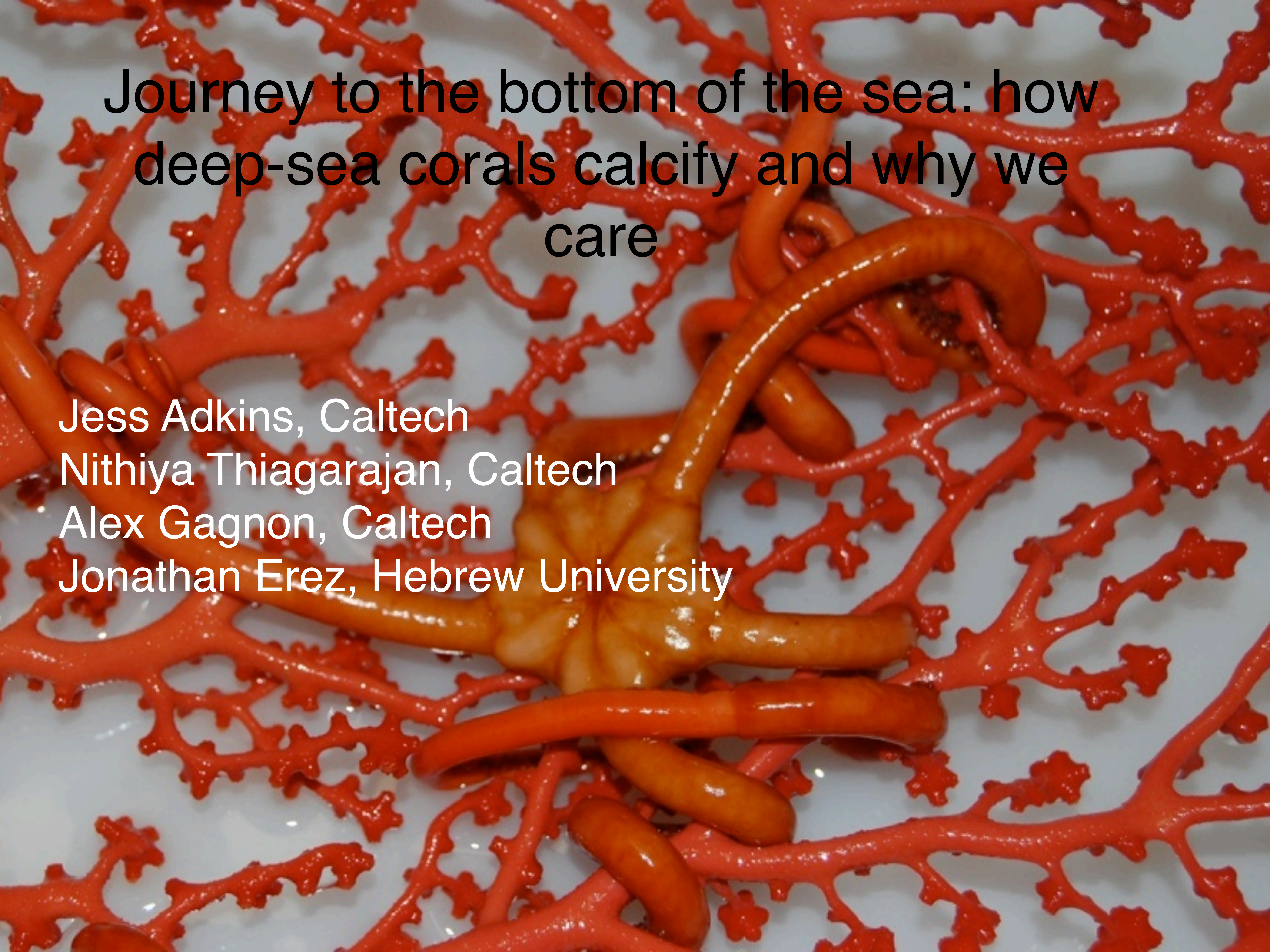
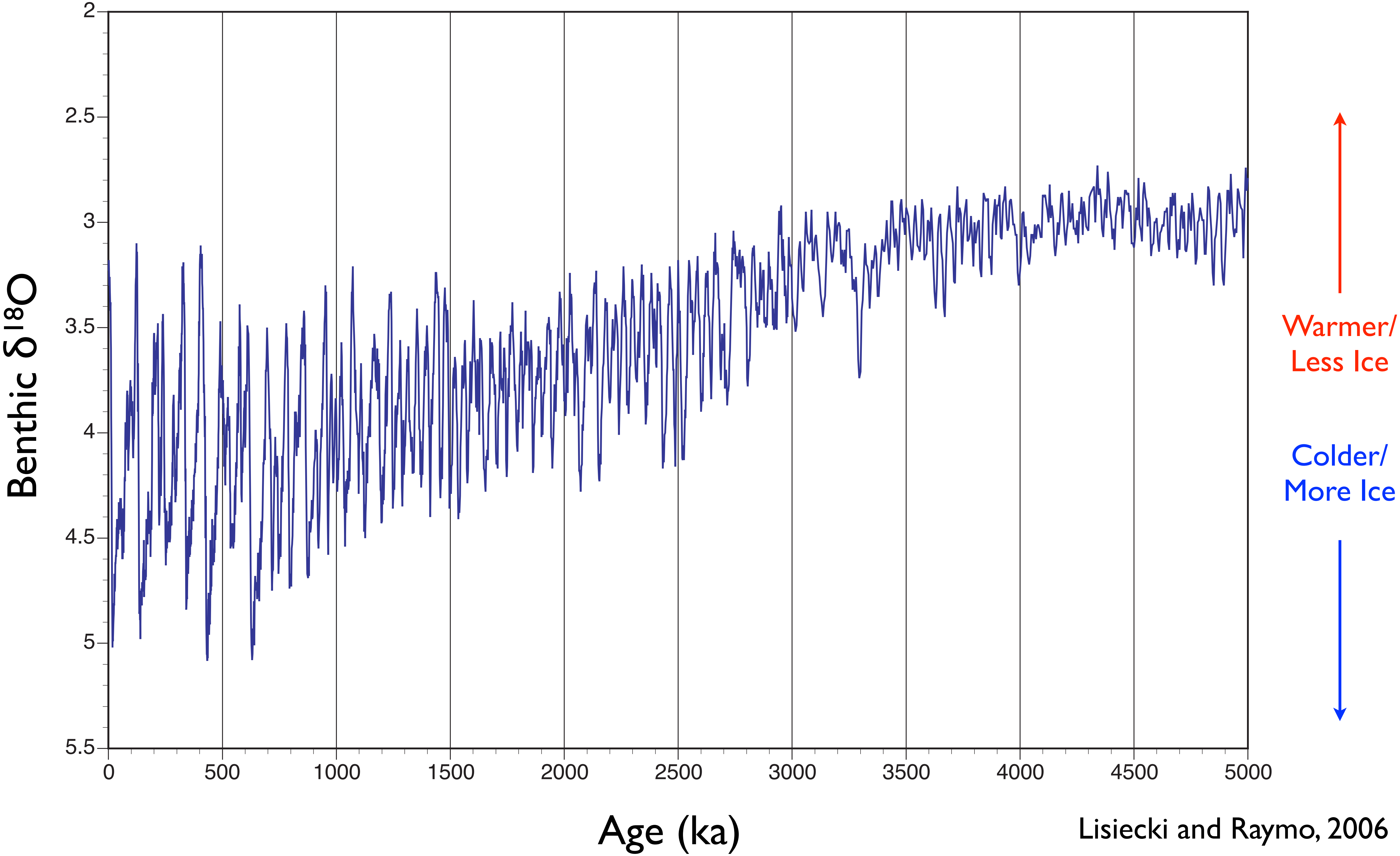


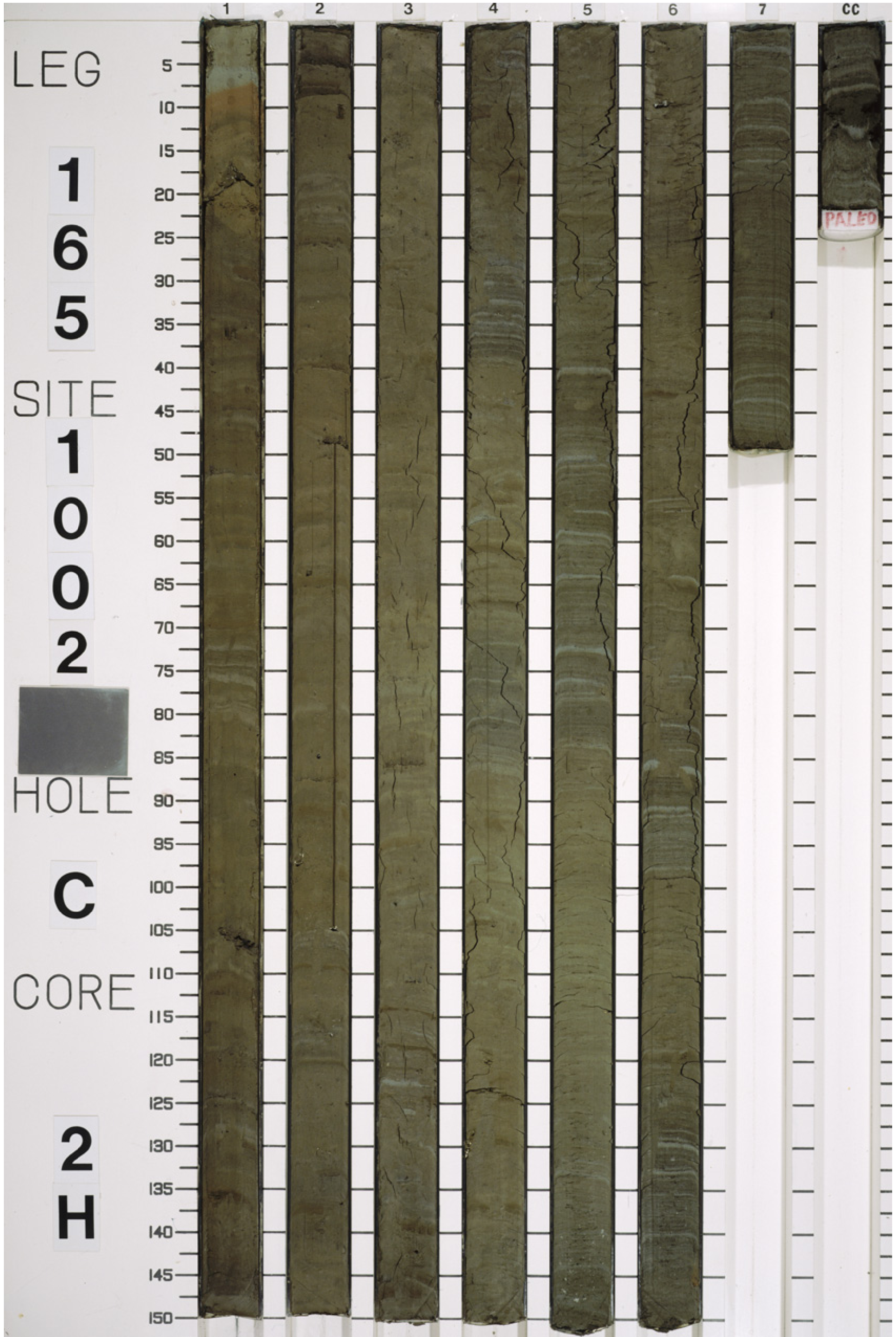
Journey to the bottom of the sea: how deep-sea corals calcify and why we care

Jess Adkins, Caltech
Nithiya Thiagarajan, Caltech
Alex Gagnon, Caltech
Jonathan Erez, Hebrew University

The marine record of the last 5 Million Years

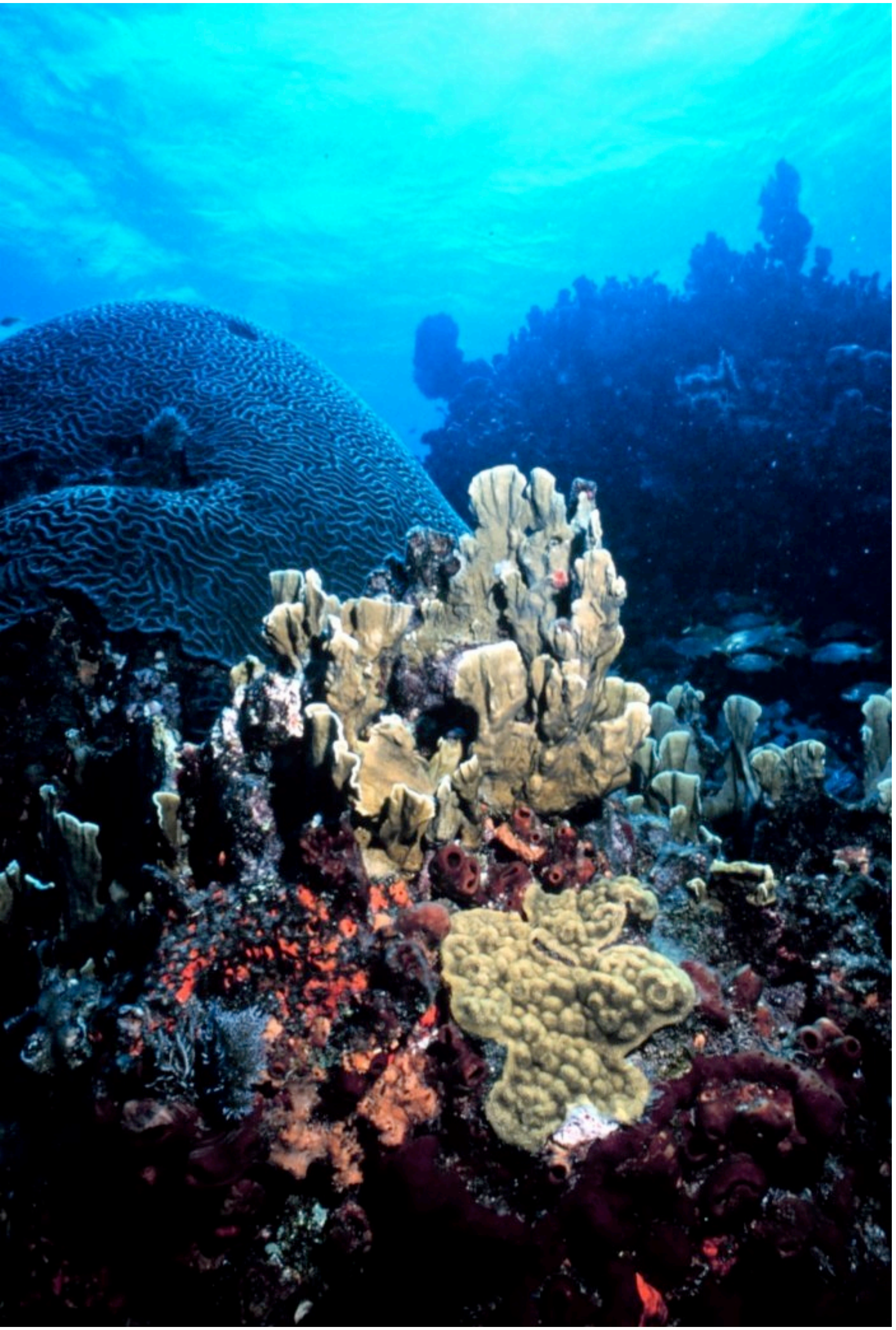


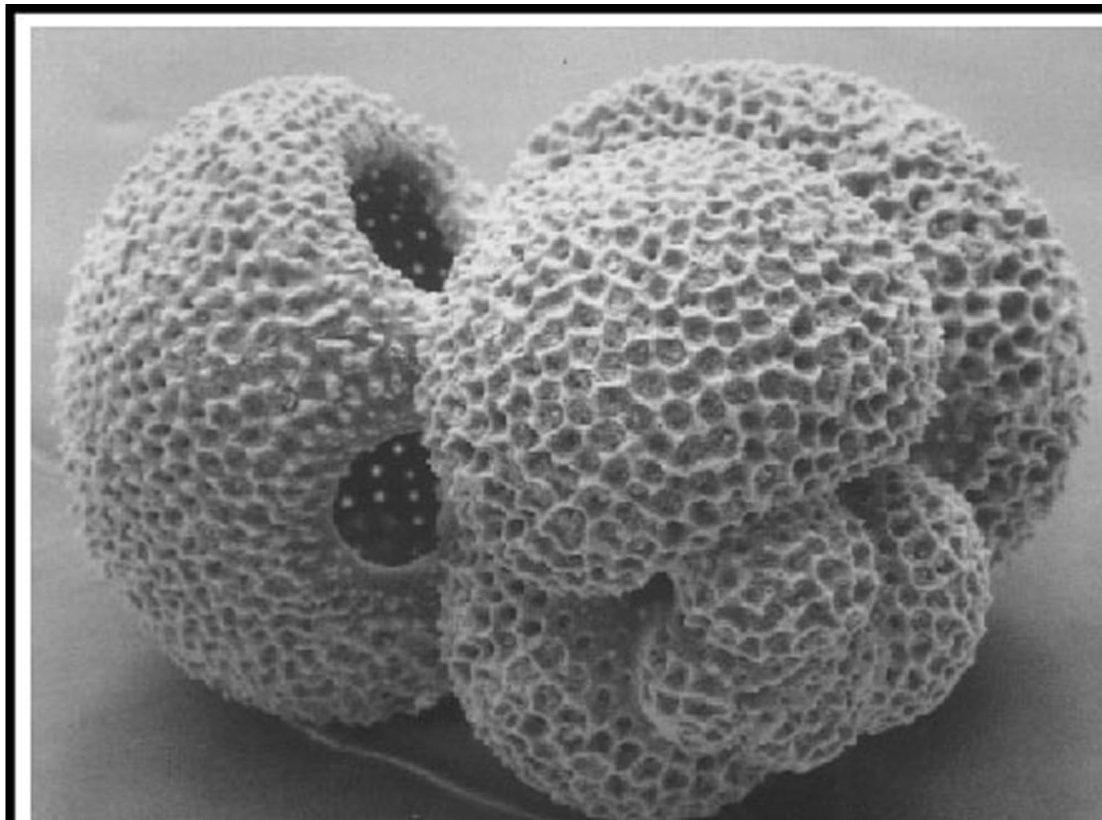
Lisiecki and Raymo, 2006



Glacial and Deglacial Sequence from the Cariaco Basin in the Caribbean

Foraminifera picked from the sediment and corals from the surface ocean are two of the main repositories of past climate information





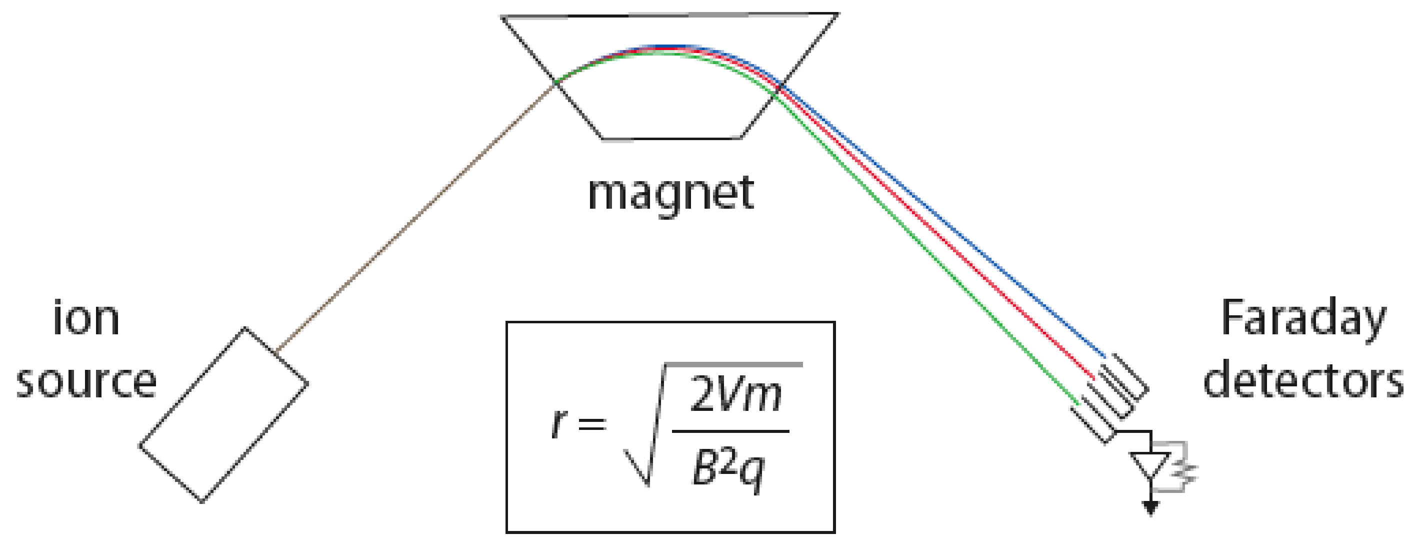
Globigerinoides ruber (white)

Carbonate dominates the record, but it is also very useful

$CaCO_3$

Me:Ca ratios

Minor: Sr, Mg
Trace: Cd, Ba, Zn
Isotopes: B, Nd, Ca, Sr, Mg



$^{12}C^{16}O^{16}O$: mass 44
$^{13}C^{16}O^{16}O$: mass 45
$^{12}C^{16}O^{18}O$: mass 46

So why is this $^{18}O/^{16}O$ ratio helpful?

$$H_2{}^{18}O + CO_3^{=} \Leftrightarrow H_2O + CO_2{}^{18}O^{=}$$

And

$$Ca^{++} + CO_3^{=} \Rightarrow CaCO_3$$

Then Overall...

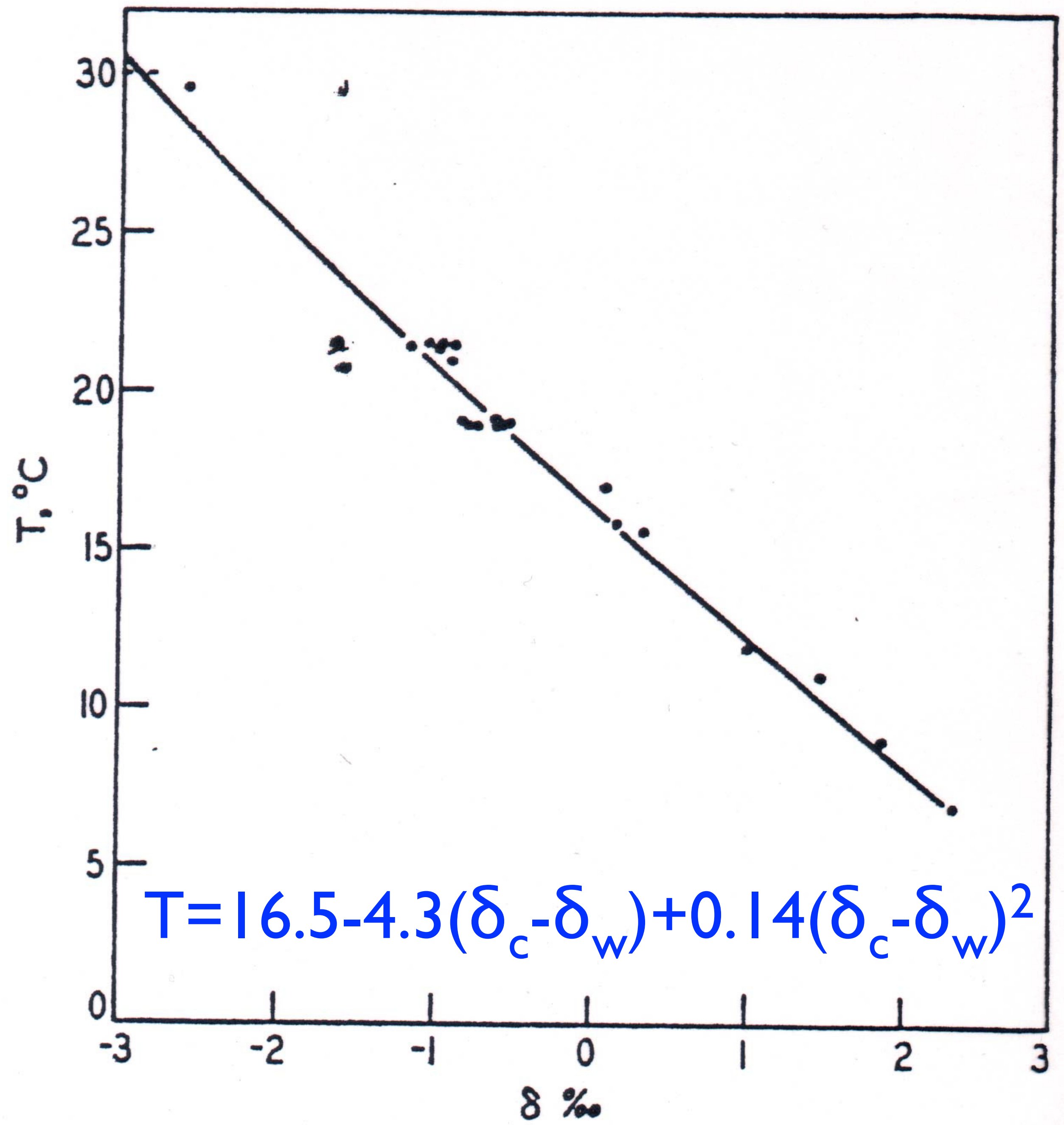
$$CaCO_3 + H_2{}^{18}O \Leftrightarrow CaCO_2{}^{18}O + H_2O$$

And...

$$\frac{(^{18}O/^{16}O)_{solid}}{(^{18}O/^{16}O)_{water}} \propto K_{eq},$$

So the isotopic ratio of the solid is a function of temperature and the $^{18}O/^{16}O$ ratio of the water.

The first Paleo-temperature Equation



$$T=16.5-4.3(\delta_c-\delta_w)+0.14(\delta_c-\delta_w)^2$$

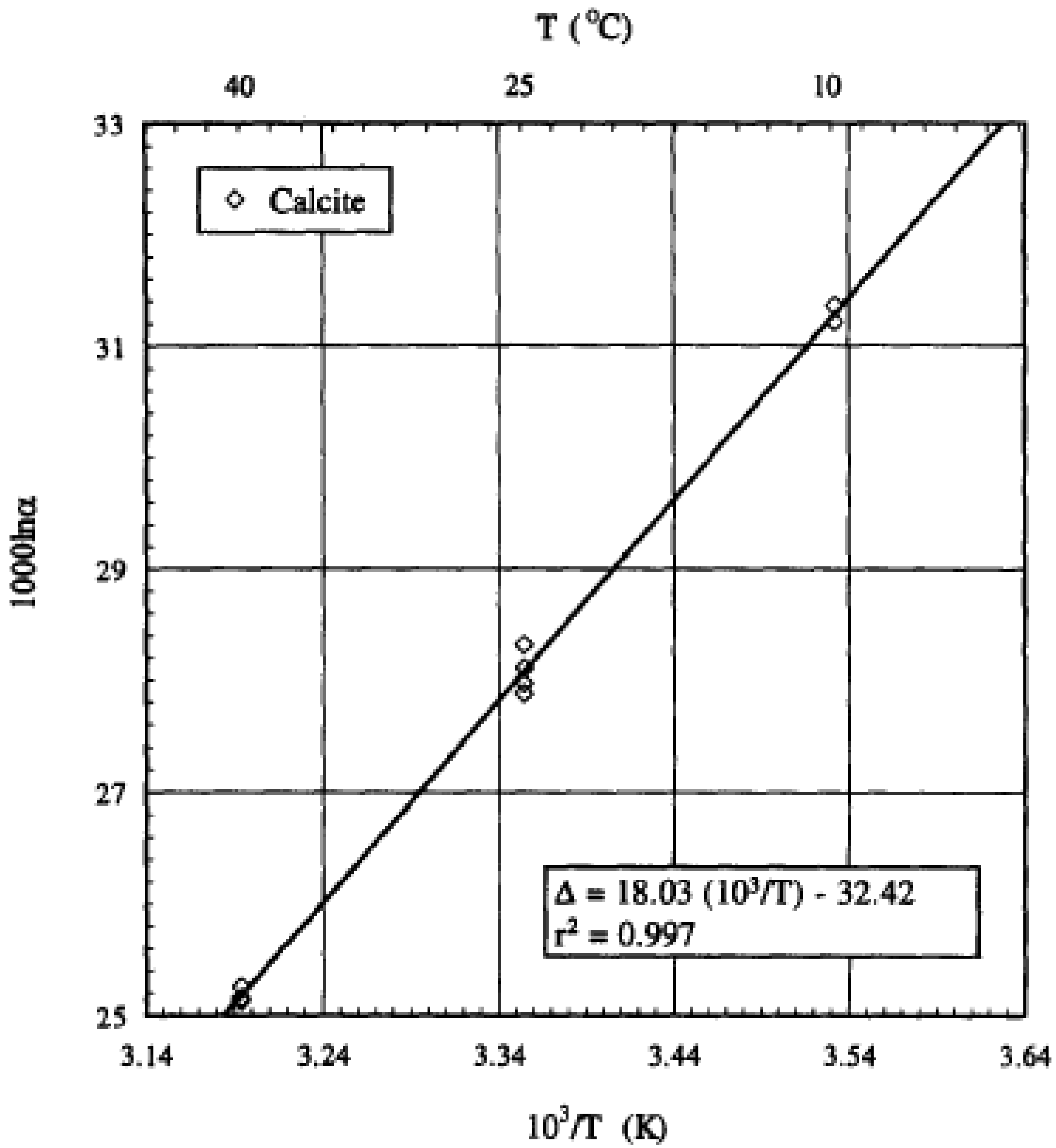
FIGURE 9.—ISOTOPIC TEMPERATURE SCALE

Epstein et al., 1953

Shackleton (1974) changes curve for cold water based on *Uvigerina* data:

$$T=16.9-4.0(\delta_c-\delta_w)$$

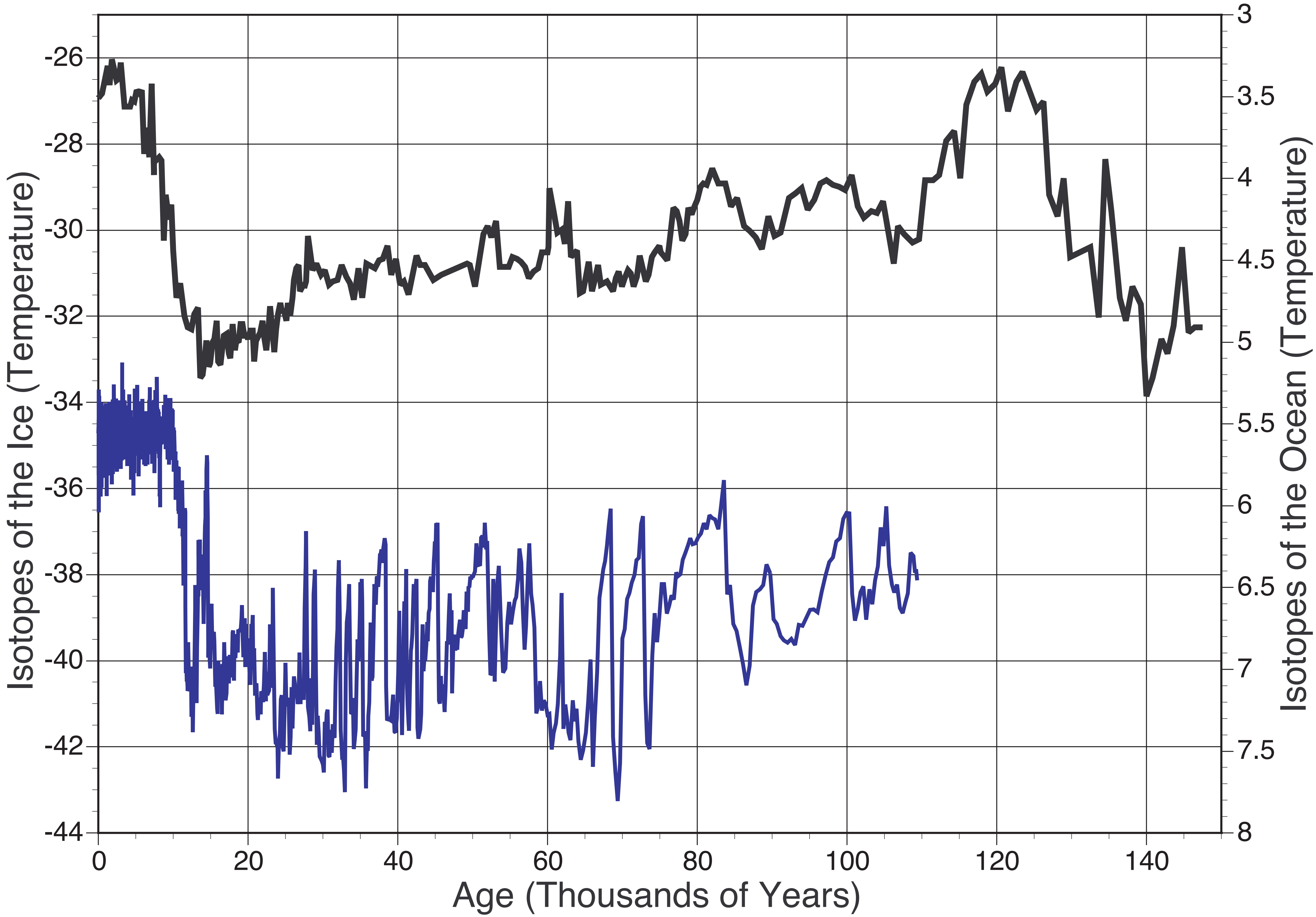
Inorganic Calcite Precipitation Experiments



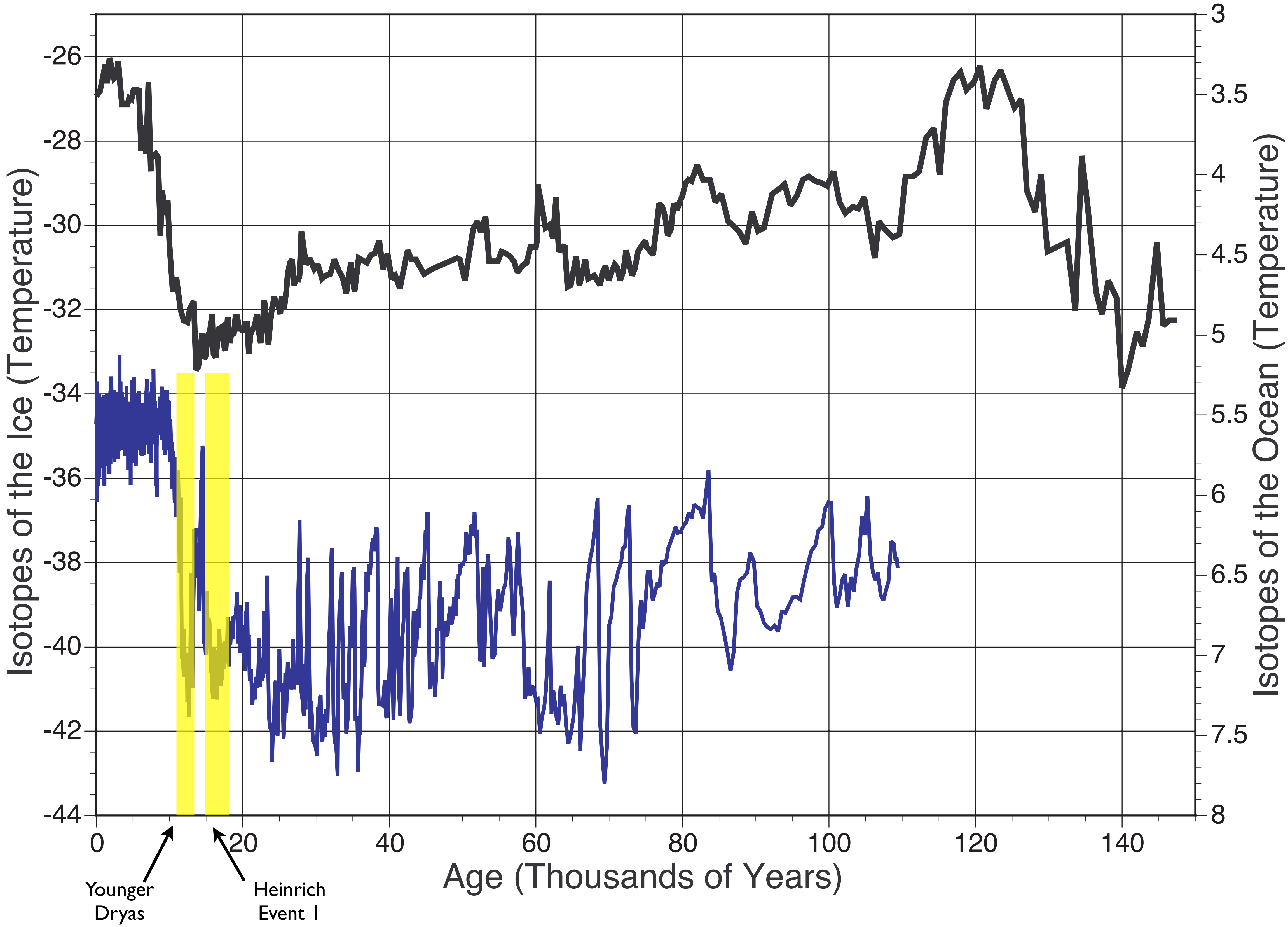
Kim and O'Neil, 1997

Where $\Delta = 1000\ln(\alpha_{Calcite-Water})$

In the early 1990's our whole view changed:



In the early 1990's our whole view changed:



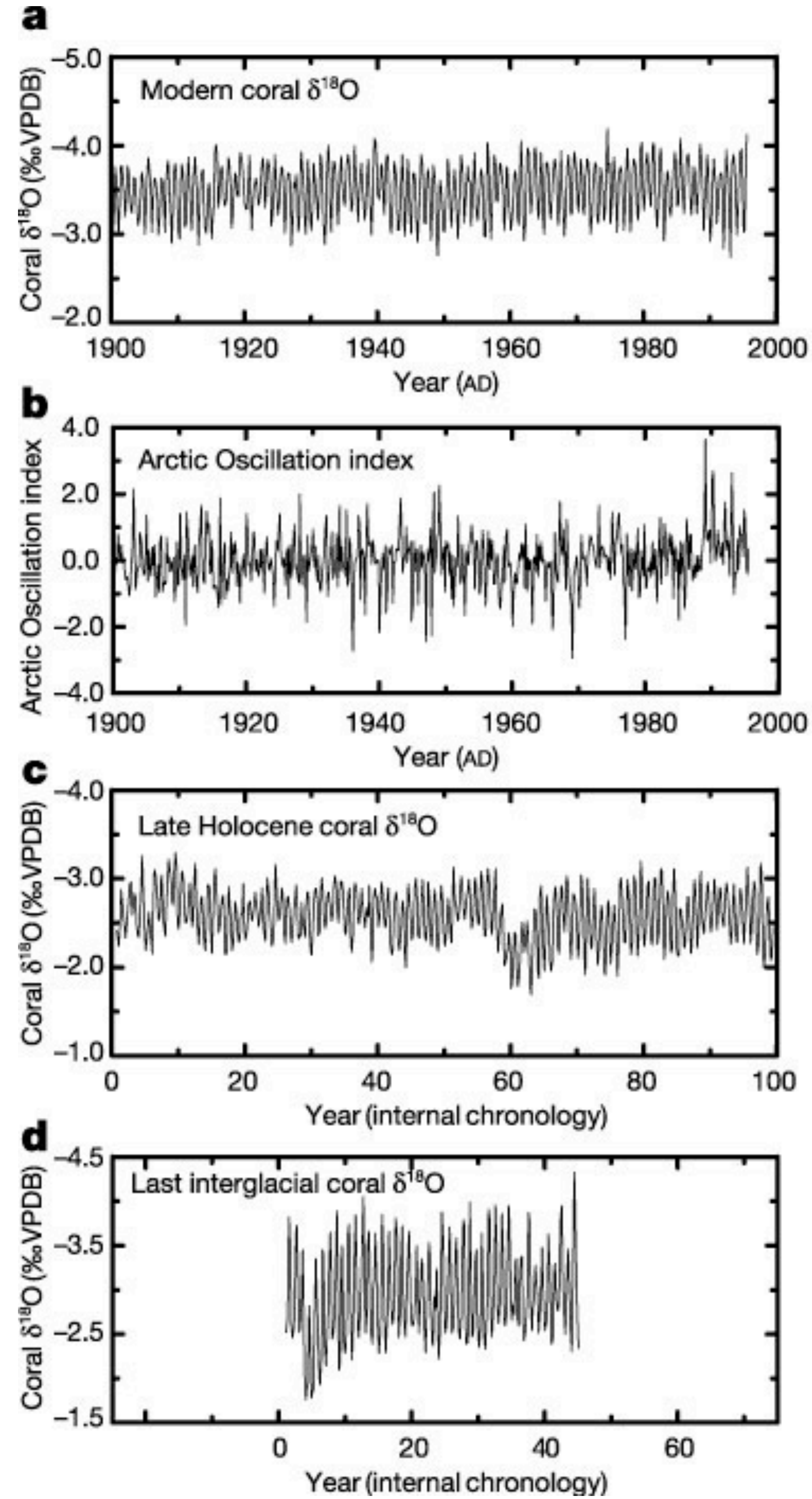
Ice Core from the Summit of Greenland

Some real success with isotopes in corals

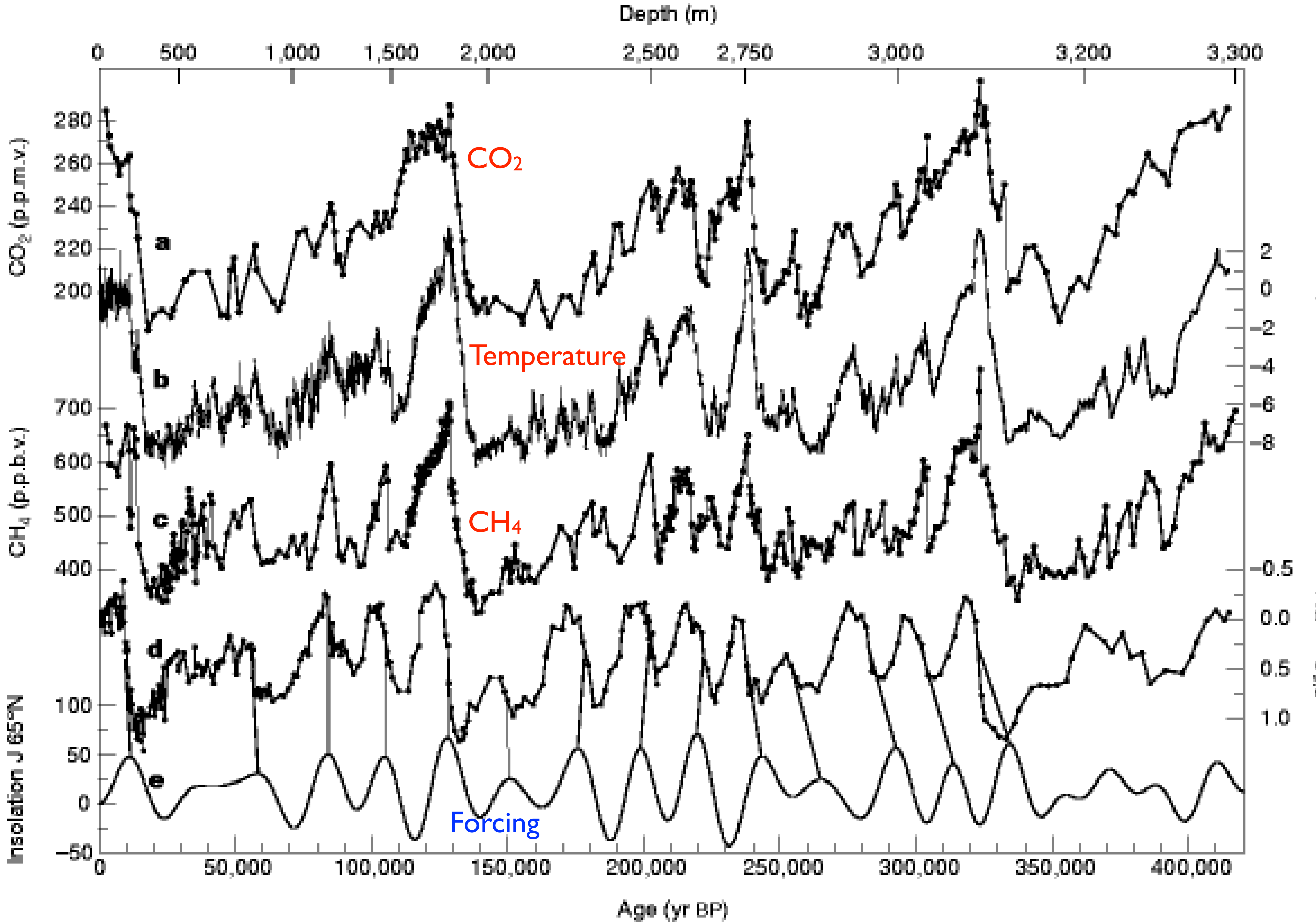
Annual density banding

Modern

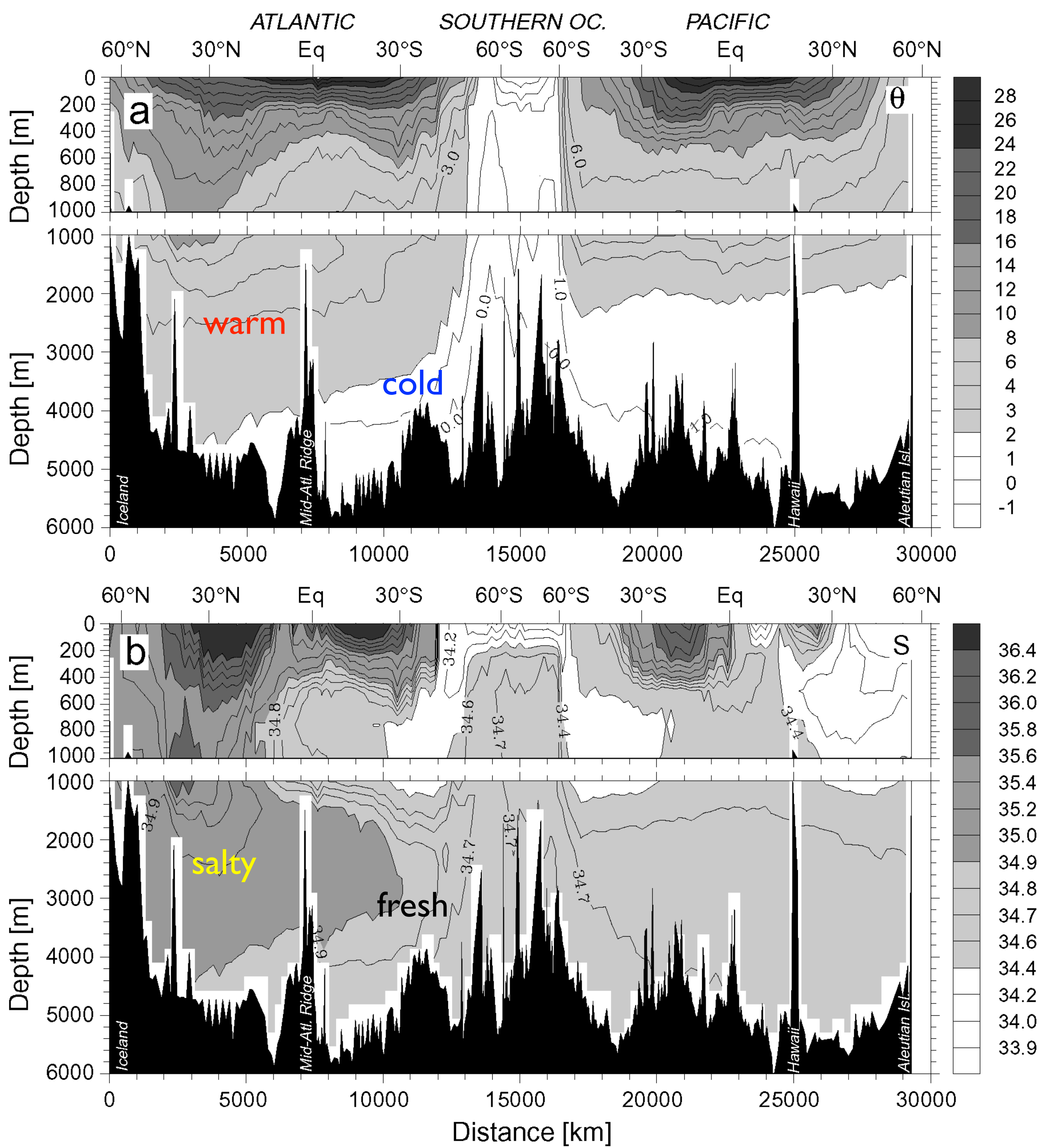
125 ka

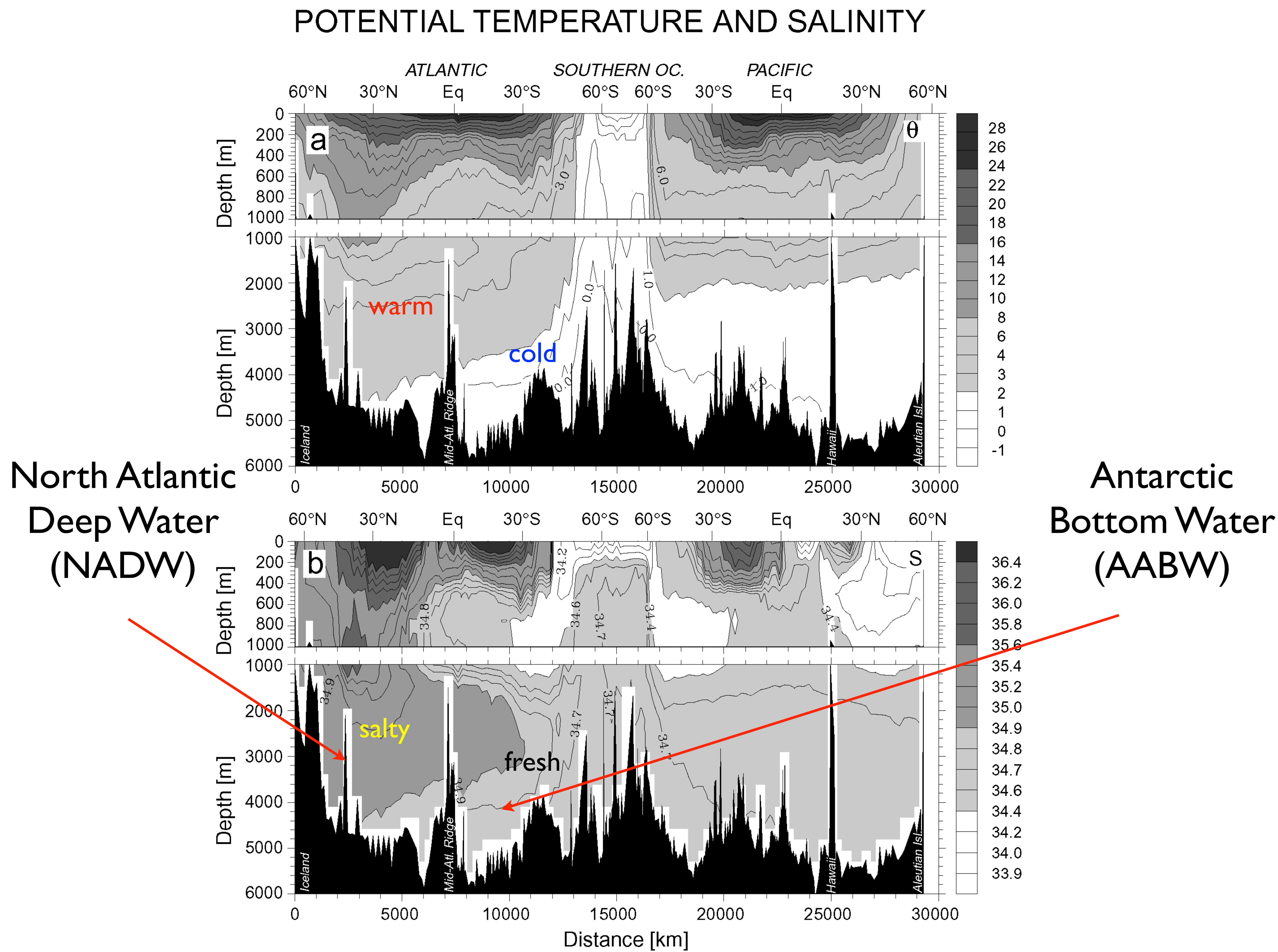


Vostok, Antarctica Ice Core Gases and Temperature



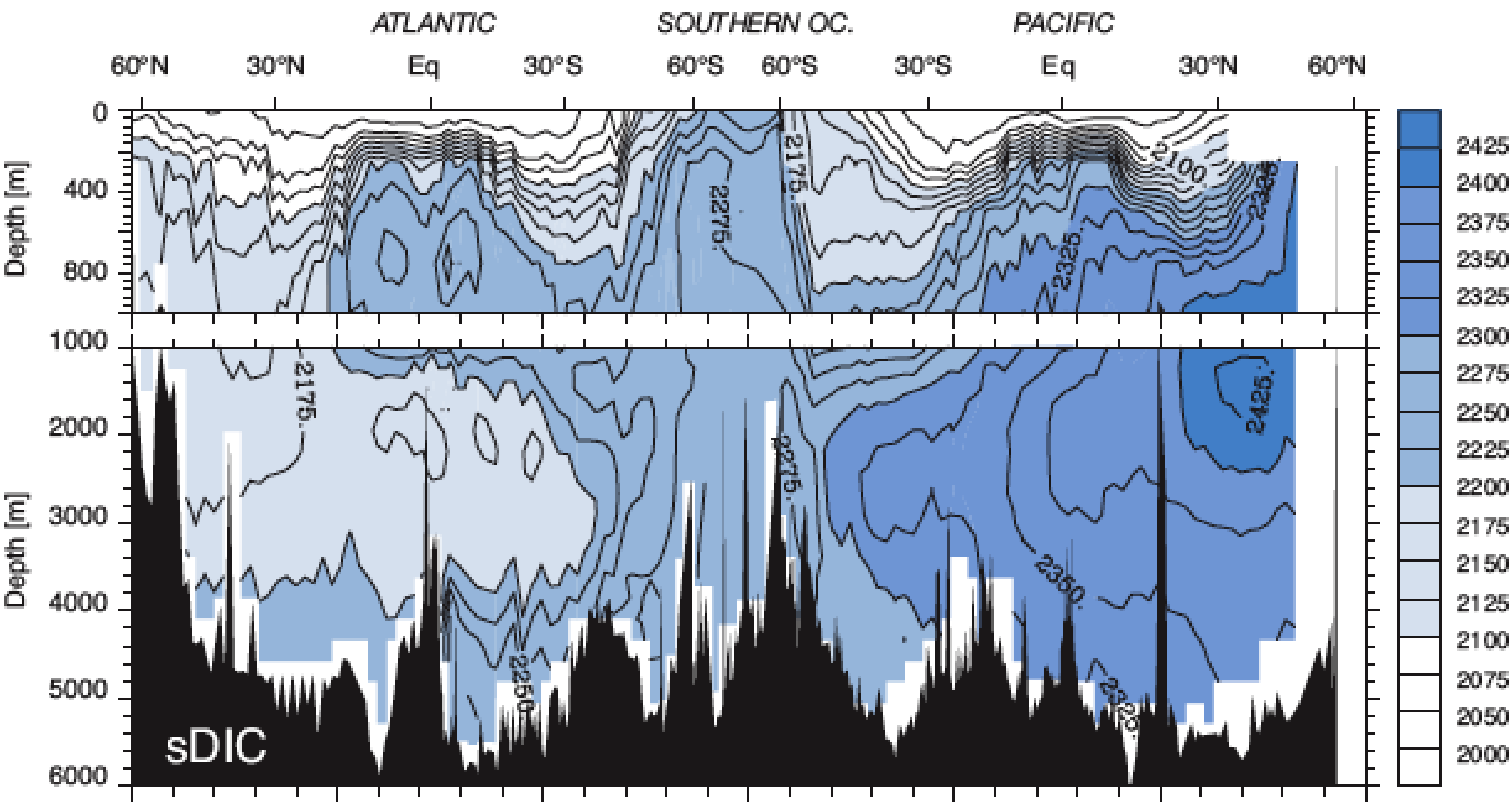
POTENTIAL TEMPERATURE AND SALINITY





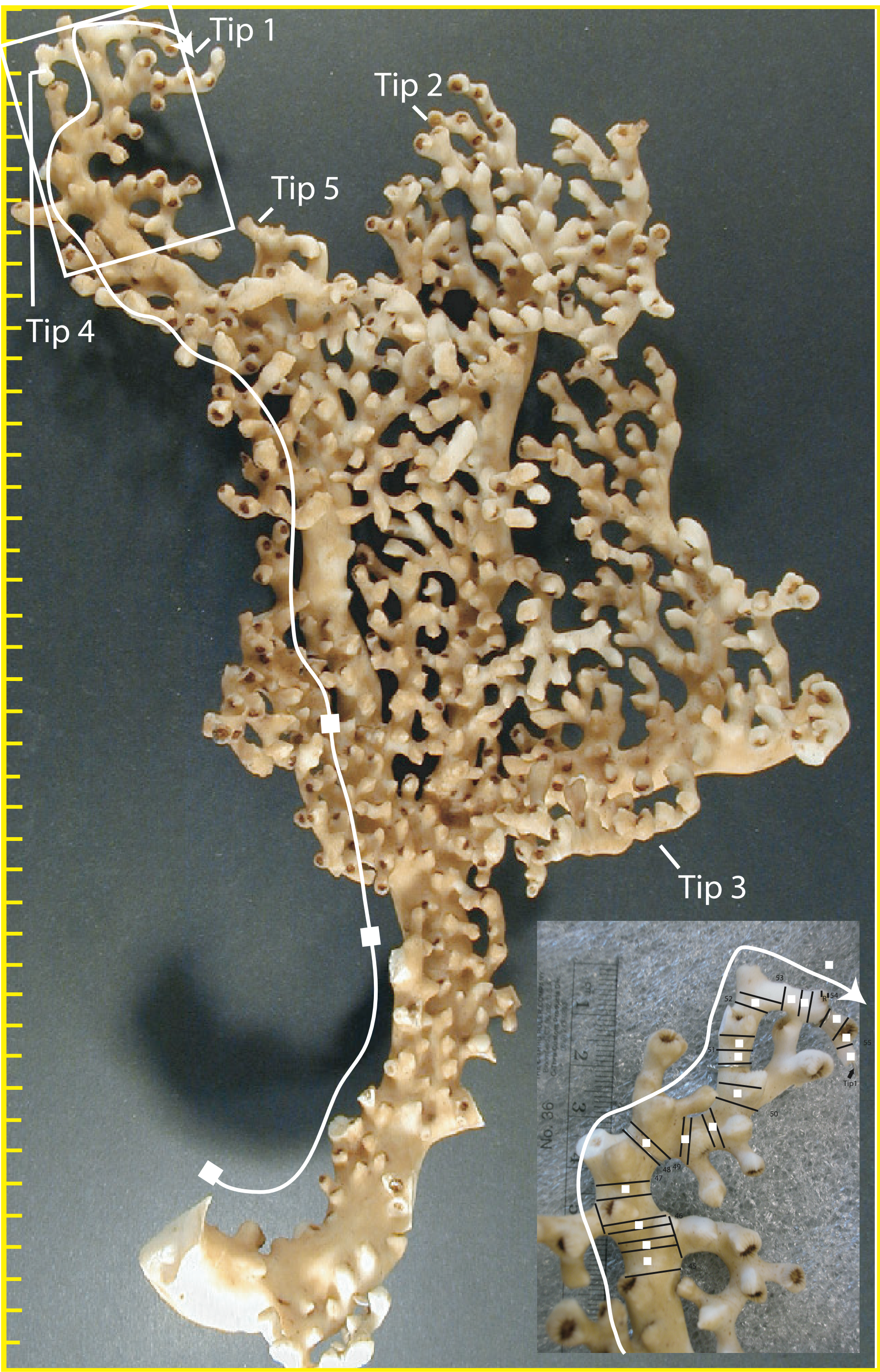
POTENTIAL TEMPERATURE AND SALINITY
ATLANTIC
SOUTHERN OC.
PACIFIC
60°N
30°N
Eq
30°S
60°S
60°S
30°S
Eq
30°N
60°N
a
θ
Depth [m]
warm
cold
Iceland
Mid-Atl. Ridge
Hawaii
Aleutian Isl.
b
S
salty
fresh
Distance [km]
North Atlantic Deep Water (NADW)
Antarctic Bottom Water (AABW)

The Distribution of Dissolved Inorganic Carbon in the Ocean



In these units the modern surface [H_2CO_3] (which sets the pCO_2) is ~25. Overall, there is ~60x more carbon in the ocean than in the atmosphere

Two of our key targets



50 cm long *E. rostrata*
-picked alive in Sept. 2001

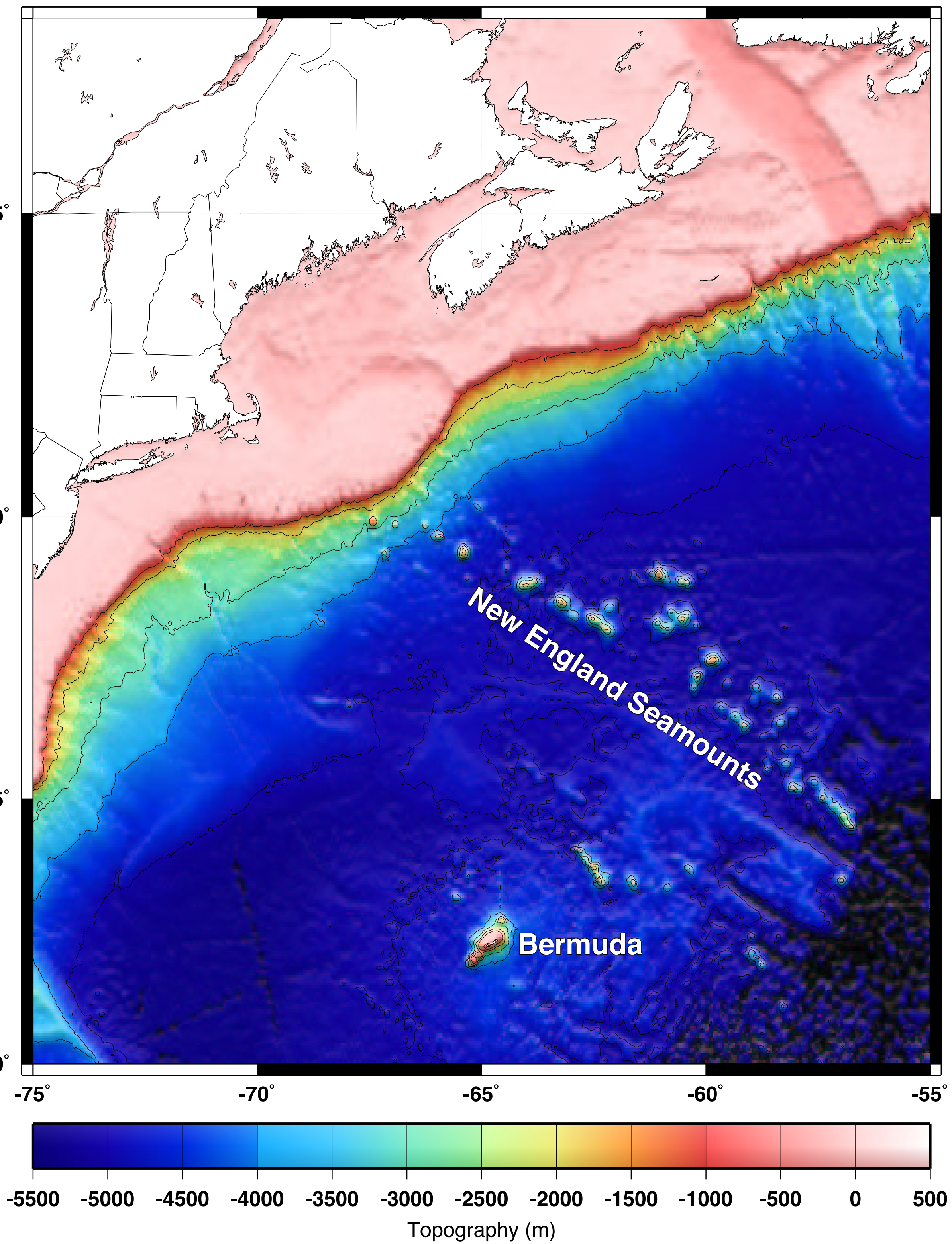
5 cm long *D. dianthus*
-fossil collected in 2003

These are Uranium rich, good absolute age control
And, not 'bioturbated', perfect relative age control

Where to go look for deep-sea corals

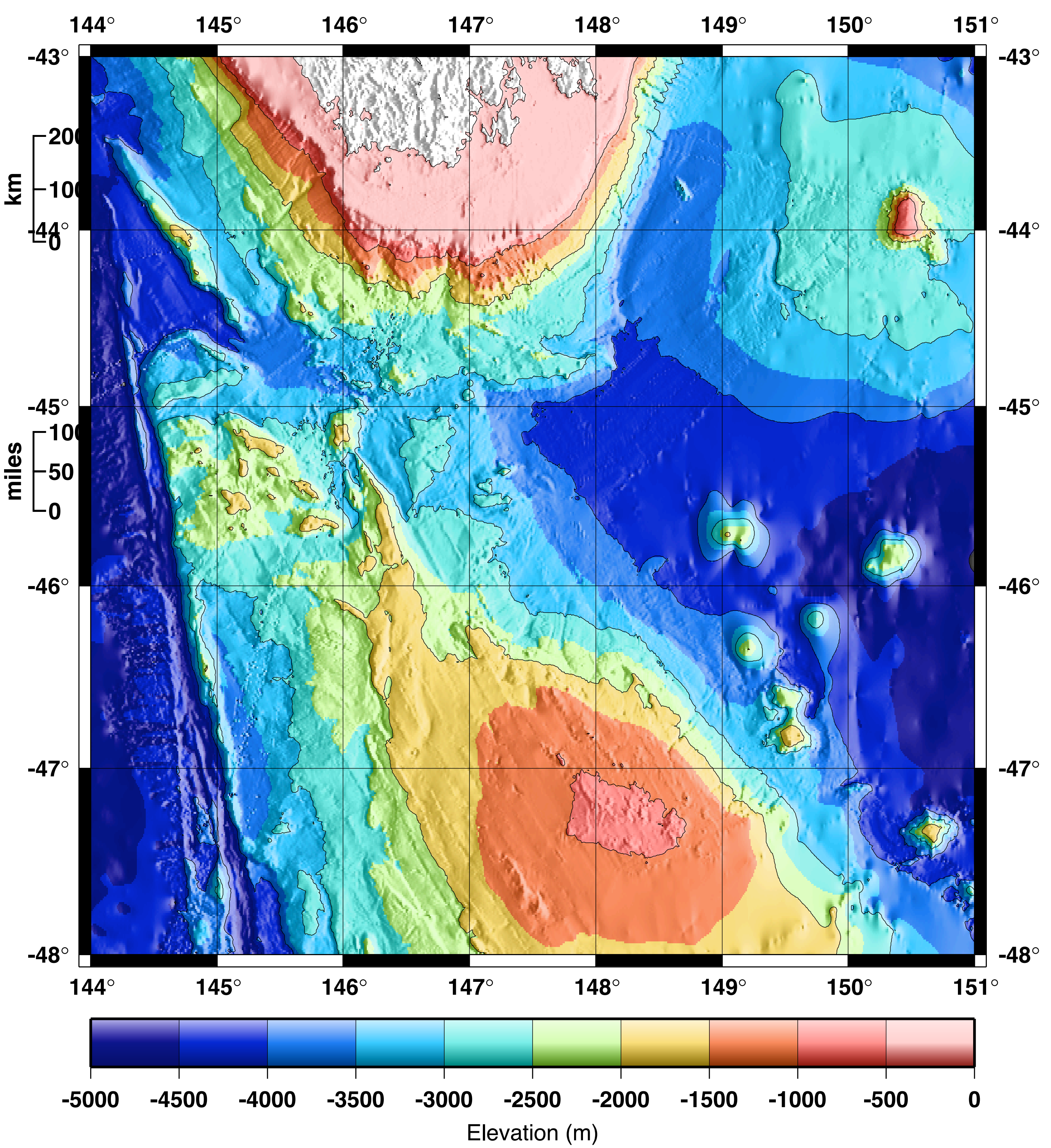
2003 North Atlantic

Alvin



2008-9 Southern Ocean

Jason

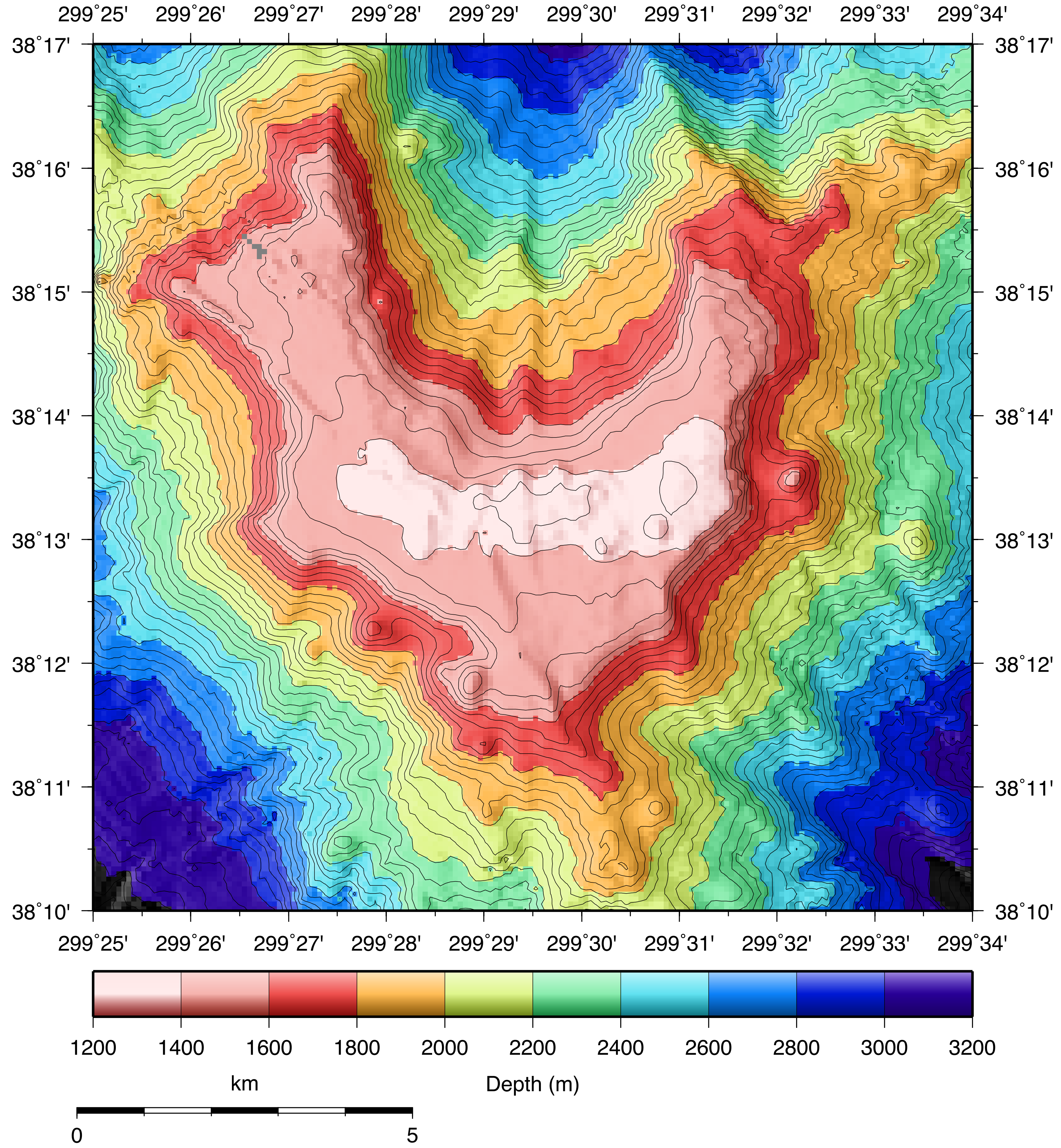


Home away from home (in 2003), the R/V Atlantis...

On the R/V Thompson's bridge in the Southern Ocean

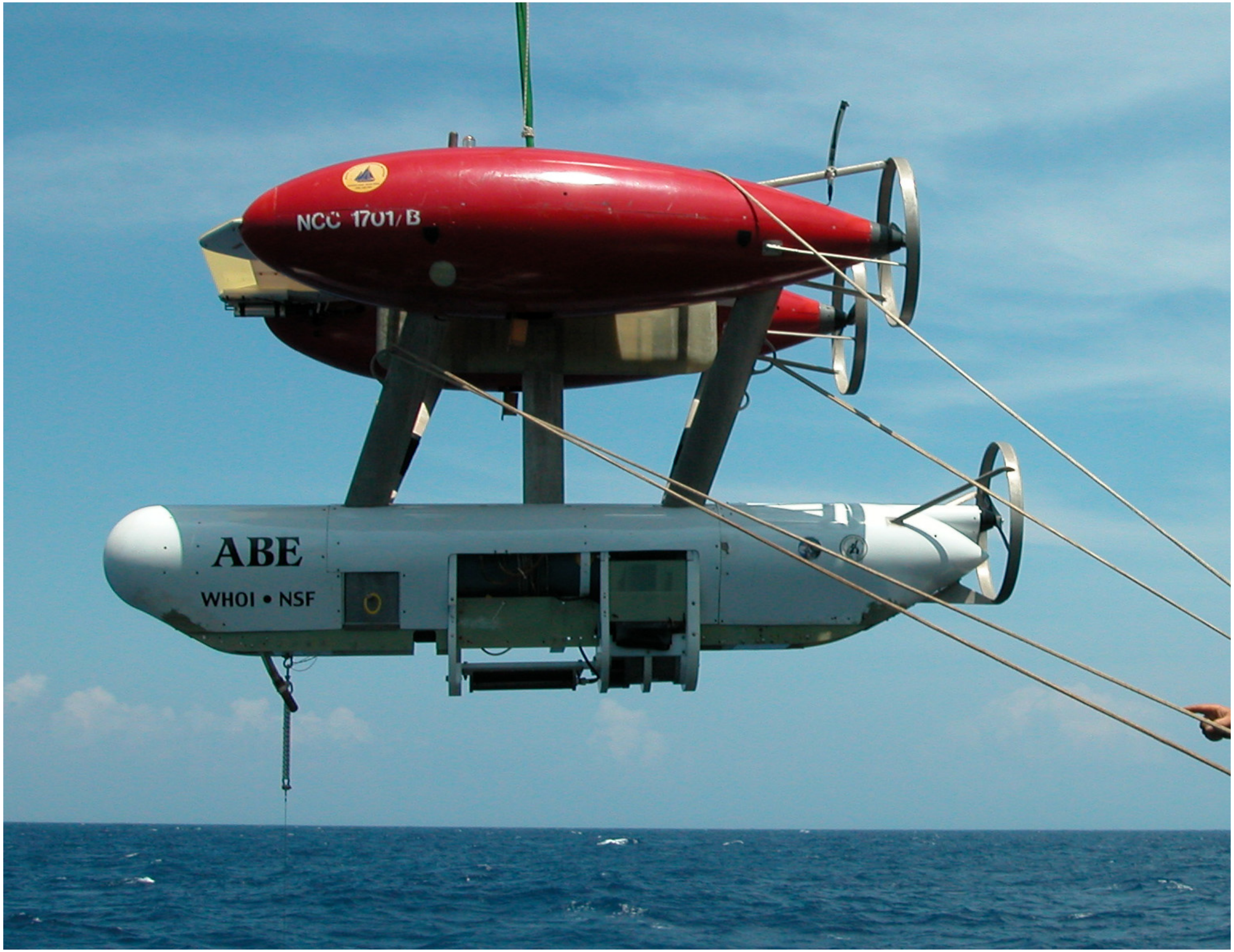
Home away from home (in 2003), the R/V Atlantis...

Summit of Manning Seamount as mapped from the surface



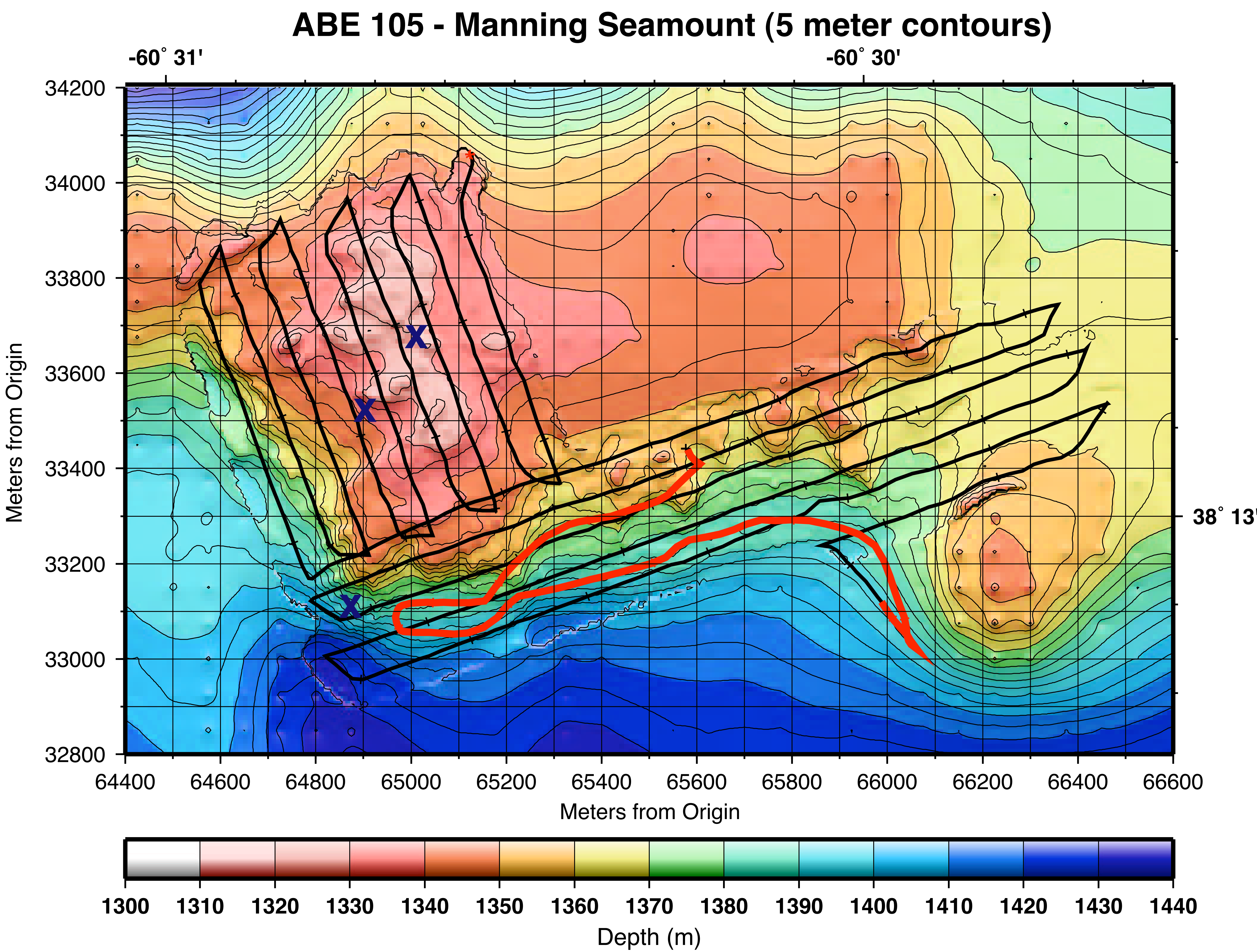
Your Window Seat View of Caltech from 2500 meters up

The Autonomous Submarine 'ABE'

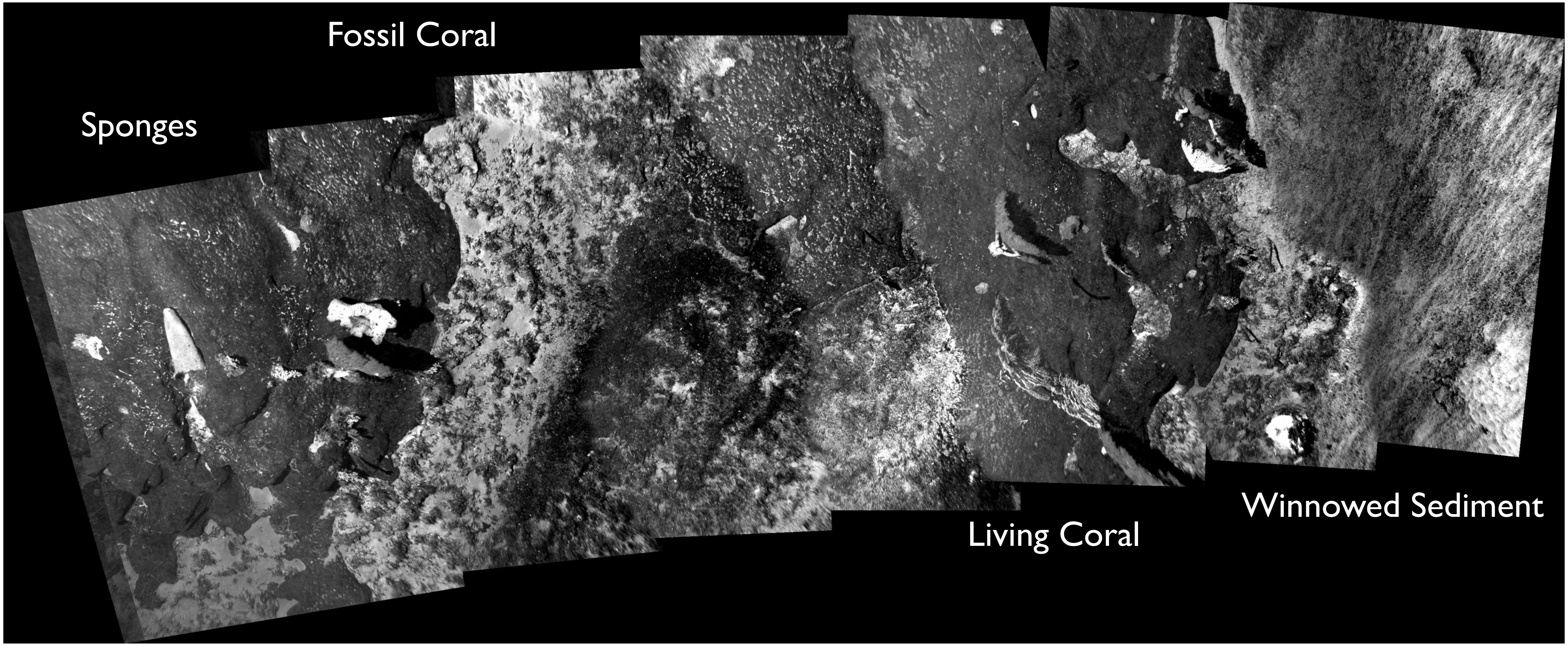


Many, many sensors, but we use the maps and photos

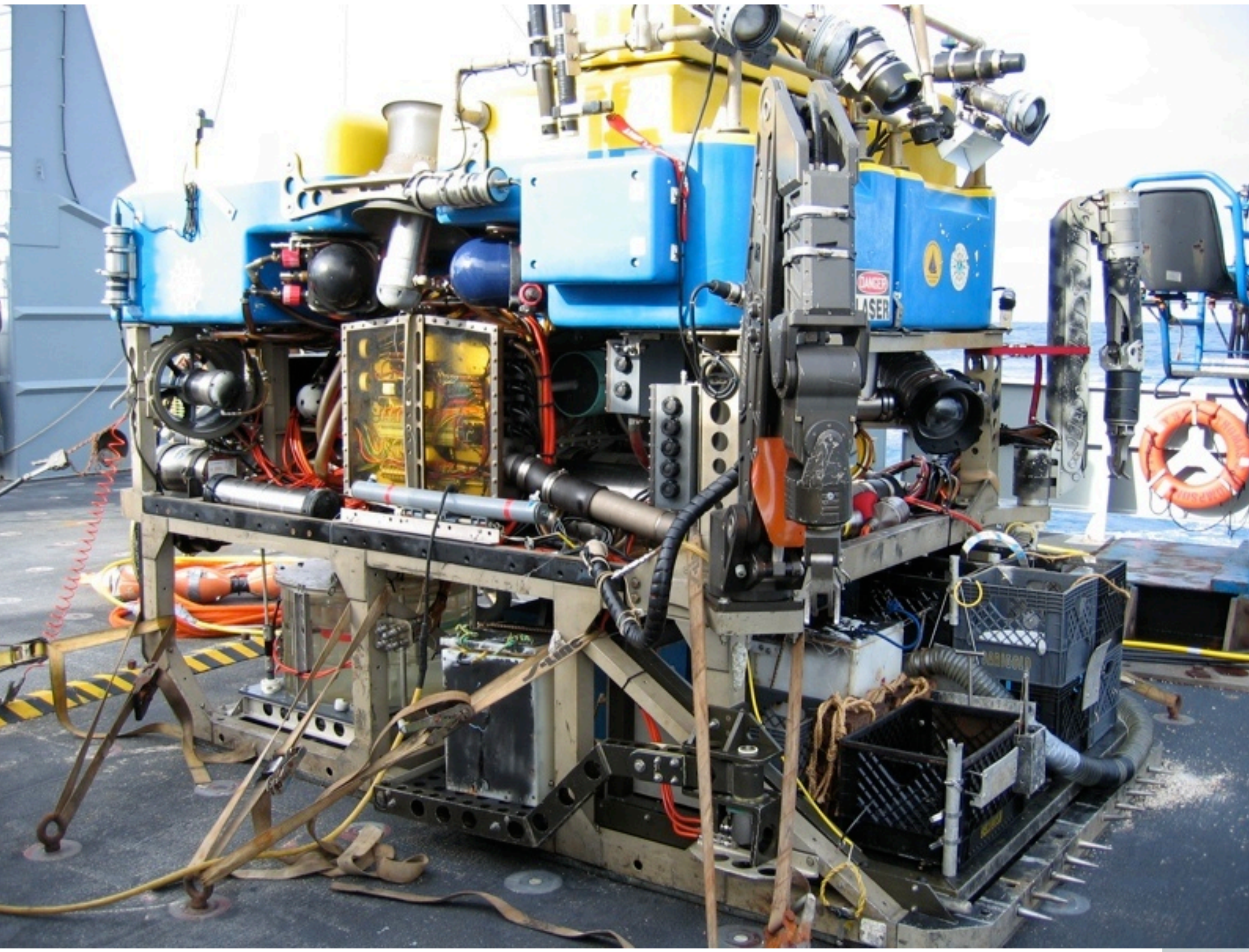
Still the summit of Manning, but now from 40 meters



ABE Photo Mosaic, from 5 meters

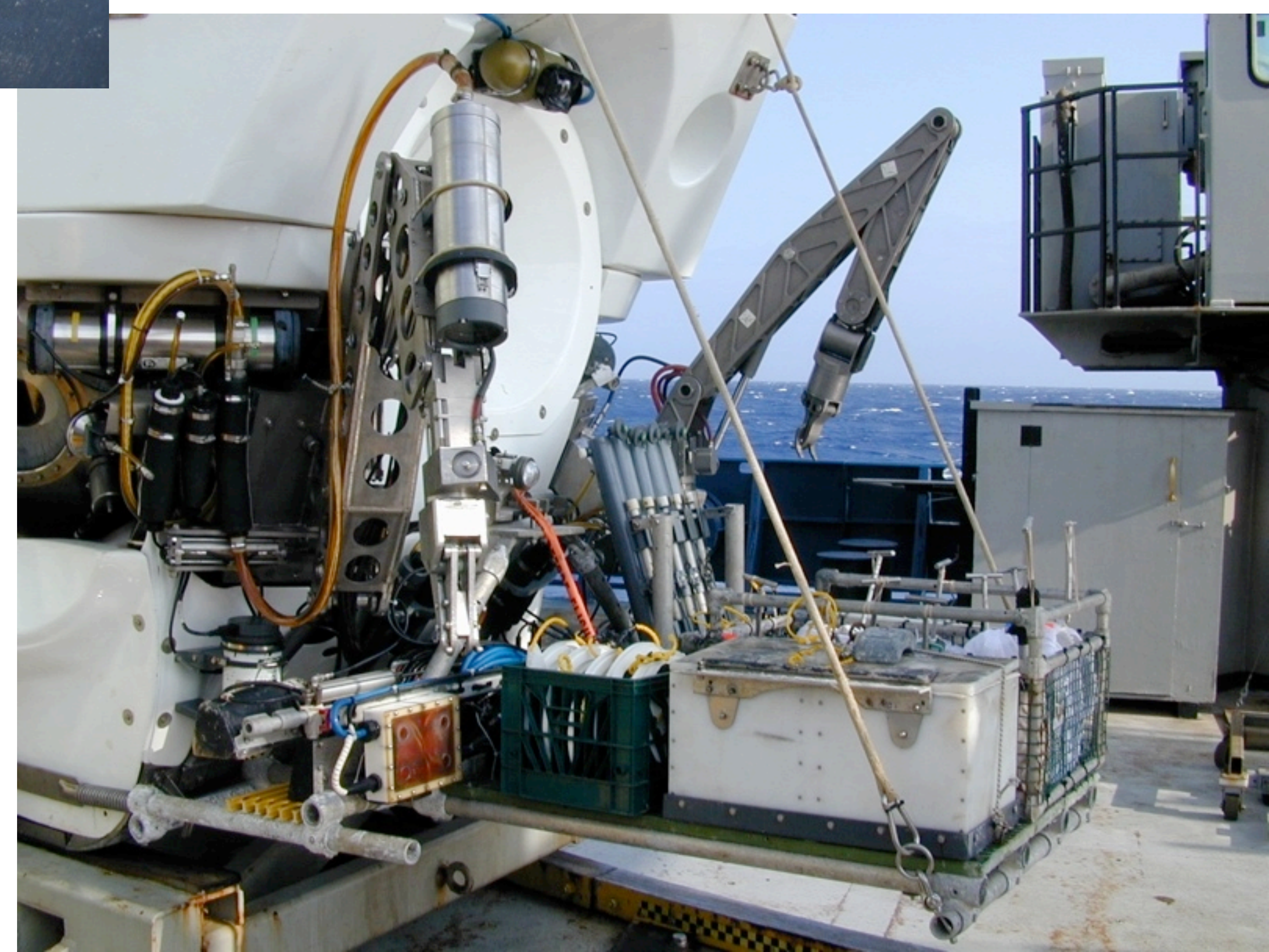


-Each image is ~5 meters wide

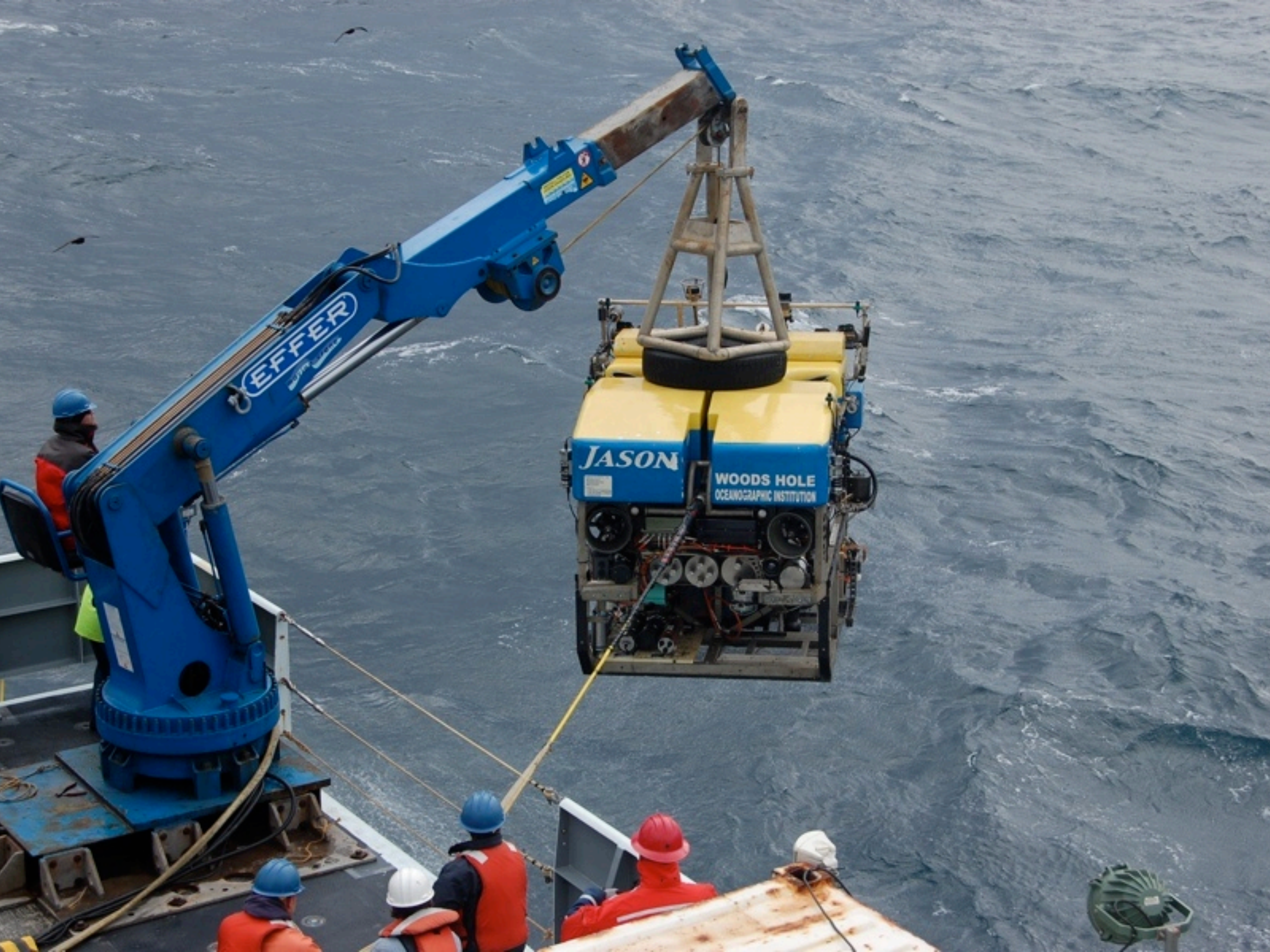


The ROV ‘Jason’

The submersible ‘Alvin’

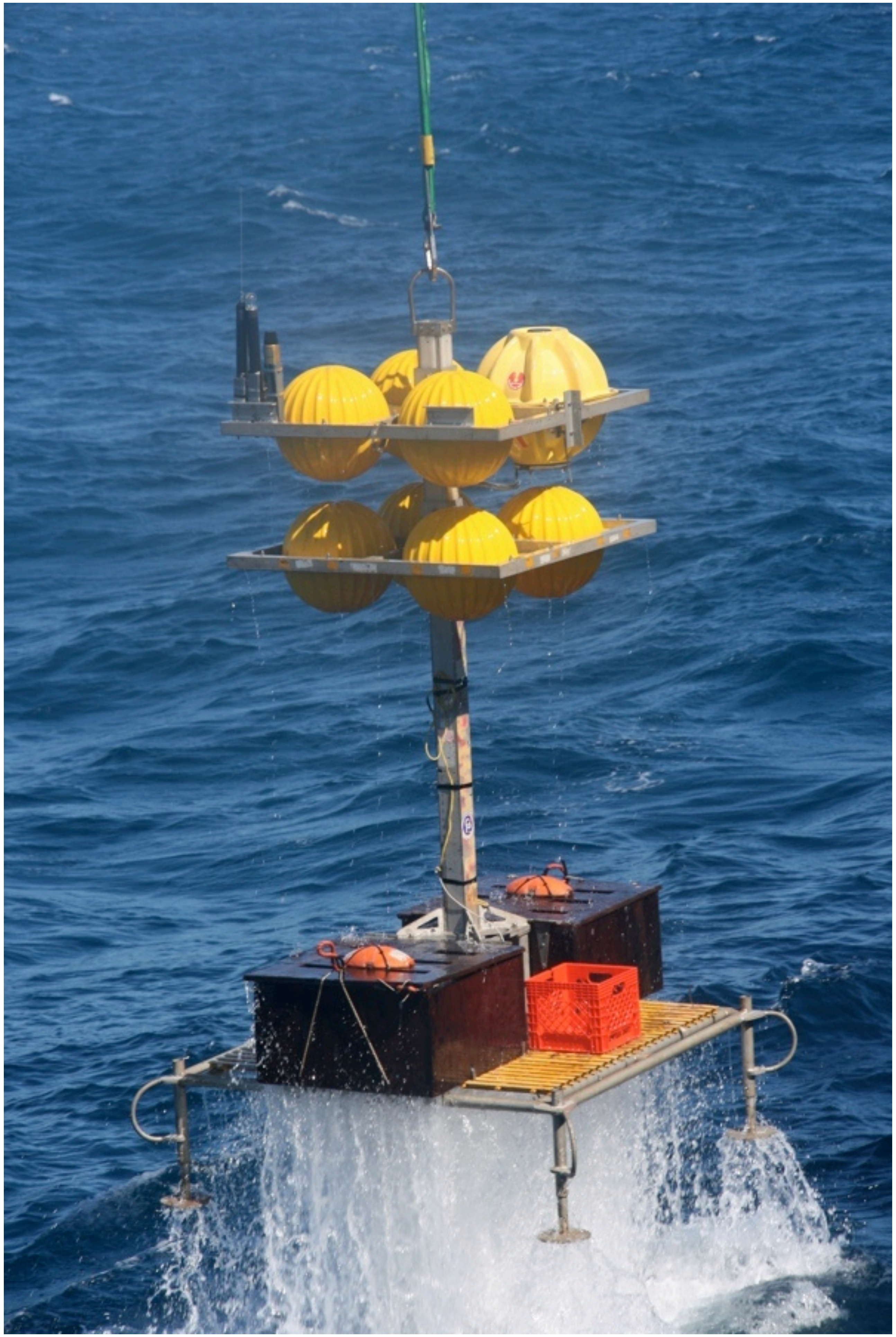


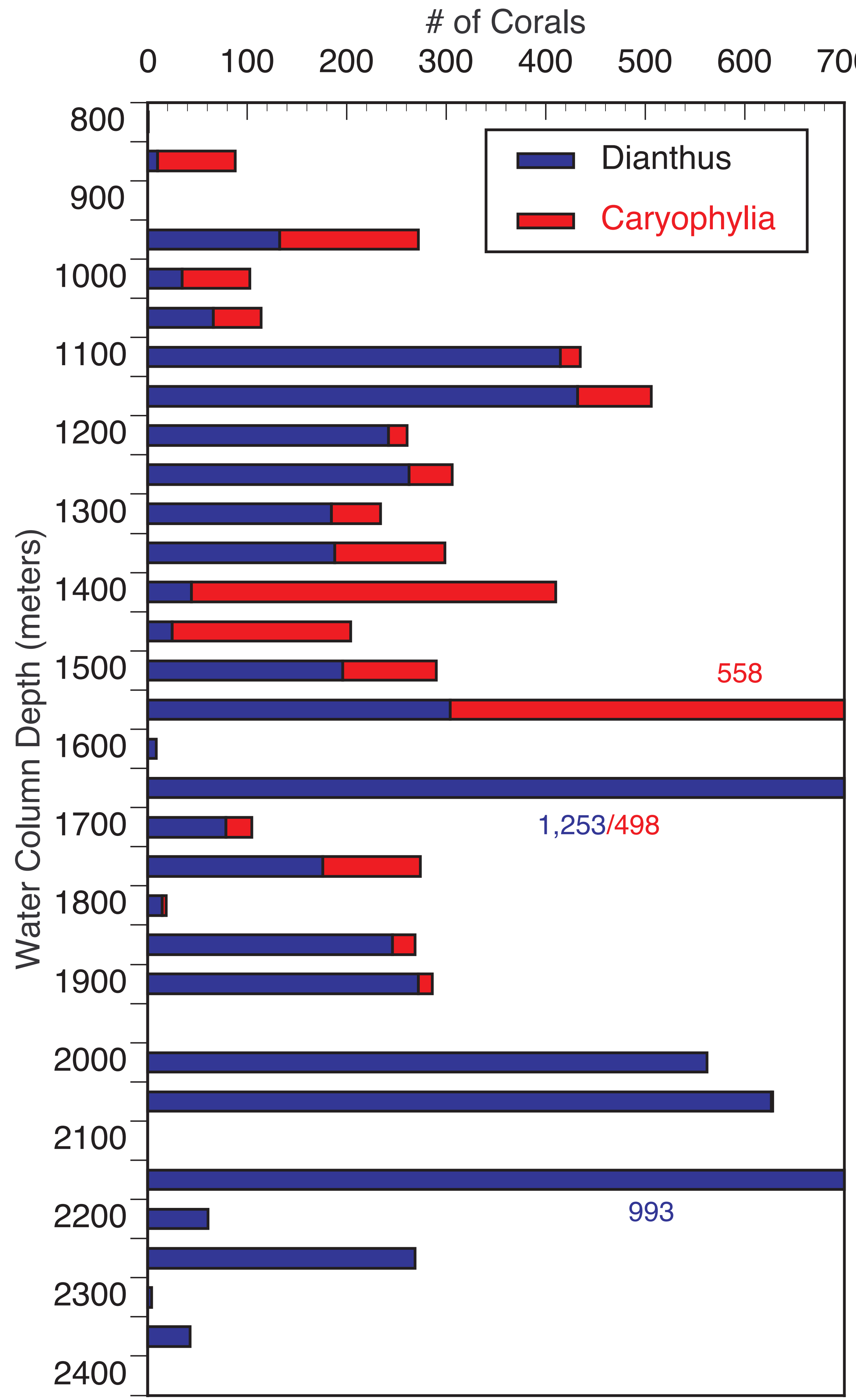
5 cm long *D. dianthus*
-fossil collected in 2003


EFFER
JASON
WOODS HOLE
OCEANOGRAPHIC INSTITUTION


CONTENTS:
DATE:
TN228-J2-382
1216-1820-1
1372-B5
TN228-J2-382-
1216-1820
TN228-
J2-382
1216-1820
14-1372
Ø16

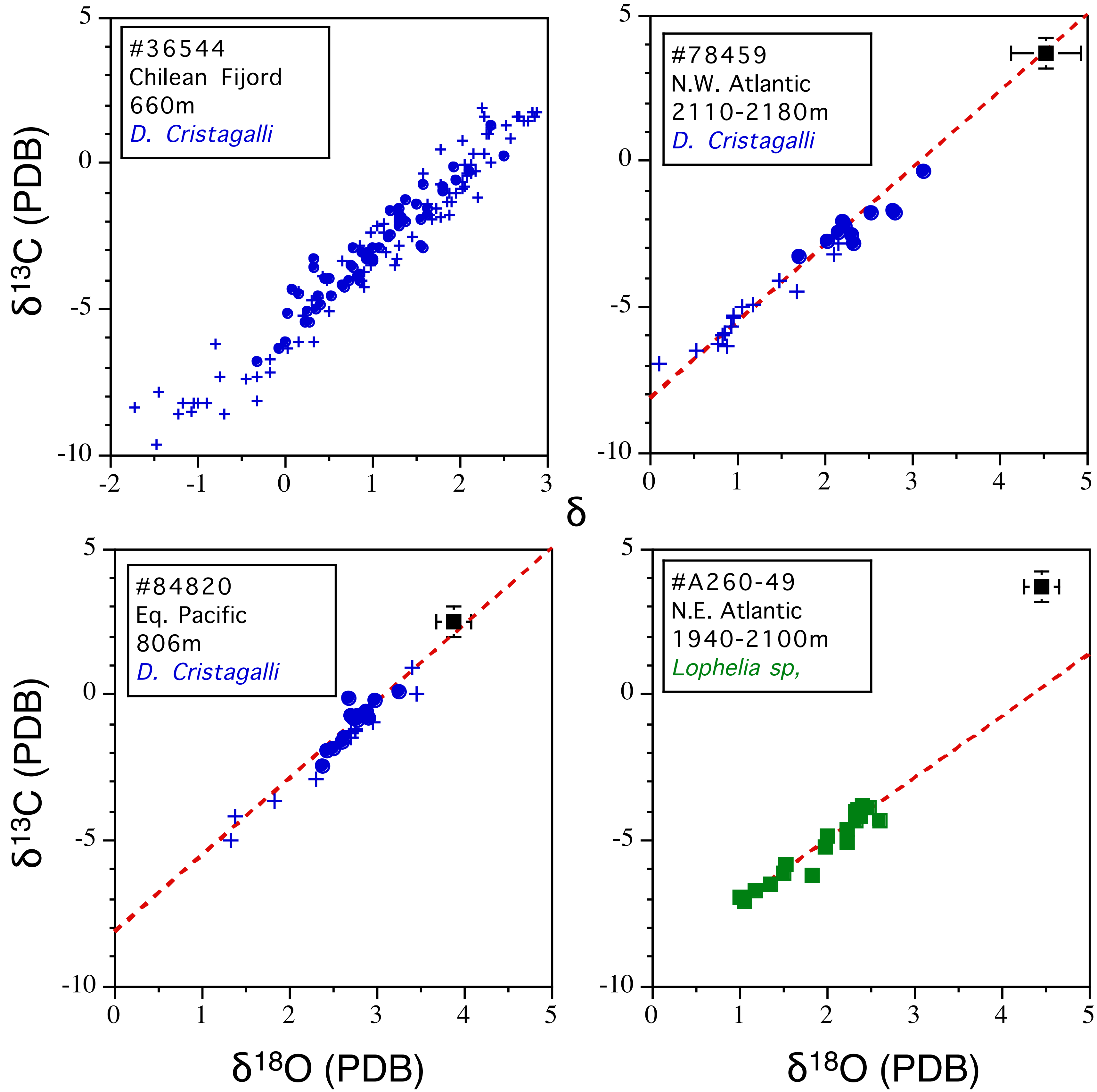

EARPLUGS
SPILL KIT

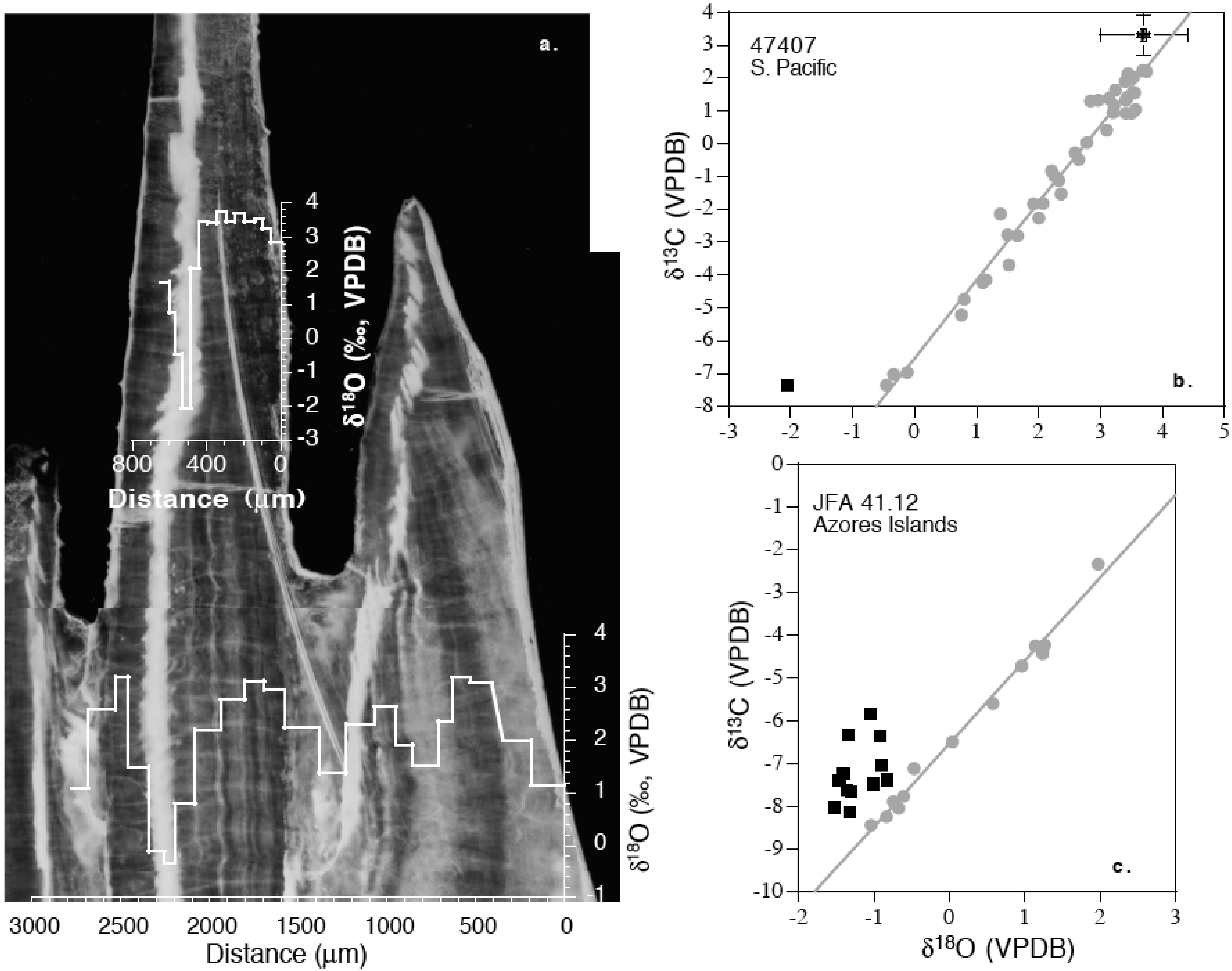




# of Corals
0
100
200
300
400
500
600
700
Water Column Depth (meters)
800
900
1000
1100
1200
1300
1400
1500
1600
1700
1800
1900
2000
2100
2200
2300
2400
Dianthus
Caryophylia
558
1,253/498
993

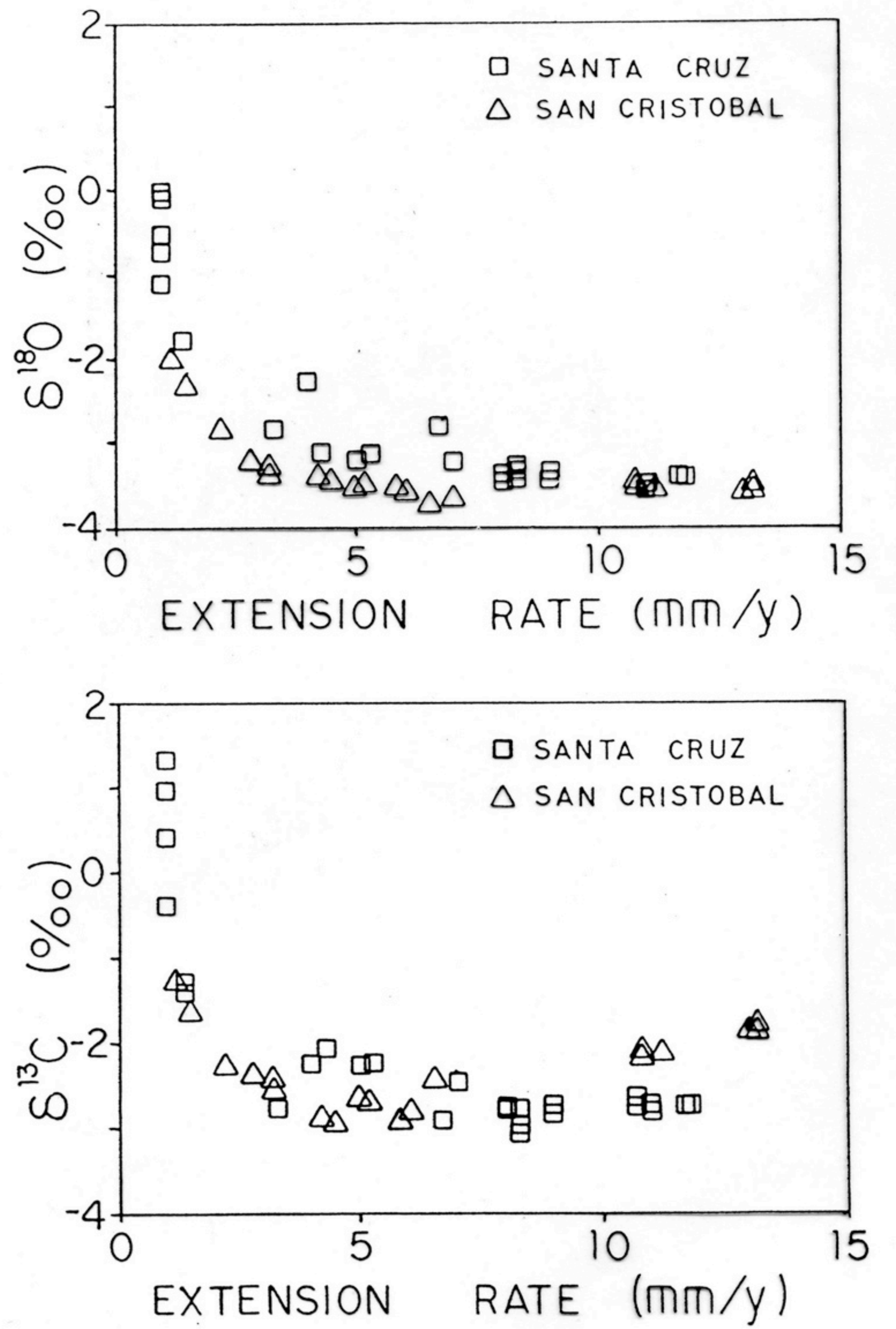
The stable isotope data from 4 separate deep corals



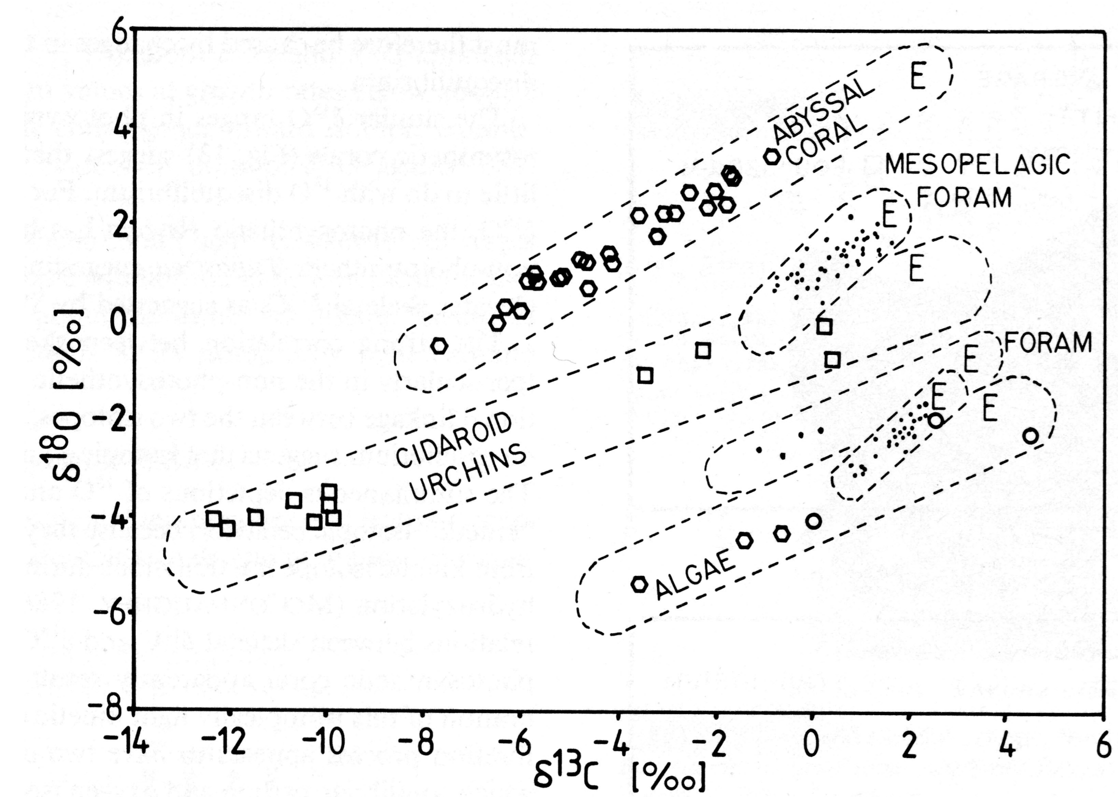


a.
δ18O (‰, VPDB)
Distance (μm)
47407
S. Pacific
b.
δ13C (VPDB)
JFA 41.12
Azores Islands
c.
δ18O (VPDB)

Ted McConnaughey's work in 1989 and the clear presence of "vital effects"



Two corals from a single time horizon



Many different marine calcifiers

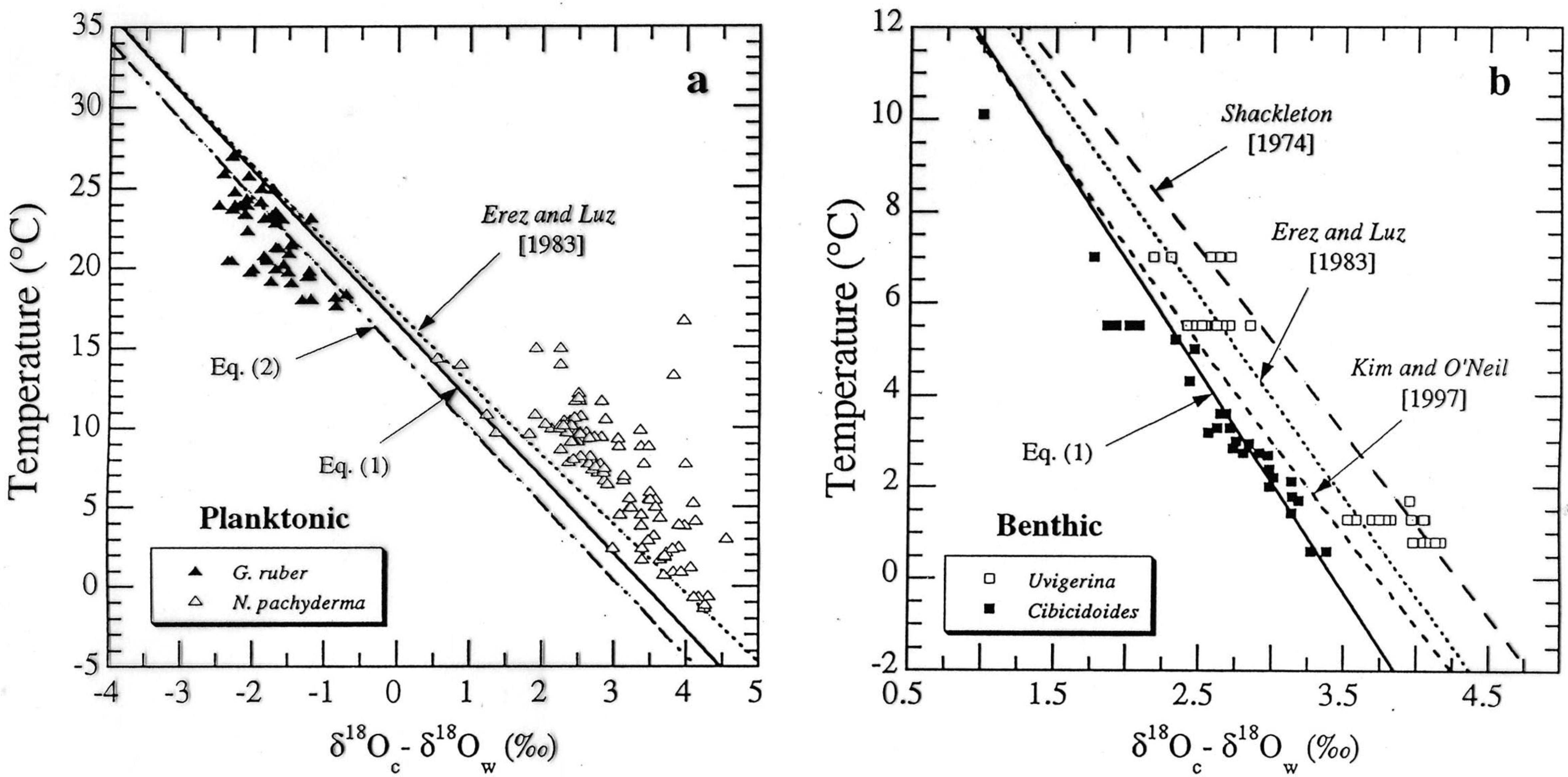
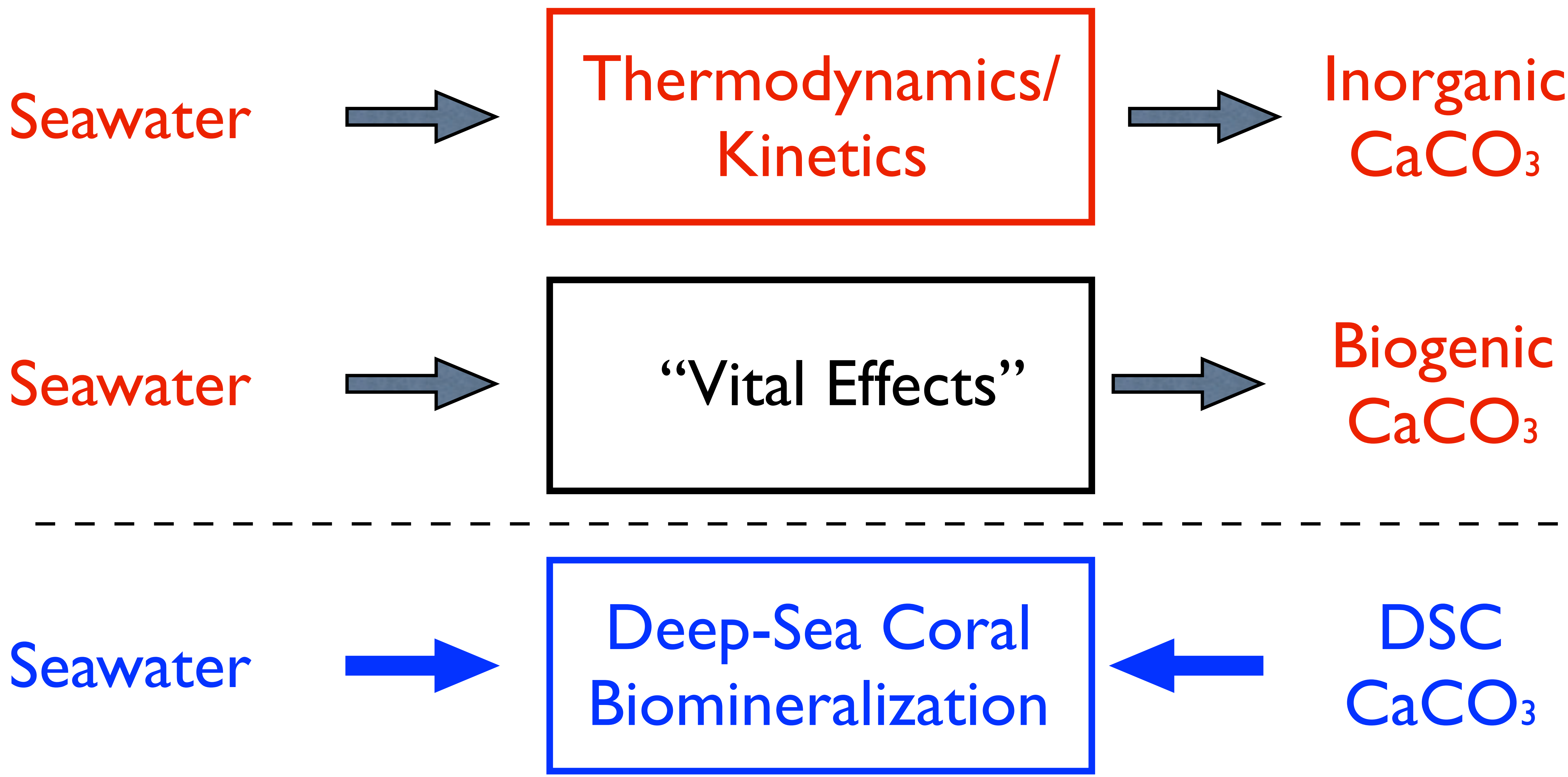


Figure 5. Published and predicted $\delta^{18}O$ values for (a) planktonic foraminifera from core tops in the equatorial to North Atlantic and the Southern Ocean [*Duplessy et al.*, 1991; *Wang et al.*, 1995; *Wu and Hillaire-Marcel*, 1994], and (b) benthic foraminifera from core tops in the Atlantic, Pacific, and Indian Oceans and the Arabian Sea and Gulf of Mexico [*Kallel*, 1988, and references therein; *Loubere et al.*, 1995; *Shackleton*, 1974]. Equation (1) provides a good fit to the *Cibicidoides* data.

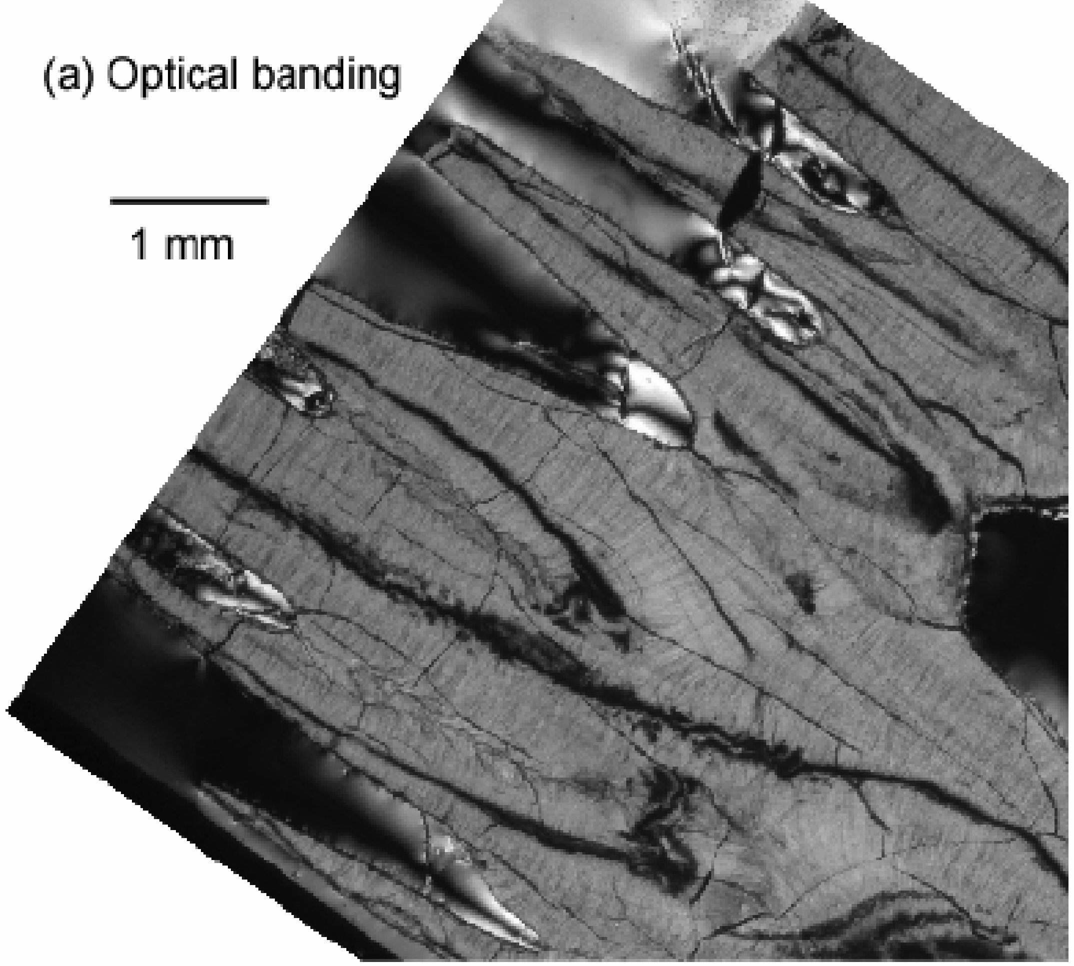
Bemis et al. (1999)

The Paleoclimate "Black Box"

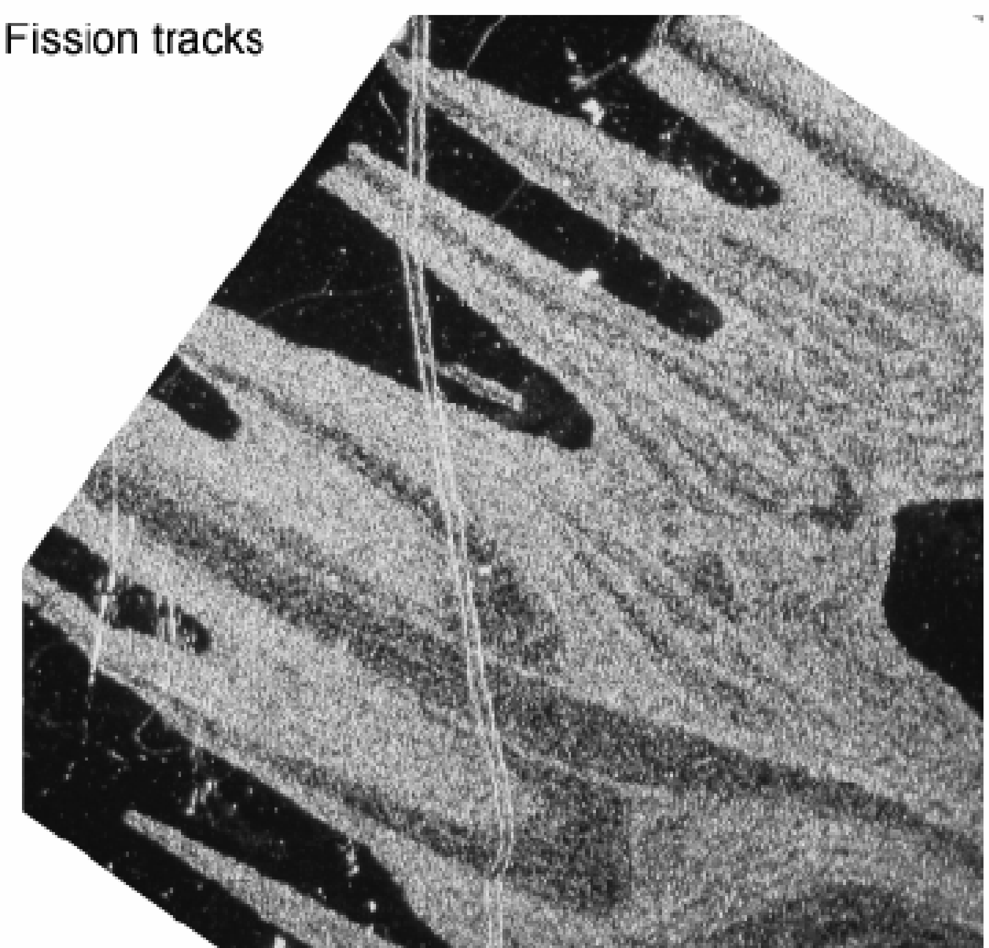


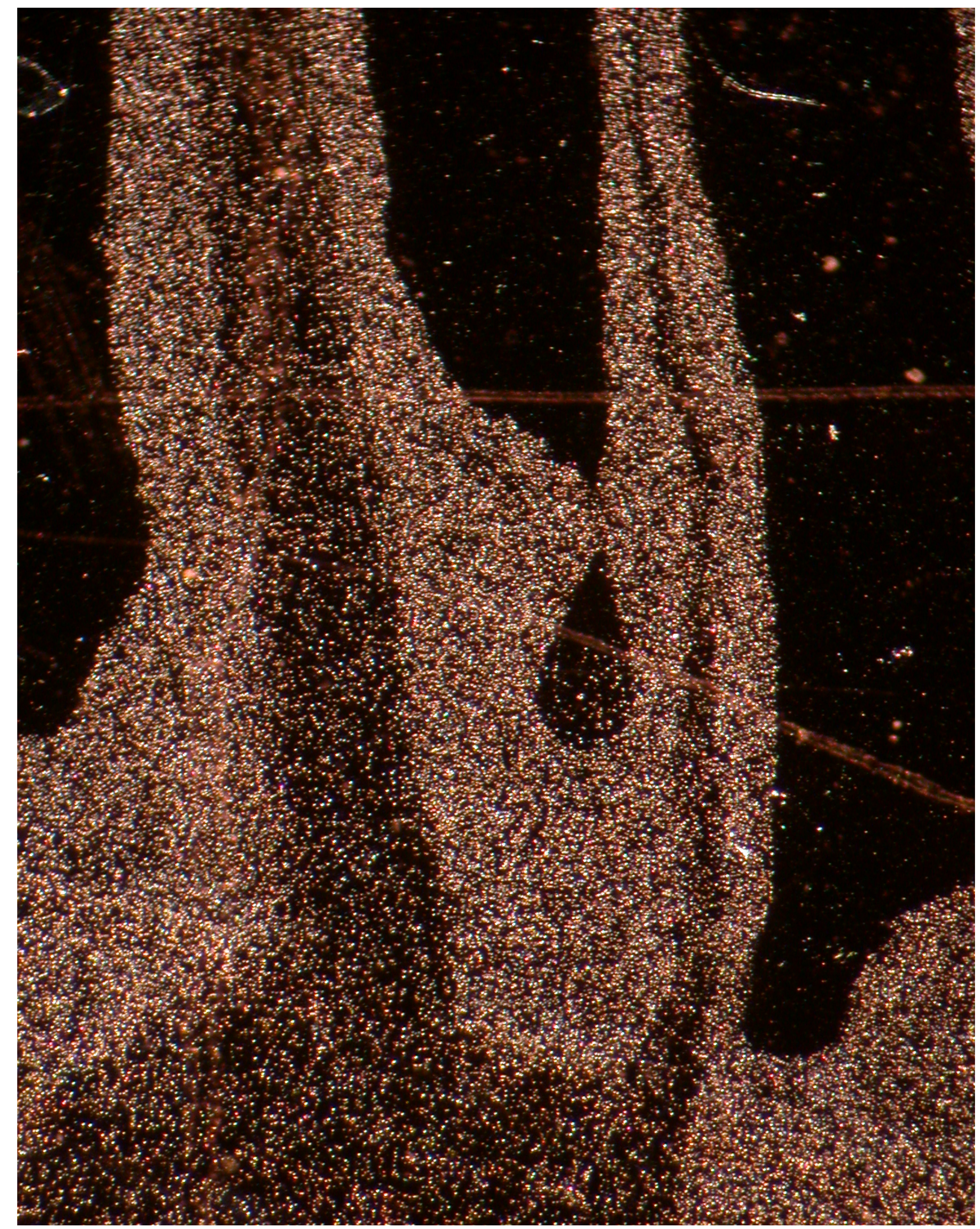
The U distribution in our corals

(a) Optical banding



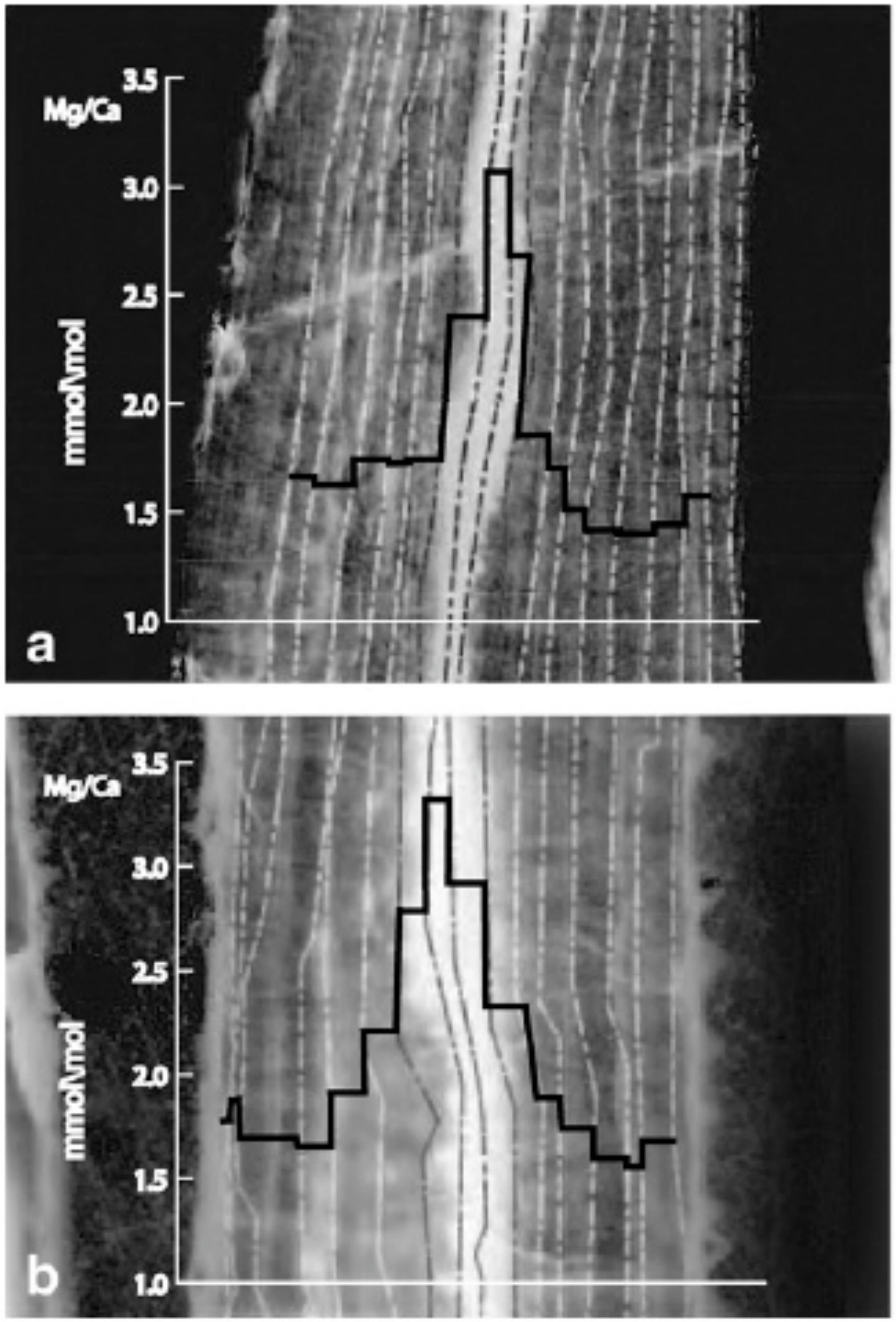
(b) Fission tracks

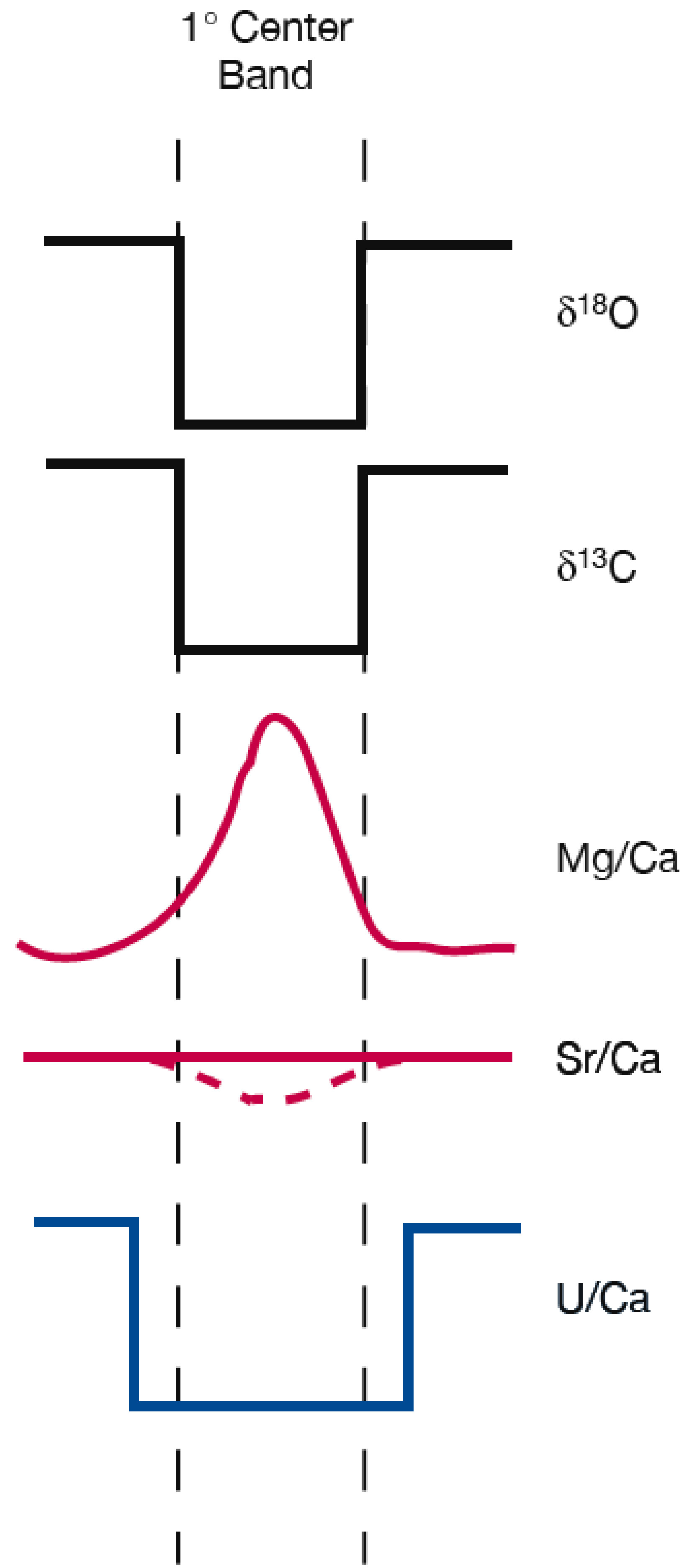




Close up of fission tracks

Mg/Ca from micromilling and ID-ICP-MS





A simplified view of the coral's "mother liquor"

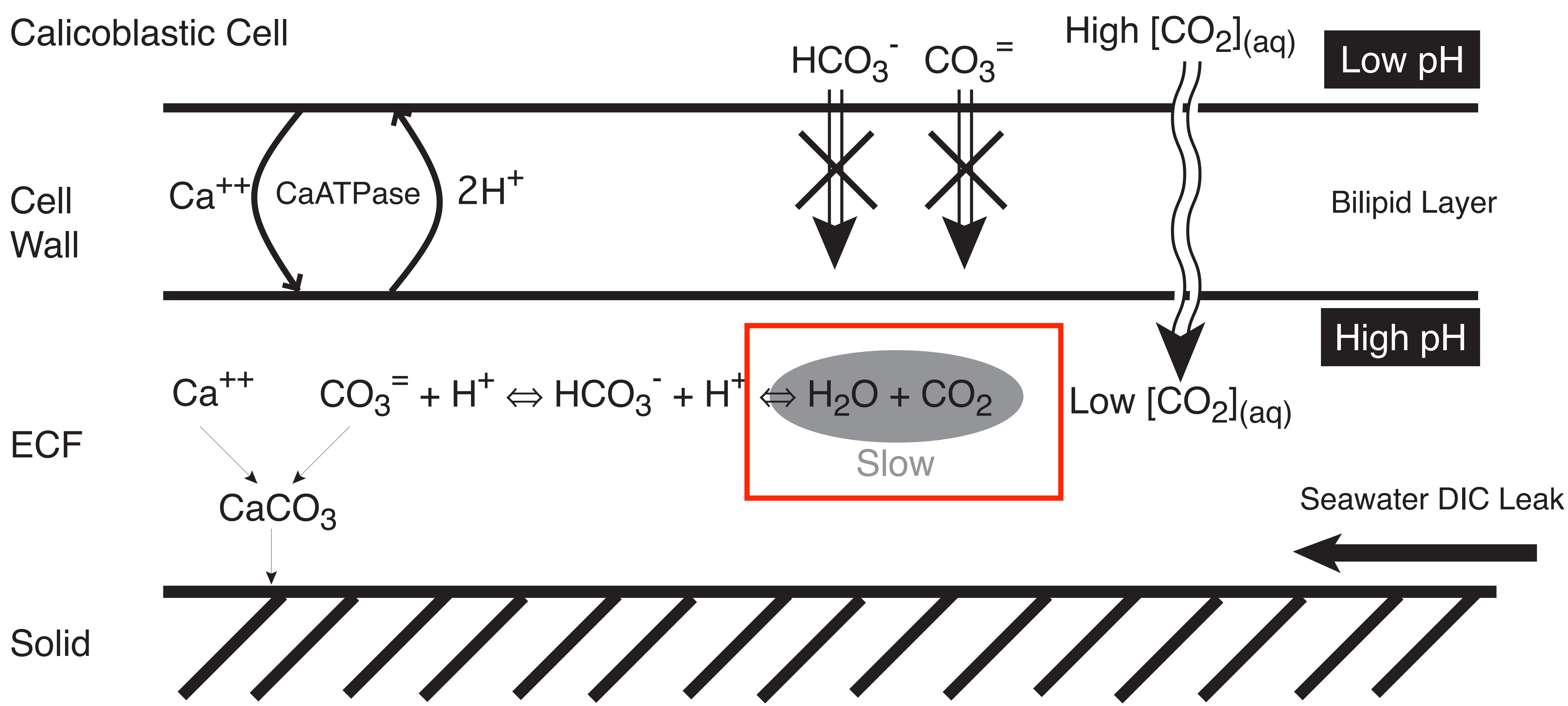
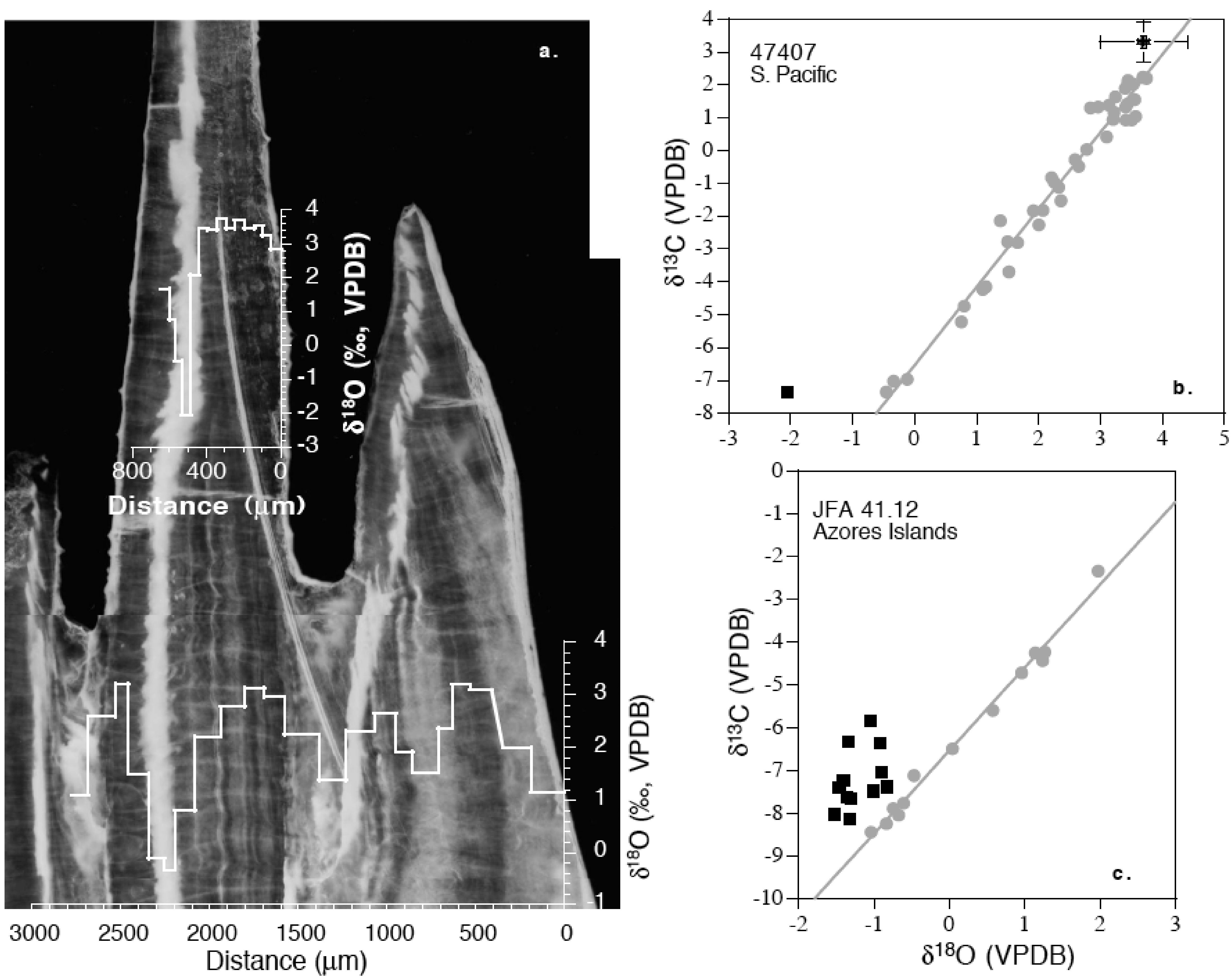
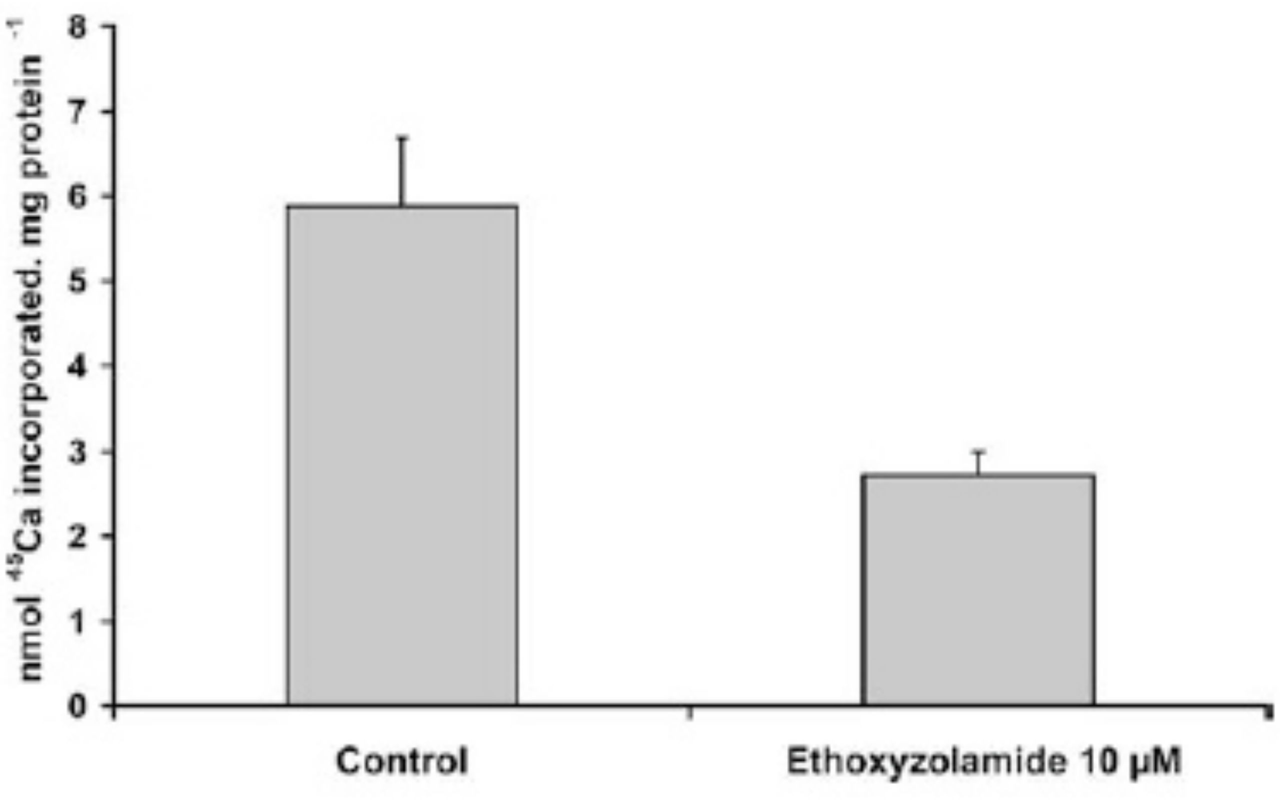


Figure 7

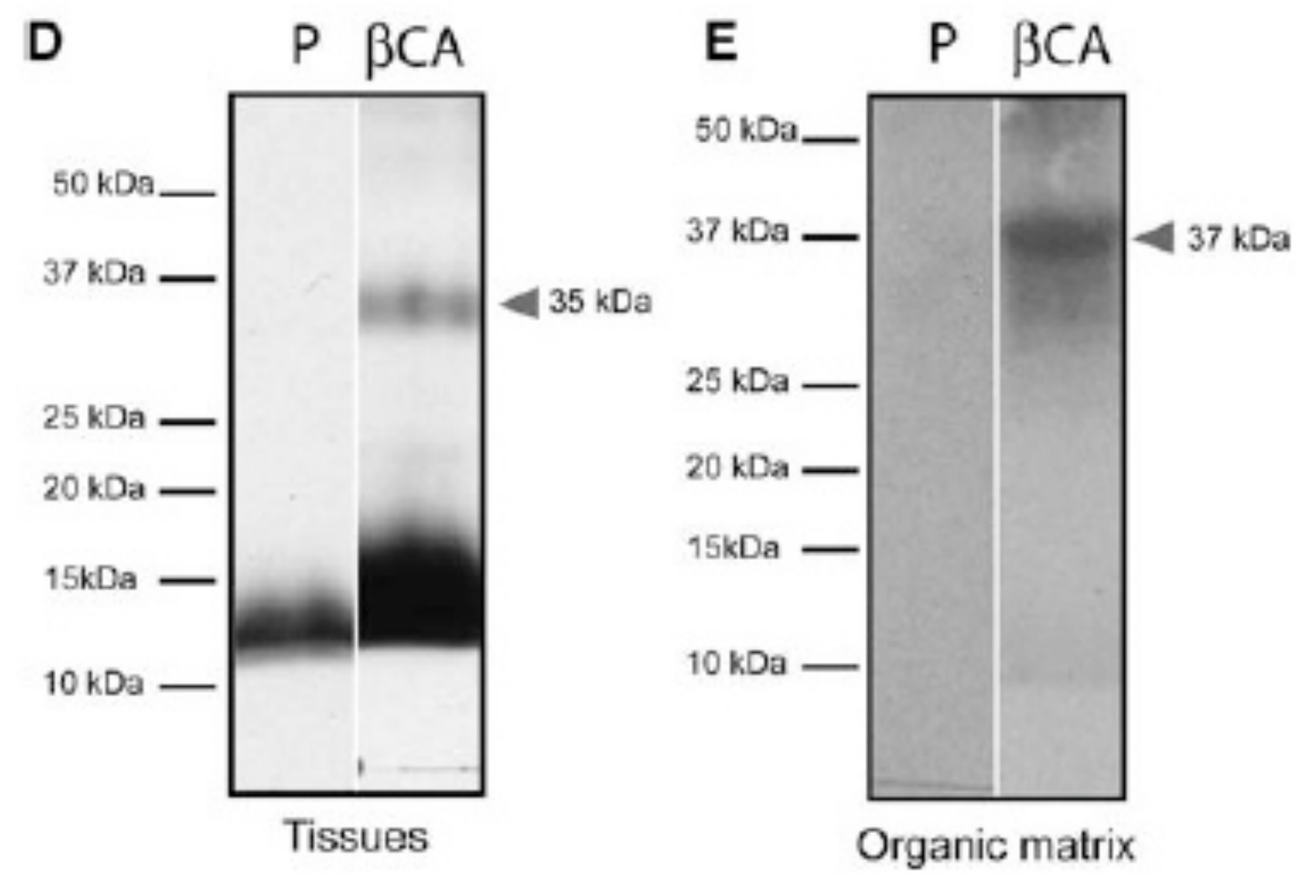
A break in the $\delta^{13}C/\delta^{18}O$ slope is trouble for kinetics



Carbonic Anydrase in the coral *Tubastrea sp.*



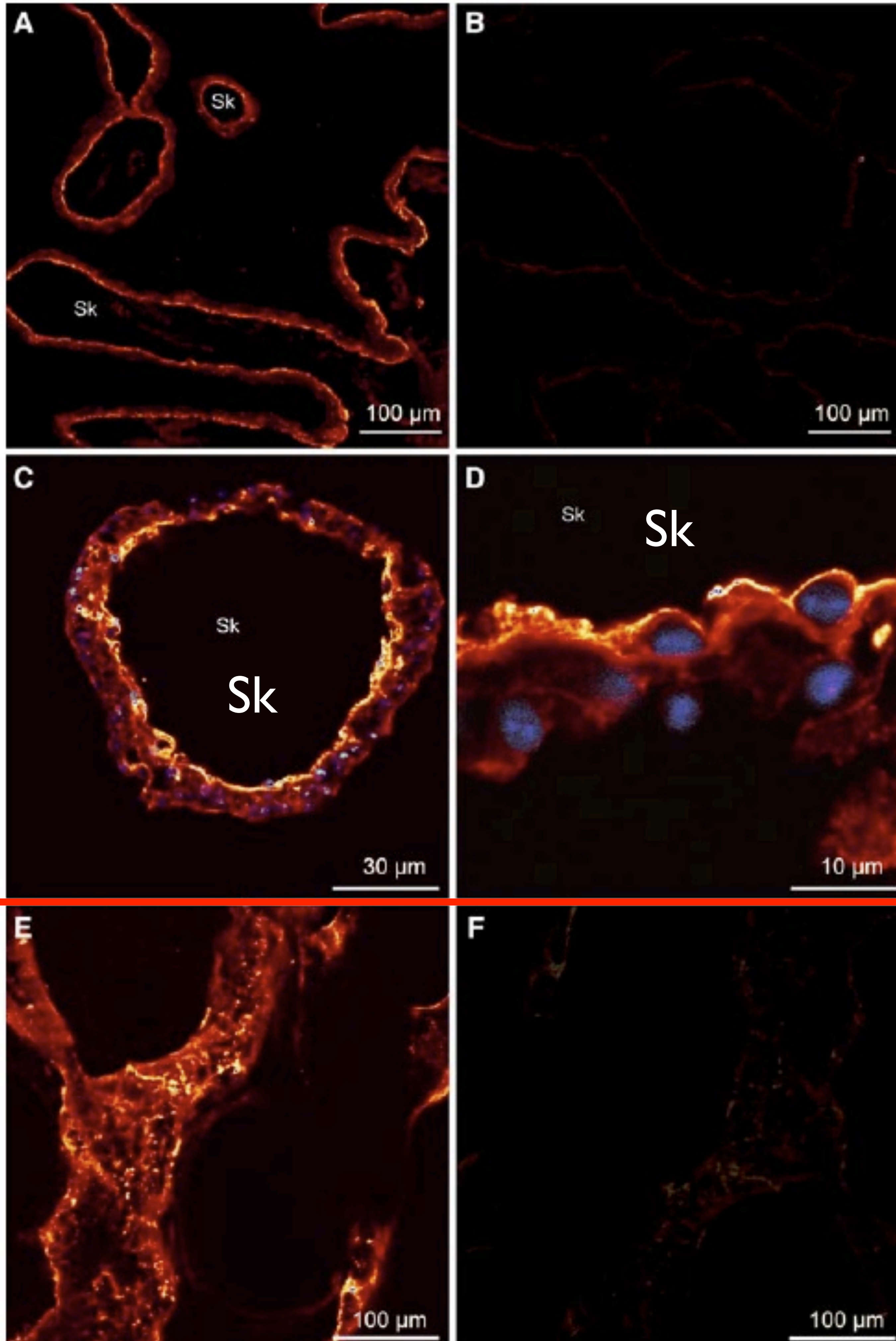
Calcification rate with a CA inhibitor



Western blots of CA in whole tissue and the skeletal organic matrix

Immunolocalization of CA in the coral calcioblastic tissue

Tissues



control

Skeleton

control

A simplified view of the coral's "mother liquor"

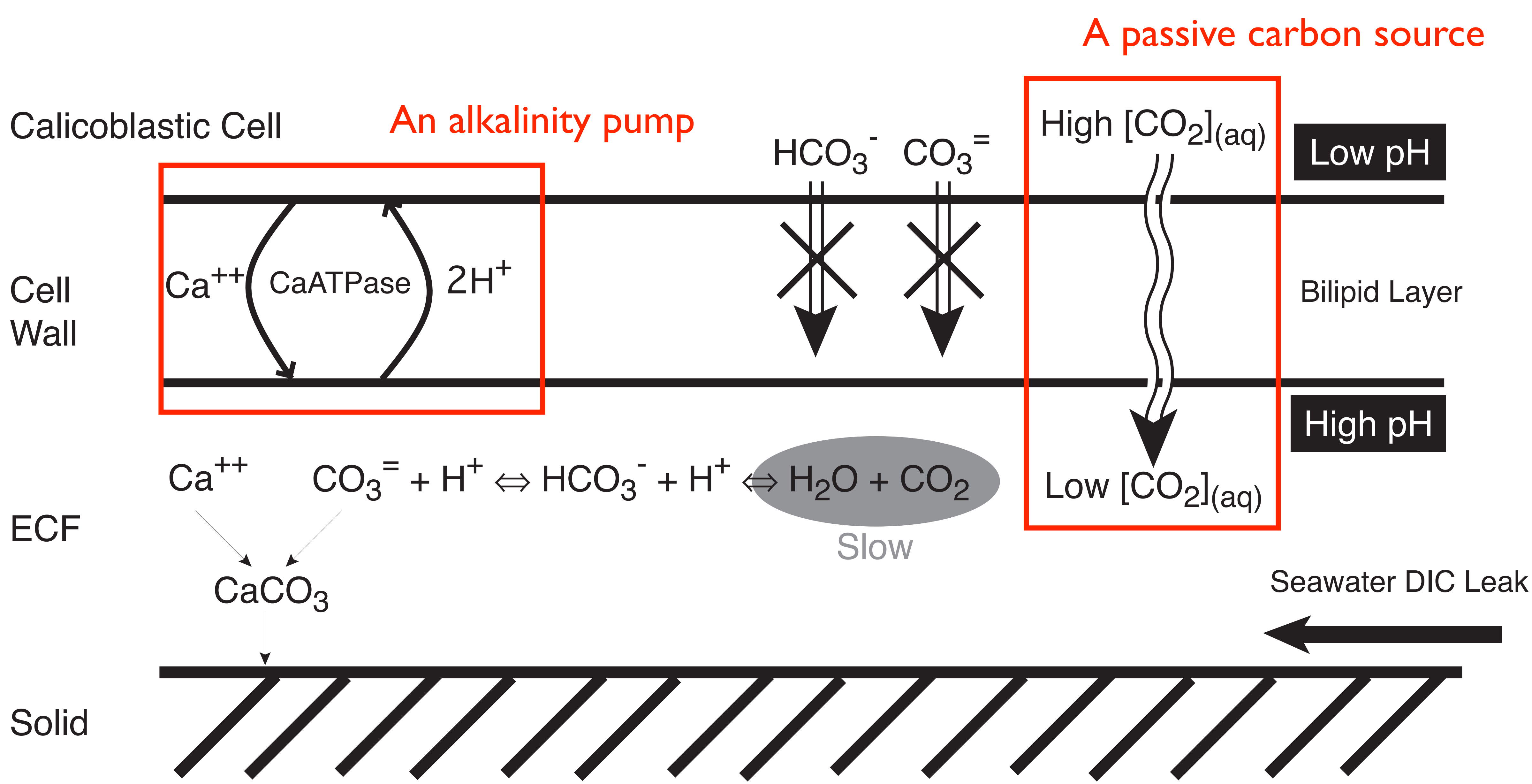


Figure 7

Carbon Isotopes at Equilibrium

$CO_{2\,(g)}$ = -8.8 ‰

Atmosphere

Ocean

$CO_{2\,(aq)}$ = -10.1 ‰

Tot CO_2=2260 µmole/kg
Alkalinity=2375 µeq/kg
$\delta^{13}C$ of DIC = 1.0 ‰

HCO_3 = 1.3 ‰

CO_3 = -1.8 ‰

Sediments

$CaCO_{3\,(solid)}$ = 2.3 ‰

Equilibrium effect of pH on oxygen isotopes

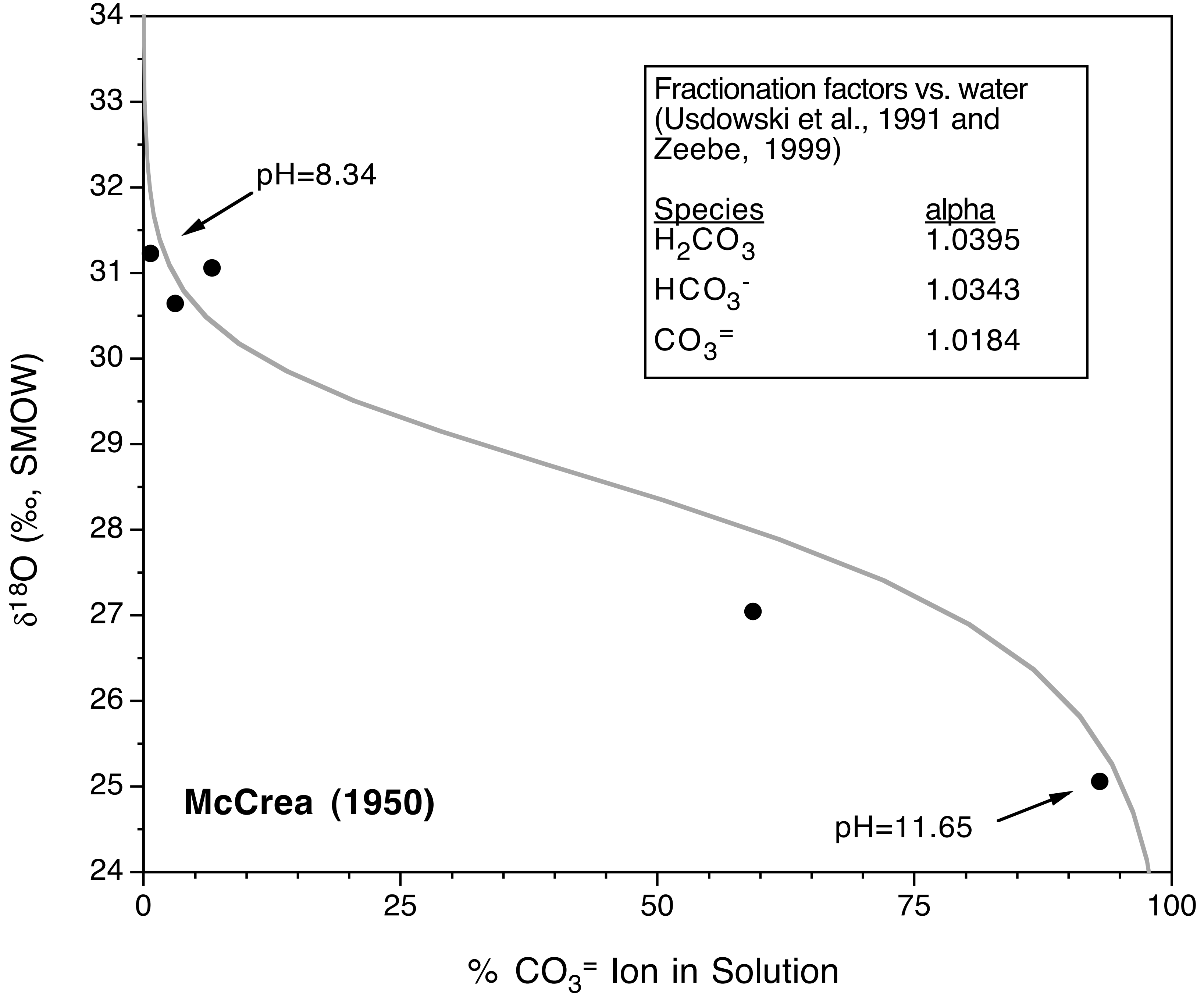


Figure 8

A simple model without kinetics

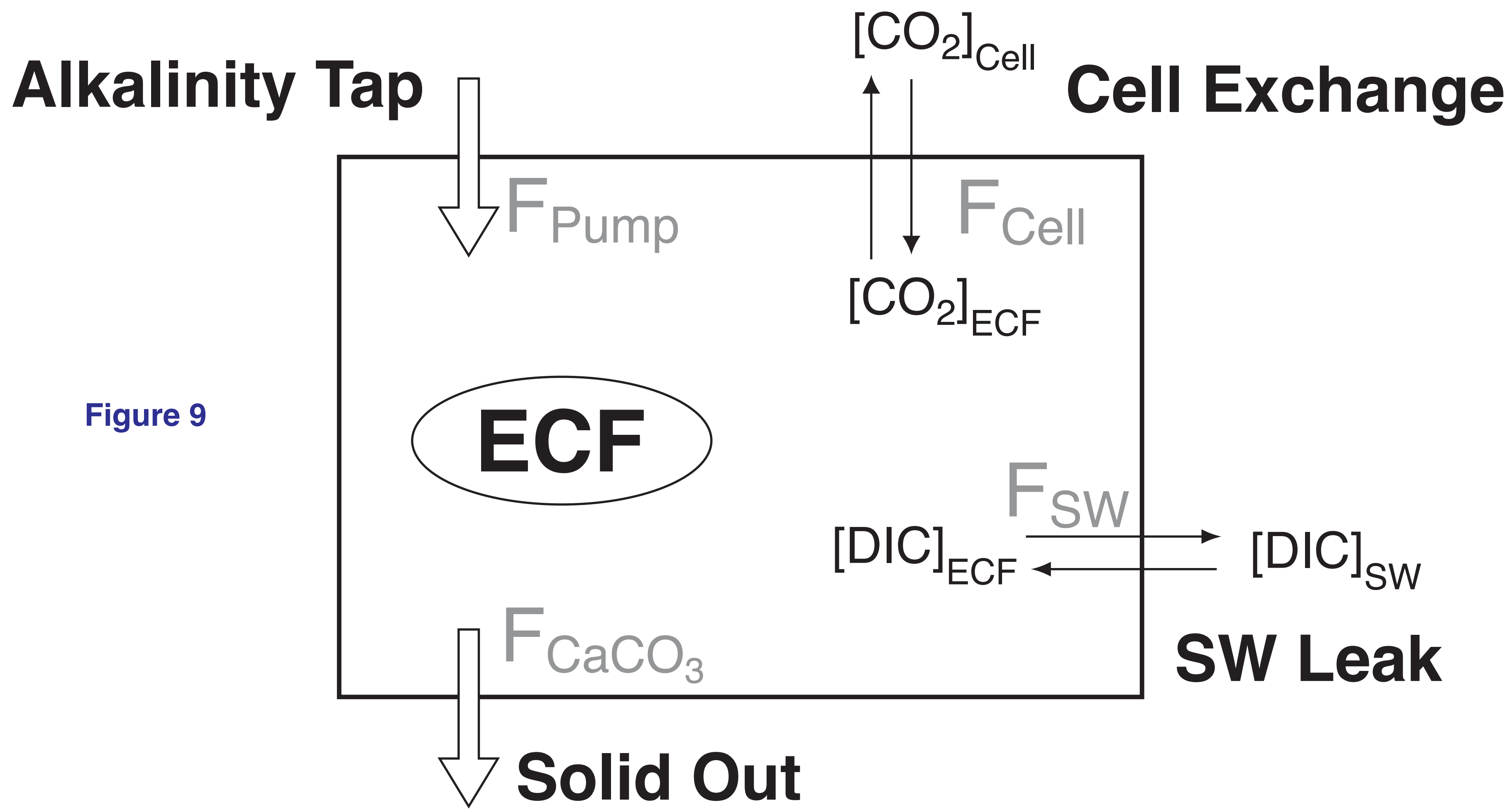


Figure 9

ECF pH Calculation

(1) $$z\frac{\partial DIC_{ECF}}{\partial t} = F_{SW}DIC_{SW} + F_{Cell}[CO_2]_{Cell} - F_{SW}DIC_{ECF} - F_{SW}DIC_{ECF}\alpha_0 - F_{CaCO_3}$$

(2) $$z\frac{\partial Alk_{ECF}}{\partial t} = F_{SW}Alk_{SW} + F_{Pump}Alk_{Pump} - F_{SW}Alk_{ECF} - 2F_{CaCO_3}$$

(3) $$z\frac{\partial [Ca]_{ECF}}{\partial t} = F_{SW}[Ca]_{SW} + \frac{f_{Ca}F_{Pump}Alk_{Pump}}{2} - F_{SW}[Ca]_{ECF} - F_{CaCO_3}$$

(4) $$Alk_{ECF} = 2DIC_{ECF}\alpha_2 + DIC_{ECF}\alpha_1$$

(5) $$F_{CaCO_3} = \frac{k_{rate}}{Surf}([Ca]DIC_{ECF}\alpha_0 - k_{sp})$$

Schematically the master variable is pH, driven by the coral's alkalinity pump

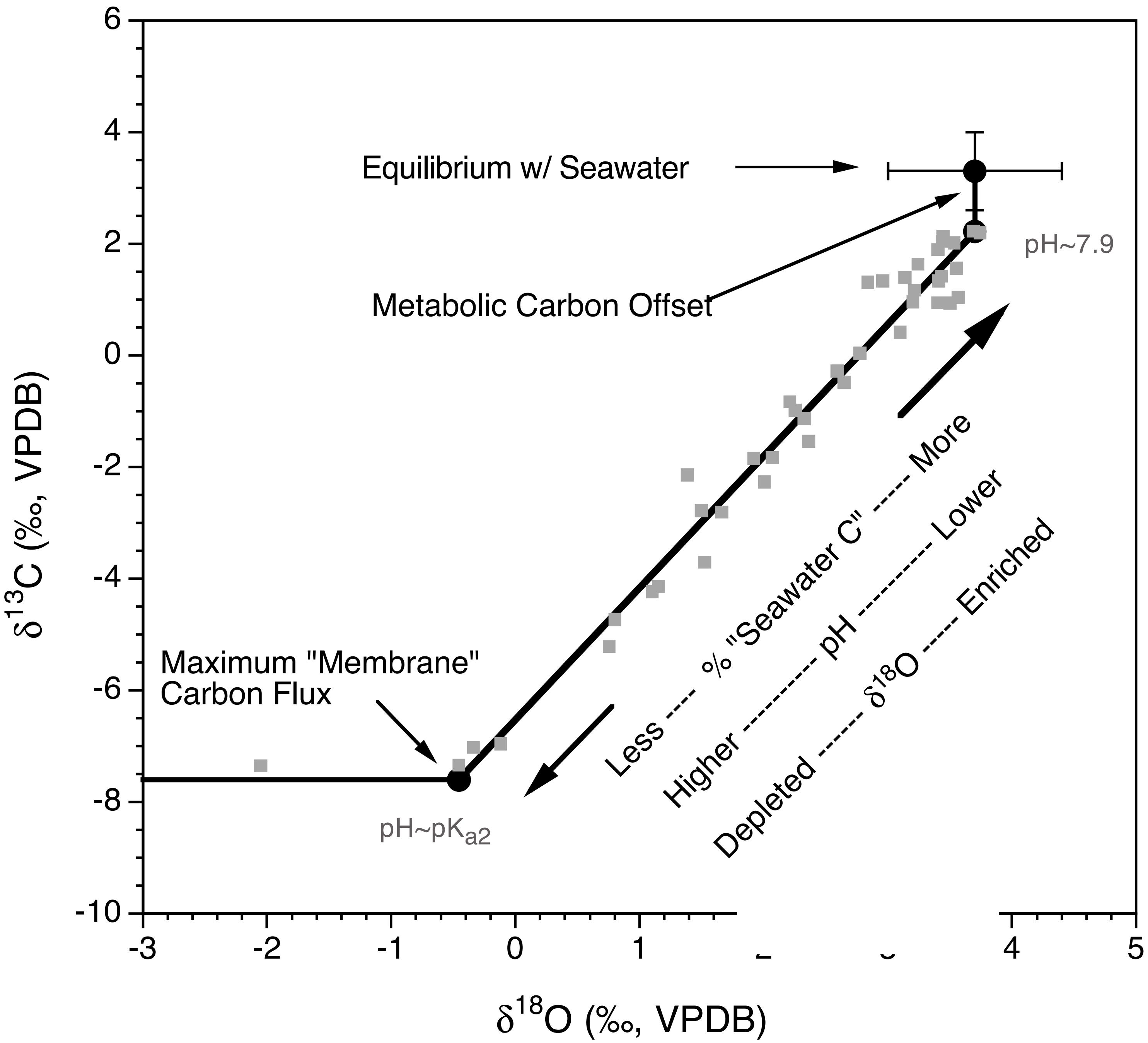
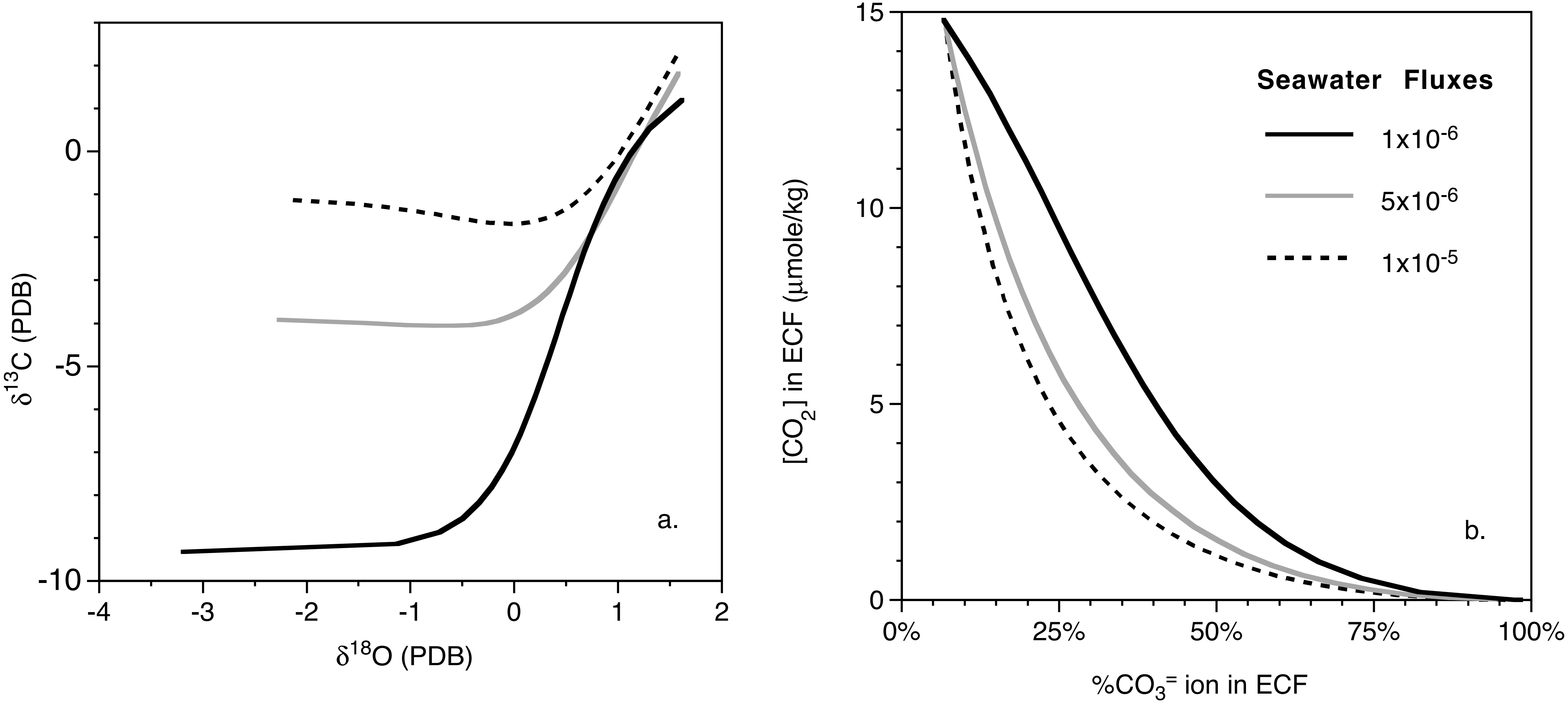


Figure 9

Steady state model results



A simplified view of the coral's "mother liquor"

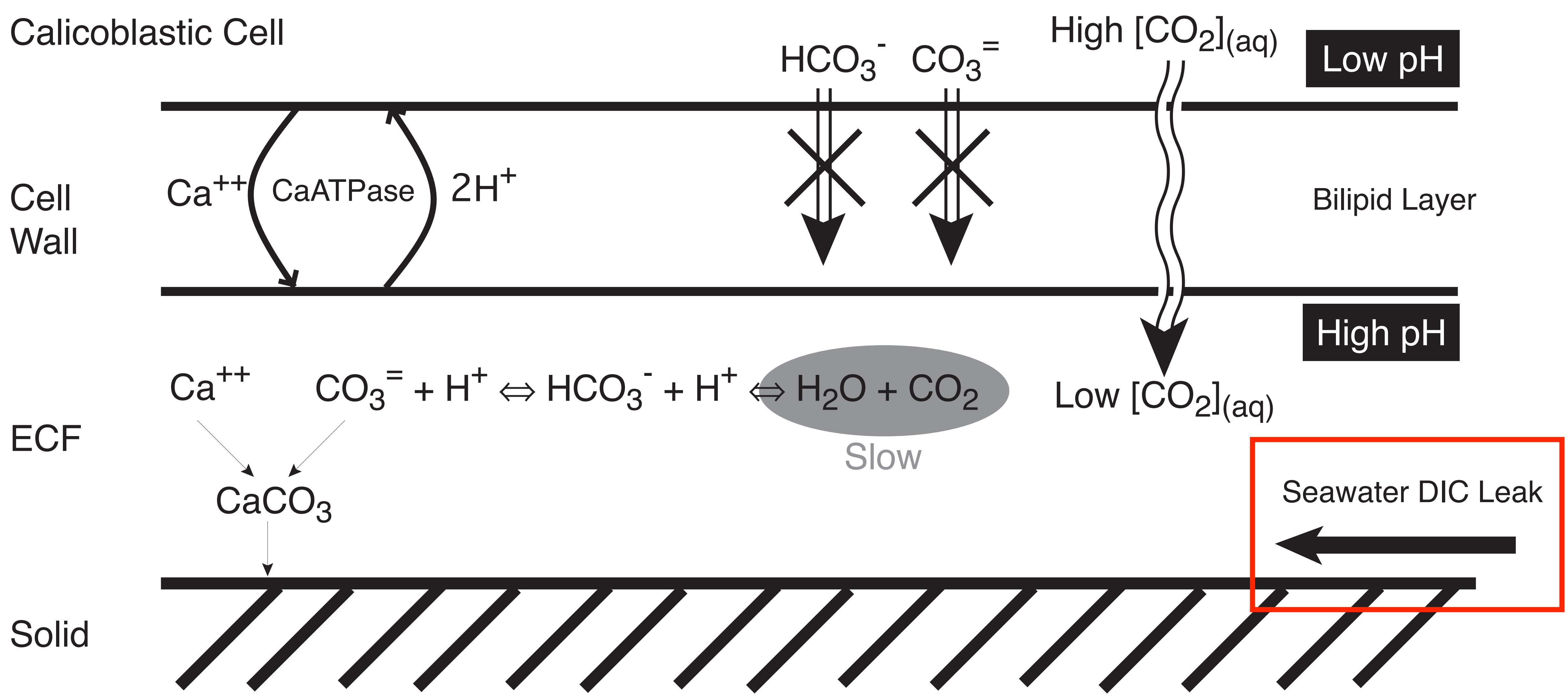
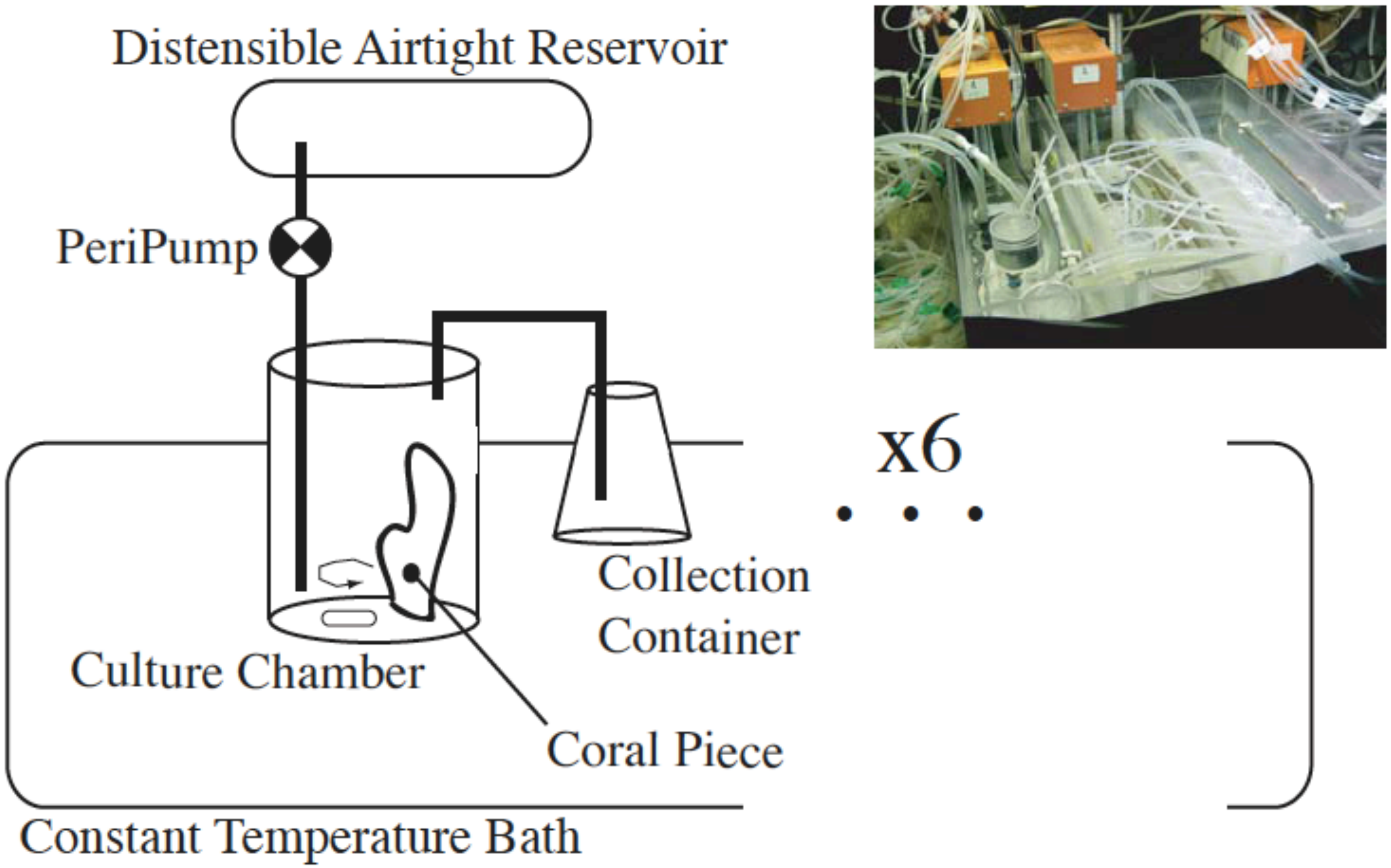
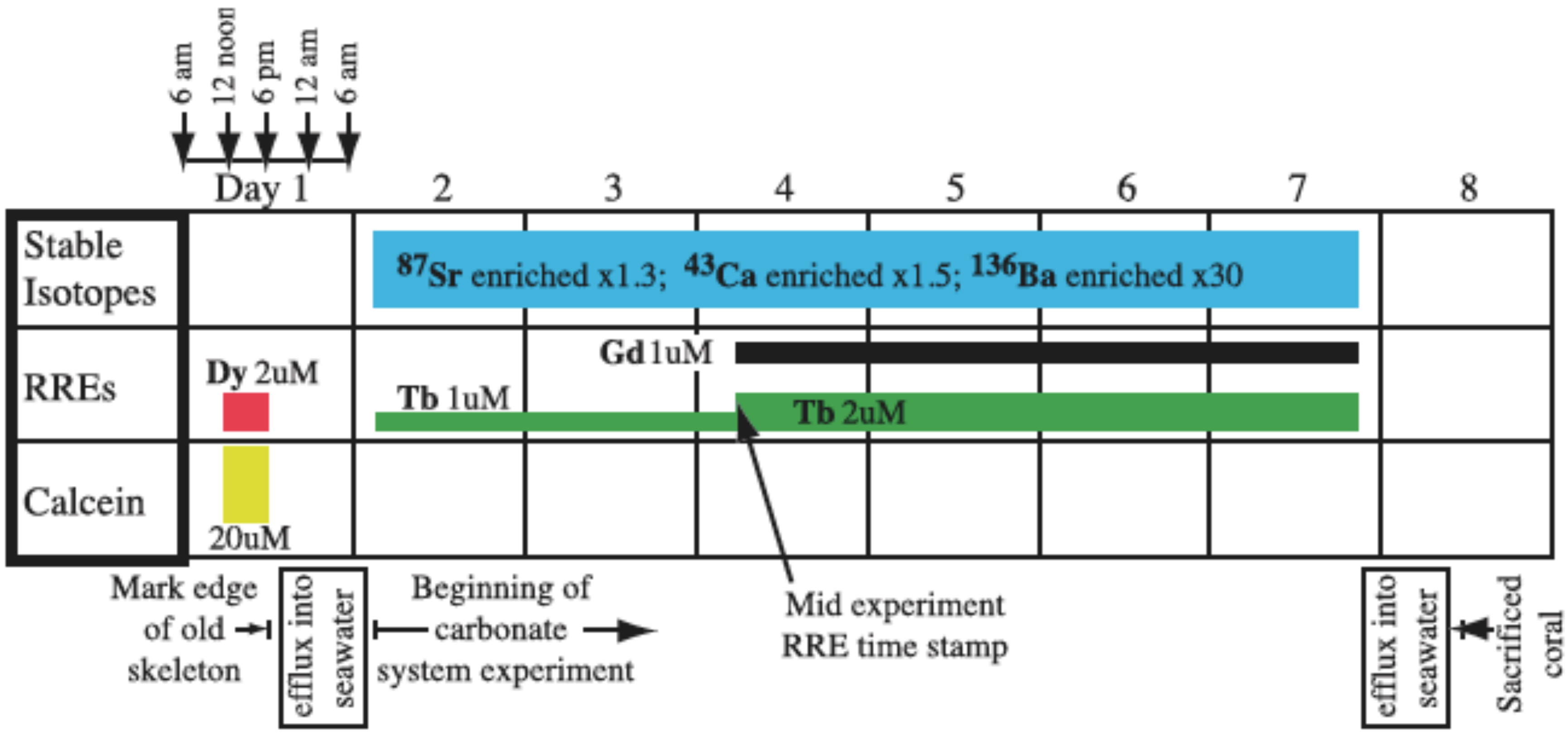
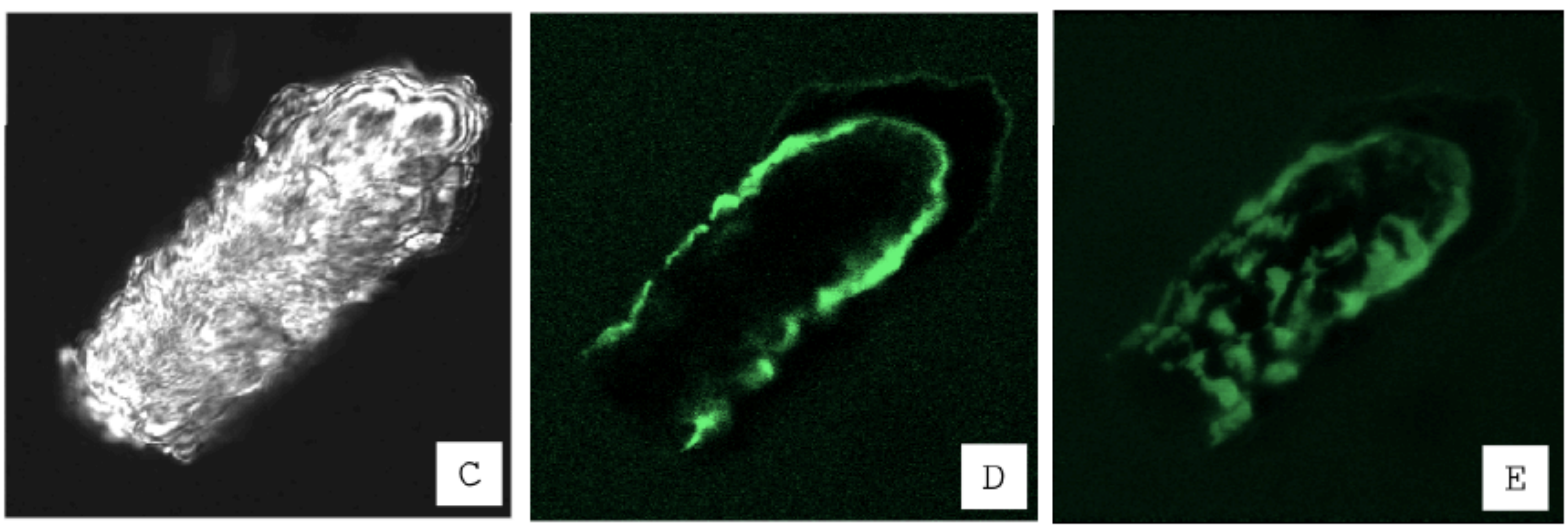


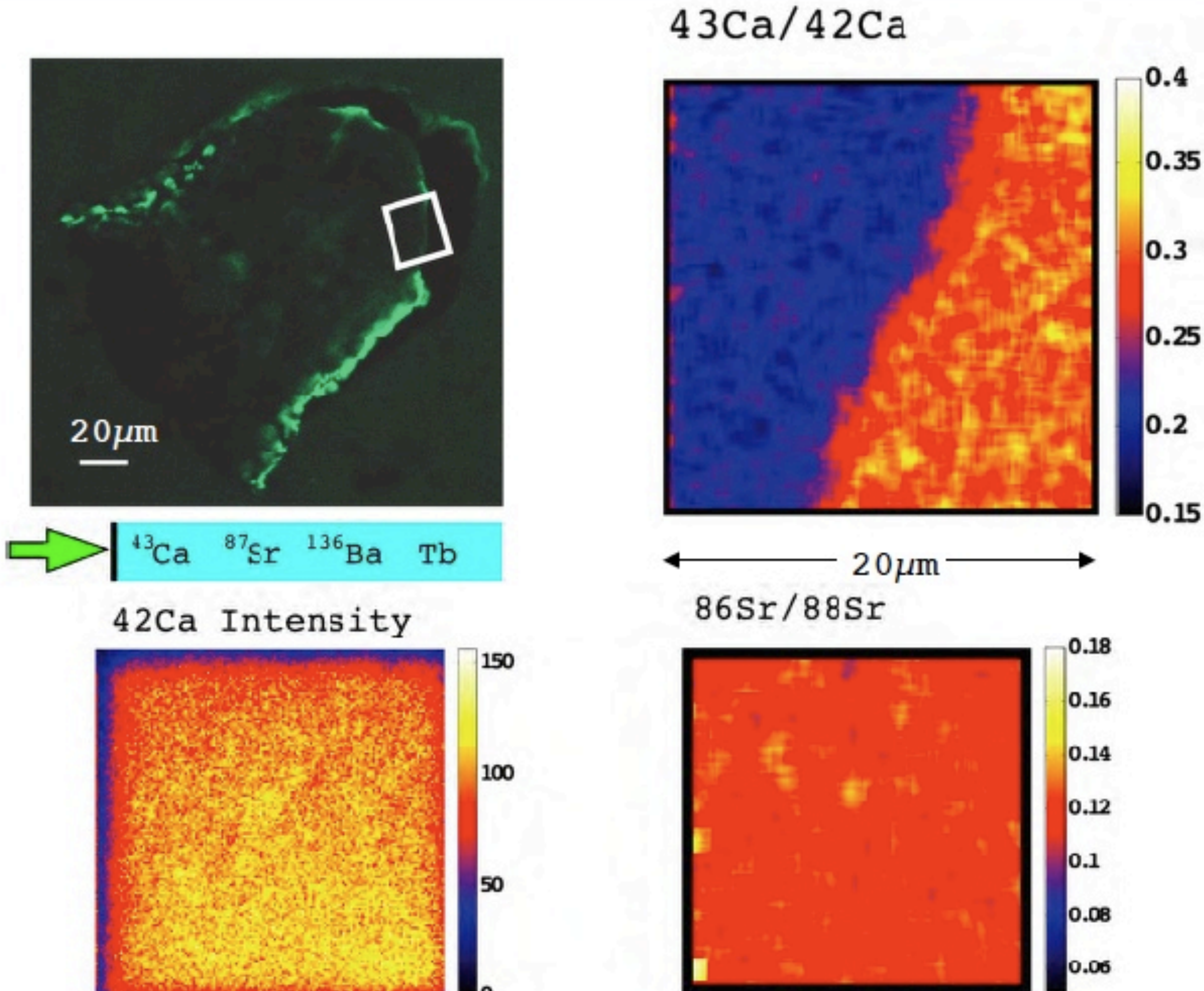
Figure 7

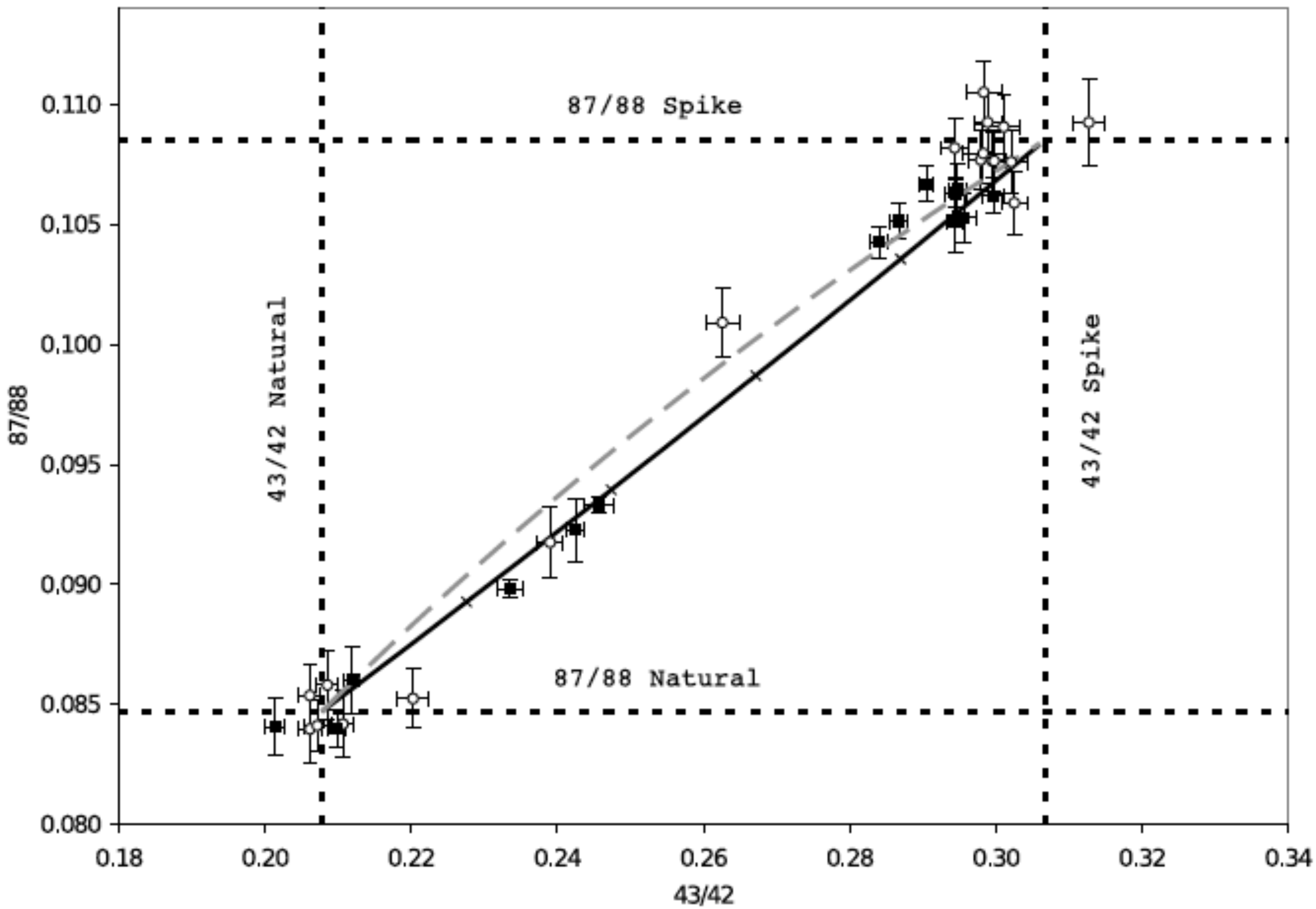

Distensible Airtight Reservoir
PeriPump
Culture Chamber
Coral Piece
Collection
Container
Constant Temperature Bath
x6


6 am
12 noon
6 pm
12 am
6 am
Day 1
2
3
4
5
6
7
8
Stable Isotopes
87Sr enriched x1.3; 43Ca enriched x1.5; 136Ba enriched x30
RREs
Dy 2uM
Gd 1uM
Tb 1uM
Tb 2uM
Calcein
20uM
Mark edge of old skeleton
efflux into seawater
Beginning of carbonate system experiment
Mid experiment RRE time stamp
efflux into seawater
Sacrificed coral


C
D
E

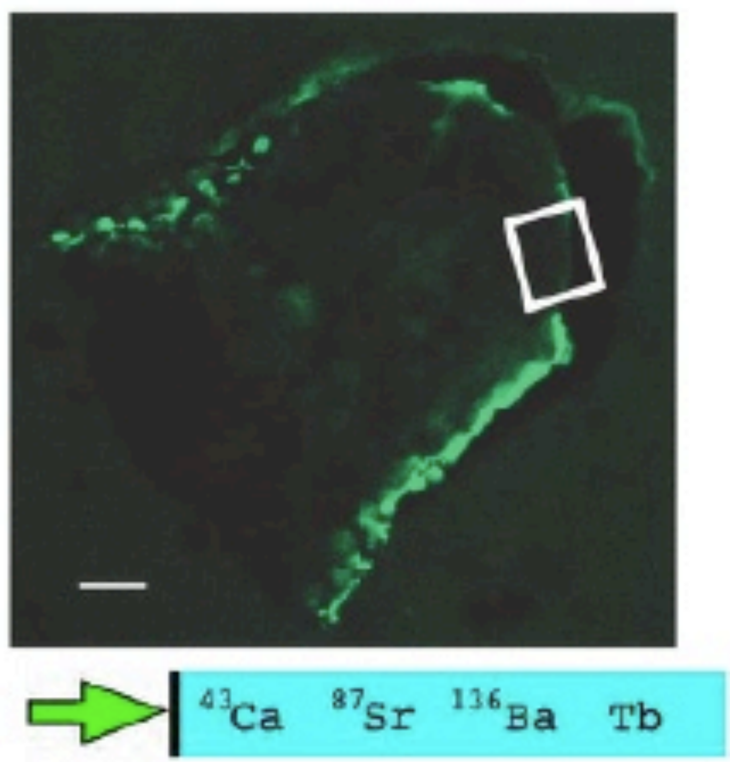
Continuous Boundary Marks Region of Experimental Growth

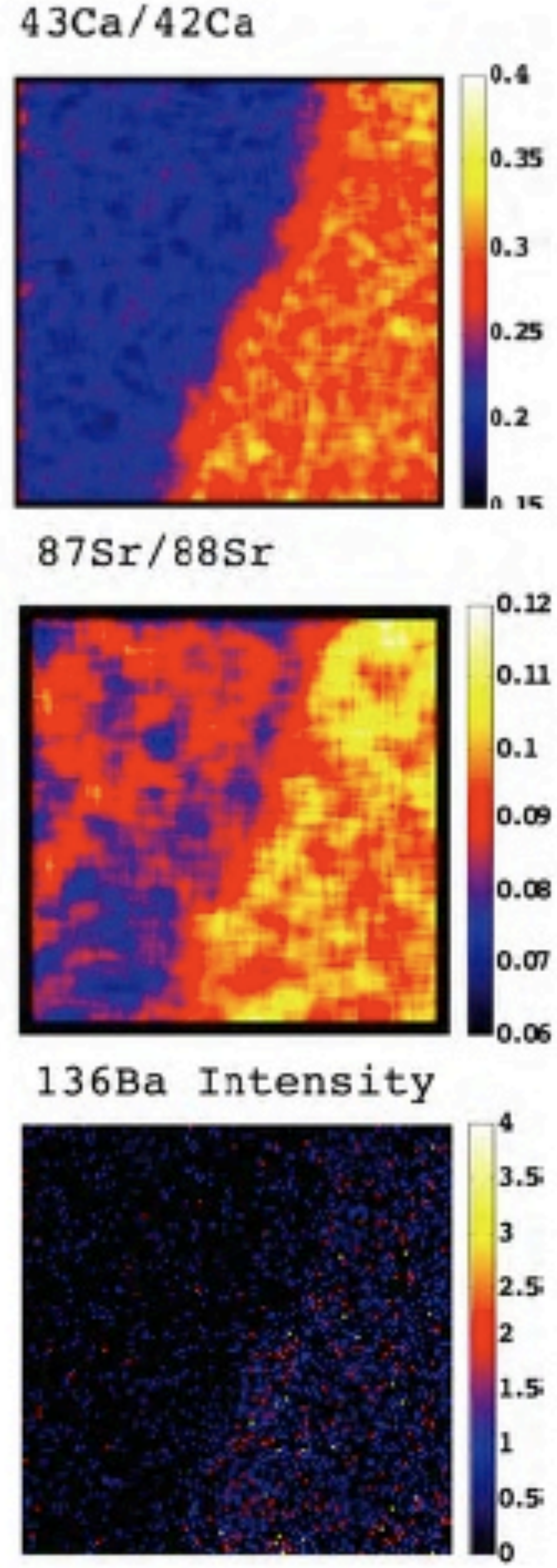


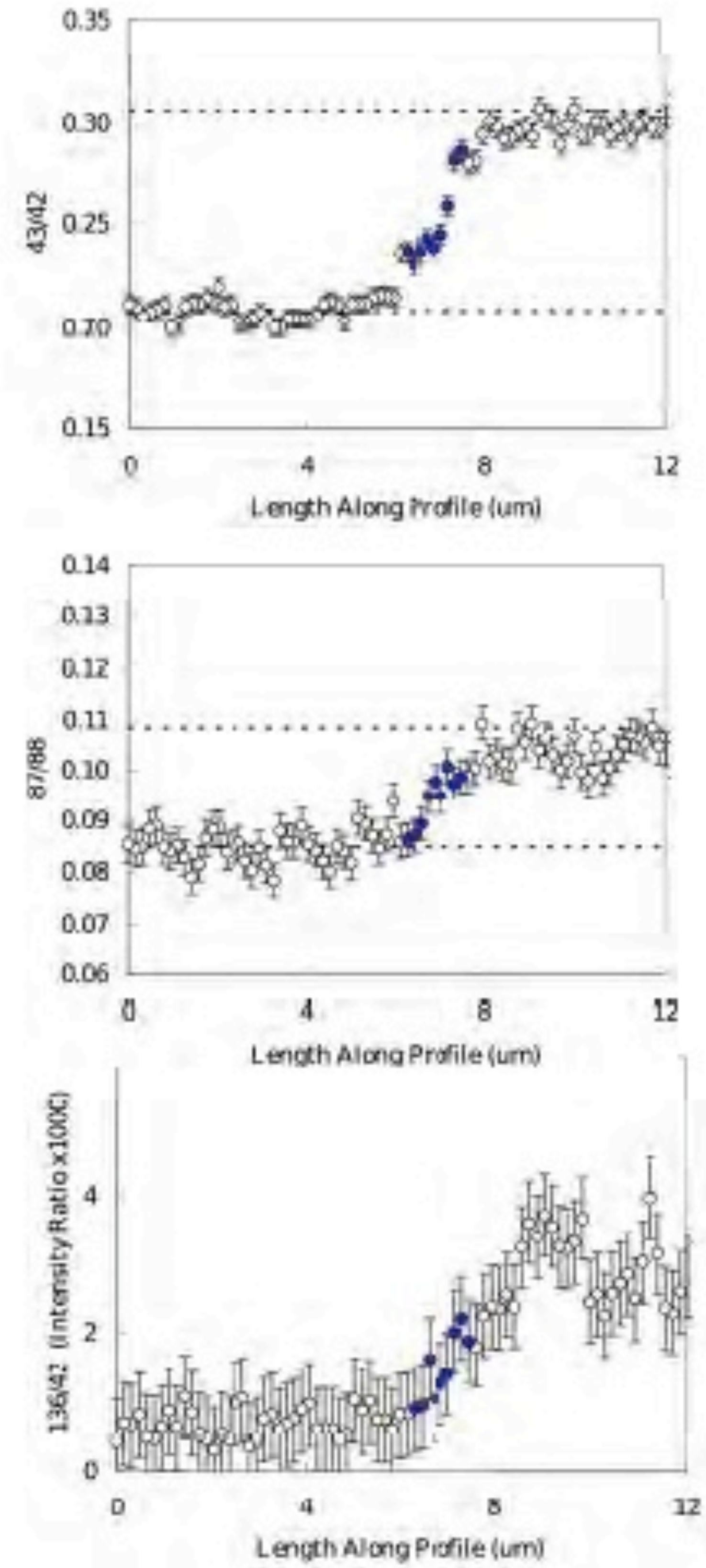


87/88 Spike
87/88 Natural
43/42 Natural
43/42 Spike
87/88
43/42
0.080
0.085
0.090
0.095
0.100
0.105
0.110
0.18
0.20
0.22
0.24
0.26
0.28
0.30
0.32
0.34

Synchronous Ion Dynamics Across Boundary

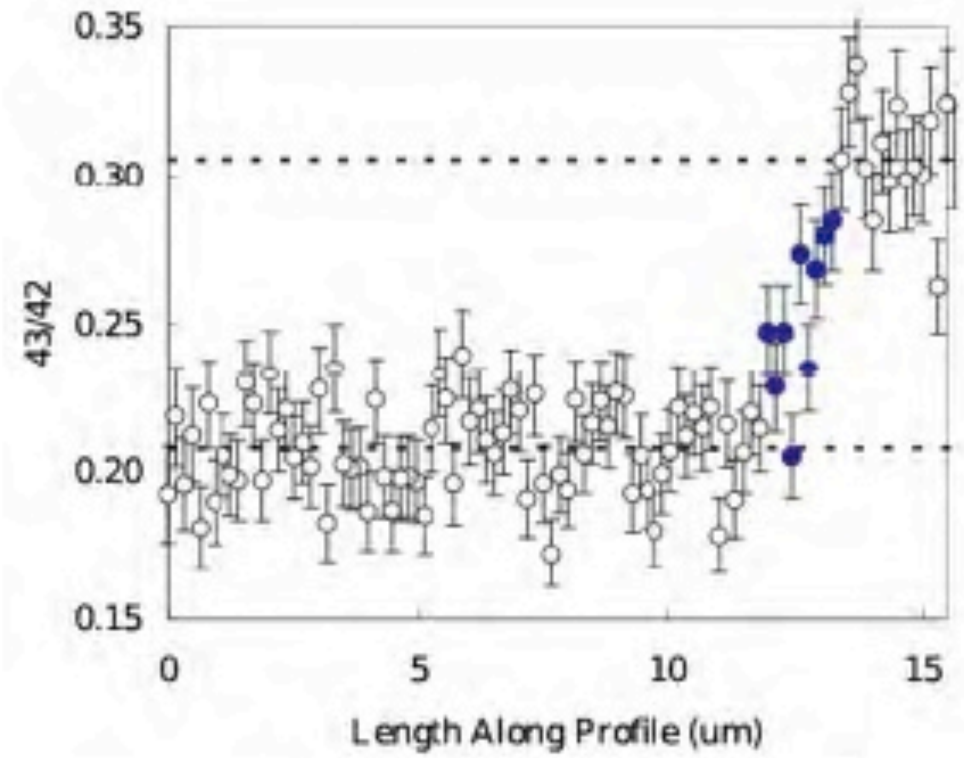


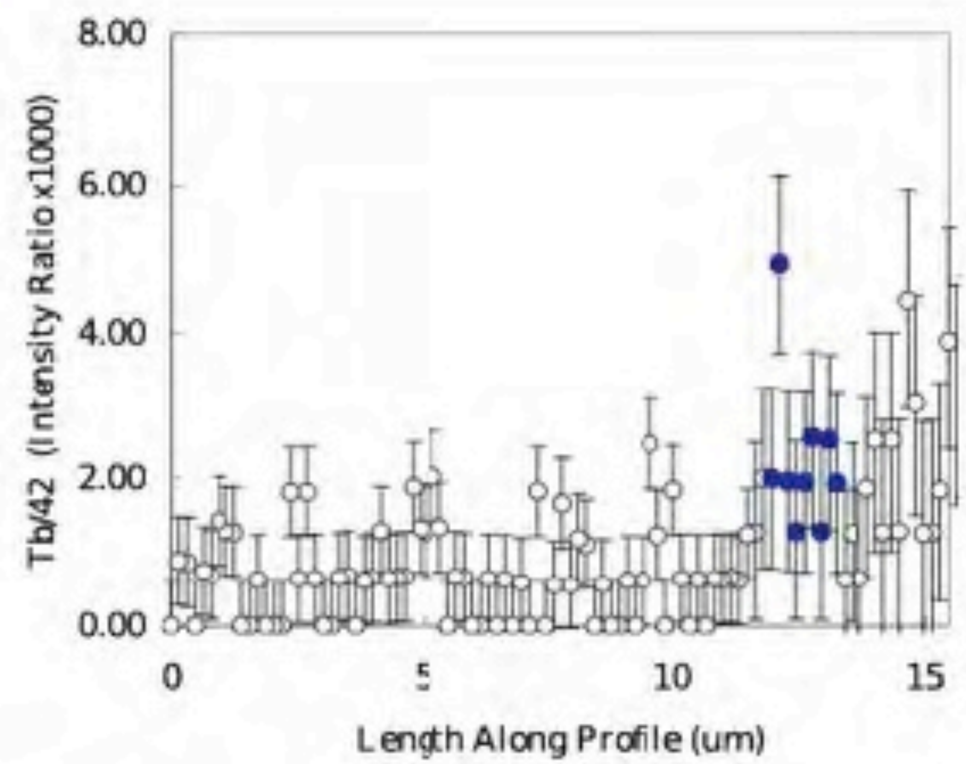




Similar results in 5 other images

Synchronous Tb^{3+} Incorporation





Synchronous ion dynamics including Tb^{3+} incorporation suggest:

direct exchange between seawater and calcifying fluid.

Localized and characterized new growth in a short (6 day) adult coral culture experiment