Precambrian  $\delta^{13}$ C variability --The ghost of the rise (and fall) of atmospheric oxygen?

- \* 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





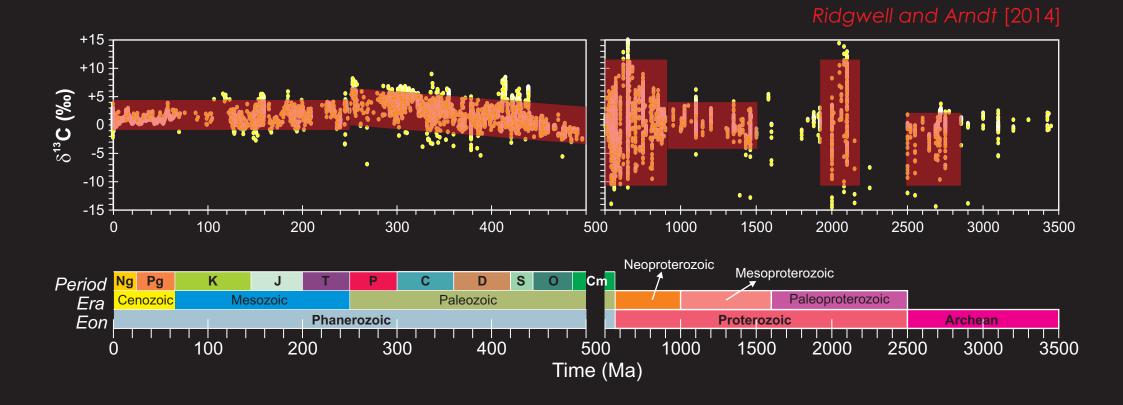














Re-partitioning of carbon between surficial reservoirs (cf. LGM)?

Injection (or removal) of isotopically light carbon?

Change in C<sub>org</sub> weathering and/or burial (at fixed carbonate weathering / burial)?

Change in carbonate weathering and/or burial (at fixed  $C_{org}$  weathering / burial)?

Carbonate diagenesis and loss of primary  $\delta^{13}$ C signal, either marine sedimentary or subaerial.



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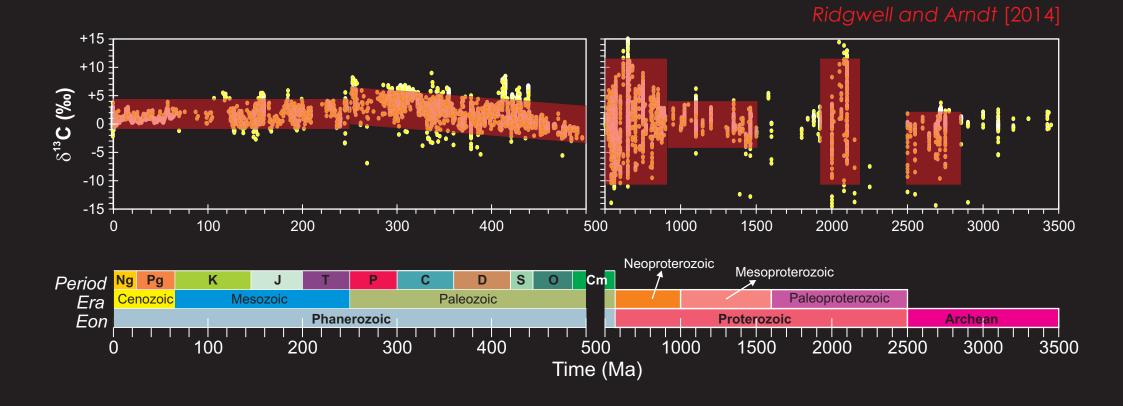
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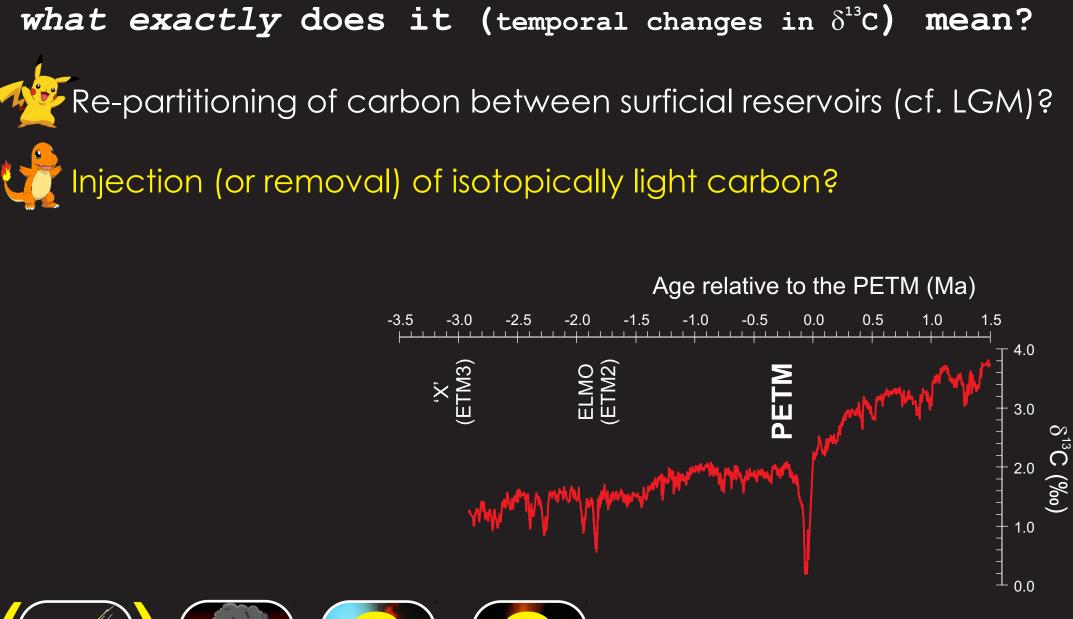
Carbonate diagenesis and loss of primary  $\delta^{13}$ C signal, either marine sedimentary or subaerial.



# what exactly does it (temporal changes in $\delta^{13}$ C) mean? Re-partitioning of carbon between surficial reservoirs (cf. LGM)?

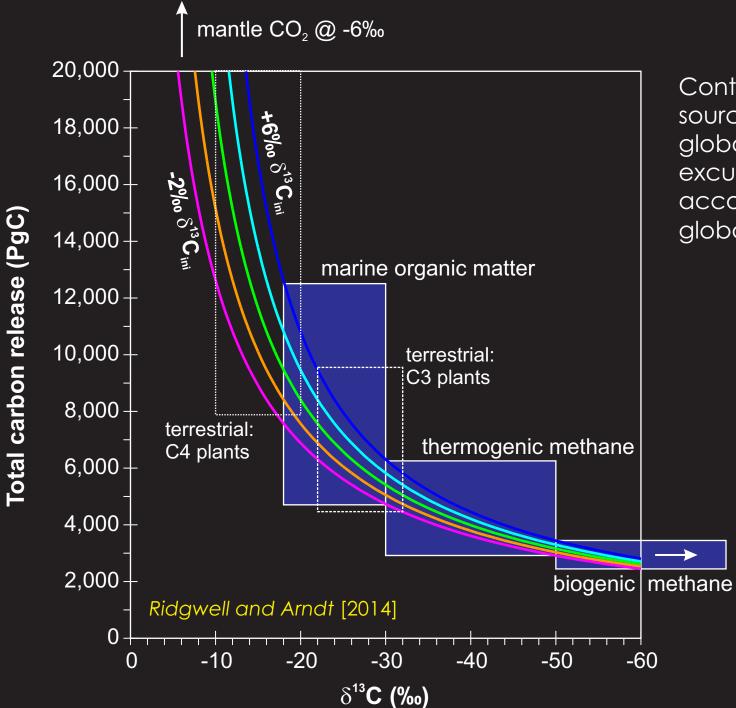






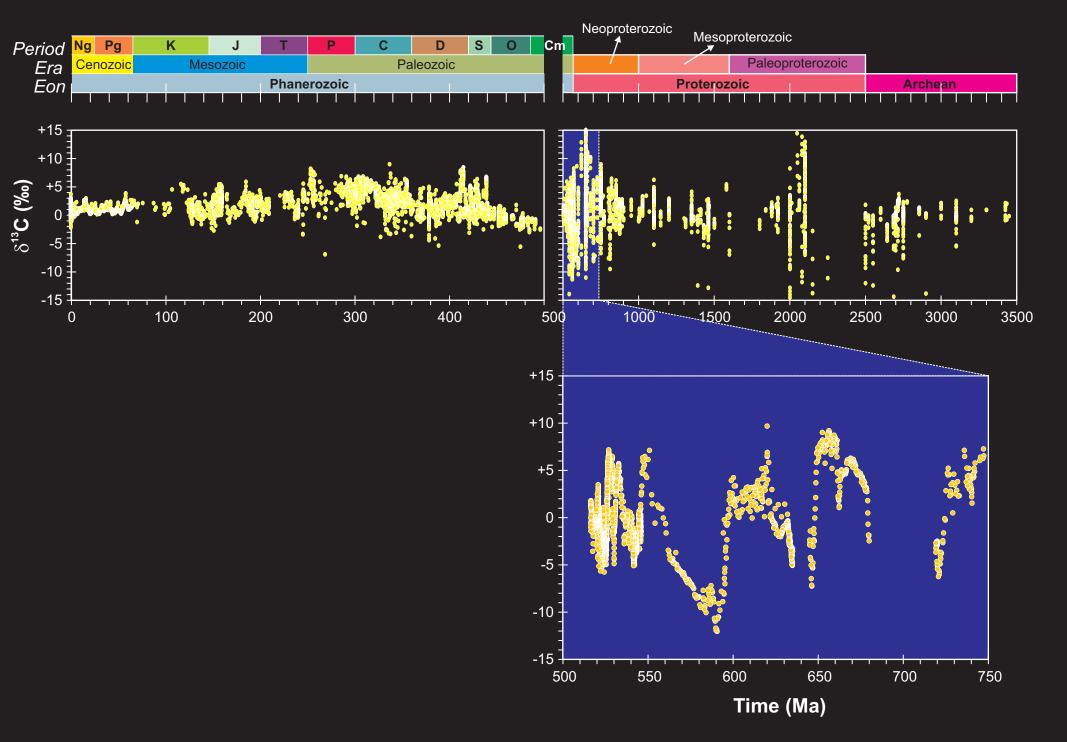






Contours of carbon release vs. source isotopic signature for a global -4‰ carbon isotopic excursion. Contours differ according to the initial mean global  $\delta^{13}$ C.

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

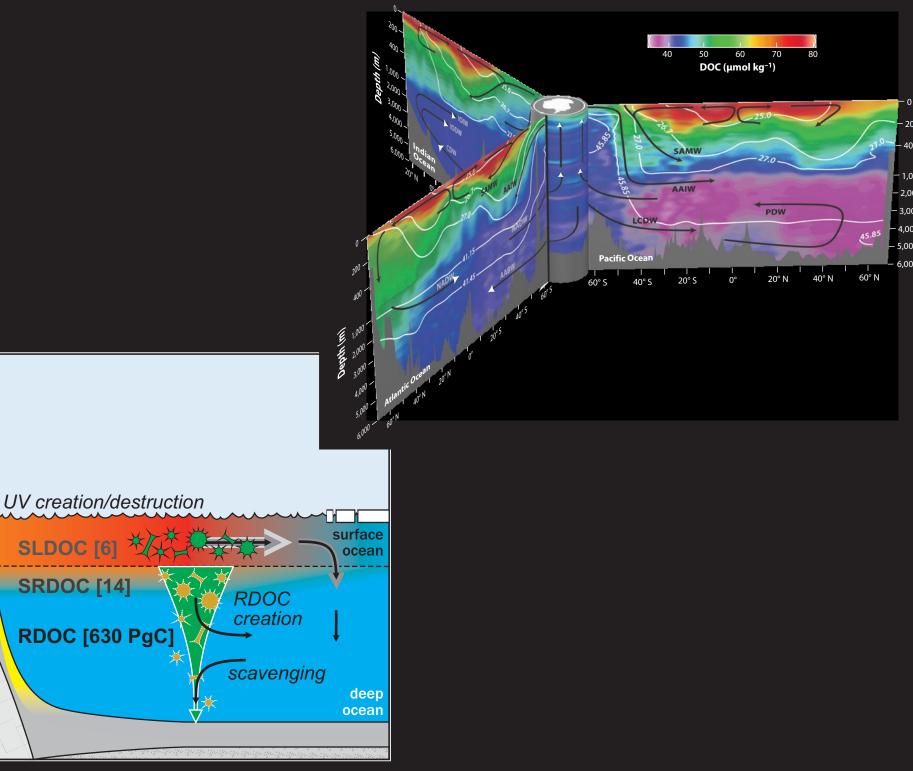


Ridgwell and Arndt [2014]

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

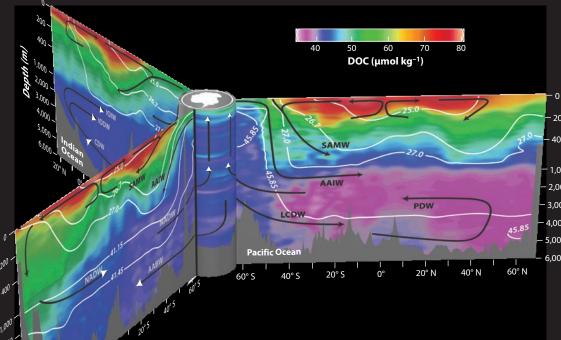
Terrestrial DOC input (?)





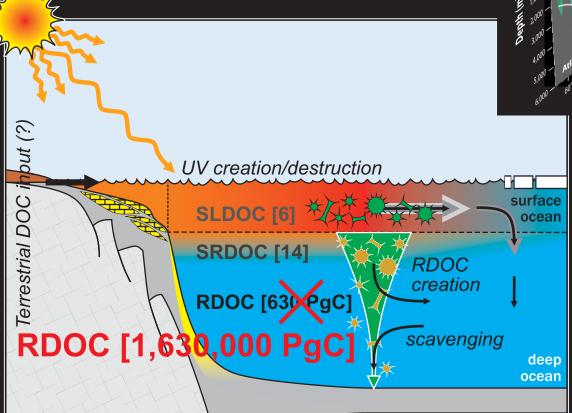
#### Carbonate $\delta^{13}$ C variability through time





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  $1.6 \times 10^6$ 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 CI<sup>-</sup>.)







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

Injection (or removal) of isotopically light carbon?



observed (recorded

Change in C<sub>org</sub> weathering and/or burial (at fixed carbonate weathering / burial)?

Change in carbonate weathering and/or burial (at fixed C<sub>org</sub> weathering / burial)?

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

$$F_{corg} / (F_{corg} + F_{caCO3}) = \sum_{ratio}^{C \text{ burial ratio}} (\delta^{13}C_{obs} - \delta^{13}C_{input}) / (\delta^{13}C_{caCO3} - \delta^{13}C_{corg})$$

$$\int_{C}^{C} (\delta^{13}C_{obs} - \delta^{13}C_{input}) / (\delta^{13}C_{caCO3} - \delta^{13}C_{corg}) = 0$$

$$\int_{C}^{C} (\delta^{13}C_{obs} - \delta^{13}C_{obs}) / (\delta^{13}C_{caCO3} - \delta^{13}C_{corg}) = 0$$



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



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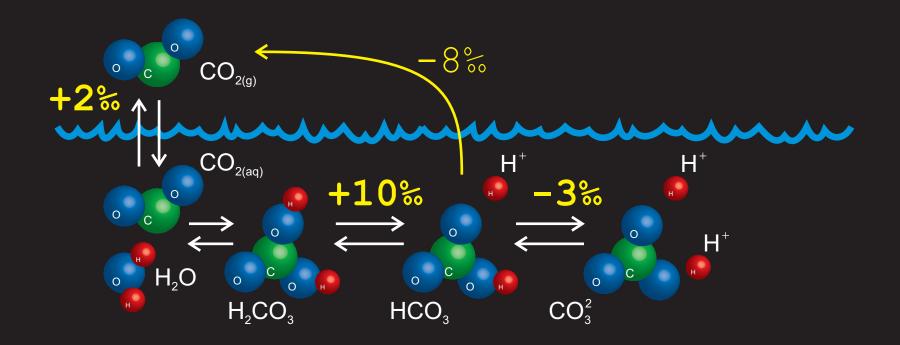


Carbonate diagenesis and loss of primary  $\delta^{13}$ C signal, beither marine sedimentary or subaerial.

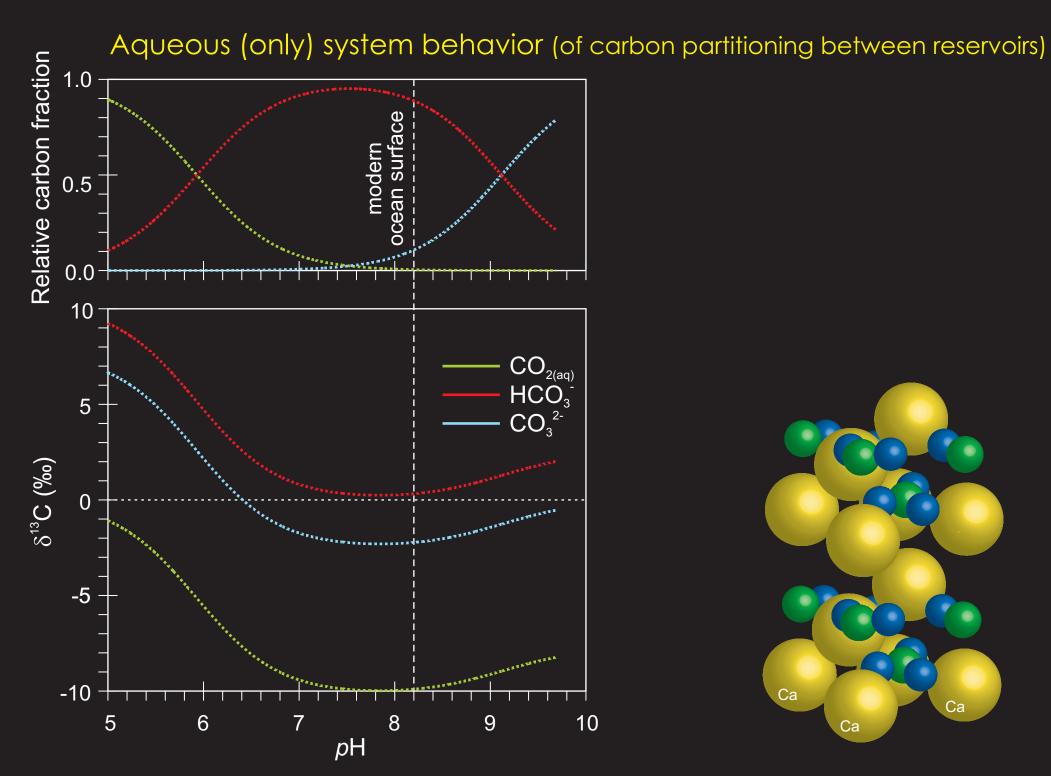
pH-driven re-partitioning of the where the isotopic composition of the mean surficial reservoir is held (and what carbonate samples) Also see: Higgins and Schrag [2003]

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

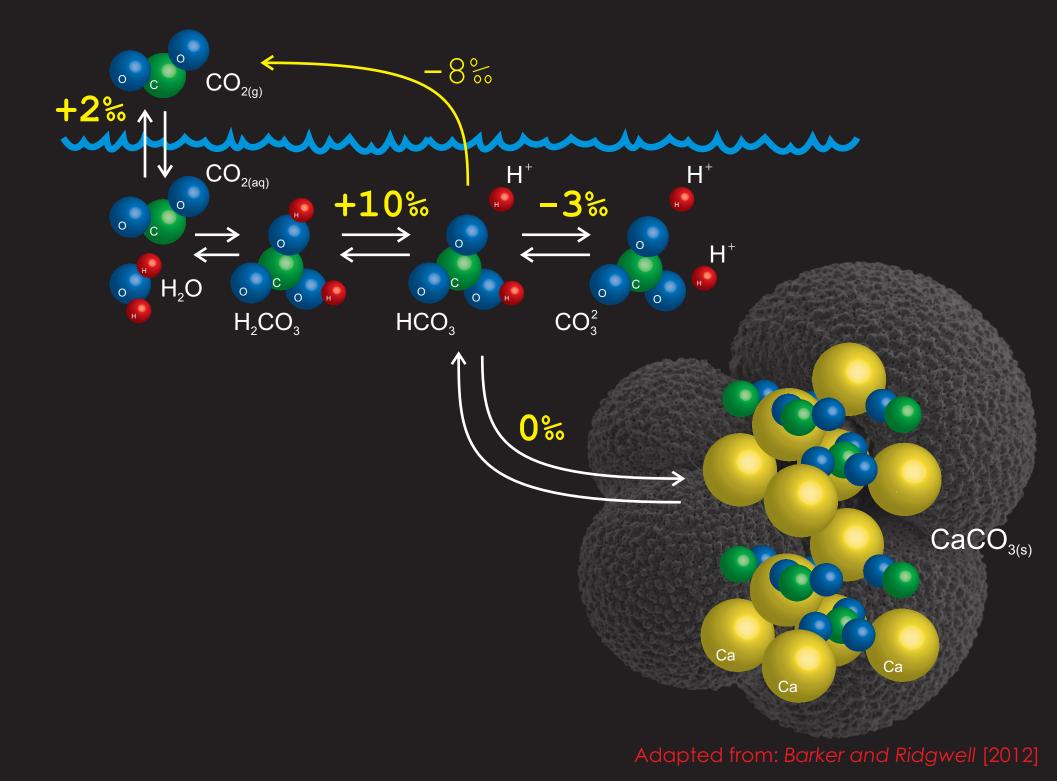




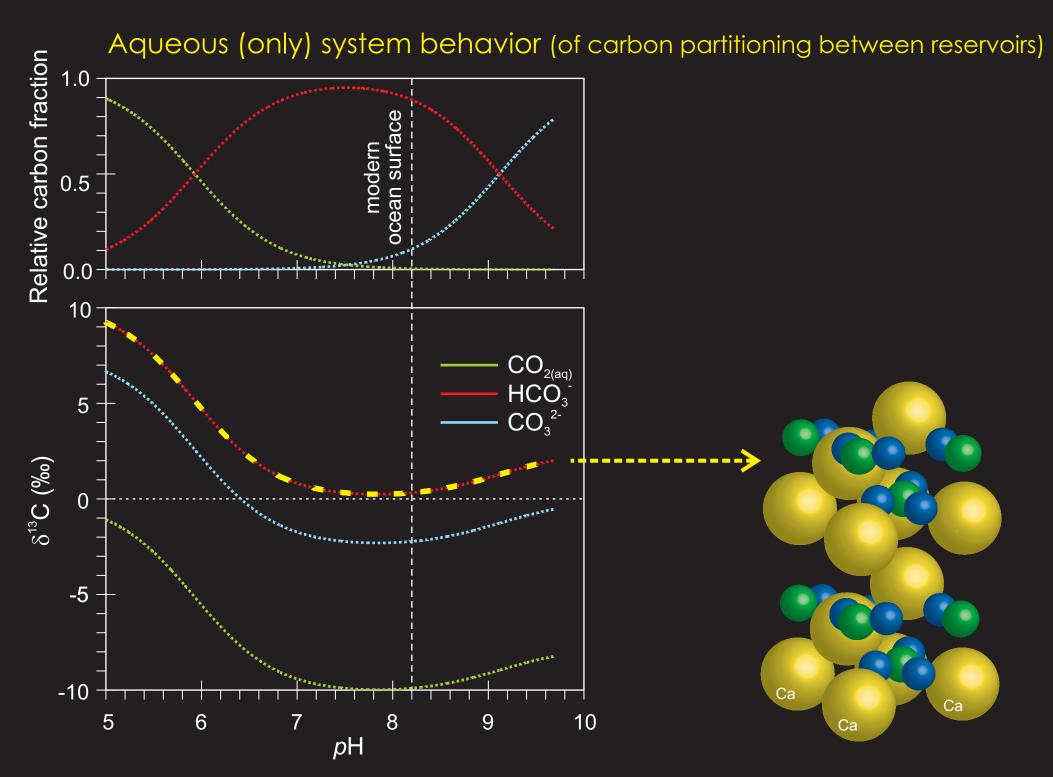




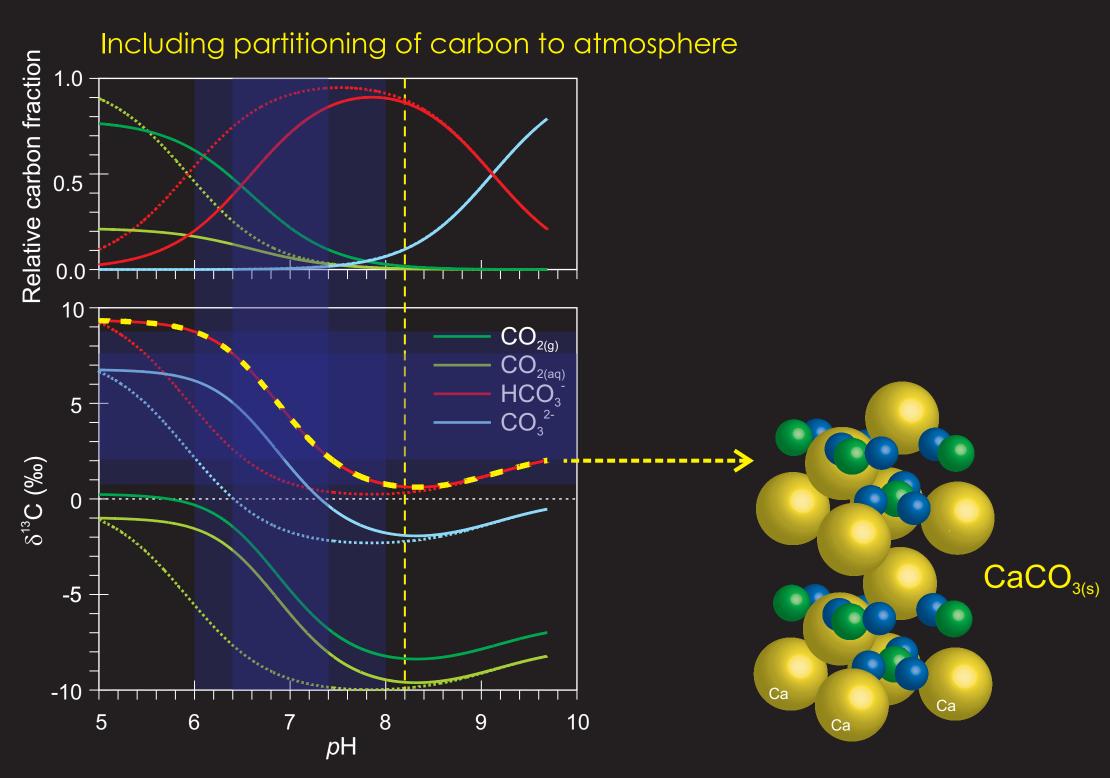




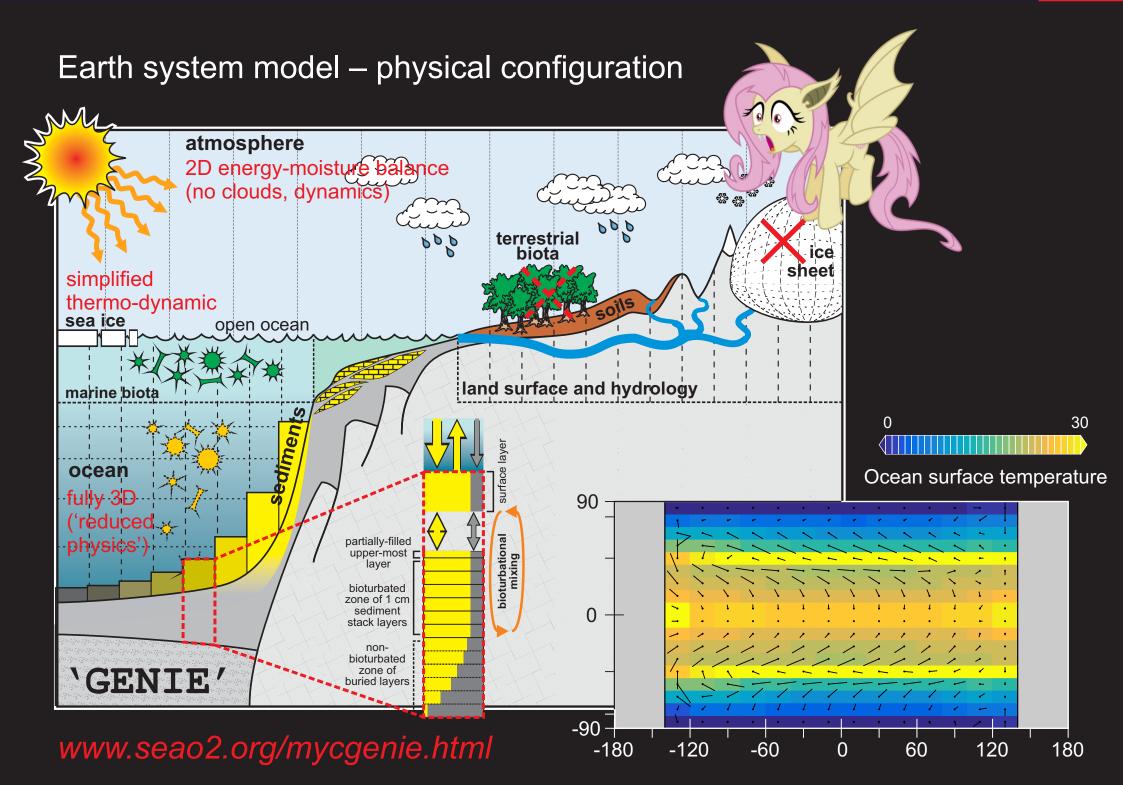




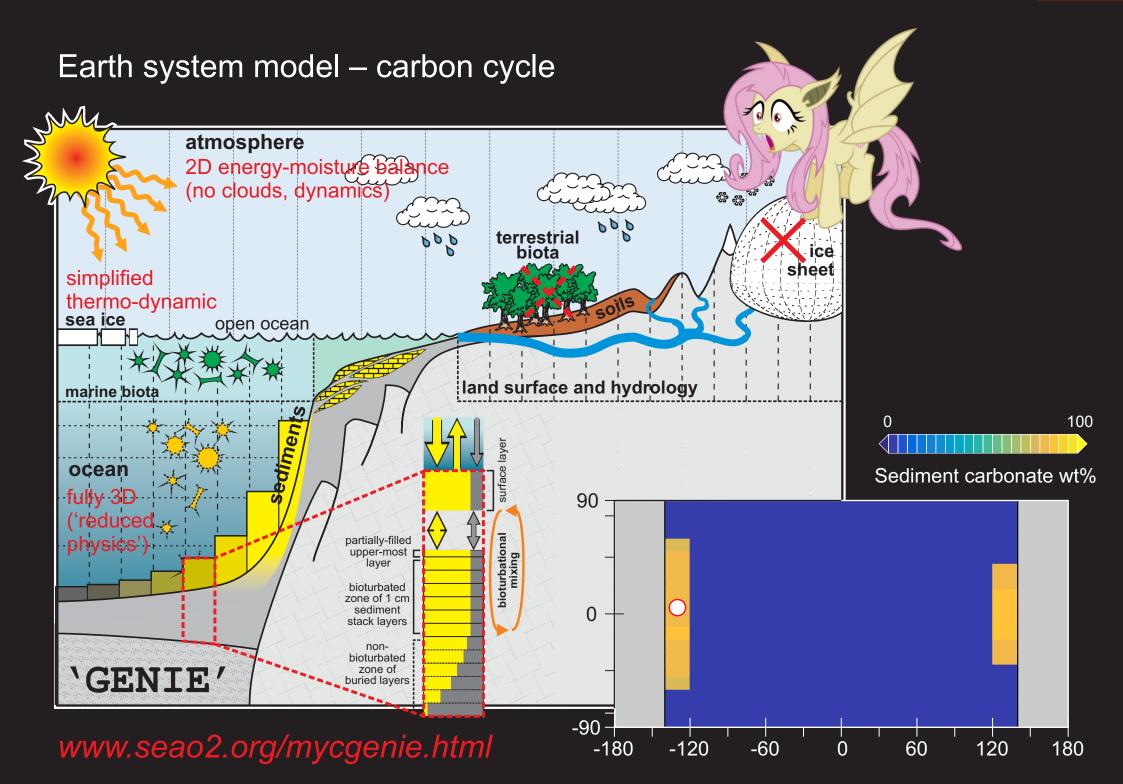




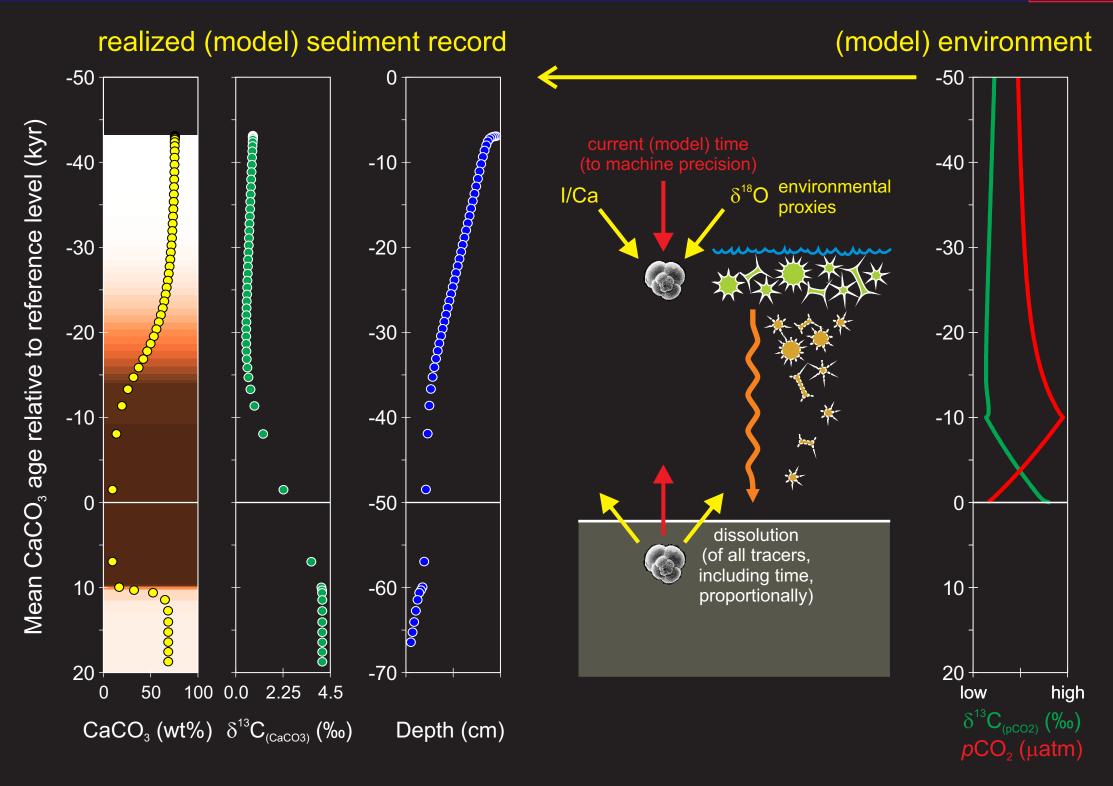






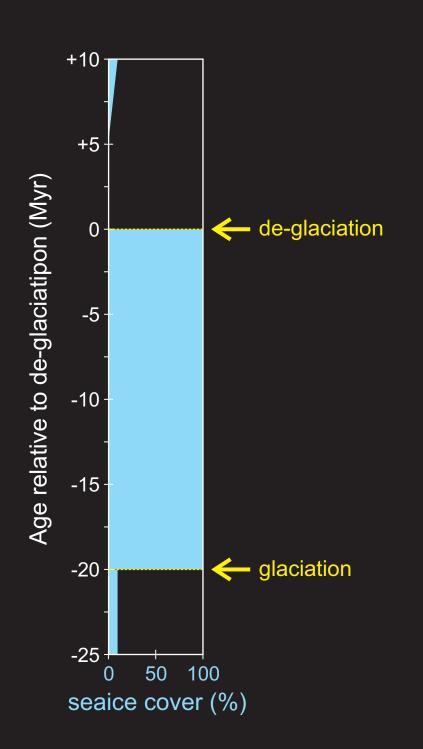


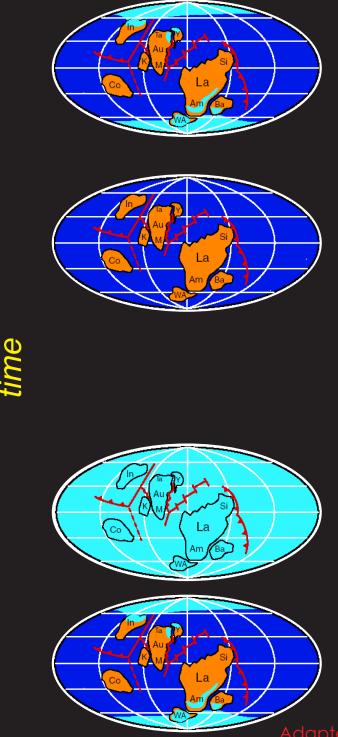




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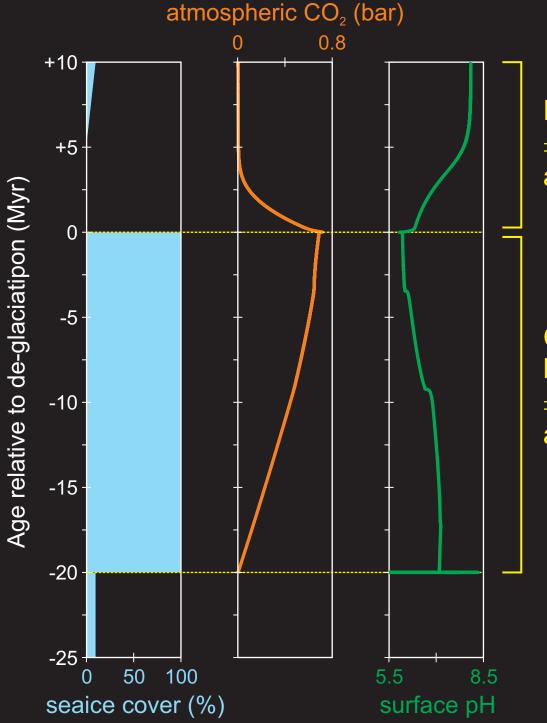




Adapted from: Hoffman and Schrag [2002]

#### Numerical modelling – Results



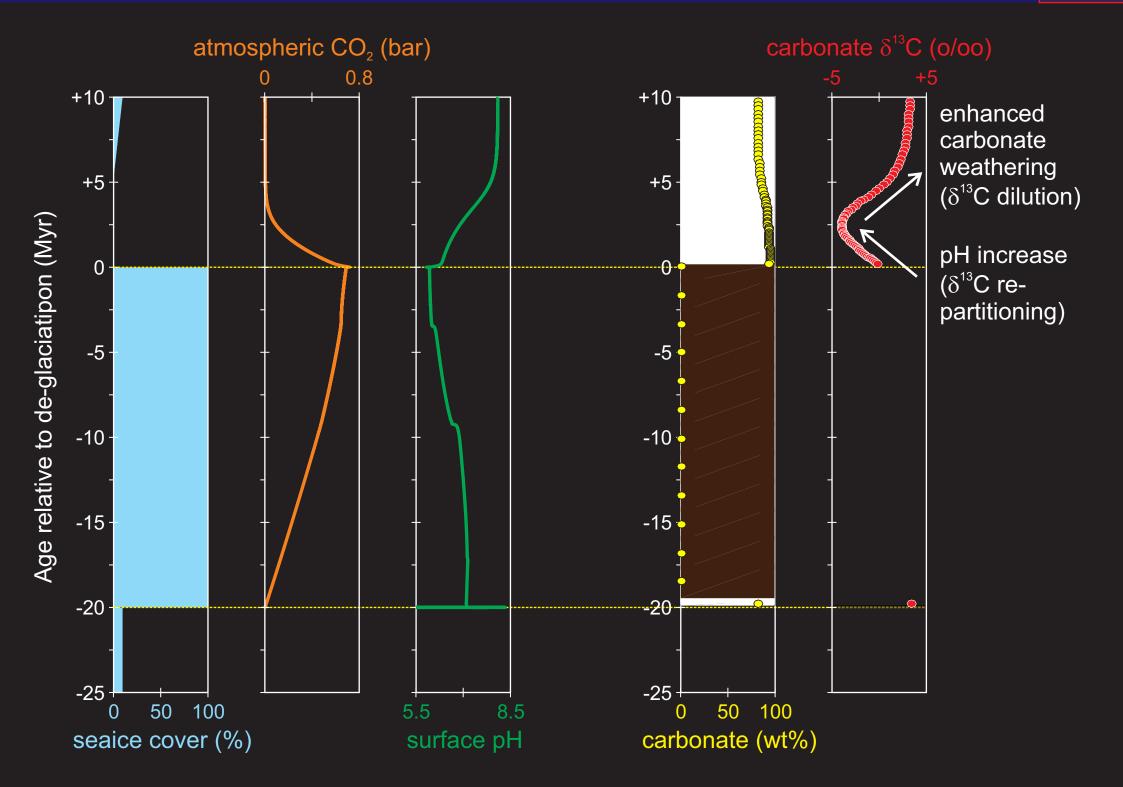


Enhanced weathering  $\Rightarrow CO_2$  draw-down and pH increase

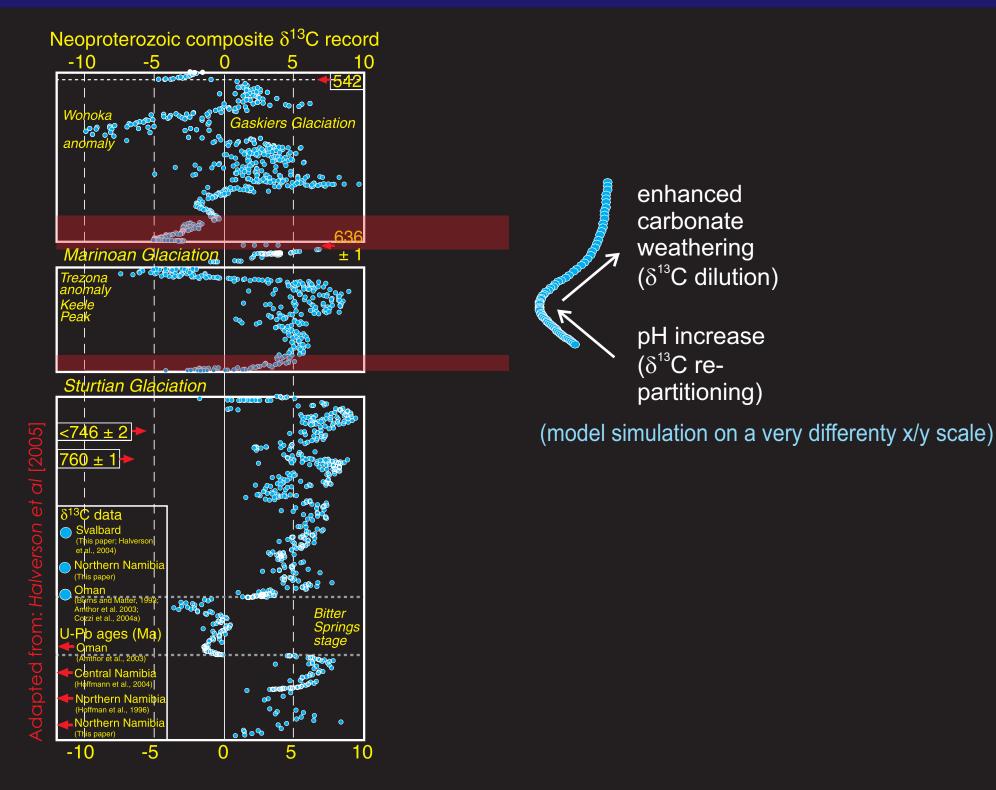
Continued  $CO_2$  out-gasssing but ... minimal weathering  $\Rightarrow CO_2$  buildup @ -6 o/oo and ocean pH decline



#### Numerical modelling – Results

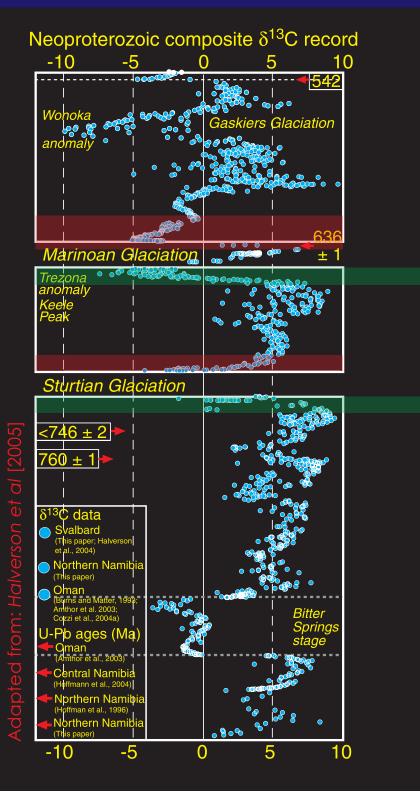






#### Deep-time inferences (aka 'speculation')





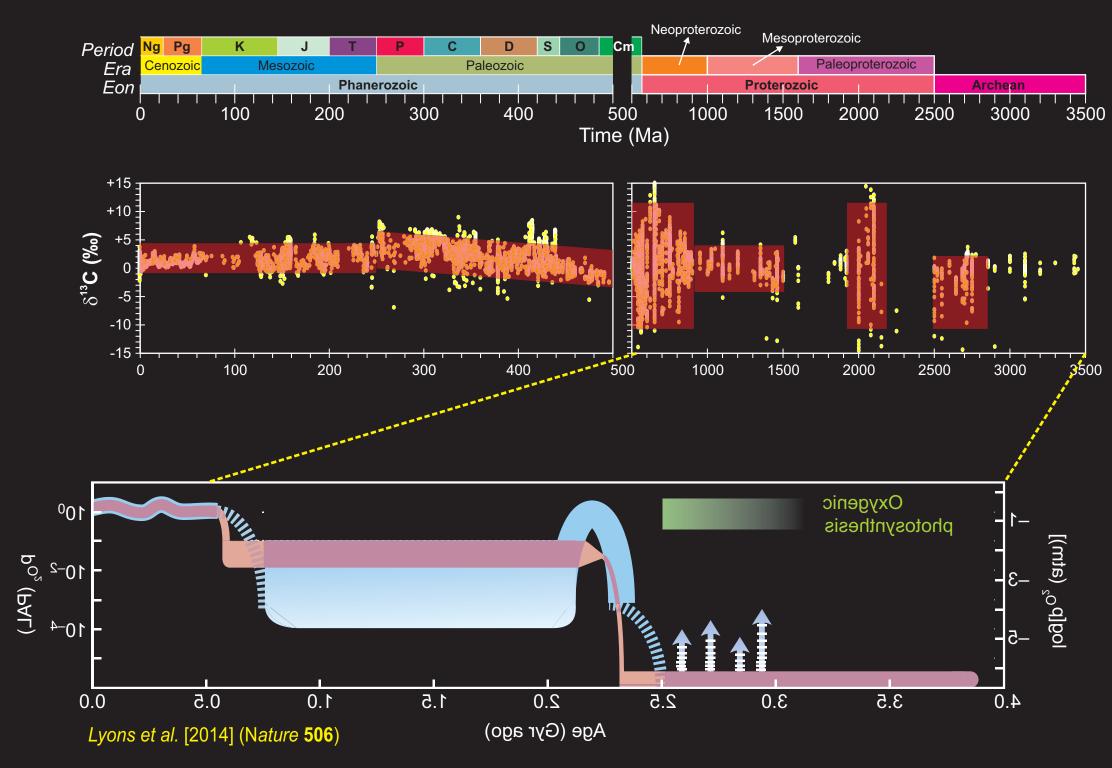
Prominent declines (and partial recovery) in  $\delta^{13}$ C prior to glacial inception.

This would be consistent with a pH increase. How?

Perhaps enhanced basaltic weathering and CO<sub>2</sub> drawdown (from a state of low pH and high CO<sub>2</sub> @ -6 o/oo)??

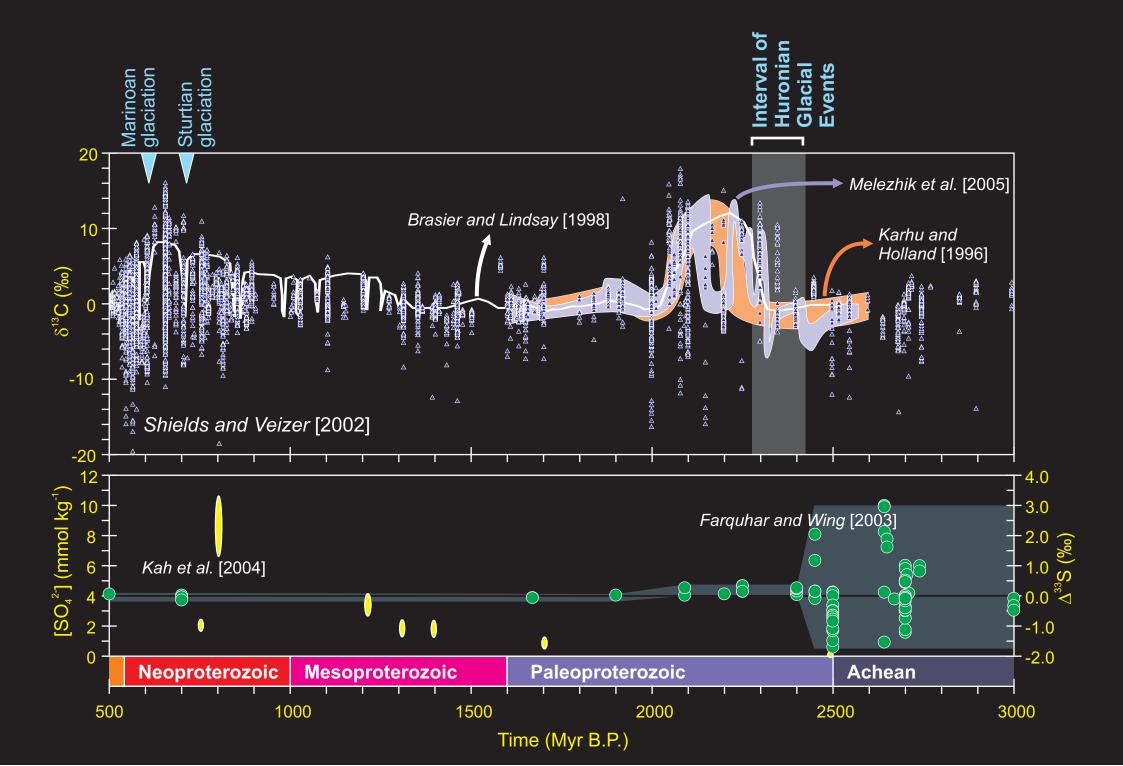
#### Deep-time inferences (aka 'speculation')





#### Deep-time inferences (aka 'speculation')





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) pH & pCO<sub>2</sub>

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

