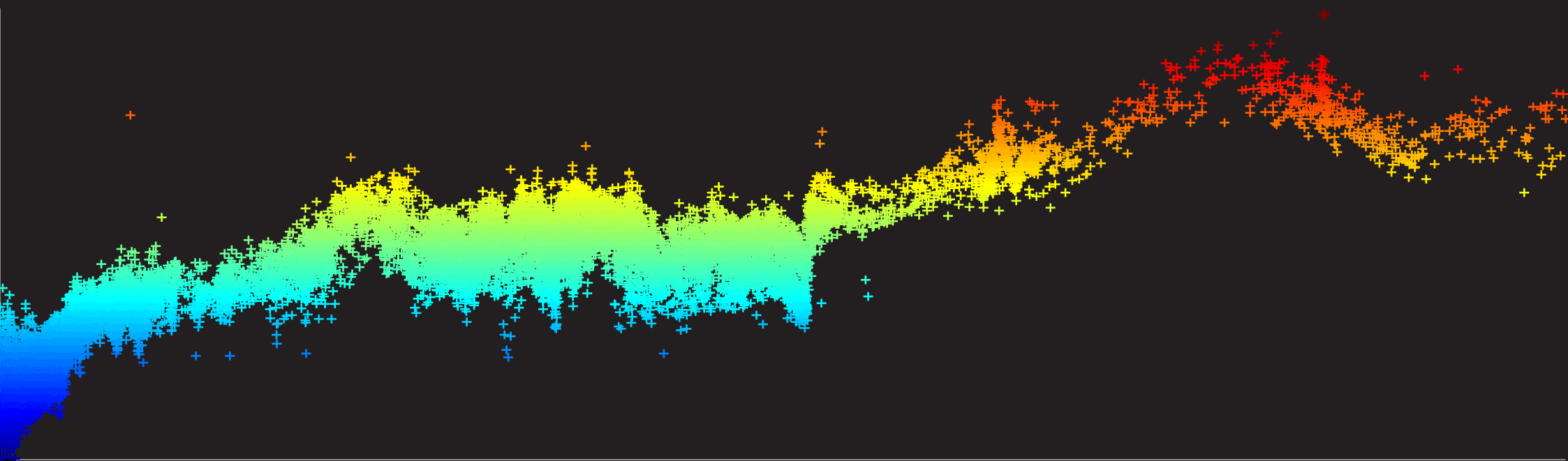


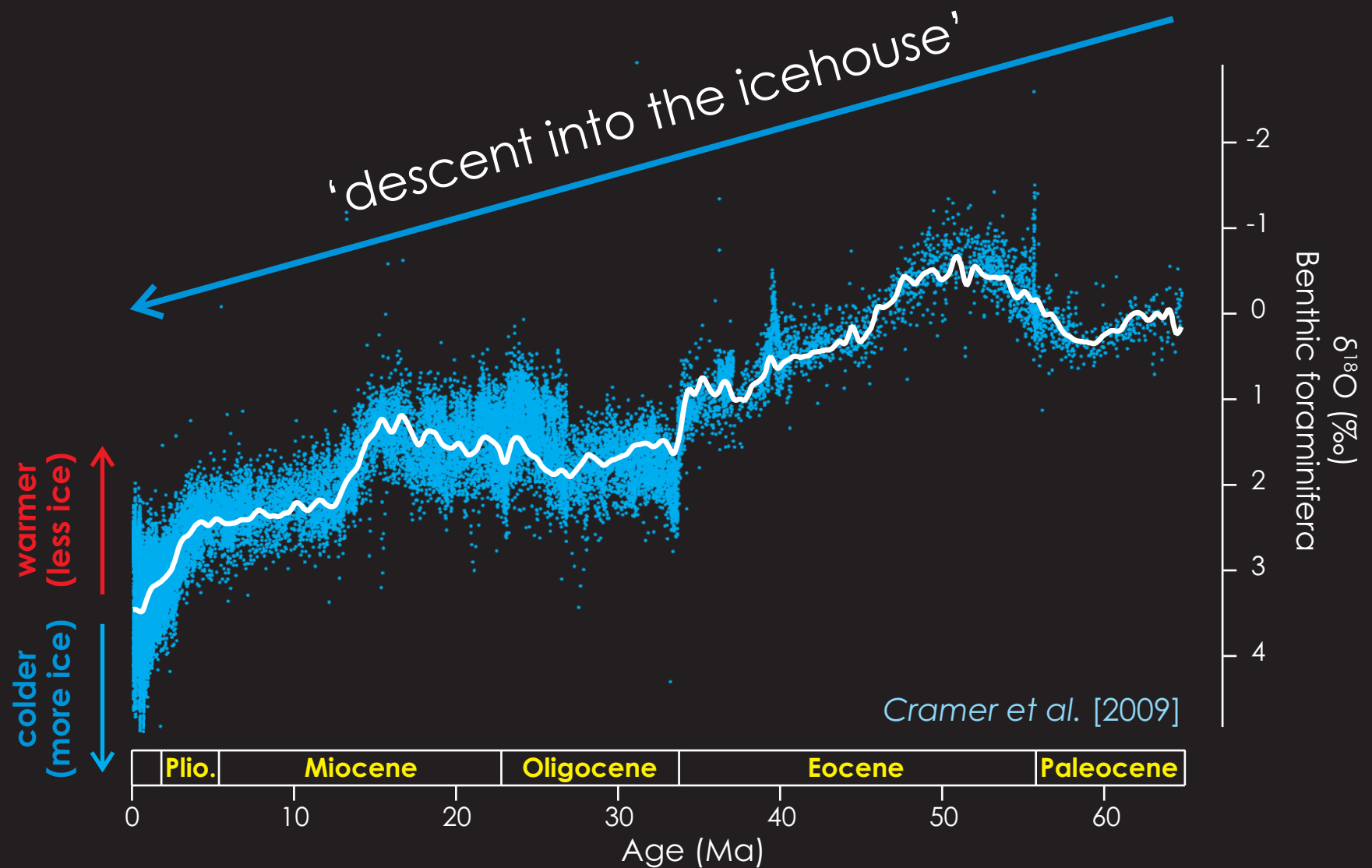
*Placing data constraints on the  
long-term evolution of CO<sub>2</sub> and climate*

aka: 'Death of a proxy'

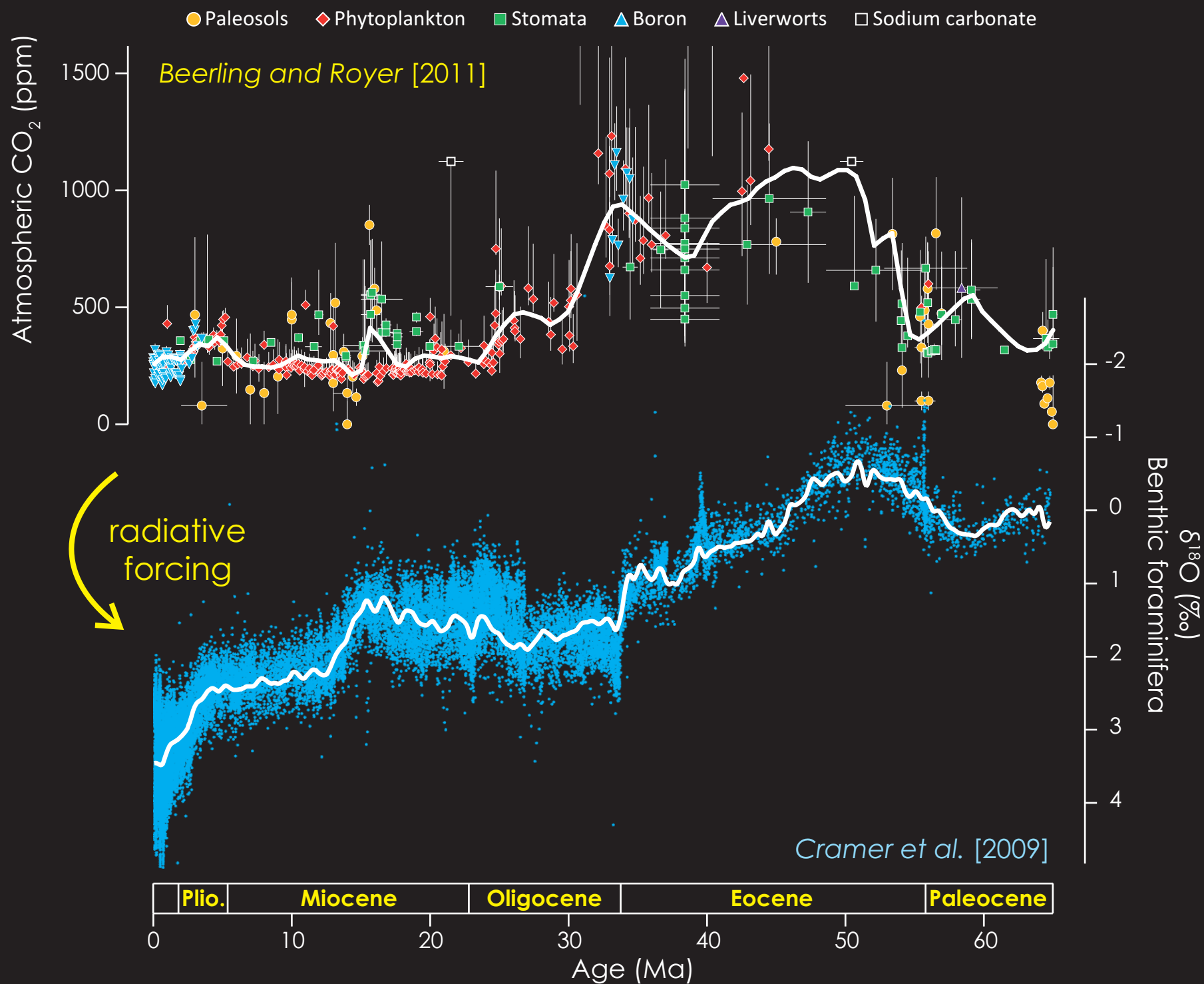
Andy Ridgwell

University of Bristol

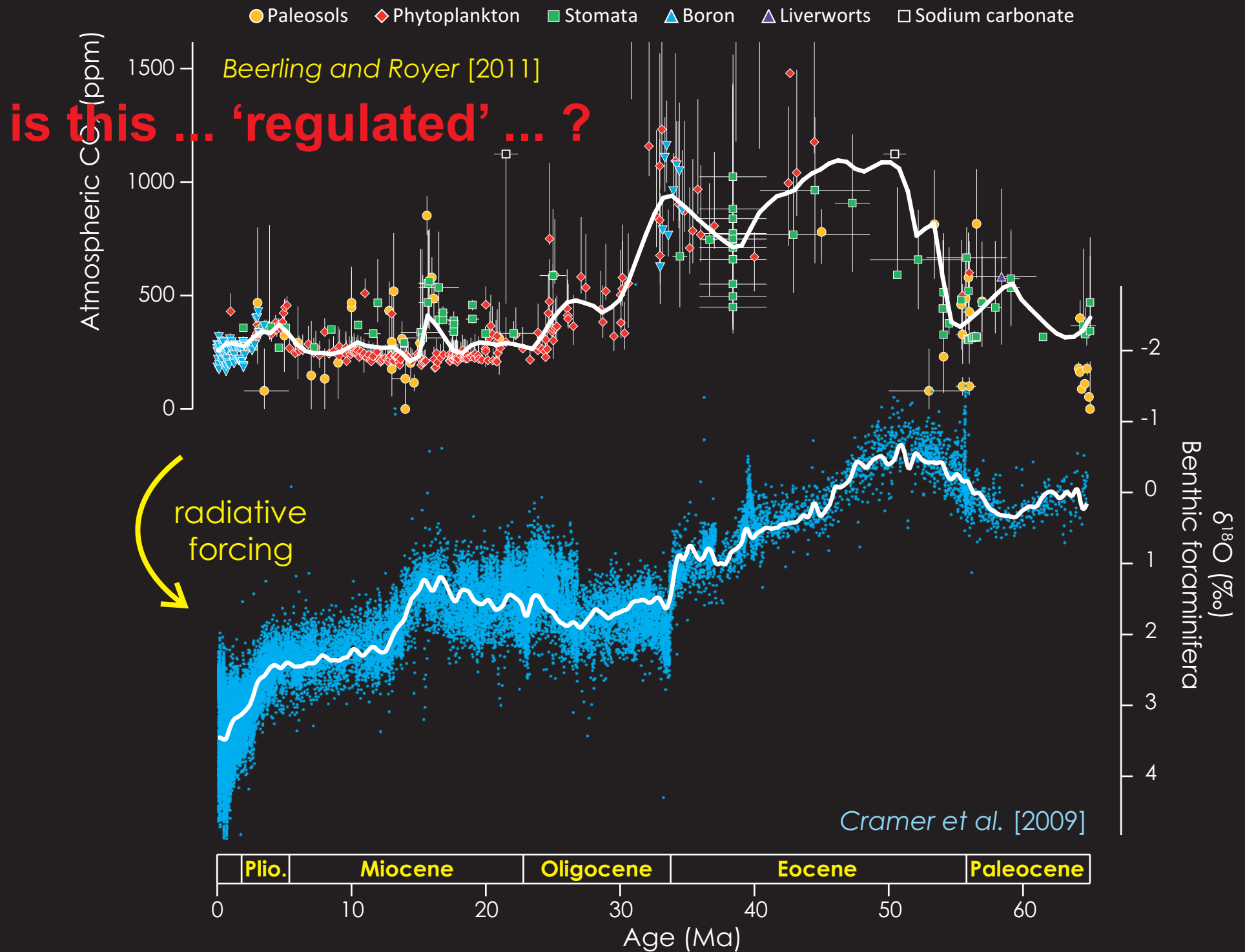




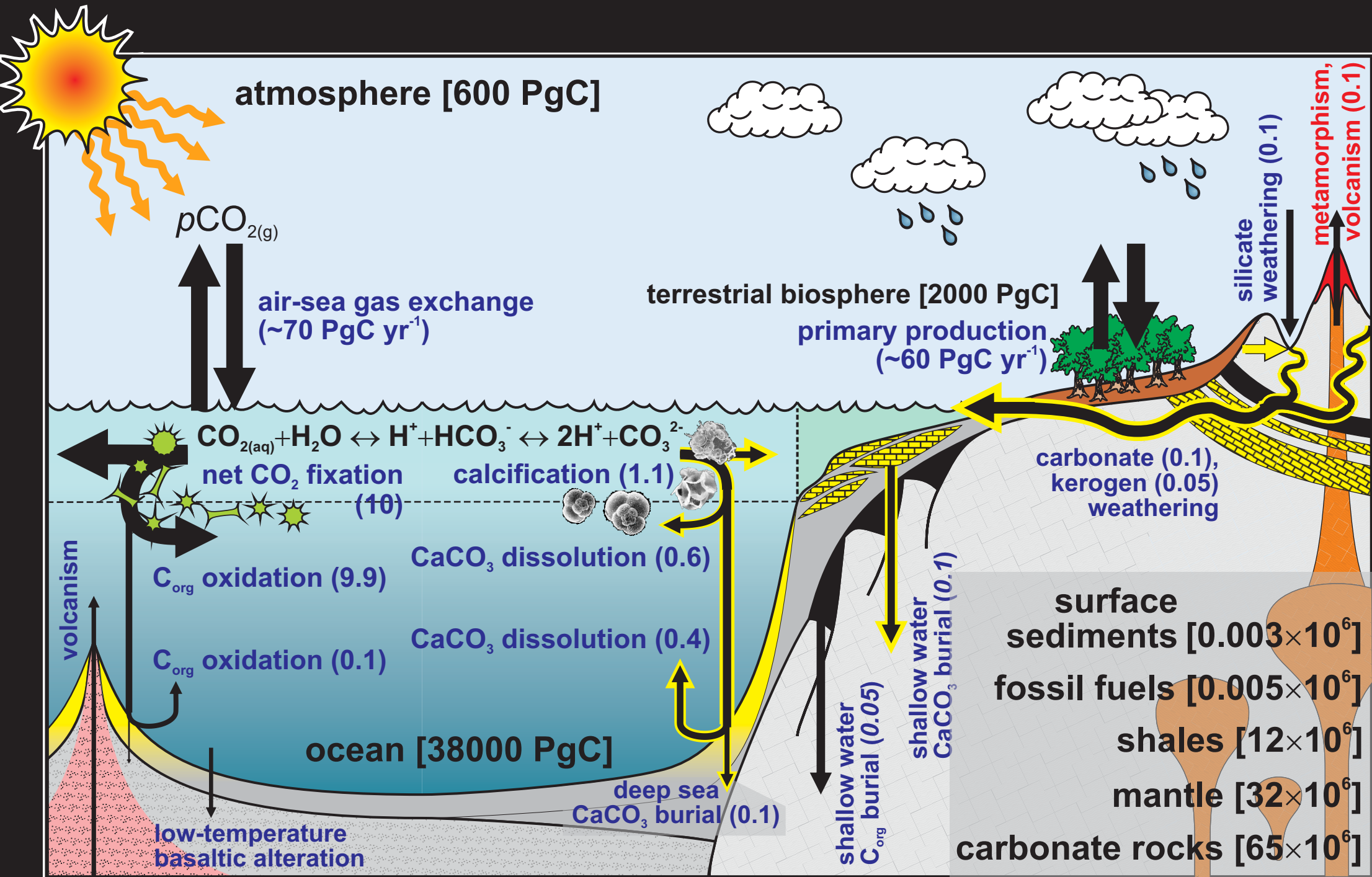
# What regulates Cenozoic climate carbon cycling?



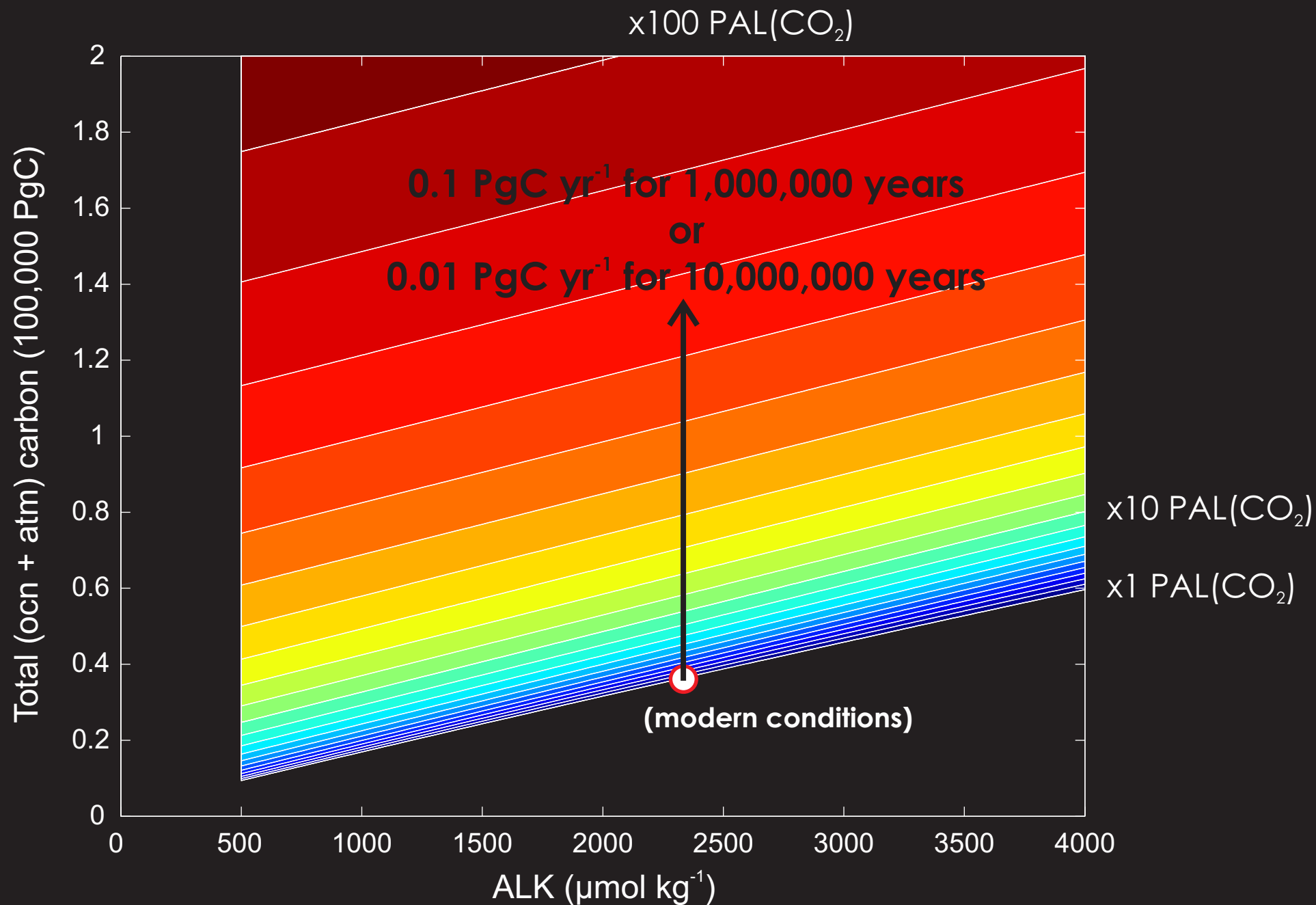
# What regulates Cenozoic ~~climate~~ carbon cycling?



# What regulates Cenozoic ~~climate~~ carbon cycling?



# What regulates Cenozoic ~~climate~~ carbon cycling?



Terrestrial weathering can be (approximately equally) divided into carbonate ( $\text{CaCO}_3$ ) and calcium-silicate (' $\text{CaSiO}_3$ ') weathering:



Ultimately, the (alkalinity:  $\text{Ca}^{2+}$ ) weathering products must be removed through carbonate precipitation and burial in marine sediments:



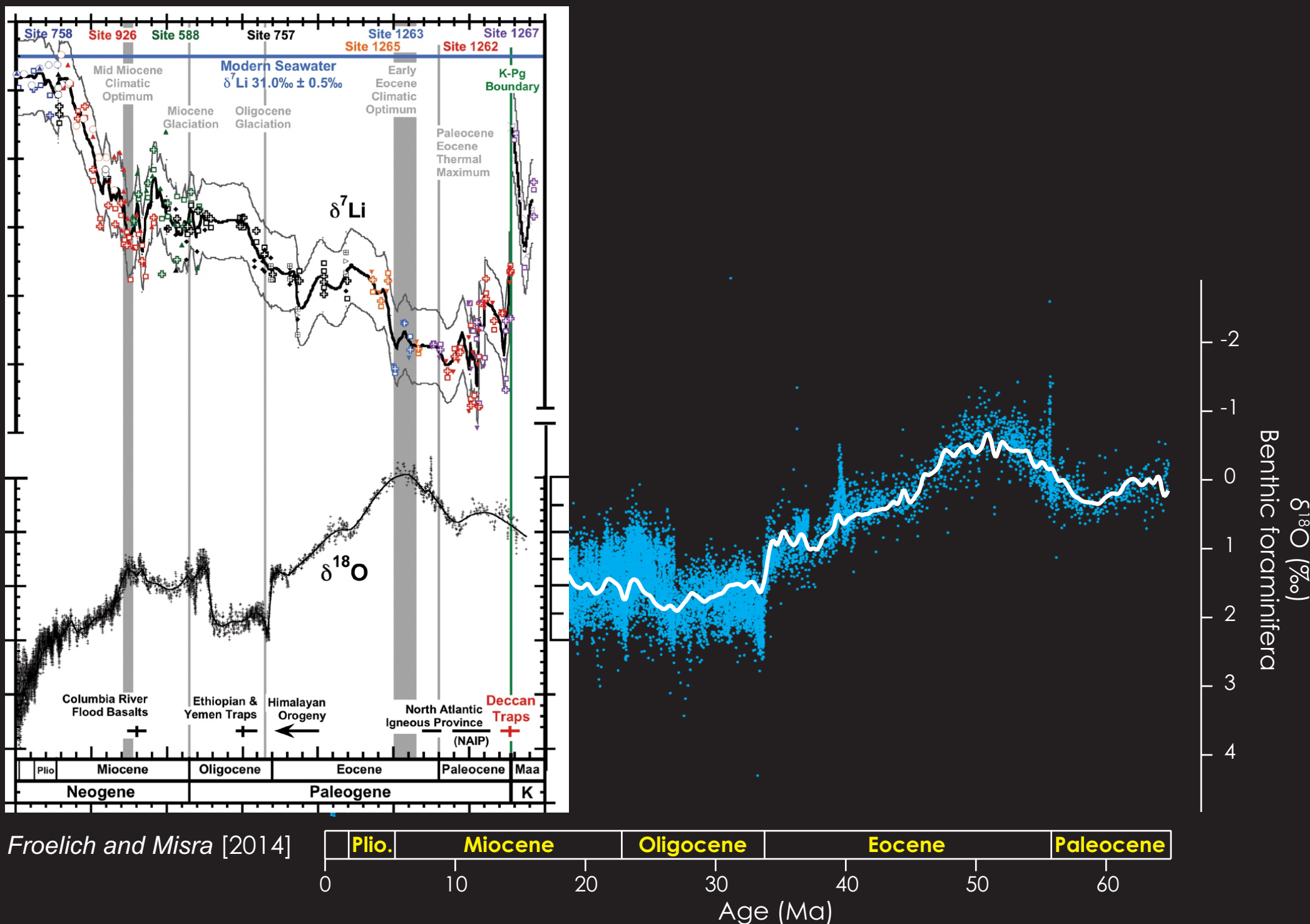
It can be seen that in (2) + (3), that the  $\text{CO}_2$  removed (from the atmosphere) during weathering, is returned upon carbonate precipitation (and burial). In (1) + (3) (silicate weathering)  $\text{CO}_2$  is permanently removed to the geological reservoir. This  $\text{CO}_2$  must be balanced by mantle (/volcanic) out-gassing on the very long term.

Furthermore, the rate of silicate weathering should scale with climate. Hence a ca. 100 kyr time-scale **silicate weathering feedback** is formed:

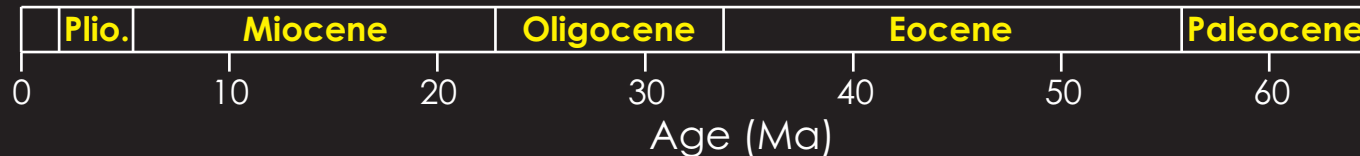
higher  $p\text{CO}_2 \rightarrow$  higher temperatures (and rainfall)  $\rightarrow$  higher weathering rates  
 $\rightarrow$  lower  $p\text{CO}_2$

(A regulating feedback system linking  $\text{CO}_2$  and climate with ocean productivity and oxygenation, and organic carbon burial, can also be formulated but not discussed further here.)

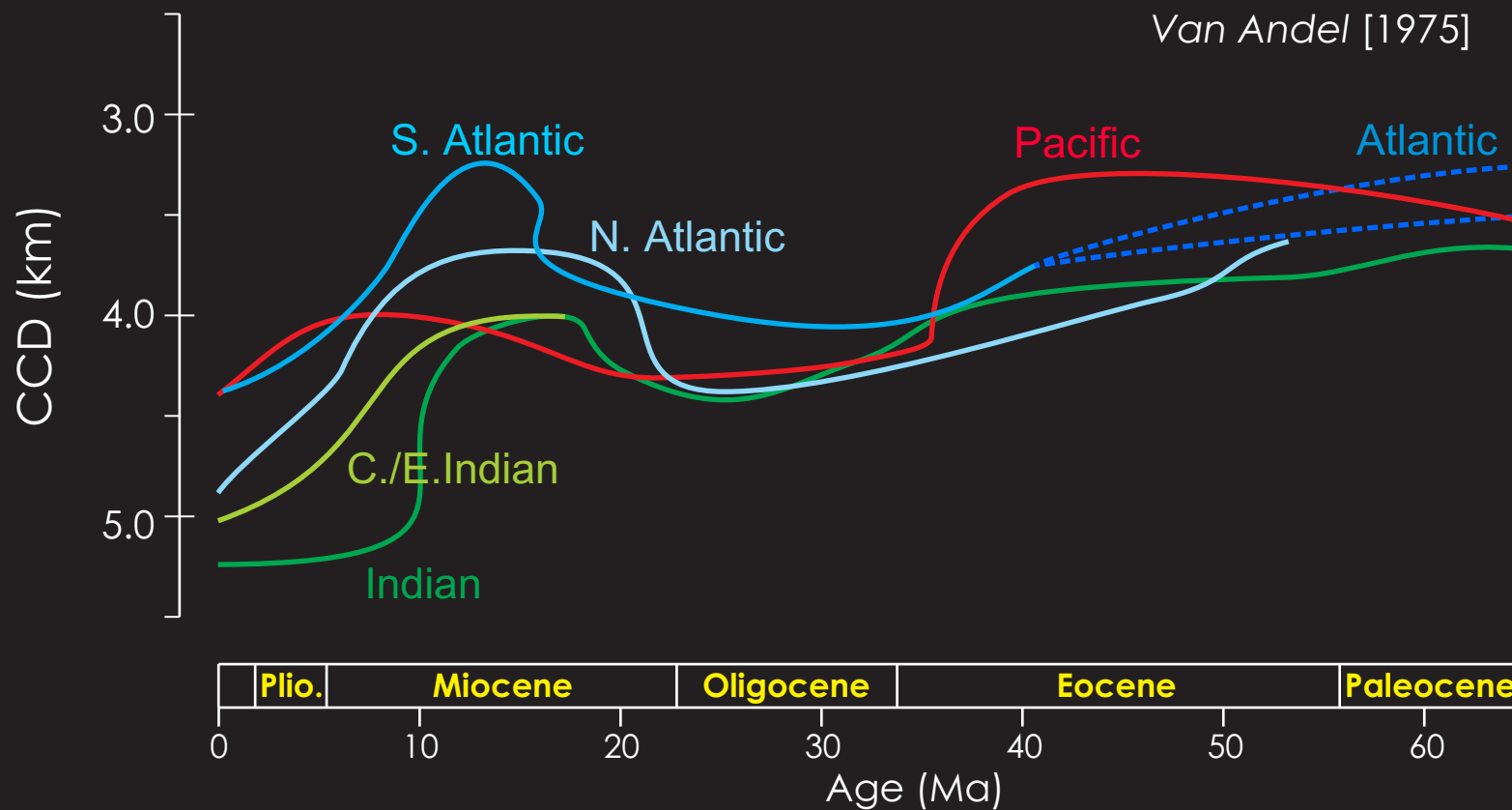
# Constraints on weathering: Li isotopes



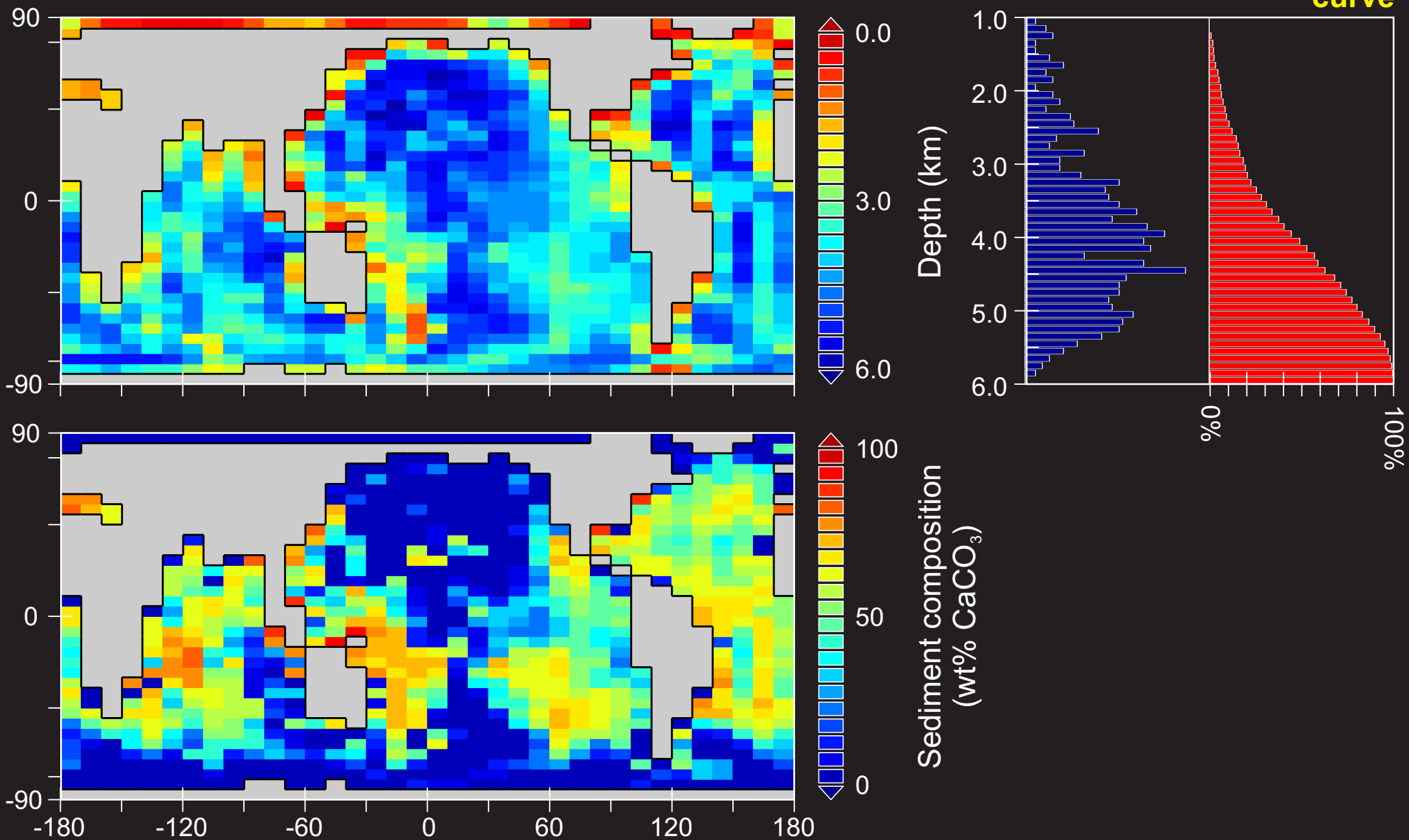
Froelich and Misra [2014]

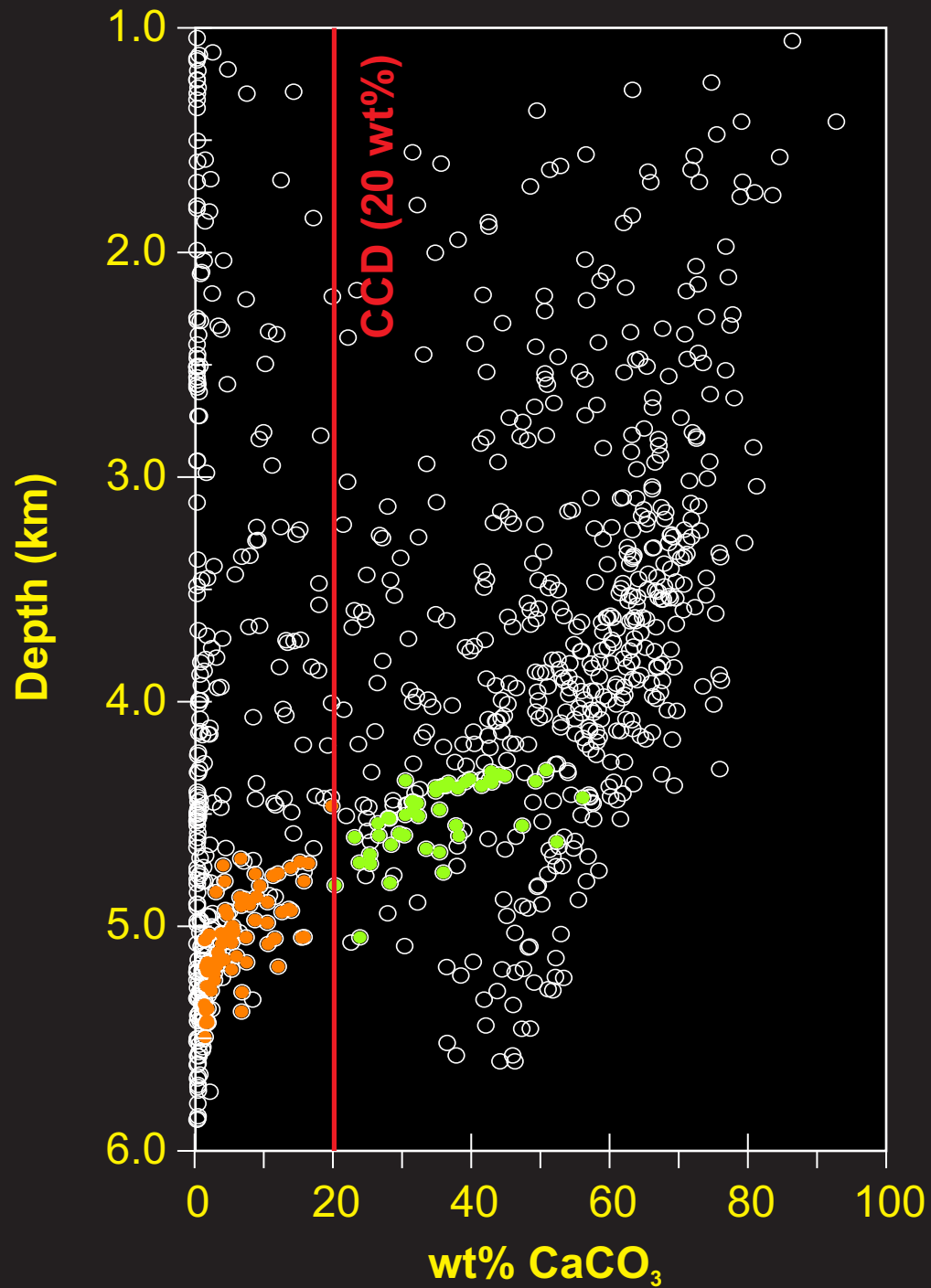


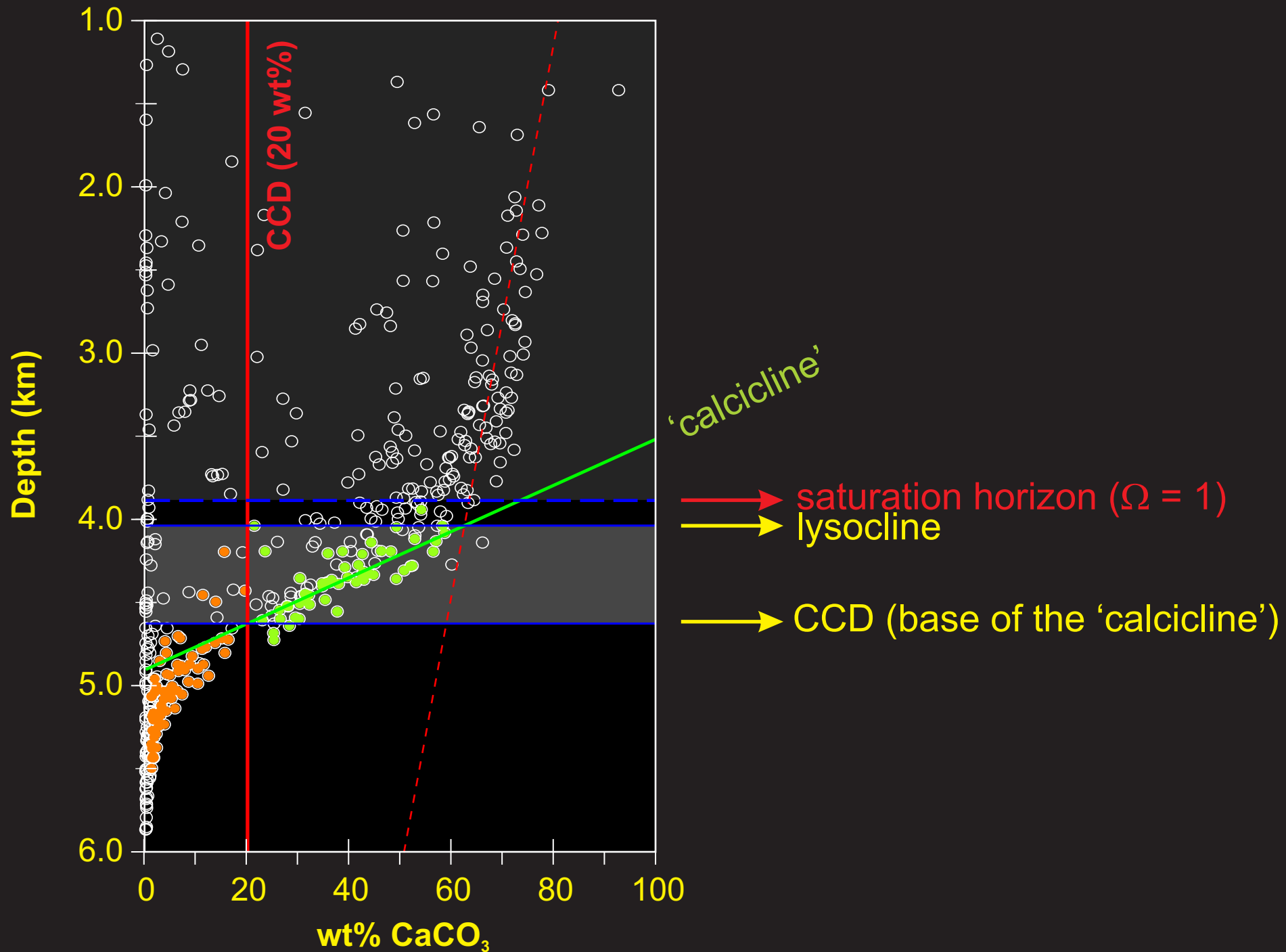


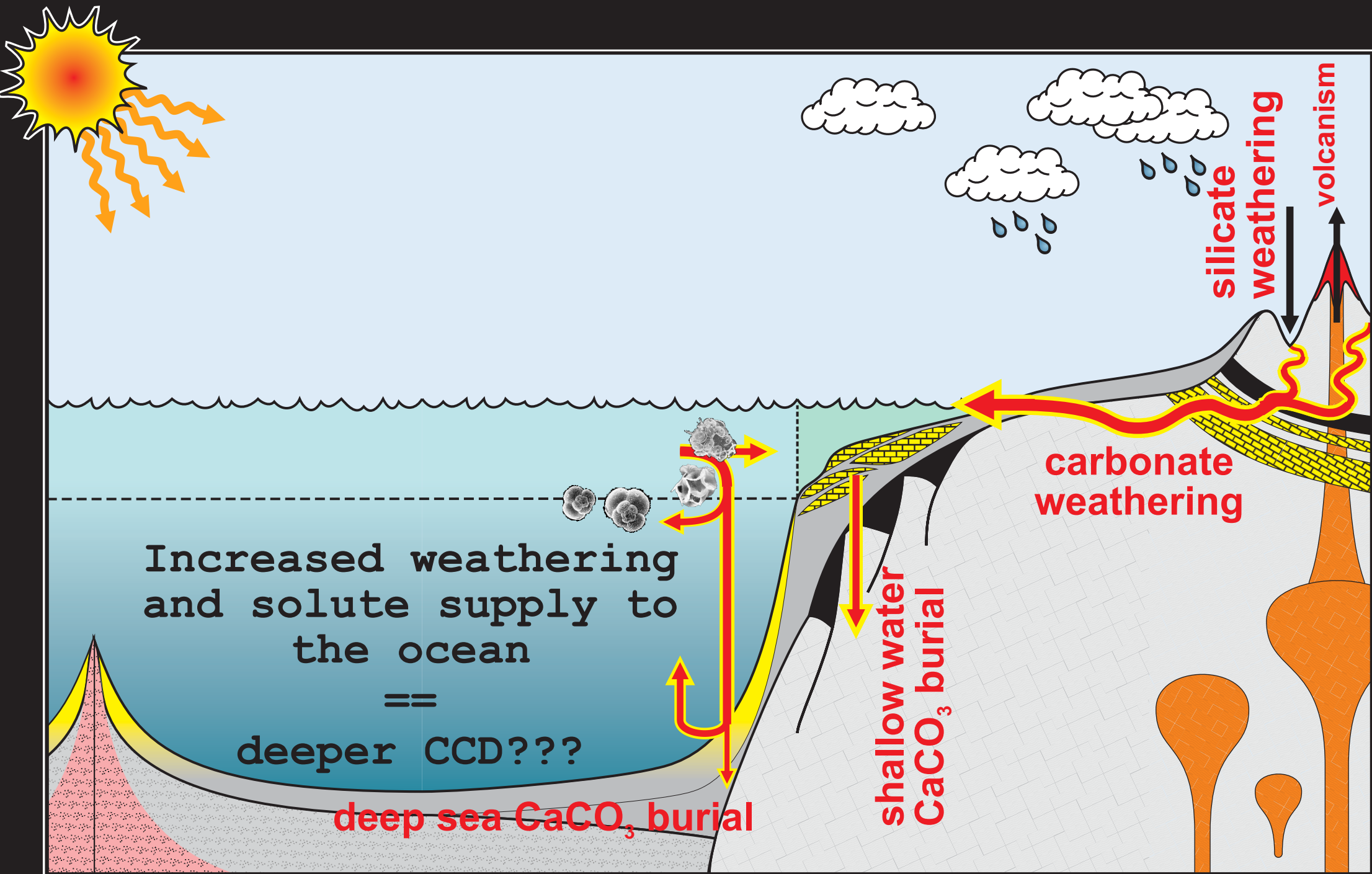


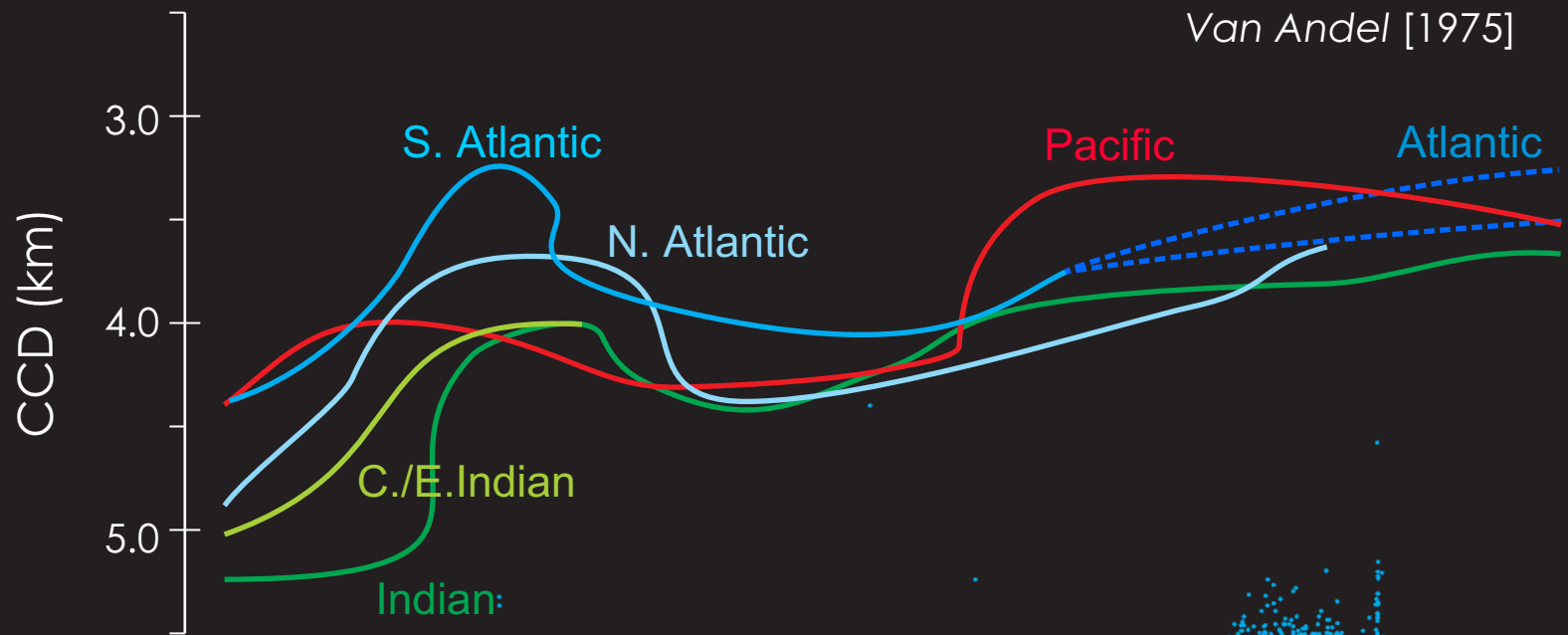
**hypso-  
metric  
curve**







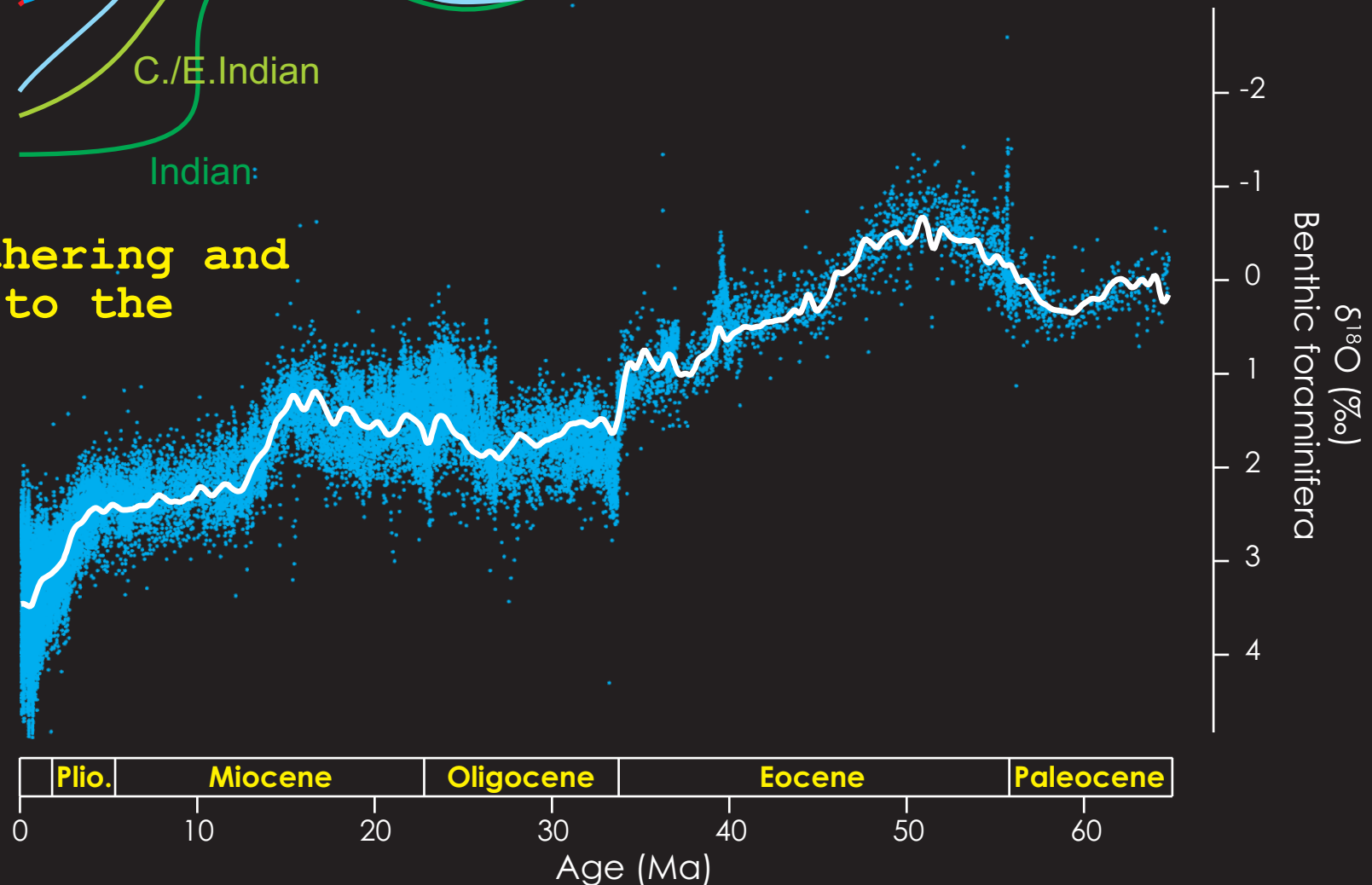


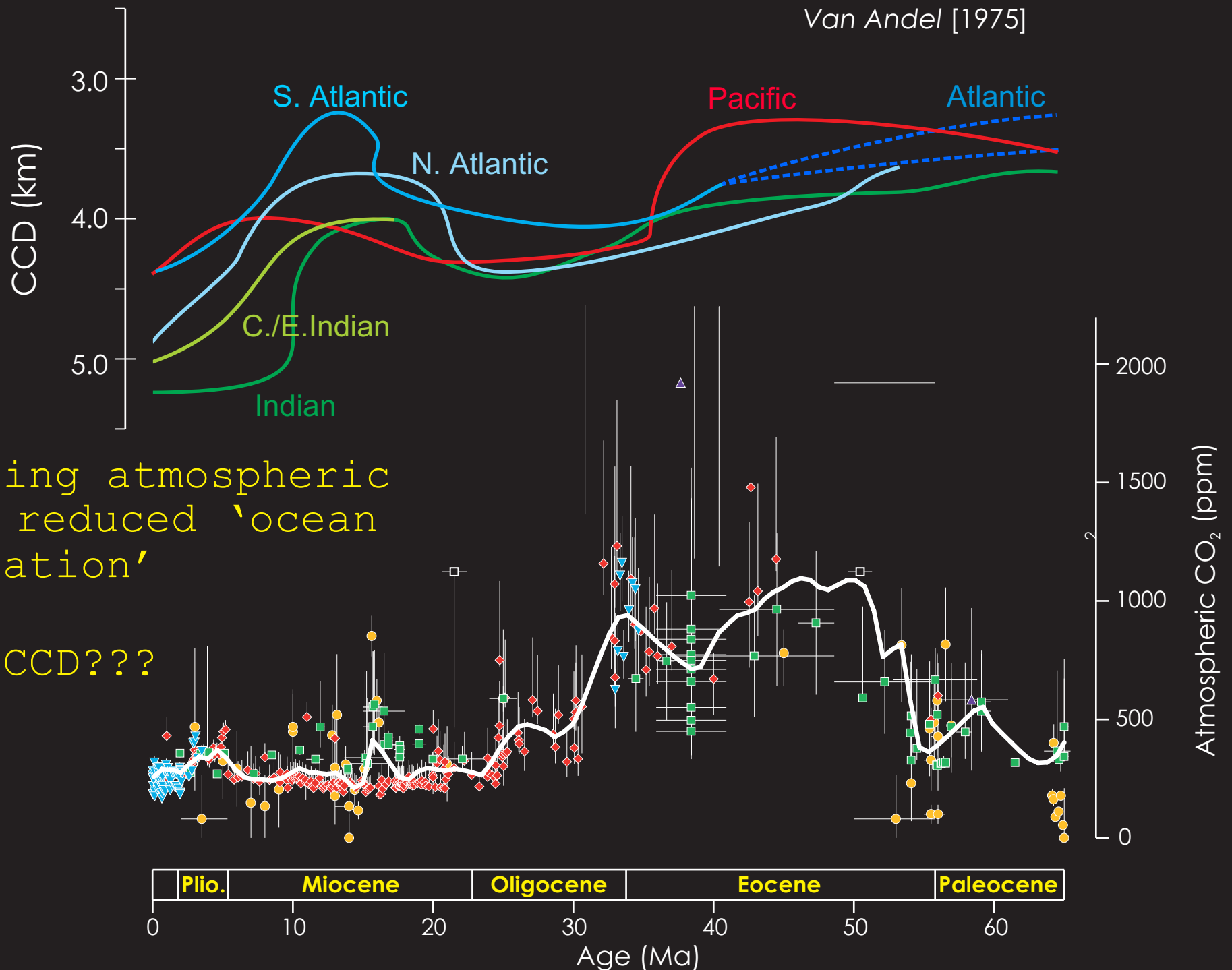


Increased weathering and solute supply to the ocean

==

deeper CCD???

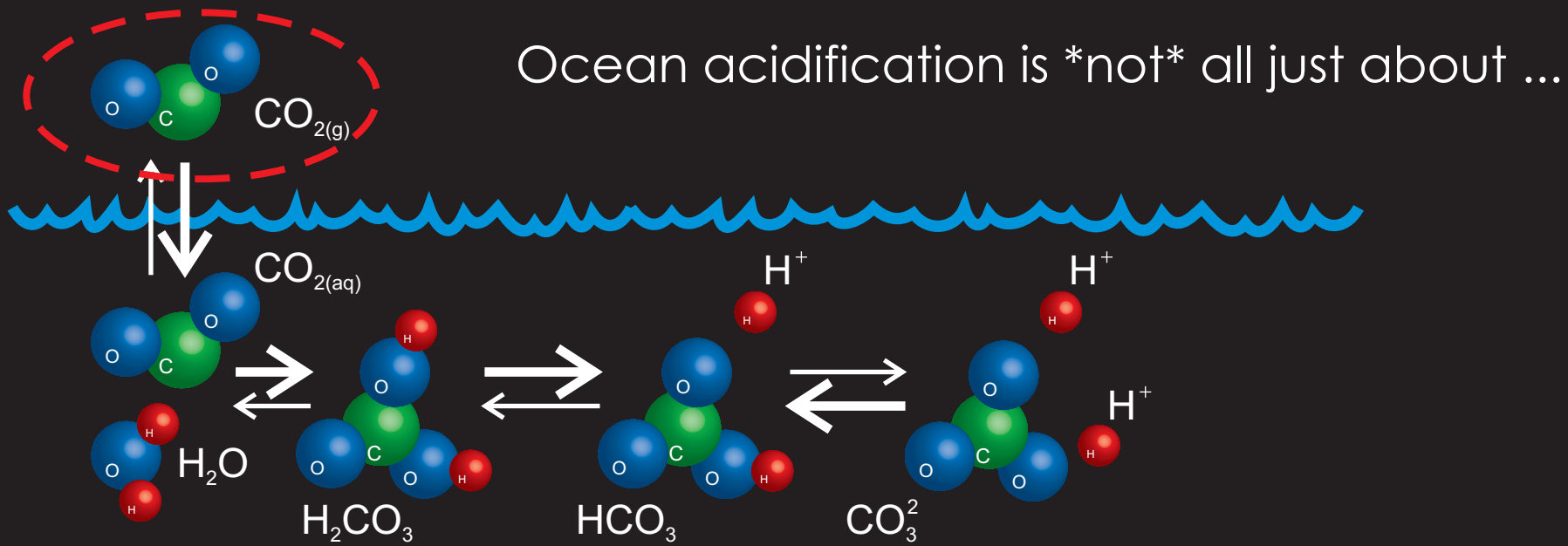




Decreasing atmospheric CO<sub>2</sub> and reduced 'ocean acidification'

==

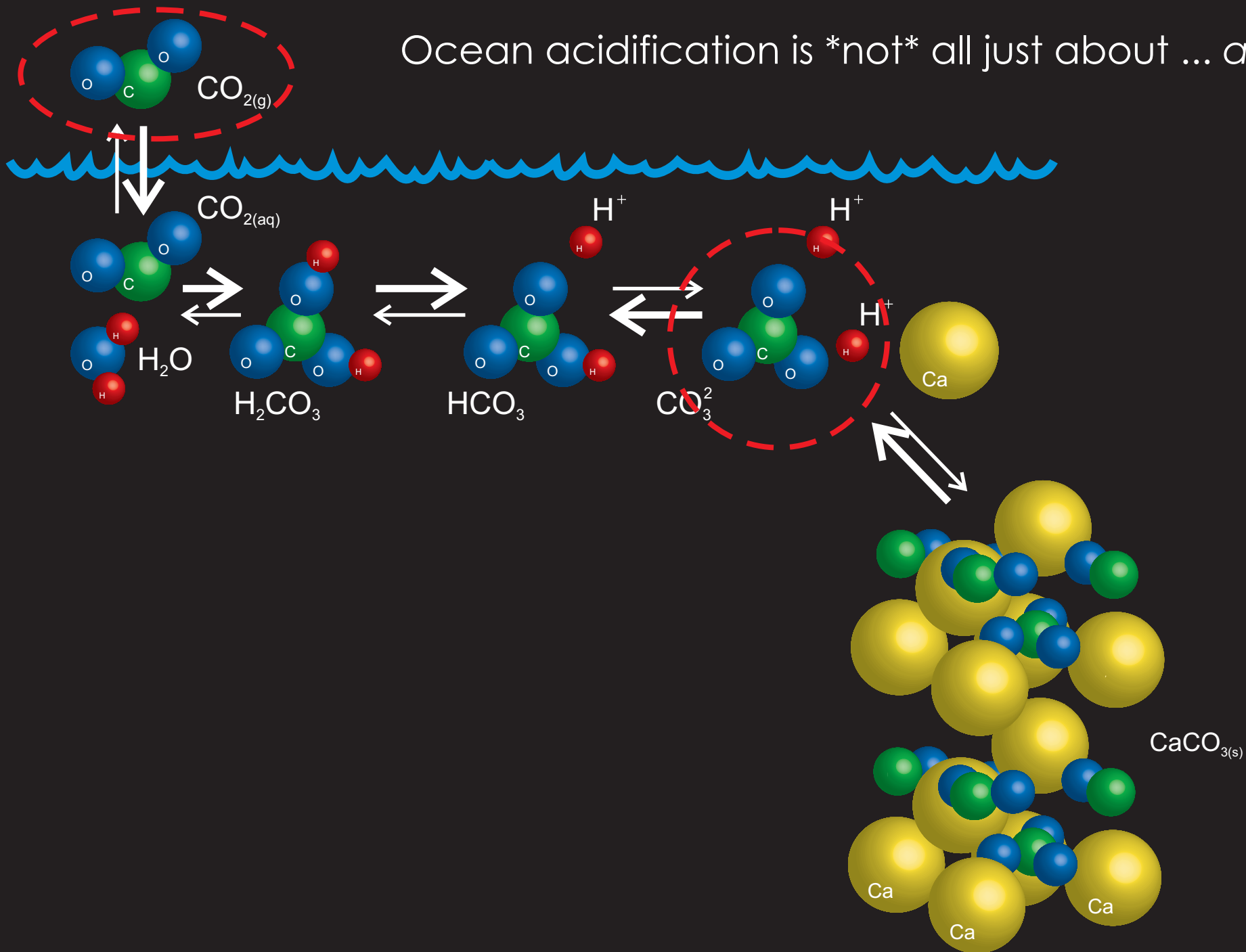
deeper CCD???





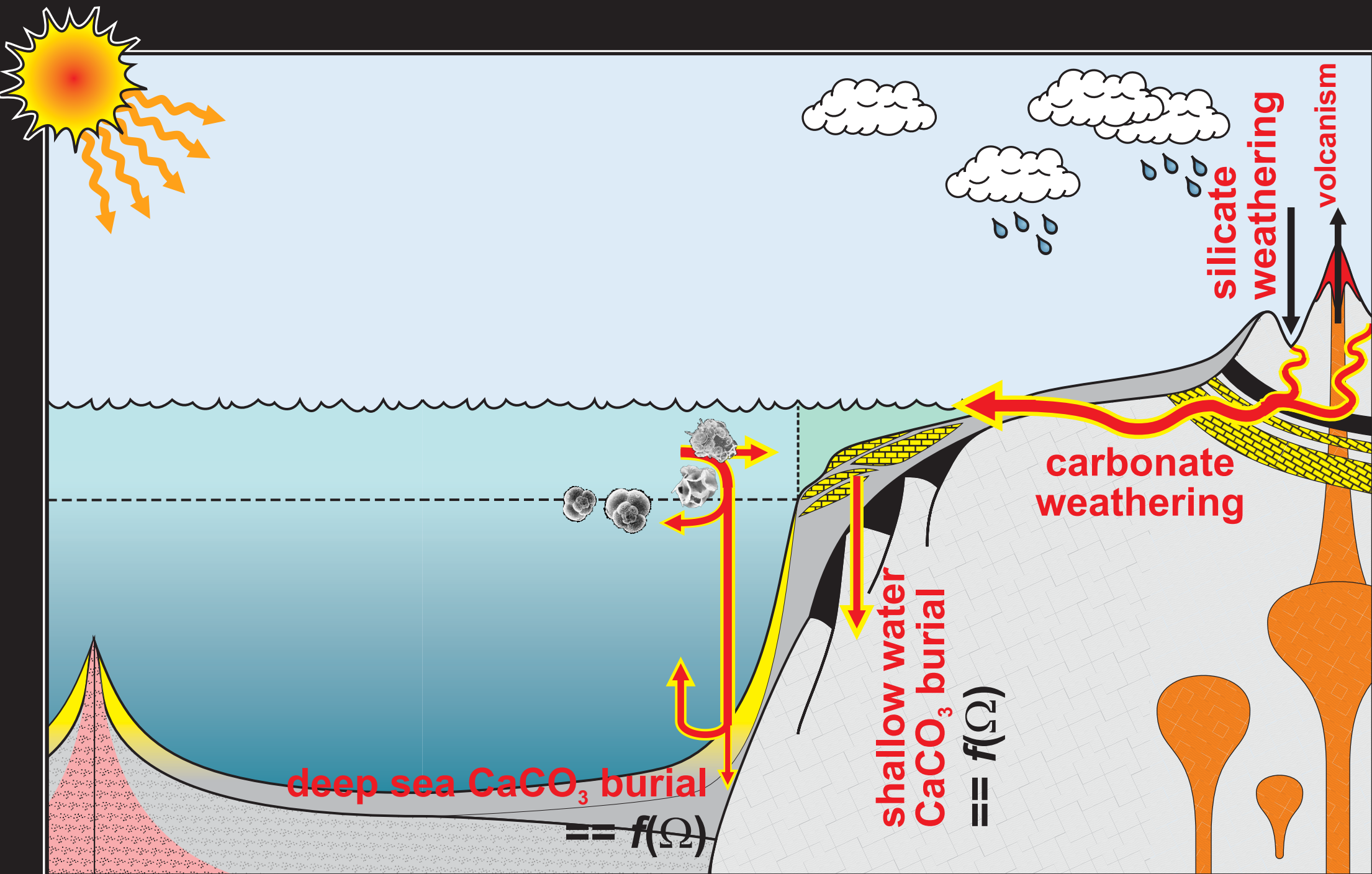
# The Carbonate Compensation Depth ('CCD')

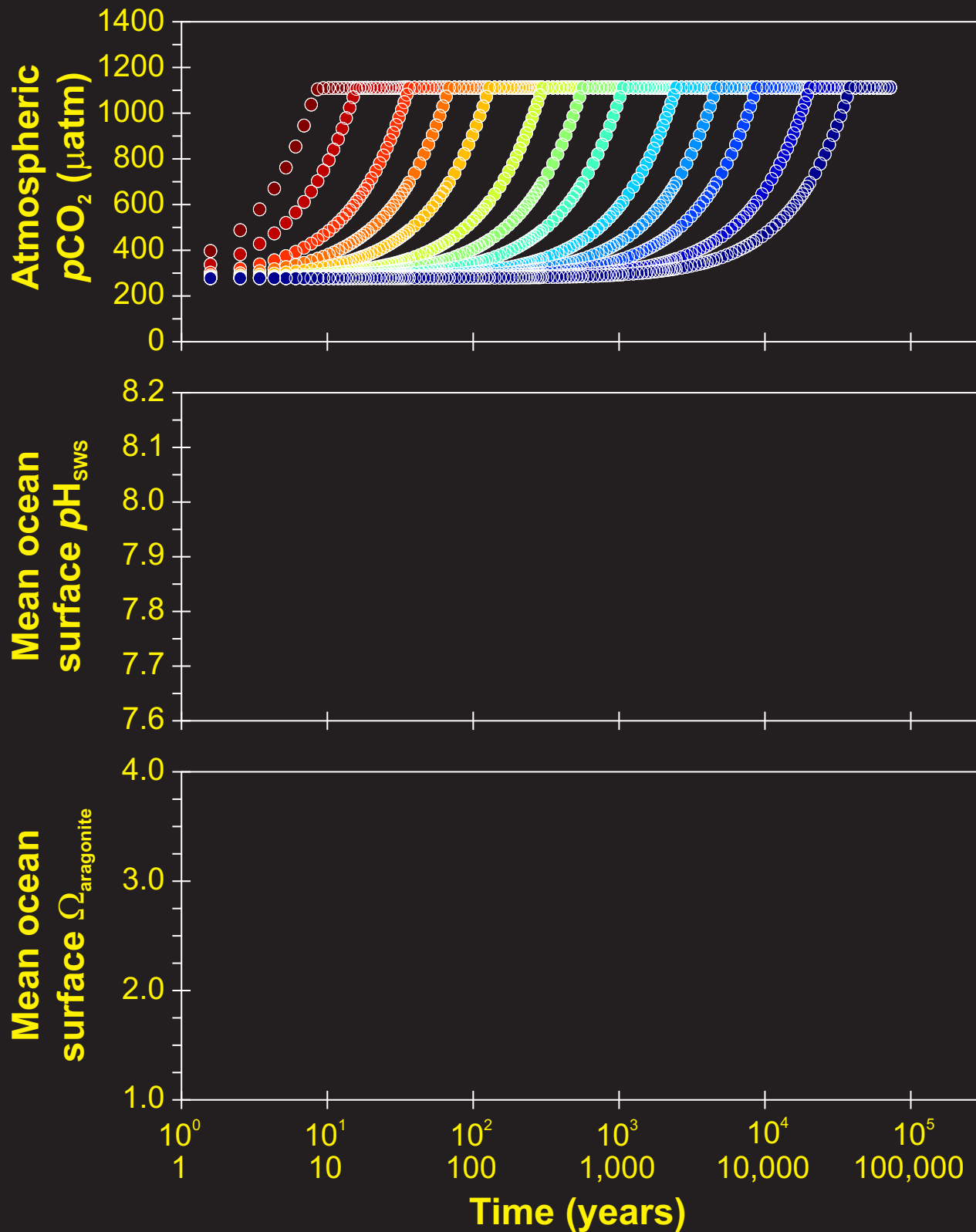
Ocean acidification is *\*not\** all just about ... acidification.



# The Carbonate Compensation Depth ('CCD')

Co-evolution of Life  
and the Planet





### anon model

```

! calculate carbonate alkalinity
loc_ALK_DIC = dum_ALK &
& - loc_H4BO4 - loc_OH - loc_HPO4 -
2.0*loc_PO4 - loc_H3SiO4 - loc_NH3 - loc_HS
&
& + loc_H + loc_HSO4 + loc_HF + loc_H3PO4

! estimate the partitioning between the
aqueous carbonate species

loc_zed = ( &
& (4.0*loc_ALK_DIC +
dum_DIC*dum_carbconst(icc_k) -
loc_ALK_DIC*dum_carbconst(icc_k))**2 + &
& 4.0*(dum_carbconst(icc_k) -
4.0)*loc_ALK_DIC**2 &
& )**0.5      loc_conc_HCO3 =
(dum_DIC*dum_carbconst(icc_k) -
loc_zed)/(dum_carbconst(icc_k) - 4.0)

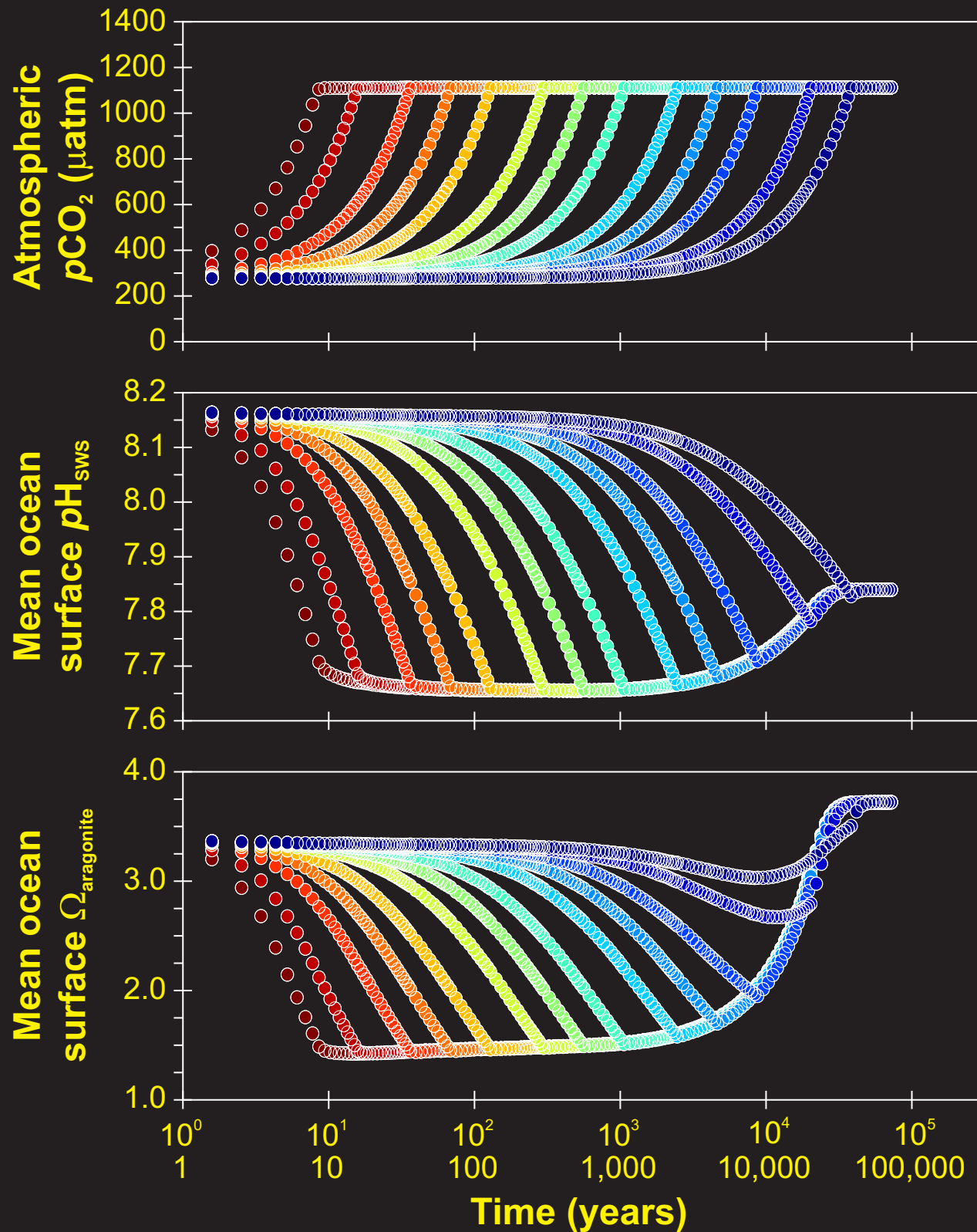
loc_conc_CO3 = &
& ( &
& loc_ALK_DIC*dum_carbconst(icc_k) -
dum_DIC*dum_carbconst(icc_k) - &
& 4.0*loc_ALK_DIC + loc_zed &
& ) &
& /(2.0*(dum_carbconst(icc_k) - 4.0))

loc_conc_CO2 = dum_DIC - loc_ALK_DIC + &
& ( &
& loc_ALK_DIC*dum_carbconst(icc_k) -
dum_DIC*dum_carbconst(icc_k) - &
& 4.0*loc_ALK_DIC + loc_zed &
& ) &
& /(2.0*(dum_carbconst(icc_k) - 4.0))

loc_H1 =
dum_carbconst(icc_k1)*loc_conc_CO2/loc_conc_
HCO3

loc_H2 =
dum_carbconst(icc_k2)*loc_conc_HCO3/loc_conc
_CO3

```



### anon model

```

! calculate carbonate alkalinity
loc_ALK_DIC = dum_ALK &
& - loc_H4BO4 - loc_OH - loc_HPO4 -
2.0*loc_PO4 - loc_H3SiO4 - loc_NH3 - loc_HS
&
& + loc_H + loc_HSO4 + loc_HF + loc_H3PO4

! estimate the partitioning between the
aqueous carbonate species

loc_zed = ( &
& (4.0*loc_ALK_DIC +
dum_DIC*dum_carbconst(icc_k) -
loc_ALK_DIC*dum_carbconst(icc_k))**2 + &
& 4.0*(dum_carbconst(icc_k) -
4.0)*loc_ALK_DIC**2 &
& )**0.5      loc_conc_HCO3 =
(dum_DIC*dum_carbconst(icc_k) -
loc_zed)/(dum_carbconst(icc_k) - 4.0)

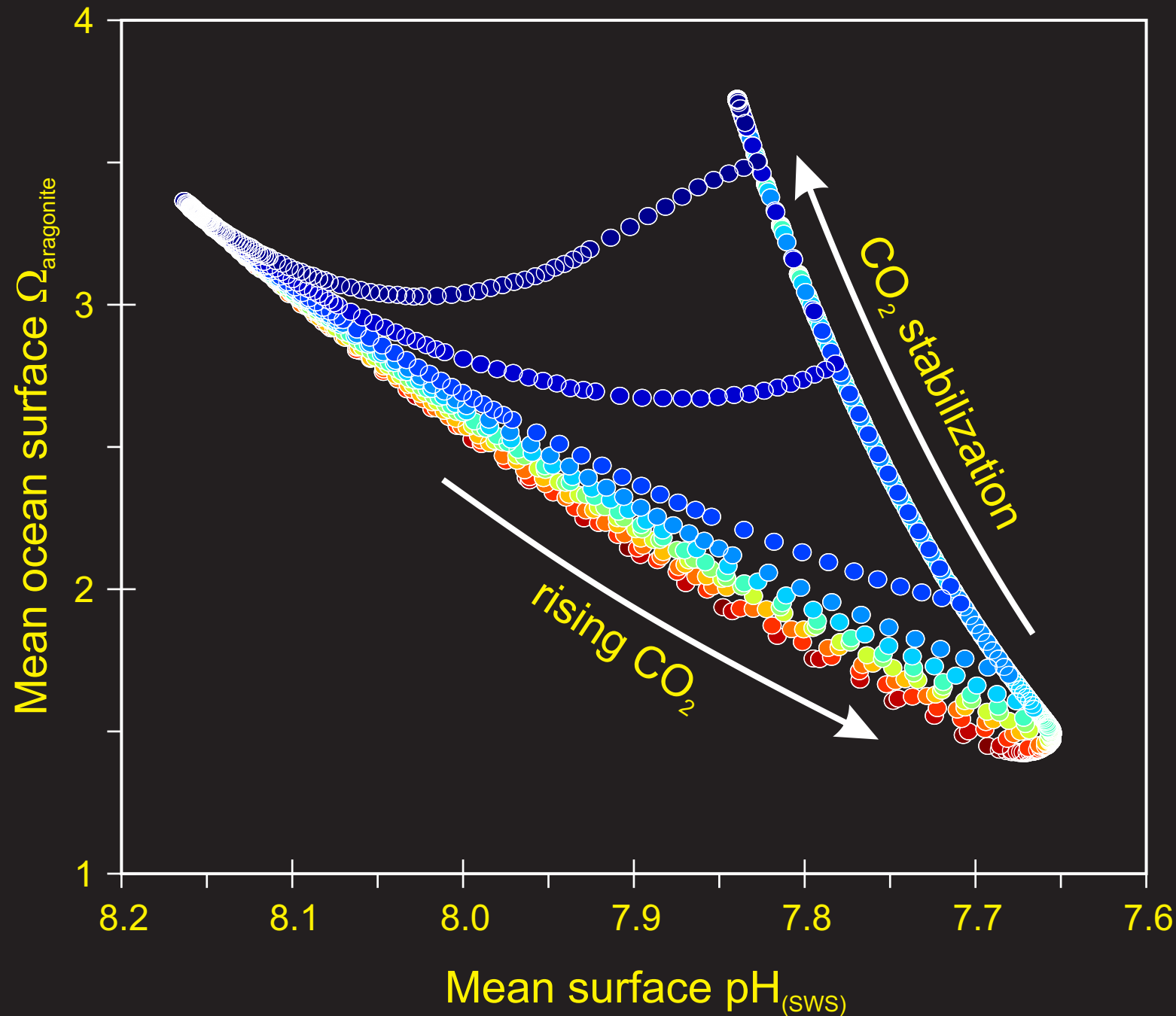
loc_conc_CO3 = &
& ( &
& loc_ALK_DIC*dum_carbconst(icc_k) -
dum_DIC*dum_carbconst(icc_k) - &
& 4.0*loc_ALK_DIC + loc_zed &
& ) &
& /(2.0*(dum_carbconst(icc_k) - 4.0))

loc_conc_CO2 = dum_DIC - loc_ALK_DIC + &
& ( &
& loc_ALK_DIC*dum_carbconst(icc_k) -
dum_DIC*dum_carbconst(icc_k) - &
& 4.0*loc_ALK_DIC + loc_zed &
& ) &
& /(2.0*(dum_carbconst(icc_k) - 4.0))

loc_H1 =
dum_carbconst(icc_k1)*loc_conc_CO2/loc_conc_
HCO3

loc_H2 =
dum_carbconst(icc_k2)*loc_conc_HCO3/loc_conc_
CO3

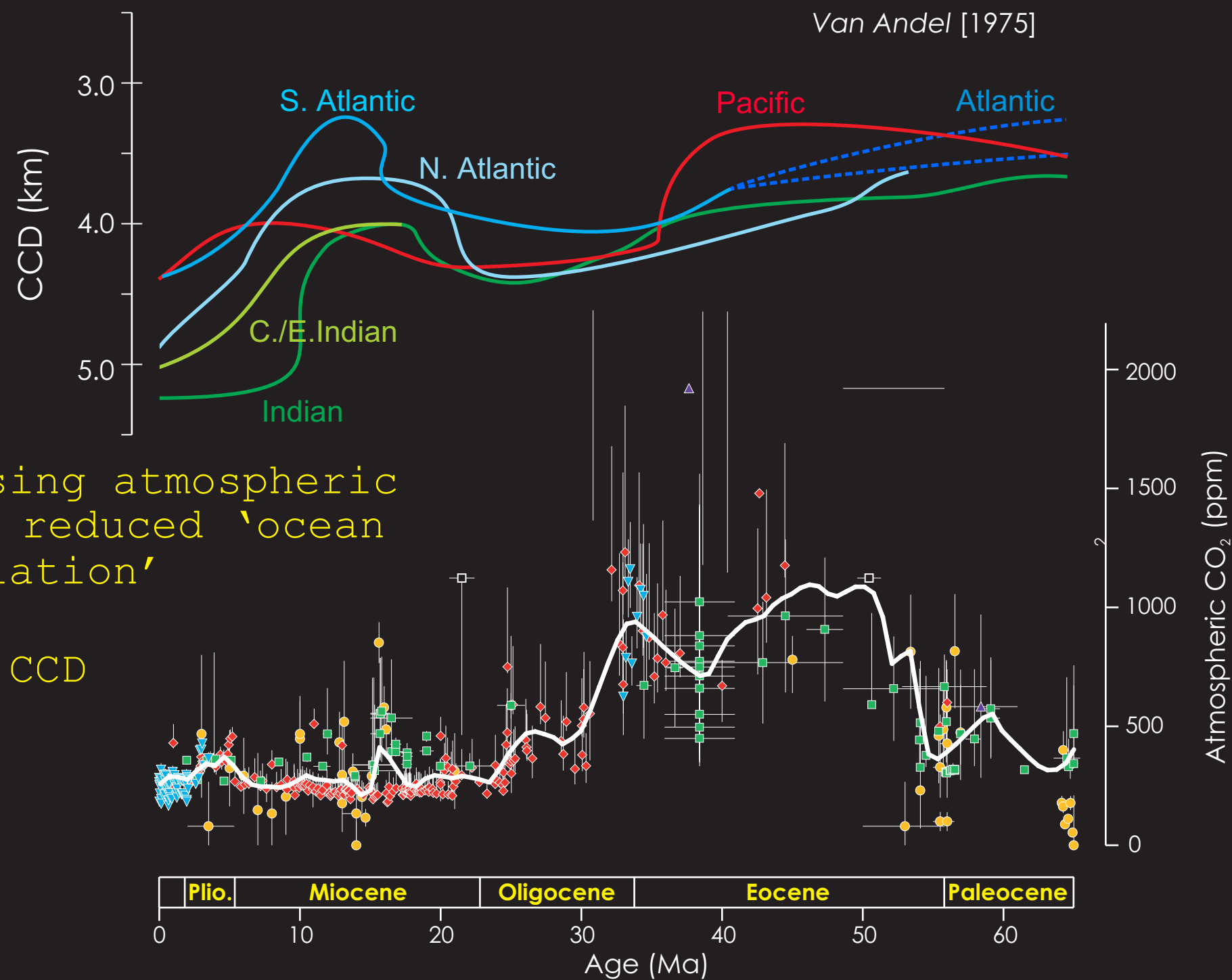
```



$10^5$   
 $10^4$   
 $10^3$   
 $10^2$   
 $10^1$

Time to a quadrupling of  $\text{pCO}_2$  (years)

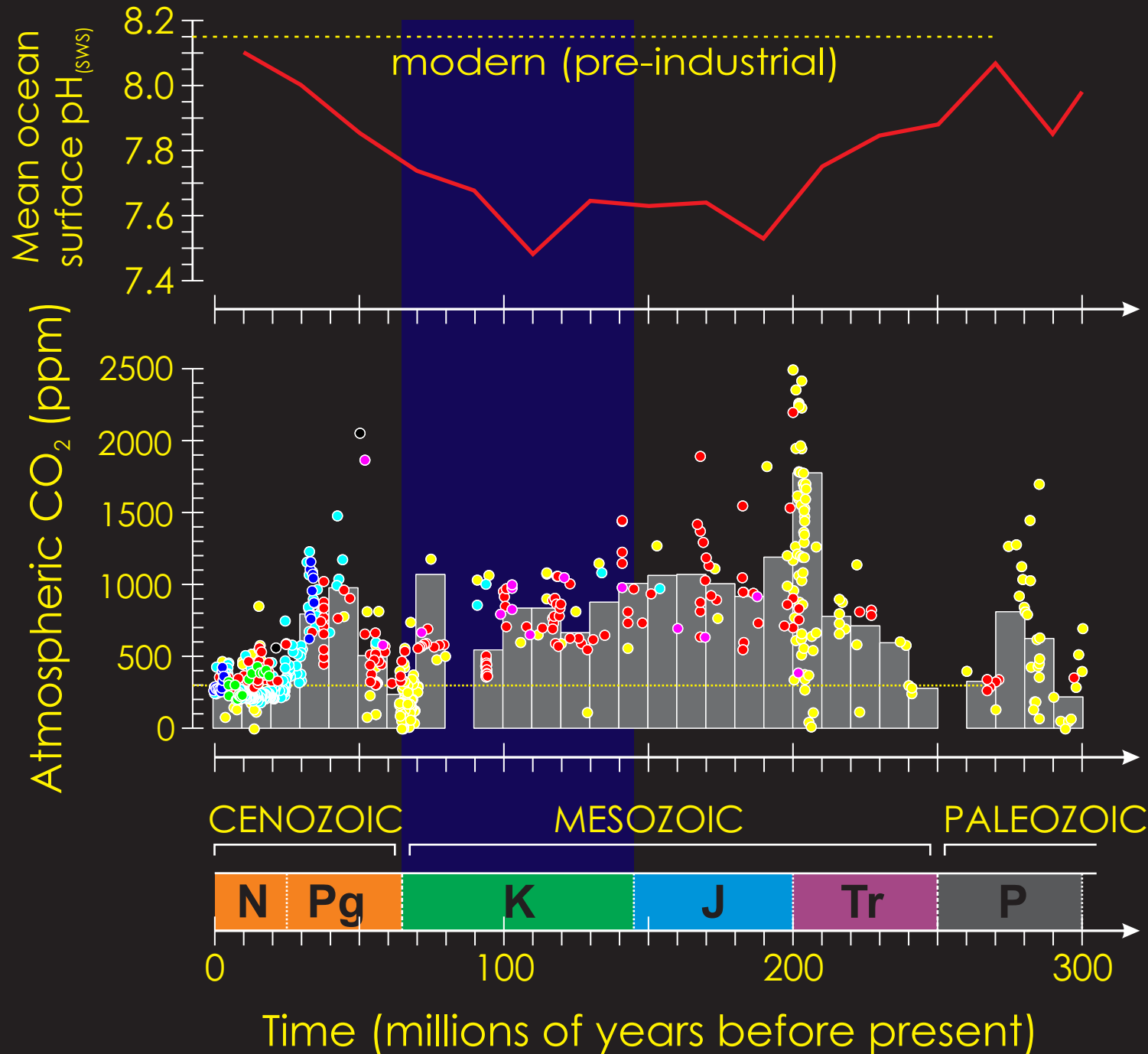


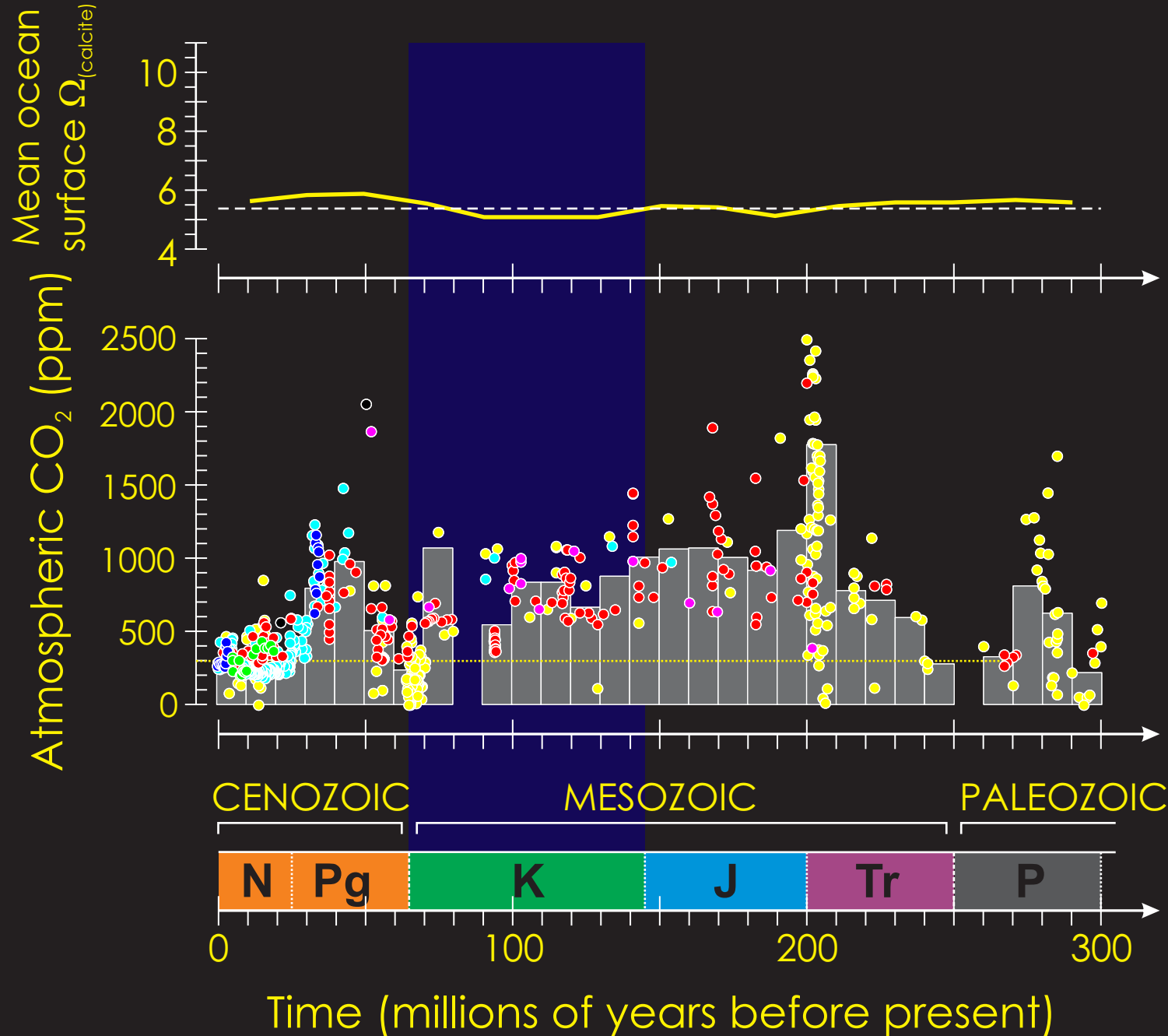


Decreasing atmospheric CO<sub>2</sub> and reduced 'ocean acidification' / = deeper CCD

# Constraining global carbon cycling with the CCD

Co-evolution of Life and the Planet



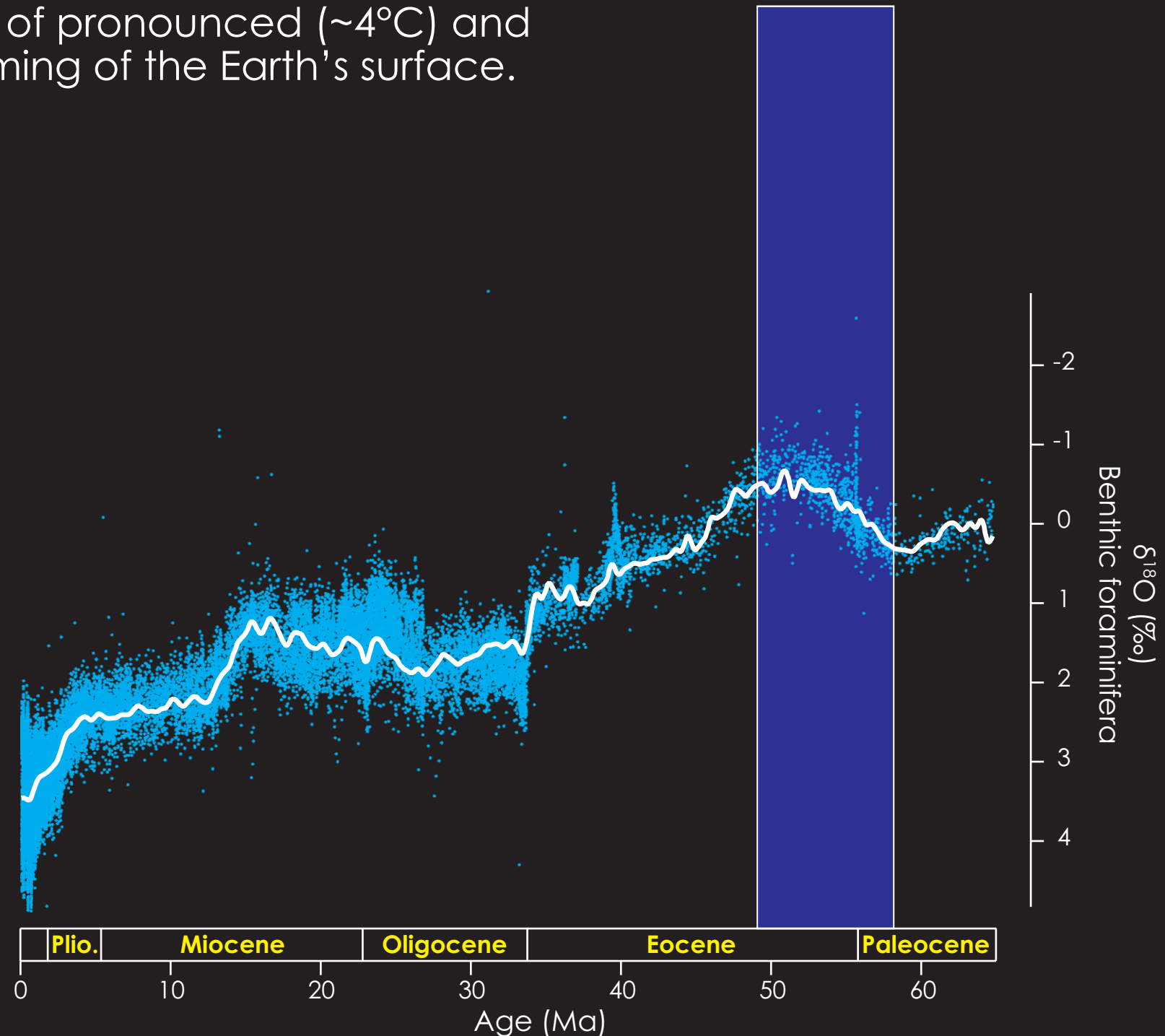




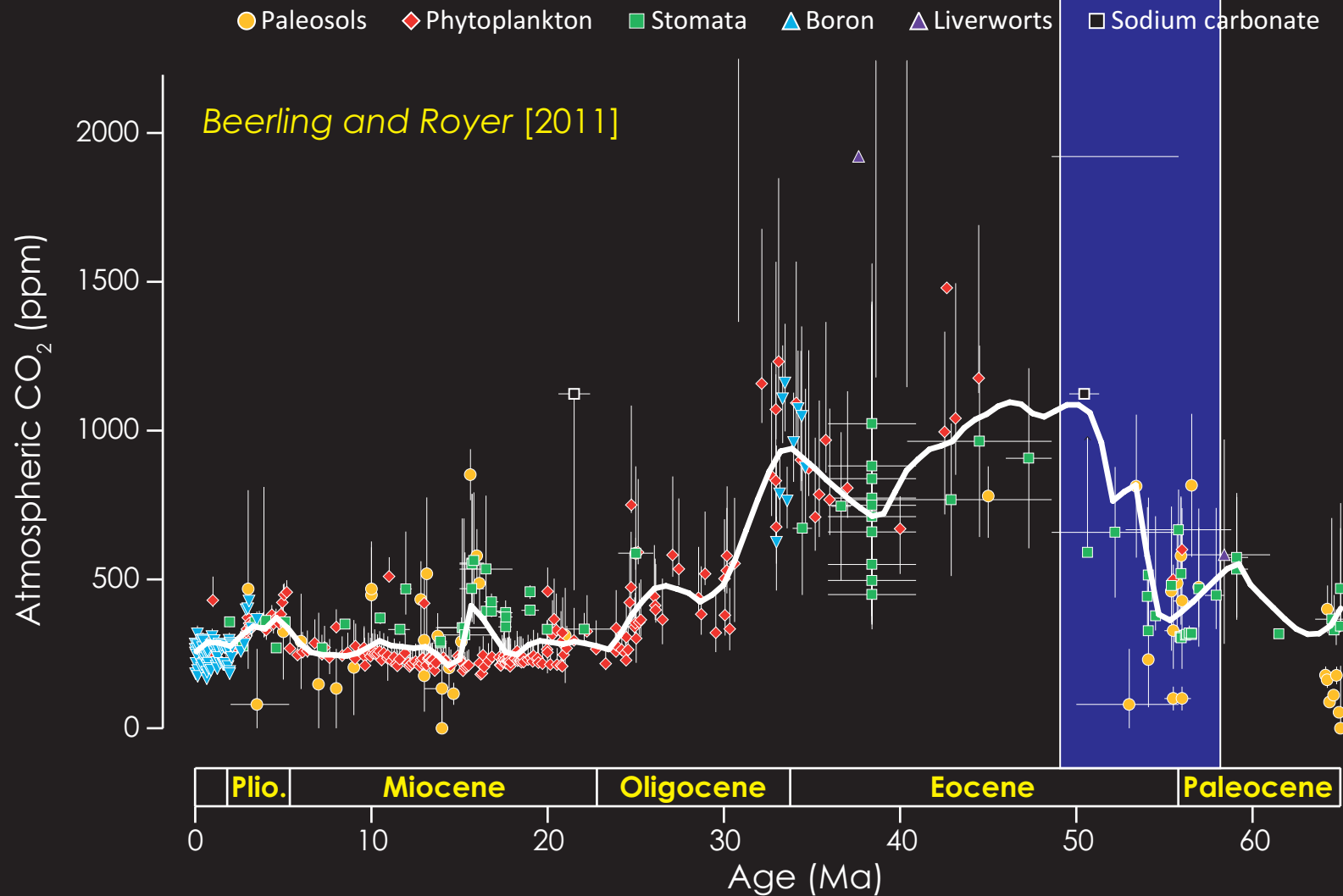


Sediments spanning the Palaeocene-Eocene boundary recovered from ODP Leg 208 (Walvis Ridge)  
Picture courtesy of Dani Schmidt (University of Bristol)

✓ ~9 Ma interval of pronounced (~4°C) and progressive warming of the Earth's surface.

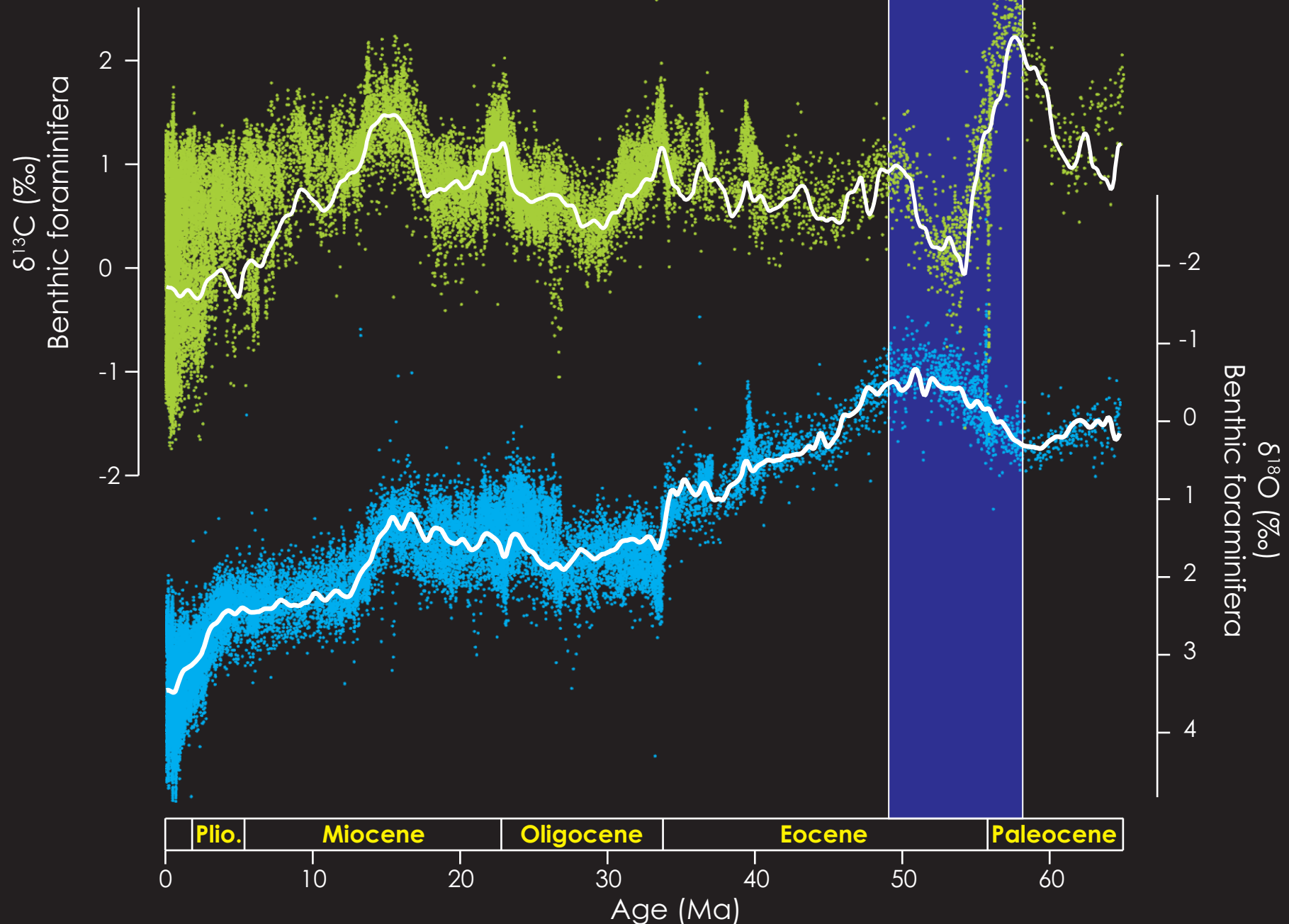


✓ Increasing atmospheric  $p\text{CO}_2$ .

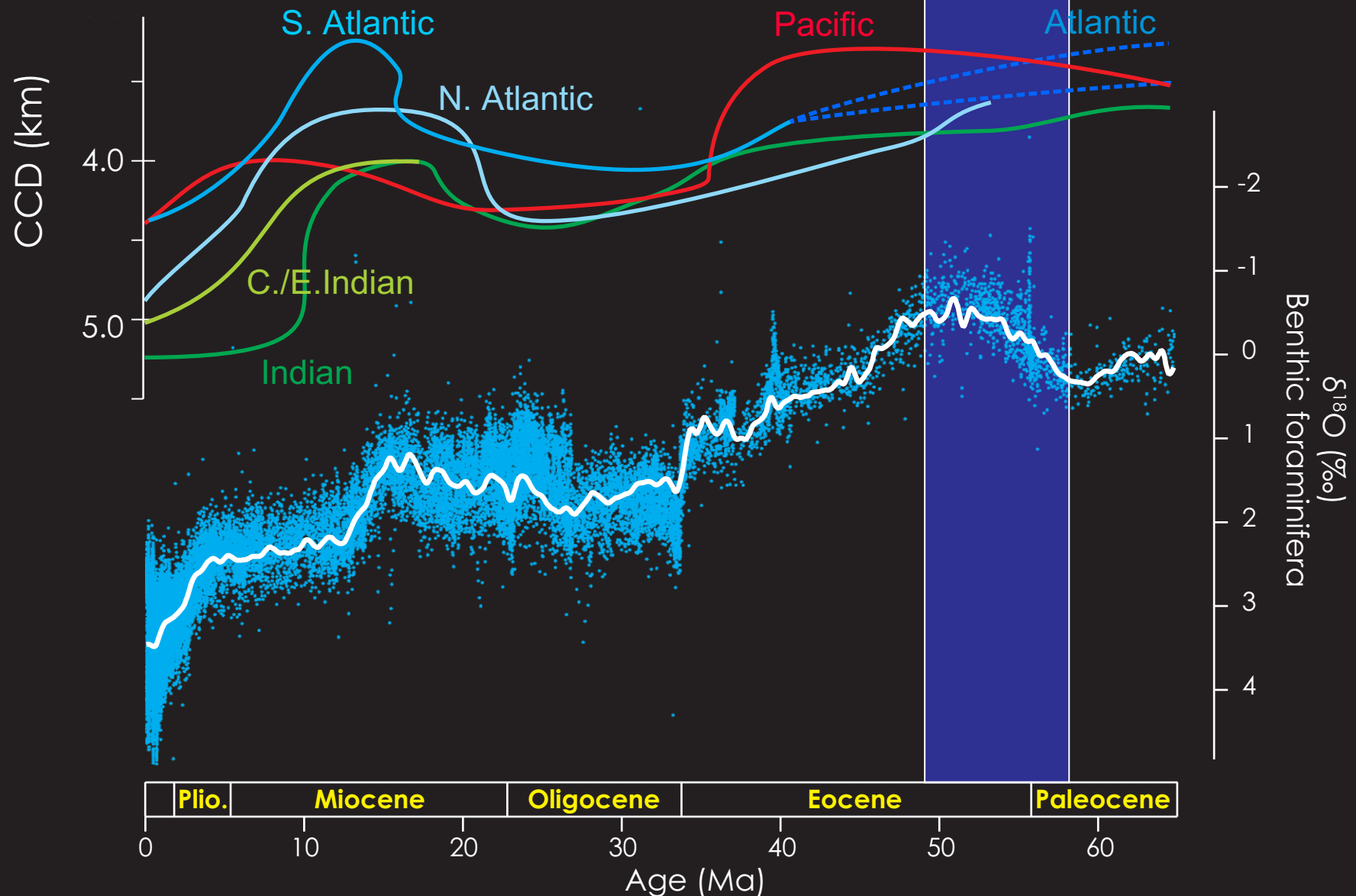


- ✓ Mostly ... characterized by declining  $\delta^{13}\text{C}$  values, consistent with net input of isotopically light carbon.

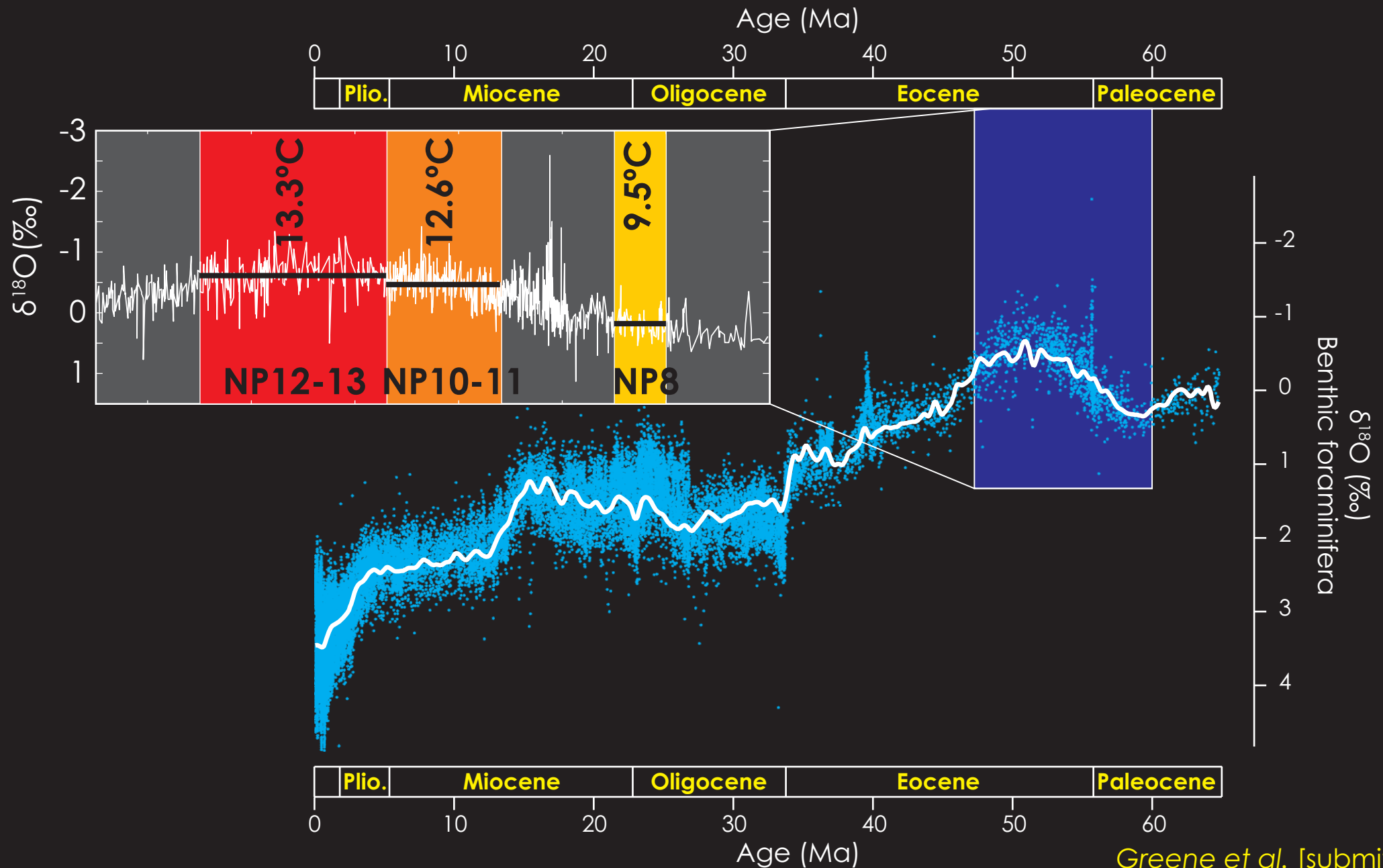
Cramer et al. [2009]



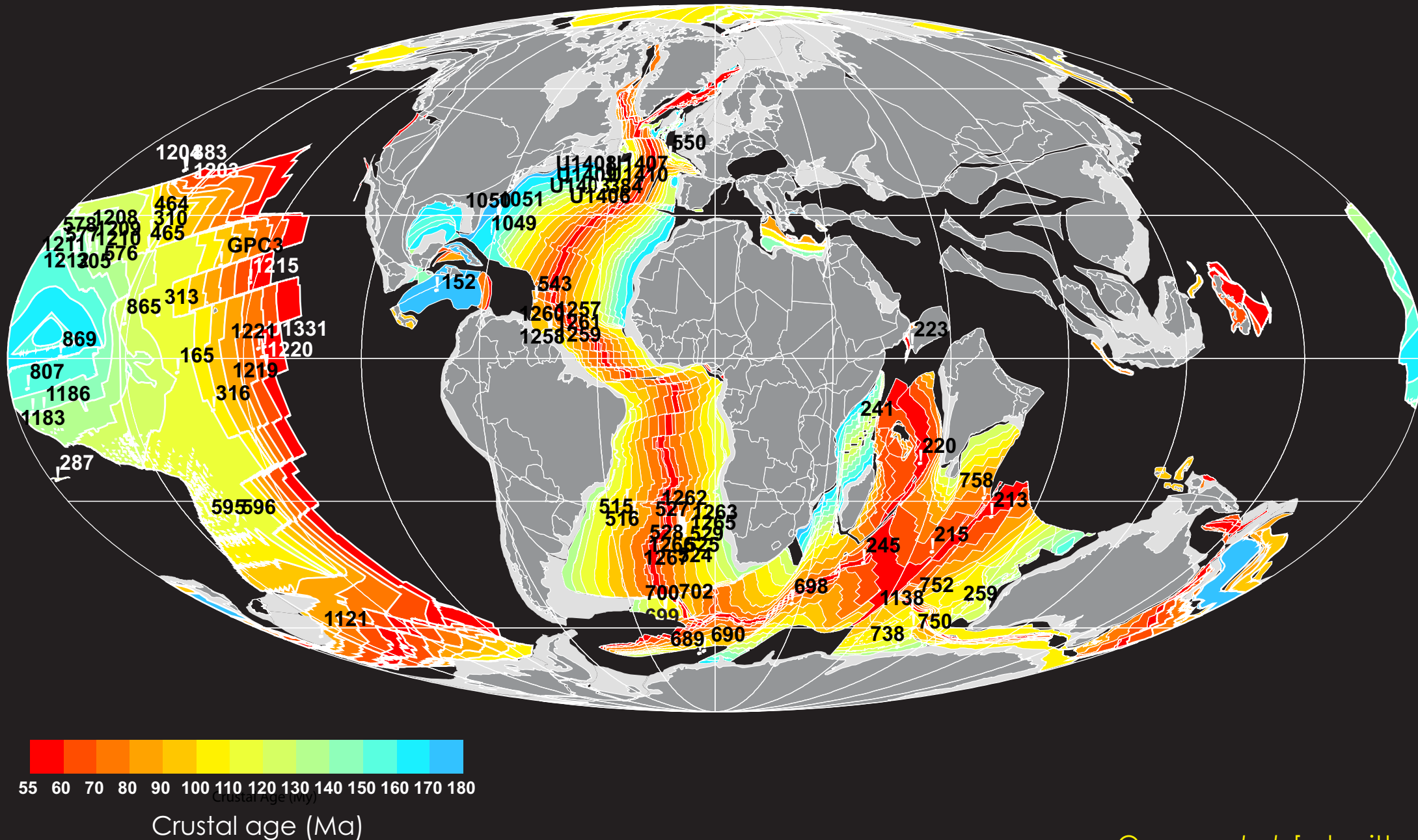
- ✗ Slightly deepening CCD ... but much less than box models predict (e.g. Komar *et al.* [2013]).
- ✗ Very sparse data coverage, not meaningfully updated since 1975.

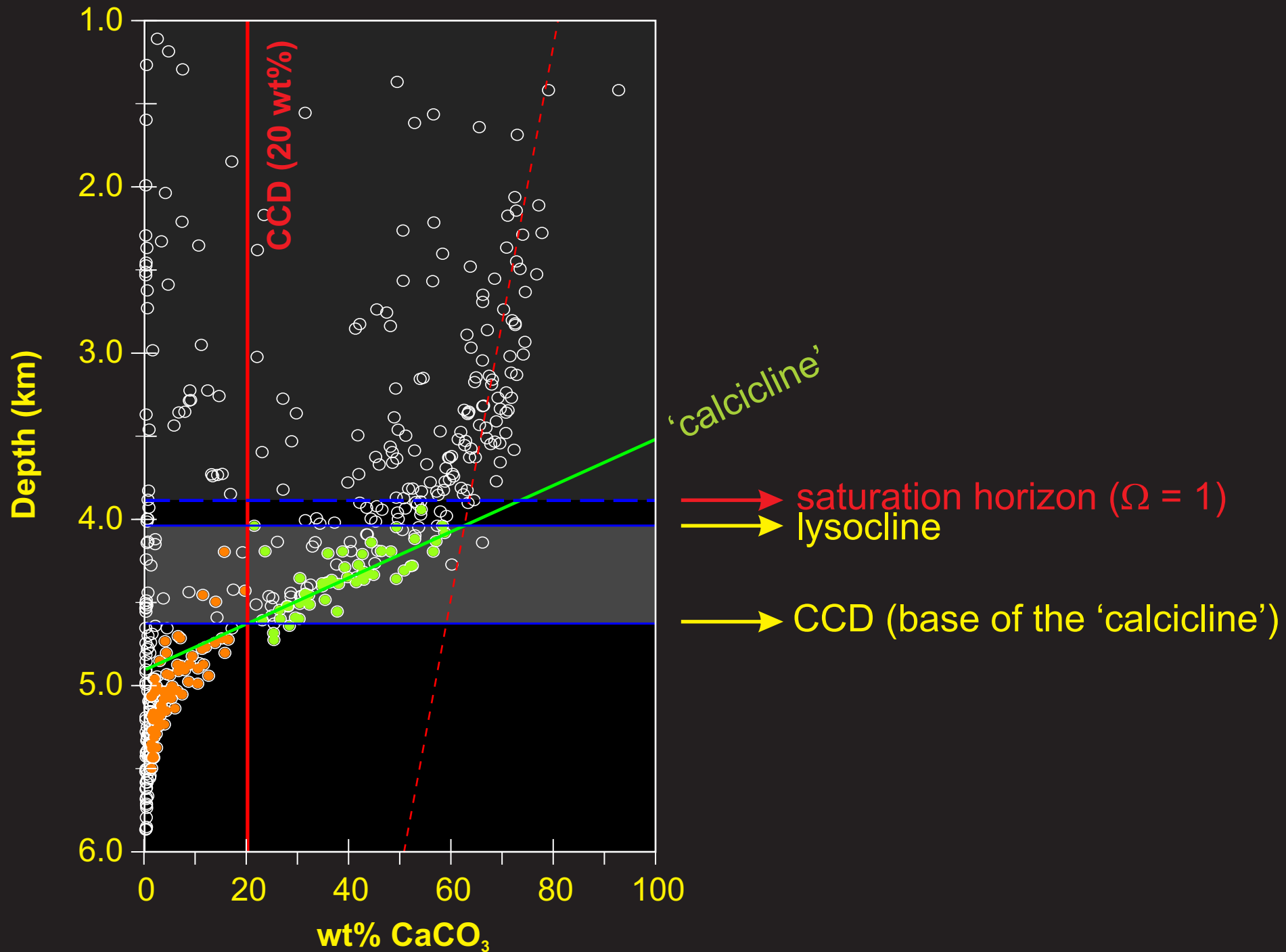


Three data slices spanning LPEE interval (and avoiding PETM).

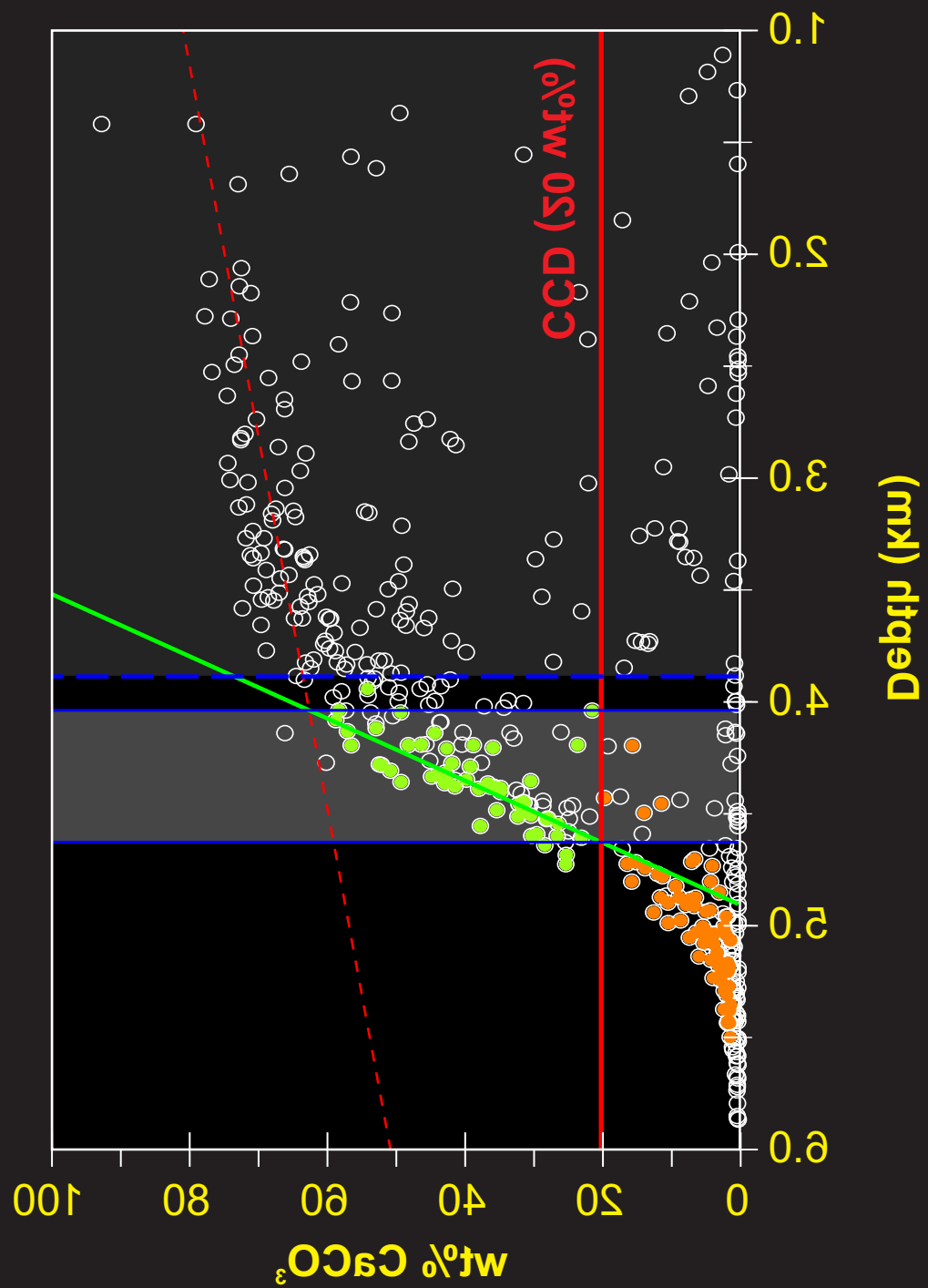


Site distribution (and existing crust older than 55 Ma).









'CCD' plots.

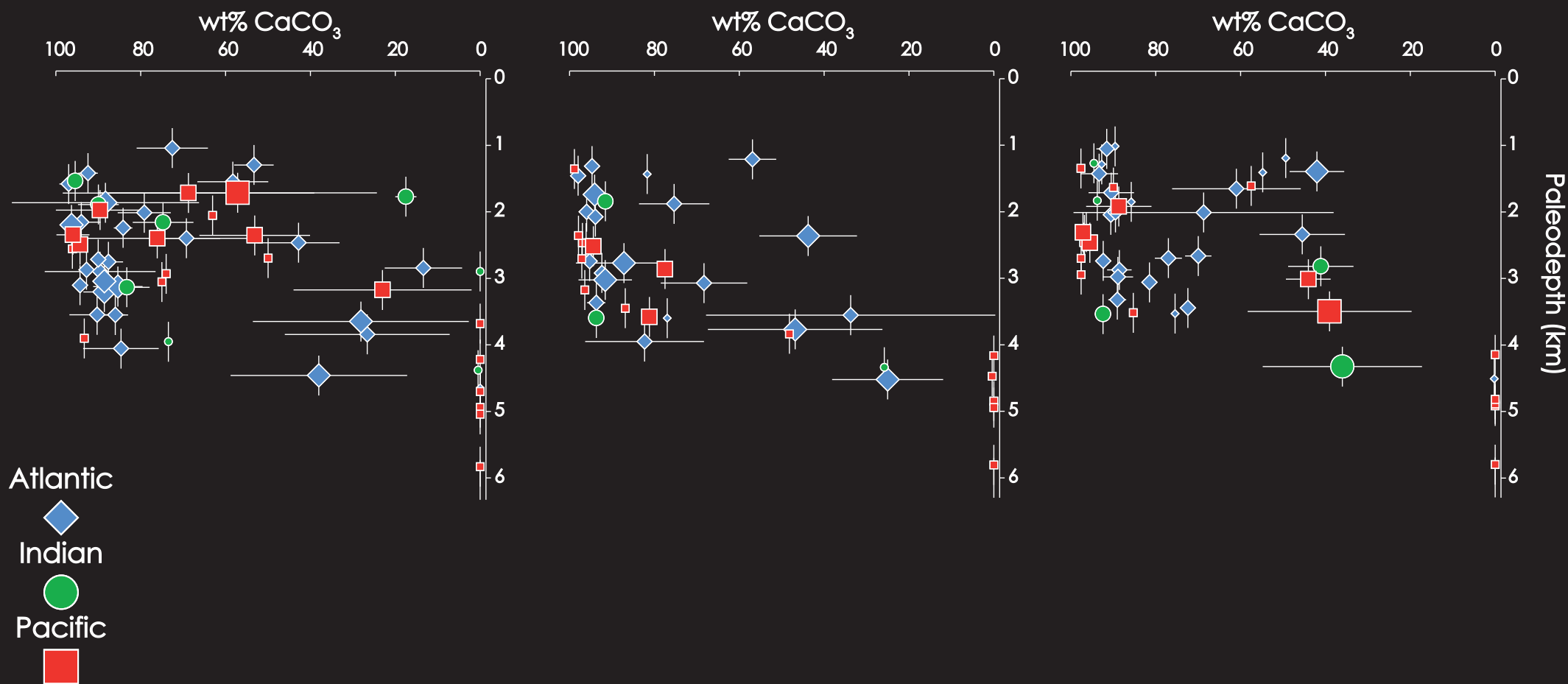
$H_0$ : warming ( $\Rightarrow$  increasing weathering?)



NP12-13 (~53-49 Ma)

NP10-11 (~55-53 Ma)

NP8 (~58-57 Ma)



'CCD' plots.

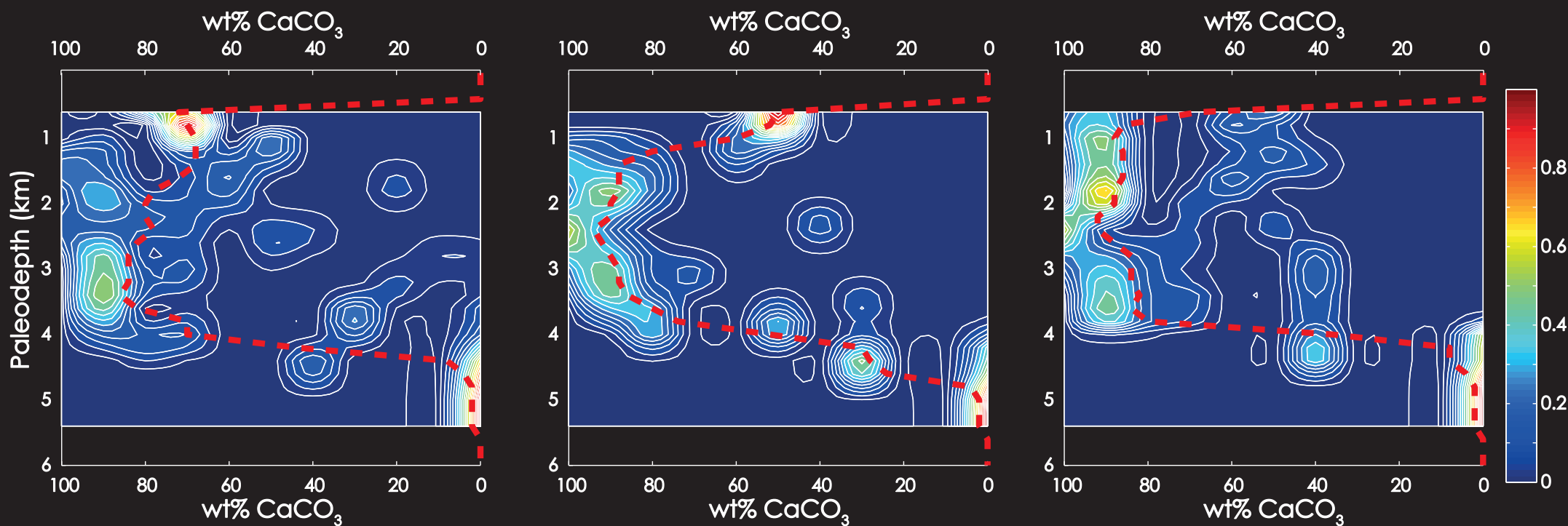
$H_0$ : warming ( $\Rightarrow$  increasing weathering?)



NP12-13 (~53-49 Ma)

NP10-11 (~55-53 Ma)

NP8 (~58-57 Ma)



Contours are of relative data density within a sliding time-window (and wt% bin).

Red contour delineates 50% of the data.

## anon model

```

! calculate carbonate alkalinity
loc_ALK_DIC = dum_ALK &
& - loc_H4BO4 - loc_OH - loc_HPO4 -
2.0*loc_PO4 - loc_H3SiO4 - loc_NH3 - loc_HS
&
& + loc_H + loc_HSO4 + loc_HF + loc_H3PO4

! estimate the partitioning between the
aqueous carbonate species

loc_zed = ( &
& (4.0*loc_ALK_DIC +
dum_DIC*dum_carbconst(icc_k) -
loc_ALK_DIC*dum_carbconst(icc_k))**2 + &
& 4.0*(dum_carbconst(icc_k) -
4.0)*loc_ALK_DIC**2 &
& )**0.5      loc_conc_HCO3 =
(dum_DIC*dum_carbconst(icc_k) -
loc_zed)/(dum_carbconst(icc_k) - 4.0)

loc_conc_CO3 = &
& ( &
& loc_ALK_DIC*dum_carbconst(icc_k) -
dum_DIC*dum_carbconst(icc_k) - &
& 4.0*loc_ALK_DIC + loc_zed &
& ) &
& /(2.0*(dum_carbconst(icc_k) - 4.0))

loc_conc_CO2 = dum_DIC - loc_ALK_DIC + &
& ( &
& loc_ALK_DIC*dum_carbconst(icc_k) -
dum_DIC*dum_carbconst(icc_k) - &
& 4.0*loc_ALK_DIC + loc_zed &
& ) &
& /(2.0*(dum_carbconst(icc_k) - 4.0))

loc_H1 =
dum_carbconst(icc_k1)*loc_conc_CO2/loc_conc_
HCO3

loc_H2 =
dum_carbconst(icc_k2)*loc_conc_HCO3/loc_conc_
_CO3

```

increased CO<sub>2</sub> out-gassing  
=> higher atm pCO<sub>2</sub> and weathering @ steady state



~3x  
pre-industrial  
pCO<sub>2</sub>

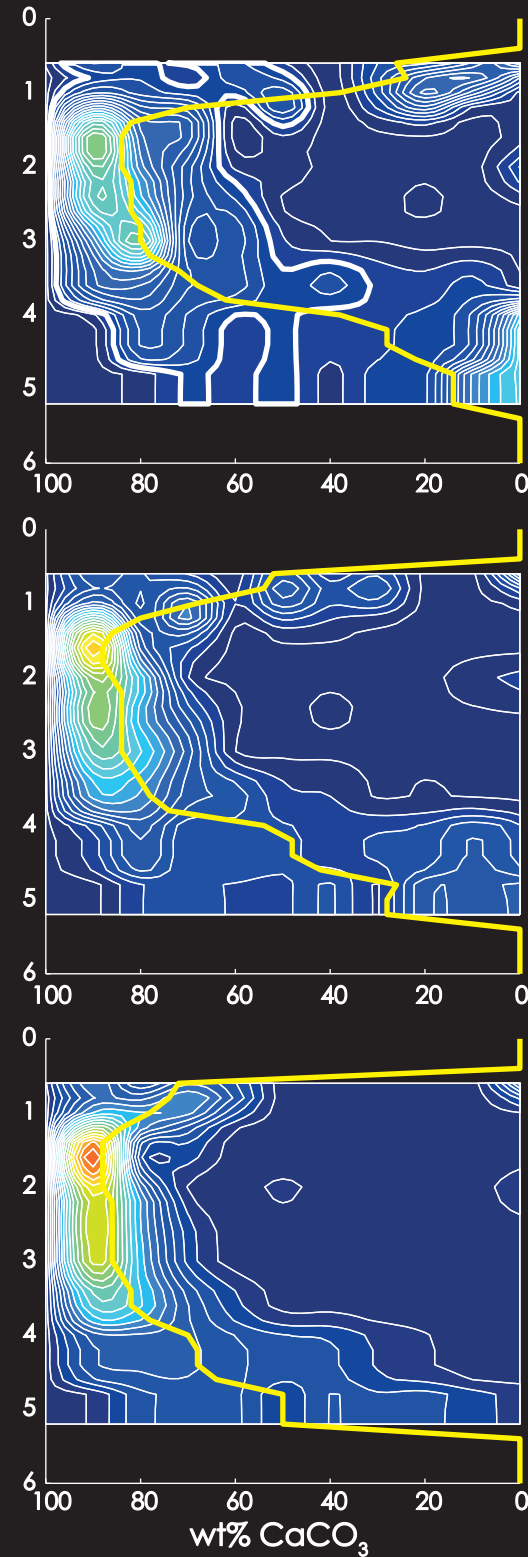
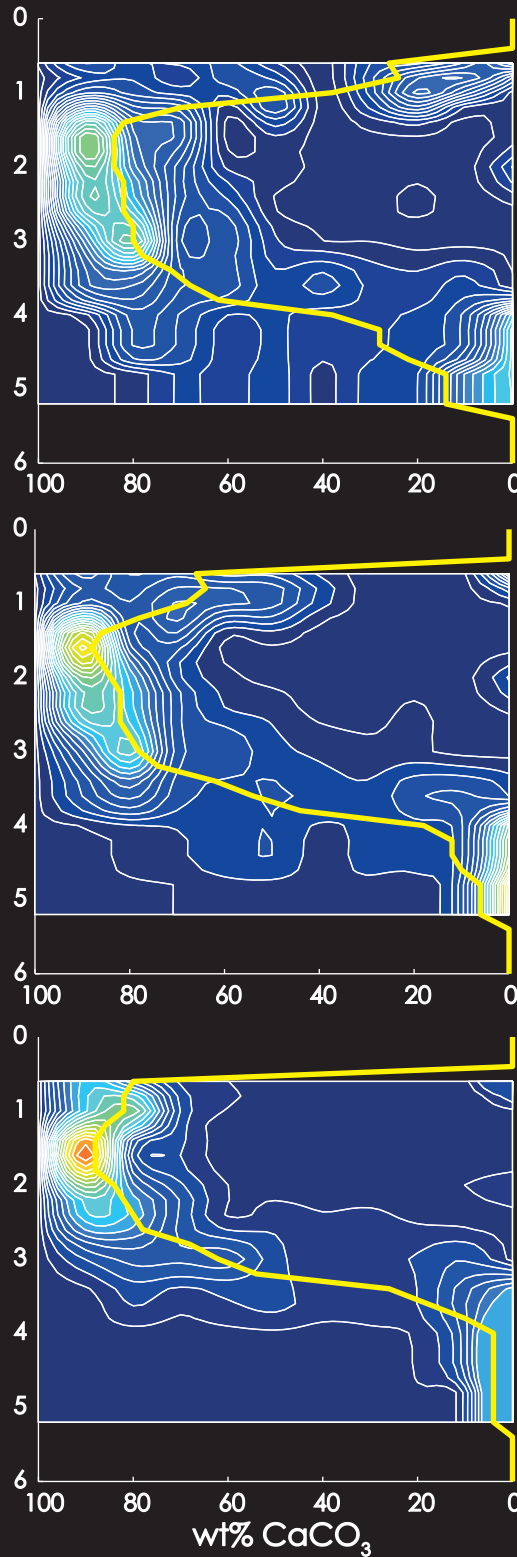
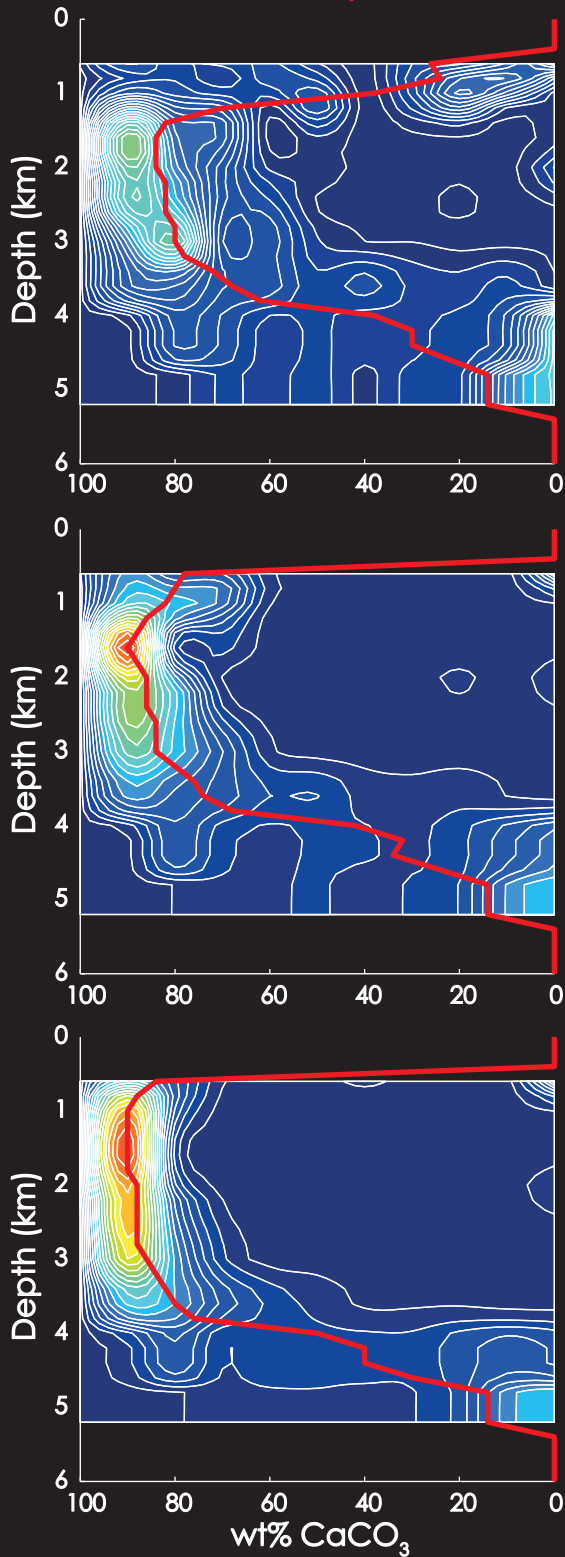
~6x  
pre-industrial  
pCO<sub>2</sub>

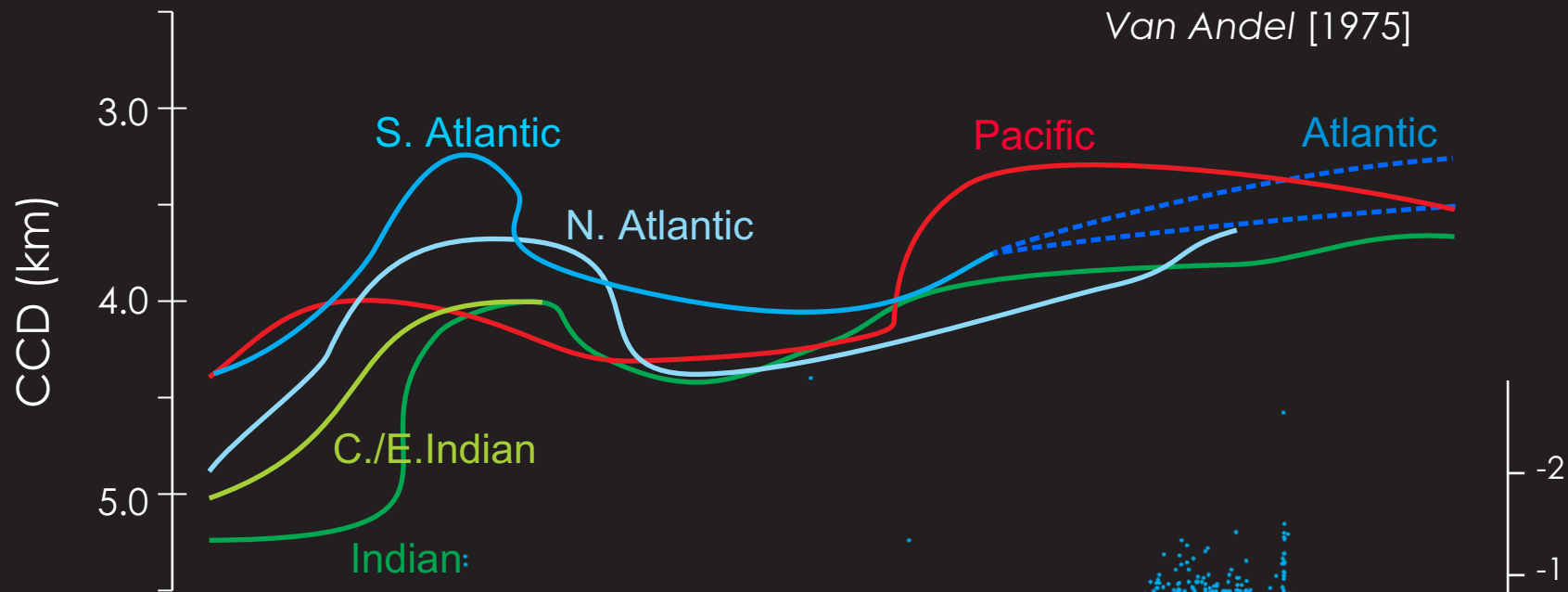
~12x  
pre-industrial  
pCO<sub>2</sub>

variable pCO<sub>2</sub>

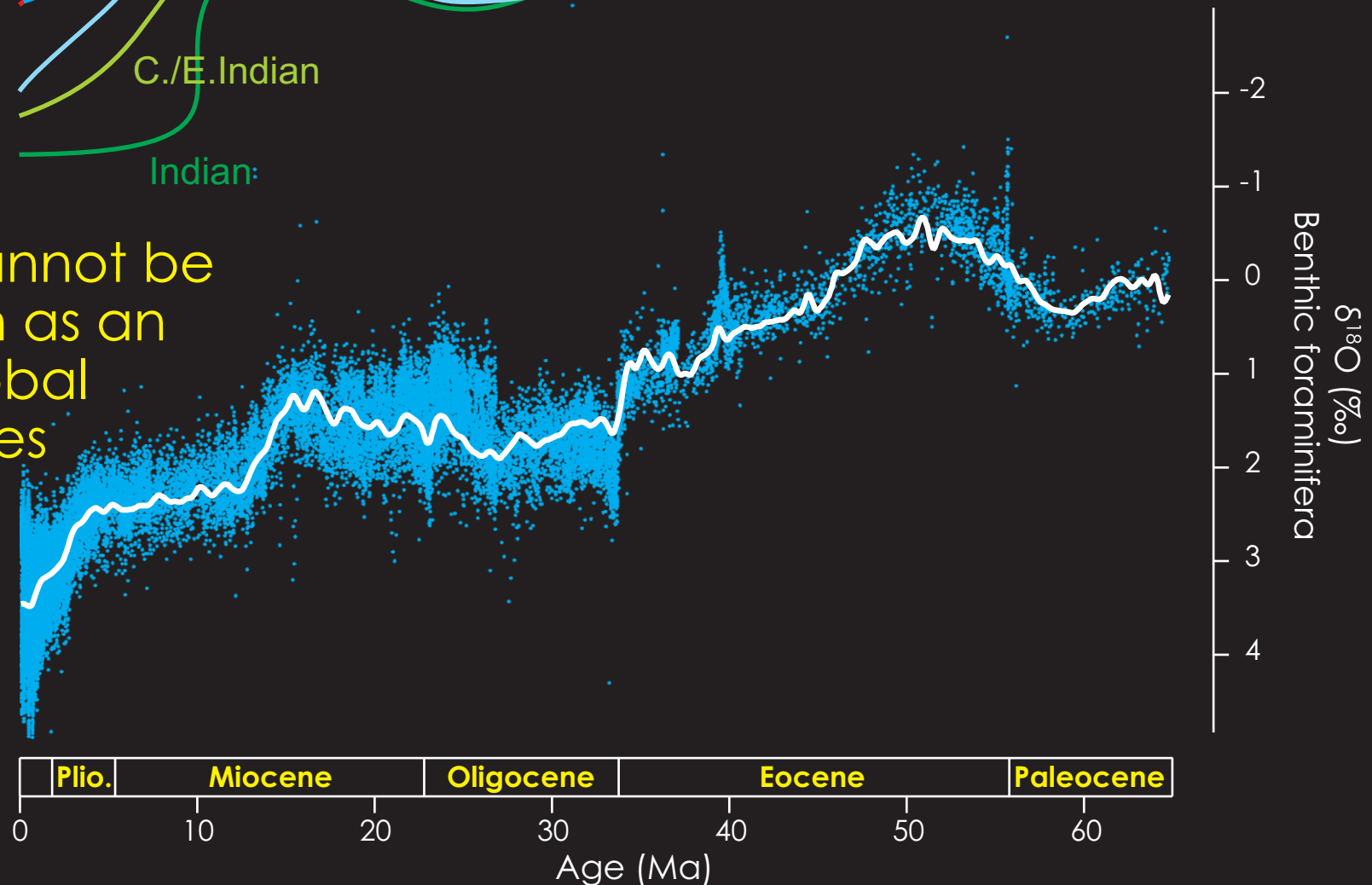
only [DIC]&[ALK] vary

only Temp. & Circulation vary





=> The CCD cannot be used on its own as an indicator of global weathering rates or climate  
#deadproxy



## Thanks to:

*Sarah Greene, Sandy Kirtland Turner, Daniela Schmidt [Bristol]*

*Ellen Thomas [Yale]*

*Heiko Pälike [Bremen]*

The Royal Society

Natural Environmental Research Council (NE/H023852/1 – ‘Evolution of Carbon Cycle Dynamics’)

