

# Geochemical Proxies

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# What can Deep Corals Tell Us?

## Ocean Archives

- Cold water coral skeletons trap trace elements and isotopes from the ambient seawater as they form.
- The composition of the skeleton reflects chemical/physical/biological processes occurring at the time.
- Skeletons therefore represent an archive of ocean conditions.

# What can Deep Corals Tell Us?

## Ocean Archives

- Cold water corals grow in a wide range of environments, including the deep oceans.
- Can provide information on short timescale processes occurring in the oceans (years to centuries)
- Sediment cores do not often provide reliable information on these timescales.



# Two Different Types

## Scleractinian Corals

- e.g. Lophelia
- Short Lived.
- Plentiful (reef builder)
- Aragonite Skeleton
- Short time-series (10s of years at most)
- Can recover fragments in long sediment cores.
- Samples in cores may be millions of years old.

Glacial Timescale Climate  
Reconstruction

## Gorgonian Corals

- e.g. Bamboo Corals
- Long Lived.
- Rare (single colonies)
- Calcite/Organic Skeleton
- Long time-series (100s – 1000s of years)
- May find sub-fossil individuals.
- Old samples possible, but very rare.

Anthropogenic Timescale Climate  
Reconstruction

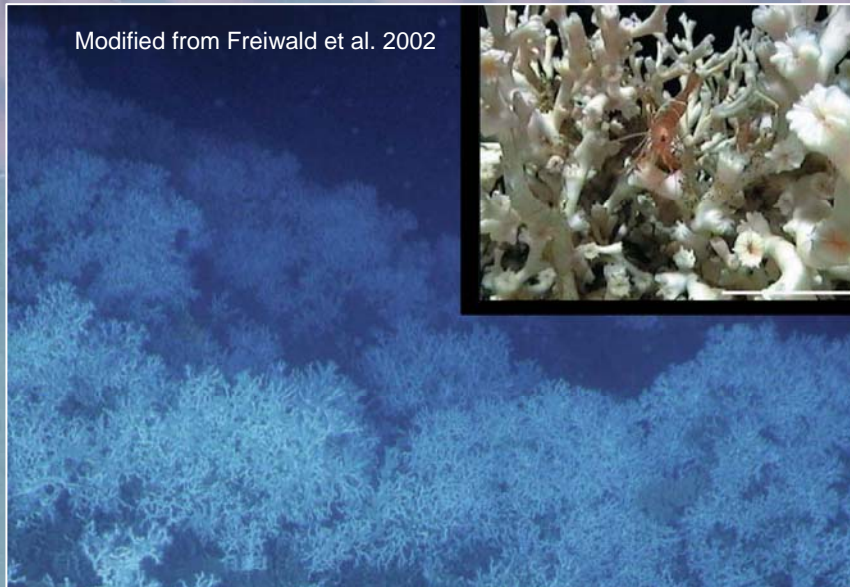
Very different strategies required for paleoceanographic reconstruction



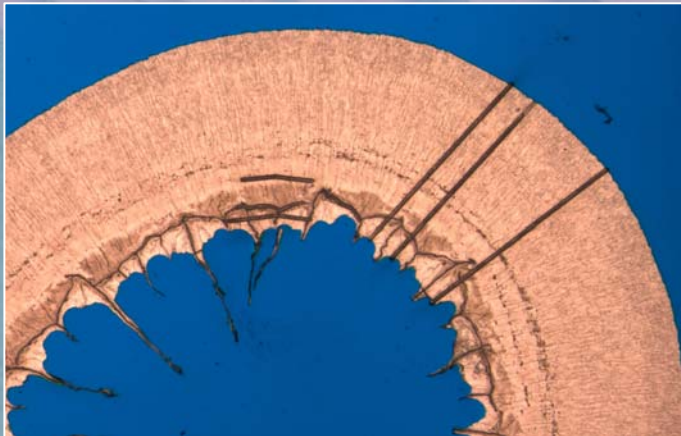
# Scleractinian Corals

## Growth Form

- Thickets of intertwined branches.
- Large polyps – each grows over several years.
- Polyps live 5-10 years before being ‘overgrown’.
- Skeleton continues to thicken during this time.

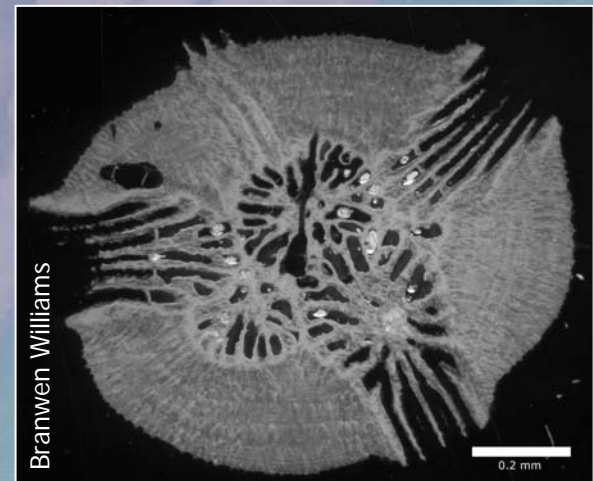
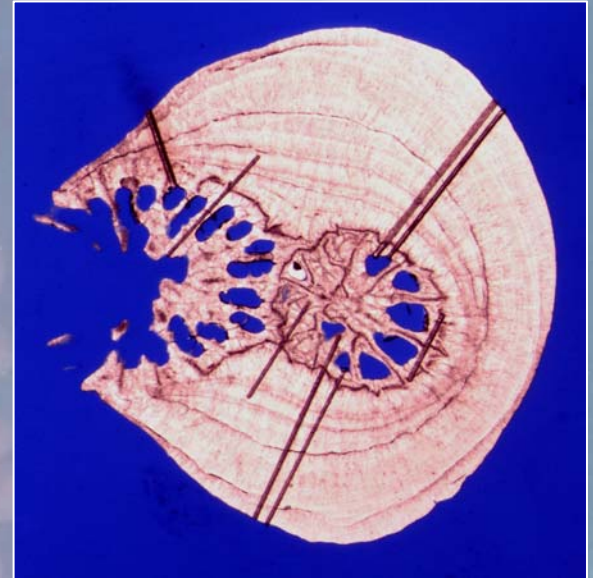


# Lophelia





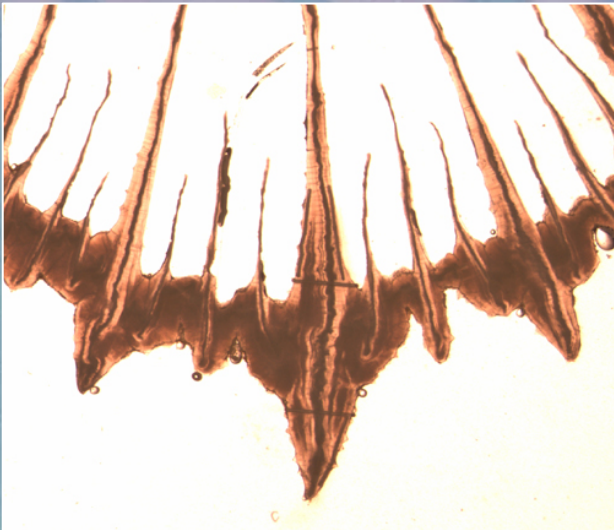
# Oculina





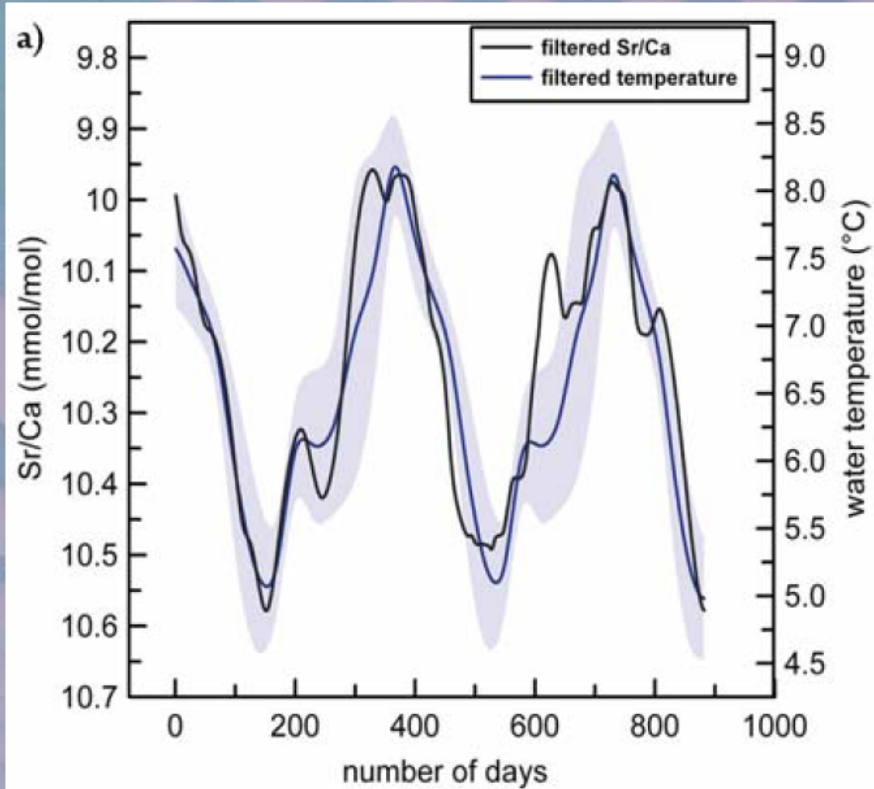
# Desmophyllum

© Greenpeace / ExploreTheAbyss.com



- Solitary Coral
- Longer Lived than Lophelia

# Interannual Variations

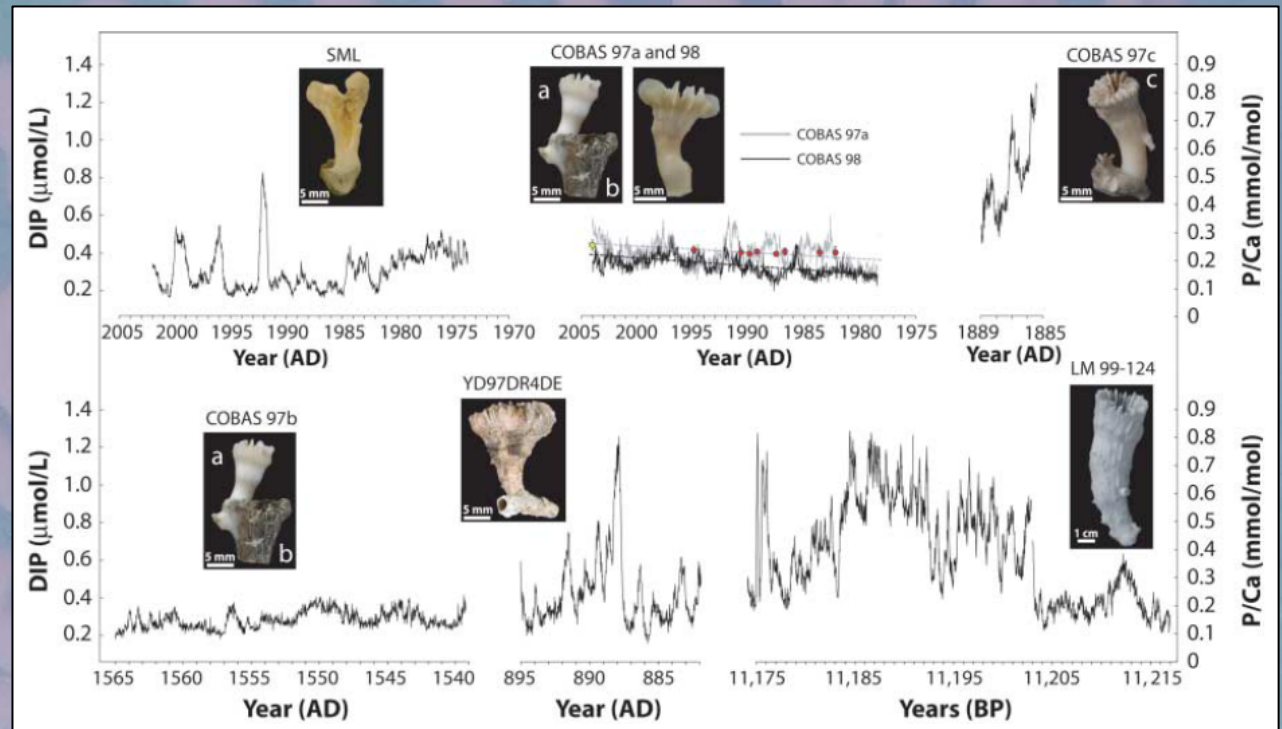
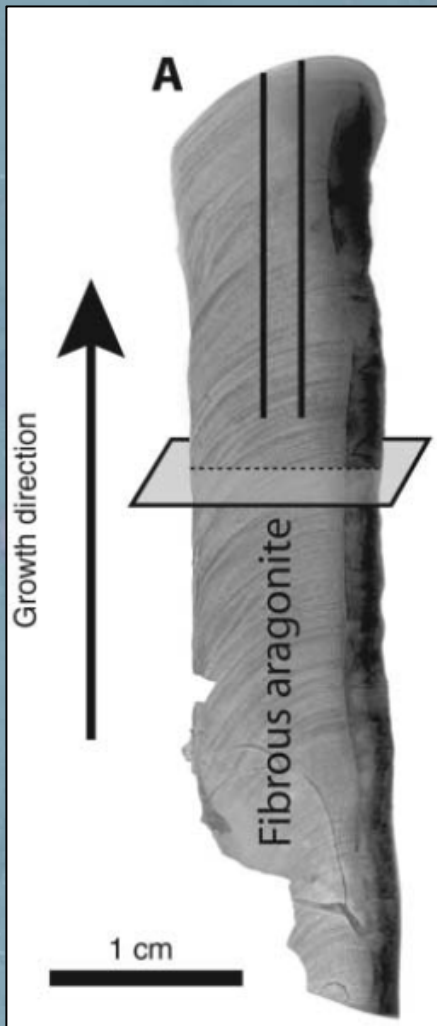


## Temperature mediated trace element inclusion

- Measured along thecal wall.
- Inorganic and biological response.
- Potential for temperature reconstruction?

From Cohen et al. 2006

# Interannual Variations



From Montagna et al. 2006

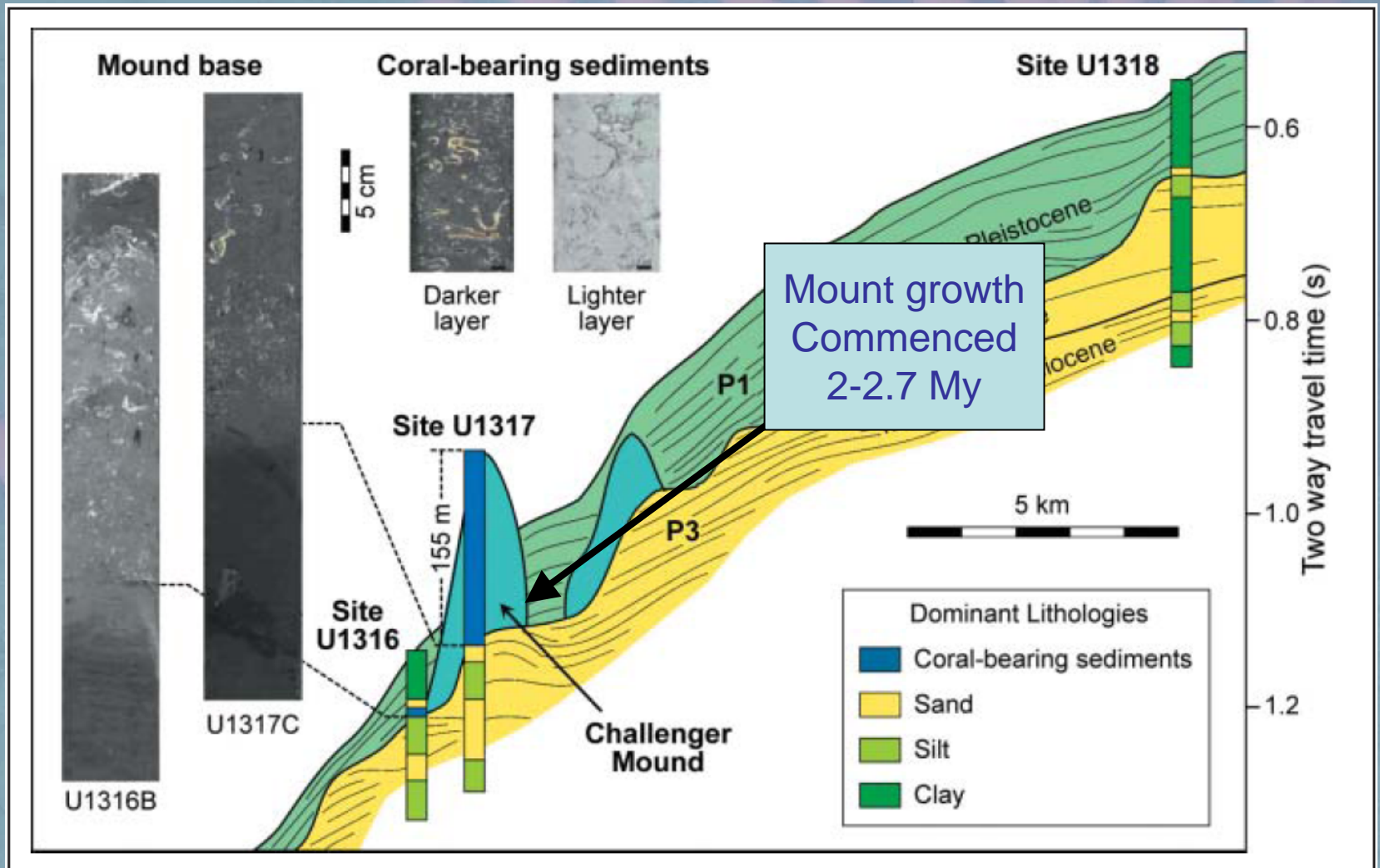
## Phosphorous as a nutrient proxy.

- Desmophyllum: longer lived than Lophelia.
- Measured along a Septum.



# Drilling Carbonate Mounds

IODP 307



# The 'Holy Grail'...

Interannual variability over 1,000,000 years!?!

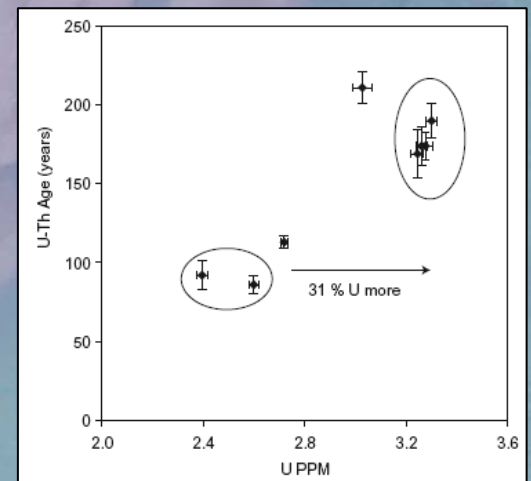
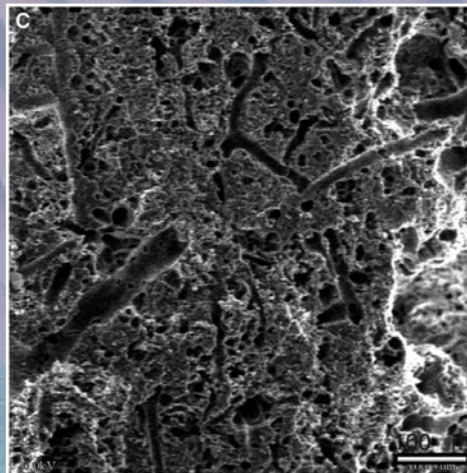
- Unfortunately...

(there's always an 'unfortunately')

# Complications

## Chemical/Physical changes to samples

- Can occur rapidly.
- Diagenesis / 'Open System'
- Bioerosion
- Old fragments may be no good for geochemistry.



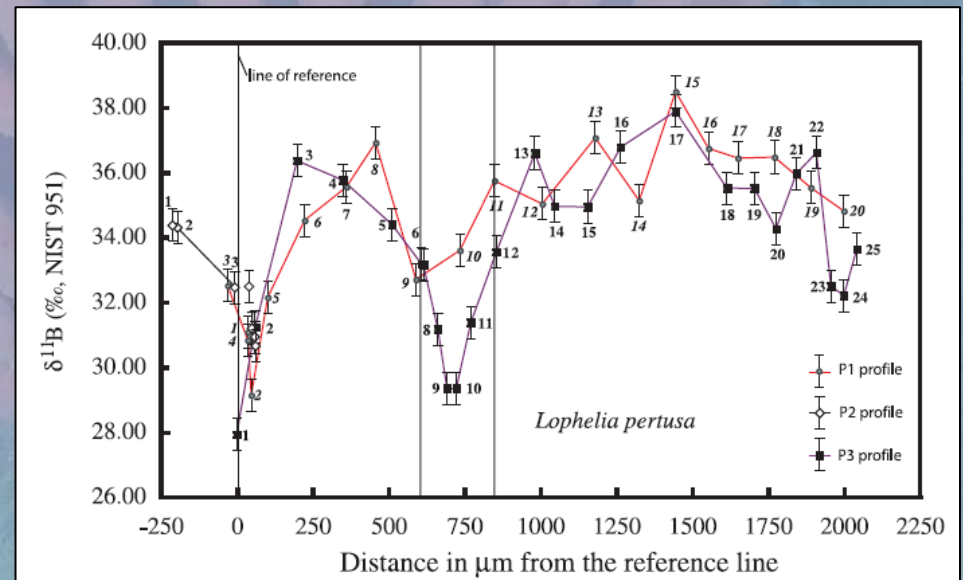
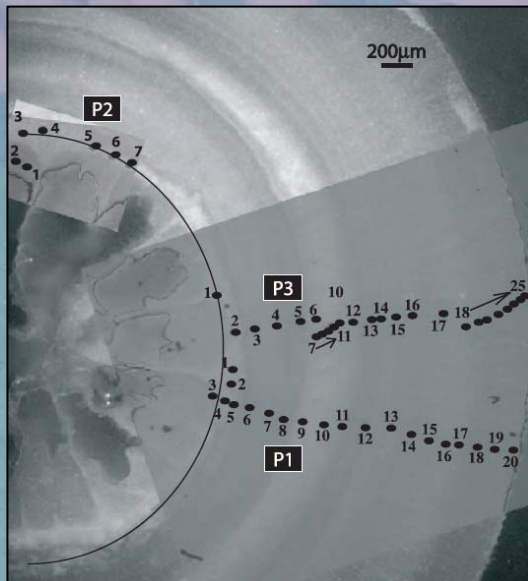


# Complications

## Chemical Tracers Affected by 'Vital Effects'

- Biology influences uptake of elements/isotopes.
- Internal structures have characteristic chemistry
- Known to affect:  $\delta^{11}\text{B}$ ,  $\delta^{18}\text{O}$ ,  $\delta^{13}\text{C}$ , Mg, U + others.
- Could it also affect Sr and P?

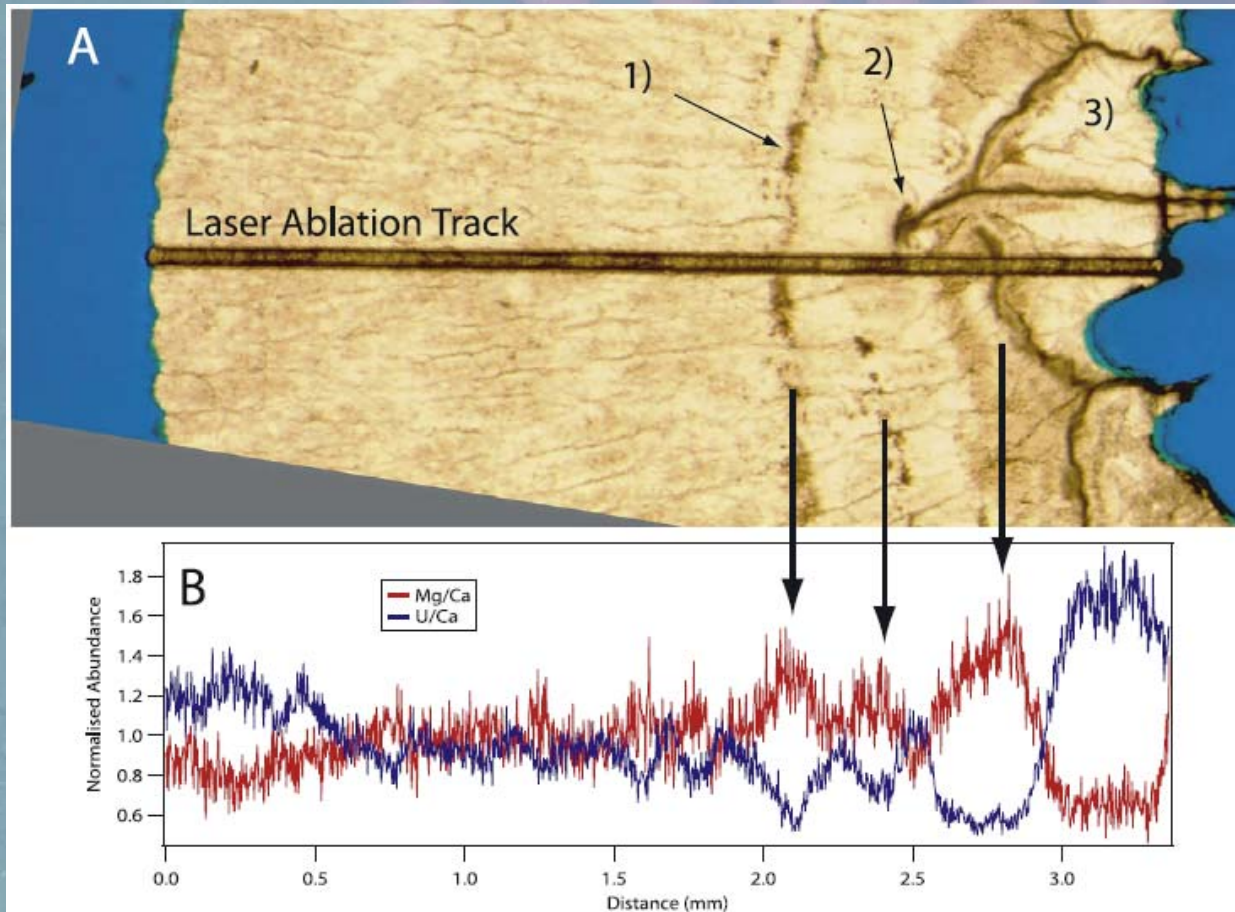
Blamart et al. 2007



# Complications

## Vital Effects

Sinclair et al. 2006



- Elements controlled by internal structure.
- Makes time-series difficult: Can't be sure whether a feature is an environmental fluctuation or an EMZ.
- Target very inside region?
- Might be able to get a time series by cutting polyp longitudinally (eg. Cohen et al. 2006, but at most get 3 years.
- Possibly get only *1 data point per coral fragment*.

# Is There Hope?

## Deep Corals Might Still Record 'Average State'

- 'Vital Effects' might complicate time-series.
- But maybe the whole coral (or selected regions) can give an 'average' of the environmental state.
  - Assumption: on average 'vital' effects are constant through time and/or are consistent between individuals.
  - People using tropical Scleractinians make these assumptions, and there are clearly cases where it works well.



# Is There Hope?

## Some Isotope Systems Might be 'Immune' from Vital Effects.

- Isotopes of heavy elements:
  - Not discriminated biologically
  - Not discriminated chemically
- May have variable environmental distributions (often one isotope is radiogenic)
- Examples: Pb isotopes, Nd isotopes (more from Norbert Frank)
- Often very low concentrations: need a lot of sample. Limits resolution of time series.

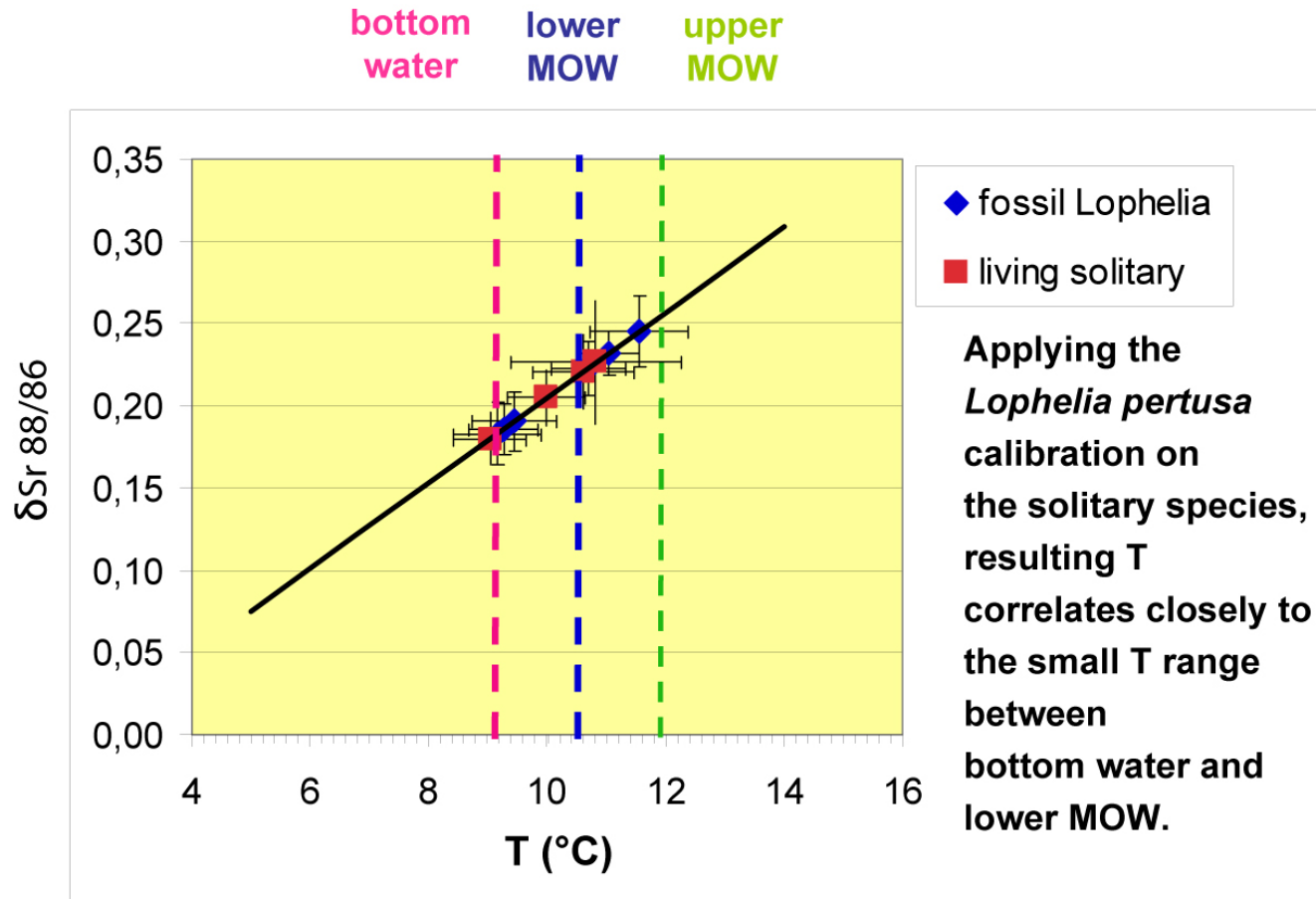
# Implications for Sampling

## One Data Point per Coral Fragment

- Need multiple corals from multiple times/locations to build up an environmental story.
  - e.g. Multiple fragments of different ages from the same location (such as a core down through a mound).
  - e.g. Multiple fragments of the same age from different locations (such as a geographical transect).
- Need for calibration studies: corals from environments with known environmental gradients - e.g. temperature/depth/nutrient transect.
- Need to set up site-monitoring as well as co-ordinate coral sampling?
- Need to plan sampling around specific environmental hypotheses.



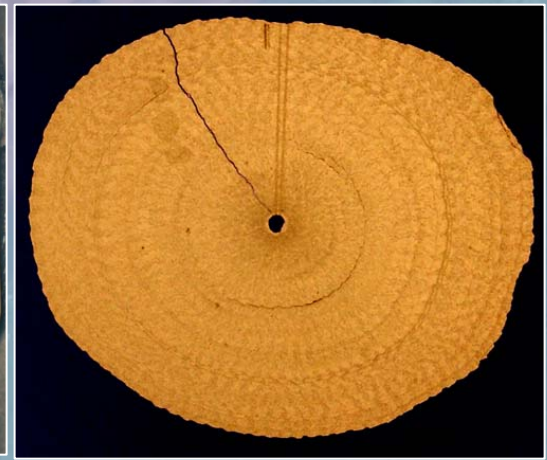
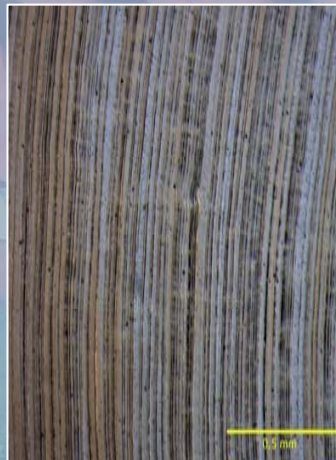
# Sr-isotopes as new tracer of temperature



# Gorgonian Corals

## Growth Form

- Single tree-like coral.
- Skeletons grow and thicken radially with periodic banding.
- Corals can be 100s to 1000s of years old!
- Potential for continuous record throughout life of coral.
- Organic and calcitic skeletons.



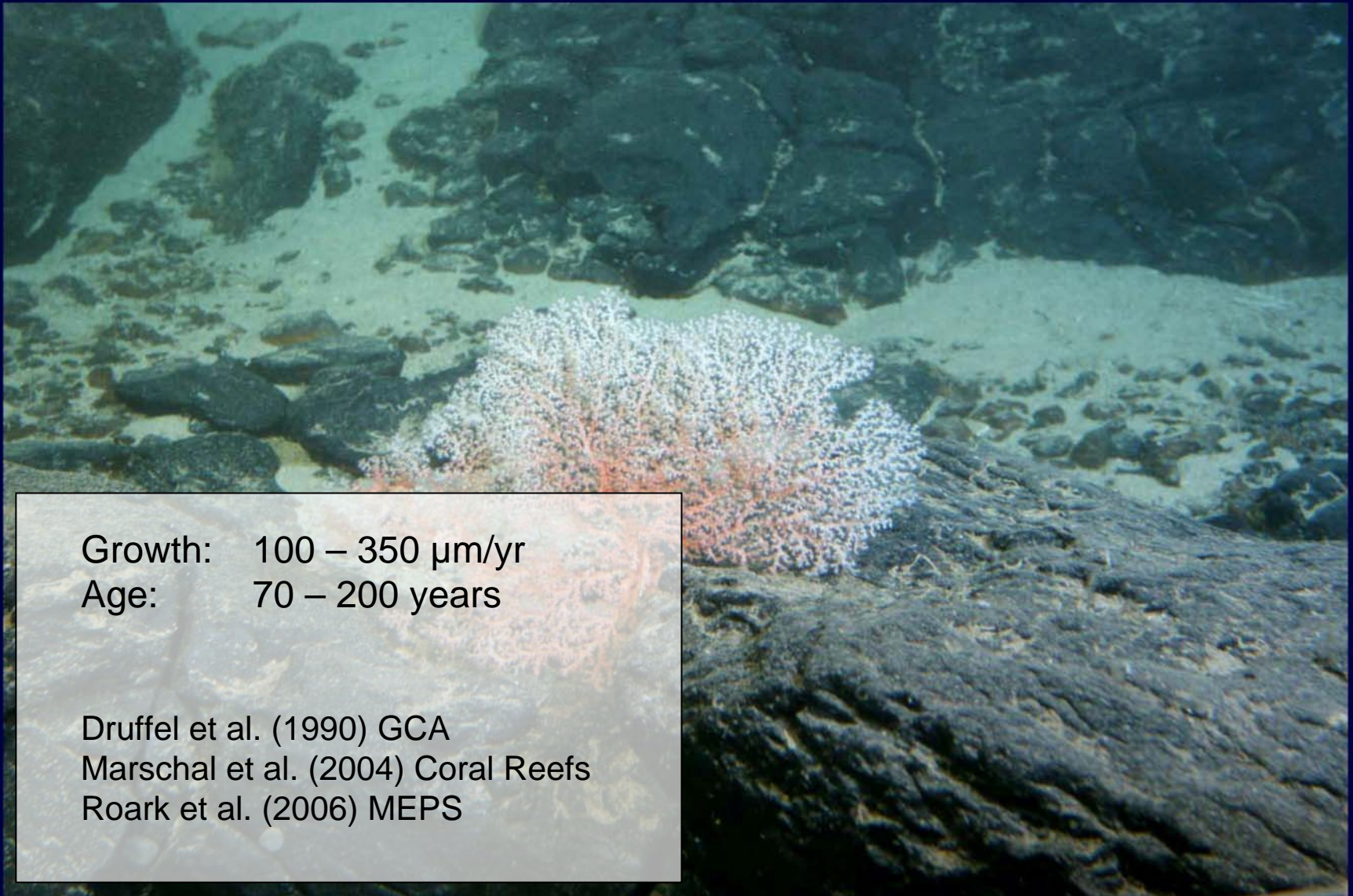


# Gorgonians

Here I shamelessly pinch slides from Brendan Roark's excellent presentation to the American TRACES workshop...



# Corallium sp.



Growth: 100 – 350  $\mu\text{m}/\text{yr}$

Age: 70 – 200 years

Druffel et al. (1990) GCA

Marschal et al. (2004) Coral Reefs

Roark et al. (2006) MEPS



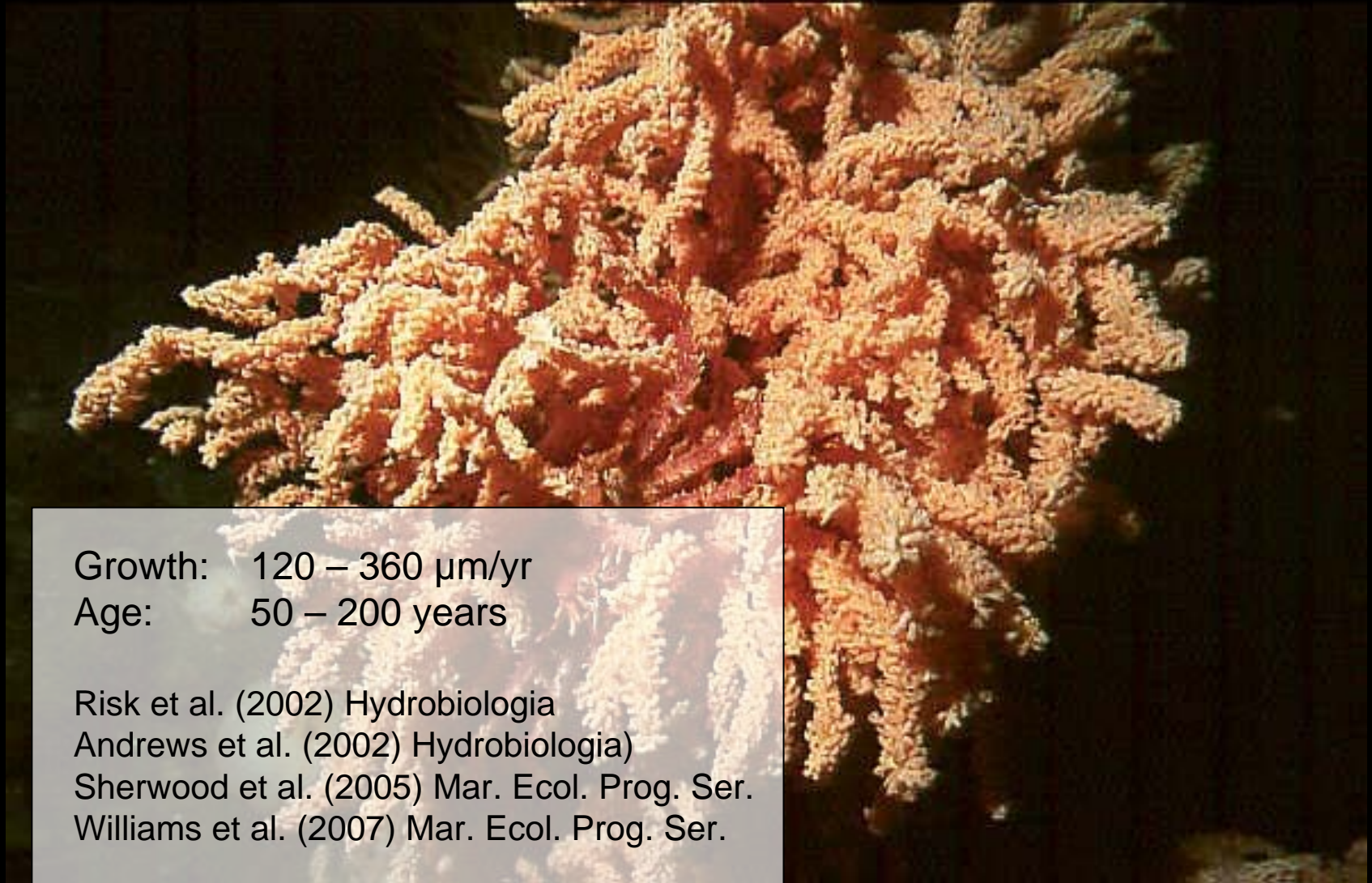
# Enallopsammia rostrata

Growth: 40 – 70  $\mu\text{m}/\text{yr}$   
Age: 200 – 600 years

Adkins et al. (2005) EPSL  
Houlbrèque et al. (in prep)



# Primnoa resedaeformis



Growth: 120 – 360  $\mu\text{m}/\text{yr}$

Age: 50 – 200 years

Risk et al. (2002) Hydrobiologia

Andrews et al. (2002) Hydrobiologia)

Sherwood et al. (2005) Mar. Ecol. Prog. Ser.

Williams et al. (2007) Mar. Ecol. Prog. Ser.



# "Bamboo Coral" Isididae



Growth: 35 – 290  $\mu\text{m}/\text{yr}$   
Age: 43 – 305 years

Roark et al. (2005) GRL  
Noe and Dullo (2006) Coral Reefs  
Tracey et al. (2007) Bull. Mar. Sci.  
Thresher et al. (2007) Bull. Mar. Sci.  
Sinclair et al. (2008) GCA (in review)



Roark TRACES meeting





Gerardia sp.

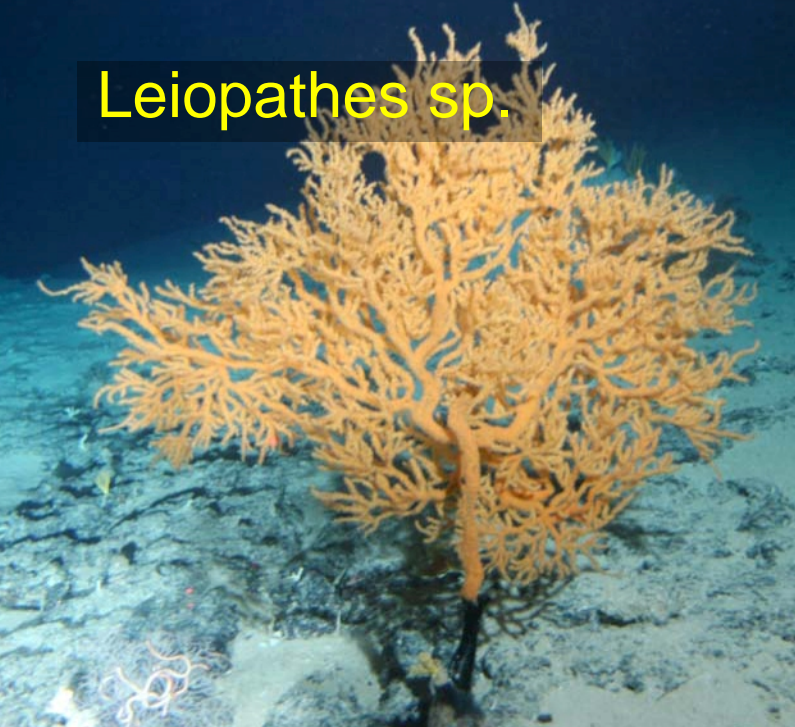
Growth: up to 1000  $\mu\text{m}/\text{yr}$   
Age: 70 – 1800 years  
(subject to dispute)

Druffel et al. (1995) GCA  
Goodfriend (1997)  
Grigg (2002)

Image filched  
from the Internet



# Leiopathes sp.



Growth: 5 – 15  $\mu\text{m}/\text{yr}$   
Age: 200 – 2300 years

Williams et al. (2006) Geology  
Roark (unpublished)

0.5 mm



RD-2001-LEIO-1





# What Can You Do With Them?

Williams et al. 2006

## Organic Skeletons:

(eg. Leiopathes)

- Skeletons can be 'peeled' after KOH soaking or demineralisation by dilute acid.
- Analyse gorgonin for stable isotopes:
  - $\delta^{15}\text{N}$  – Sewerage
  - $\delta^{13}\text{C}$  – C source
- Trace Elements?
  - Nobody has tried.

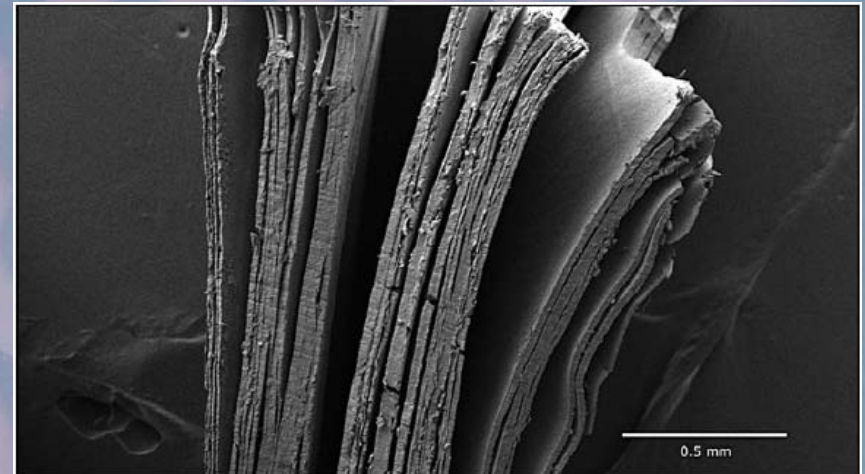
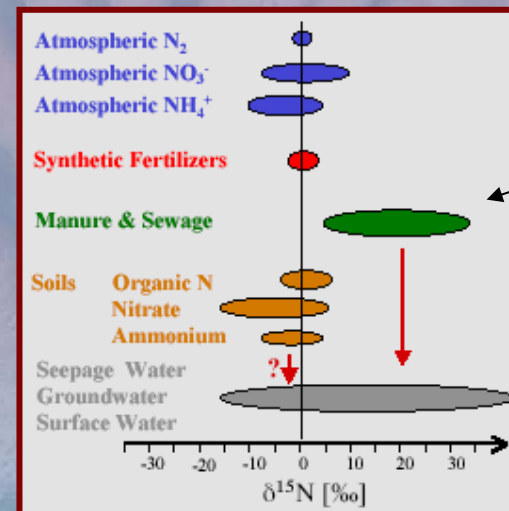
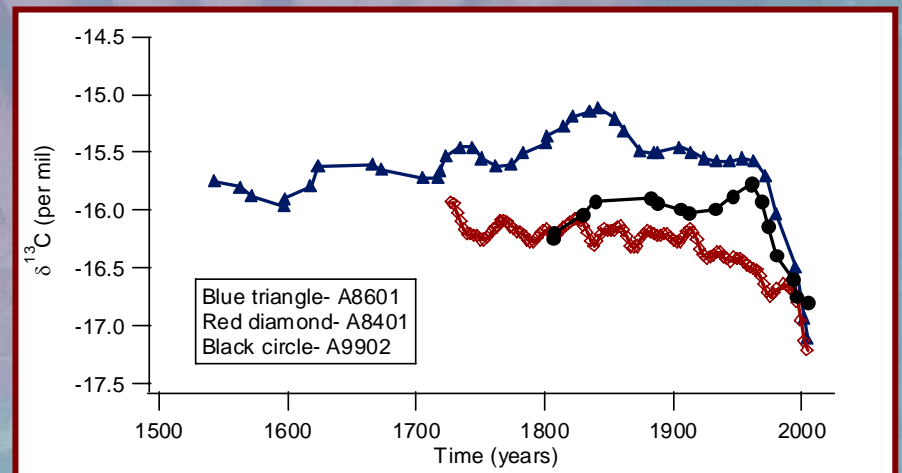
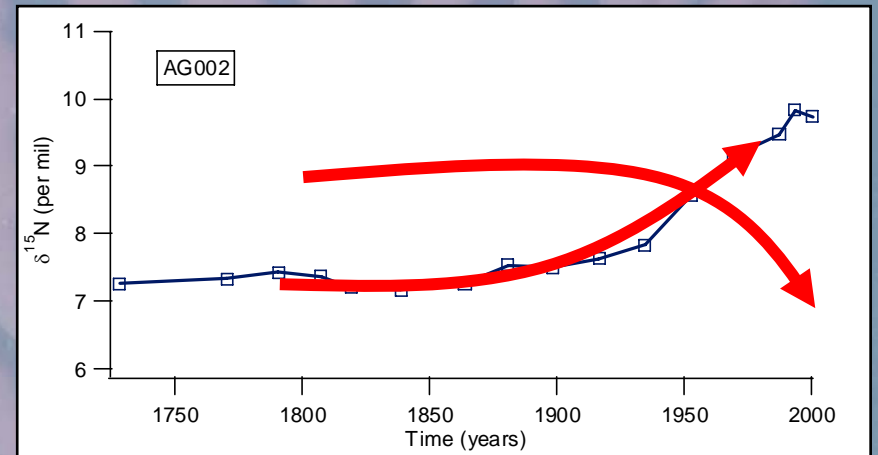


Figure 3. Cross section of specimen A8601 after KOH treatment.



Sewerage  
enriched in  
 $^{15}\text{N}$

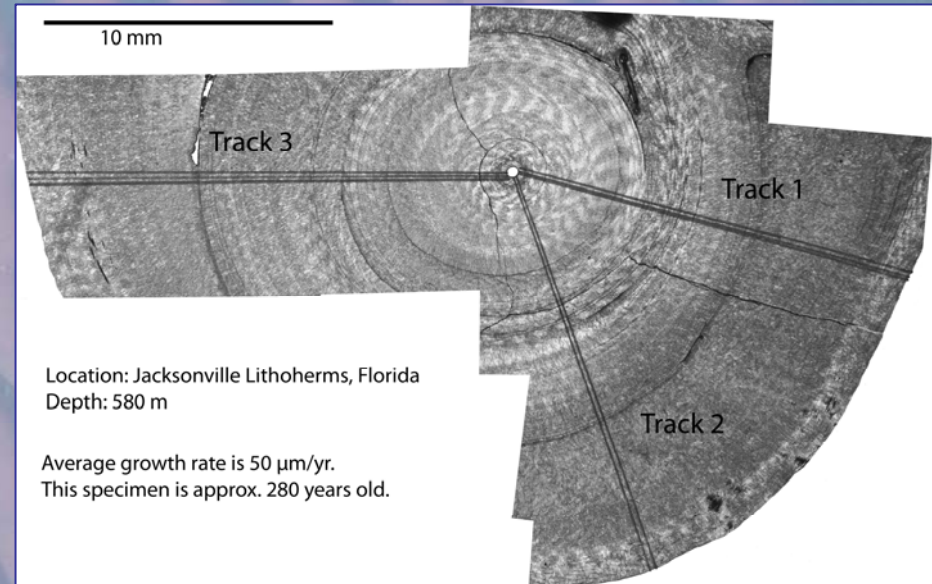




# What Can You Do With Them?

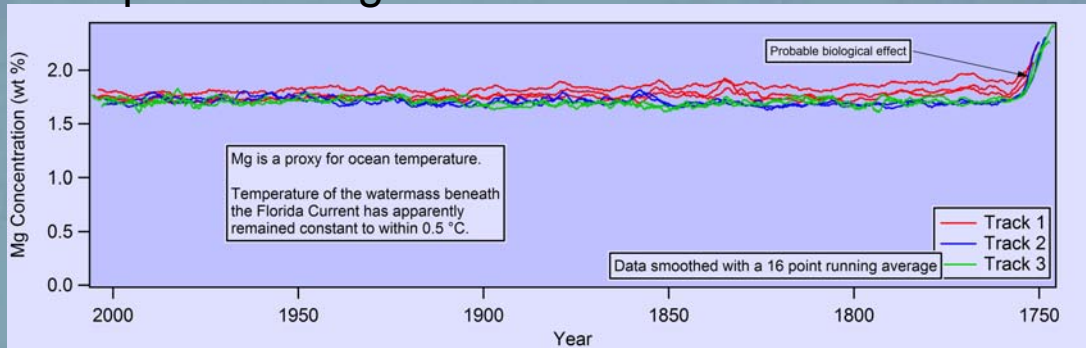
## Calcitic Skeletons: (eg. Keratoisis)

- Minor Element Analysis using Microbeam methods
  - (LA-ICP-MS, SIMS, etc)
  - Sr, Mg, Ba, Pb, Mn
- Physical Sampling
  - Low level metals
  - Isotope systems

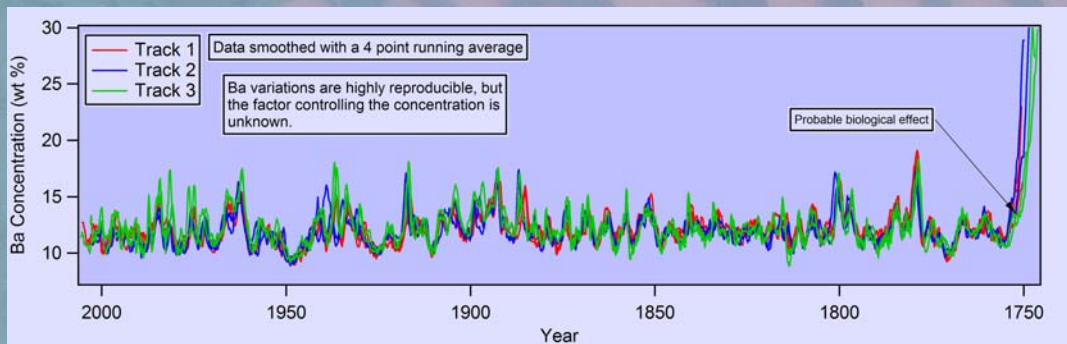


Sinclair et al. 2008 I, II (GCA – in review)

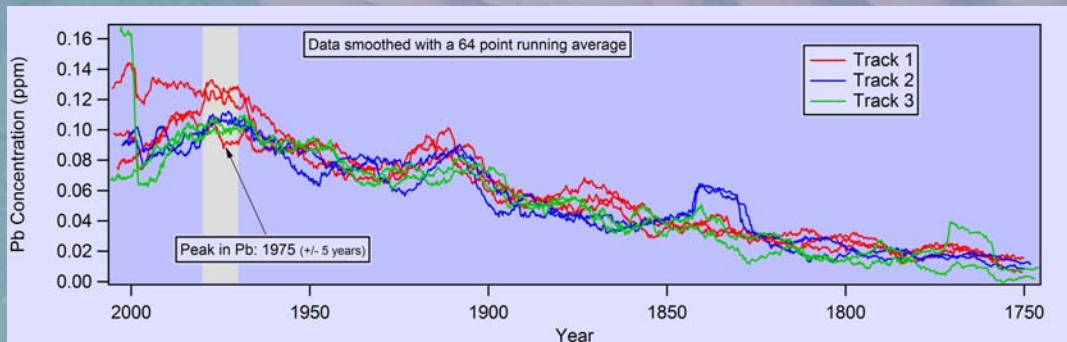
## Temperature Signal – Stable Gulf Stream



## Possibly productivity Signal



## Industrial Pb

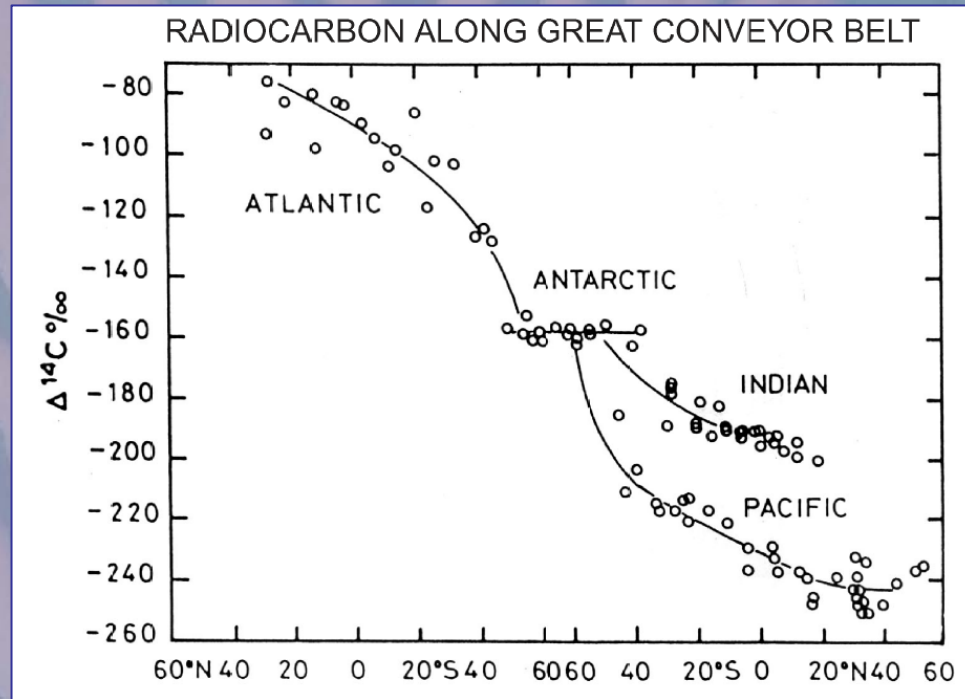




# What Can You Do With Them?

## All deep sea corals:

- Radiocarbon measurements
- Many applications: Norbert Frank to summarise!
- At the moment – probably the most useful oceanographic tracer (and one of the most expensive!)



From the North American TRACES talk by Jess Adkins

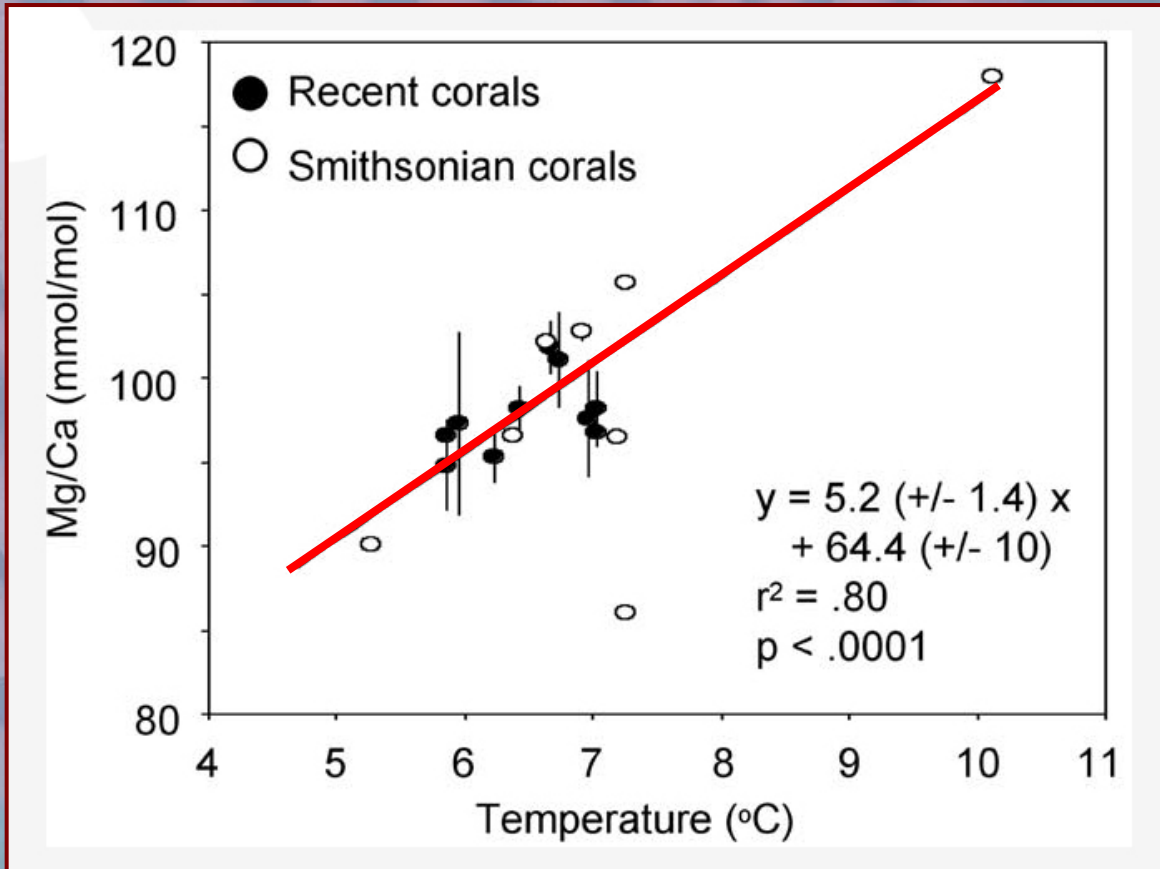
# Temperature Calibration

$$\text{Mg/Ca} = 5 \times T + 60$$

1 °C = 7 %  
change in Mg

Sherwood et al. (2005)

- Mg/Ca in calcite is T dependent
- 17 *Primnoa* colonies
- NW Atlantic Margin
- Calibrated to instrumental T



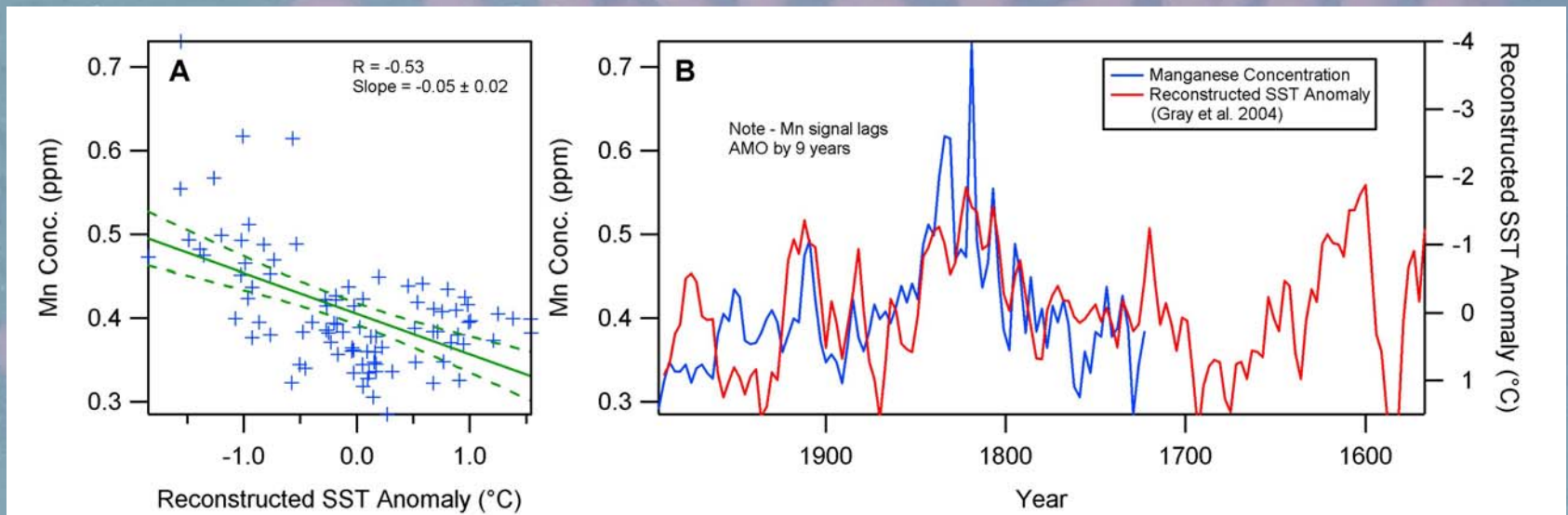
From Sherwood et al. (2005)



# An Interesting Application

## African Dust in Florida Corals (?)

Sinclair et al. 2008 (GCA – in review)



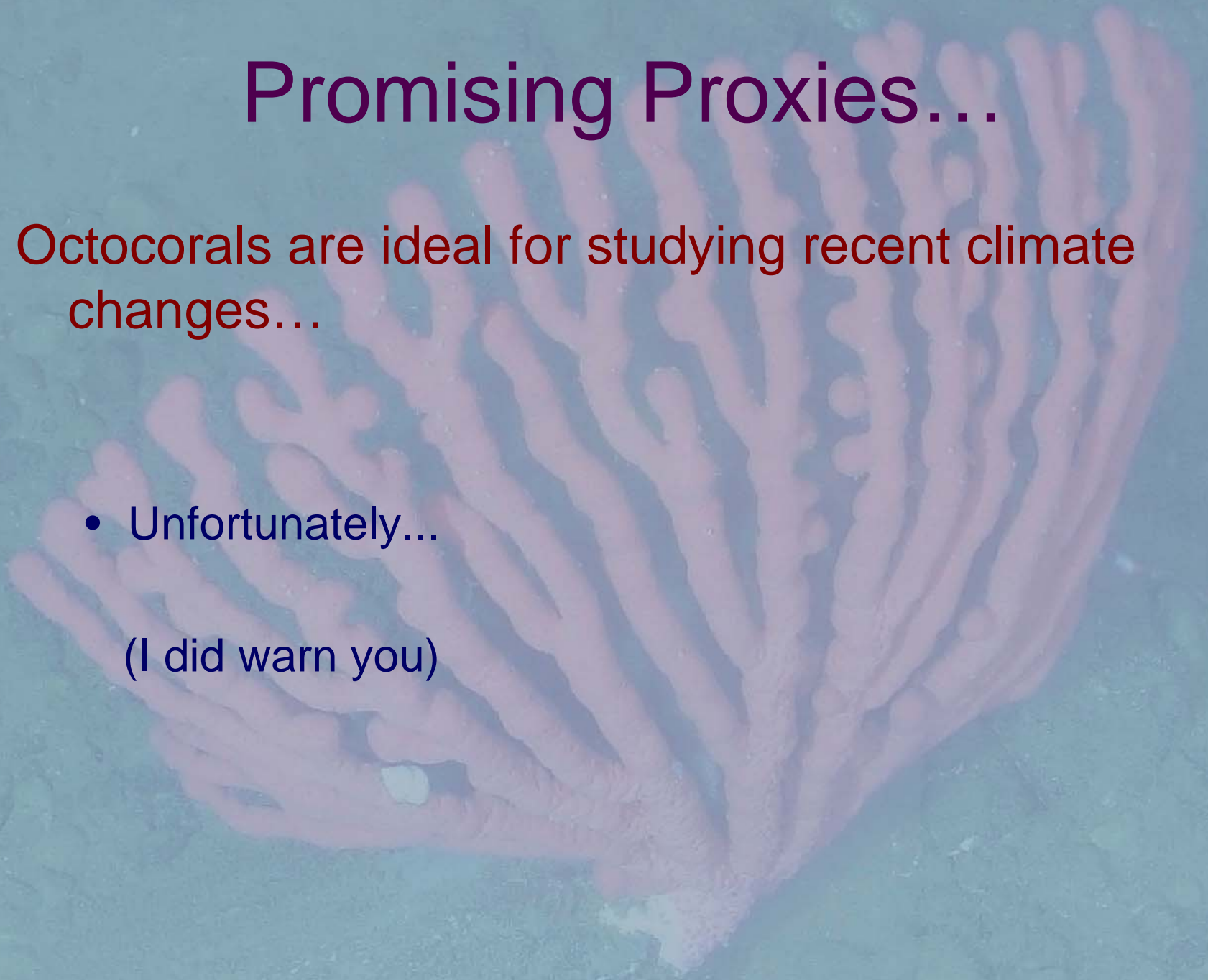
- Mn correlated with the Atlantic Multidecadal Oscillation.
- Droughts in the Sahel tend to occur when the Atlantic is cool (negative phase of the AMO).
- Leads to greater dust flux – rich in Mn.

# Promising Proxies...

Octocorals are ideal for studying recent climate changes...

- Unfortunately...

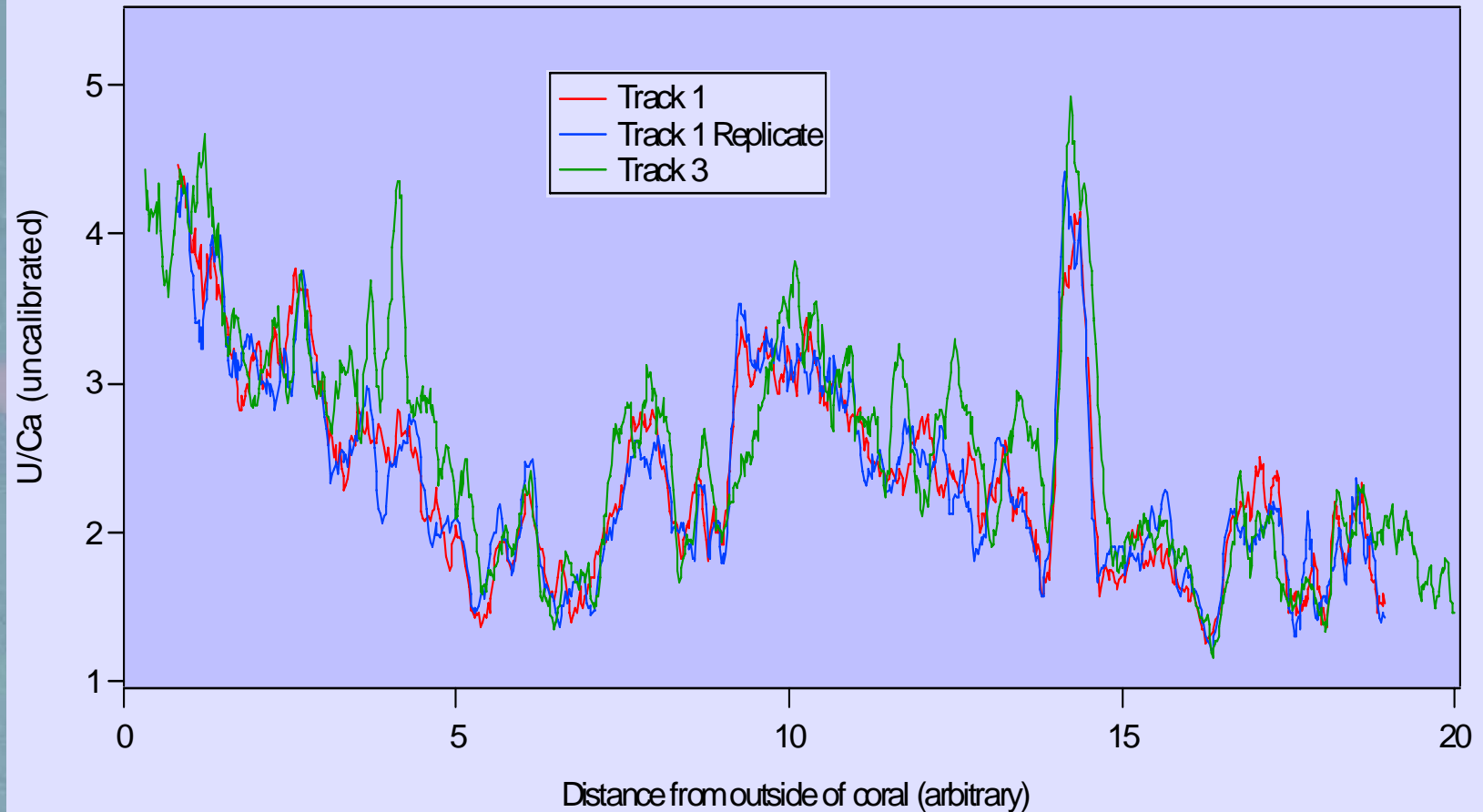
(I did warn you)





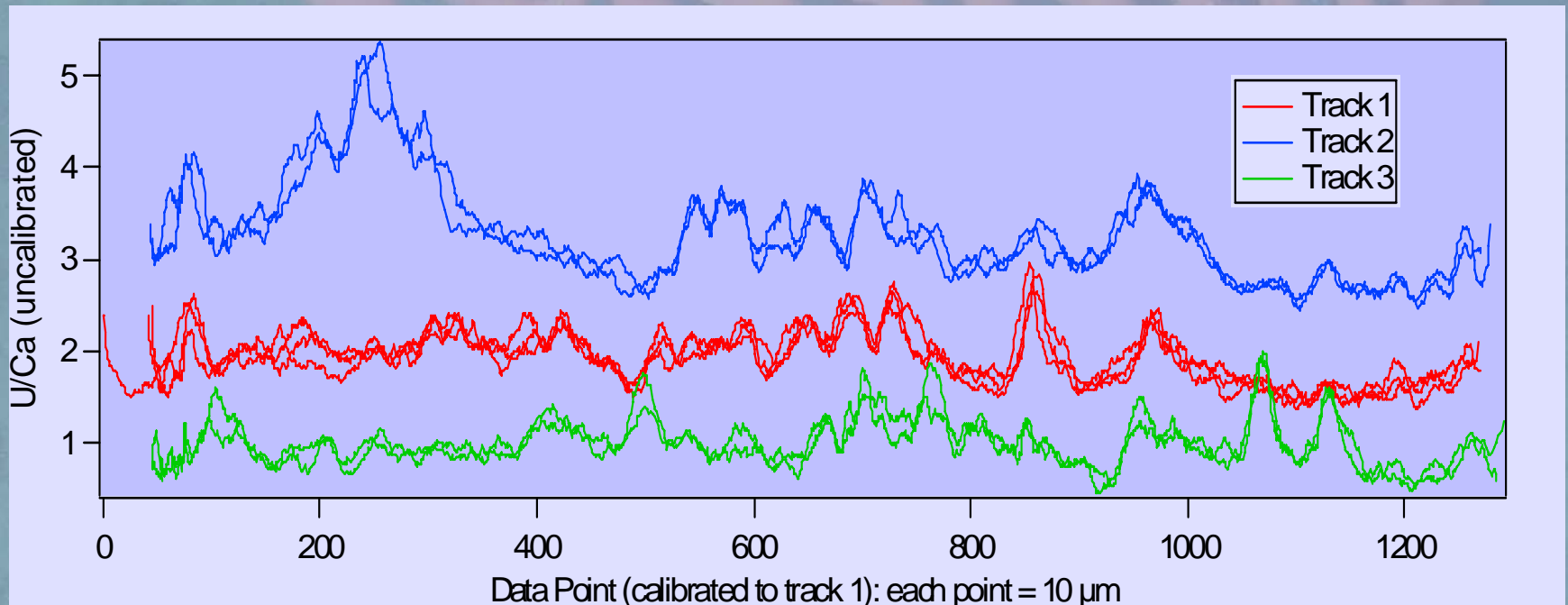
# Complications

Uranium in *Primnoa resedaeformis*



# Complications

Uranium in Keratoisis (note – tracks offset for clarity)



Outside  
(youngest)

Inside  
(oldest)



# Imperfect Recorders

Deep sea octocorals do not always faithfully record environmental processes.

- Biological or diagenetic processes result in a heterogeneous skeleton.
- Where there is no reproducibility, there is no information.
- Need to test corals and reproduce records wherever possible.

# Implications for Sampling

## Octocorals are relatively scarce

- Opportunistic sampling
- Co-ordinate between biologists and geochemists

## Can't trust a single record

- Wherever possible take several samples
- Sample from a geographic transect
- (Ideal) Obtain organic and calcitic genera from the same location.

## Most useful for studying modern climate

- Target regions where instability will be most evident
- Target regions of oceanographic significance: upwelling, downwelling, watermass boundaries, gateways, etc



# Sub-fossil Gerardia





# Wrap Up

## Pollutants/Anthropogenic

- $\delta^{15}\text{N}$  Nutrient source/sewerage
- $\delta^{13}\text{C}$  C source/Suess Effect
- Mn Dust
- Pb Industrial inputs
- Zn + metals Pollutants

## Oceanographic

- Sr Temperature? Growth?
- Ba Nutrients + productivity?
- Sr isotopes Temperature?
- Pb isotopes Ocean watermass
- Nd isotopes Ocean watermass
- Radiocarbon Upwelling + water age



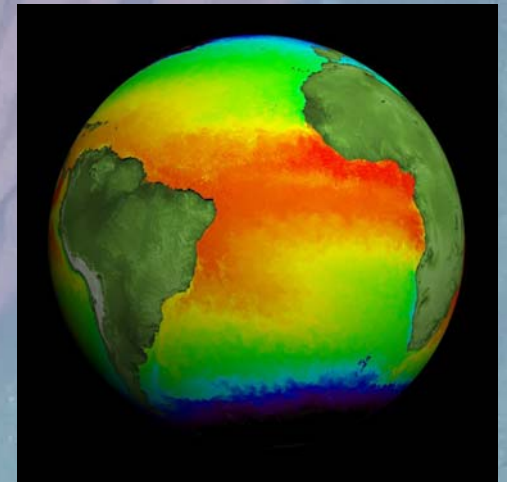
# Wrap Up

## Proxy Development Wish List

- Reliability testing
- Calibration
  - collections from environmental gradients
  - culturing
- Site monitoring + ocean observatories
- New proxies
  - Salinity proxy!
  - Nutrients/Productivity
- Co-ordinate geochemistry

## Science Questions

- Ocean acidification
- Southern ocean
- Thermohaline shutdown
- Teleconnections – What drives what?



# A Parting Thought...

Paleoceanographers salivate over the prospect of a 4000 year coral record...

- But...

Does the science justify destroying an organism that has survived millennia?





# Thanks To:

TRACES



SAMS

SAGES



Murray Roberts, Vikki Gunn + Many Others