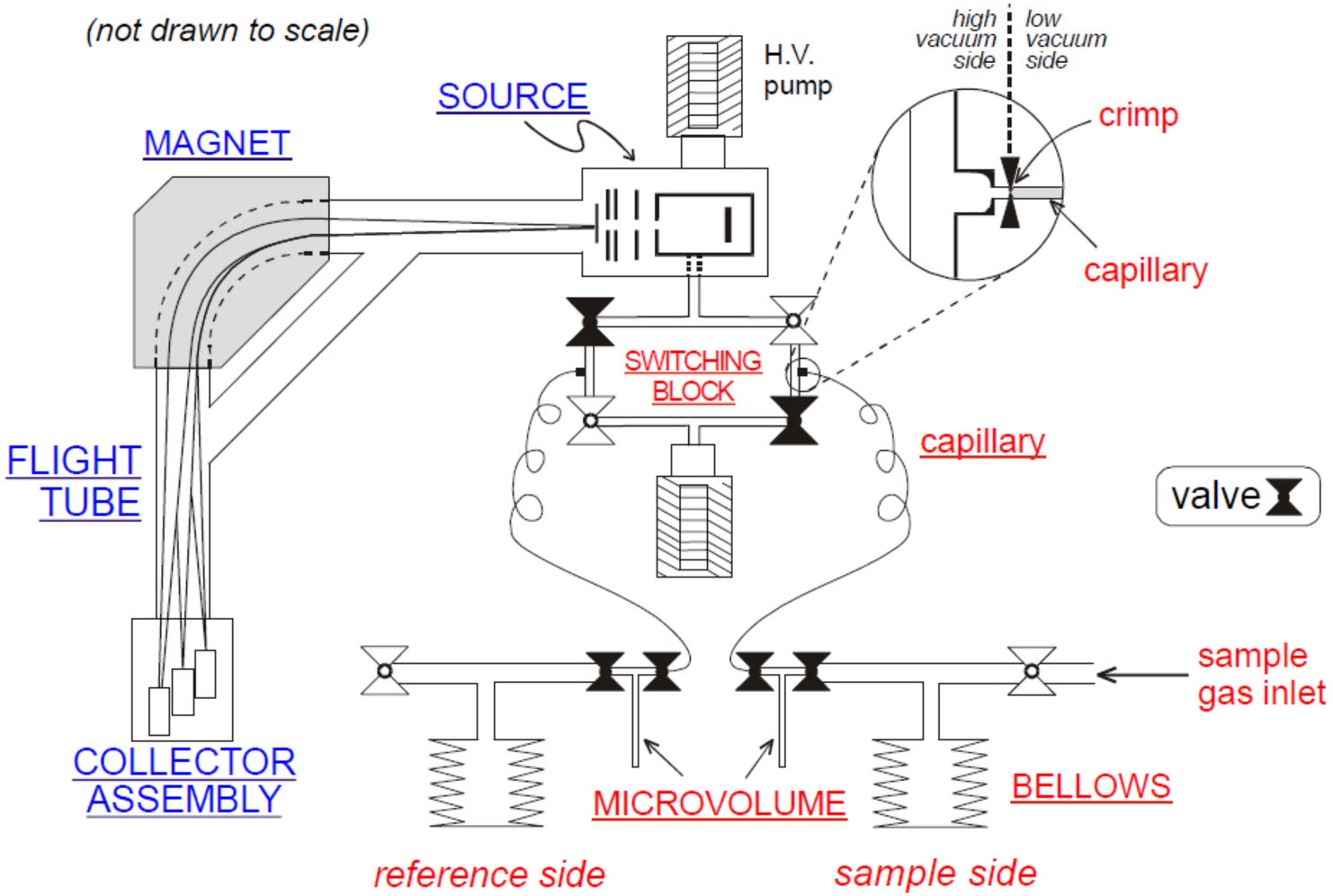
Lecture 16: Stable isotopes

1. Equilibrium fractionation of stable isotopes
2. Pleistocene climate

We acknowledge and respect the lək̓ʷəŋən peoples on whose traditional territory the university stands and the Songhees, Esquimalt and W̱SÁNEĆ peoples whose historical relationships with the land continue to this day.


(not drawn to scale)
SOURCE
H.V.
pump
high
vacuum
side
low
vacuum
side
crimp
capillary
MAGNET
SWITCHING
BLOCK
capillary
FLIGHT
TUBE
valve
sample
gas inlet
COLLECTOR
ASSEMBLY
MICROVOLUME
BELLOWS
reference side
sample side

"Before the discovery of isotopes, it was generally assumed that all atoms of an element were identical in all respects. With their discovery it was evident that such atoms may differ in atomic weights, but it was believed that their chemical and physical properties were identical except for those properties directly related to mass such as densities of gases and condensed phases, rates of diffusion and evaporation, and others of this kind. As a result of the theoretical and experimental studies reviewed in this paper, we now know that isotopes and isotopic compounds differ in their thermodynamic properties. These differences are small except in the case of the hydrogens and they generally decrease with increasing atomic weight. These small differences... may have important applications as a means of determining the temperatures at which geological formations were laid down."

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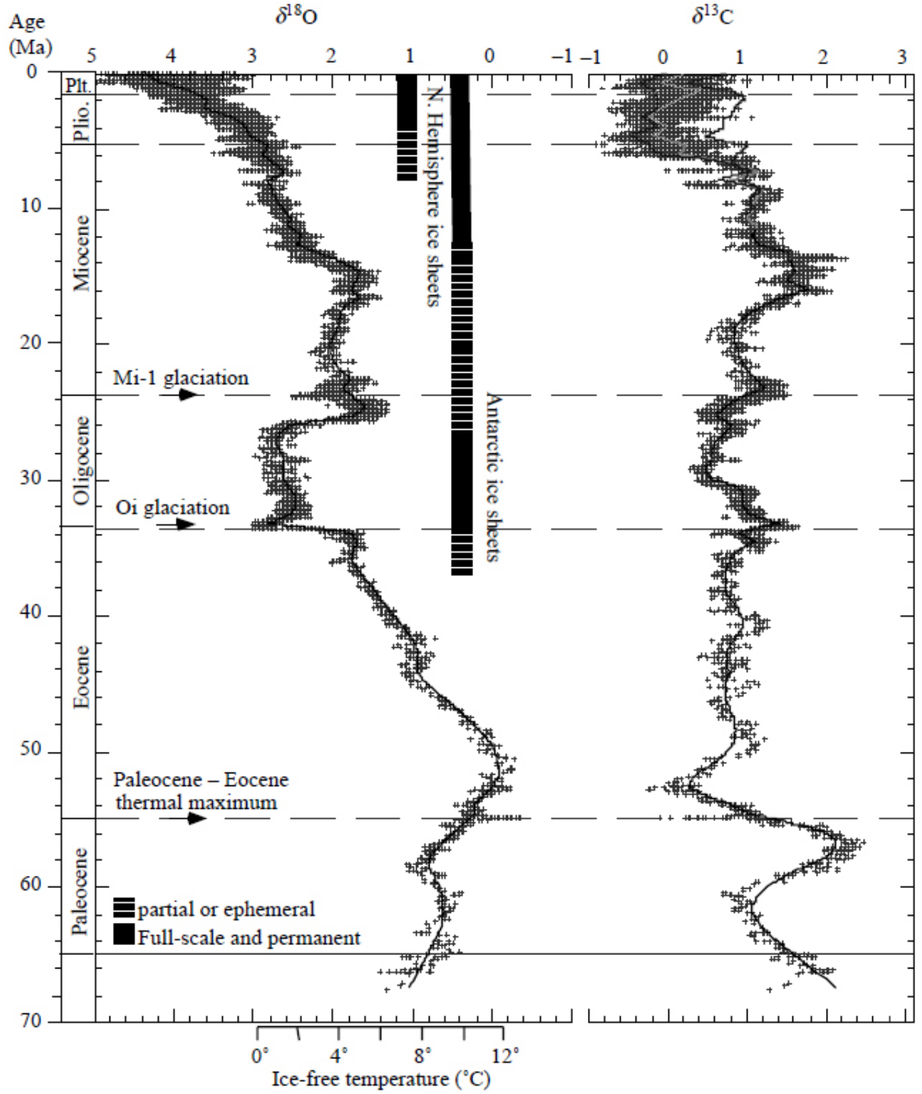
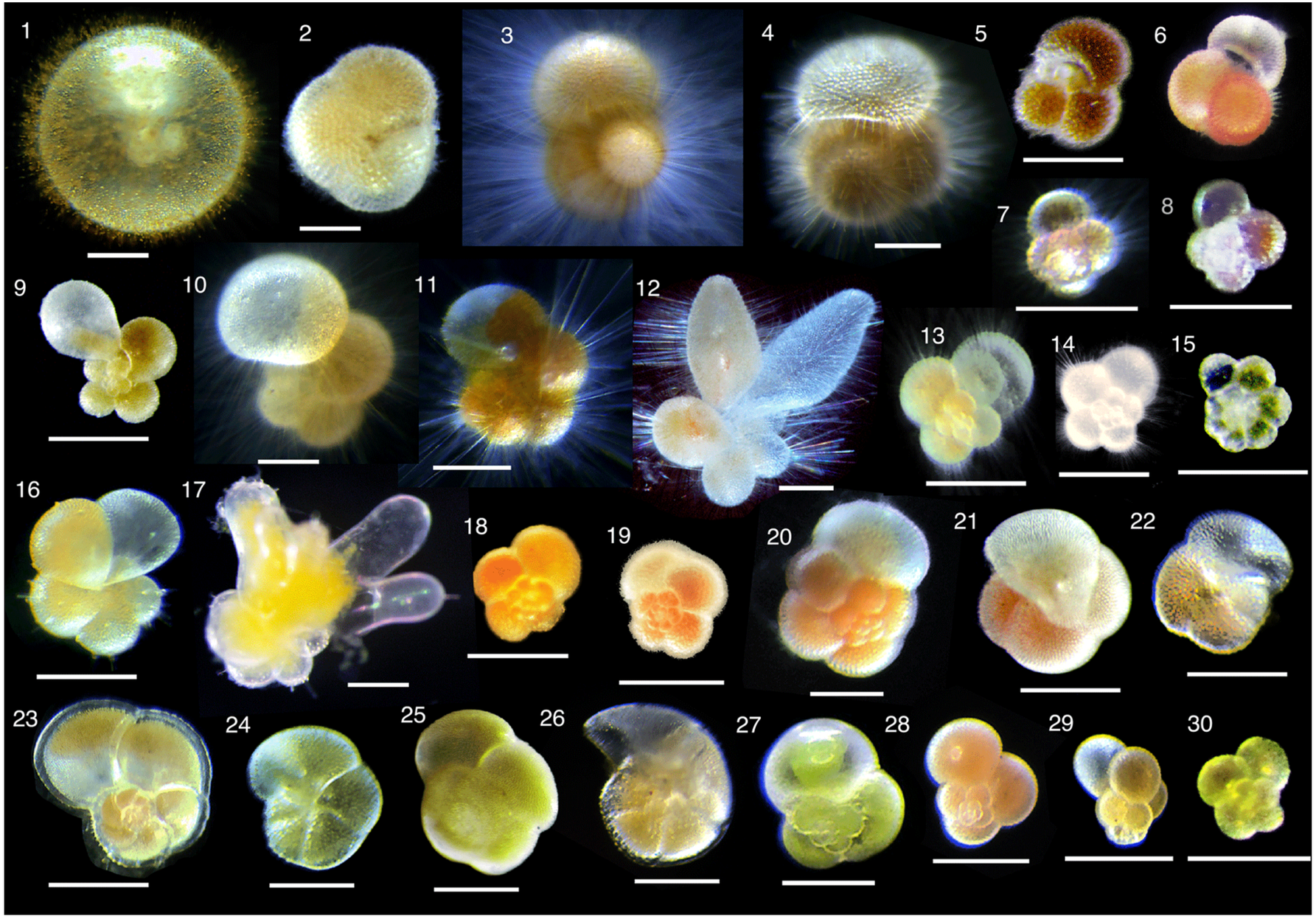


Compilation from Zachos *et al.*, 2001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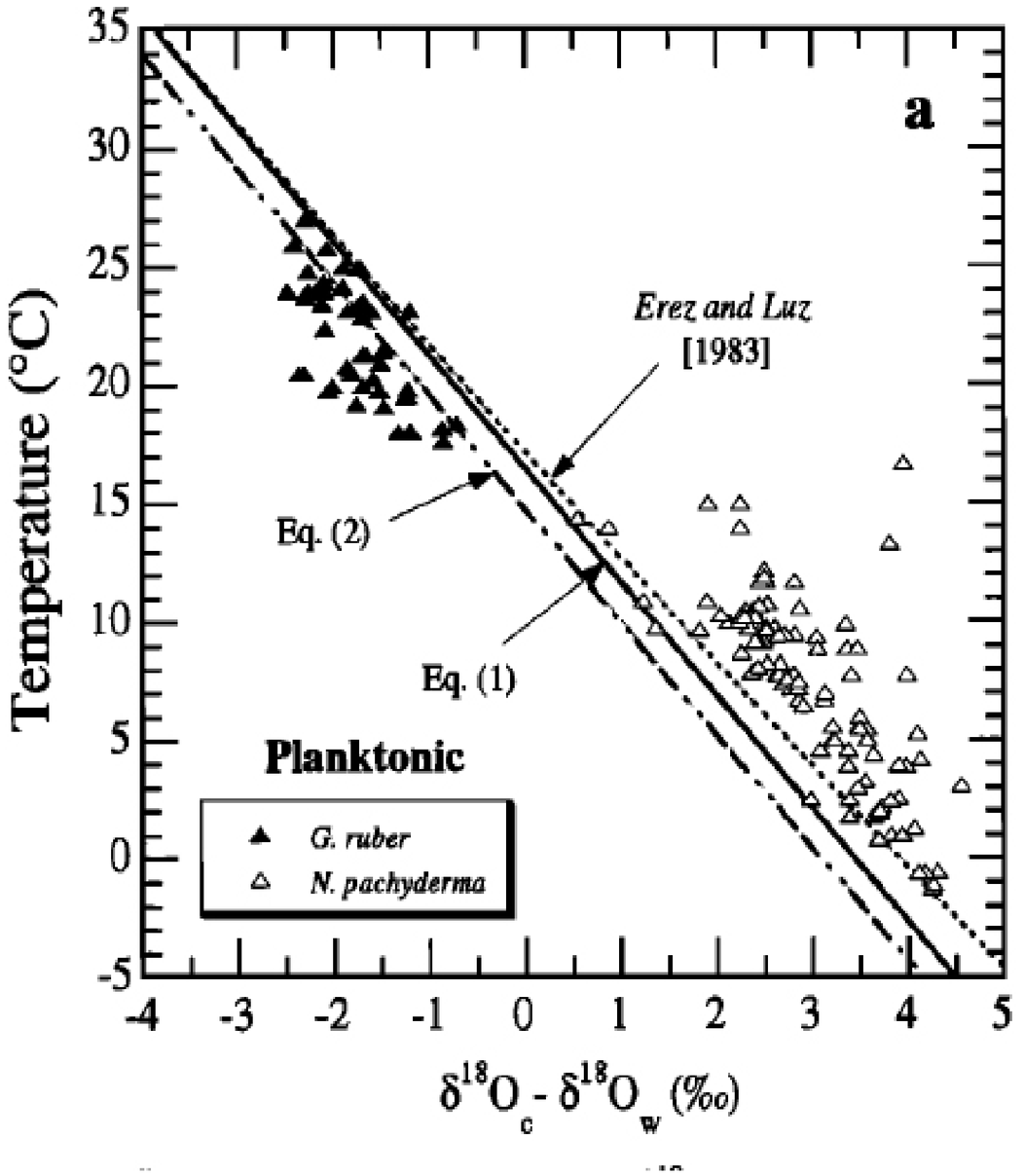
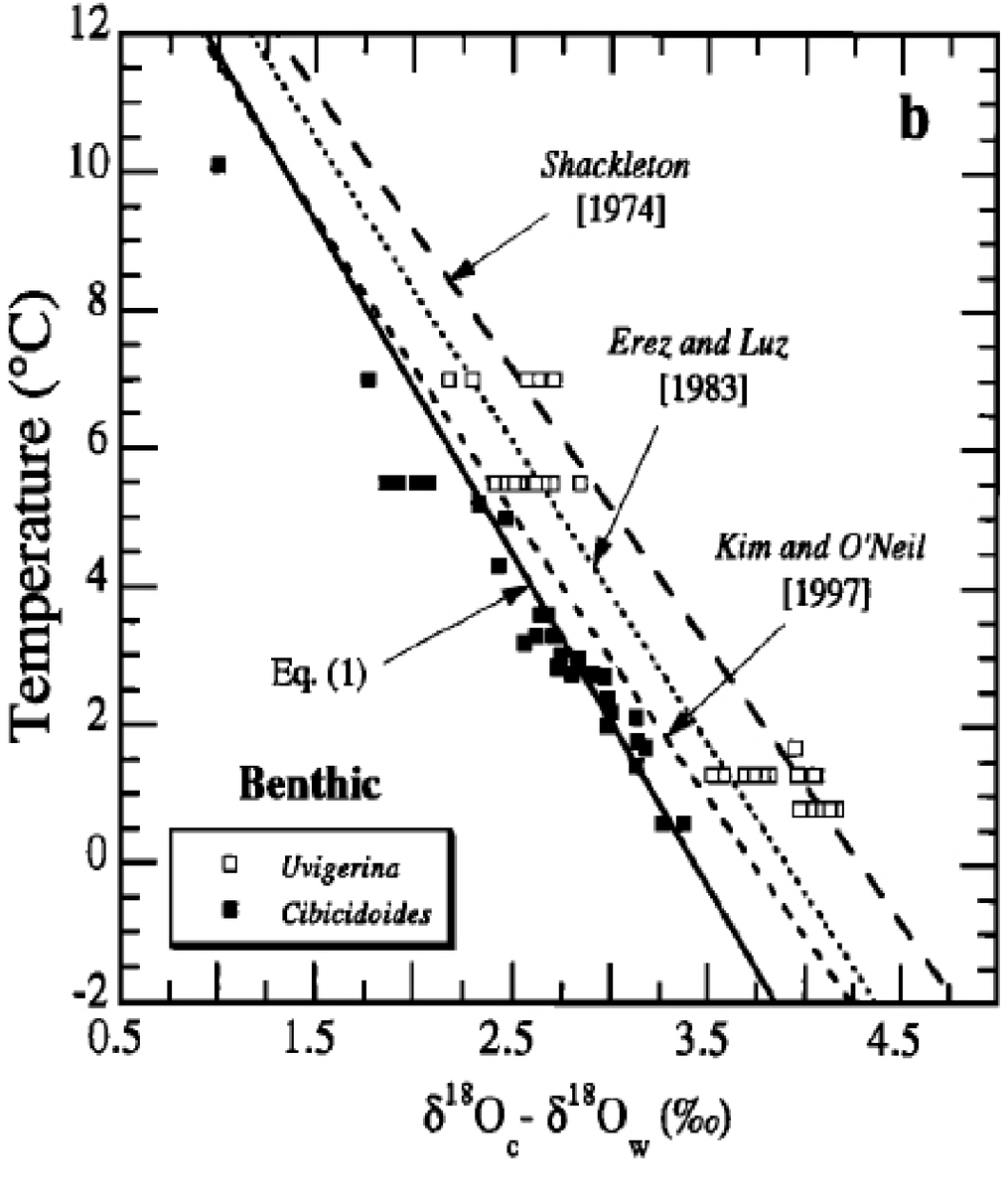

a
Temperature (°C)
35
30
25
20
15
10
5
0
-5
-4
-3
-2
-1
0
1
2
3
4
5
δ18Oc - δ18Ow (‰)
Erez and Luz
[1983]
Eq. (2)
Eq. (1)
Planktonic
G. ruber
N. pachyderma


b
Temperature (°C)
12
10
8
6
4
2
0
-2
0.5
1.5
2.5
3.5
4.5
δ18Oc - δ18Ow (‰)
Shackleton
[1974]
Erez and Luz
[1983]
Kim and O'Neil
[1997]
Eq. (1)
Benthic
Uvigerina
Cibicidoides

$$CaC^{18}O_3 + H_2{}^{16}O \longleftrightarrow CaC^{16}O_3 + H_2{}^{18}O$$

$$Q = \frac{[CaC^{16}O_3][H_2{}^{18}O]}{[CaC^{18}O_3][H_2{}^{16}O]} \approx \frac{99.76}{0.24}\cdot\frac{0.24}{99.76} \approx 1$$

$^{16}O = 99.76\%$

$^{18}O \approx 0.24\%$

What if ^{18}O more likely to be in $CaCO_3$?

$Q \neq 1$

$\ln 1 = 0$

at equilibrium:

$$\Delta G^\circ = -RT \ln Q \quad \text{if } Q \neq 0 \text{ then } \Delta G^\circ \neq 0$$

recall from L3 that ΔG° is the sum of the chemical potential of the products minus the sum of the chemical potential of the reactants

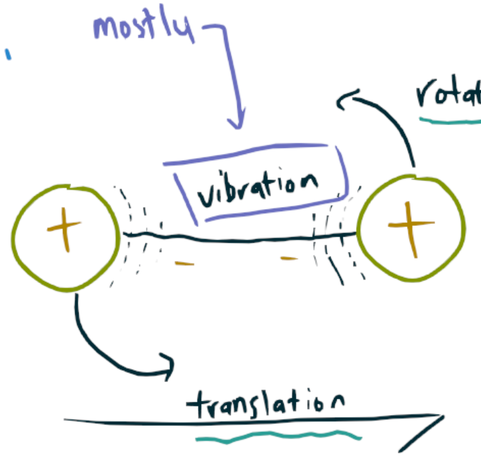
$$\mu_{CaC^{16}O_3} + \mu_{H_2O^{18}} - \mu_{CaC^{18}O_3} - \mu_{H_2O^{16}} = \Delta G^\circ \neq 0$$

μ must depend on mass

$\Delta \mu$ must depend on mass

↑

what is this difference in energy?

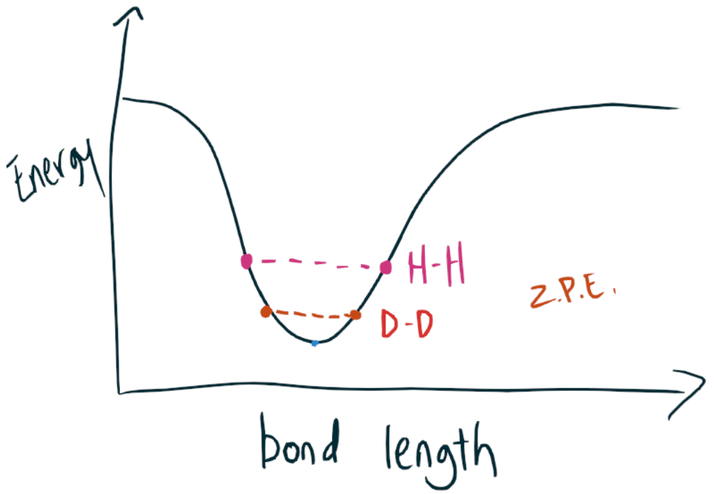


Electrical

↑ doesn't depend on mass

R and T ~ 0 in solids

Consider H_2



spring constant

2 masses on a spring

$F = -kx$

x ↑ difference from Bond length at the true minimum E

freq of vibration is directly proportional to energy

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

reduced mass

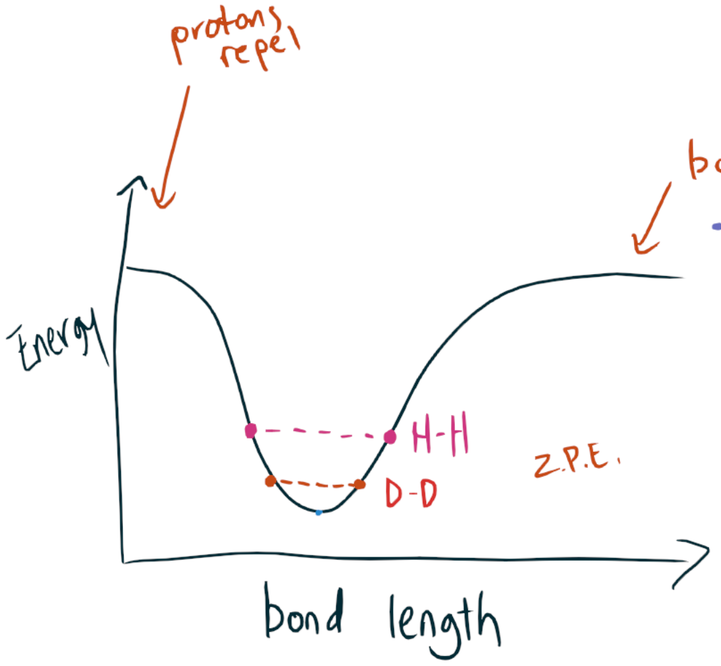
Vibrations only exist in specific levels (energy is quantized)

lowest level is the zero point energy

high ν = high E

$$\mu = \frac{M_1 \cdot M_2}{M_1 + M_2}$$

lower ν ⟶ $\mu_{H\text{-}D} = \frac{1 \cdot 2}{3} = 0.\bar{6}$ $\mu_{H\text{-}H} = \frac{1 \cdot 1}{2} = 0.5$

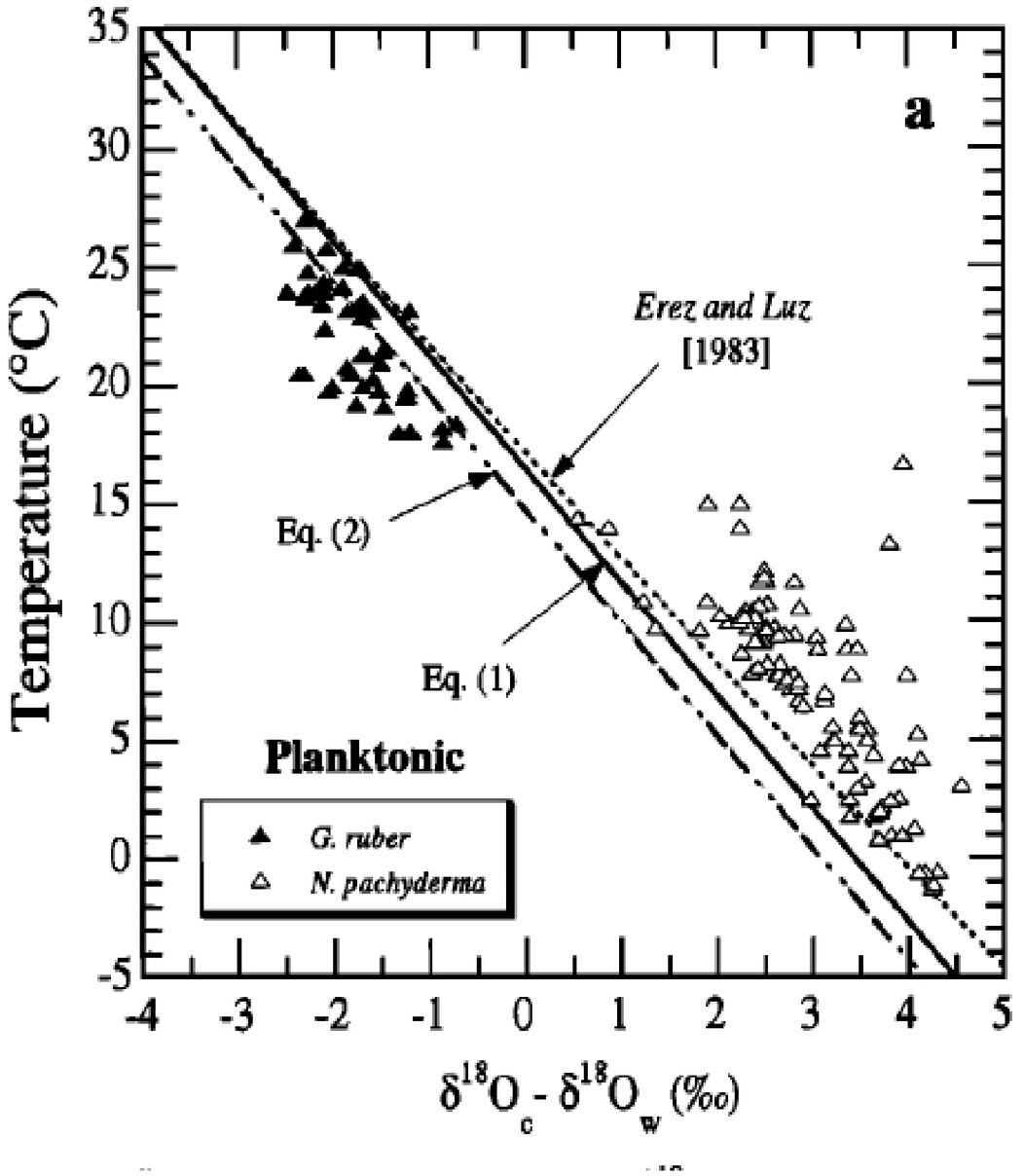


- Heavy isotopes have lower ZPE

* can we use this fact to predict which phases heavy isotopes prefer?

reactions minimize energy of the system so heavy isotopes prefer the phase with the greatest difference in ZPE_{LIGHT} and ZPE_{HEAVY}

- often the strongest bonds ie mineral over H_2O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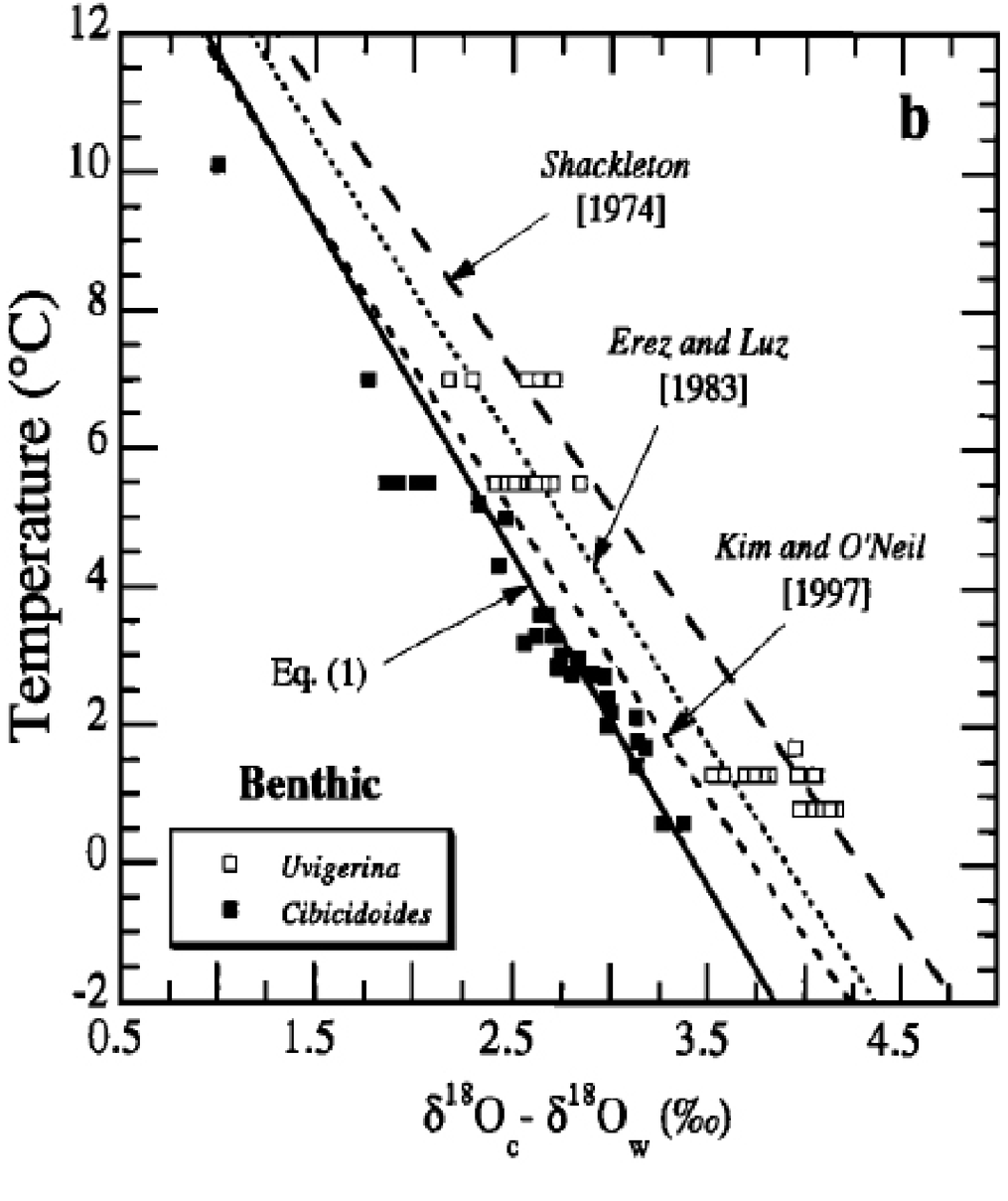
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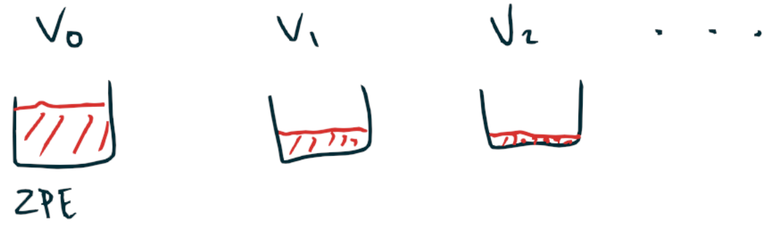
Kim and O'Neil
[1997]
Eq. (1)
Benthic
Uvigerina
Cibicidoides

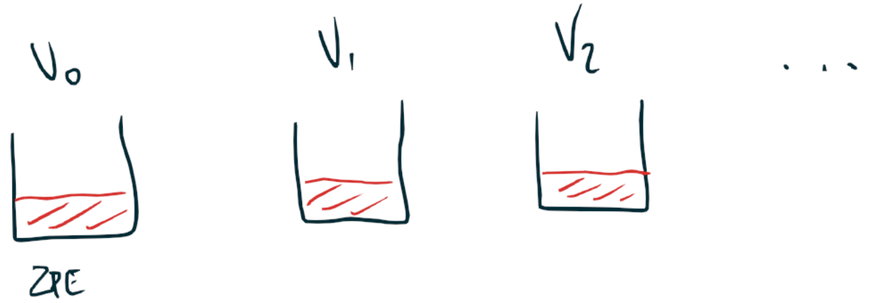
What about the sensitivity to Temp?

low T

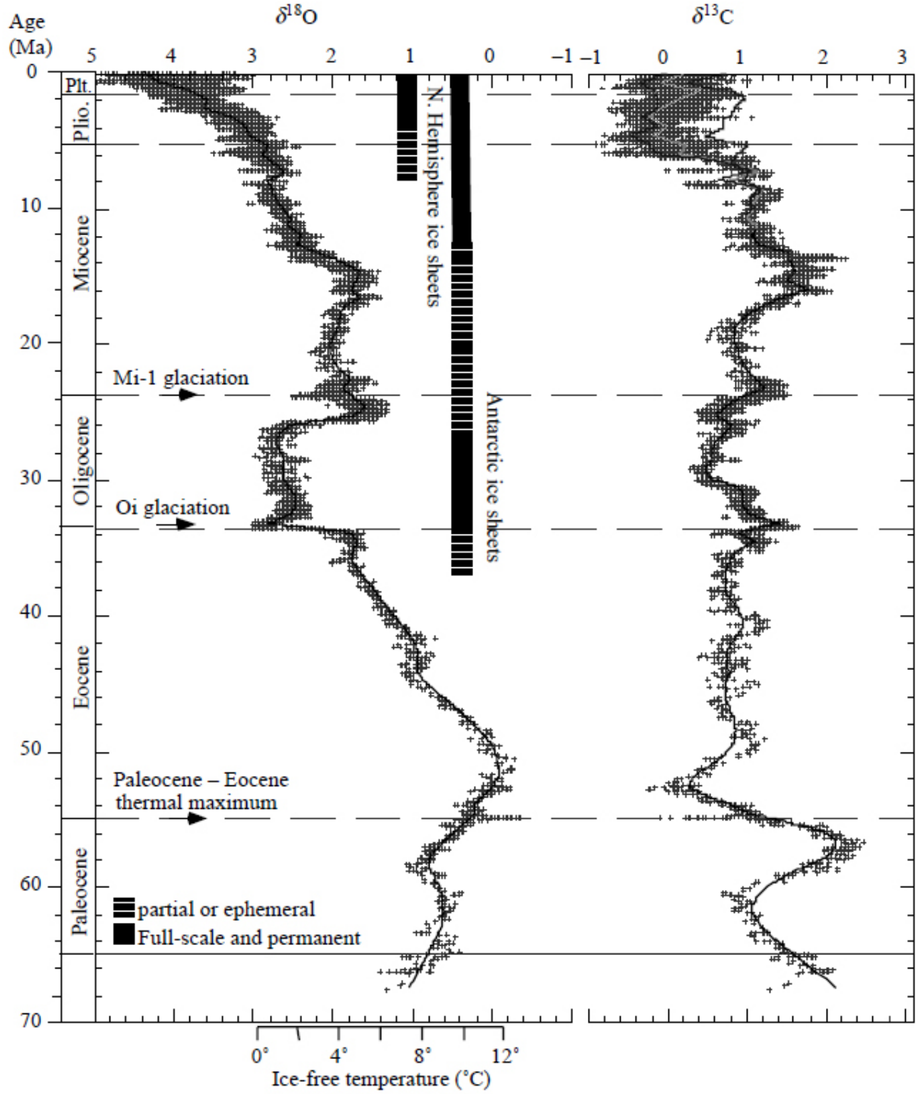


high T

even distribution at $T = \infty$



- MORE bonds vibrating at V_0, MORE energy difference between H-H and H-D



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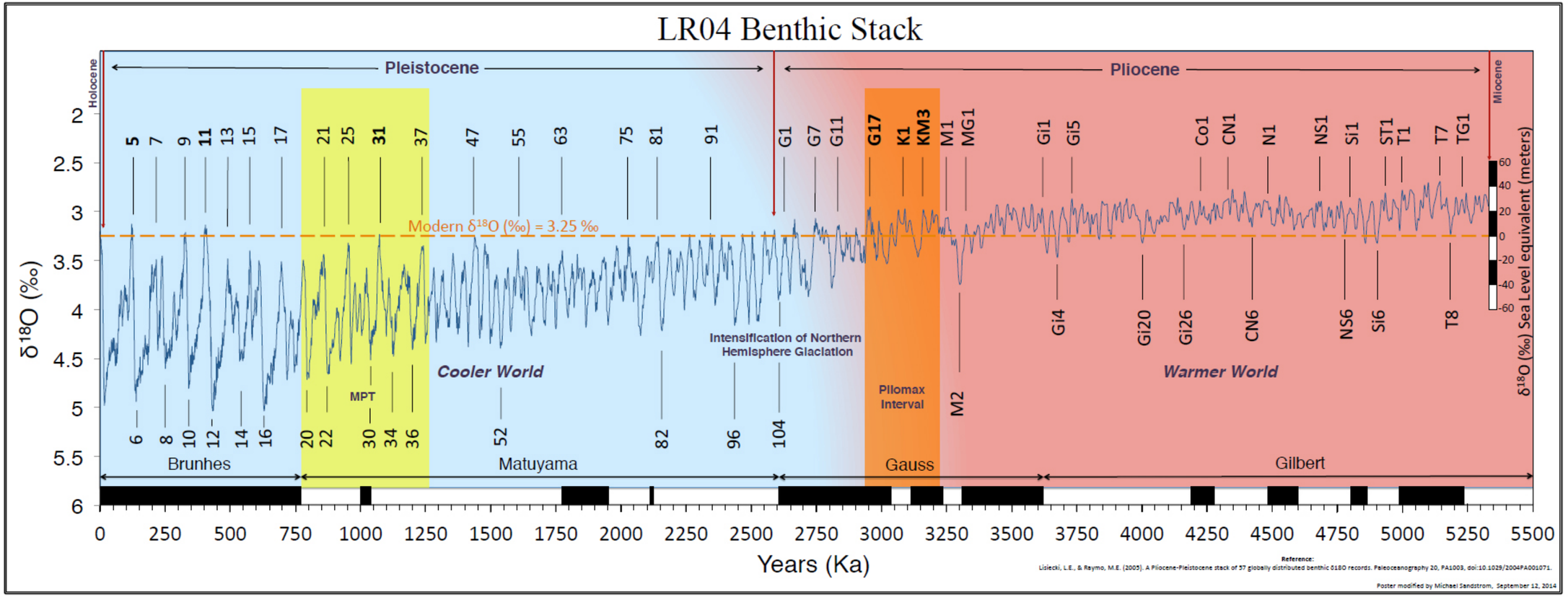
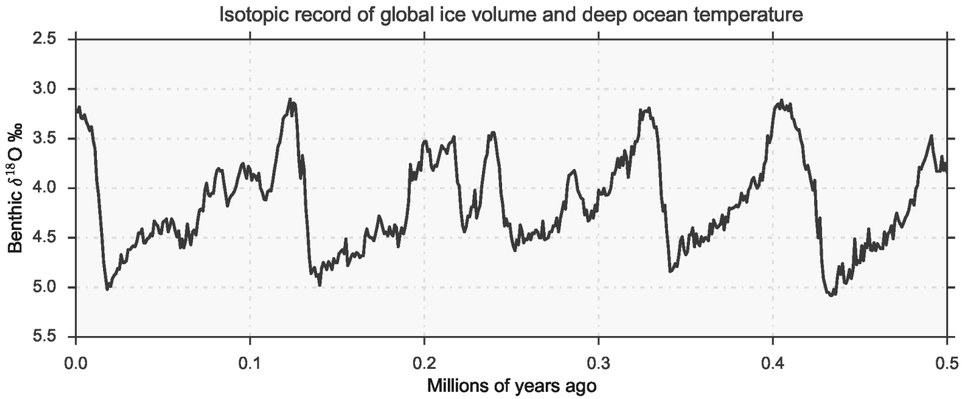
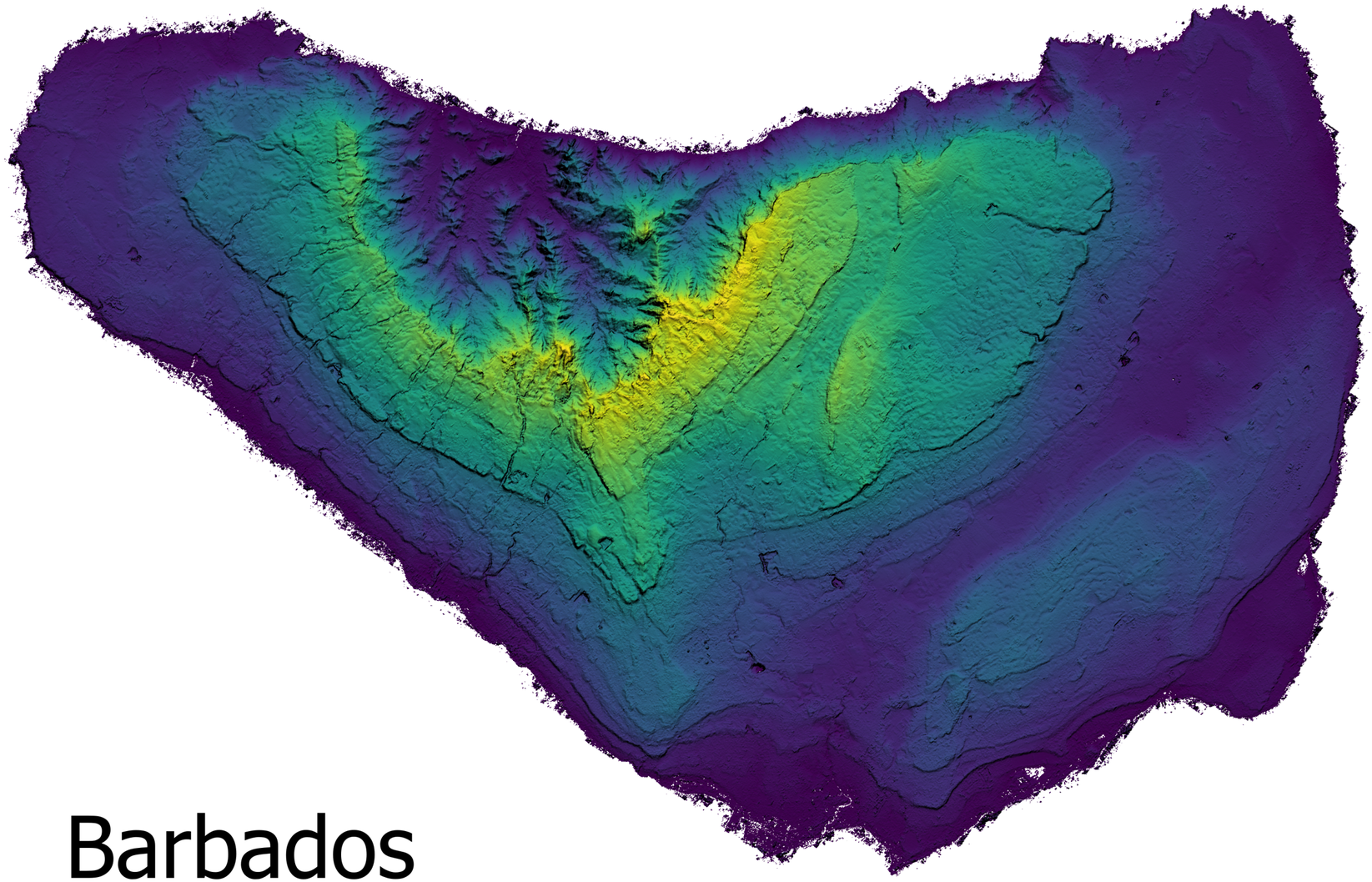


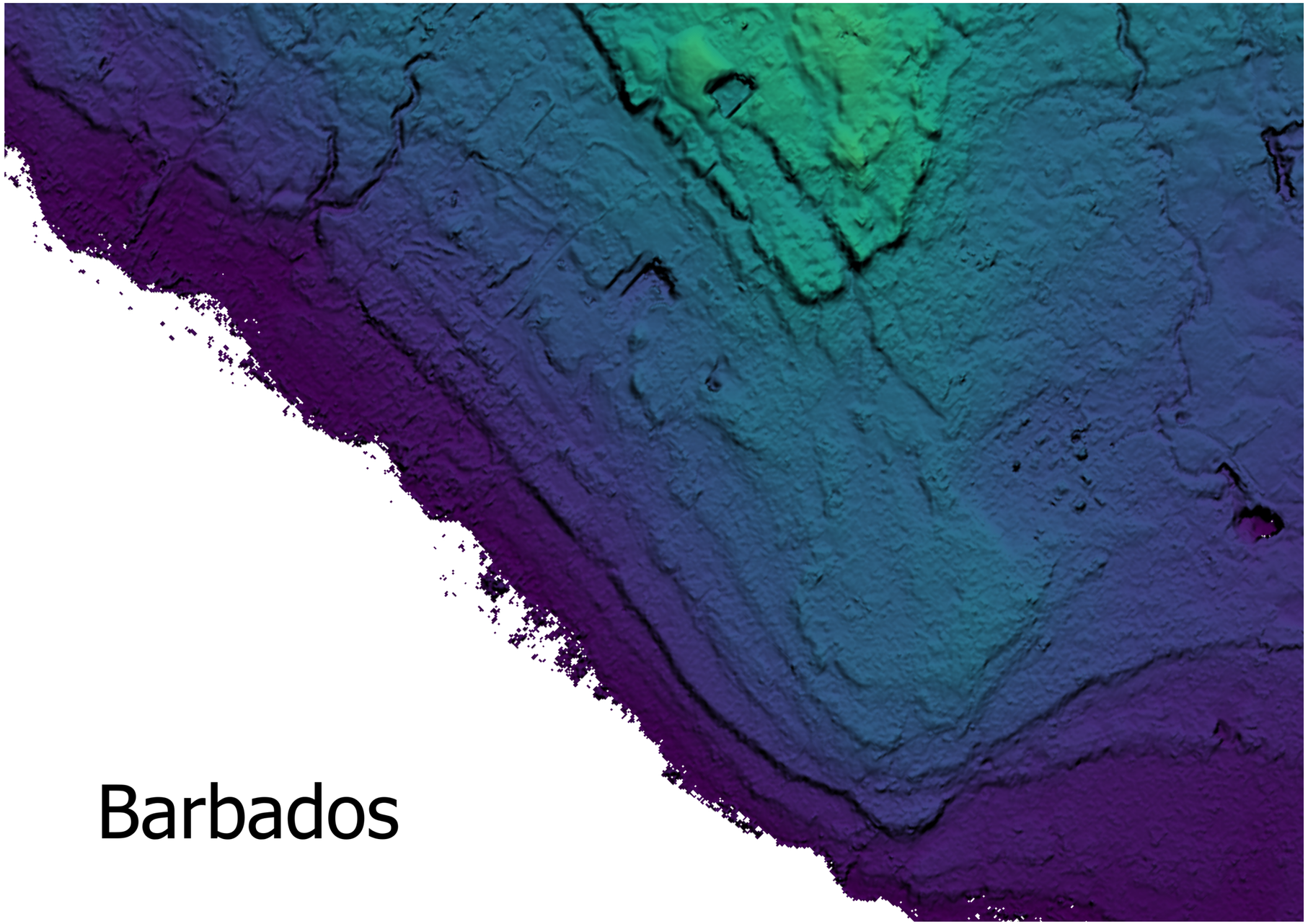
from Lisiecki and Raymo, 2004


Isotopic record of global ice volume and deep ocean temperature
Benthic $\delta^{18}O$ ‰
2.5
3.0
3.5
4.0
4.5
5.0
5.5
0.0
0.1
0.2
0.3
0.4
0.5
Millions of years ago

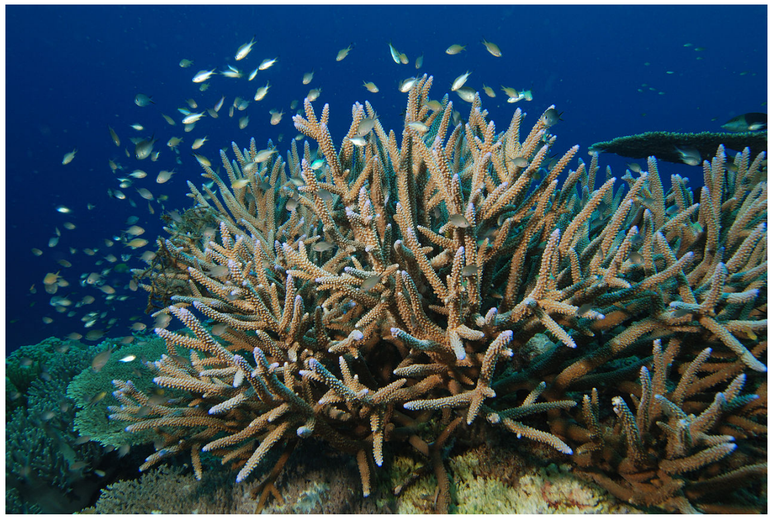

Barbados

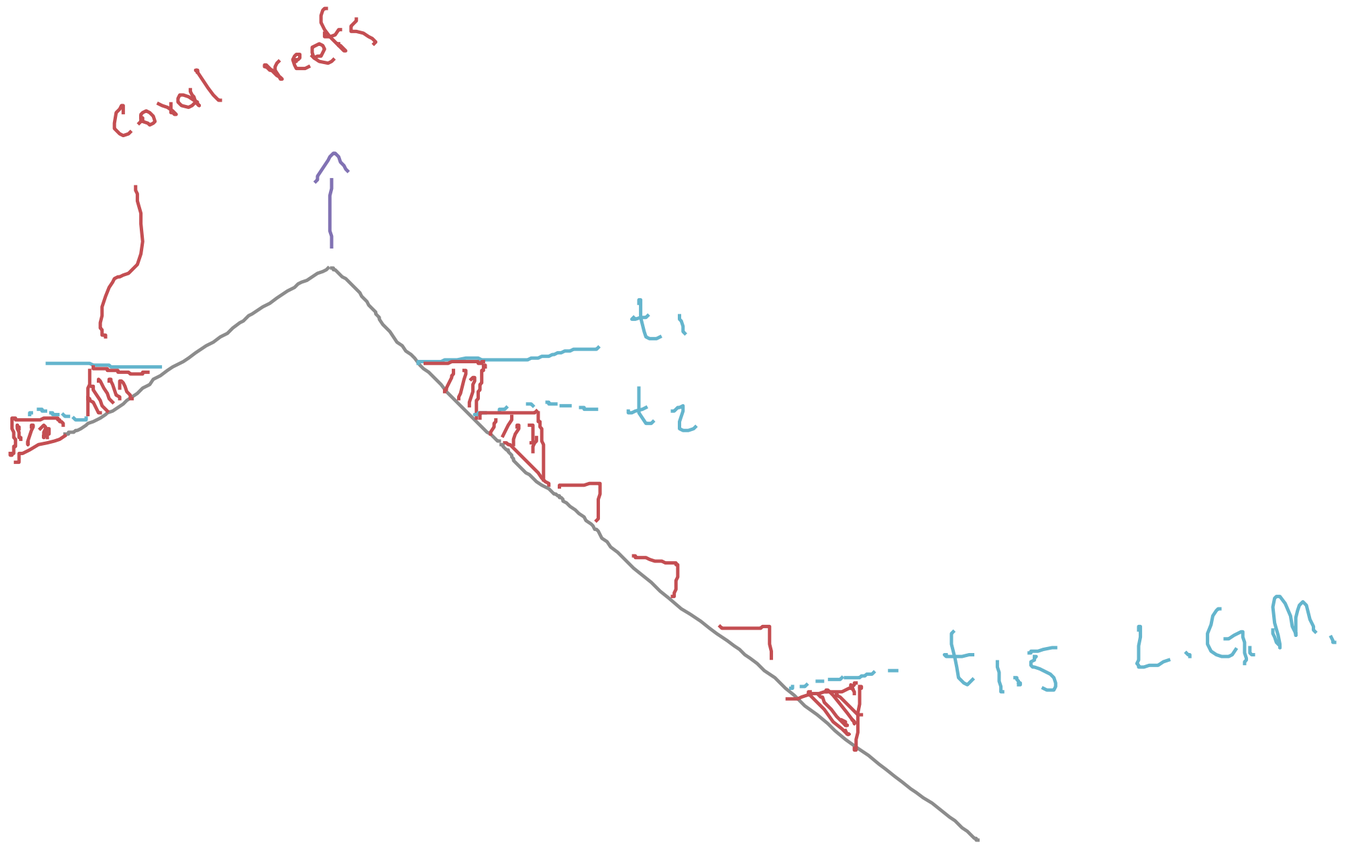


Barbados



Barbados




Coral reefs
t1
t2
t1.5
L.G.M.