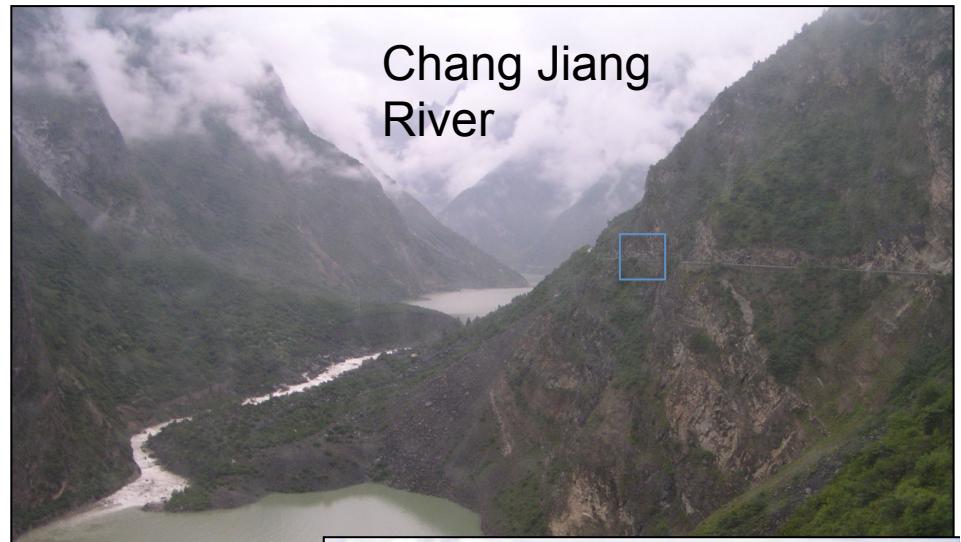
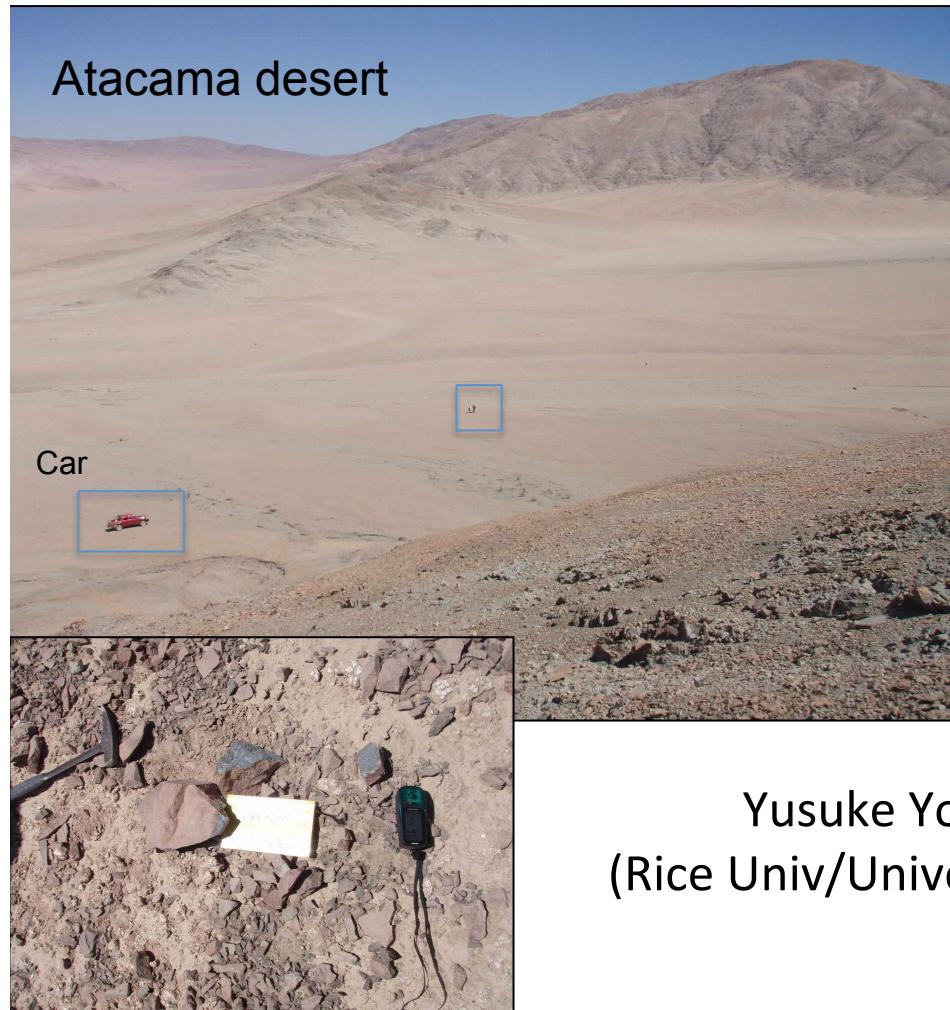
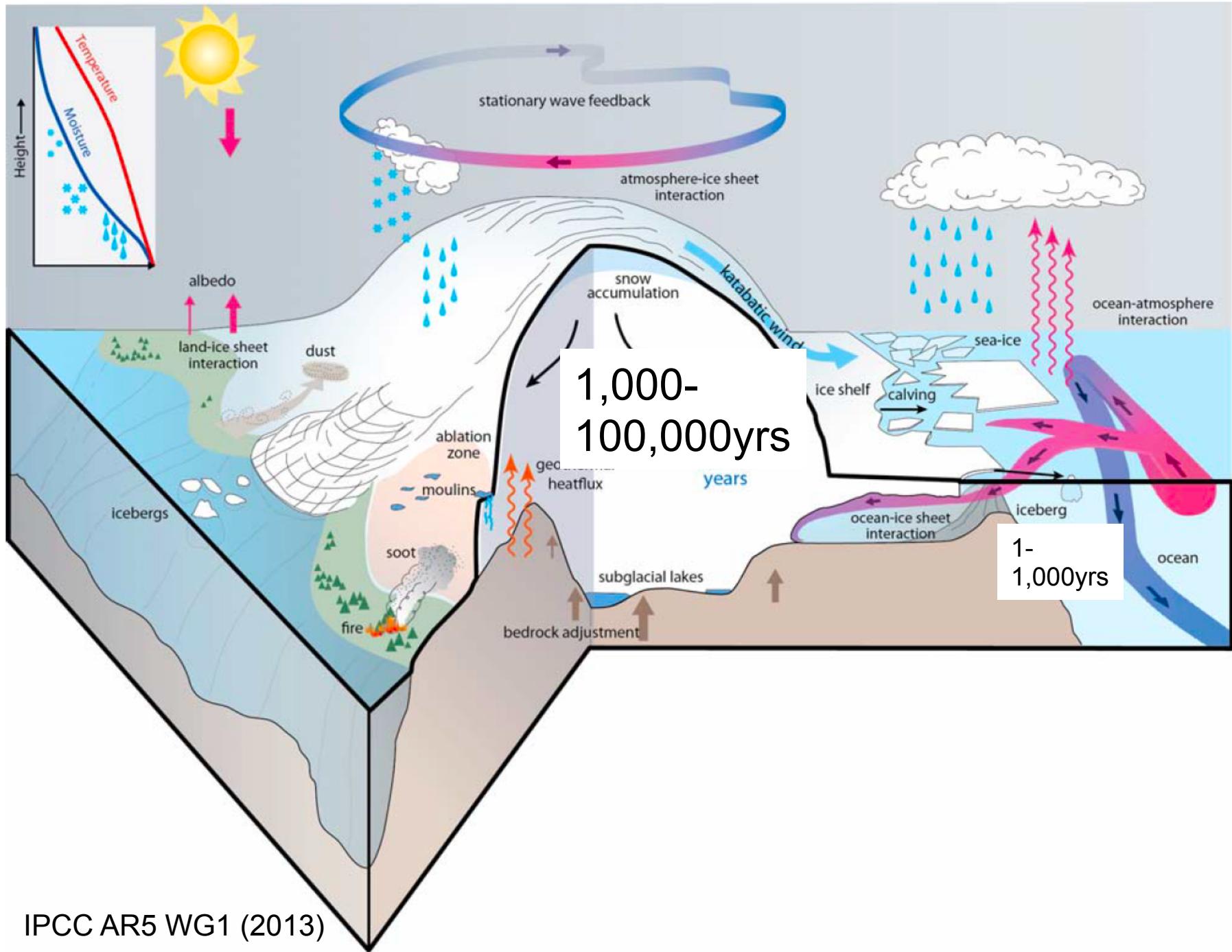


# Paleoclimate records, biogeochemistry, erosion and weathering

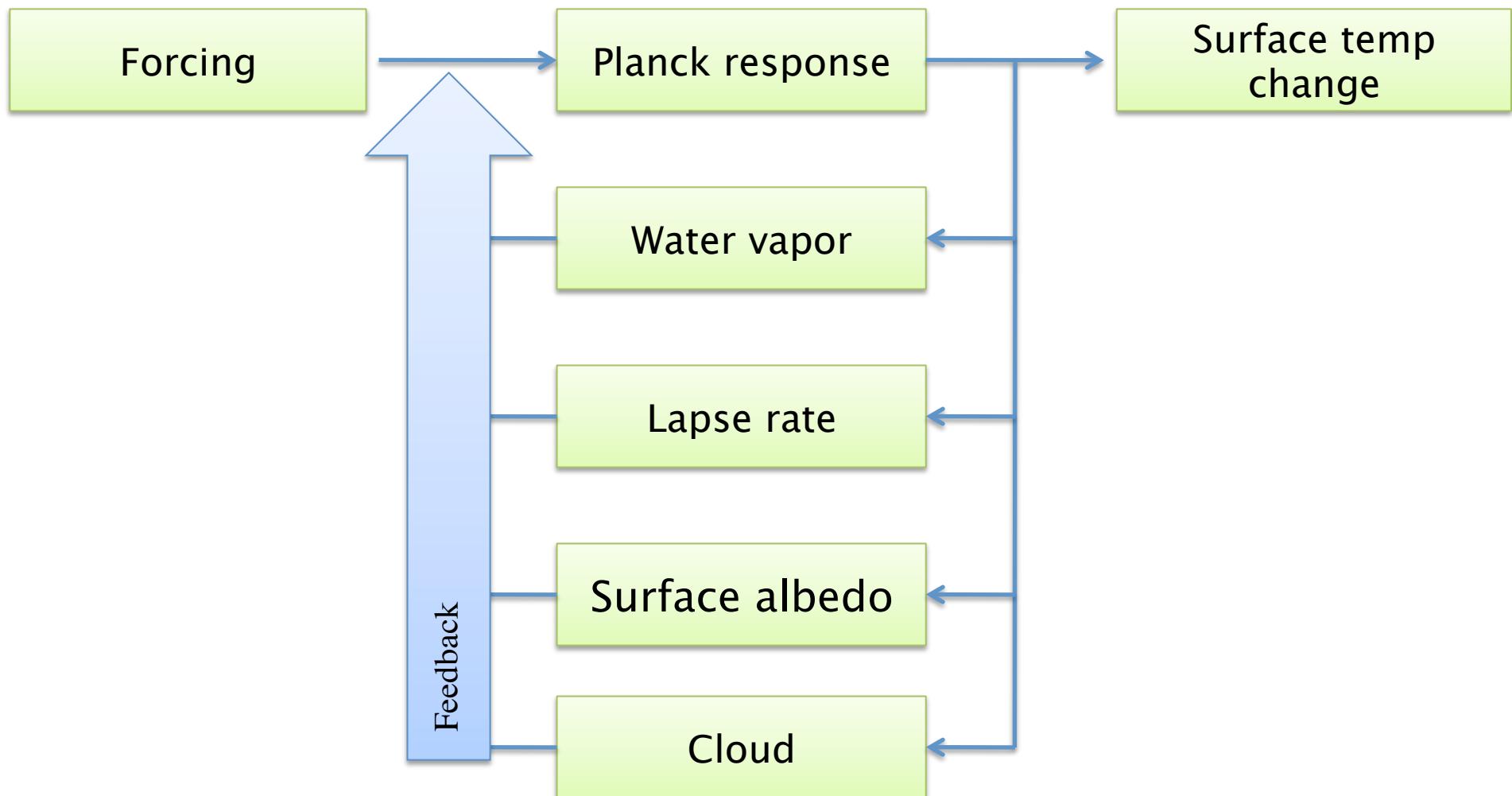


Yusuke Yokoyama  
(Rice Univ/University of Tokyo)



IPCC AR5 WG1 (2013)

# Climate feedback loop



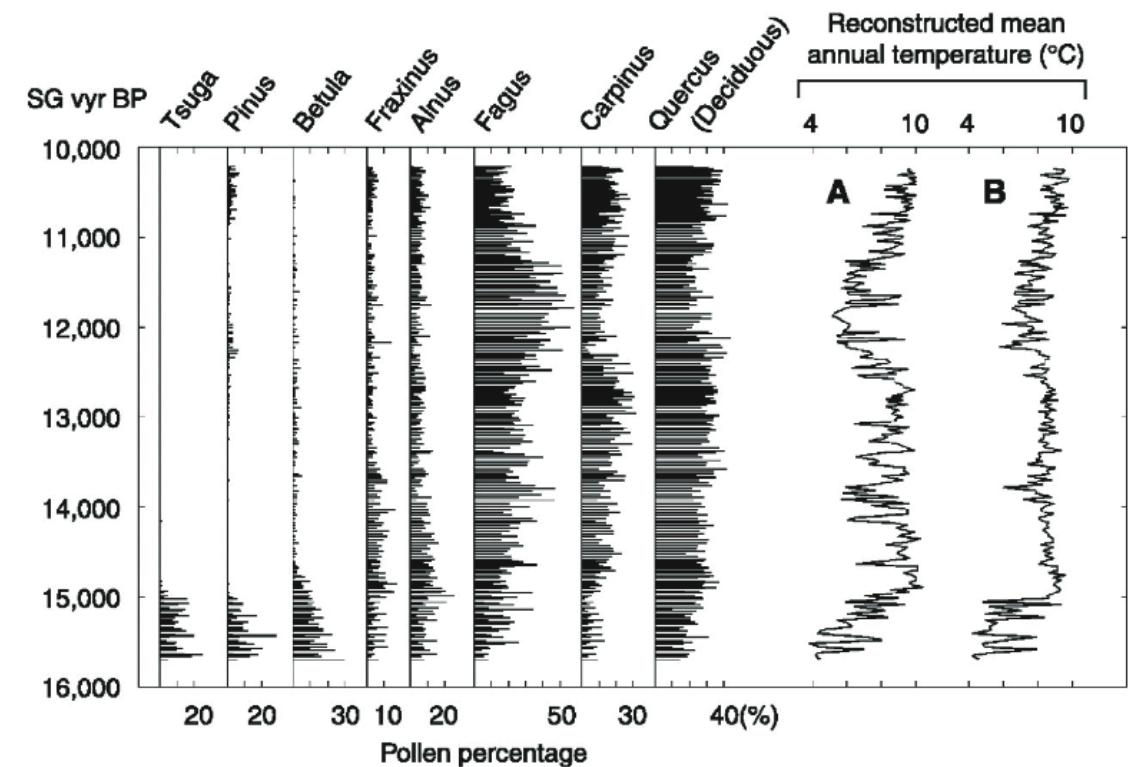
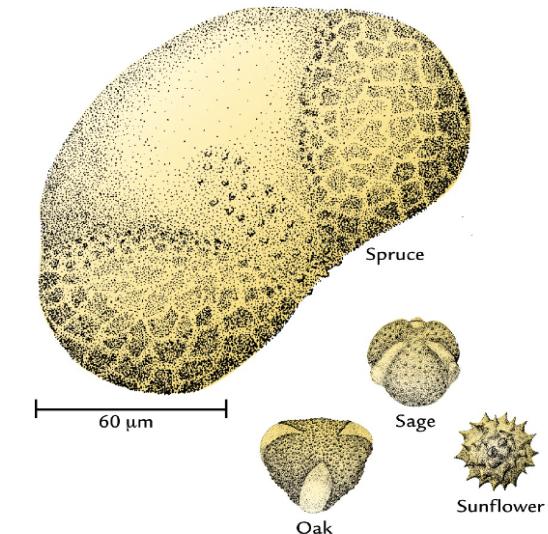
# Background and History of Paleoclimatology (1)



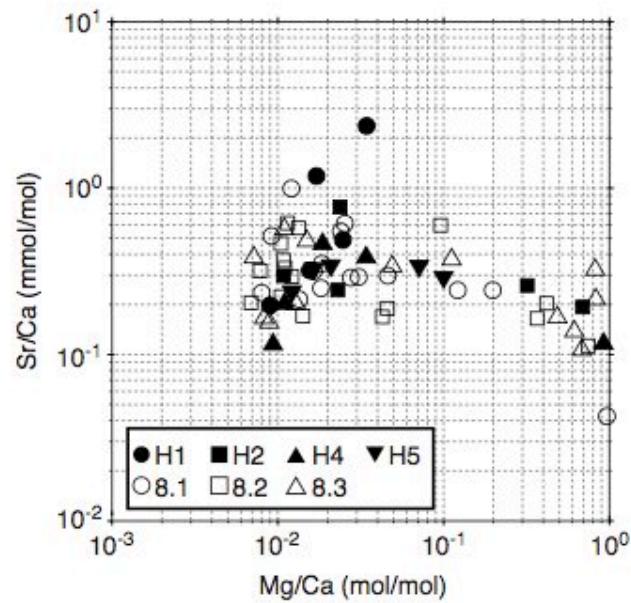
Planktonic foraminifera

- 1a-c: *Globorotalia truncatulinoides*
- 2a-c: *Globigerinoides sacculifer*
- 3a-c: *Globorotalia scitula*
- 4a-c: *Globigerinoides ruber*

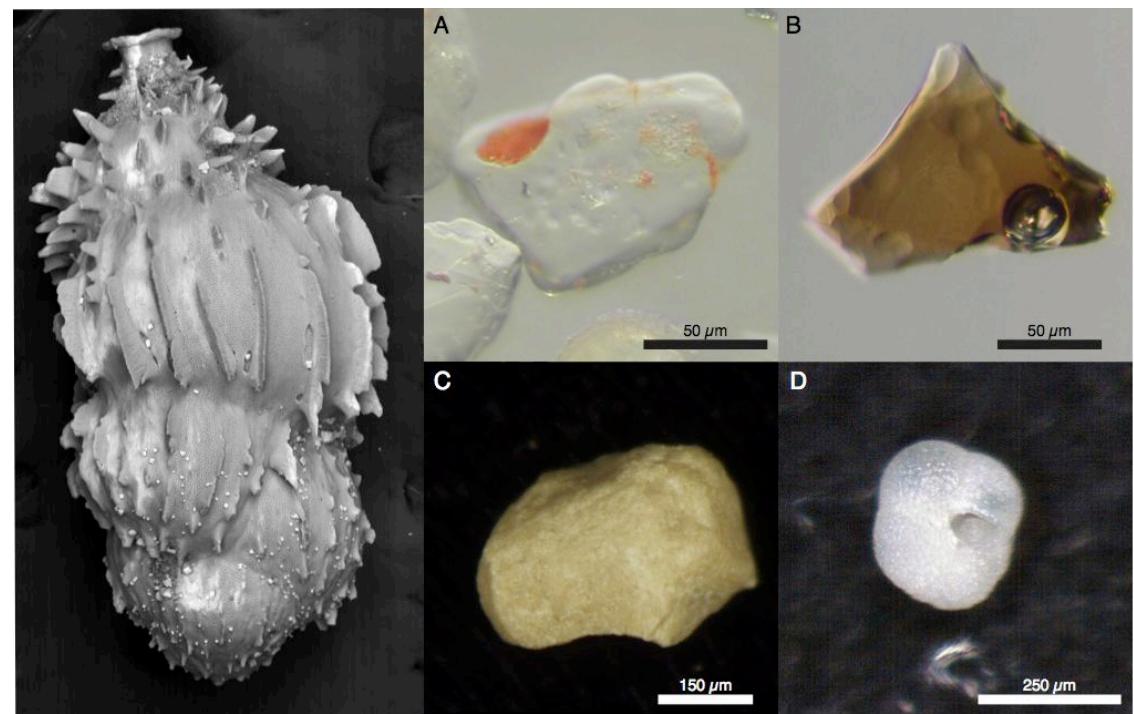
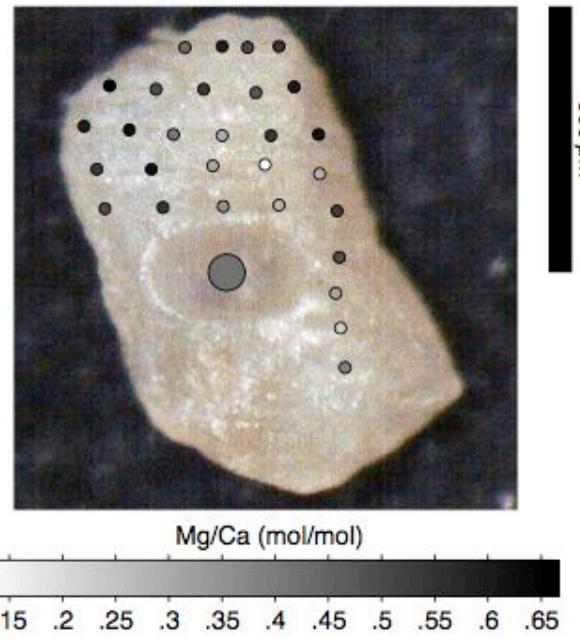
Scale bar=100μm.



# Various climate proxies



B: Single Grain



Obrochta, Yokoyama et al. (2014 EPSL)

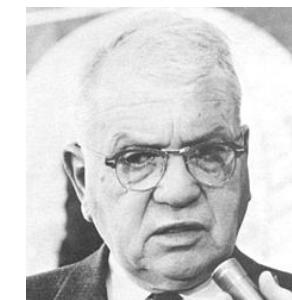
# Background and History of Paleoclimatology (2)

→ Louis Agassiz (1840): Realizing “ice age”



[http://en.wikipedia.org/wiki/Louis\\_Agassiz](http://en.wikipedia.org/wiki/Louis_Agassiz)

→ Harold Urey (1947): The thermodynamic properties of isotopic substances



[http://en.wikipedia.org/wiki/Harold\\_Urey](http://en.wikipedia.org/wiki/Harold_Urey)

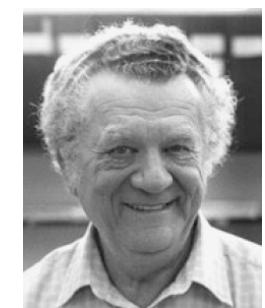
★ Prediction of temperature dependence of oxygen isotopic fractionation between ( $H_2O$ ) and carbonate ( $CaCO_3$ )

★ Proposing  $\delta^{18}O$  as a paleothermometer

→ Samuel Epstein (Urey's post-doc)

★ Cultured bivalves in different temperature setting

$$\star \Delta = \delta^{18}O_{cal} - \delta^{18}O_{water} = 15.36 - 2.673(16.52 + T)^{0.5}$$



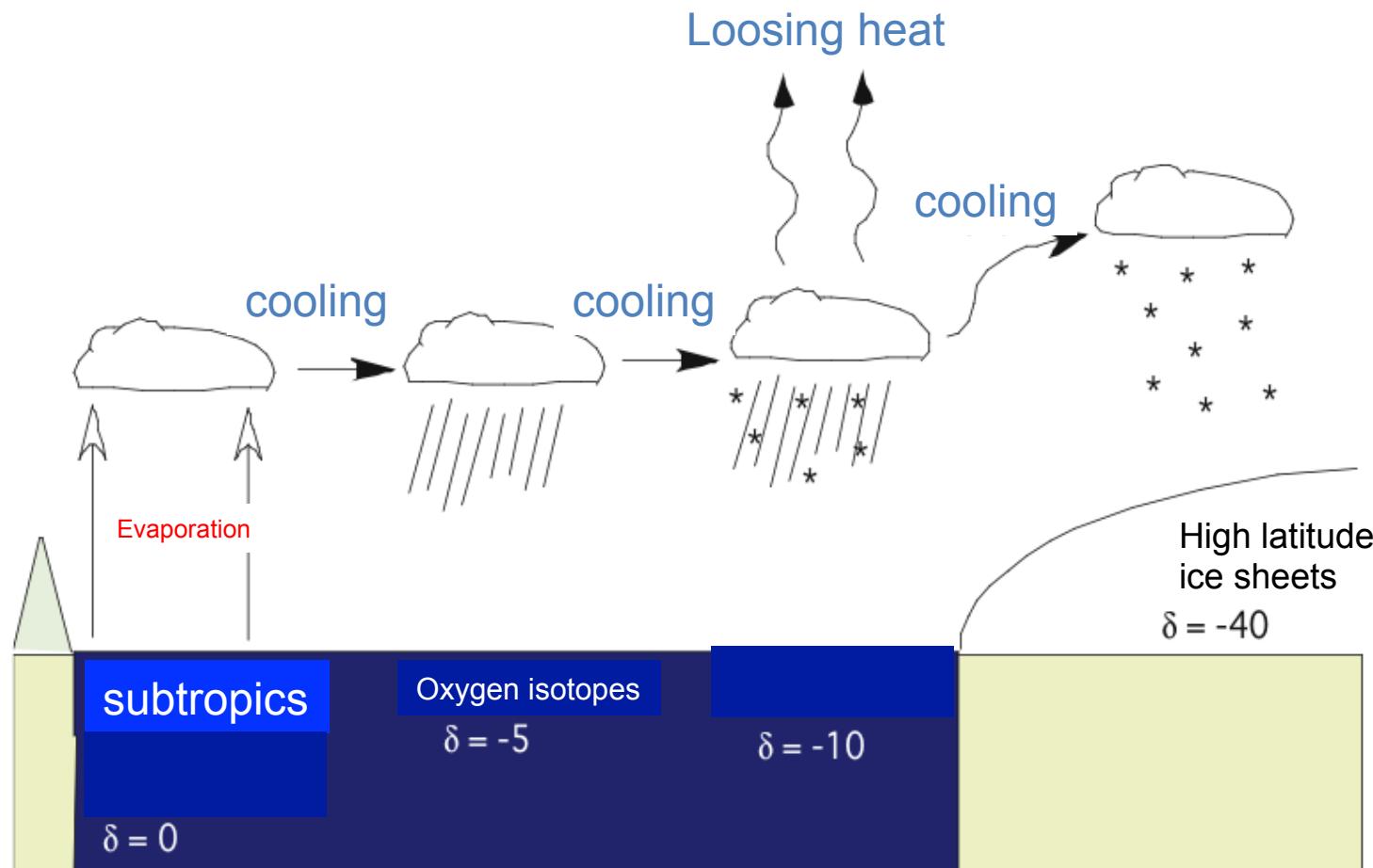
<http://caltech.library.caltech.edu/4030/>

# Summary of major Paleotemperature techniques

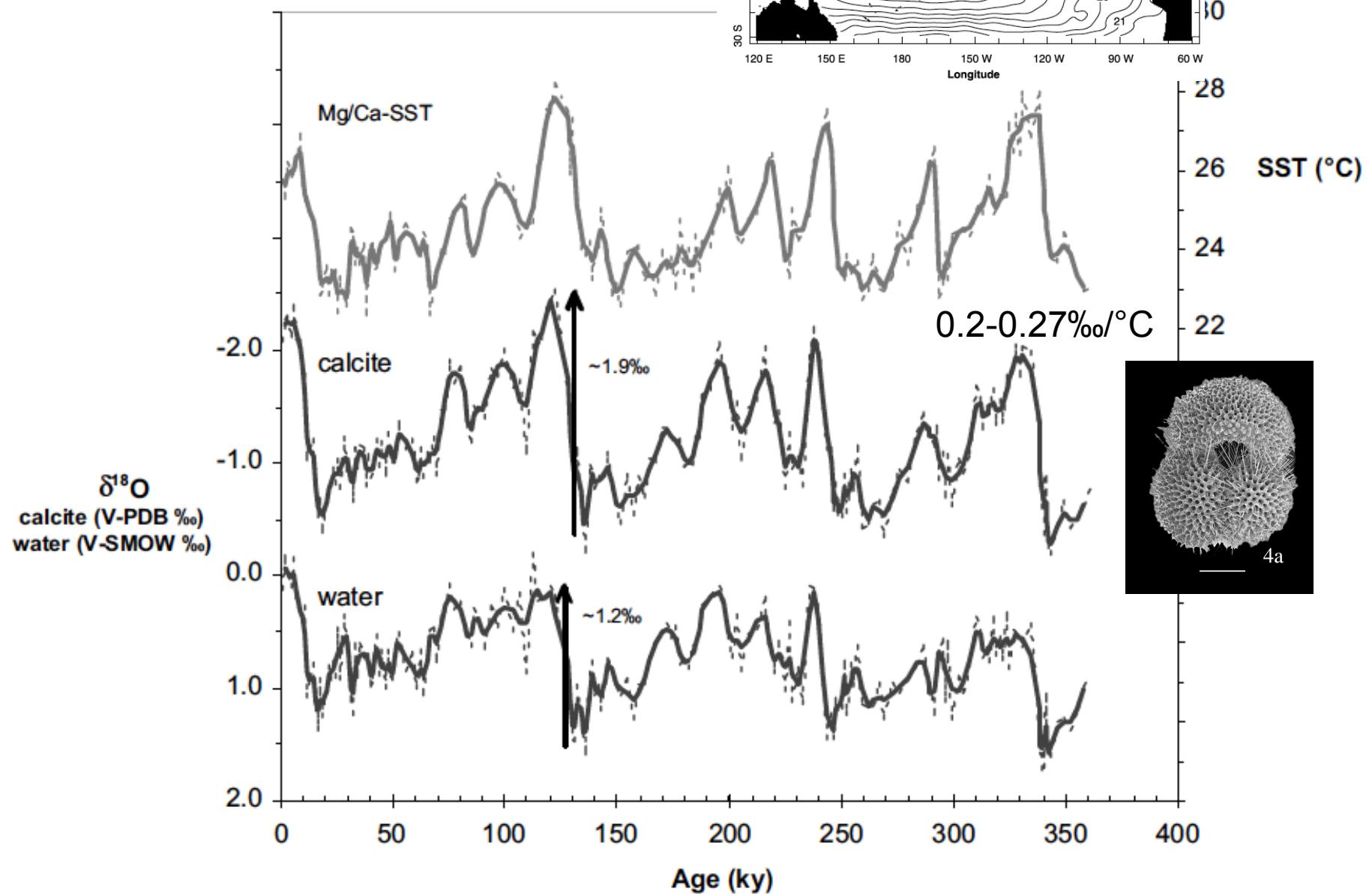
	<i>Phases</i>	<i>Sensitivity (per °C)</i>	<i>Estimated SE</i>	<i>Major secondary effects</i>	<i>Time scale<sup>a</sup></i>
Oxygen Isotopes	Foraminifera	0.18–0.27‰	0.5 °C if $\delta^{18}\text{O}$ -sw is known	Effect of $\delta^{18}\text{O}$ -sw	0–100 Ma
	Corals	~0.2‰	0.5 °C if $\delta^{18}\text{O}$ -sw is known	Kinetic effects Effect of $\delta^{18}\text{O}$ -sw	0–130 ka
	Opal			Effect of $\delta^{18}\text{O}$ -sw	0–30 ka
Mg/Ca	Foraminifera	9 ± 1%	~1 °C	Dissolution Secular Mg/Ca variations (>10 Ma)	0–40 Ma
	Ostracodes	~9%	~1 °C	Dissolution? Calibration	0–3.2 Ma
Sr/Ca	Corals	−0.4 to −1.0‰	0.5 °C?	Growth effects Secular Sr/Ca changes (>5 ka)	0–130 ka
Ca isotopes	Foraminifera	0.02–0.24‰	unknown	Species effects, calcification	0–125 ka
Alkenone unsaturation index <sup>b</sup>	Sediment organics	0.033 (0.023–0.037) in U <sub>37</sub> <sup>Kd</sup>	~1.5 °C (global calib.)	Transport, species variation	0–3 Ma
Faunal transfer functions <sup>c</sup>	Foraminifera, Radiolaria, Dinoflagellates	NA	1.5 °C	Ecological shifts	0–?

<sup>a</sup> Timescale over which the technique has been applied. <sup>b</sup> Chapter 6.15. <sup>c</sup> (Imbrie and Kipp, 1971) <sup>d</sup> (Müller *et al.*, 1998 and Pelejero and Calvo, 2003).

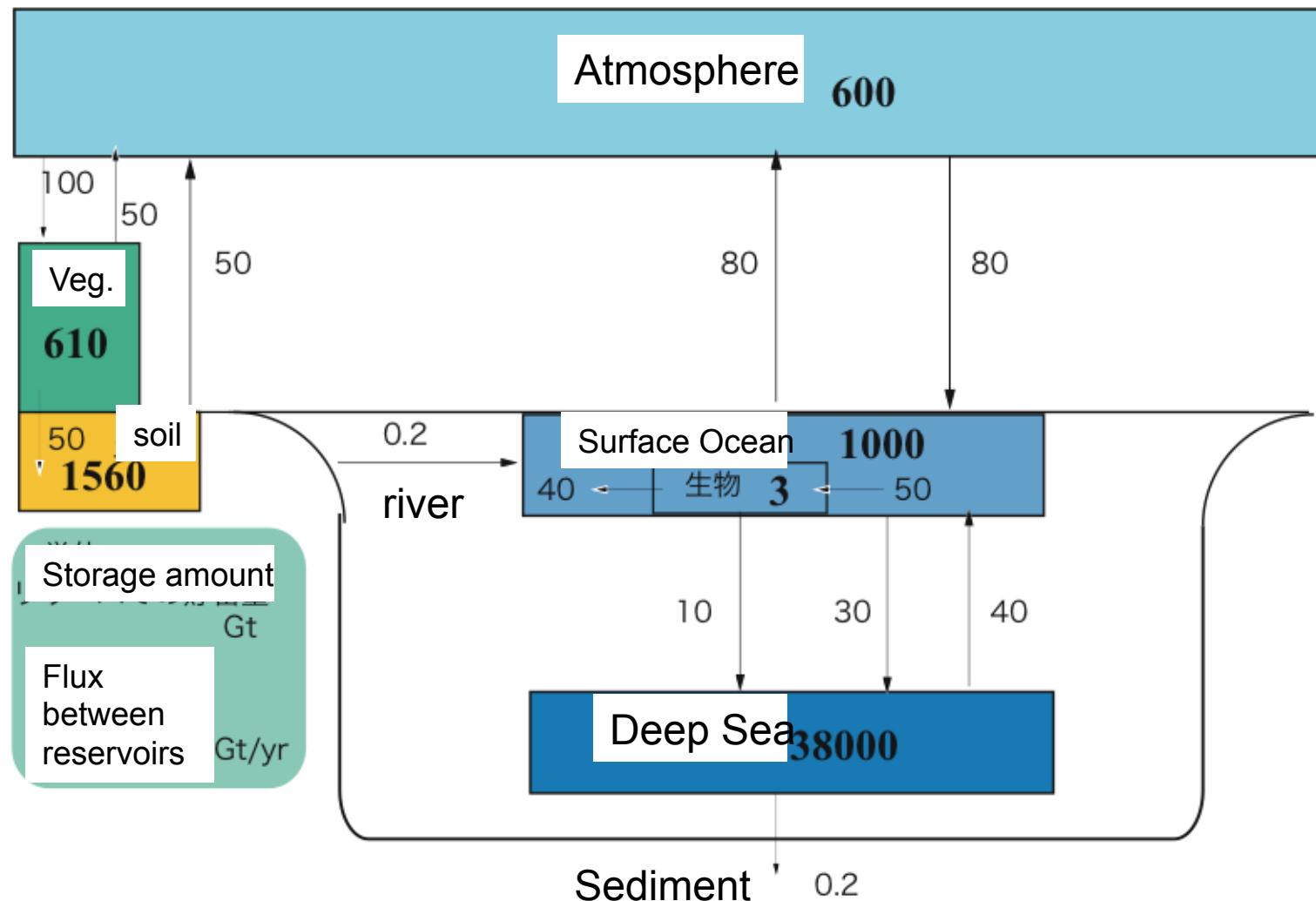
# Ocean and ice core oxygen isotopes



# Multiple proxies approach

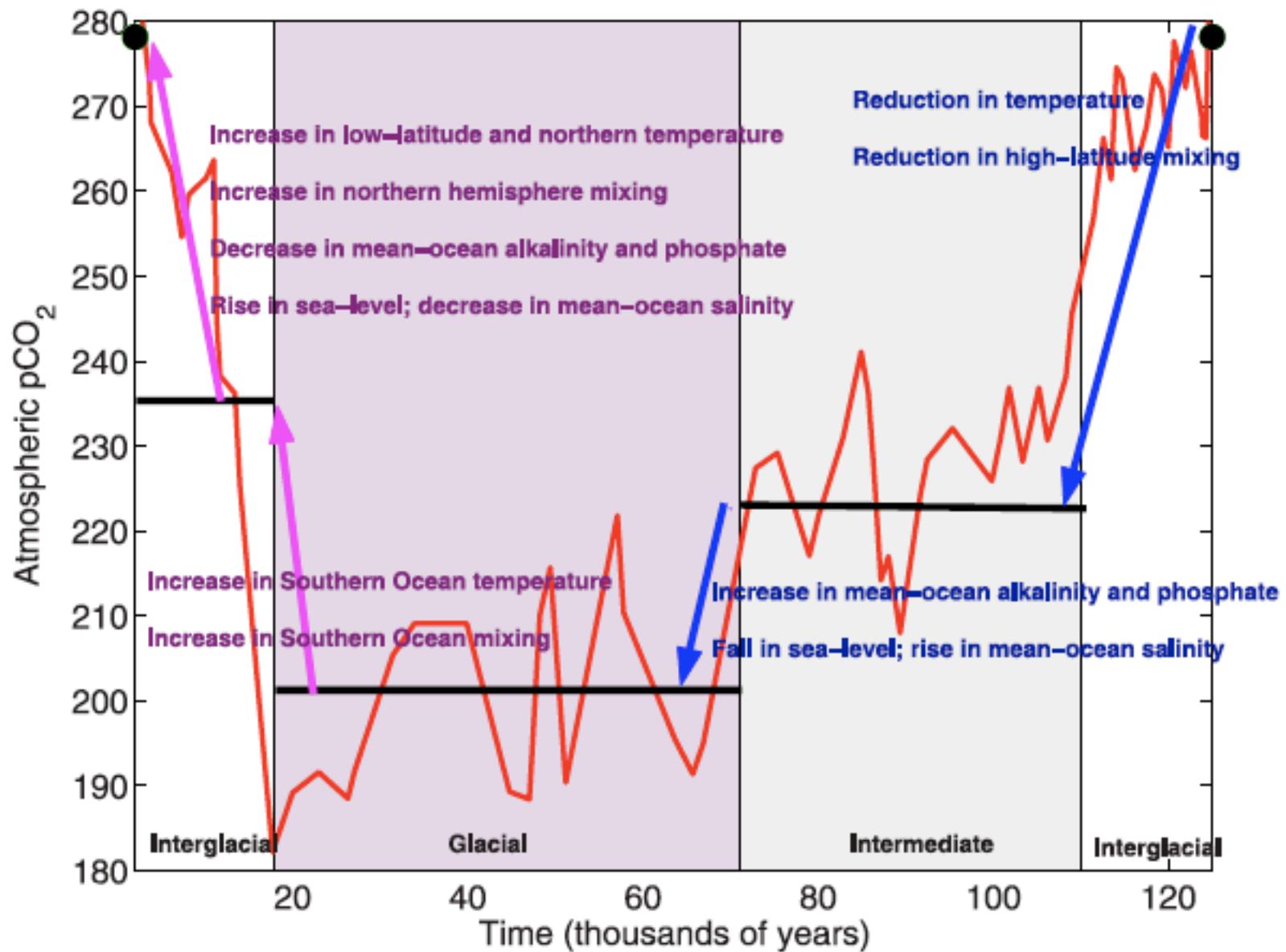


# Present day carbon cycle



Data from National Research Council

# Glacial-Interglacial pCO<sub>2</sub> change and potential mechanisms



(Peacock et al., 2006)

## Glacial/interglacial carbon cycling



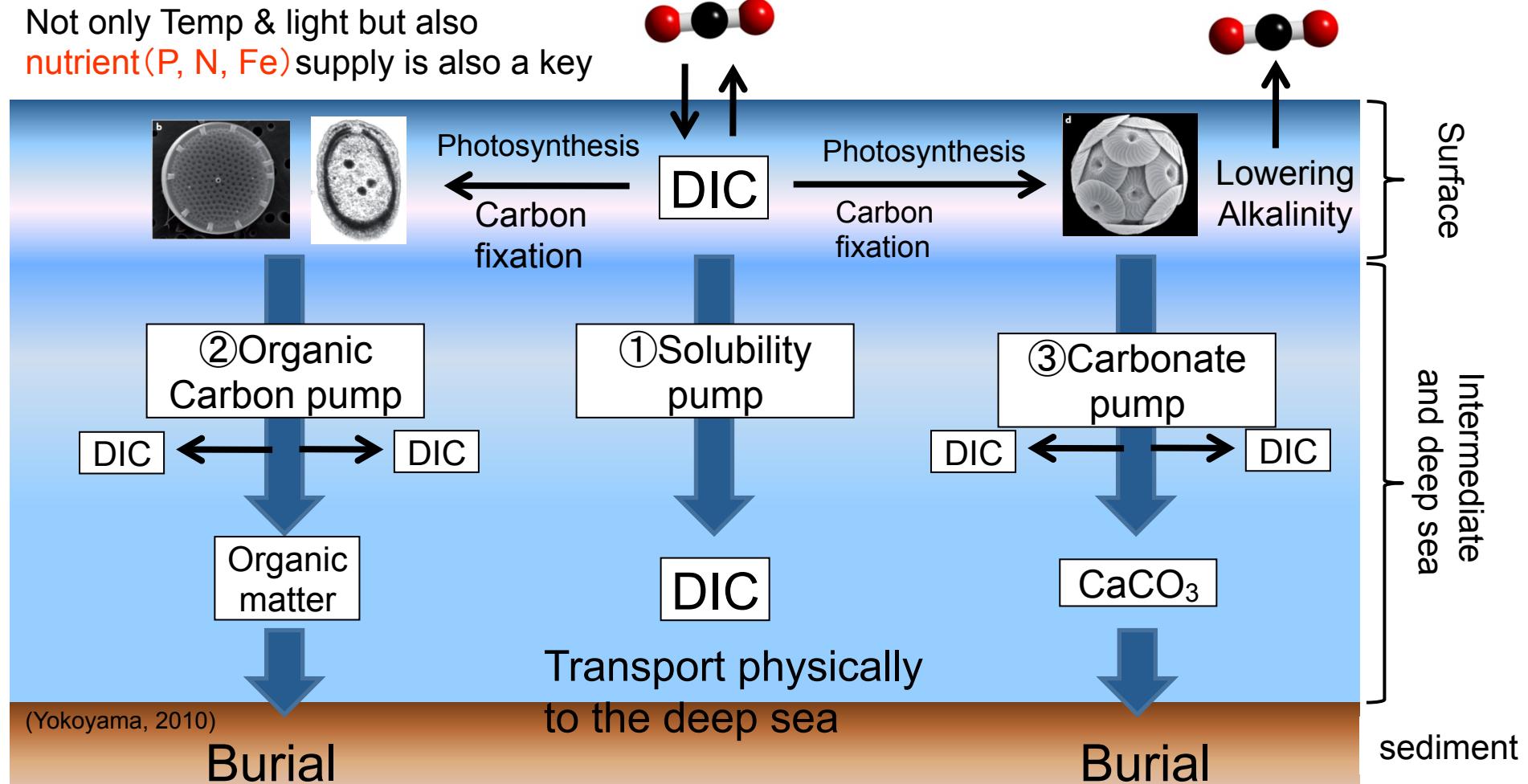
3 pumps are important to deliver carbon to **Deep sea** (Maximum reservoir of Carbon in the surface of the Earth)



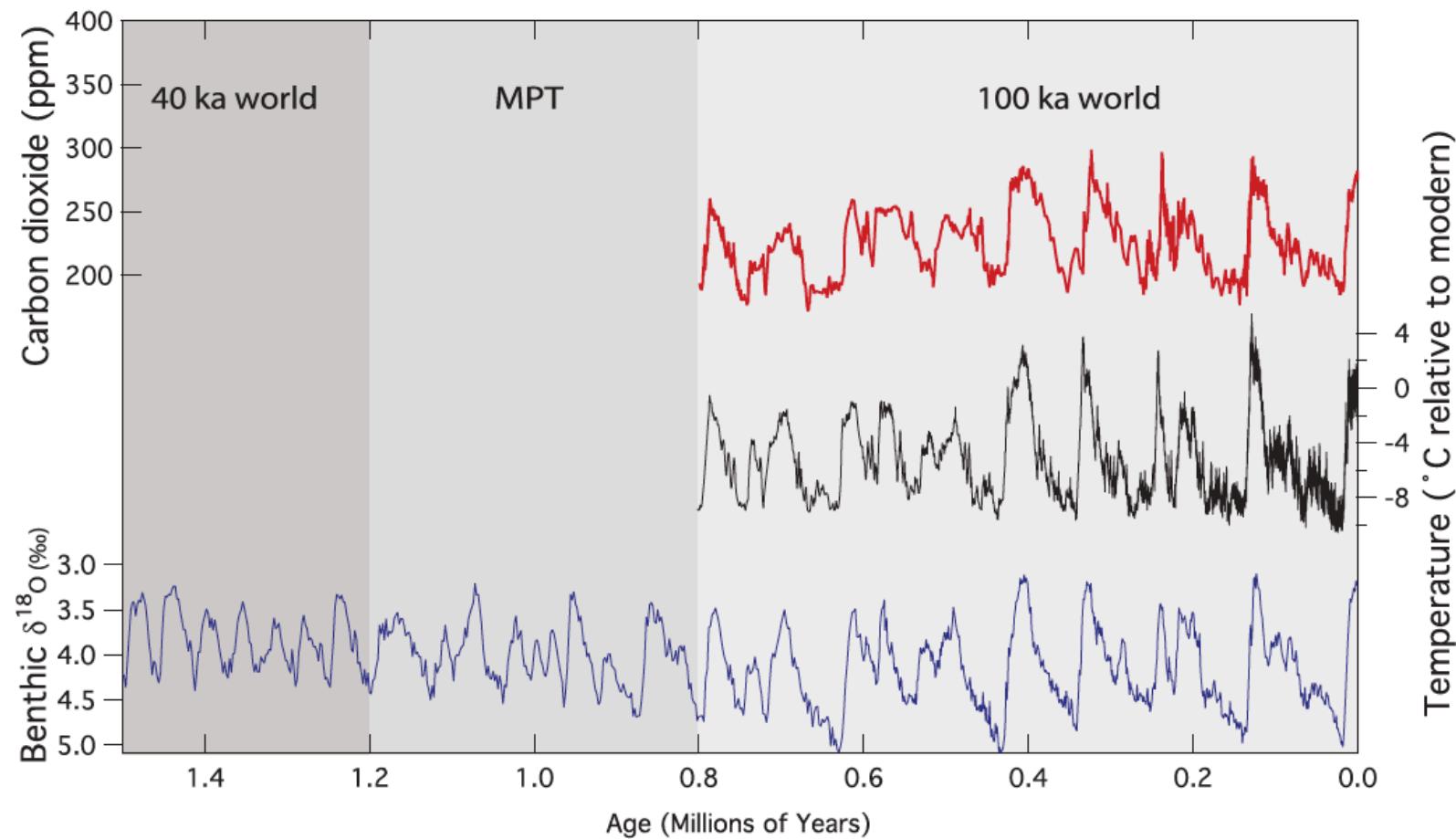
- ① Solubility
- ② Organic Carbon
- ③ Carbonate

Gas exchange: SST, SSS, Wind, Sea ice

Not only Temp & light but also nutrient (P, N, Fe) supply is also a key

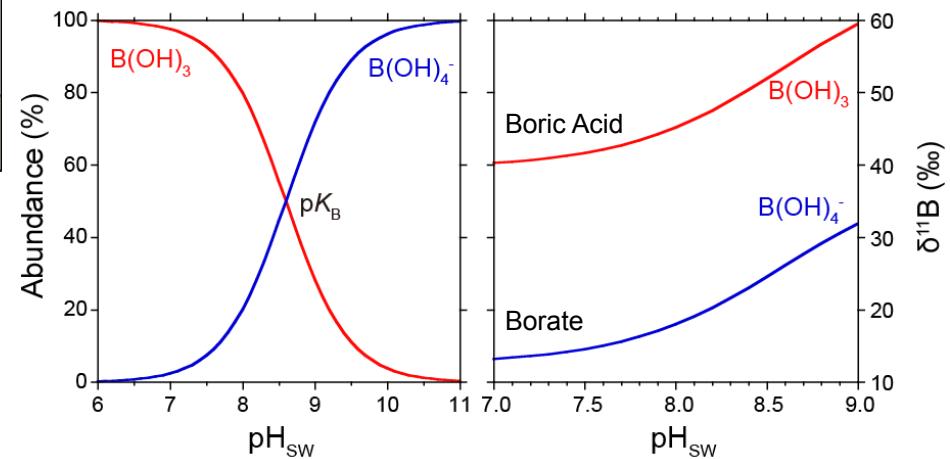
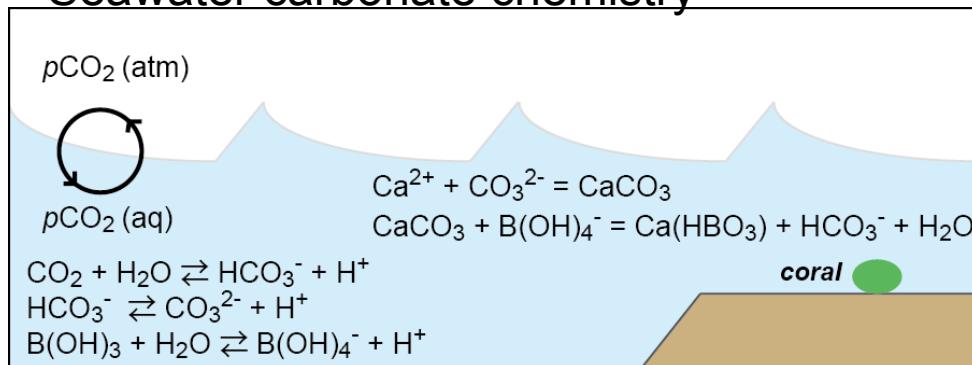


## Paleoclimate record from Ice core and Deep Sea



# Boron isotopes as an seawater pH indicator

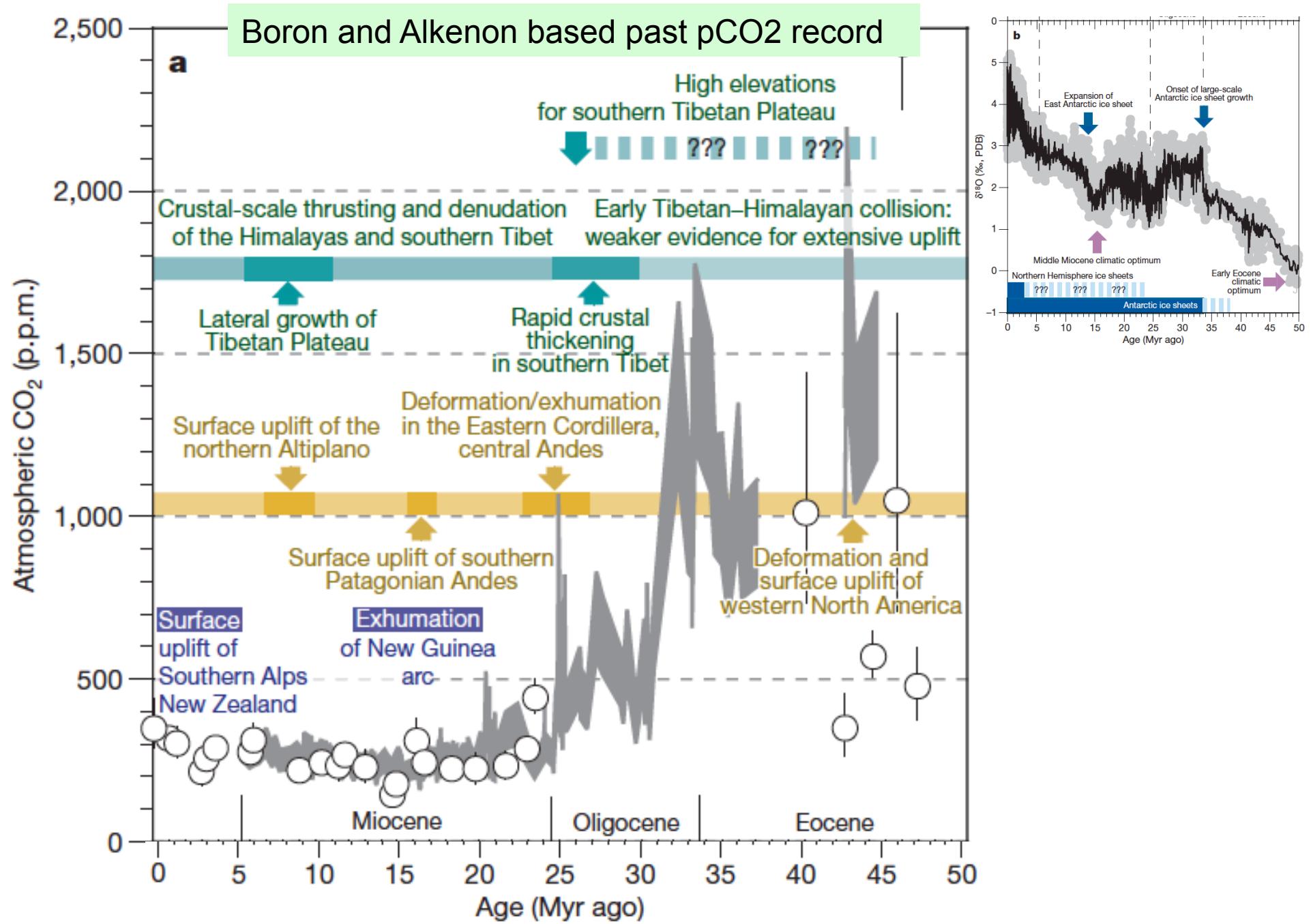
## Seawater carbonate chemistry



$$\delta^{11}\text{B} = \left( \frac{(^{11}\text{B} / ^{10}\text{B})_{\text{sample}}}{(^{11}\text{B} / ^{10}\text{B})_{\text{std}}} - 1 \right) * 10^3$$

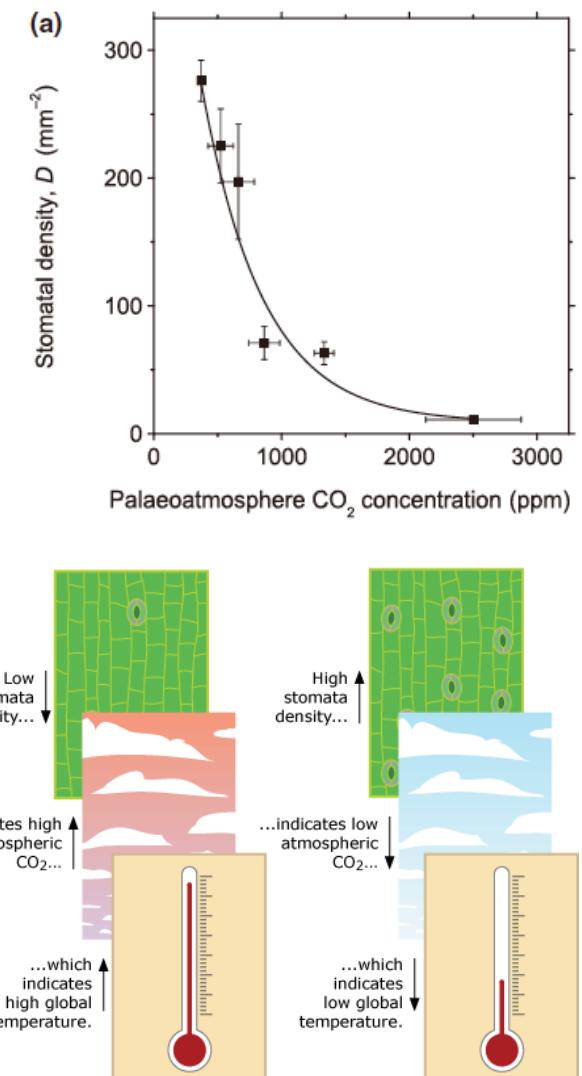
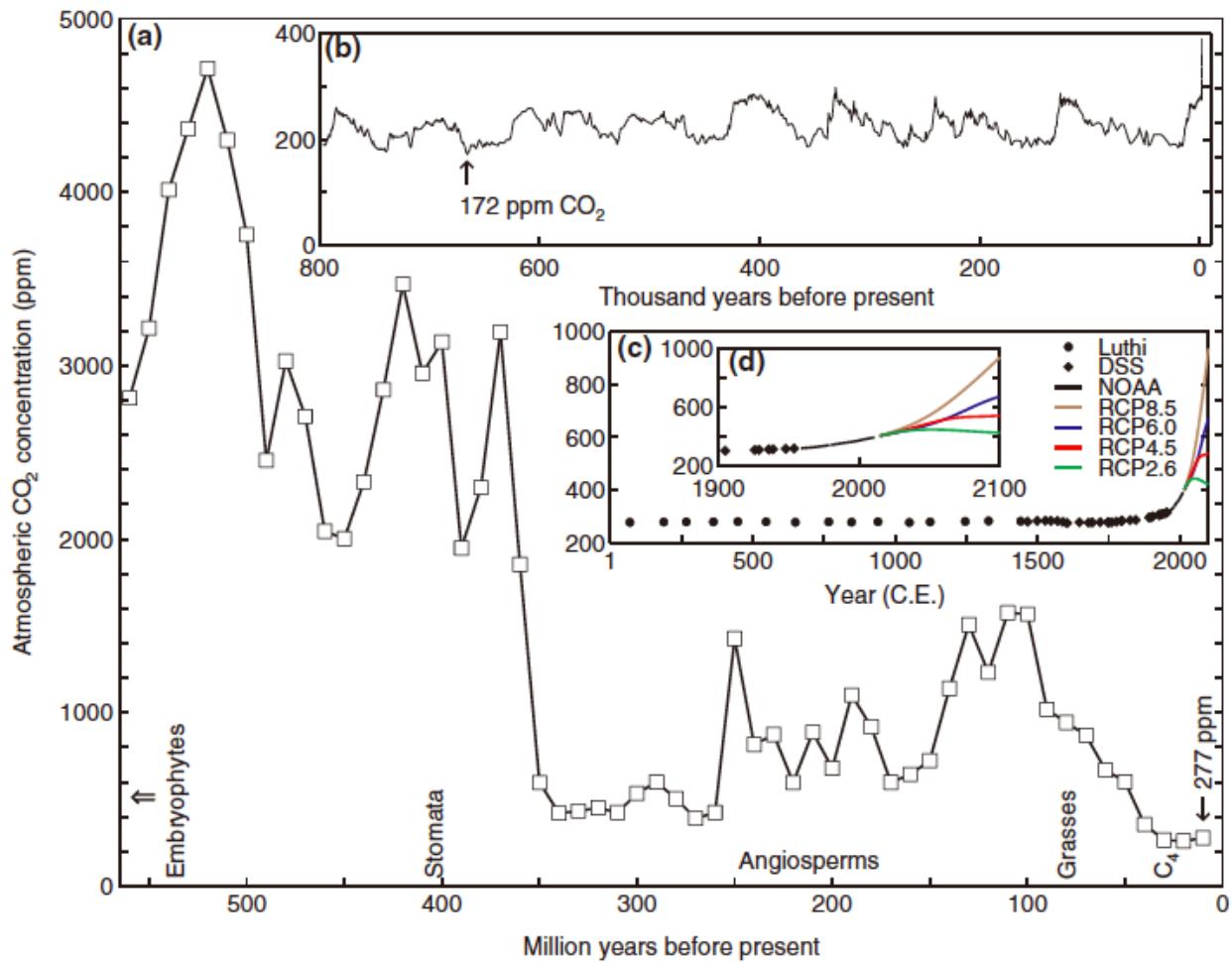
Only Borate,  $\text{B(OH)}_4^-$ , is incorporated into coral skeleton

$$\text{pH} = \text{p}K_B - \log \left( \frac{\delta^{11}\text{B}_{\text{SW}} - \delta^{11}\text{B}_{\text{coral}}}{\alpha_{3-4} * \delta^{11}\text{B}_{\text{coral}} - \delta^{11}\text{B}_{\text{SW}} + 10^3 * (\alpha_{3-4} - 1)} \right)$$



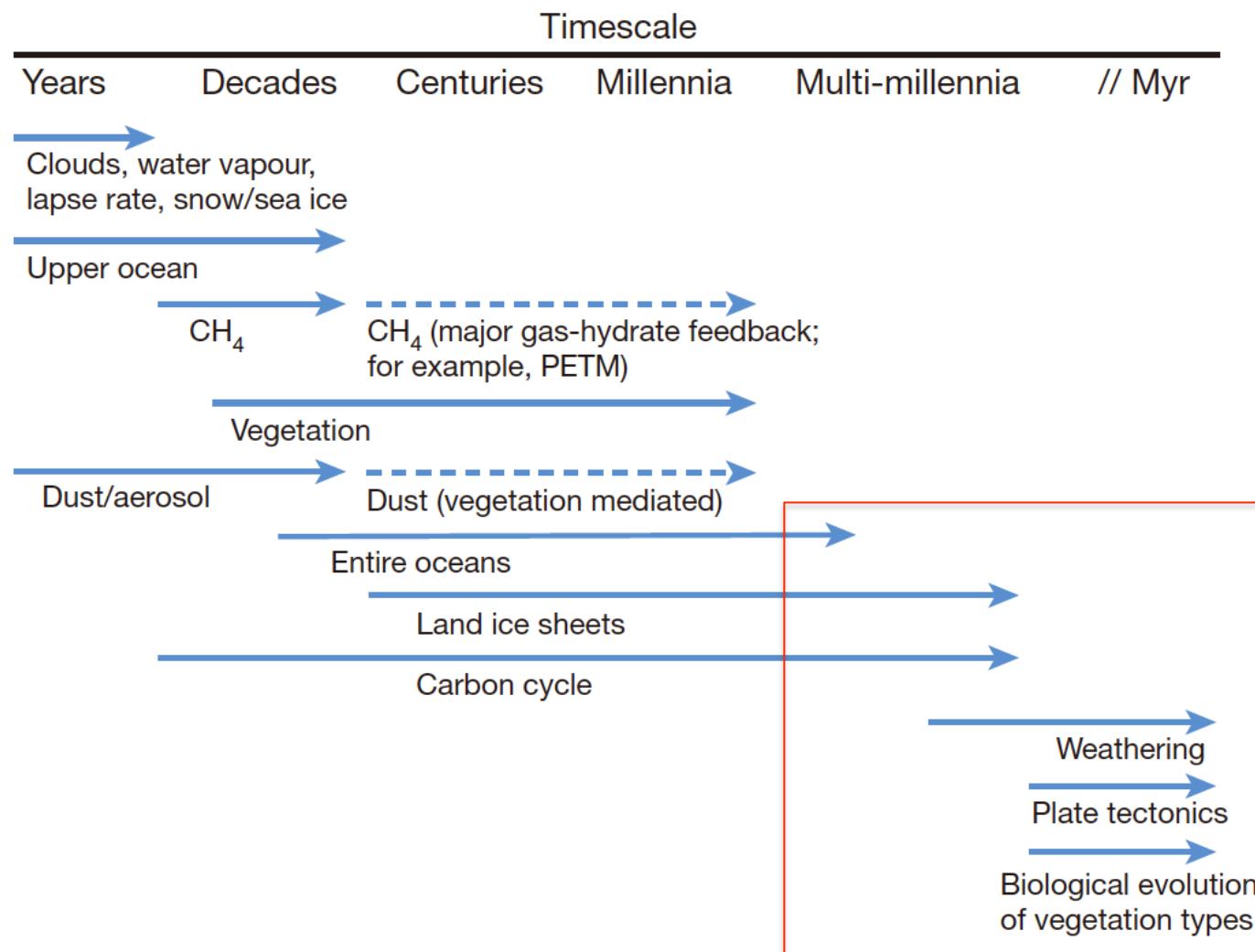
(Pagani et al. 2009 Nature)

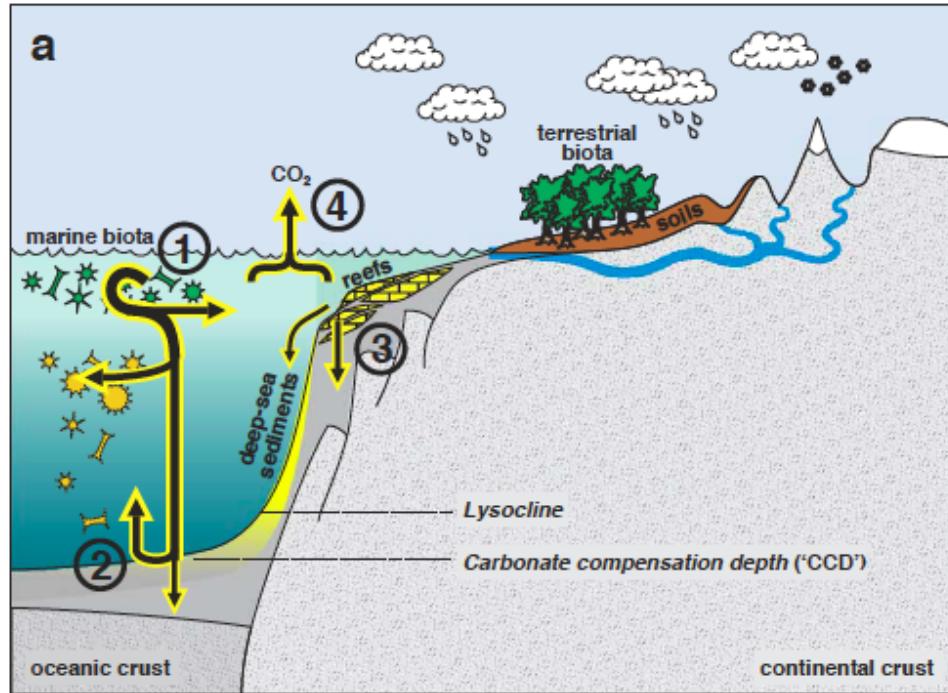
# Atmospheric CO<sub>2</sub> and plants



[http://evolution.berkeley.edu/evolibrary/search/imagedetail.php?id=372&topic\\_id=&keywords=](http://evolution.berkeley.edu/evolibrary/search/imagedetail.php?id=372&topic_id=&keywords=)

(Franks et al. 2013 New Phytologist)





## Sinks of Carbon Cycle

1 Carbonate precipitation by biomineralization



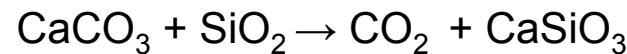
2 Carbonate dissolution in deep sea

3 Carbonate precipitation by coral reefs

4 CO<sub>2</sub> release due to carbonate precipitation

5  $\text{CO}_2 + \text{H}_2\text{O} + \text{CaCO}_3 \rightarrow \text{Ca}^{2+} + 2\text{HCO}_3^-$

6 Thermal breakdown of Carbonate

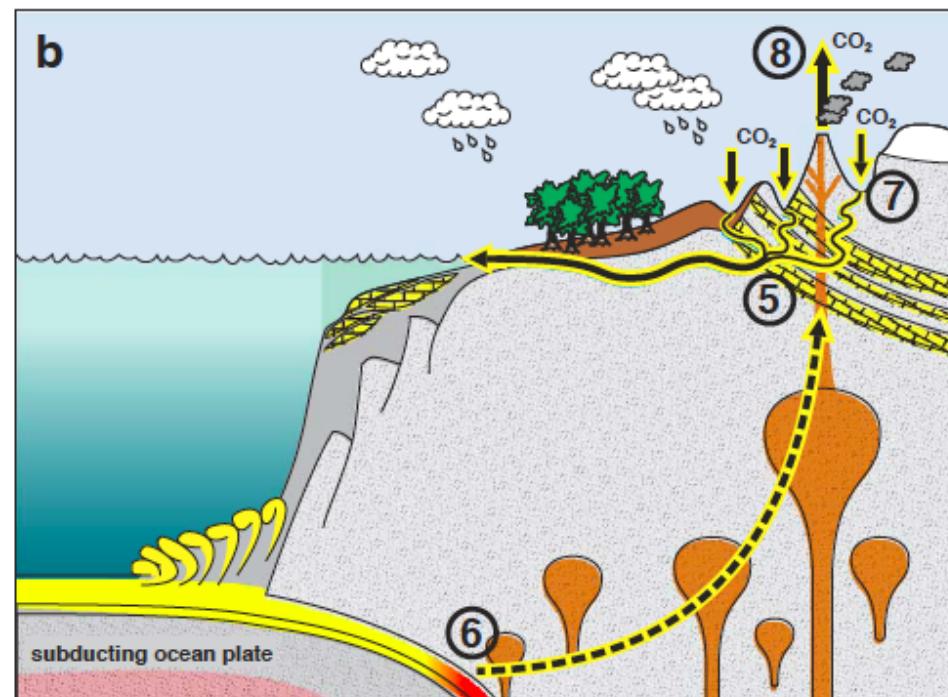


7 Silicate weathering

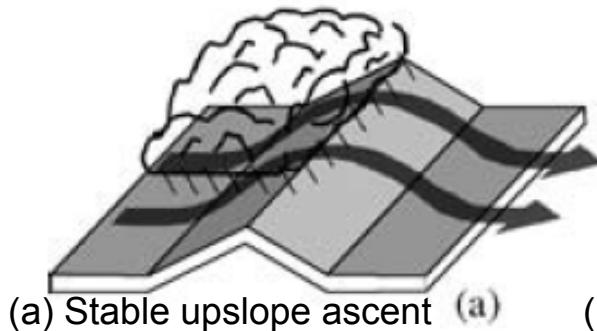


8 Volcanic degassing

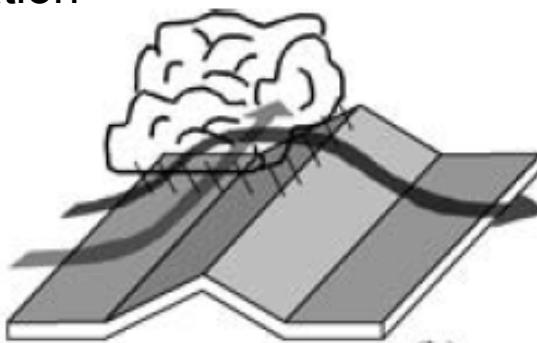
(Ridgwell and Zeebe, 2005 EPSL)



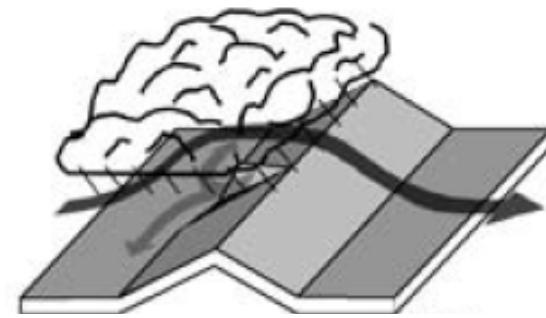
## Various Orographic Precipitation



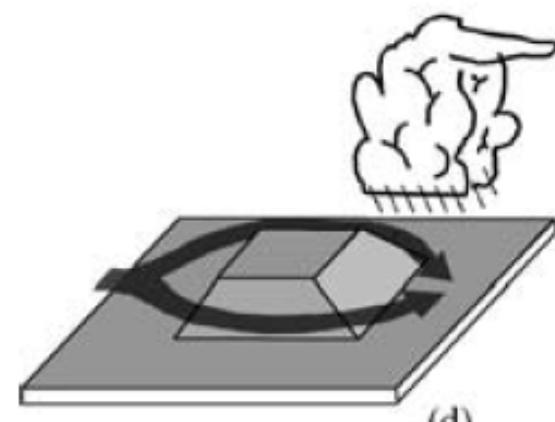
(a) Stable upslope ascent



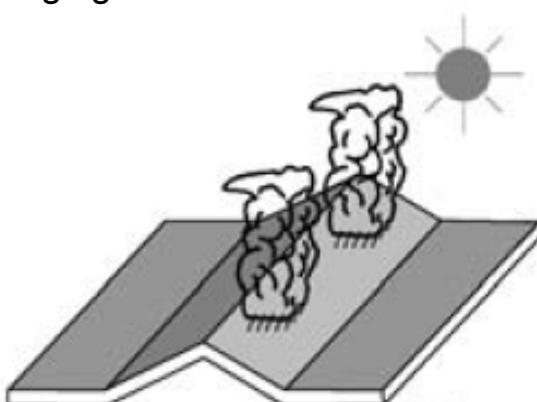
(b) Partial blocking of the impinging air mass



(c) Down valley flow induced by evaporative cooling



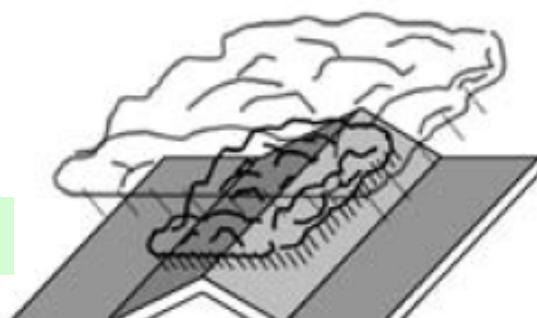
(d) lee-side convergence



(e) Convection triggered by solar heating



(f) Convection owing to mechanical lifting above level of free convection

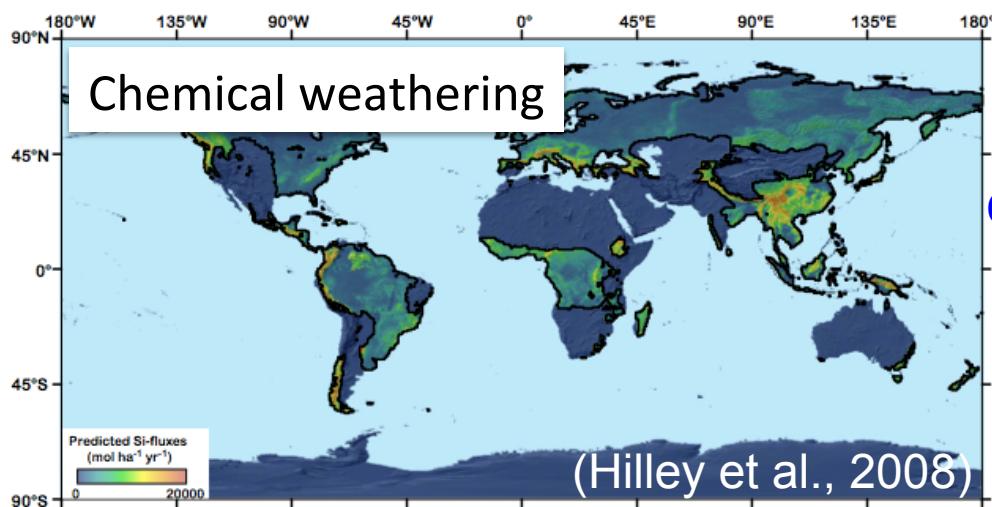
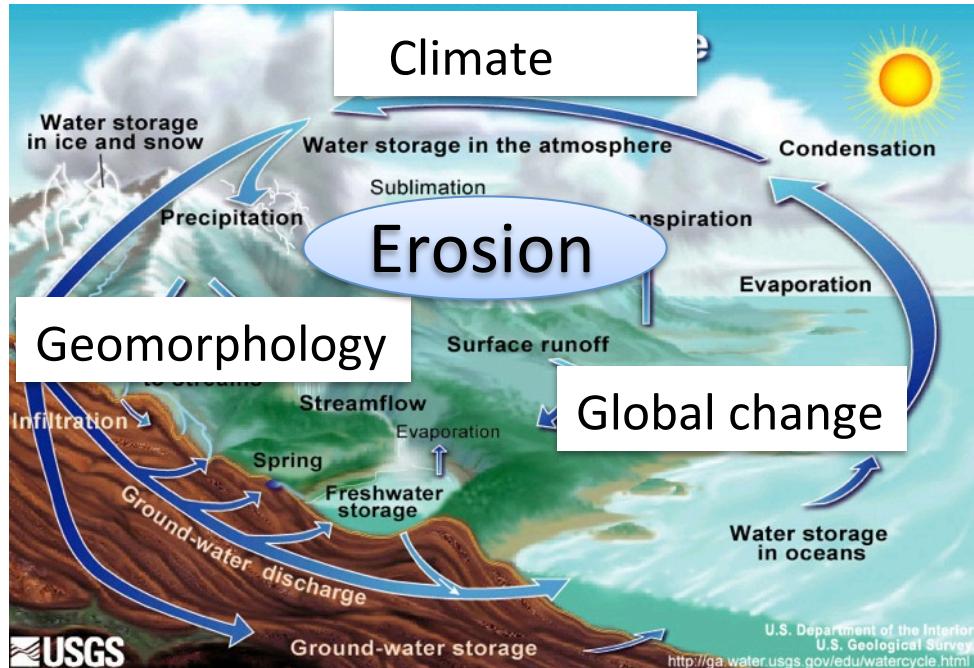


(g) Seeder-feeder mechanism

Changing in hydrological cycle

(Roe 2005)

# Erosion

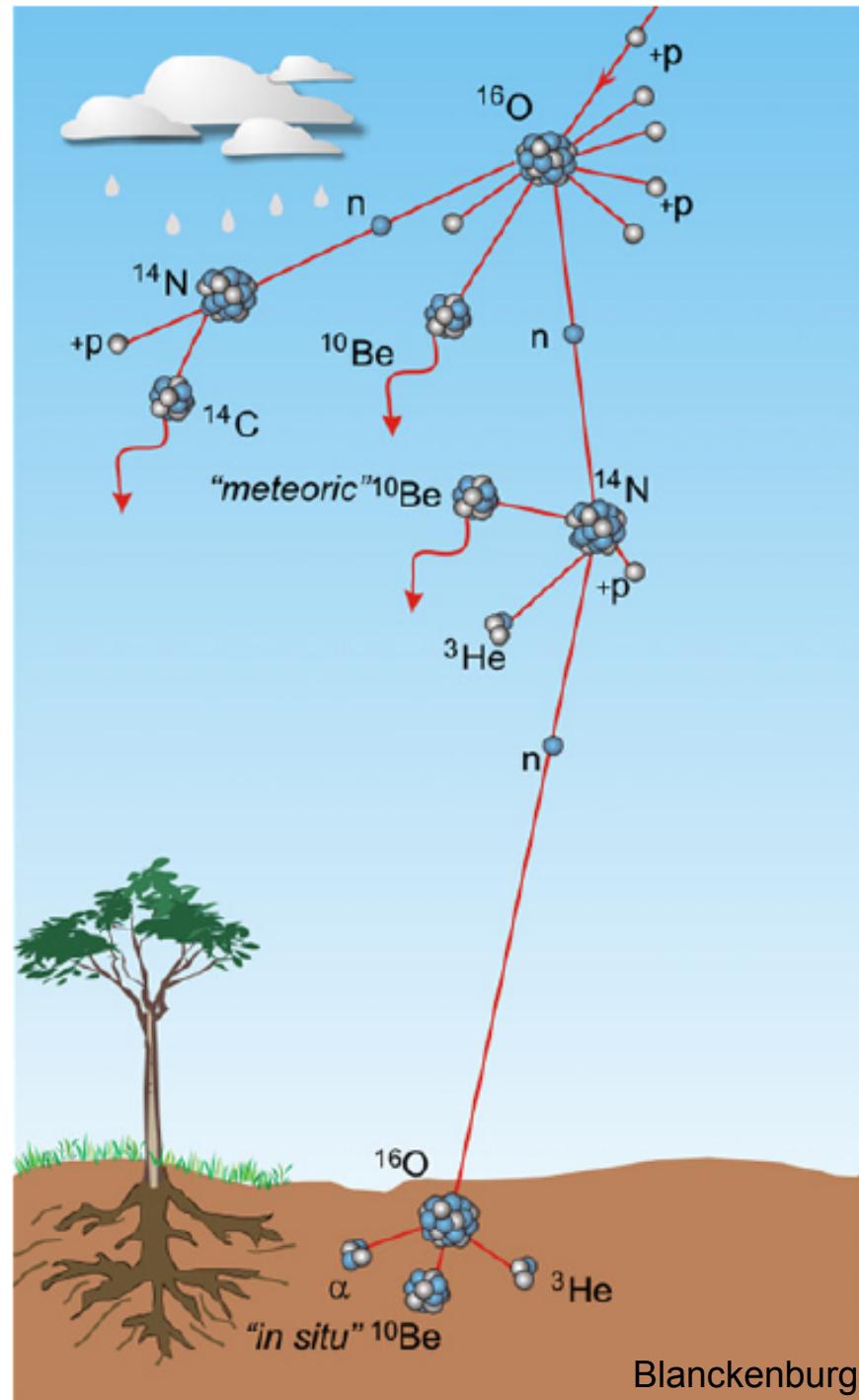


- Seawater alkalinity ,  $\text{pCO}_2$   
(Berner et al., 1983; Raymo et al., 1988)
- Physical erosion - weathering  
(Hilley et al., 2008; Willenbring et al., 2013)

It had been difficult to quantify erosion rate

Quantities of sand deposited (Beaty, 1970)

Cosmogenic radionuclides (Lal, 1991)  
Depth profile of CRN (Siame 2008)



# Interactions with Earth surface elements (Si, O, Ca, K, Mg, Fe)

Secondly cosmic ray



In situ nuclides



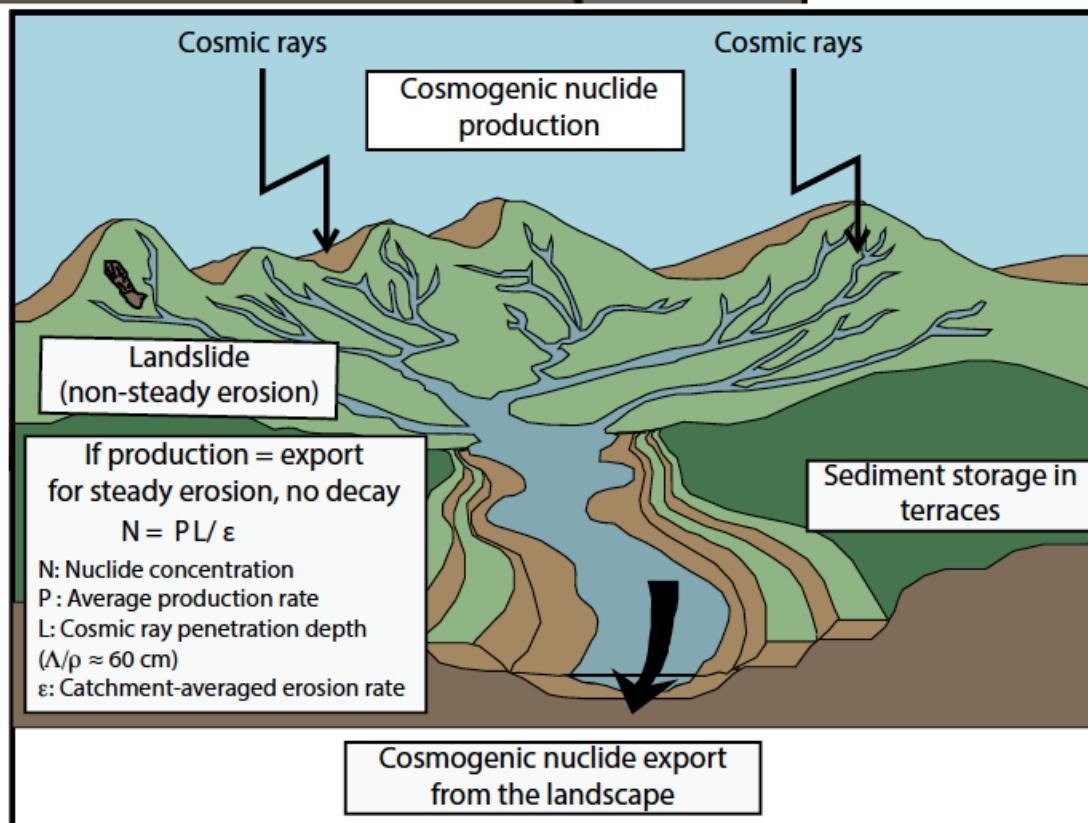
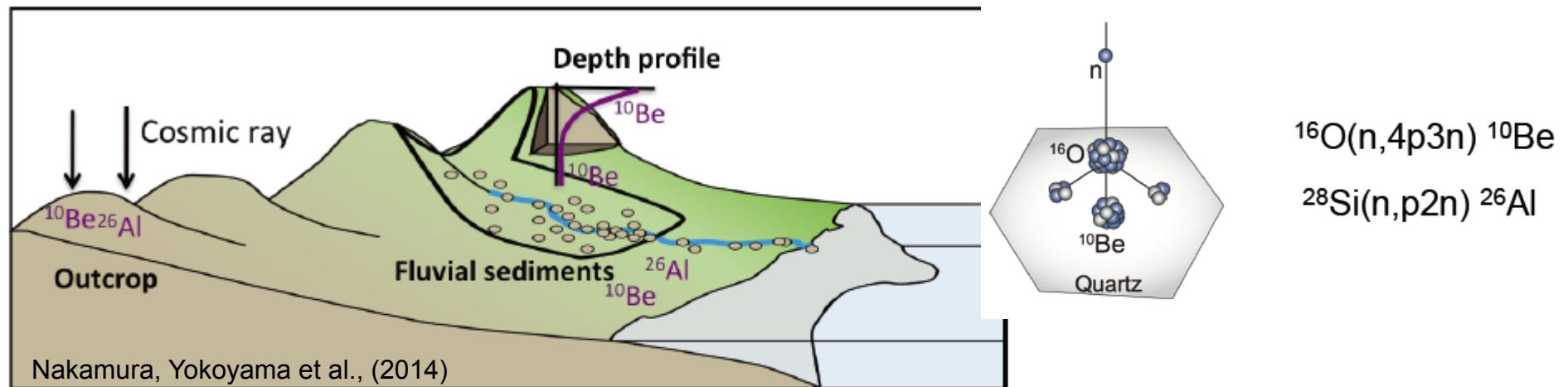
Land surface

Nuclide	Half-life (years)	Important target element(s) in terrestrial rocks
$^3\text{He}$	Stable	O, Mg, Si, Fe
$^{10}\text{Be}$	$1.5 \times 10^6$	O, Mg
$^{14}\text{C}$	$5.73 \times 10^3$	O
$^{21}\text{Ne}$	Stable	Mg, Al, Si
$^{26}\text{Al}$	$7.1 \times 10^5$	Si
$^{36}\text{Cl}$	$3.0 \times 10^5$	Cl, K, Ca, Fe
$^{36}\text{Ar}$	Stable	Cl, K, Ca
$^{38}\text{Ar}$	Stable	K, Ca
$^{41}\text{Ca}$	$1.0 \times 10^5$	Ca, Ti, Fe
$^{53}\text{Mn}$	$3.7 \times 10^6$	Fe
$^{129}\text{I}$	$1.56 \times 10^7$	Te, Ba, REE

Terrestrial material

Yokoyama et al. (2005 J.  
Geol Soc J)

# Direct comparison of site-specific and basin-scale erosion rate



# Basin scale averaged erosion rate

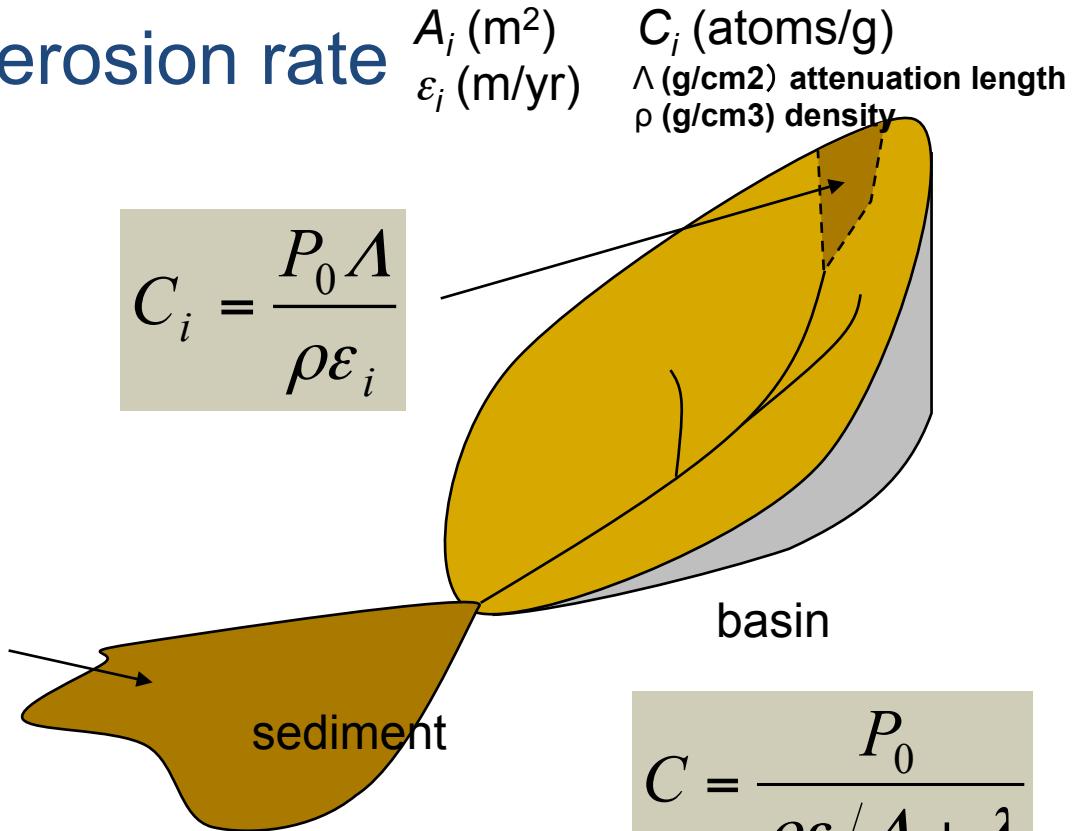
Considering sediments in basin.

If we divide basin in polygons,  $n$

$$\bar{\varepsilon} = \sum_{i=1}^n \varepsilon_i A_i \Bigg/ \sum_{i=1}^n A_i$$

$$\bar{C} = \sum_{i=1}^n C_i \varepsilon_i A_i \Bigg/ \sum_{i=1}^n \varepsilon_i A_i$$

When  $\Lambda/\rho \ll \tau\varepsilon_i \Leftrightarrow \rho\varepsilon_i/\Lambda \gg \lambda$



$$\bar{C} = \frac{P_0 \Lambda}{\rho} \sum_{i=1}^n A_i \Bigg/ \sum_{i=1}^n \varepsilon_i A_i = \frac{P_0 \Lambda}{\bar{\varepsilon} \rho}$$

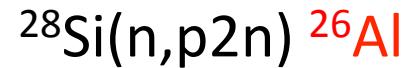
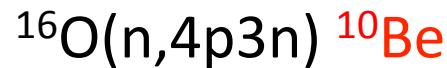
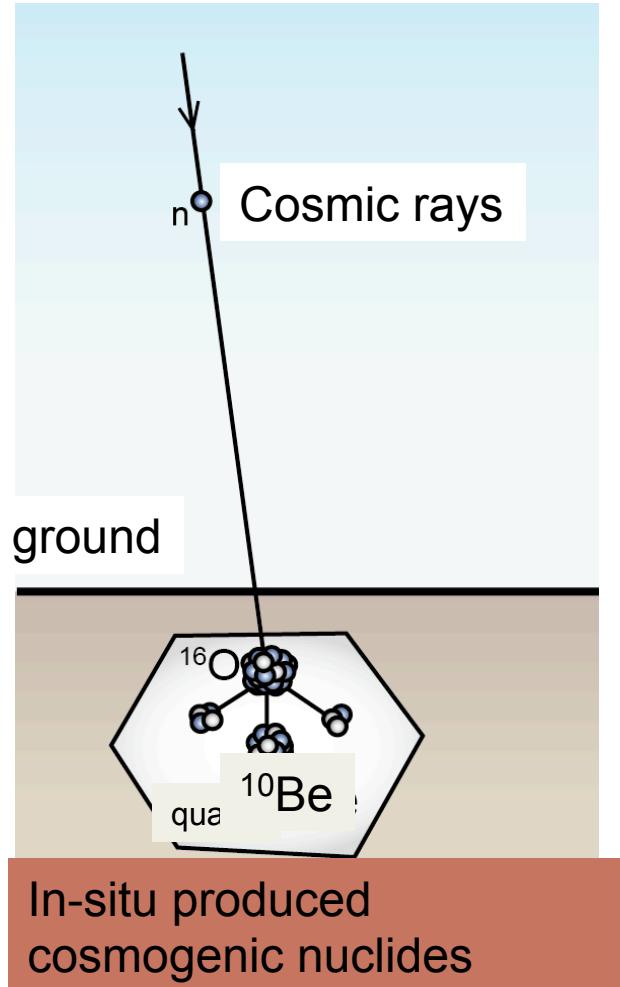
Inheritance

$$\bar{\varepsilon} = \frac{P_0}{\bar{C}} \cdot \frac{\Lambda}{\rho}$$

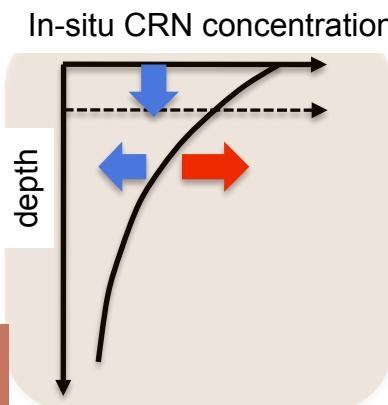
Spatially averaged erosion rate

(Brown et al., 1995; Granger et al., 1996)

# Erosion rate calculation using CRN



$$\frac{\partial C}{\partial t} = P_0 e^{-\rho x} + \varepsilon \frac{\partial C}{\partial x} - C \lambda \quad (\text{Lal et al., 1991})$$



C nuclide concentration (atoms/g)

t time (yr)

x depth (cm)

$P_0$  production rate at the surface (atoms/g/yr)

$\Lambda$  attenuation length ( $\text{g}/\text{cm}^2$ )

$\lambda$  radioactive decay constant

$\rho$  density

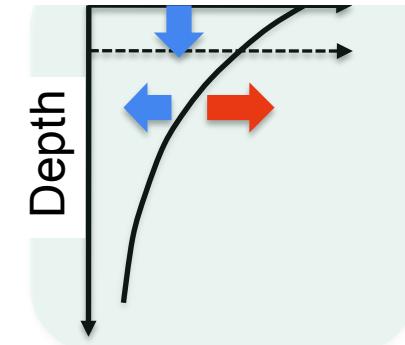
$\varepsilon$  erosion rate (cm/yr)

# Depth profile is depending on steady state erosion rate

$$\frac{\partial C}{\partial t} = P_0 e \frac{-\rho x}{\Lambda} + \varepsilon \frac{\partial C}{\partial x} - C \lambda$$

prod      erosion

Cosmogenic Nuclides concentration



Neutron spallation

$$C(x,t) = \frac{P_0 P_{spal}}{\frac{\rho \varepsilon}{\Lambda_{spal}} + \lambda} e^{\frac{-\rho x}{\Lambda_{spal}}} \left( 1 - e^{-\left(\lambda + \frac{\rho \varepsilon}{\Lambda_{spal}}\right)t} \right)$$

Muon capture

$$C(x,t) = \frac{P_0 P_{stop}}{\frac{\rho \varepsilon}{\Lambda_{stop}} + \lambda} e^{\frac{-\rho x}{\Lambda_{stop}}} \left( 1 - e^{-\left(\lambda + \frac{\rho \varepsilon}{\Lambda_{stop}}\right)t} \right)$$

High energy muon reaction

$$C(x,t) = \frac{P_0 P_{fast}}{\frac{\rho \varepsilon}{\Lambda_{fast}} + \lambda} e^{\frac{-\rho x}{\Lambda_{fast}}} \left( 1 - e^{-\left(\lambda + \frac{\rho \varepsilon}{\Lambda_{fast}}\right)t} \right)$$

$\varepsilon$  (erosion rate) = stable

$C$  nuclide concentration (atoms/g)

$t$  time (yr)

$x$  depth (cm)

$P_0$  production rate at the surface (atoms/g/yr)

$\Lambda$  attenuation length ( $\text{g}/\text{cm}^2$ )

$\lambda$  radioactive decay constant

$\rho$  density

$\varepsilon$  erosion rate (cm/yr)

$P_{spal}$ ,  $P_{stop}$ ,  $P_{fast}$ , contribution rates

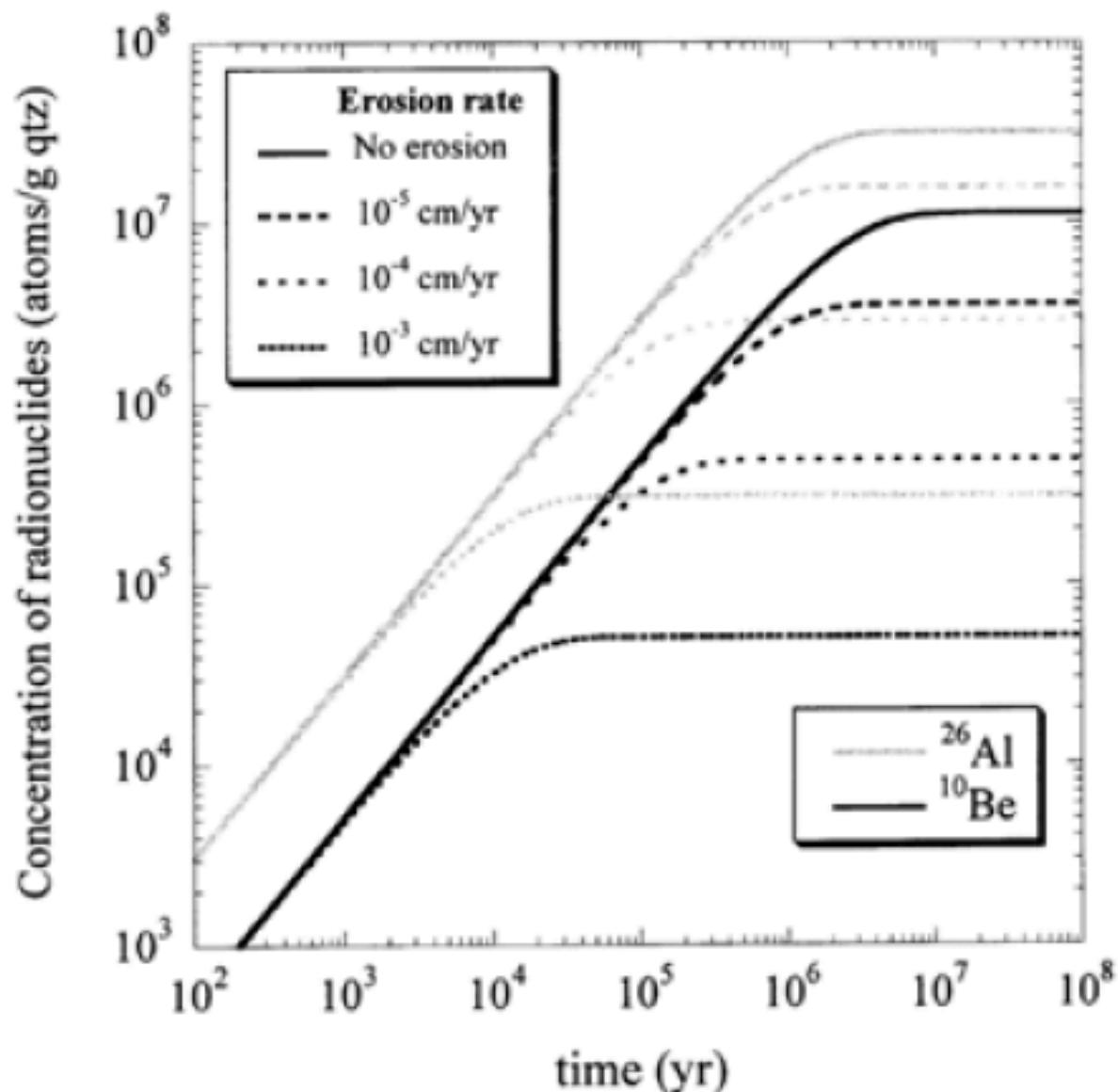
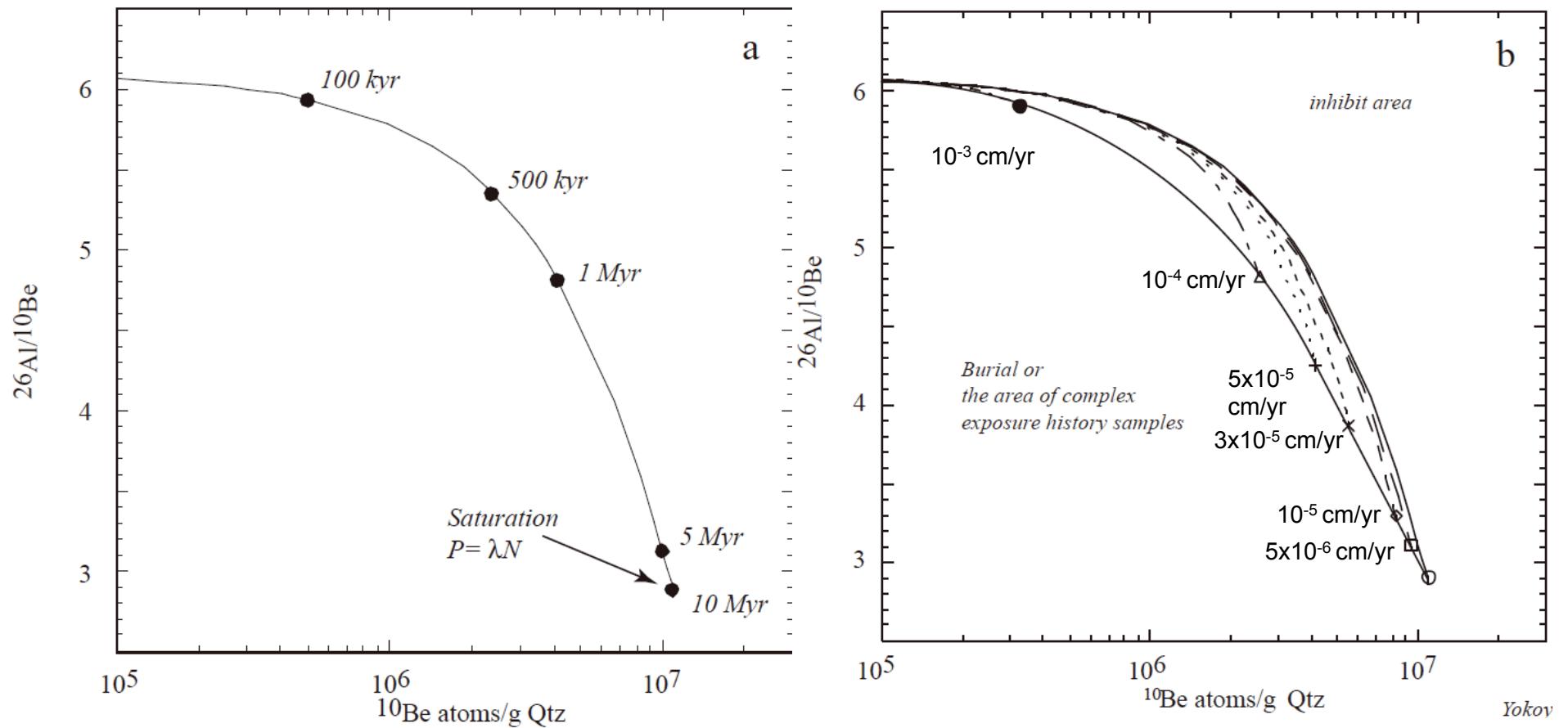


Fig. 3. Production of  $^{10}\text{Be}$  and  $^{26}\text{Al}$  (production rate (Stone, 2000);  $P_{\text{Be}} = 5.1$  atoms/g quartz yr,  $P_{\text{Al}} = 31.1$  atoms/g quartz yr). Solid lines display radionuclides production in case of no erosion at a surface. Dashed lines indicate radionuclides production that a surface erode with rates of  $10^3$ ,  $10^4$ ,  $10^5$  cm/yr.

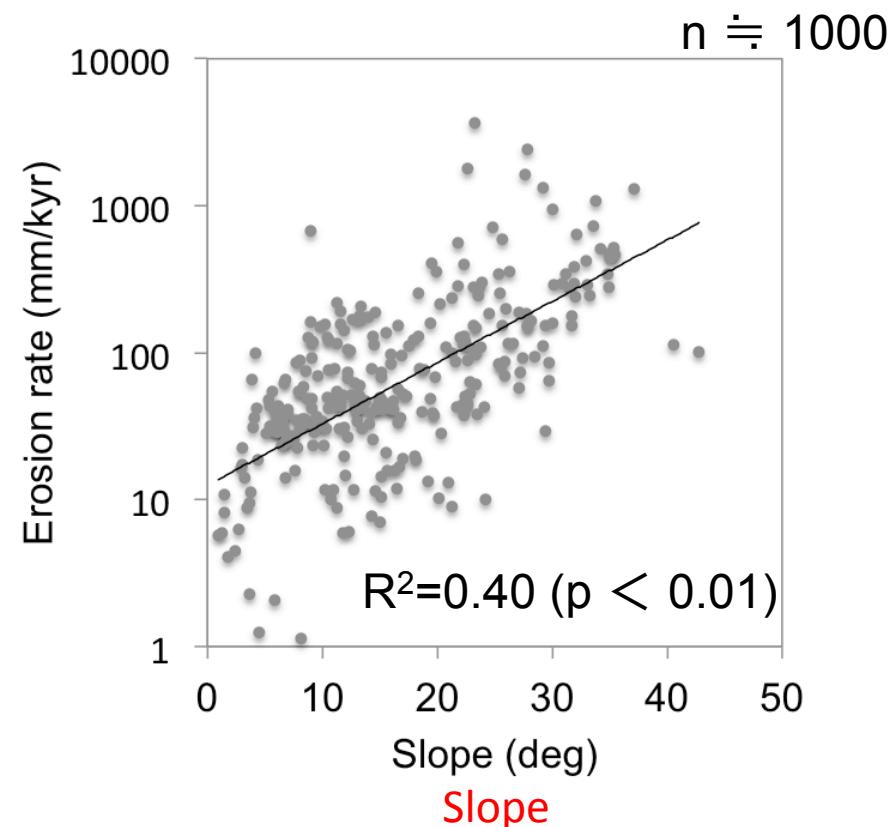
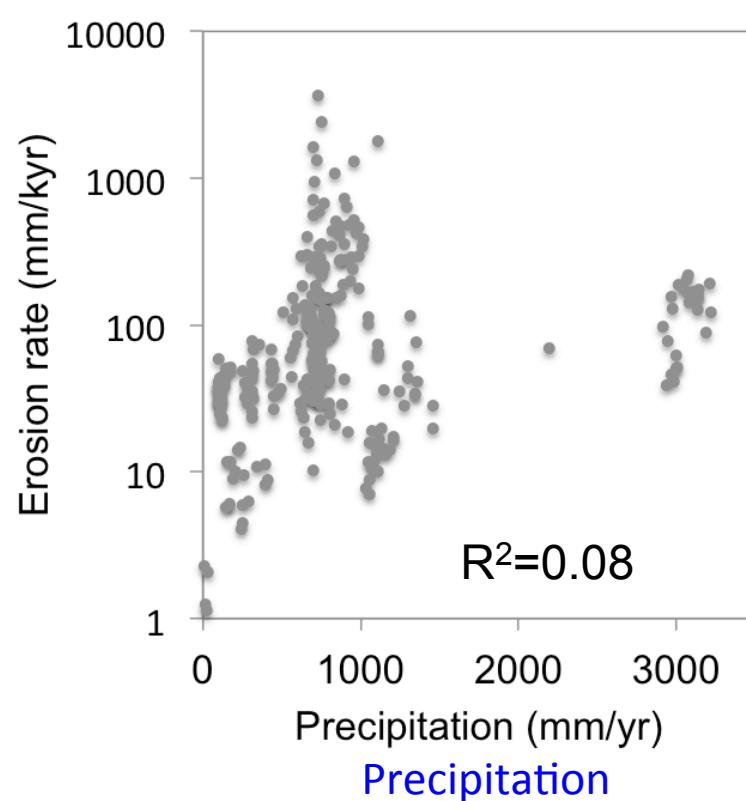
# Erosion “island”



Yokoyama et al. (2005)

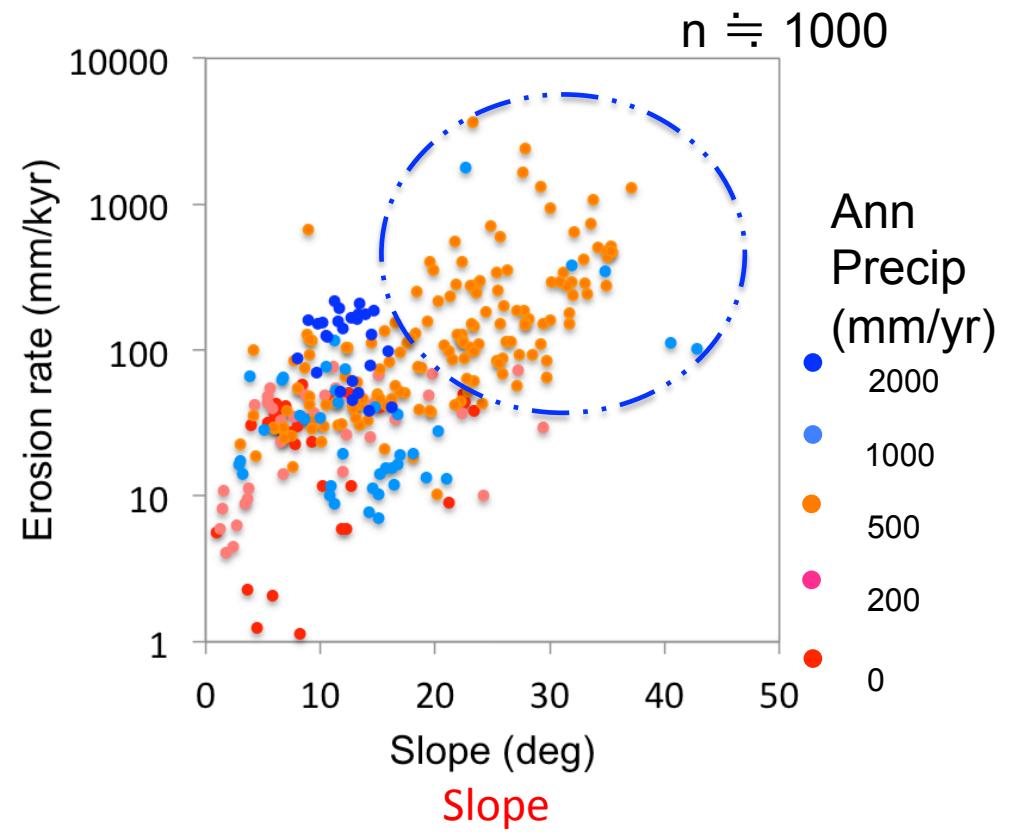
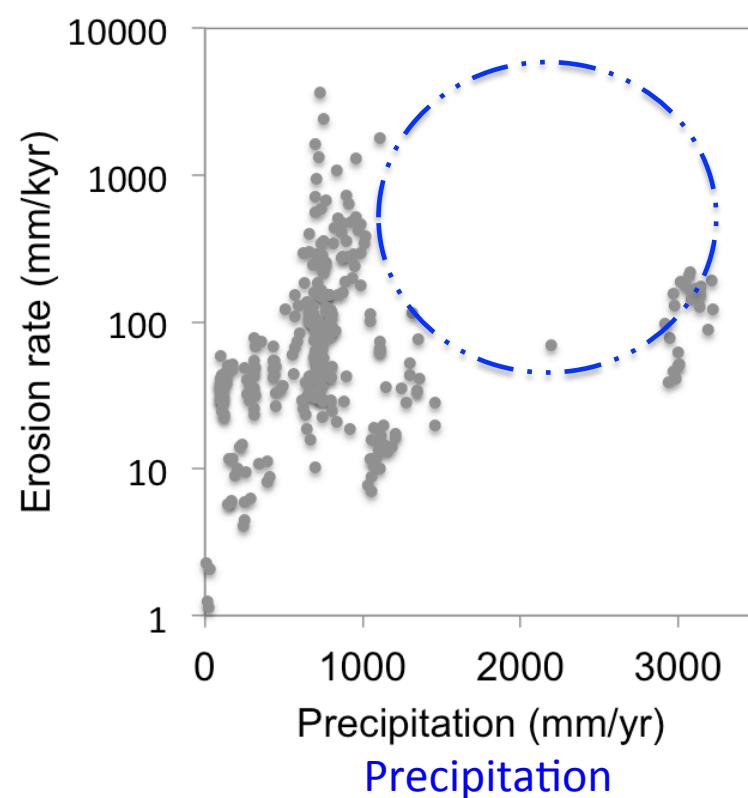
# What controls erosion rate?

Erosion rate =  $f$ ( Precipitation, Slope, tectonics, Temp, lithology, relief, vegetation. etc)  
(Portenga et al., 2011; Willenbring et al., 2013)



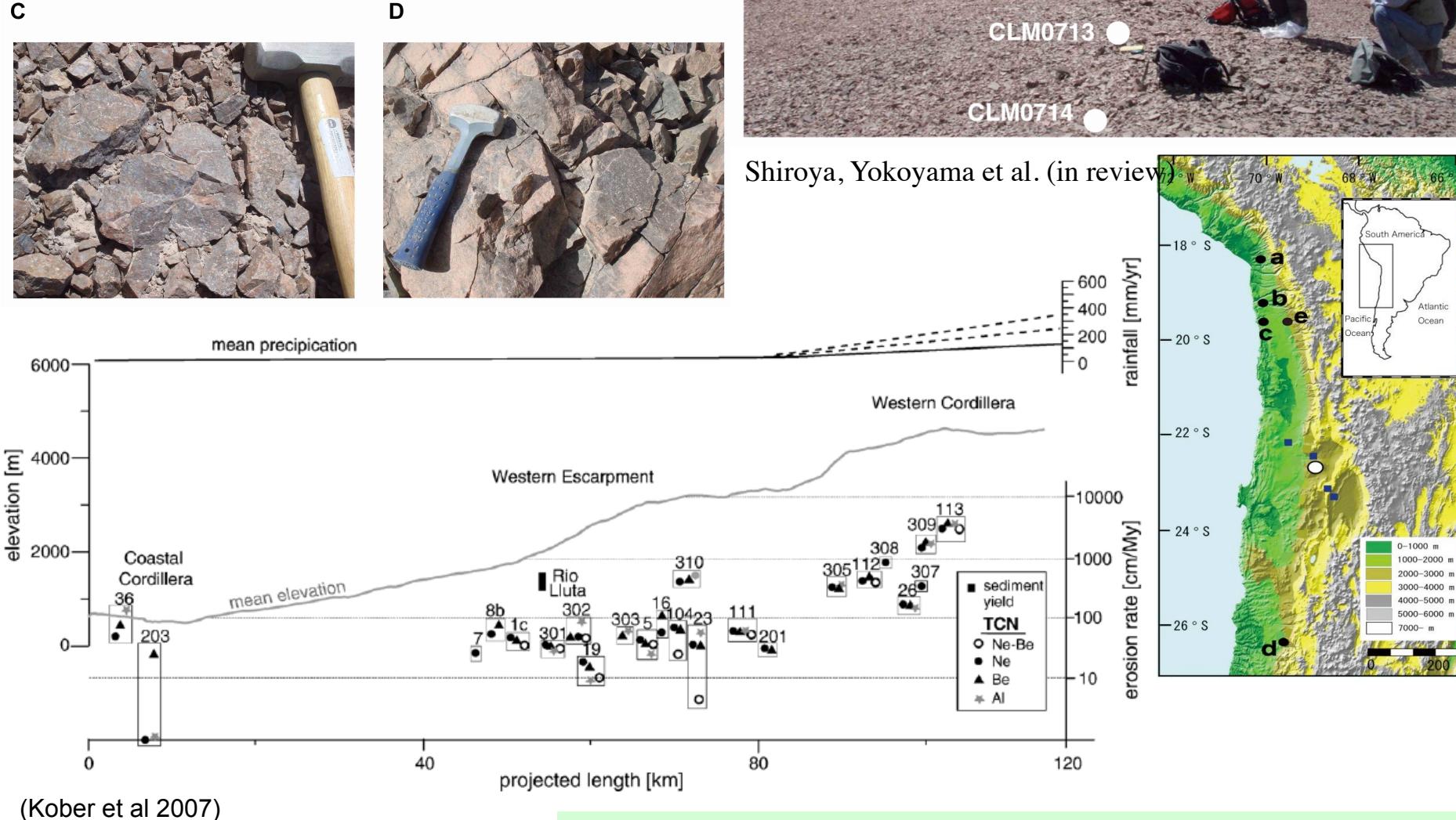
# What controls erosion rate?

Erosion rate =  $f$ ( Precipitation, Slope, tectonics, Temp, lithology, relief, vegetation. etc)  
(Portenga et al., 2011; Willenbring et al., 2013)



Lack of data for mid latitude high precipitation areas

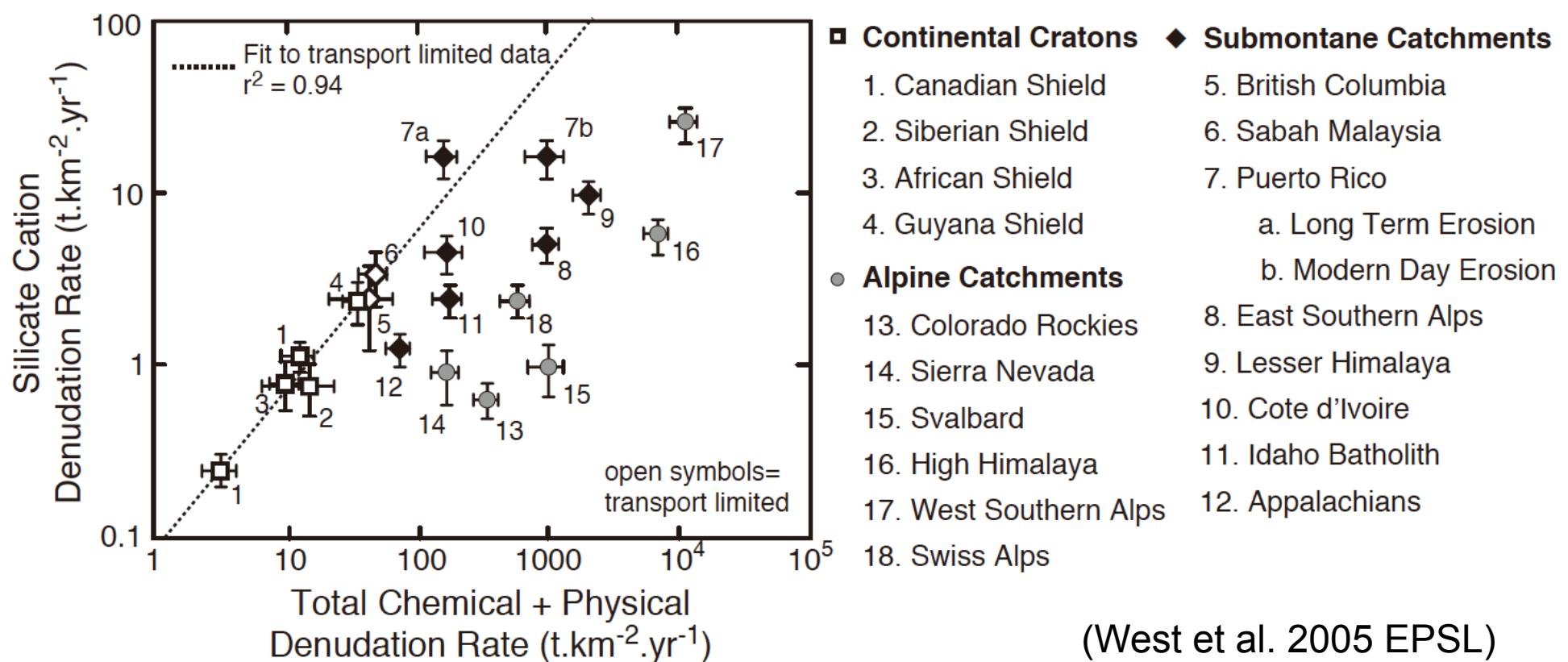
# Atacama Desert



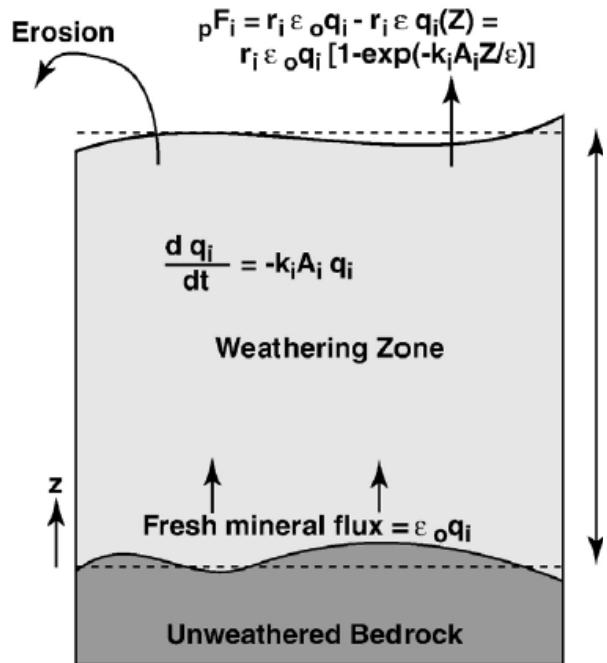
# Transport vs kinetic limitation with regards to silicate cation denudation rate

[Chemical weathering]  $\propto$

mineral type reactivity, the supply of minerals, water and acid reactants



## Silicate weathering rates are controlled by erosion rate/ fresh mineral supply



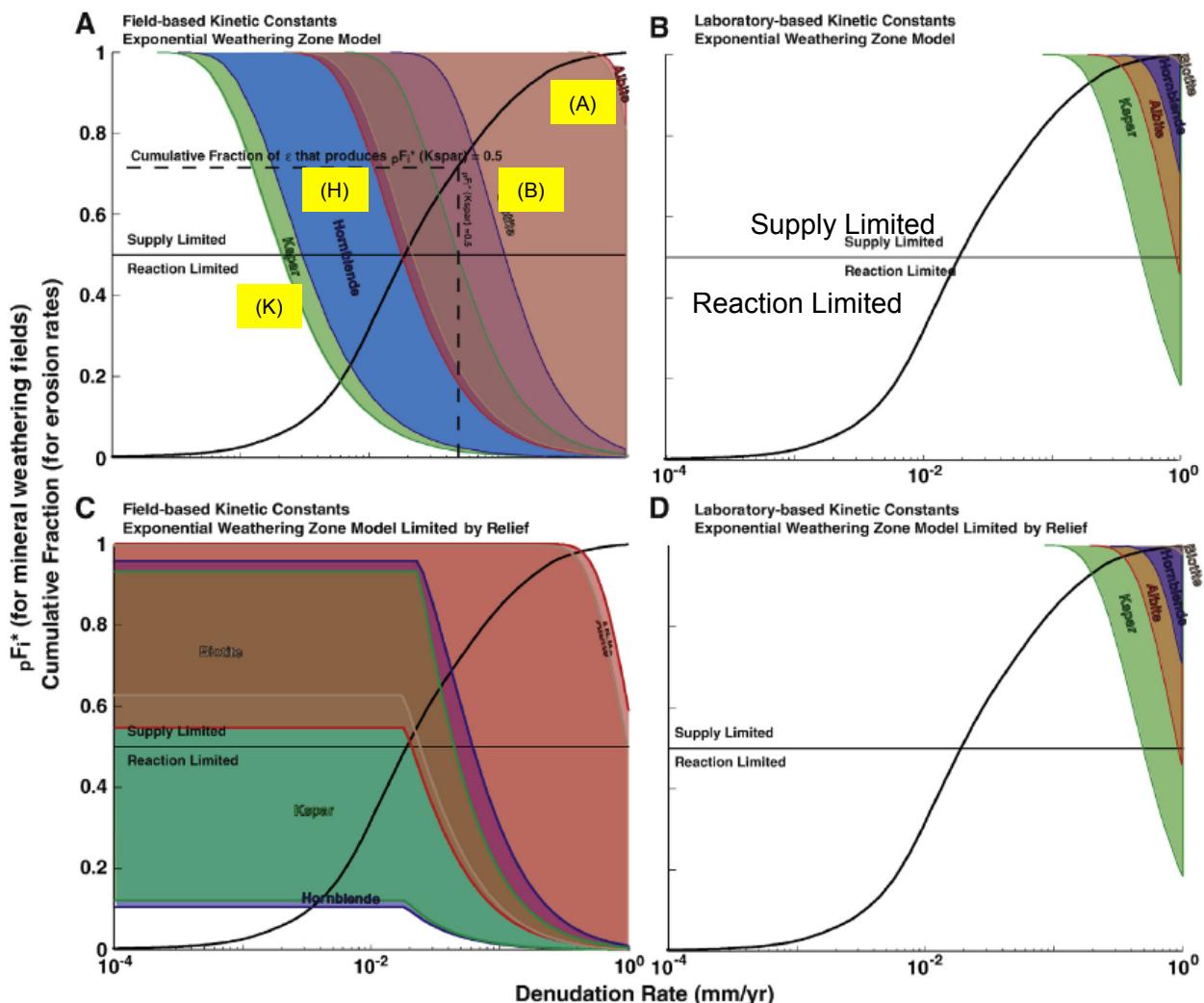
Erosion rate (ie. providing fresh minerals) is the most important factor to control chemical weathering

(Hilley et al. 2010 EPSL)

**Table 1**

Range of laboratory- and field-based reaction rates used in this study (compiled from White and Brantley, 2003).

Mineral phase	Laboratory-based		Field-based
	$\log_{10} k_f A_i$ range (1/s)	$\log_{10} k_f A_i$ range (1/s)	
Albite	(A)	-10.9 to -9.2	-13.3 to -10.9
K-feldspar	(K)	-11.4 to -9.0	-14.4 to -13.4
Hornblende	(H)	-10.6 to -8.3	-14.2 to -12.9
Biotite	(B)	-10.1 to -8.1	-13.2 to -11.0



## Prediction of chemical weathering

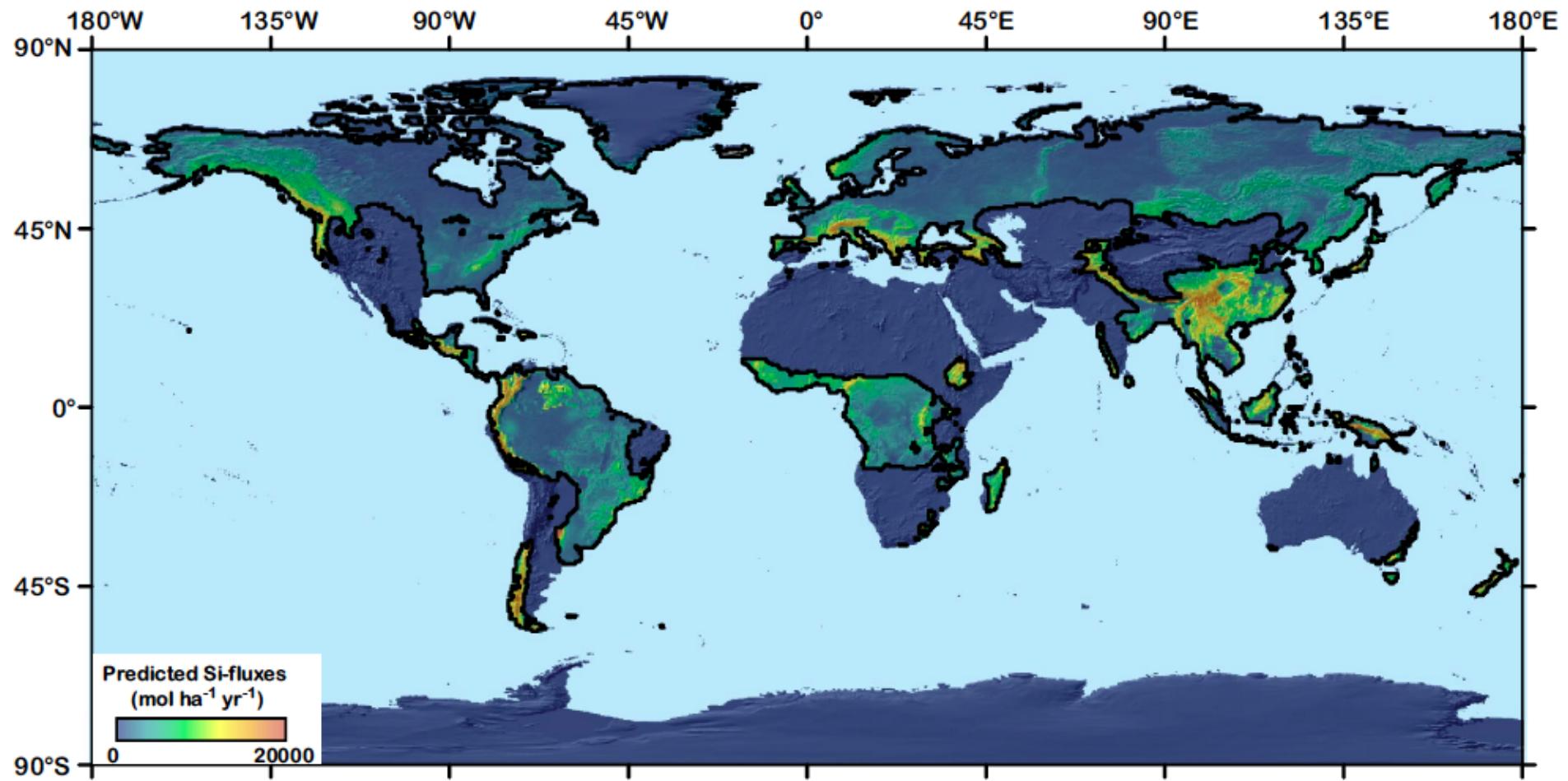
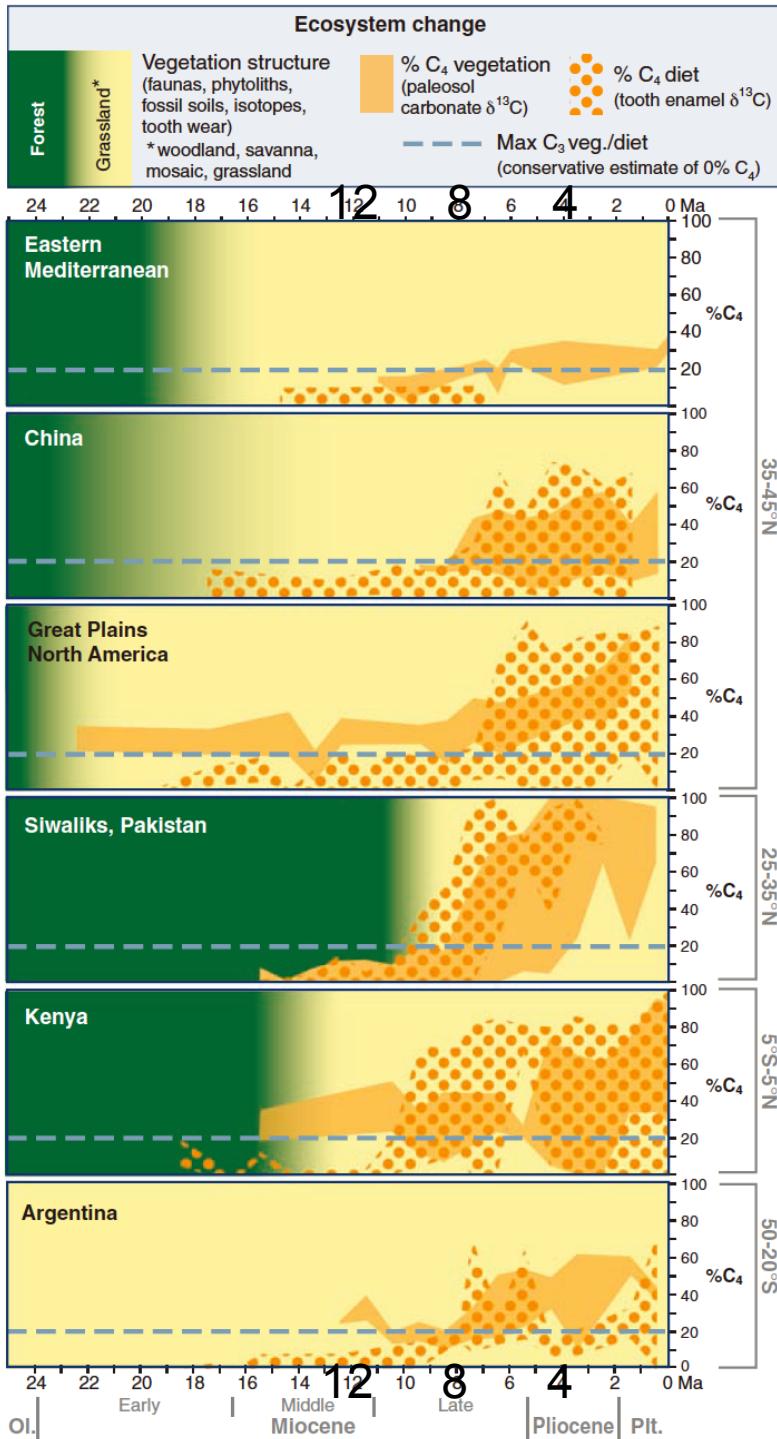
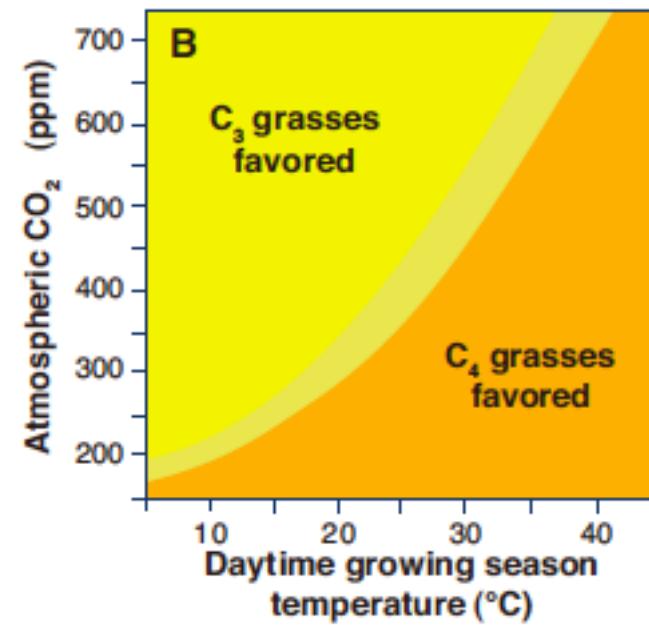


Fig. 1. Spatially explicit predicted Si fluxes ( $\text{mol} \cdot \text{ha}^{-1} \cdot \text{year}^{-1}$ ) for each  $0.5^\circ \times 0.5^\circ$  region (excluding Antarctica). The black line highlights the regions where  $\text{P} > \text{PEt}$ , all other regions are assumed not to contribute to silicate weathering. The scenario shown here is based on modern dust fluxes and our deep weathering zone scenario (DWZ). LGM and SWZ scenarios, evaluated for both P-Et 0 and P-Et 500 are available in [SI](#).

(Hilley and Porder 2008 PNAS)



## C<sub>3</sub> and C<sub>4</sub> vegetation changes

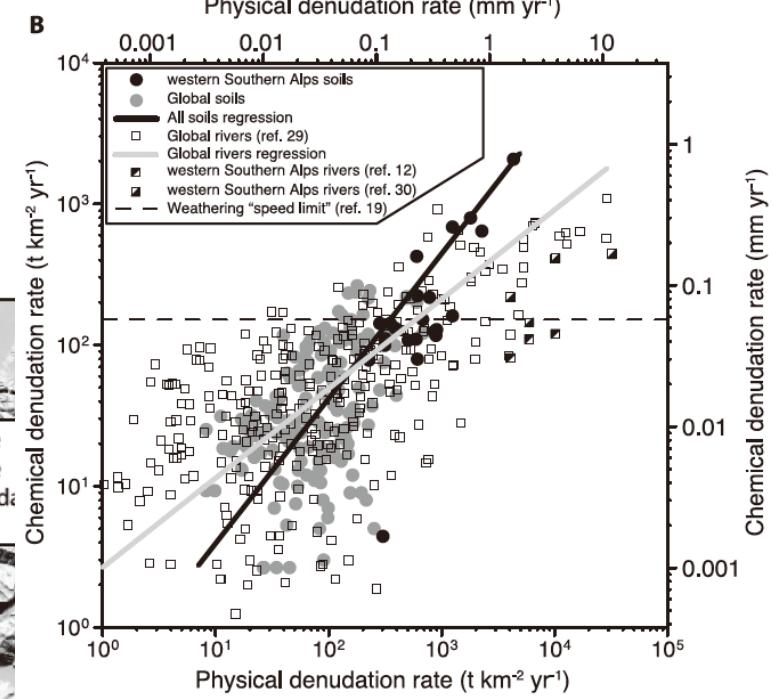
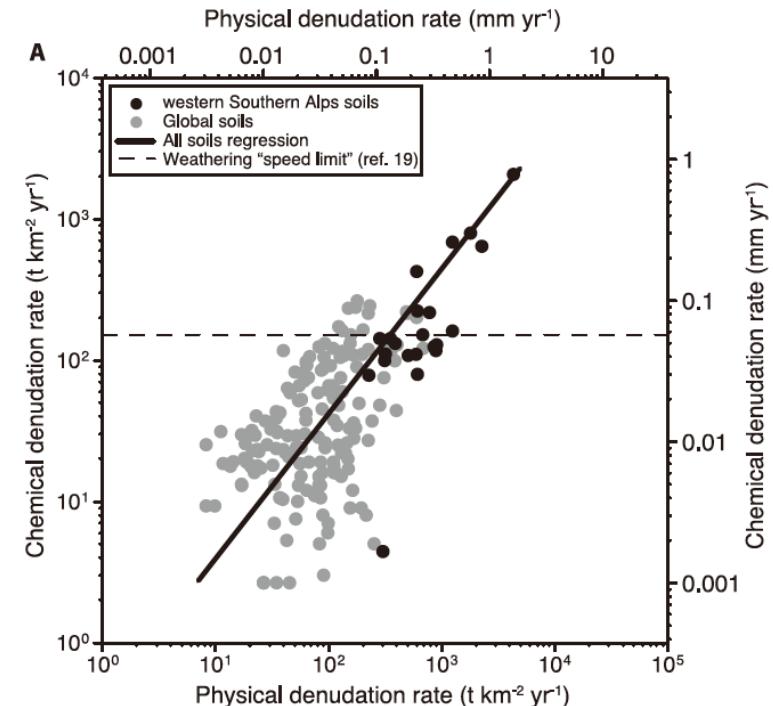
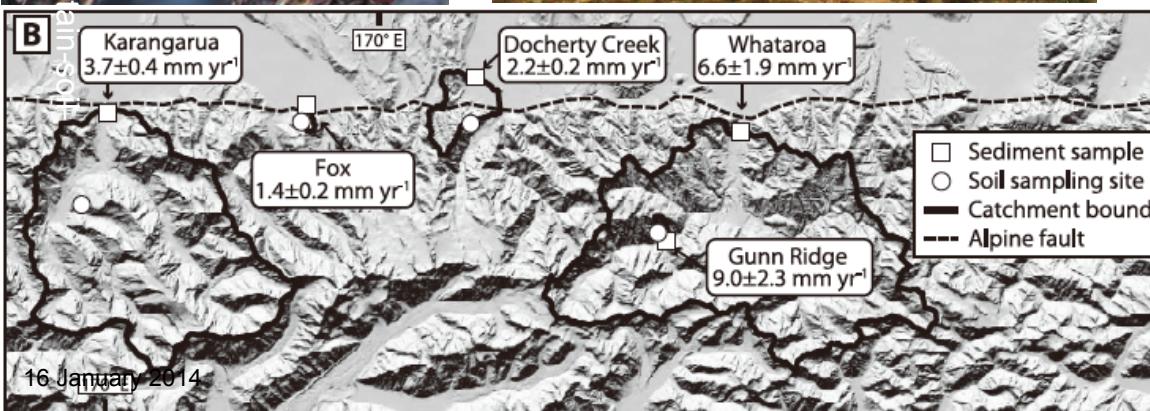
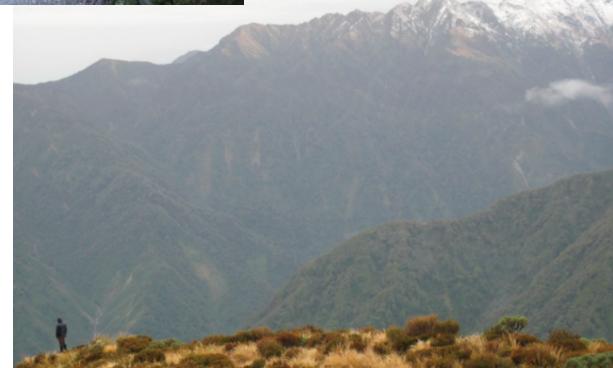
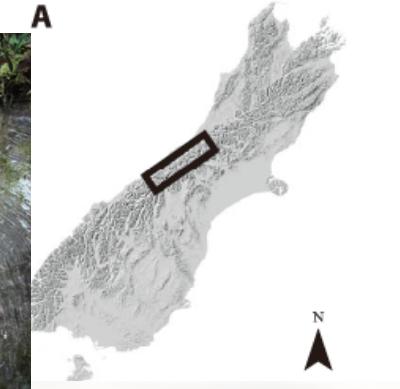


Grasses evolved at around 3-8 Ma that using C<sub>4</sub> photosynthesis

(Edwards et al 2010 Science)

Soil production rate is “roof less” and reached up to 2.5mm/yr

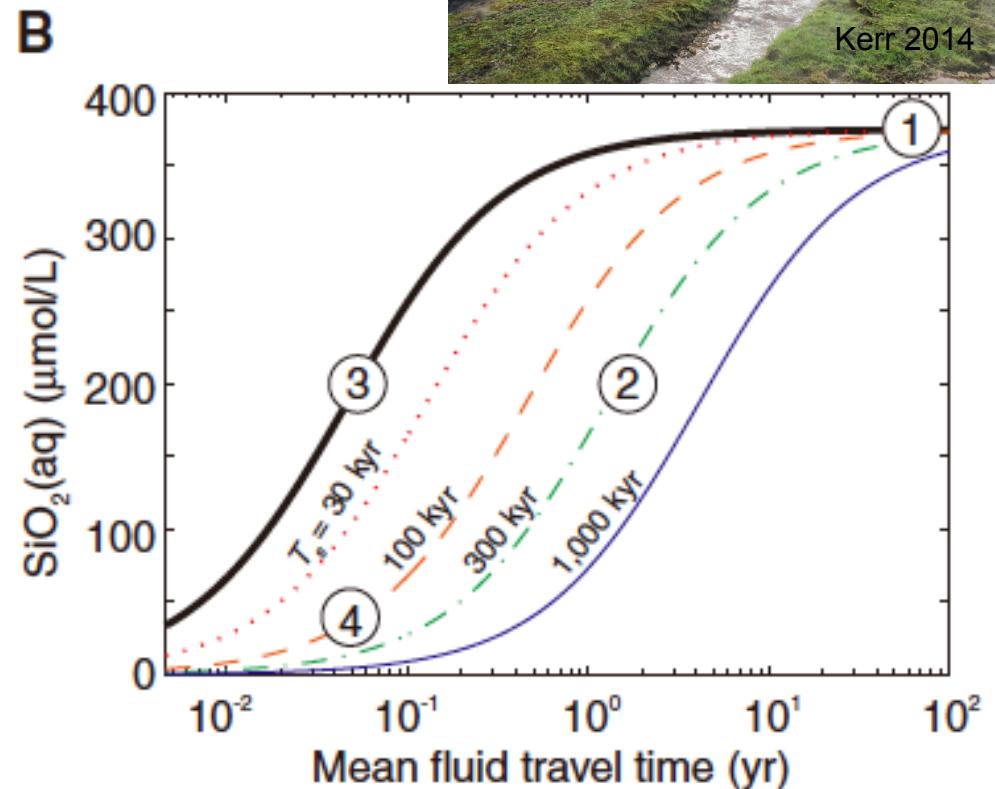
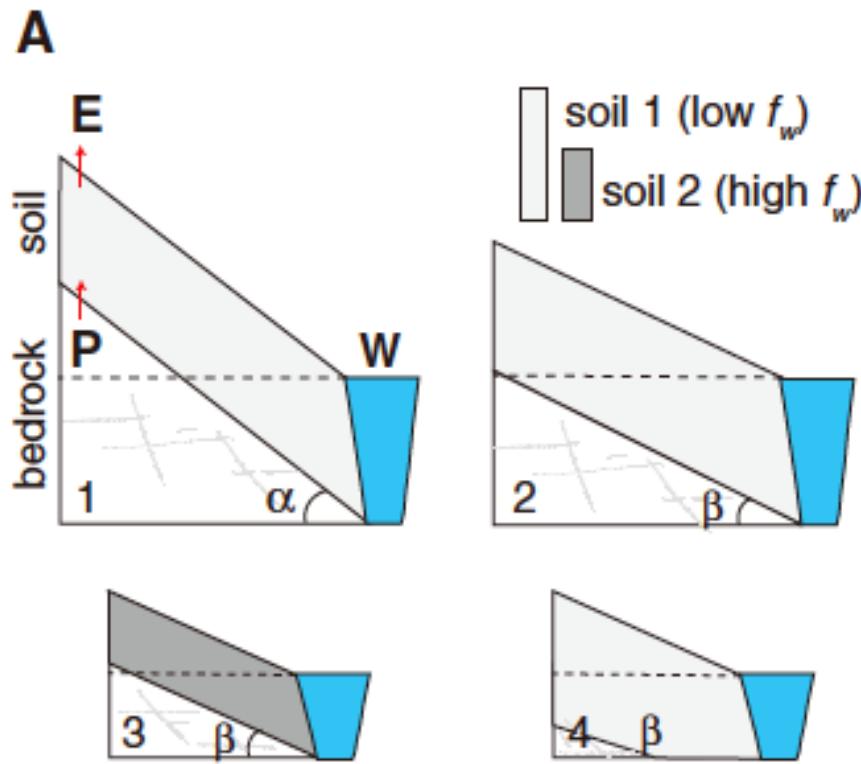
Larsen et al.  
(2014 Science)



Cooling mechanism, not freezing...

## Hydrologic regulation of Chemical weathering

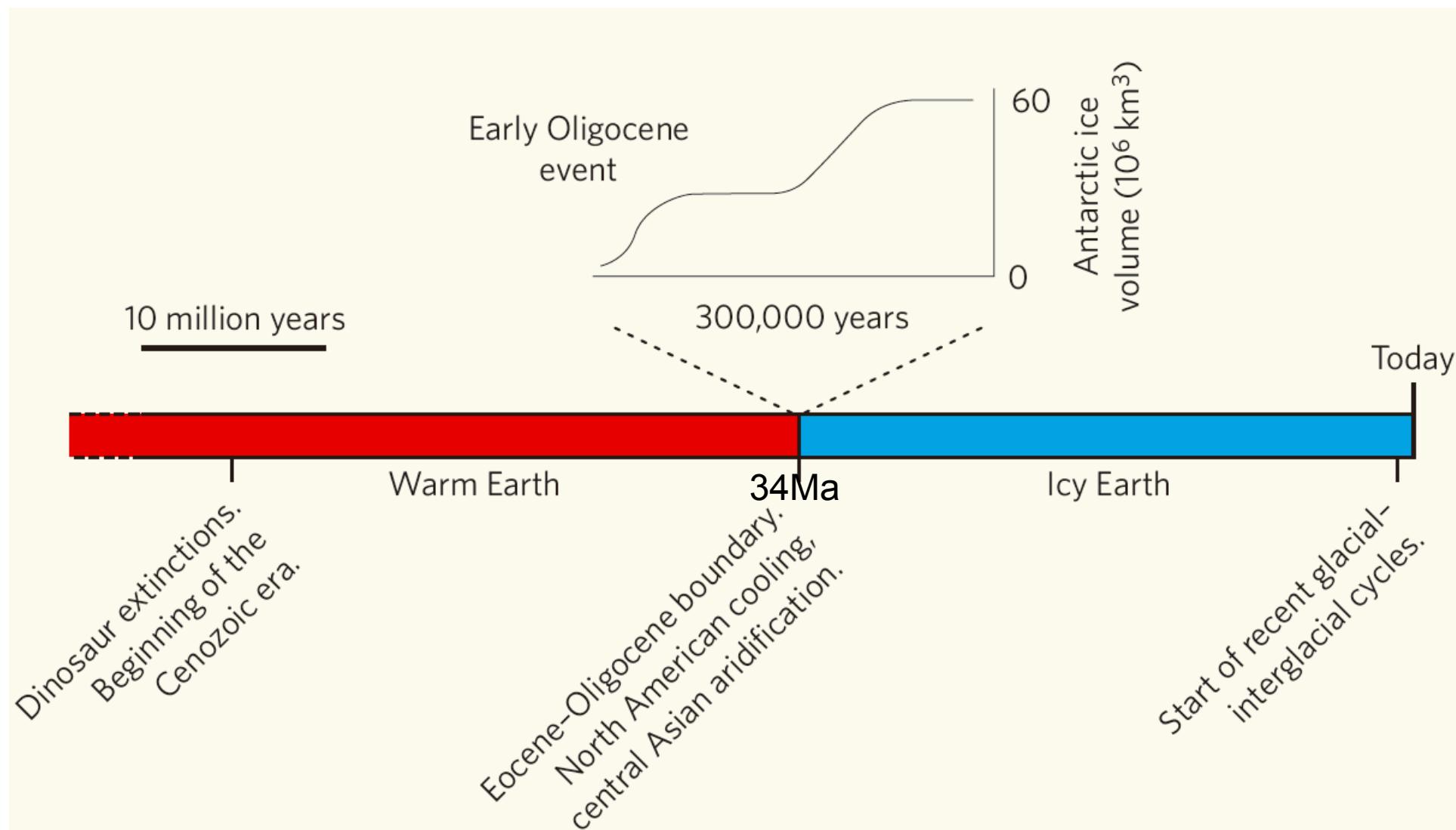
(Maher and Chamberlain 2014 Science )



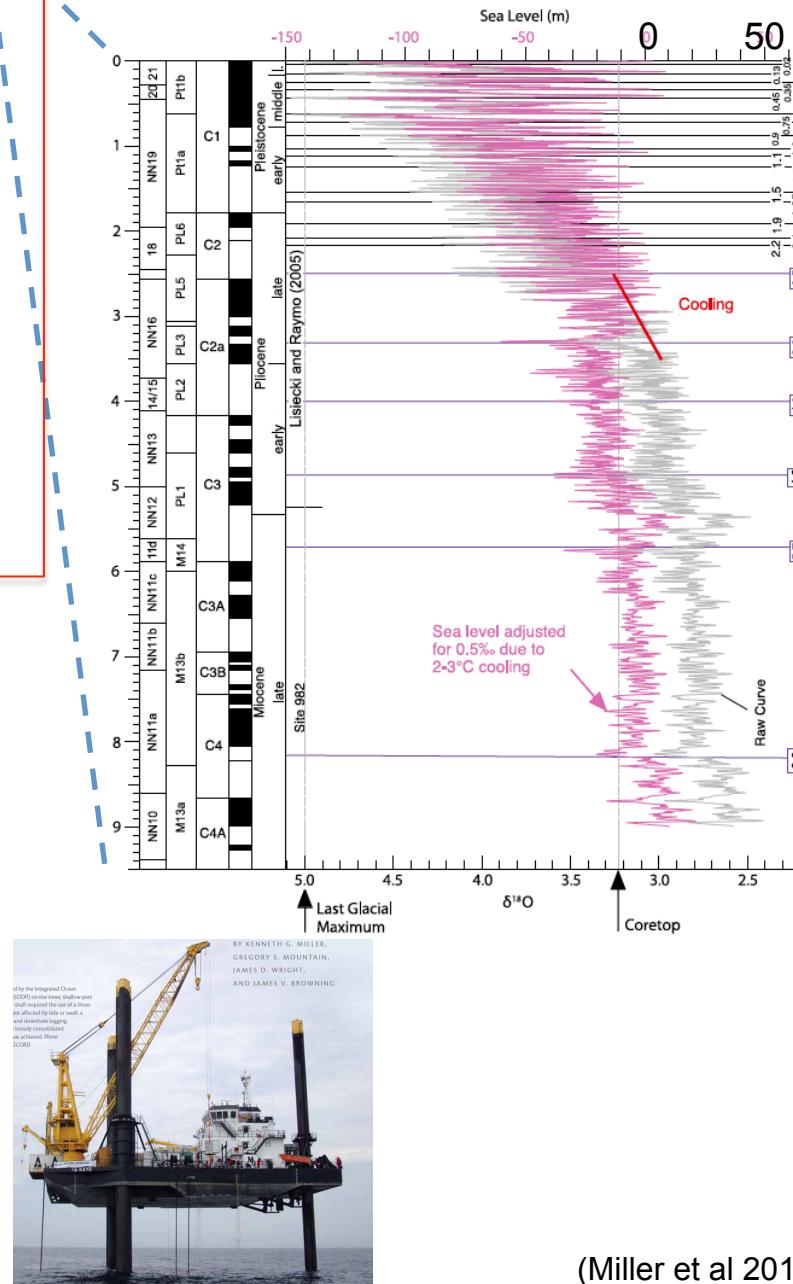
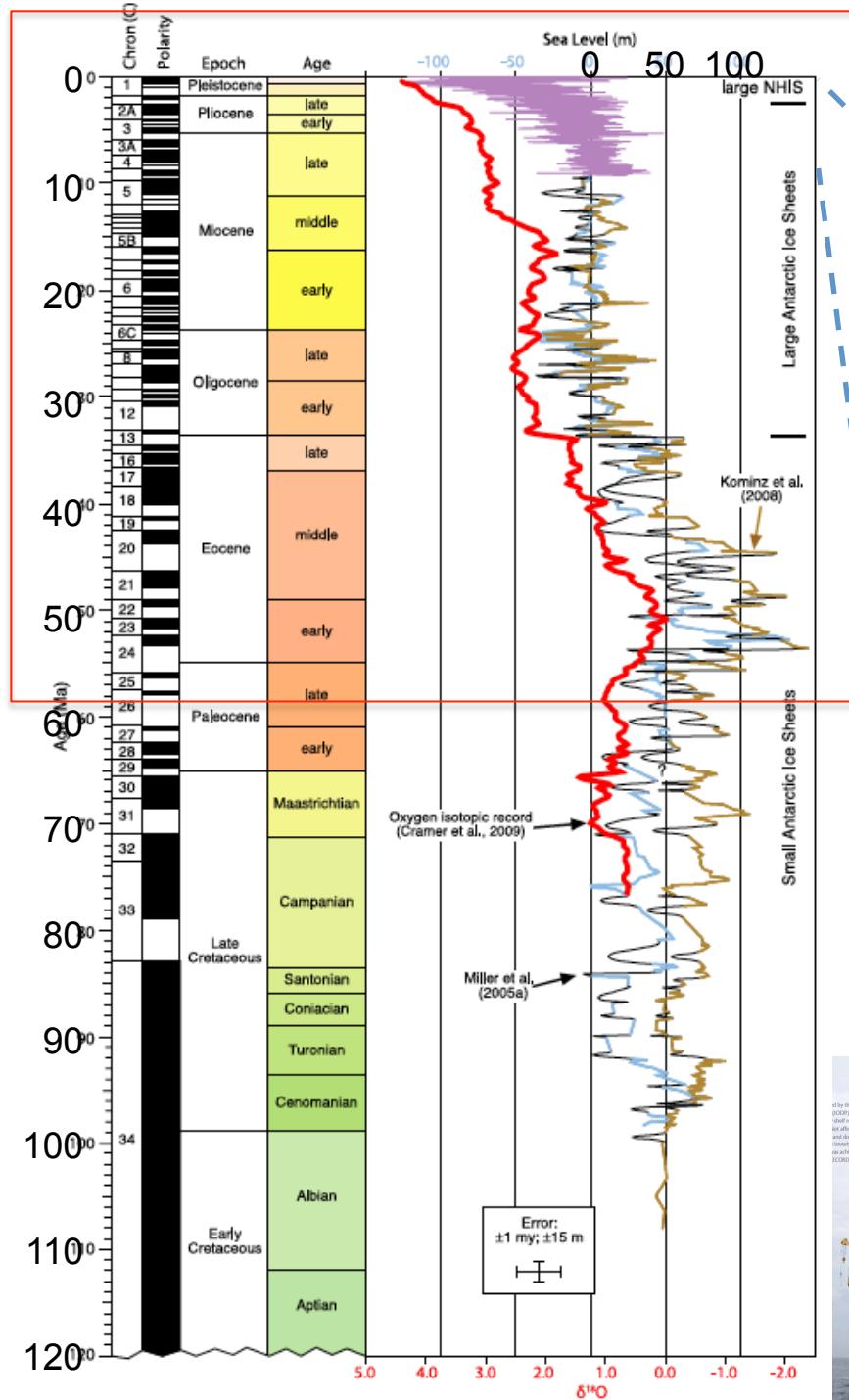
Chemical weathering → Runoff and duration of silicate minerals contacting to fluids are important

Mountain building modify hydrologic cycle that can affect weathering via solute production  
→ thermodynamic load limit and low temp. reins weathering prevent runaway cooling effect

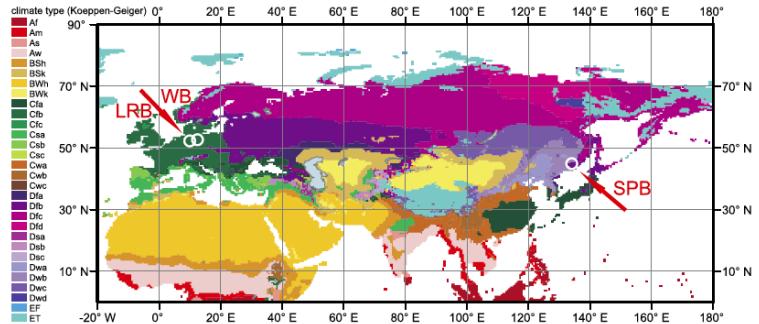
Climate shifted into colder states since 34 Ma...



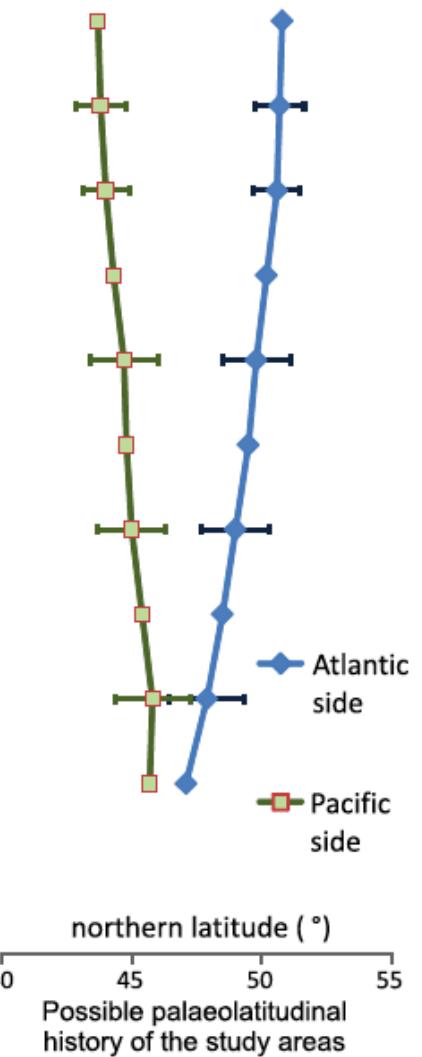
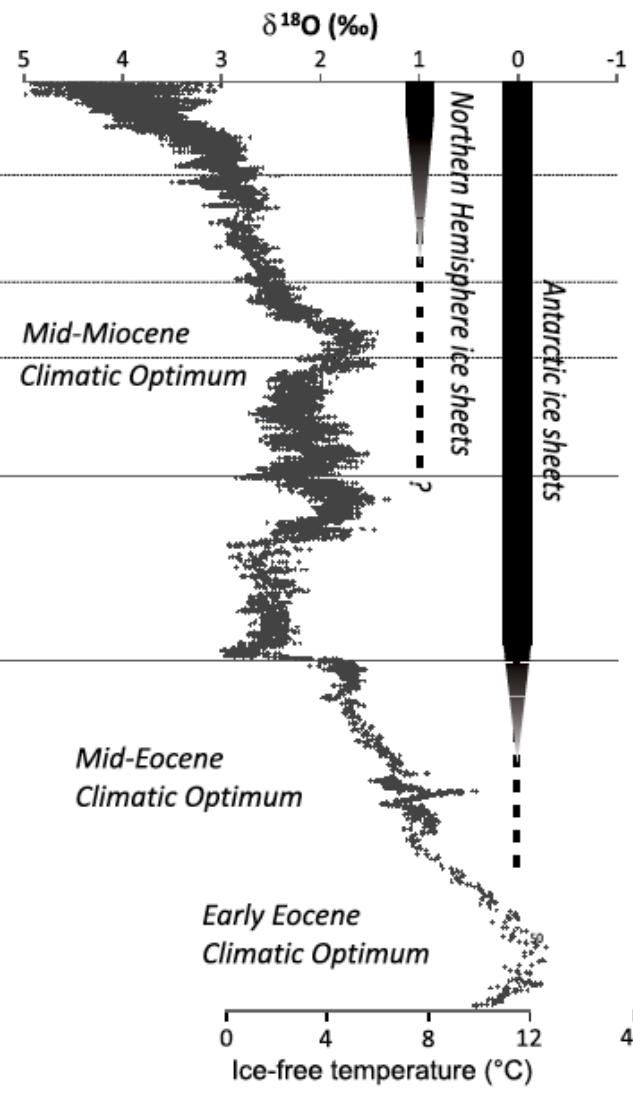
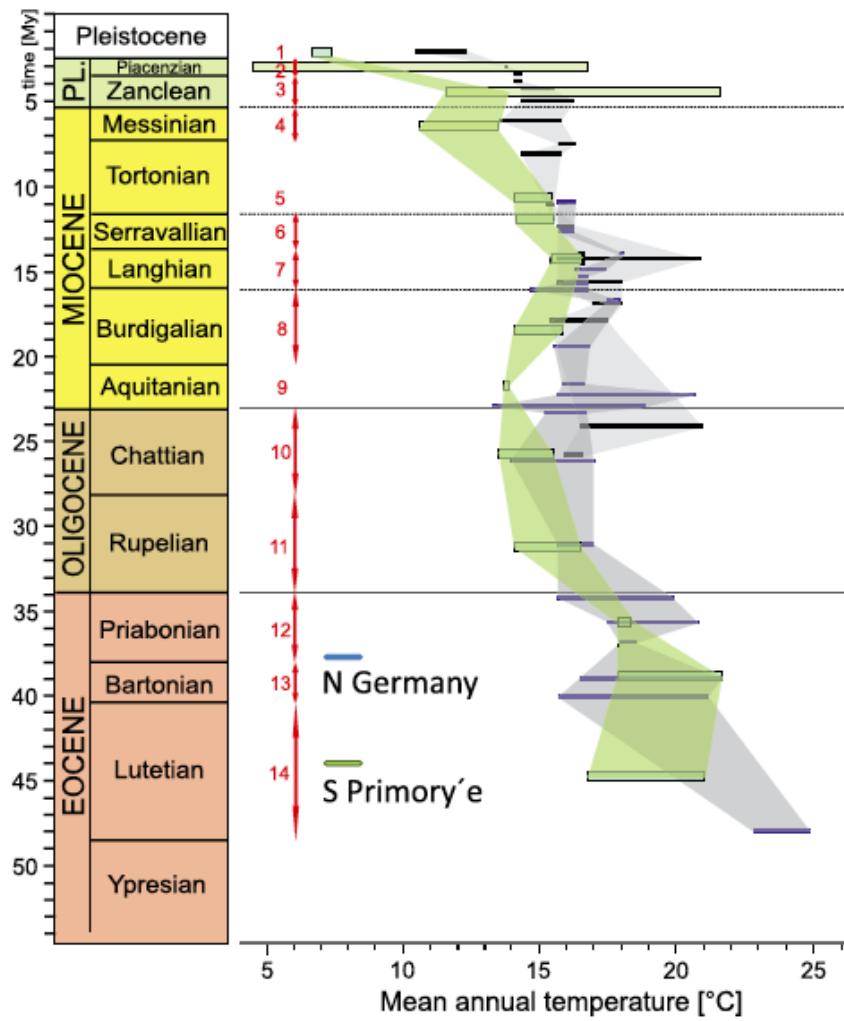
# Sea level for the last 120 Ma



(Miller et al 2011 Oceanography)

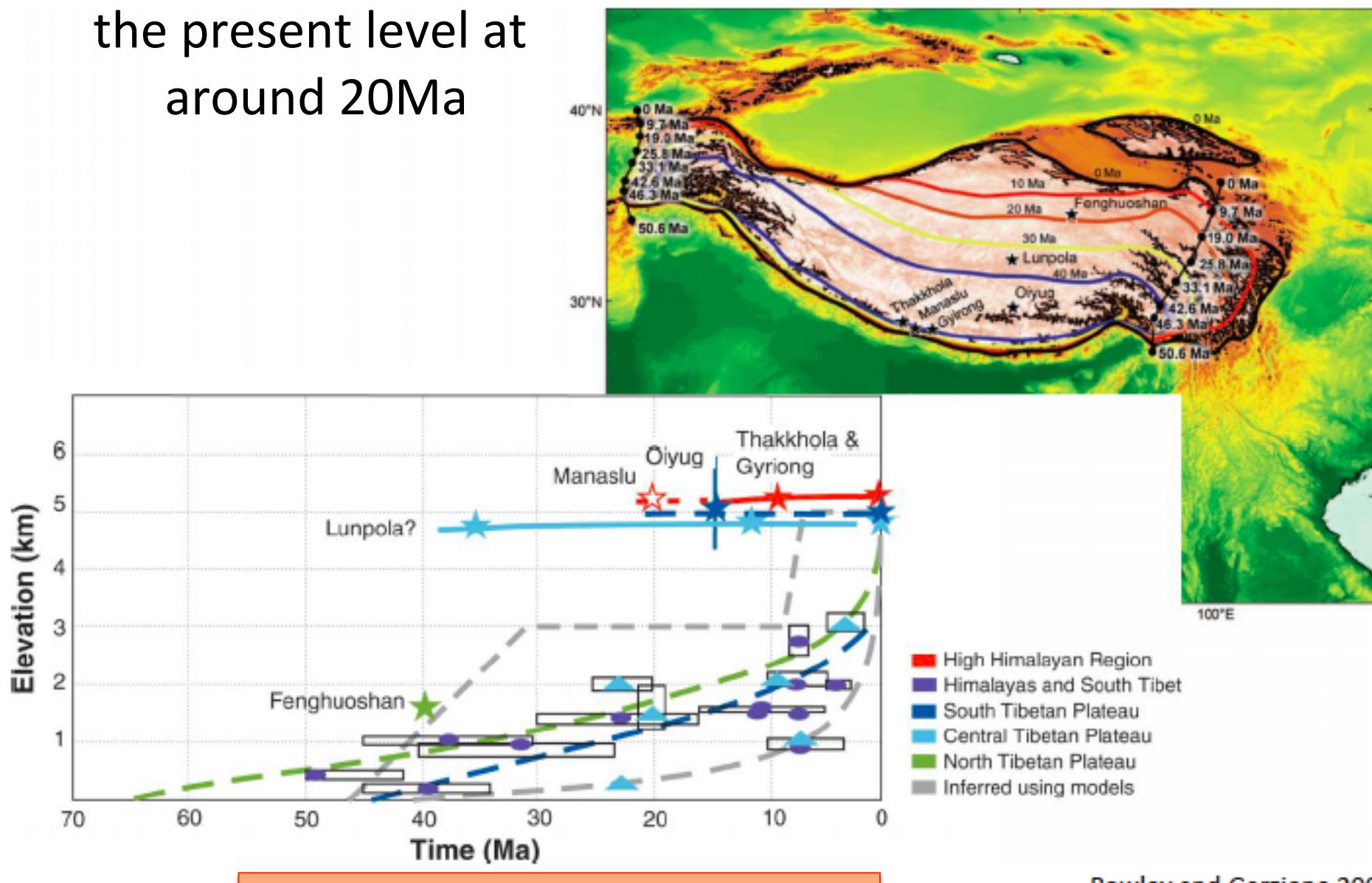


# Plant type based paleoclimate record on land



(Utescher et al EPSL 2015)

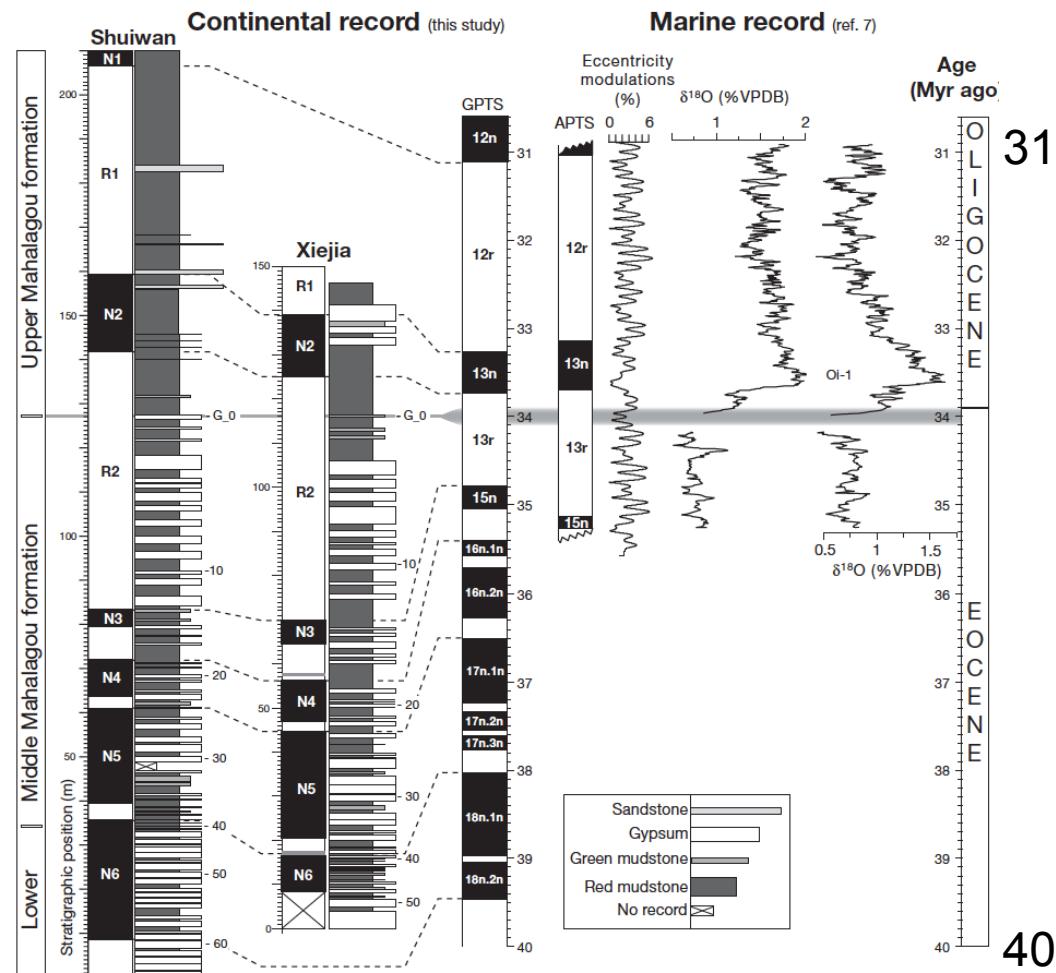
Himalaya reached to the present level at around 20Ma



Rowley and Garzione 2007

Modified from Laurence's talk

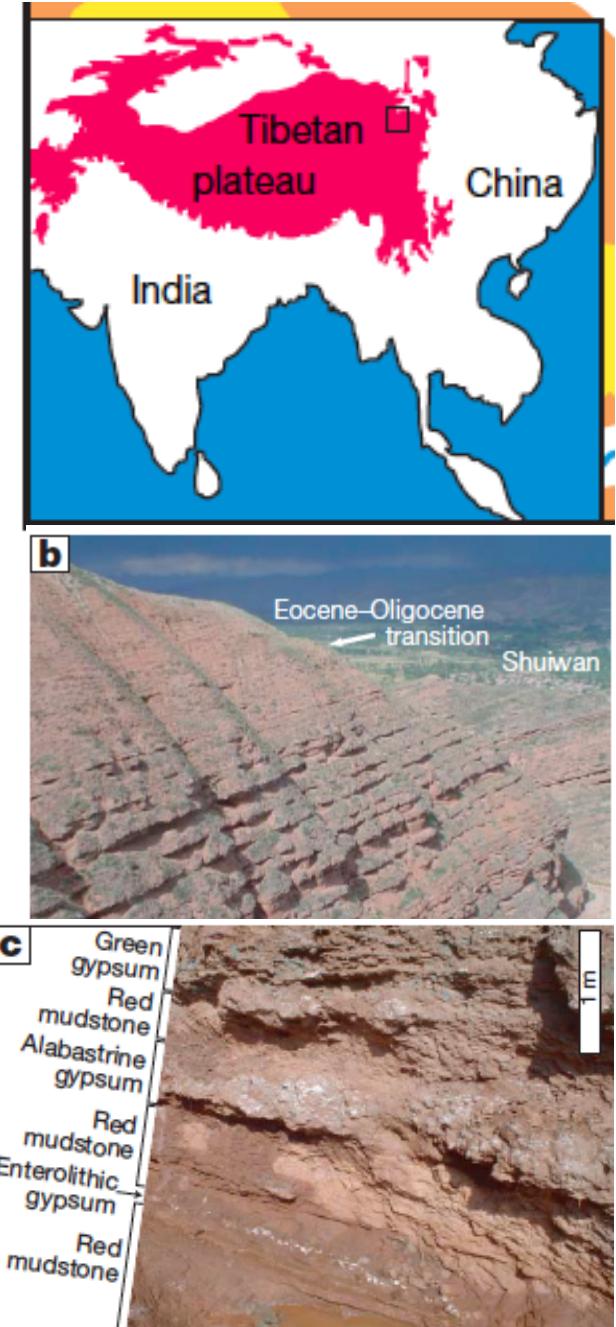
# Global cooling and Tibetan Plateau aridification at the Eocene-Oligocene transition



- Pollen captured cooling signal
- Uplift was earlier than the cooling

(Dupont-Nivet et al 2008, Geology)

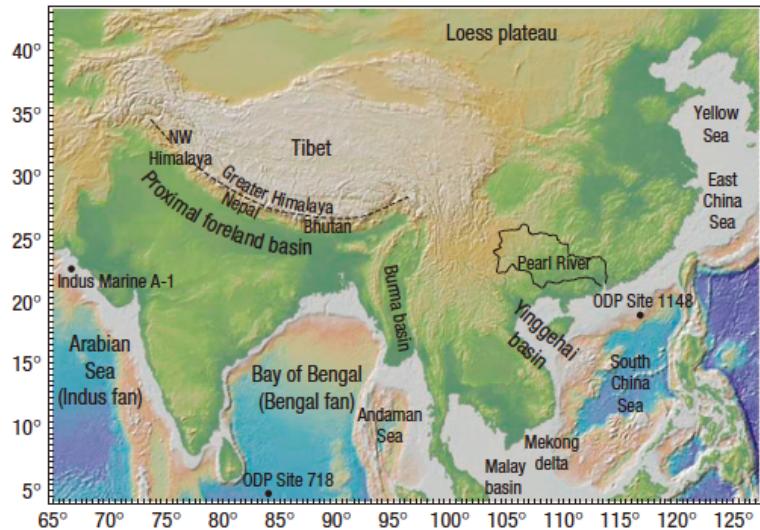
Tectonic driven climate change??



(Dupont-Nivet et al 2007, Nature)

# Uplift of Himalaya and Monsoon

(Clift et al Nature Geo 2008)



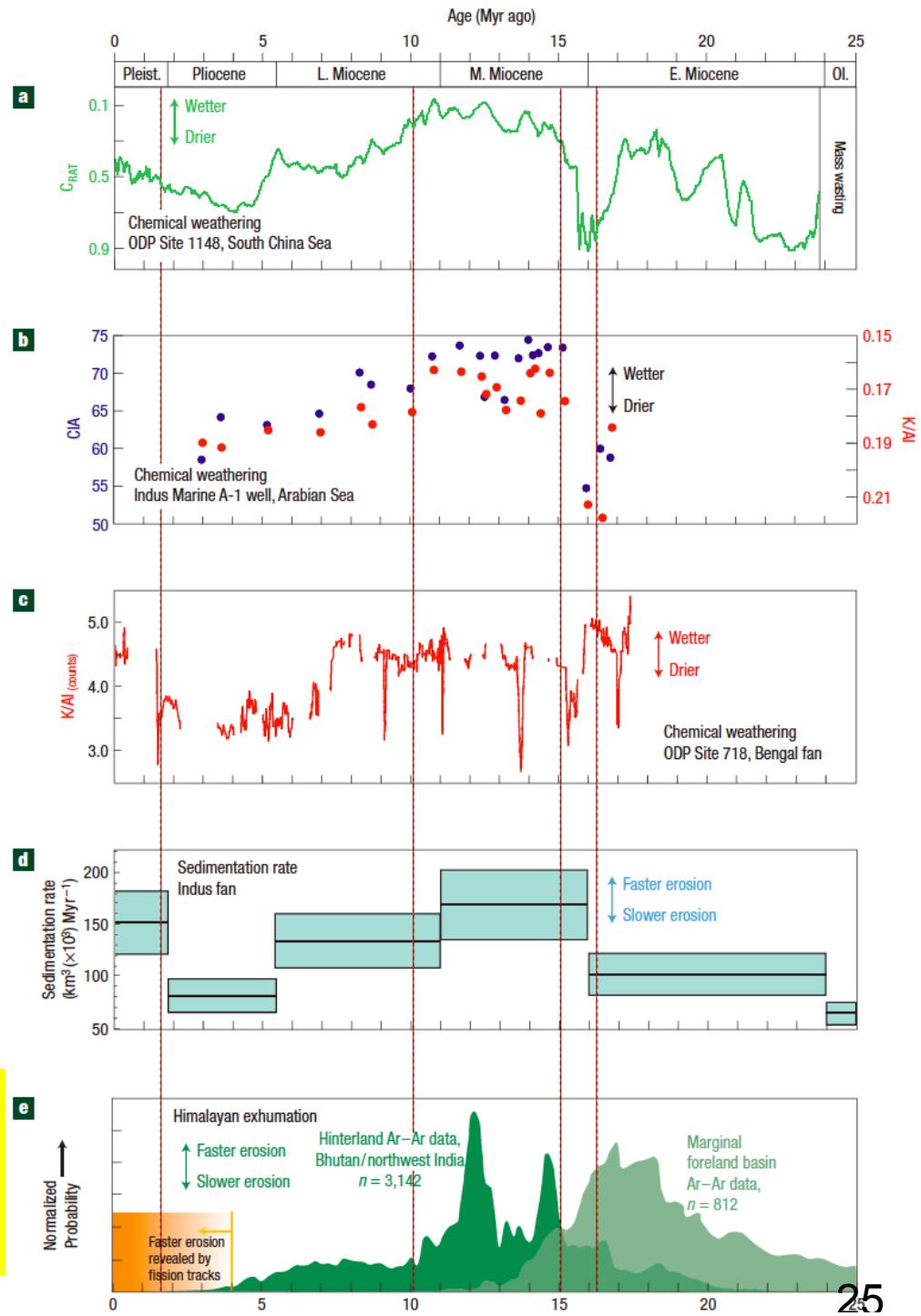
Al vs Na, K, Ca

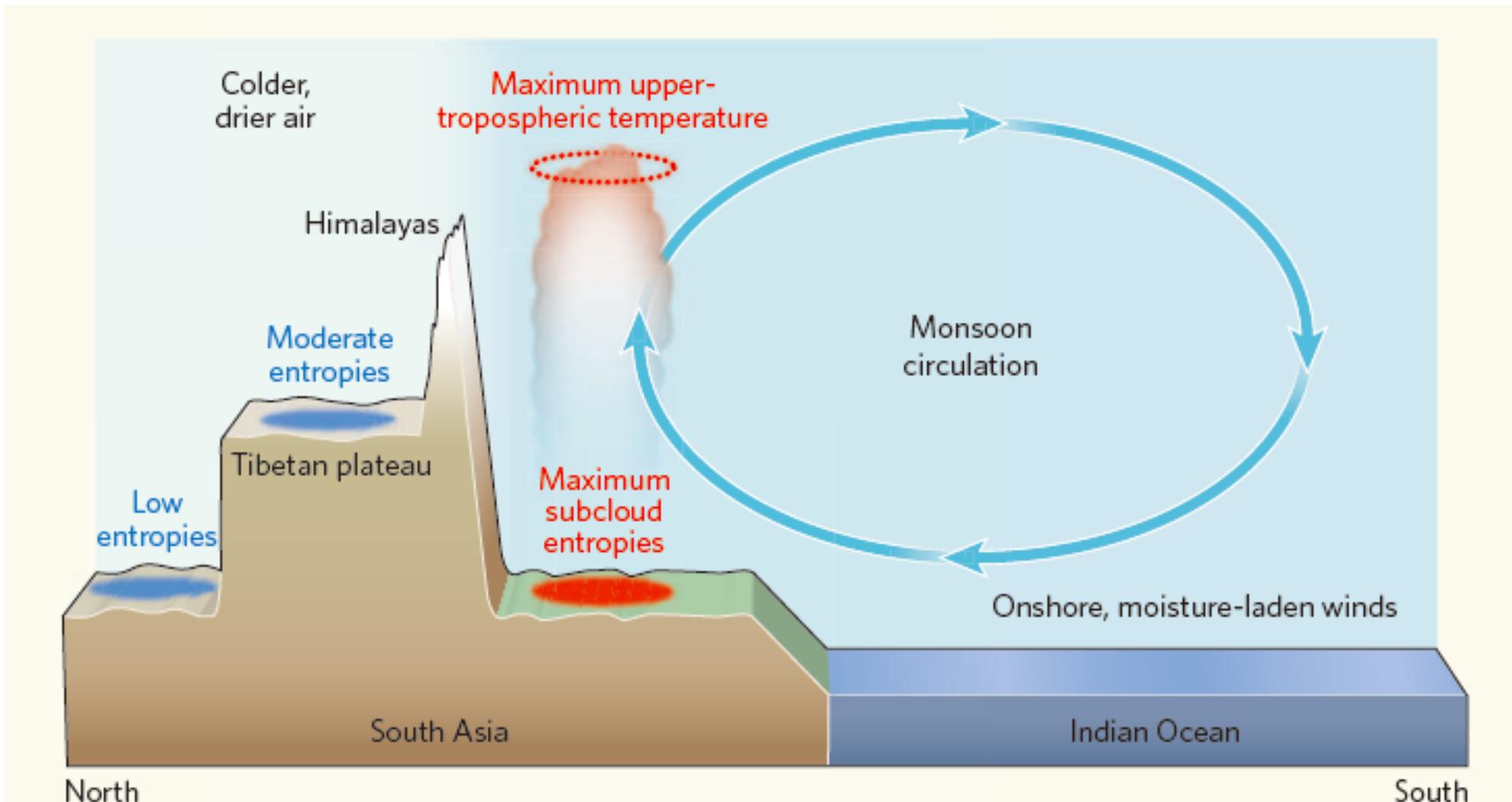
$$CIA = \frac{[Al_2O_3]}{[Al_2O_3 + CaO^* + Na_2O + K_2O]} \times 100$$

where  $CaO^*$  is the amount of  $CaO^*$  incorporated in the silicate fraction of the rock (Nesbitt and Young 1982 Nature)

- Closure of Tethys: 45-55Ma
- Himalayan-Tibetan orogen: <23Ma
- Monsoon start >23 Ma (29Ma)

*A strengthening of the East Asian Monsoon after 22–23 Ma, followed by an extended period of monsoon maximum between 18 and 10 Ma, then weakening.*

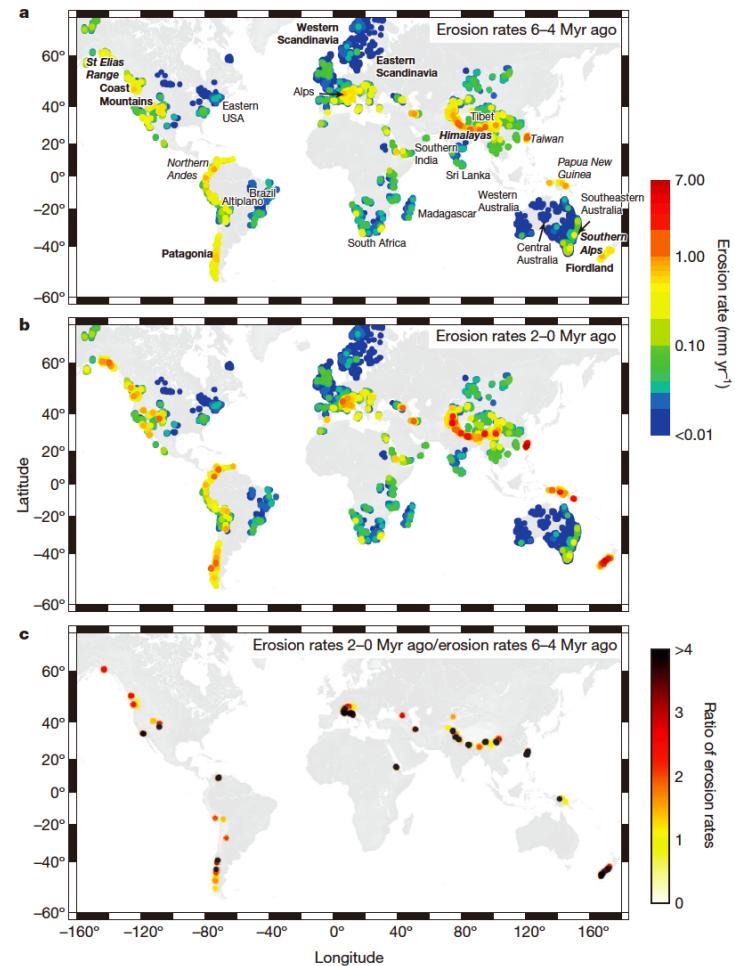




**Figure 1 | A new model monsoon.** Boos and Kuang's thinking<sup>1</sup> centres on the role of moisture convection rather than heat absorbed and radiated by the Tibetan plateau. Maximum subcloud moist entropy occurs south of the Himalayas, and the heat released as water vapour rises and condenses is reflected in peak temperatures in the overlying upper troposphere. The Himalayas keep the moist warm air over South Asia separated from the colder, drier air to the north, so the high energy of this air mass is undiluted, remains favourable for moisture-driven convection and underlies the strength of the South Asian monsoon.

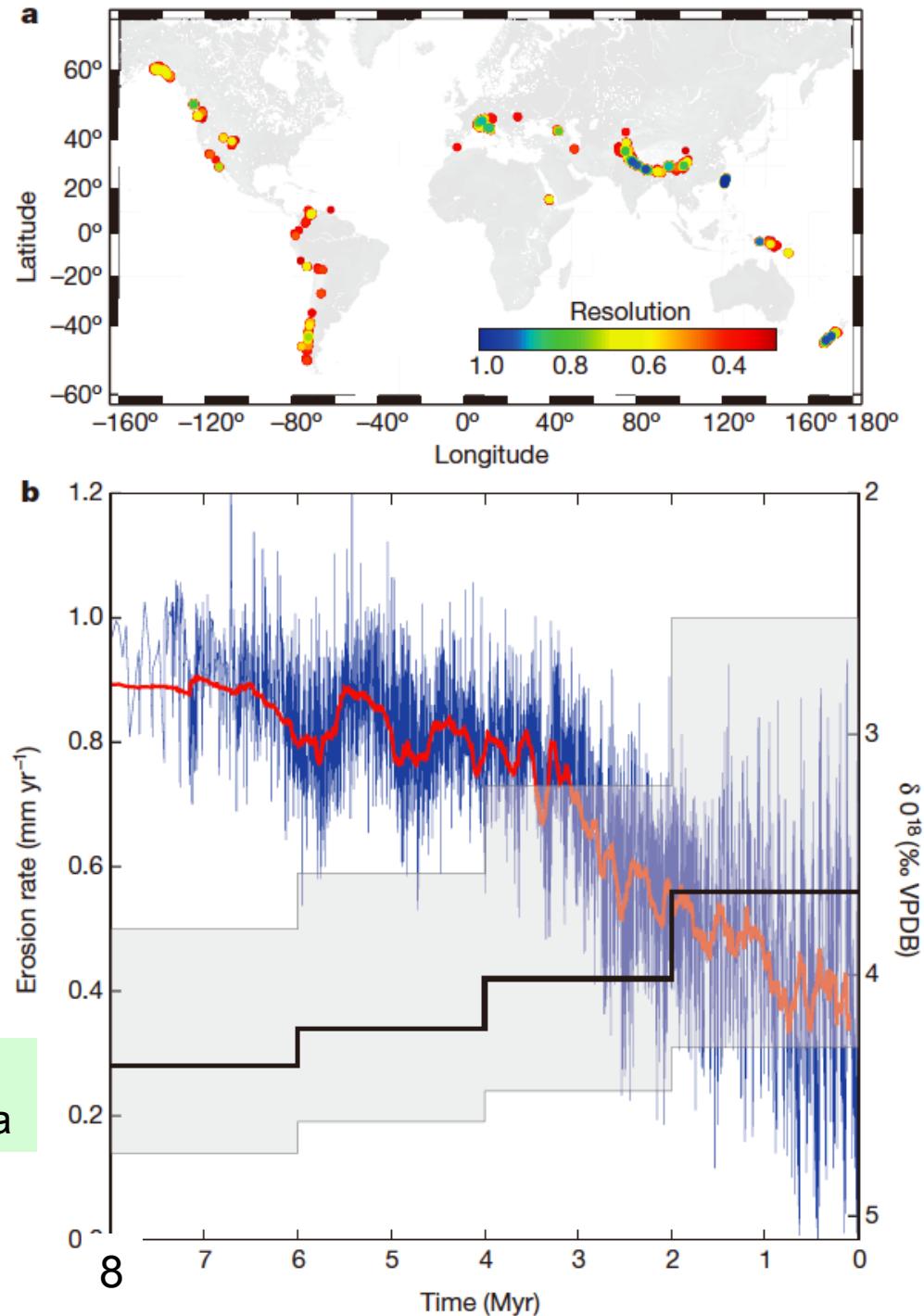
(Cane 2010 Nature)

# Accelerating erosion of mountains



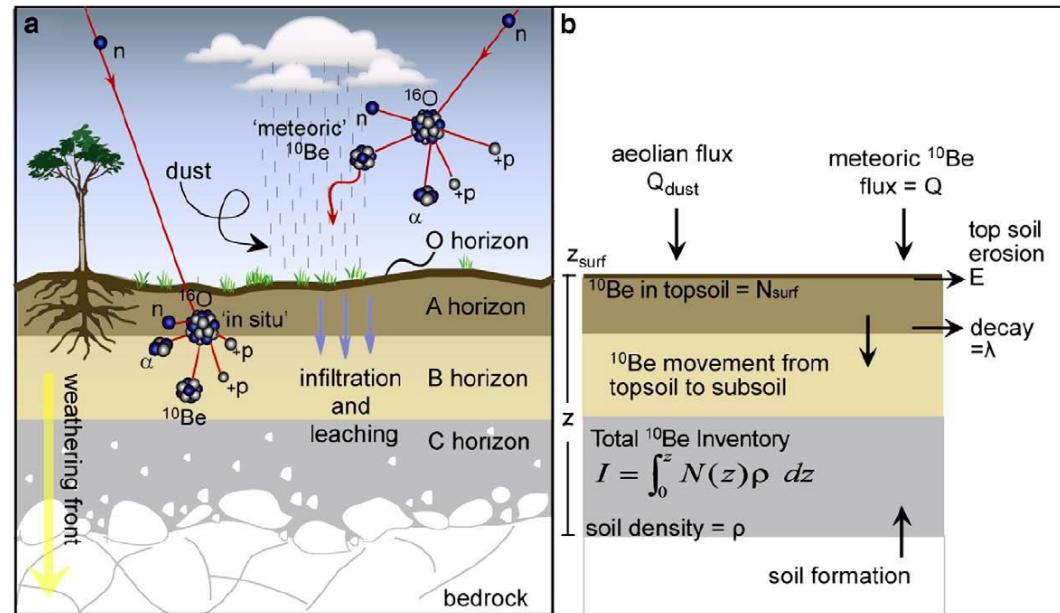
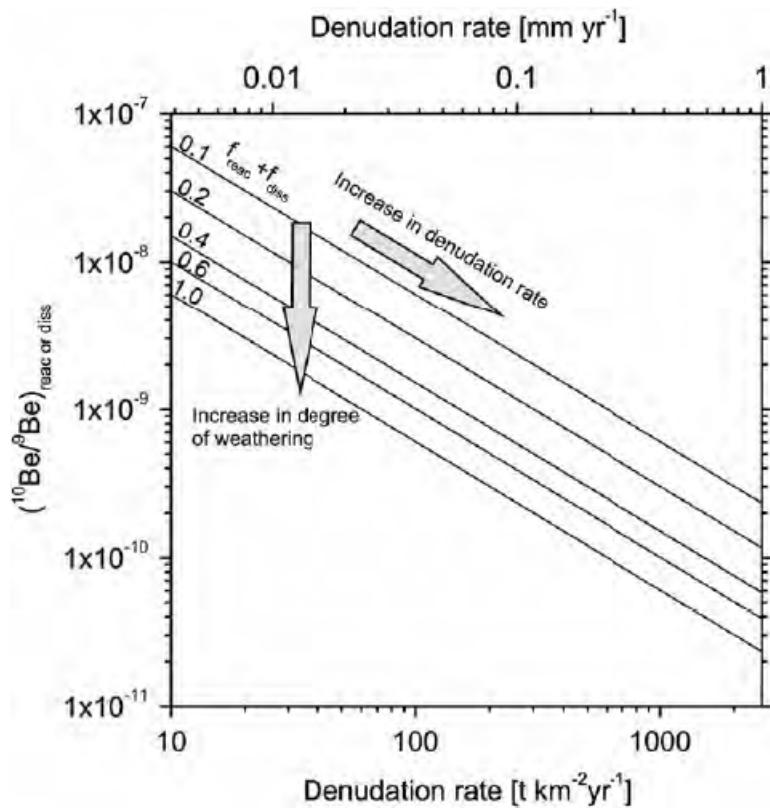
- Using compiled thermochronology data
- Rates of erosion increased for the last 8Ma

(Herman et al. 2013 Nature)



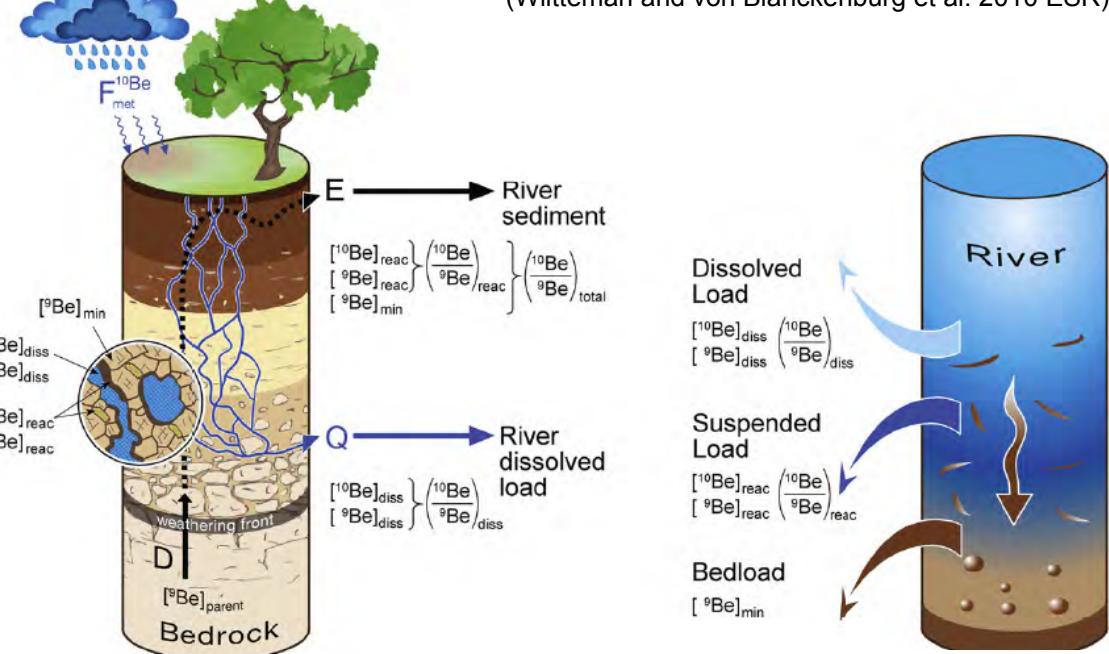
# Meteoric $^{10}\text{Be}/^{9}\text{Be}$ as a tracer for chemical weathering

$^{10}\text{Be}/^{9}\text{Be}$  decrease when chemical weathering increased

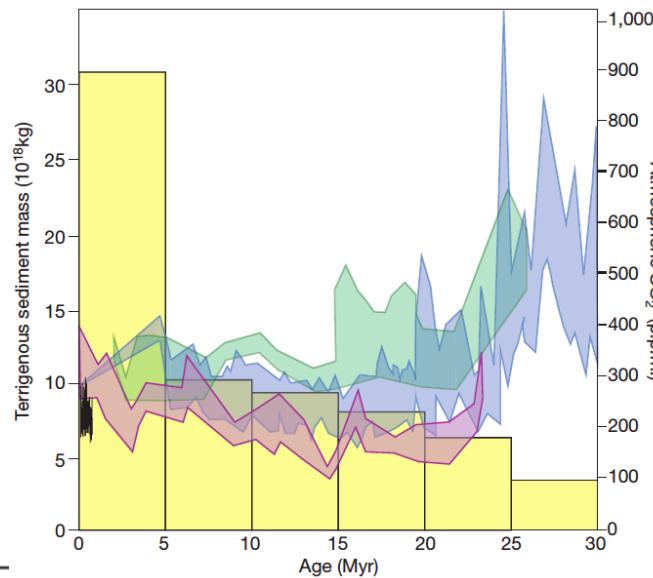
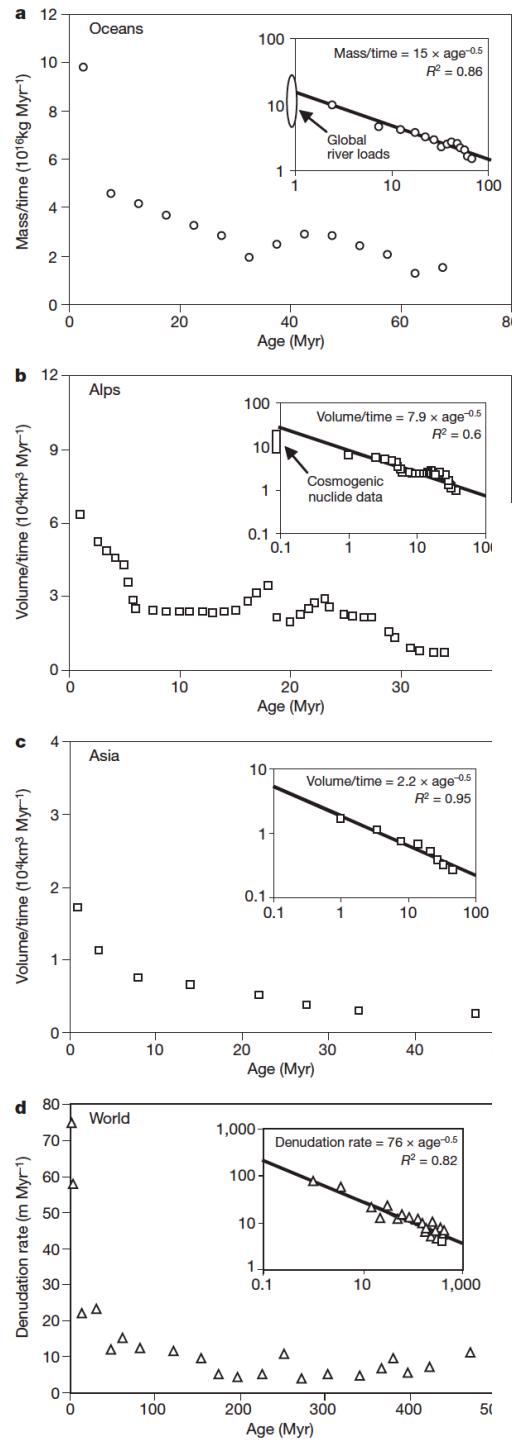


Schematic diagram of a soil profile and the ways in which  $^{10}\text{Be}$  can become incorporated into the soil. The weathering front follows the downward movement of water from surface precipitation and (not shown) ground water. (b) Schematic diagram of a soil profile and definitions of variables in Eqs. (4)–(21).

(Wiltman and von Blanckenburg et al. 2010 ESR)

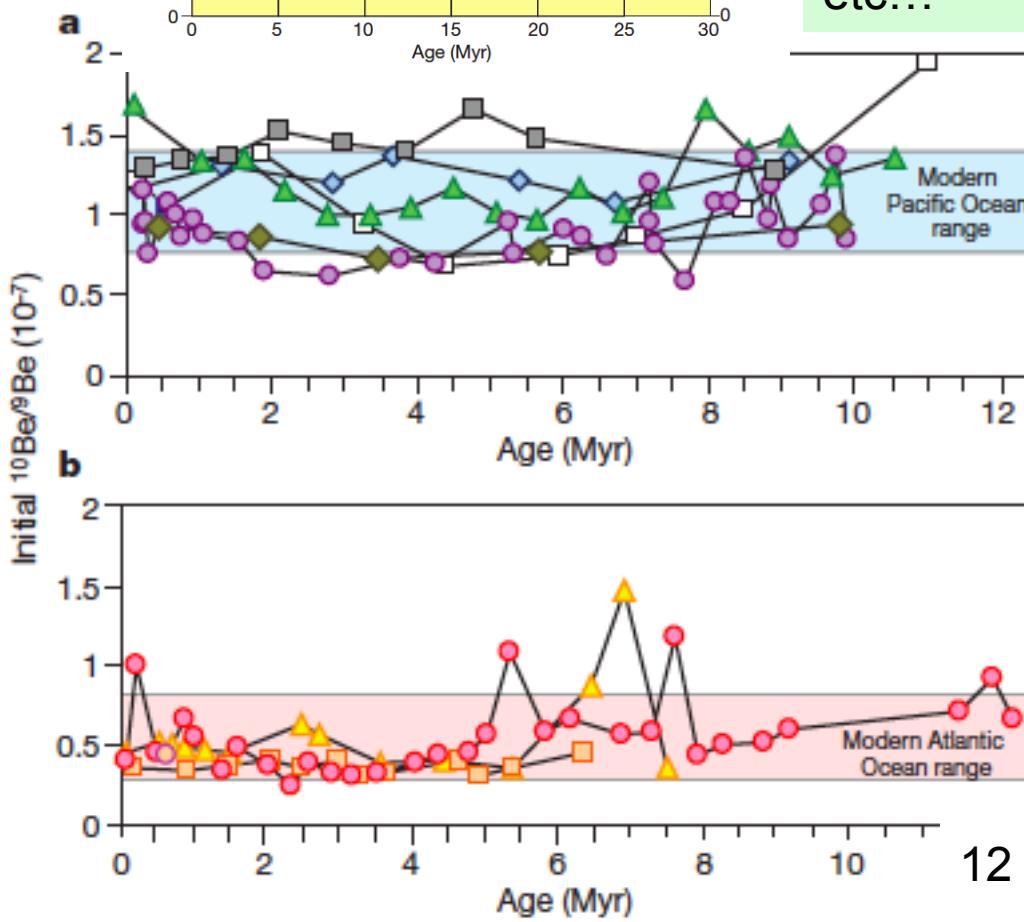


(von Blanckenburg et al. 2012 EPSL)



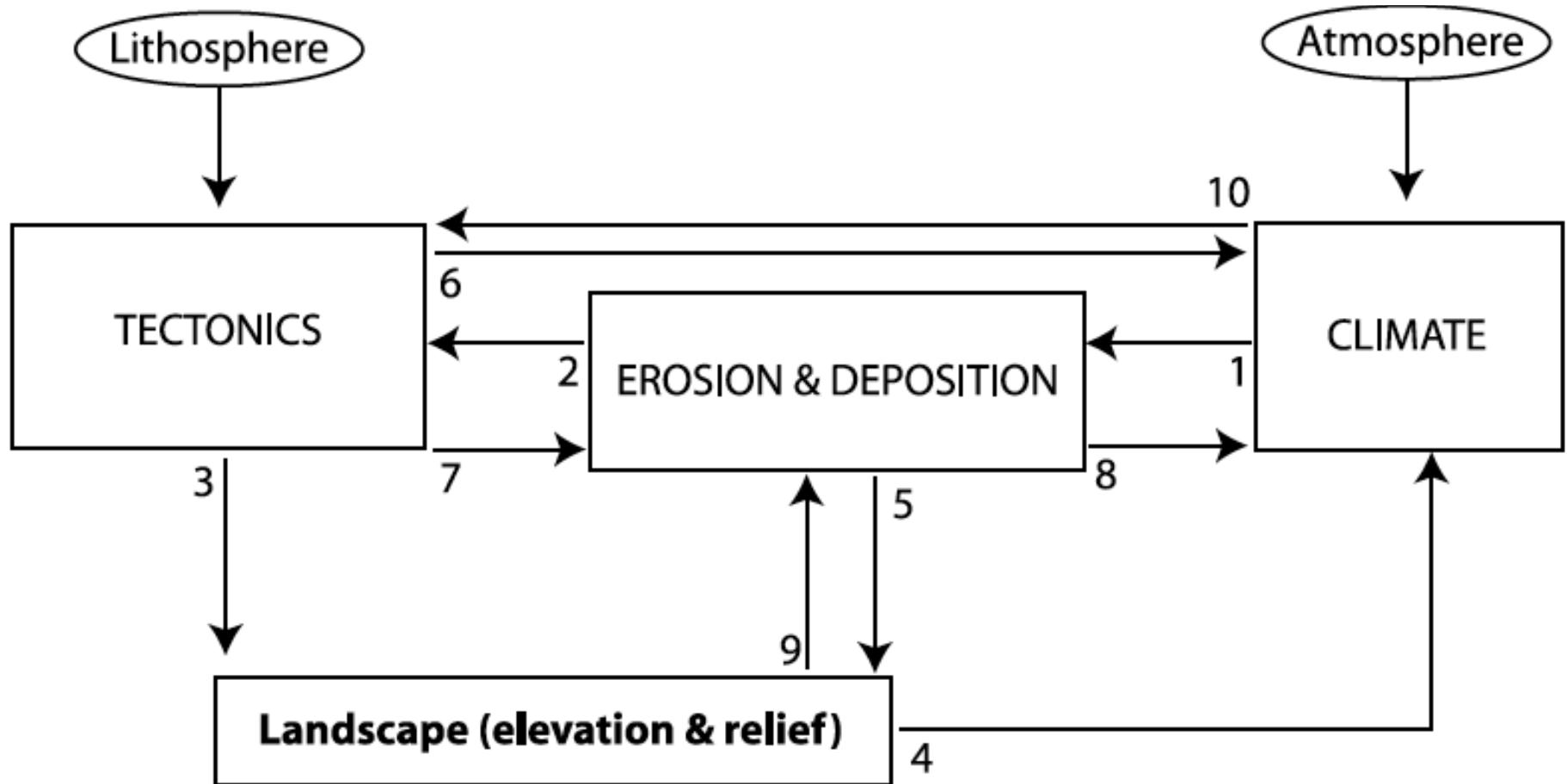
$^{10}\text{Be}/^{9}\text{Be}$  shows constant erosion

“Traditional” sed rate estimates has several issues: compaction, age determination, hiatus etc...



(Willenbring and von Blanckenburg 2010)

## Tectonics, Climate and Mountain topography



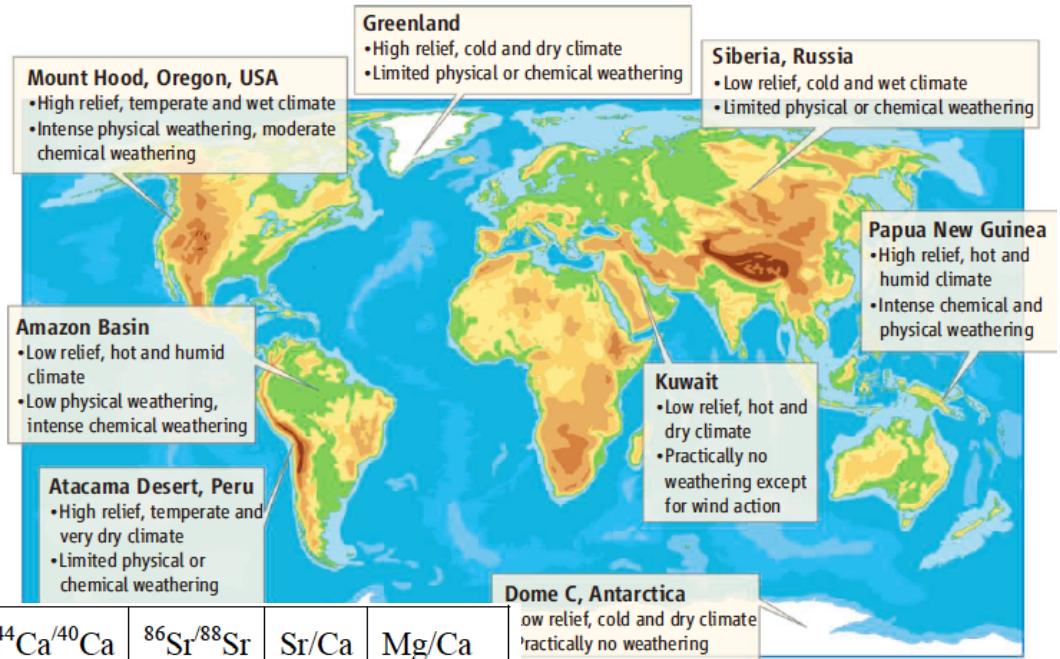
Are there anyways to untangle the complex relations? ...

The way to move forward...

Need to consider different types of weathering regimes. Thus...

Multi Proxy-Multi Process Matrix

Proxy Process	$^{7\text{Li}}/^{6\text{Li}}$	$^{87\text{Sr}}/^{86\text{Sr}}$	$^{187}\text{Os}/^{188}\text{Os}$	$^{44}\text{Ca}/^{40}\text{Ca}$	$^{86}\text{Sr}/^{88}\text{Sr}$	Sr/Ca	Mg/Ca
River Flux (total weathering input)	✓	✓	✓	✓	✓	✓	✓
Rock Type Weathered							
Calcite	-	✓	-	✓	✓	✓	✓
Aragonite	-	✓	-	✓	✓	✓	✓
Dolomite	-	✓	-	✓	✓	✓	✓
Silicates	✓	✓	✓	✓	✓	✓	✓
Shales	-	✓	✓	-	-	-	-
Basalts	✓	✓	✓	✓	✓	✓	✓
Evapoites	-	*	-	*	?	✓	✓
Weathering Regime	✓	-	-	-	-	-	-
Hydrothermal Flux	✓	✓	✓	✓	✓	-	✓
Sedimentation/Dissolution of Seafloor/Shelf Carbonates	-	*	?	✓	✓	✓	✓
Reverse Weathering	✓	-	-	-	-	-	✓
Cosmogenic Dust Input	-	-	✓	-	-	-	-
Subduction Fluid Expulsion	✓	-	-	-	-	-	-
**Other (temperature, vital effects)	-	-	-	✓	✓	✓	✓



(Paytan 2012)