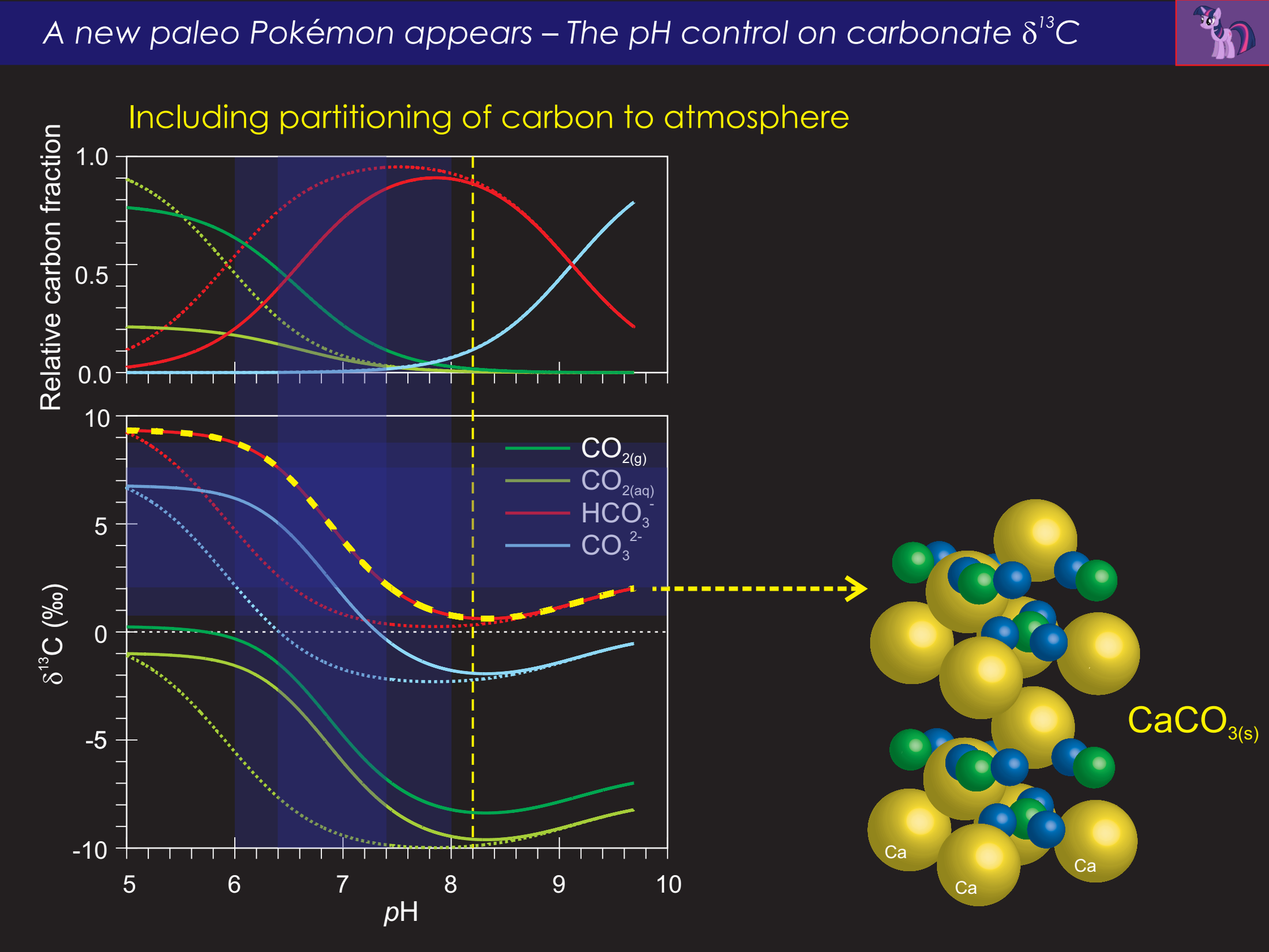
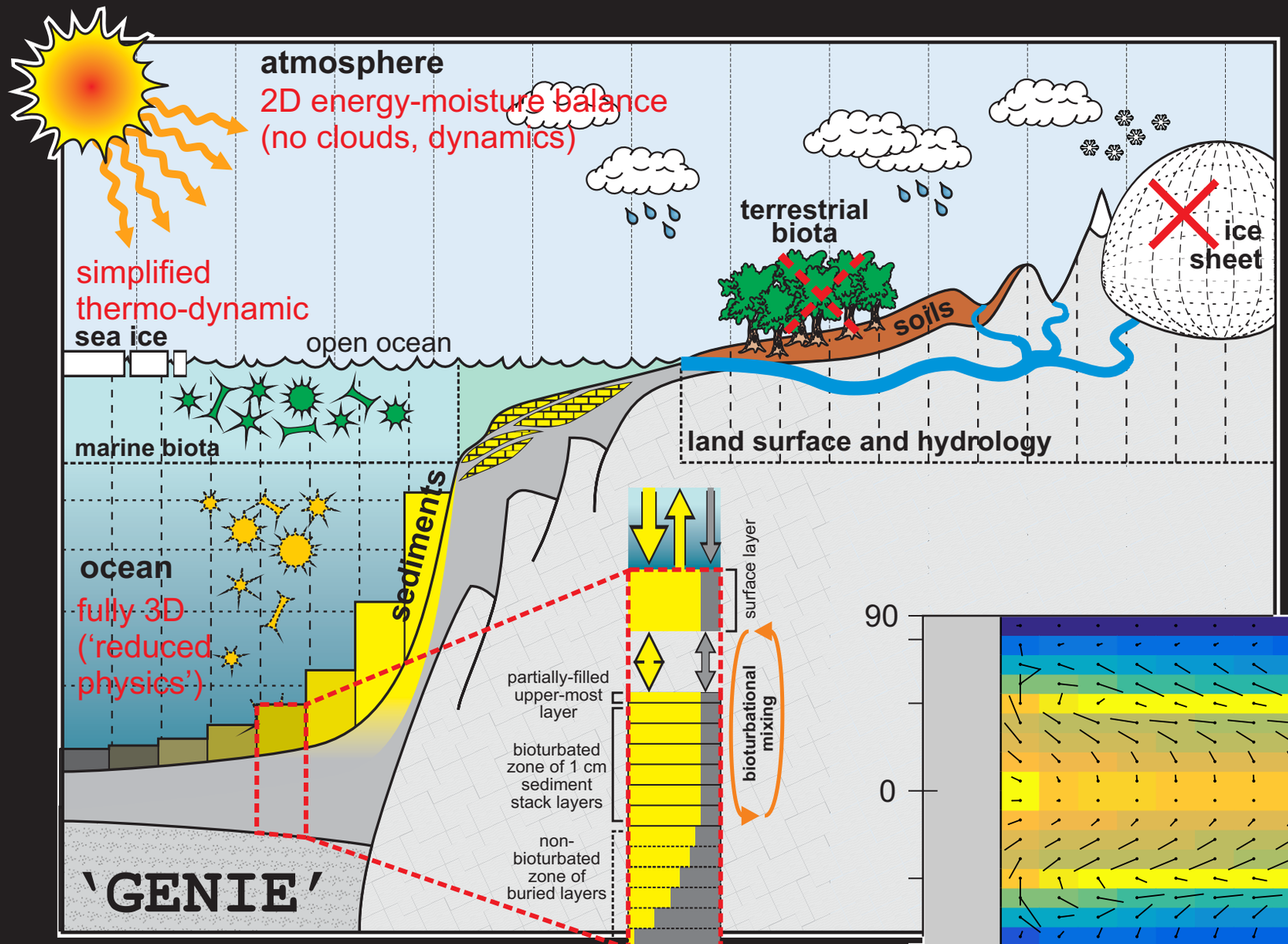
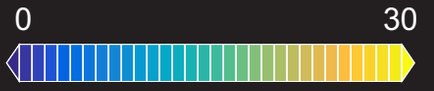
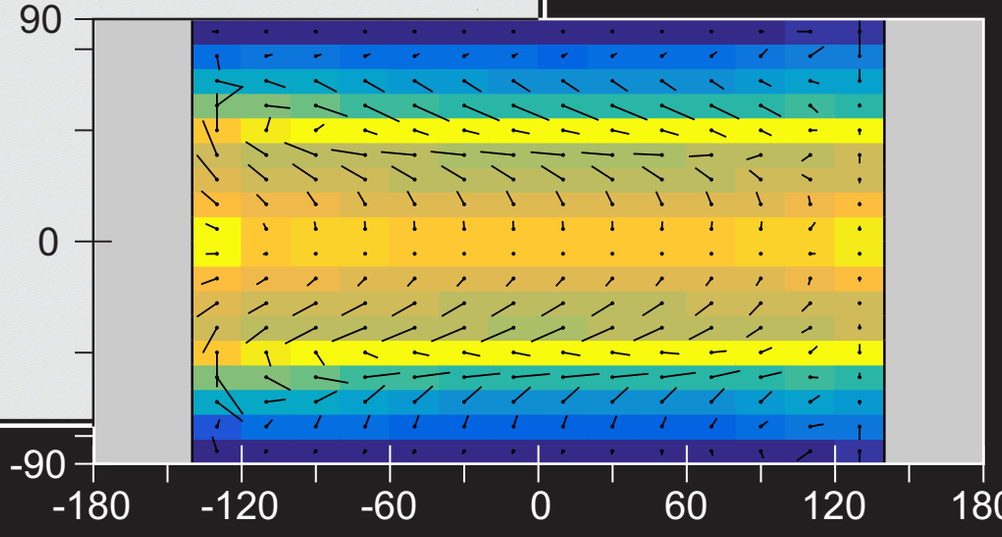


Earth system model – physical configuration

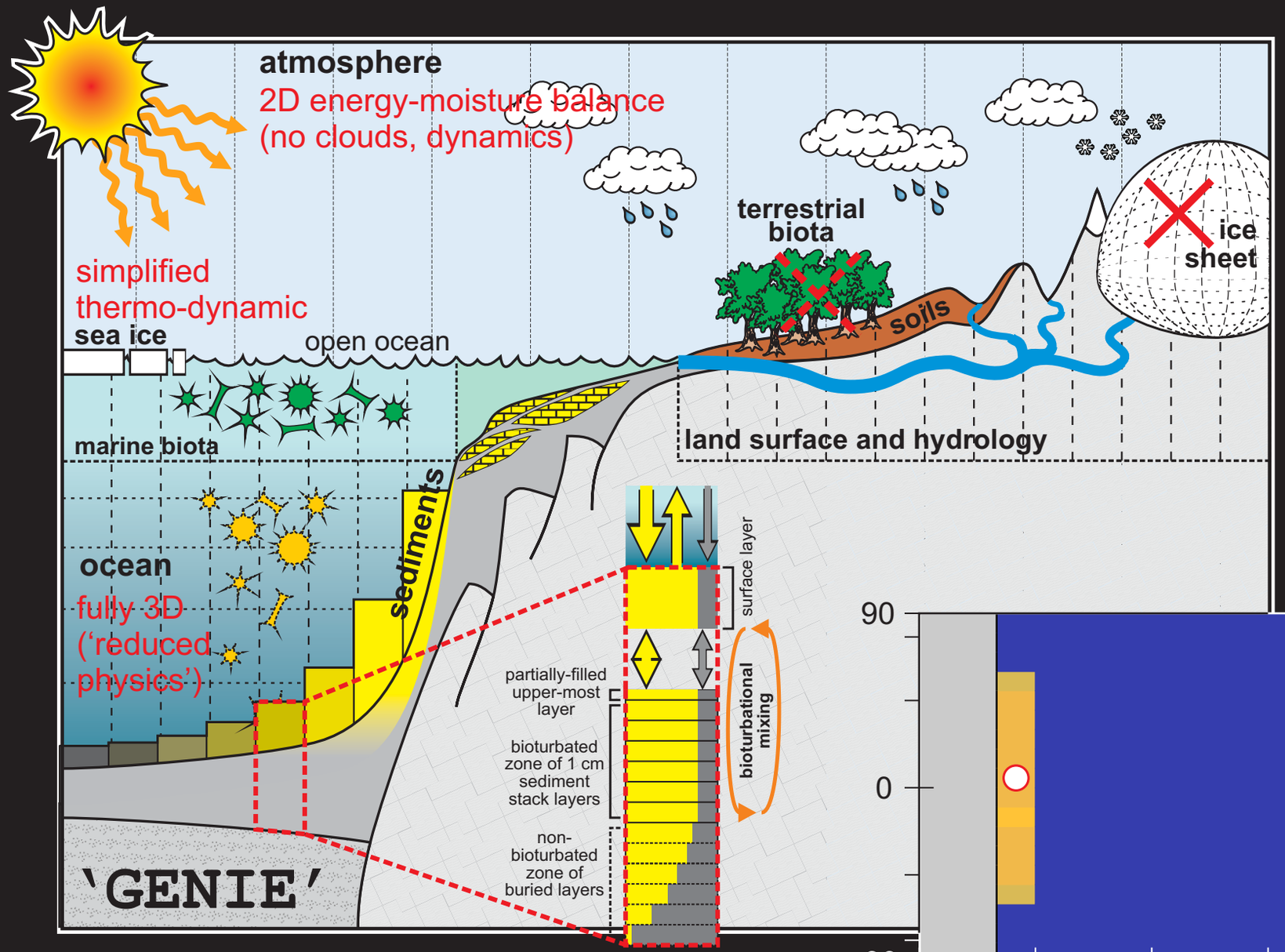


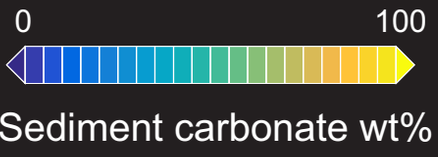


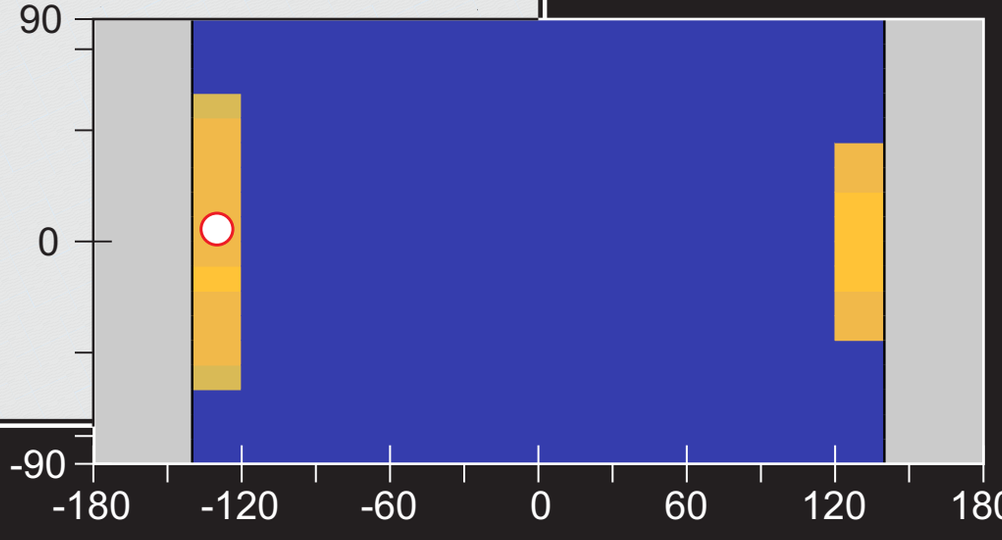


www.seao2.org/mycgenie.html

Earth system model – carbon cycle (sedimentary) configuration







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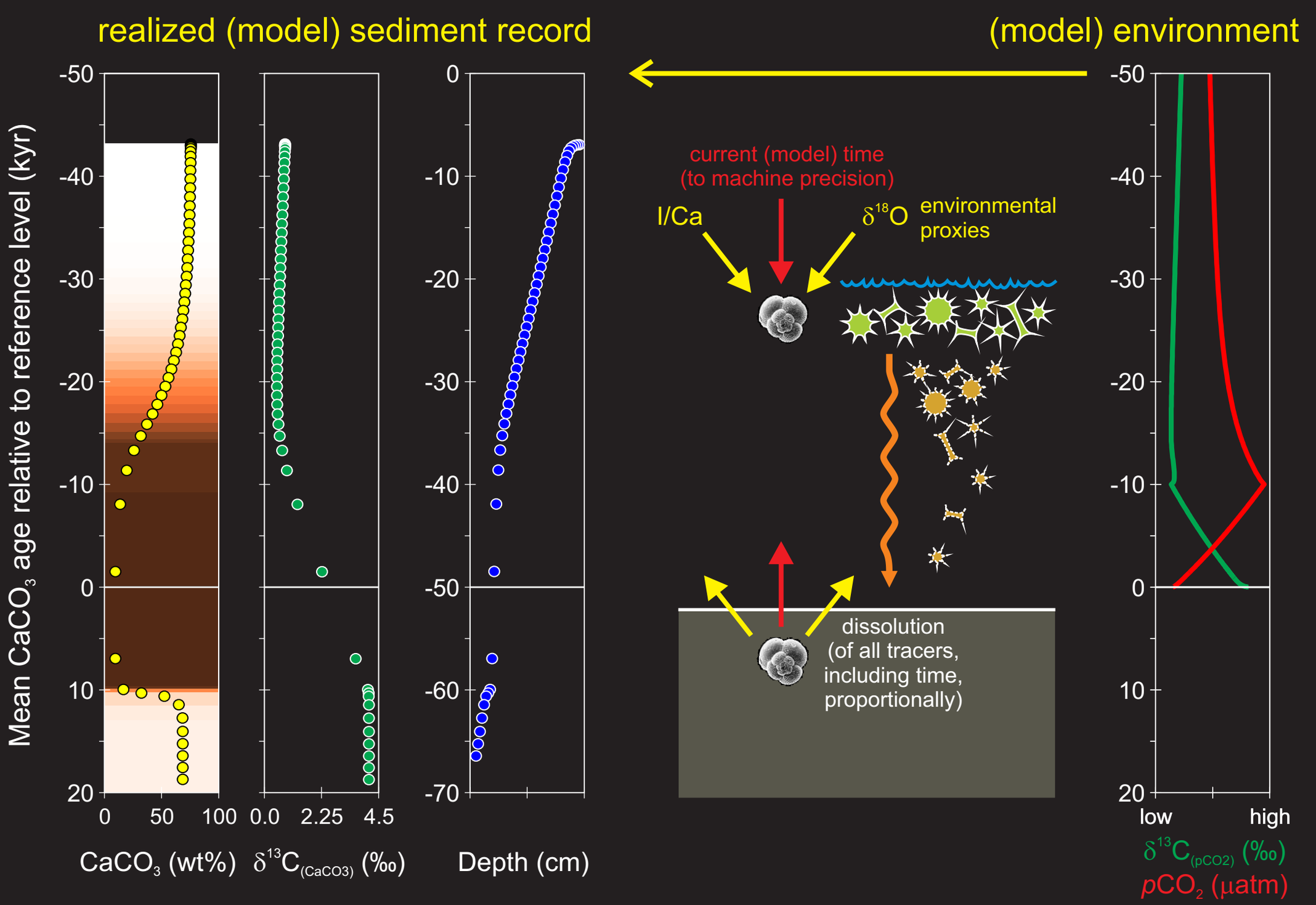
Numerical modelling – Approach



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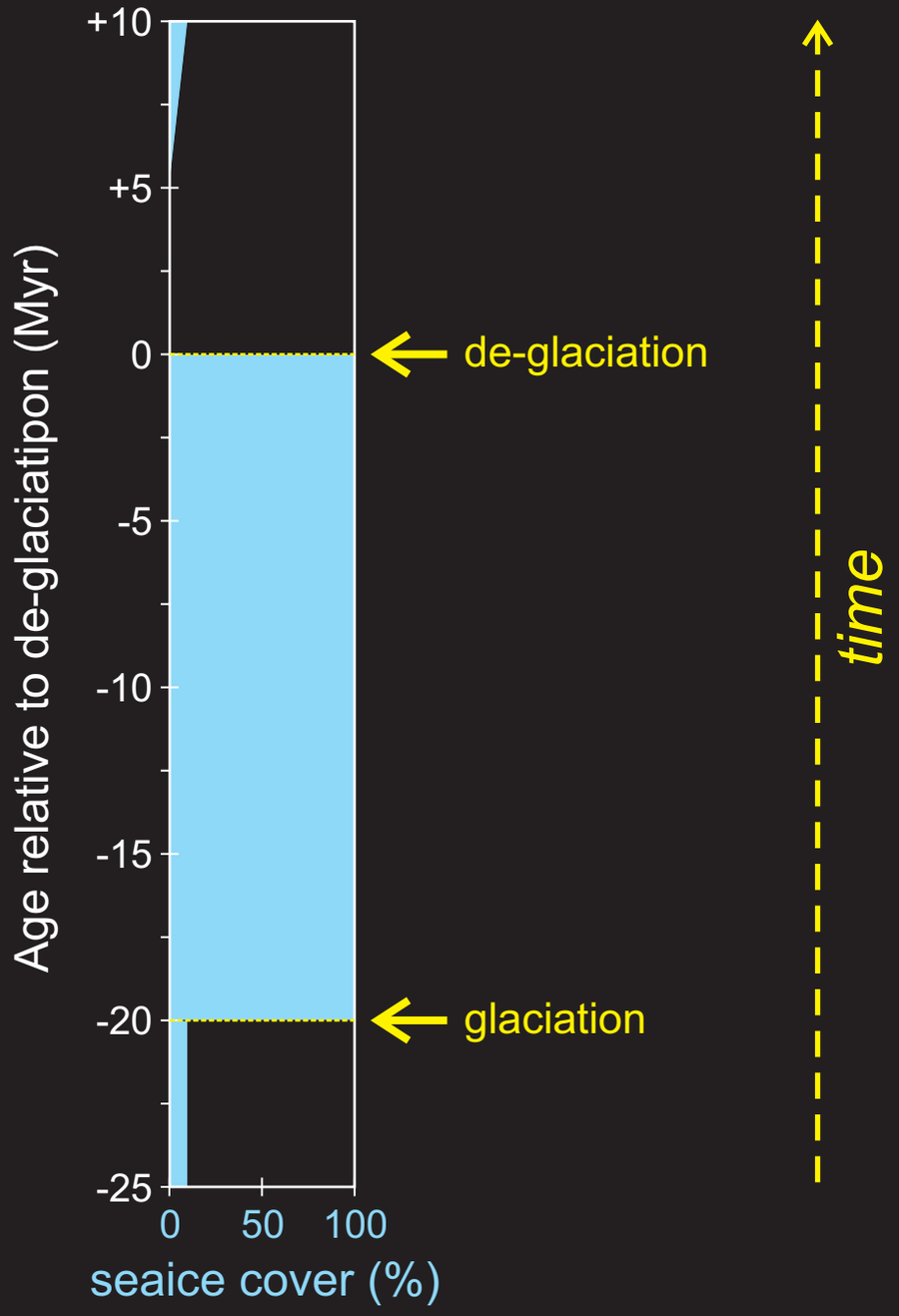
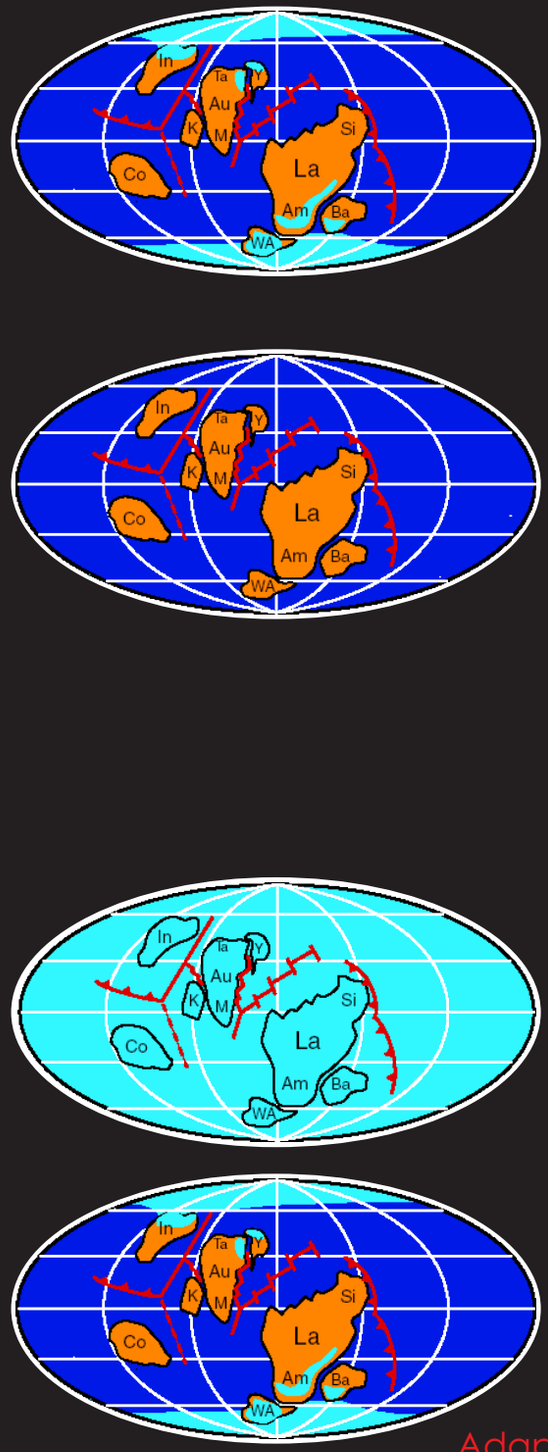
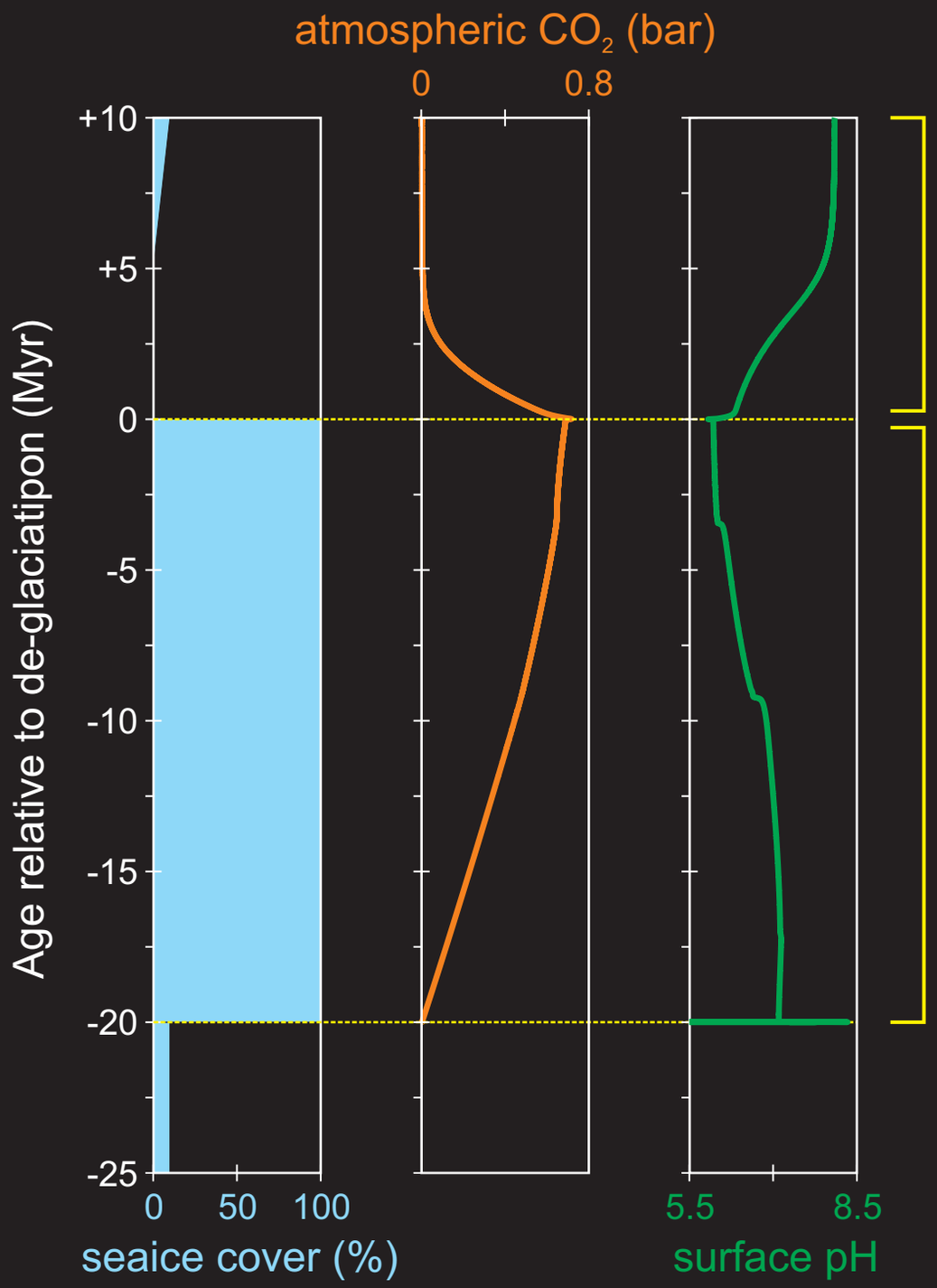


time



Adapted from: *Hoffman and Schrag* [2002]

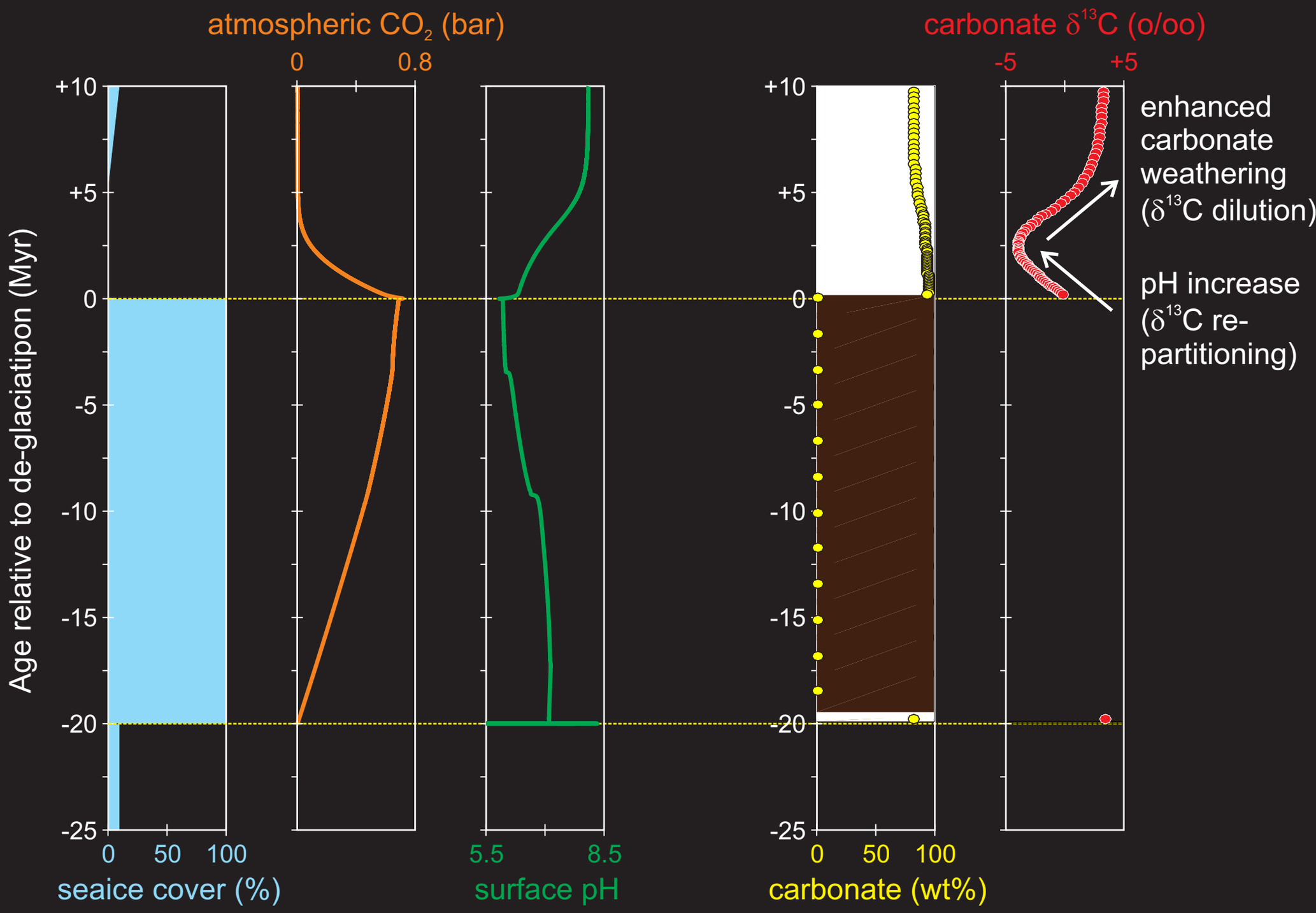
Numerical modelling – Results



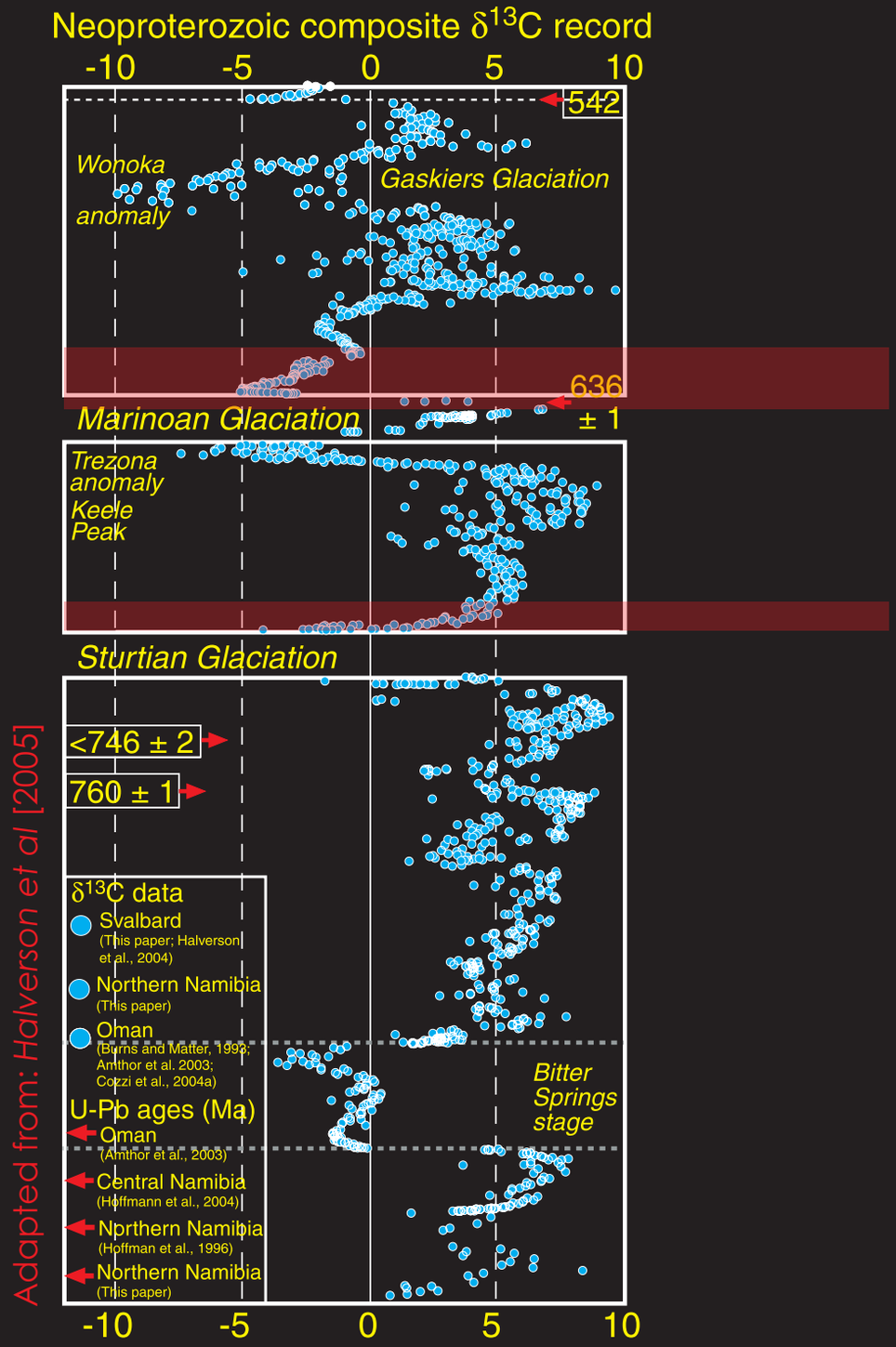
Enhanced weathering
$\Rightarrow$ CO_2 draw-down
and pH increase

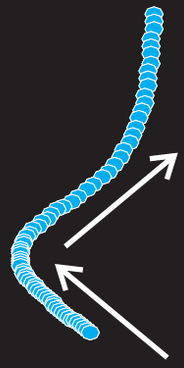
Continued CO_2 out-gasssing
but ... minimal weathering
$\Rightarrow$ CO_2 buildup @ -6 o/oo
and ocean pH decline

Numerical modelling – Results



Deep-time inferences (aka 'speculation')



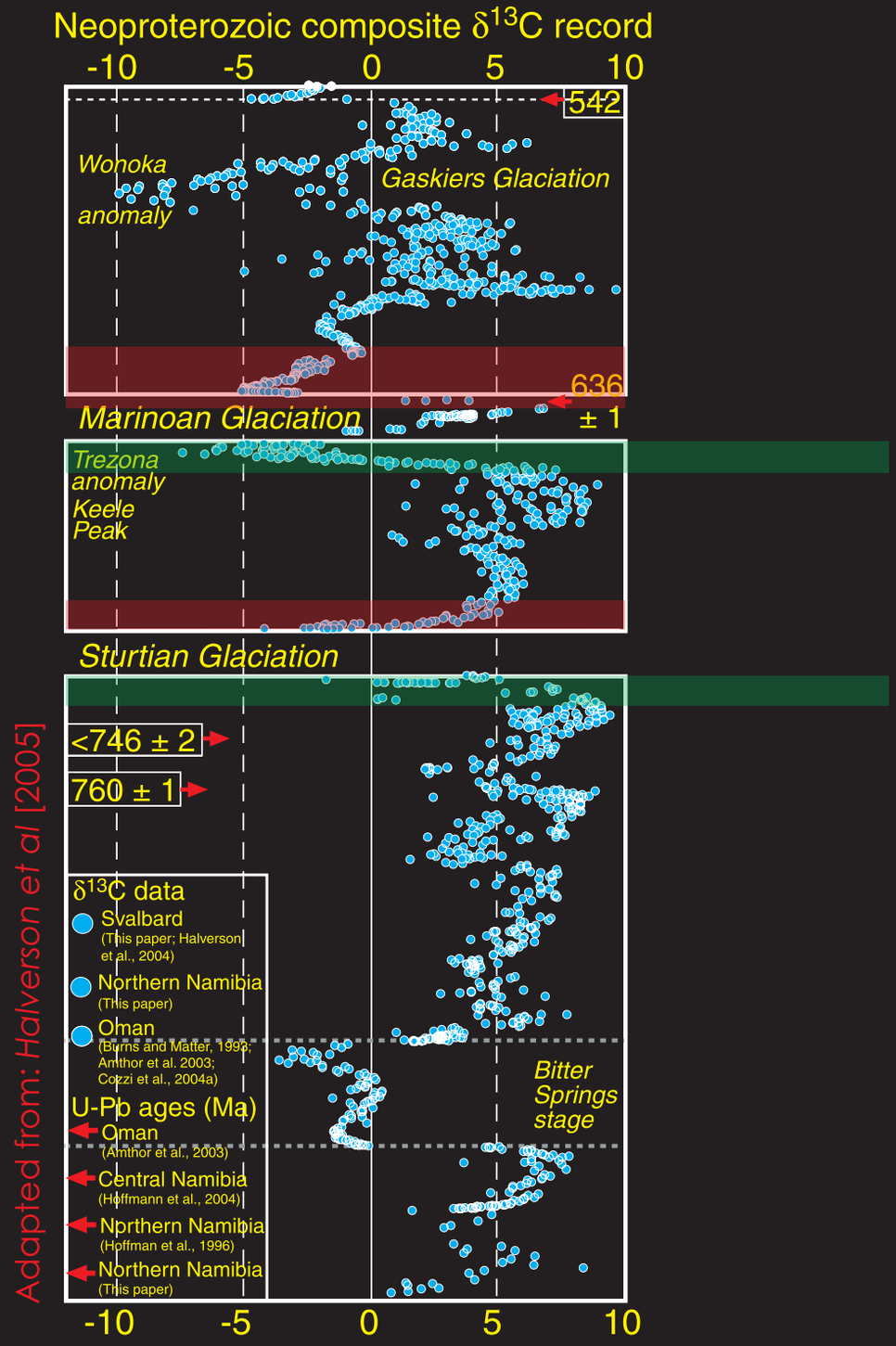


enhanced carbonate weathering ($\delta^{13}C$ dilution)

pH increase ($\delta^{13}C$ re-partitioning)

(model simulation on a very differenty x/y scale)

Deep-time inferences (aka 'speculation')

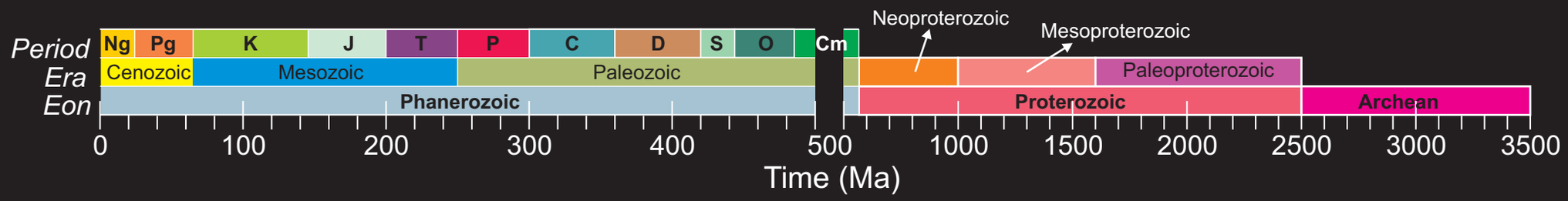


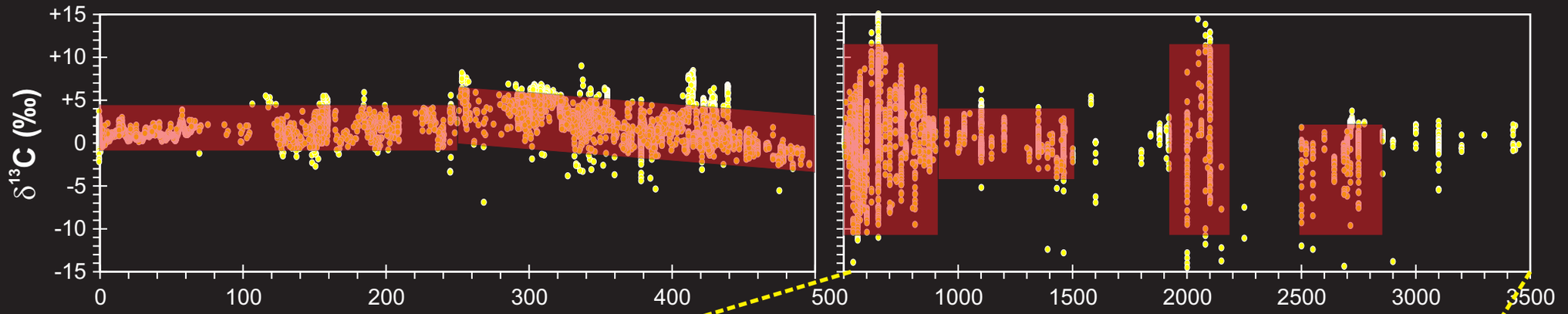
Prominent declines (and partial recovery) in $\delta^{13}C$ prior to glacial inception.

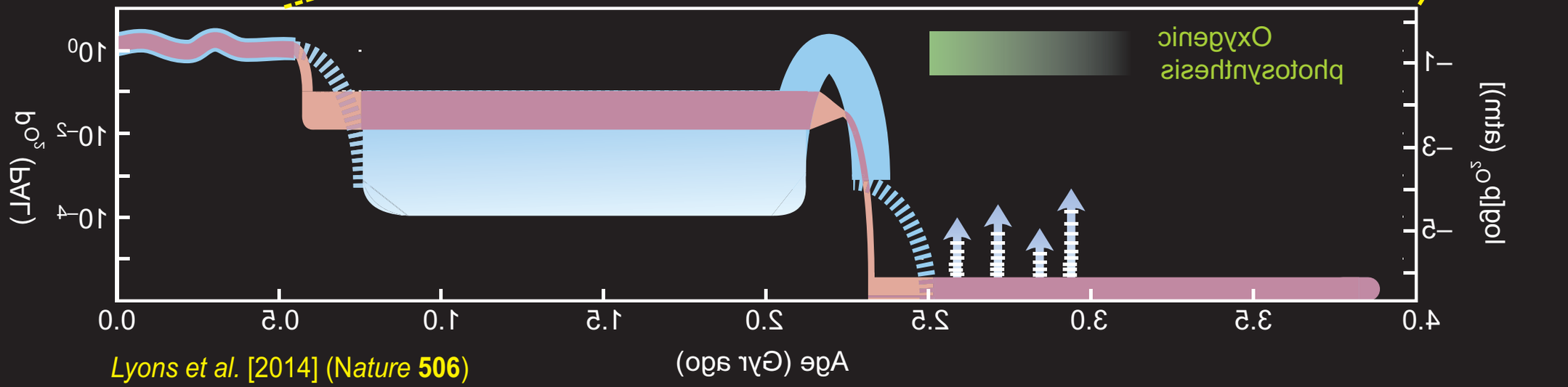
This would be consistent with a pH increase. How?

Perhaps enhanced basaltic weathering and CO_2 drawdown (from a state of low pH and high CO_2 @ -6 o/oo)??

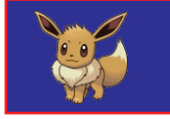
Deep-time inferences (aka 'speculation')







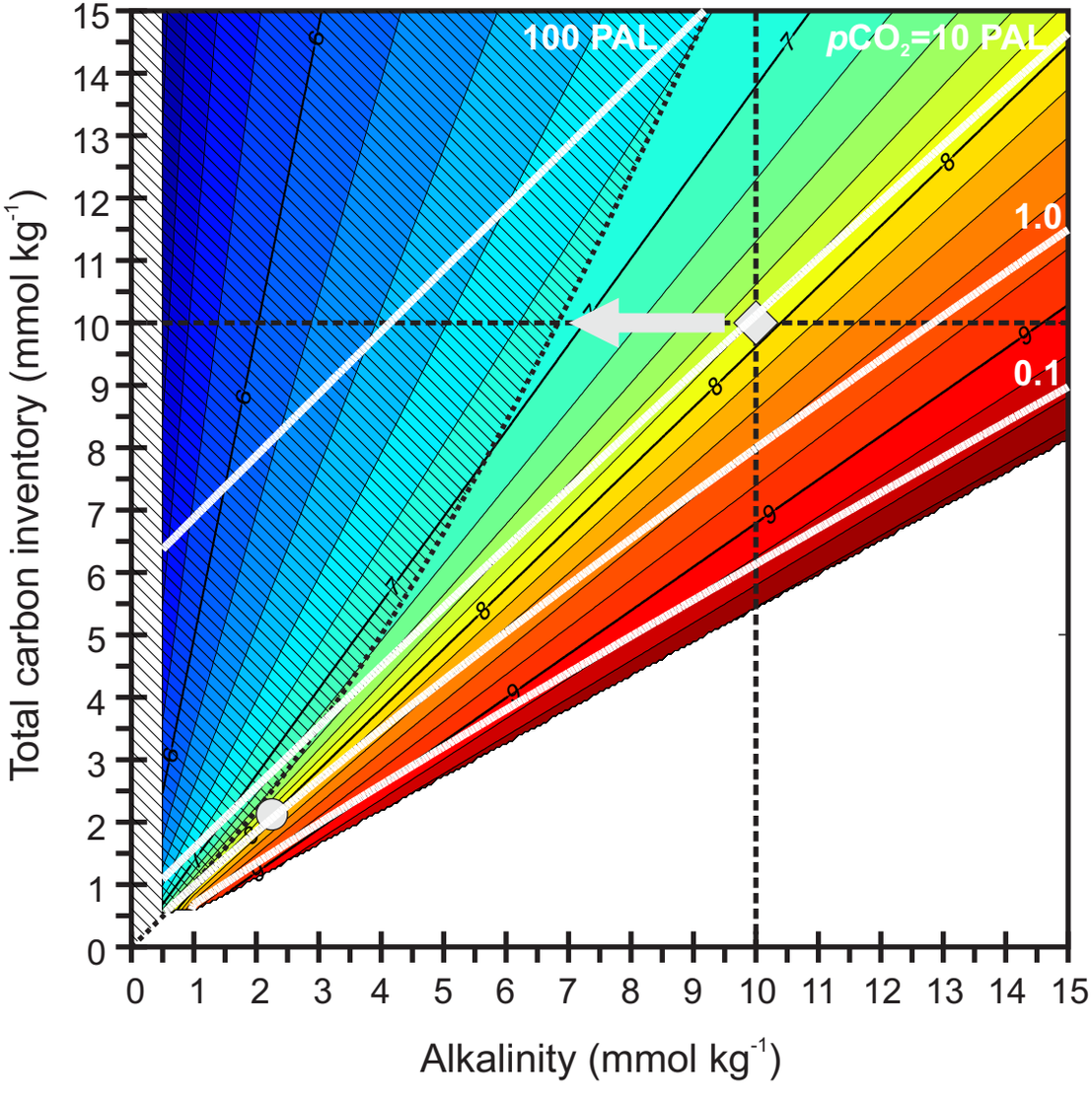
Lyons et al. [2014] (*Nature* **506**)



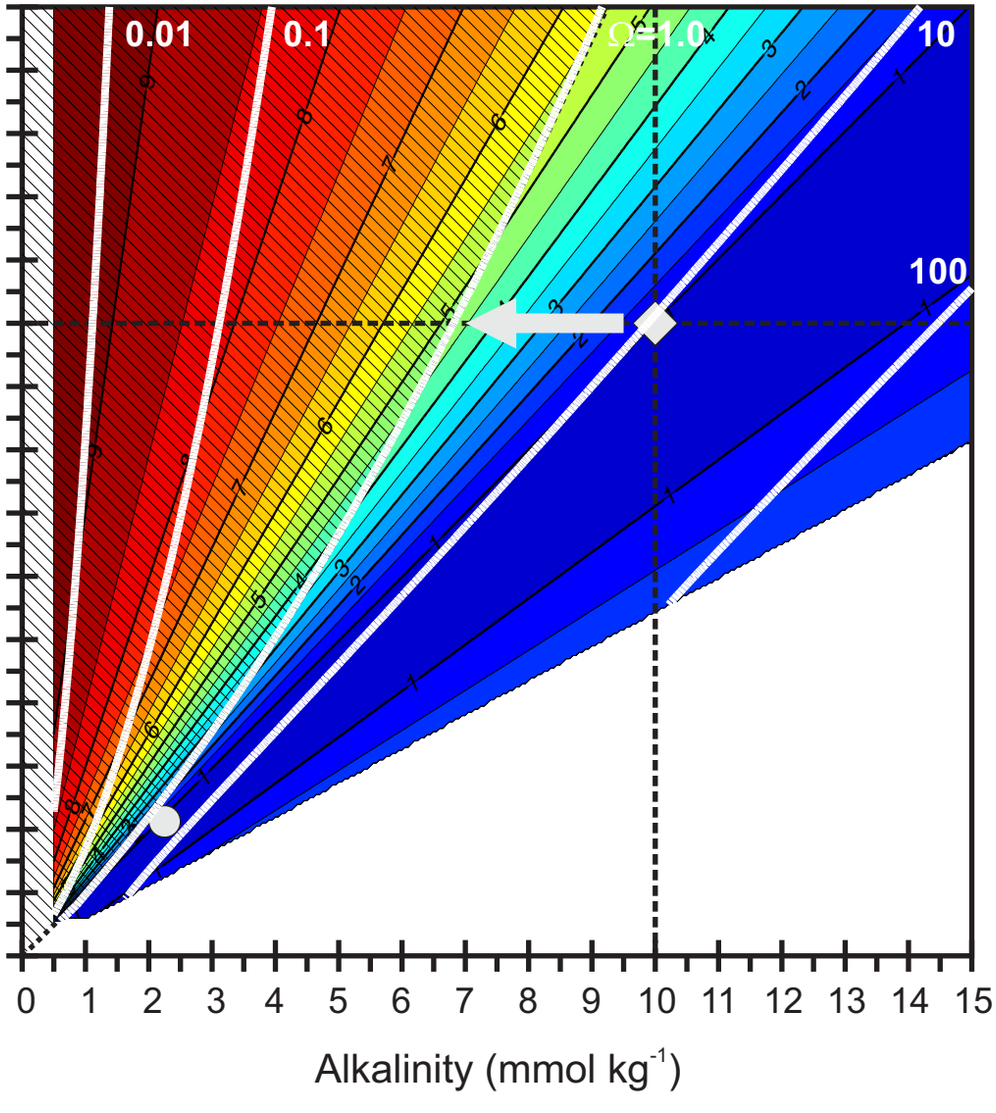
What does it take (e.g. sulphate increase/decrease) to change pH sufficiently?

How does it all (global carbonate cycling and carbonate buffering) pan out?

Mean ocean (surface) *p*H & pCO_2



Bicarbonate $\delta^{13}C$ & calcite Ω



vs.