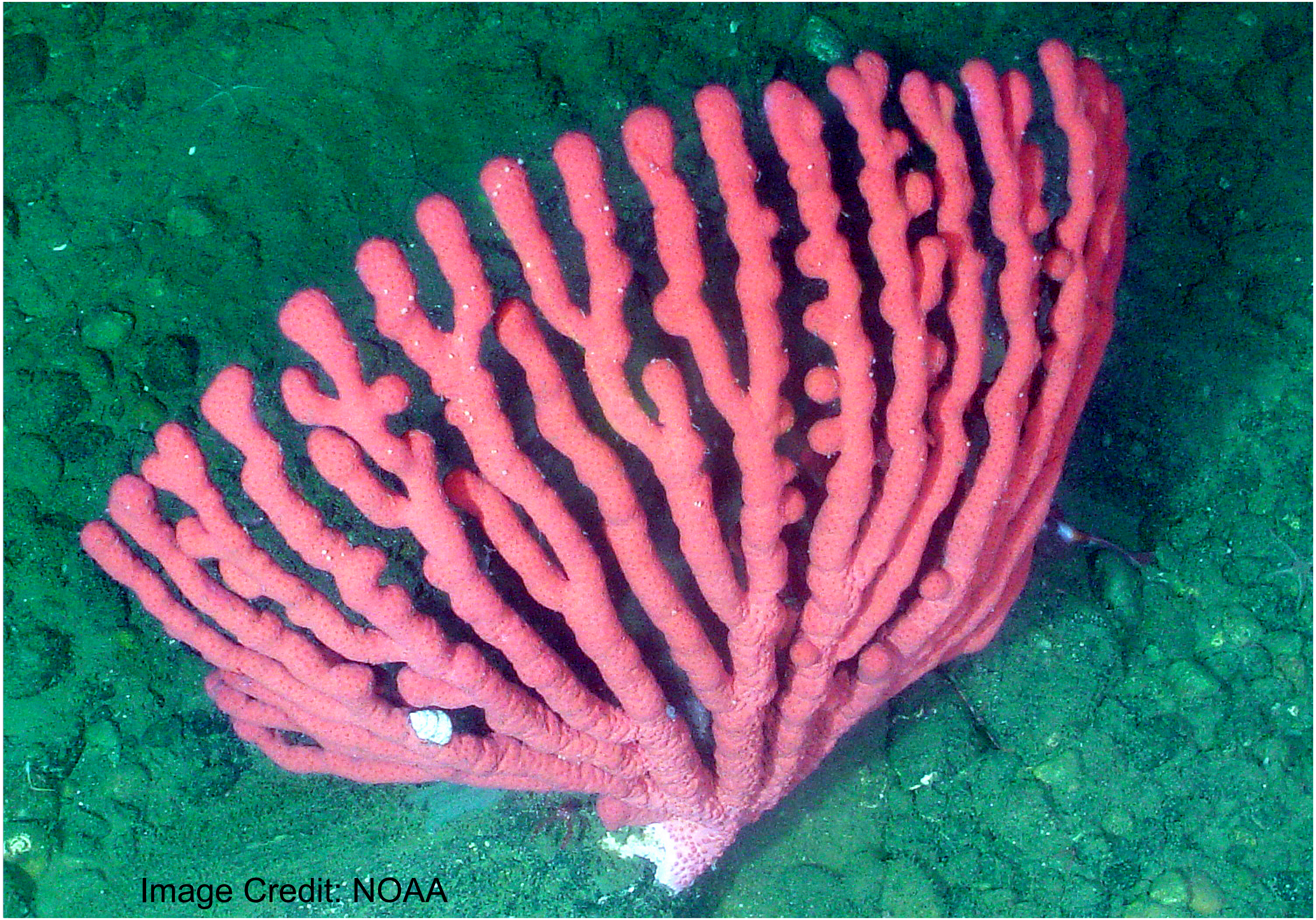


Image Credit: NOAA

# Deep Sea Coral $\delta^{15}N$

Dan Sinclair
Institute of Coastal and Marine Sciences
Rutgers University

# Notes About This Presentation

This archive-version of the presentation has been modified from the one that I gave at the PAGES-NICOPP Meeting in May. Specifically I have removed content which is regarded as being sensitive (either unpublished or subject of active research grant applications). I apologise for this. More information may be obtained by private communication with the people involved.

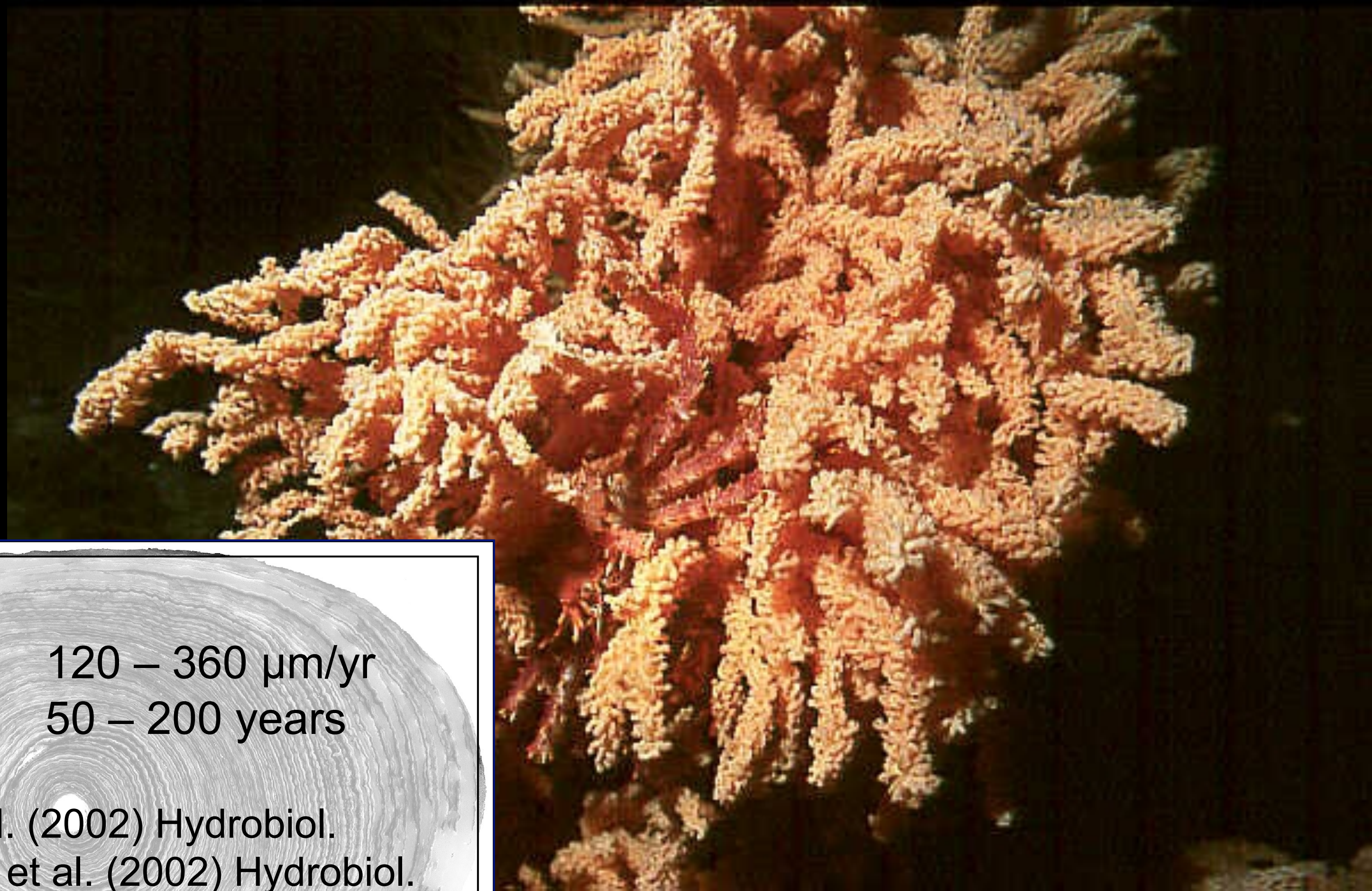
I would also like to note that much of the work presented here is not my own, but was carried out by my colleagues in the NSERC-funded Deep Coral Research Project (primary grant held by Prof. M. Risk) which ran from 2001 through 2005. I am grateful to Branwen Williams, Owen Sherwood Dave Scott and Mike Risk, and associated collaborators Claude Hillaire-Marcel, Steve Ross, Jeff Heikoop, Andrea Grottoli and Evan Edinger.

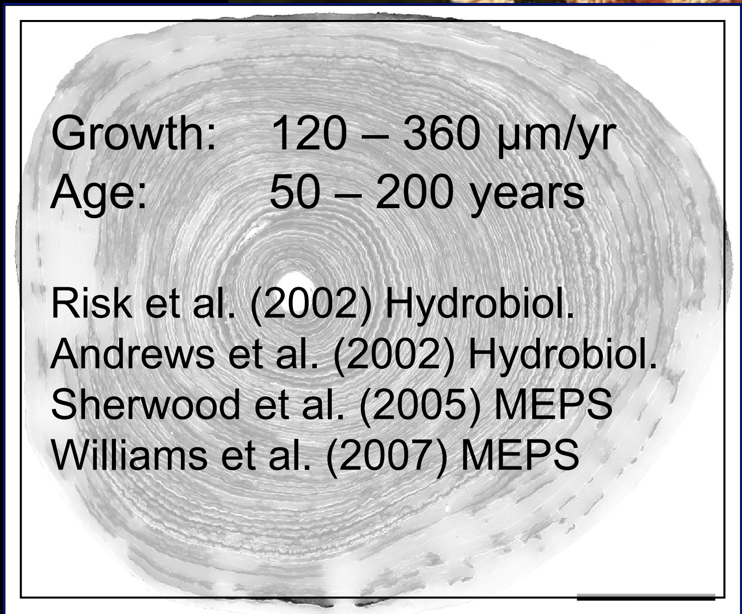

Organic Skeleton ‘Corals’

# Organic Skeleton ‘Corals’

Credit for the following slides: modified from Brendan Roark’s excellent presentation to the American TRACES workshop in 2008.

# Primnoa resedaeformis



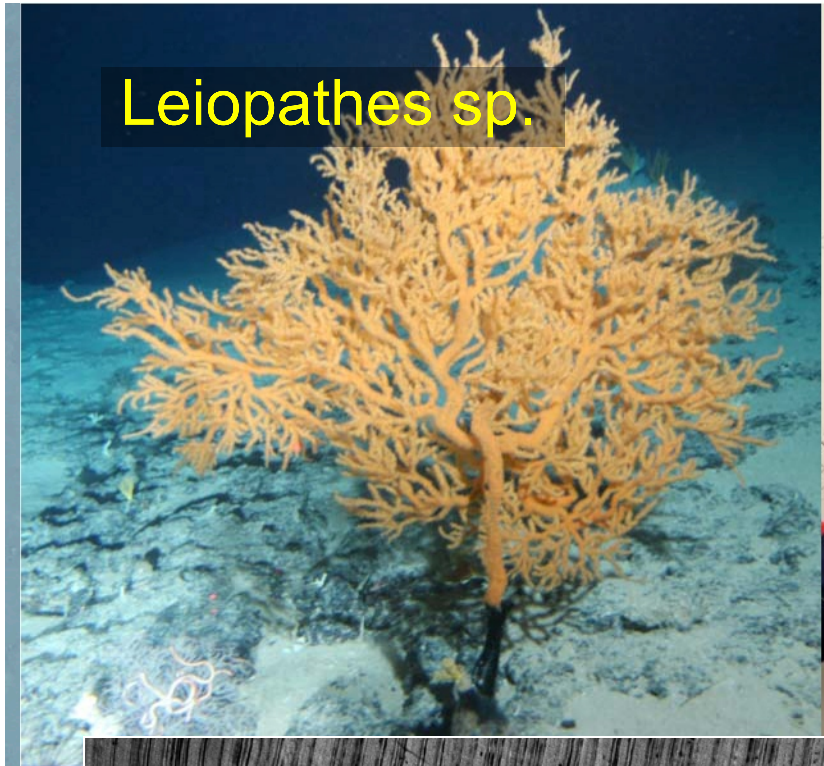


Growth: 120 – 360 µm/yr
Age: 50 – 200 years

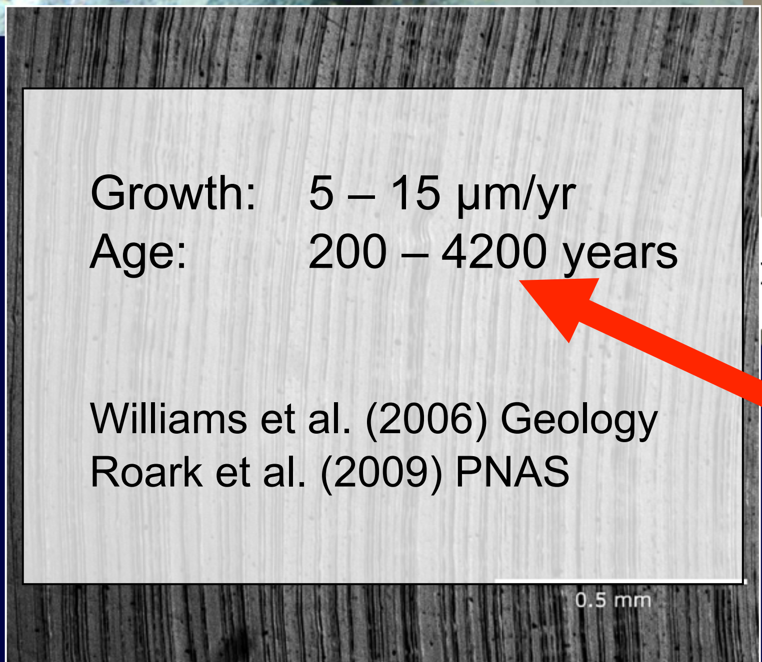
Risk et al. (2002) Hydrobiol.
Andrews et al. (2002) Hydrobiol.
Sherwood et al. (2005) MEPS
Williams et al. (2007) MEPS

F. E. Moen

# Leiopathes sp.

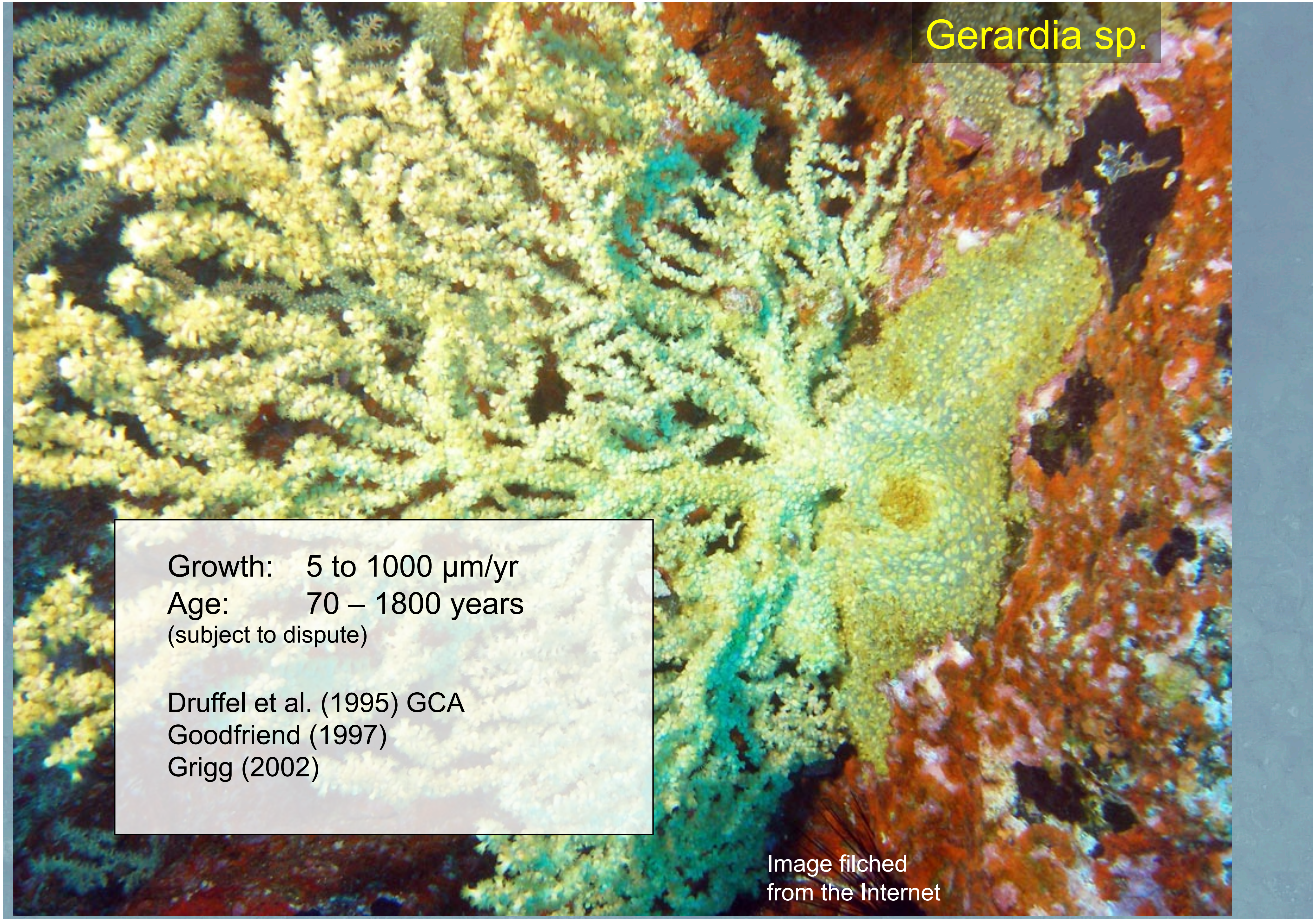






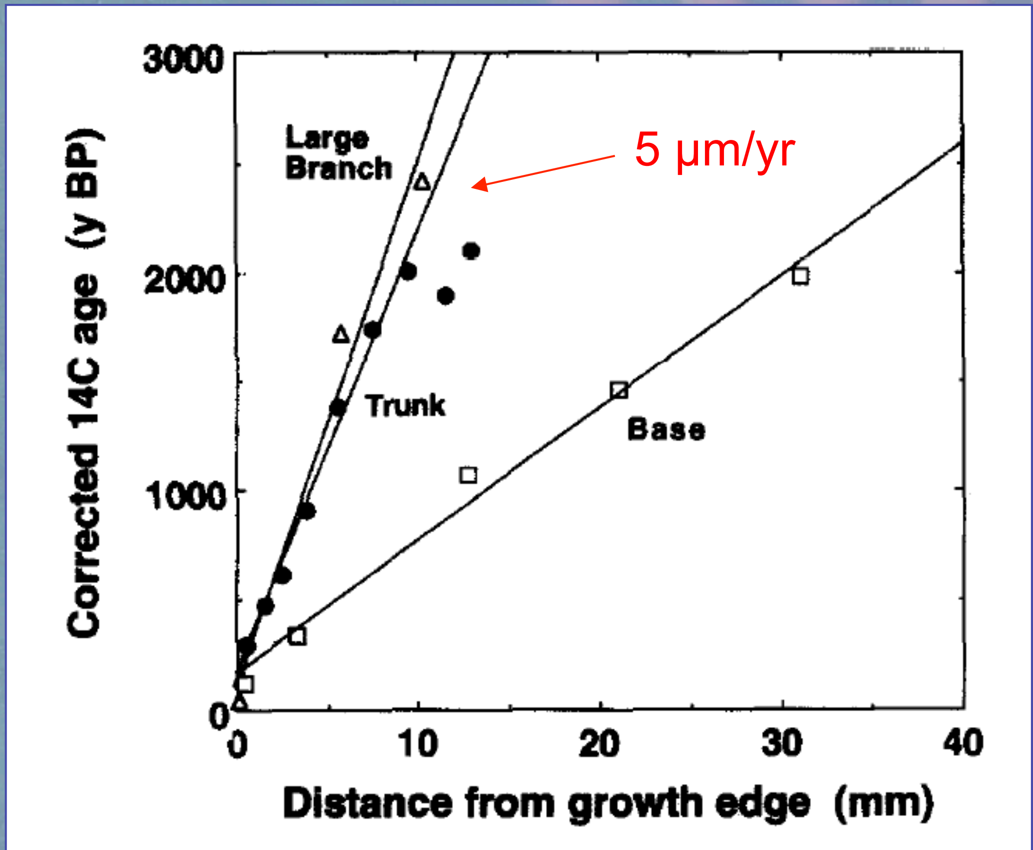

Growth: 5 – 15 µm/yr
Age: 200 – 4200 years

Williams et al. (2006) Geology
Roark et al. (2009) PNAS


Gerardia sp.
Growth: 5 to 1000 µm/yr
Age: 70 – 1800 years
(subject to dispute)
Druffel et al. (1995) GCA
Goodfriend (1997)
Grigg (2002)
Image filched
from the Internet

# Extremely Slow Growth

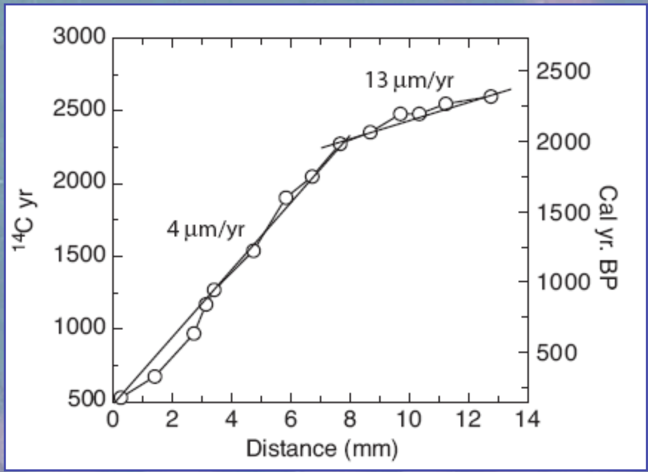
# Extremely Slow Growth

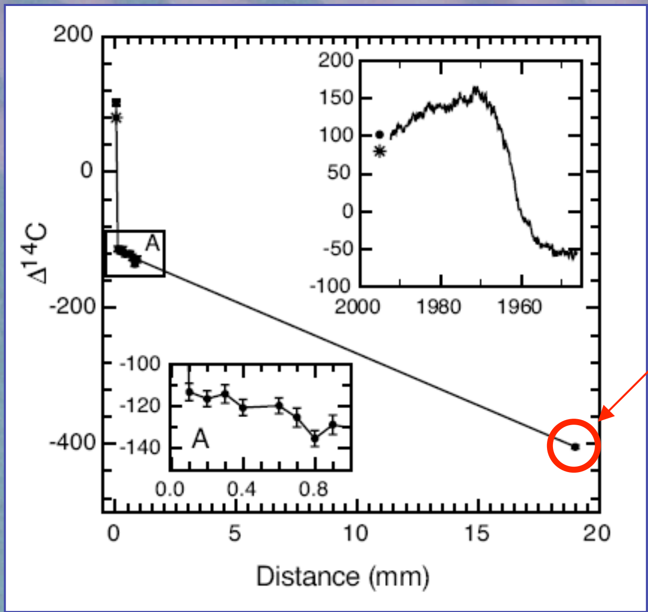



From Druffel et al. GCA 1995

- Gerardia Specimen from Little Bahama Bank (620 m).
- Linear Age vs Depth relationship suggests constant growth rate.
- Slope of lines for Trunk and Branches suggests a radial growth rate of 5 µm per year!
- Specimen age estimated at 1800 years!!

# Extremely Slow Growth



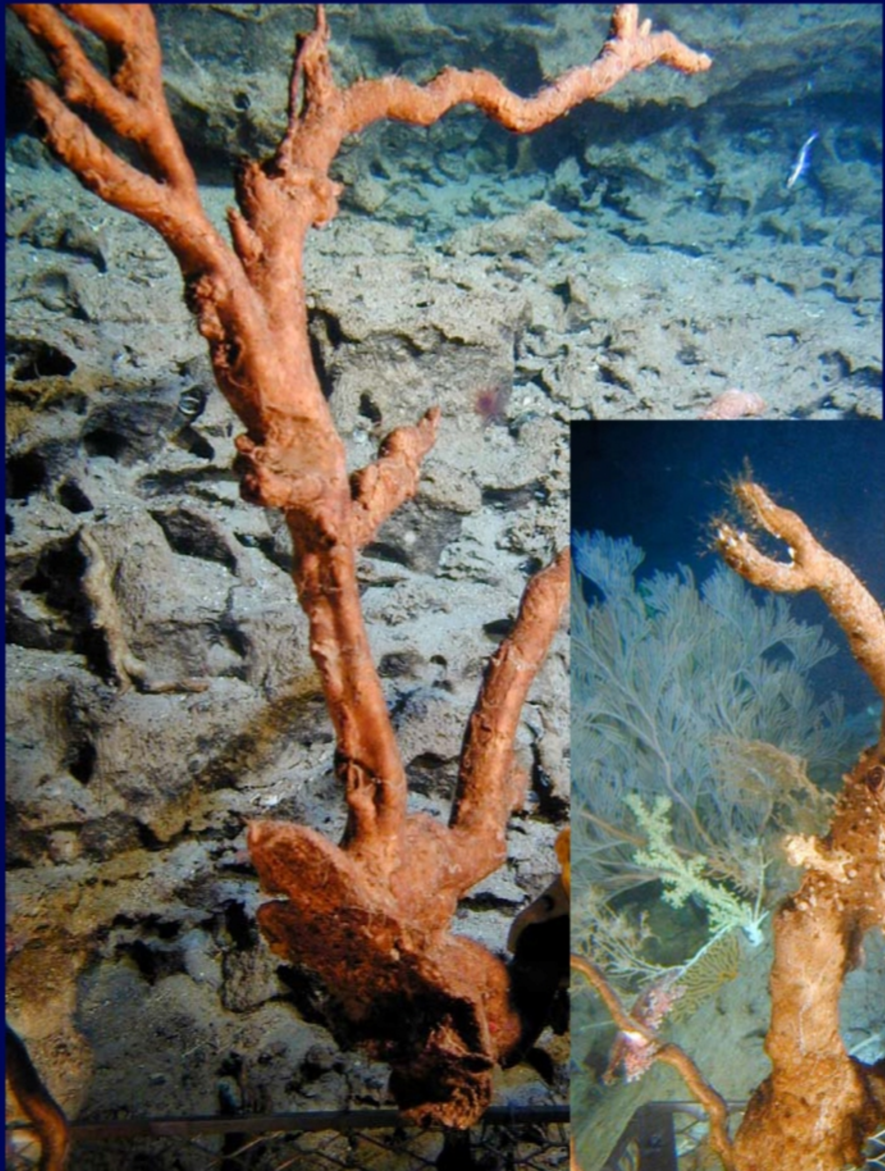



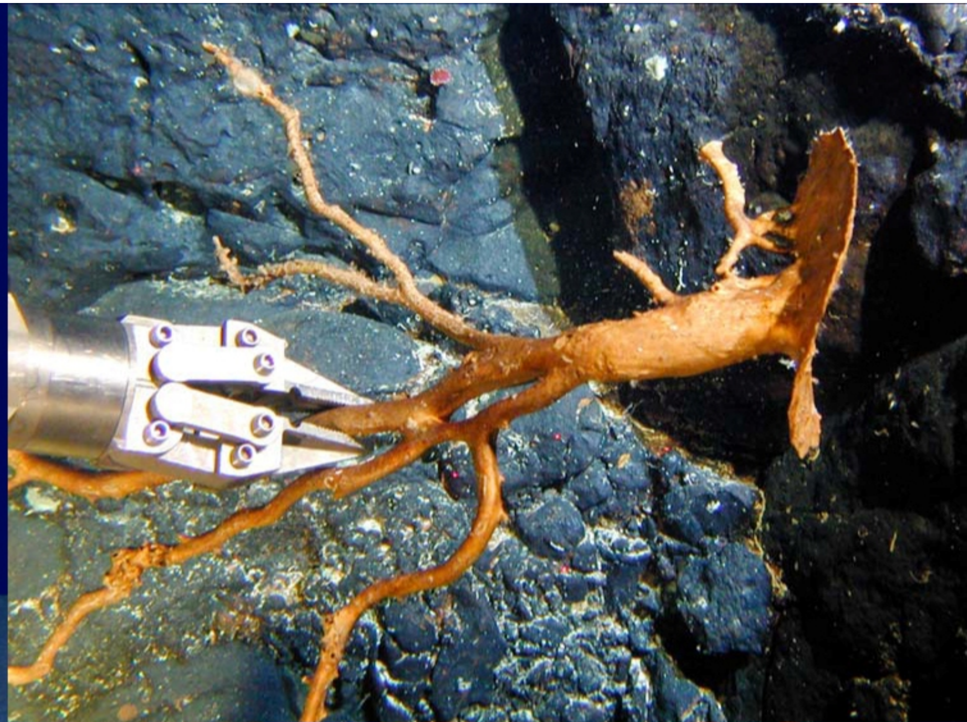

- Leiopathes Specimen from Hawaii (300 - 500 m).
- Growth rate as low as 4 μm per year.
- Oldest specimen estimated as 4200 years old!!

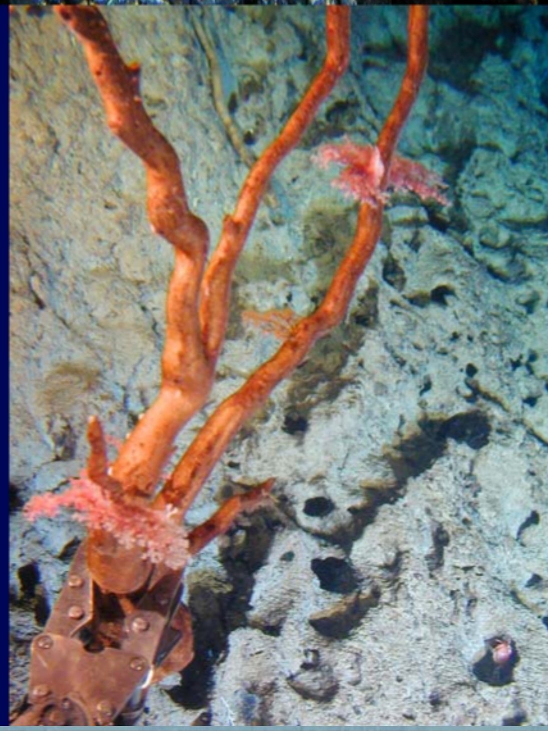
~ 4200 years bp

From Roark et al. 2009 PNAS

# Sub-fossil Gerardia

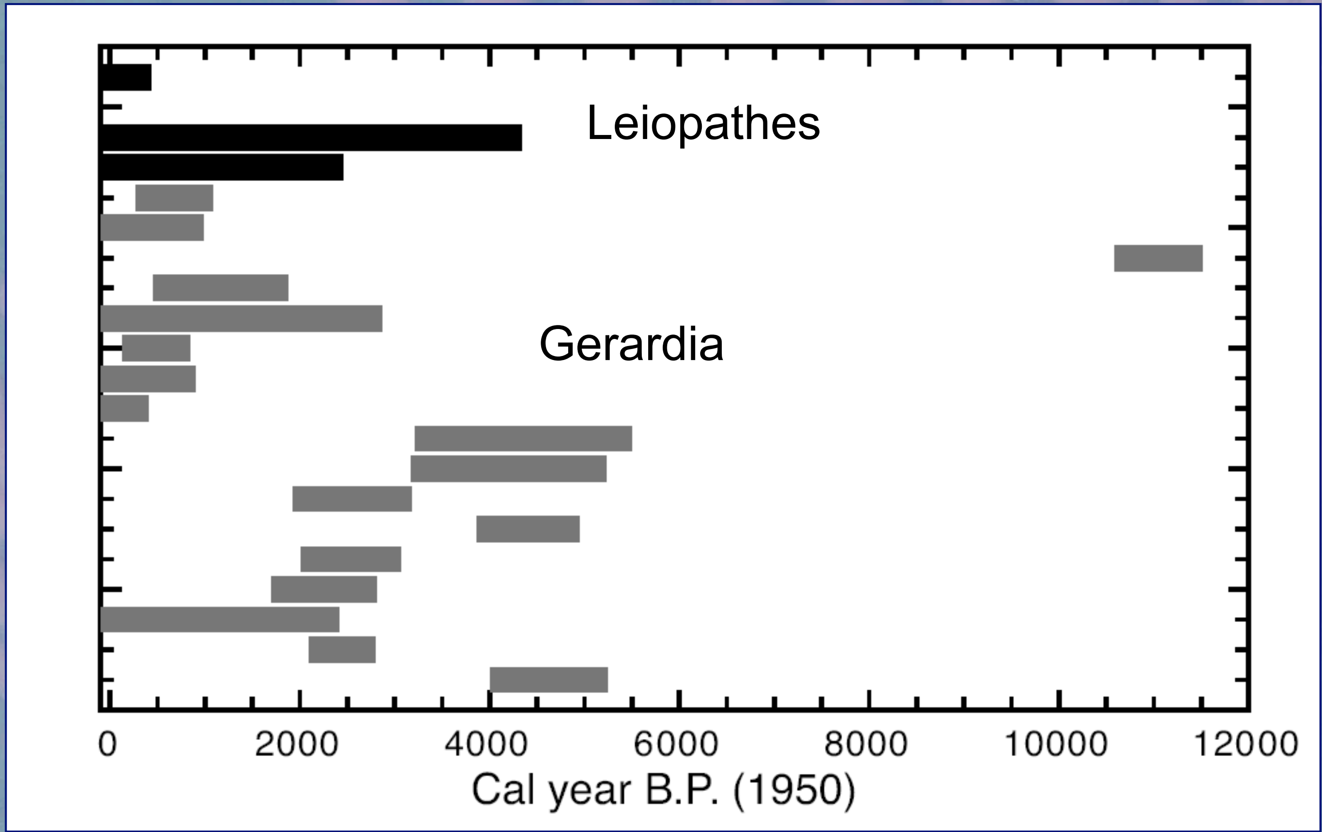




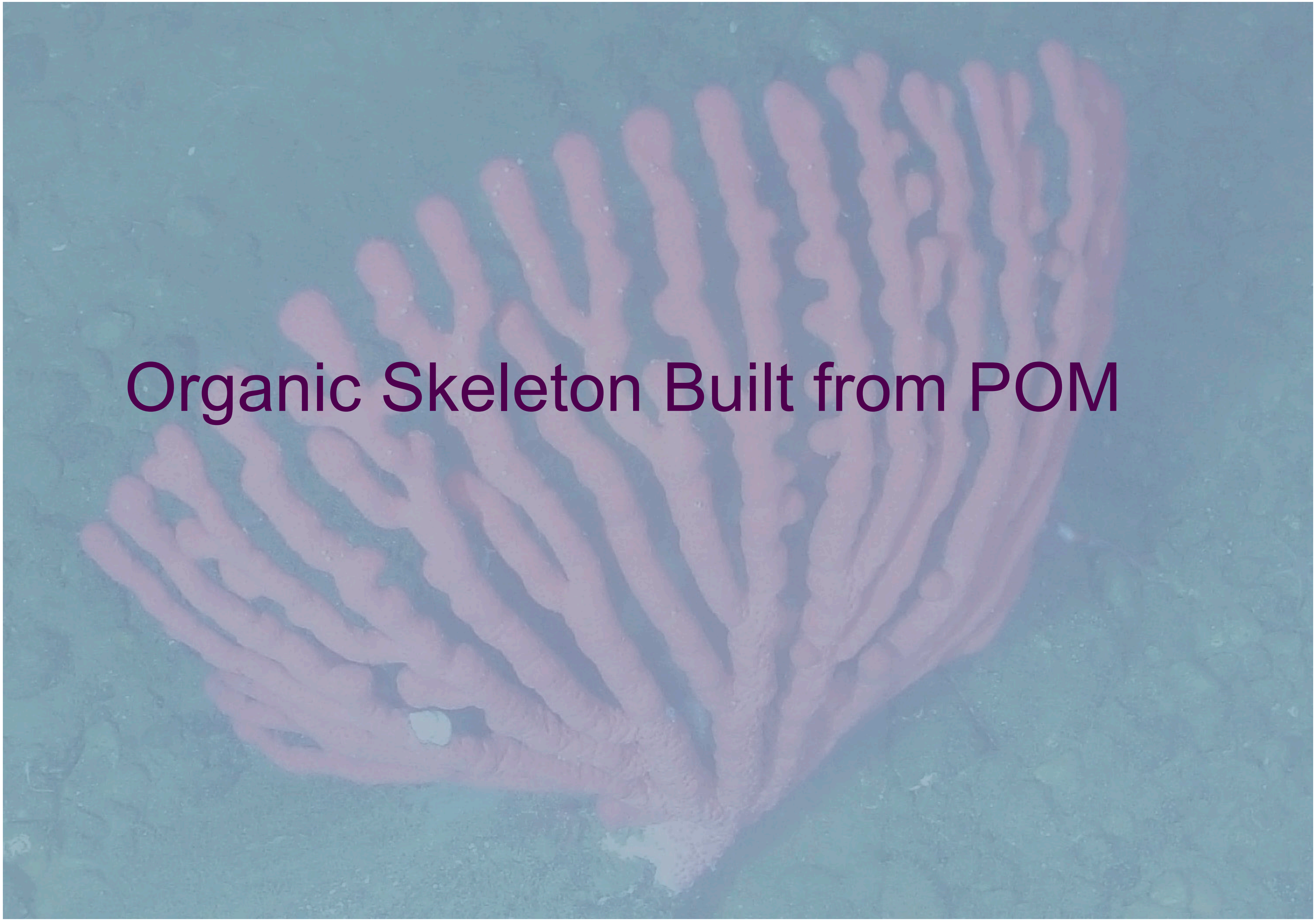


Roark TRACES meeting

# Overlapping Timeseries




Overlapping sub-fossil specimens potentially span 5,500 years (Roark et al. 2009)


Organic Skeleton Built from POM

# Organic Skeleton Built from POM

## Evidence Part 1:

Presence of bomb $^{14}C$ in younger parts of corals growing in deep water (where the signal hasn't migrated into the DIC or DOC pool) clearly indicates a surface source for the carbon. Skeleton must be built from a surface C pool: ie. settling POM.

- Gerardia
  - Griffin and Druffel 1989
  - Druffel et al. 1995
  - Roark et al. 2009
- Primnoa
  - Heikoop et al. 1998
  - Sherwood et al. 2005
- Leiopathes
  - Roark et al. 2009
- Bamboo Corals
  - Roark et al. 2005

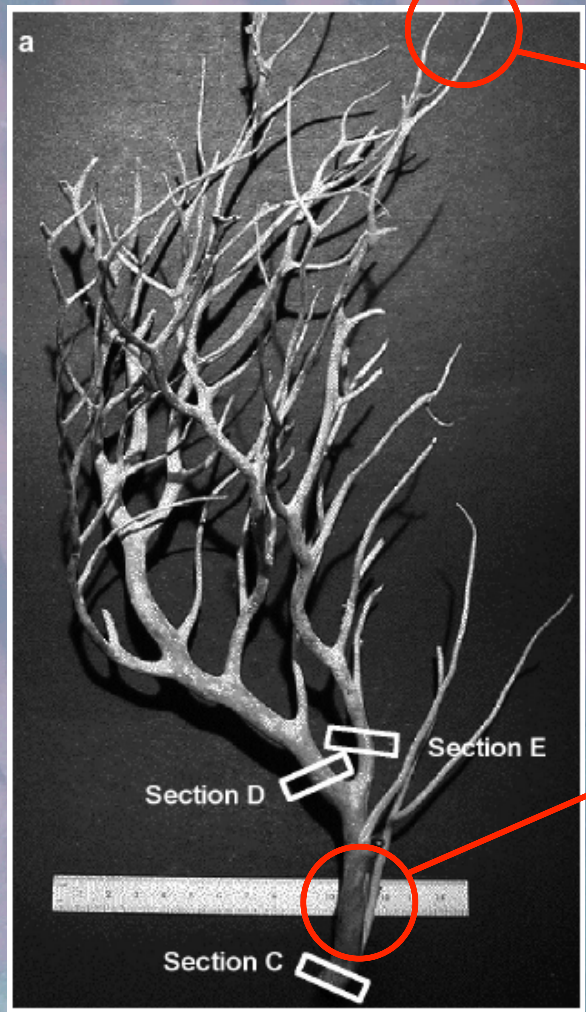



Image From Sherwood et al. (2005a) MEPS

Tips: $\Delta^{14}C$ up to + 100 ‰

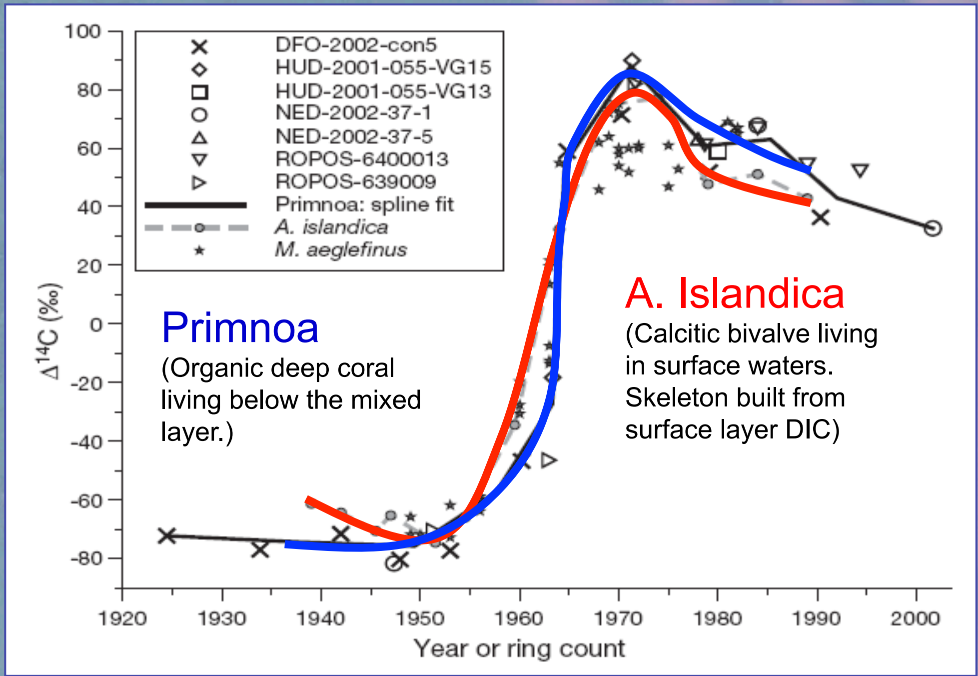
(Bomb radiocarbon Druffel et al. 1995)

Base: $\Delta^{14}C$ ~ - 50 ‰

(roughly pre-bomb Surface DIC Druffel et al. 1995)

# Organic Skeleton Built from POM

From Sherwood et al. MEPS 2005a




## Evidence Part 2:

- Similar $\Delta^{14}C$ profiles for Primnoa resedaeformis (250 - 475 m) and Arctica islandica (75 m).
- Suggests that they incorporate the same C pool.
- A. islandica (calcitic bivalve) incorporates inorganic DIC into its calcite from surface mixed layer.
- If Primnoa incorporated in-situ DIC you would expect much lower $\Delta^{14}C$ (samples are from below the mixed layer).
- The only way for Primnoa to incorporate surface DIC is through packaging into settling POC.

## Evidence Part 3:

- There is no difference in the timing or amplitude of the bomb $^{14}C$ spike between the deeper water organism (Primnoa) and the shallower water organism (A. islandica). If the C came from a deeper 'pool', the bomb spike would be smaller in amplitude and more 'spread out'.
- Similar argument advanced by Roark et al. (2009) who saw no difference between deep coral $^{14}C$ profiles and surface seawater reconstructions from tropical corals.

# Organic Skeleton Built from POM

| $\delta^{13}C$ | $\delta^{15}N$ | Coral |
|---|---|---|
| -22.6 ‰ | +10.3 ‰ | Primnoa |
| (-18 to -24 ‰) | (+8 to +14 ‰) | (range) |
| -19.3 ‰ | +8.3 ‰ | Gerardia |
| -19.7 ‰ | +9.3 ‰ | Leiopathes |
| -18 to -22 ‰ | +2 to +6 ‰ | Surface POM |

Data from Heikoop et al. 1998; Sherwood et al. 2005b; Roark et al. 2009.
See also Williams et al. 2006.

## Evidence Part 4:

- DeNiro and Epstein (1978, 1981) establish a connection between the $\delta^{13}C$ and $\delta^{15}N$ of animal tissues (including bone collagen) and the isotopic values of their diet.
- Polyp $\delta^{13}C$ values in these corals are very close to the value of surface settling POM.
- Polyp $\delta^{15}N$ values in these corals are similar to the value of surface settling POM, shifted by ~ 1 trophic level.
- Organic skeletons are similar or slightly elevated in $\delta^{15}N$ relative to polyps, but polyp and skeleton are strongly correlated (Heikoop et al. 2002).

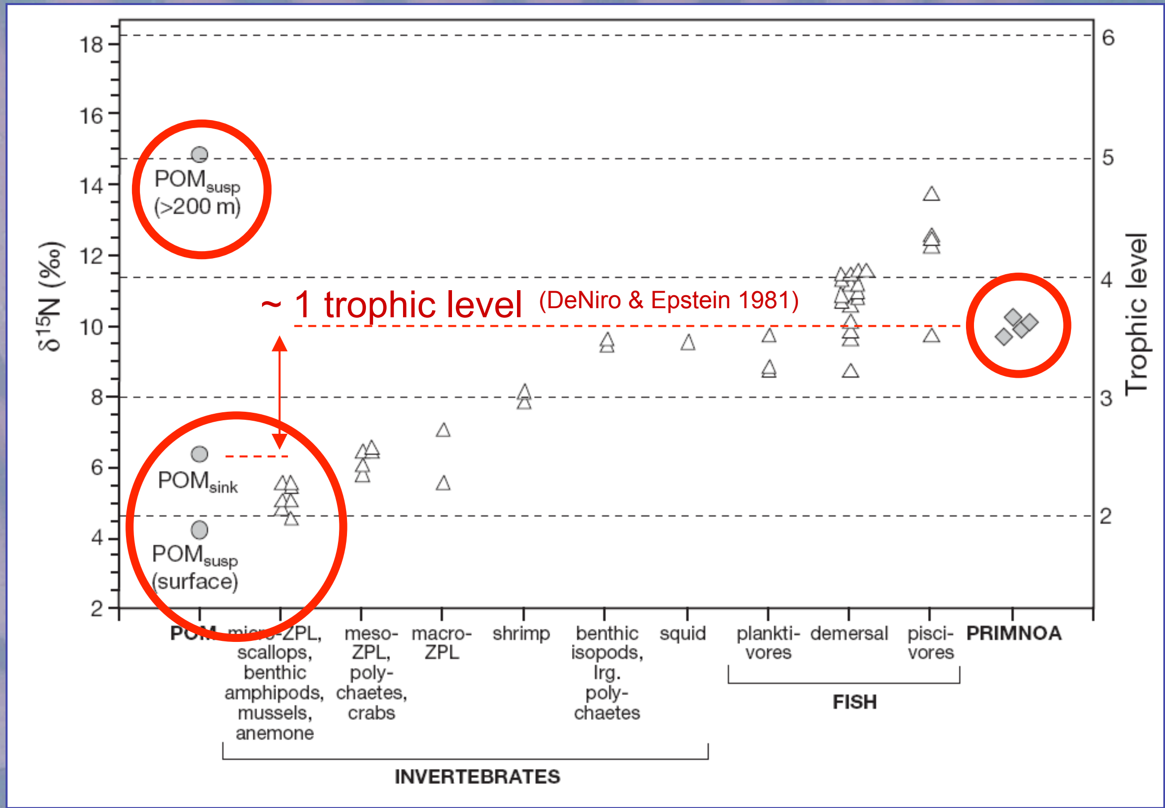
These results support the earlier evidence that these deep sea corals build their skeletons from settling POM *derived primarily from the surface ocean.* This accords with observations that other benthic deep sea corals feed primarily on POM and zooplankton (Ribes et al. 1999; 2003; Orejas et al. 2003)

# Organic Skeleton Built from POM

## Trophic Level

$\delta^{15}N$ indicates that Primnoa is primarily carnivorous: on the same level as planktivorous fish.

Relatively 'low' $\delta^{15}N$ suggests Primnoa is not consuming highly degraded suspended POM.




From Sherwood et al. MEPS 2005b

# Reconstructing Surface $\delta^{15}N$

# Reconstructing Surface $\delta^{15}N$

Since $\delta^{15}N$ in the skeleton is connected to diet, and corals are eating settling POM from the surface, $\delta^{15}N$ in organic skeleton deep sea corals may provide archives of *surface nutrient processes*.

- First proposed by Druffel et al. (1995) (see also preliminary work in Griffin and Druffel 1989).
- Given longevity and growth rate, *millennial-duration decadal scale reconstructions* of surface ocean productivity could be possible.

The overarching assumption is that surface POM reflects the $\delta^{15}N$ of the primary N source for phytoplankton growth.

Attention now turns to testing this possibility:

- Is N geochemically stable in the coral skeleton?
- Are $\delta^{15}N$ profiles reproducible within a specimen?
- Are $\delta^{15}N$ profiles reproducible between specimens?
- Are $\delta^{15}N$ profiles correlated with surface productivity/processes?

# Reconstructing Surface $\delta^{15}N$

The organic protein (Gorgonin) that makes up the coral skeleton is one of the most chemically inert proteins known (Goldberg 1976) and thus very resistant to diagenesis.

Modern and fossil specimens have similar:

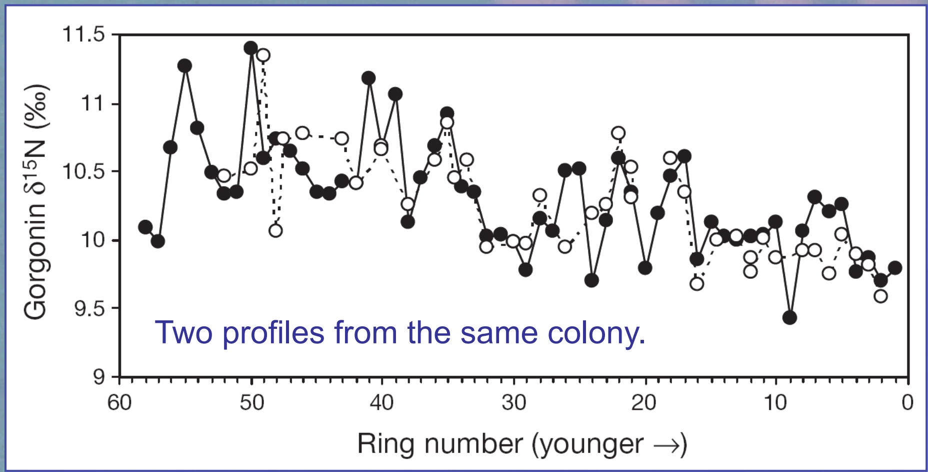
- C:N
- $\delta^{13}C$
- $\delta^{15}N$
- Amino acid abundances

"Over millennial timescales, isotope abundances in *Primnoa* are preserved, making these corals durable archives of paleoceanographic information."

- Sherwood et al. MEPS (2005b)

# Reconstructing Surface δ$^{15}$N

## δ$^{15}$N profiles are reproducible within and between specimens.



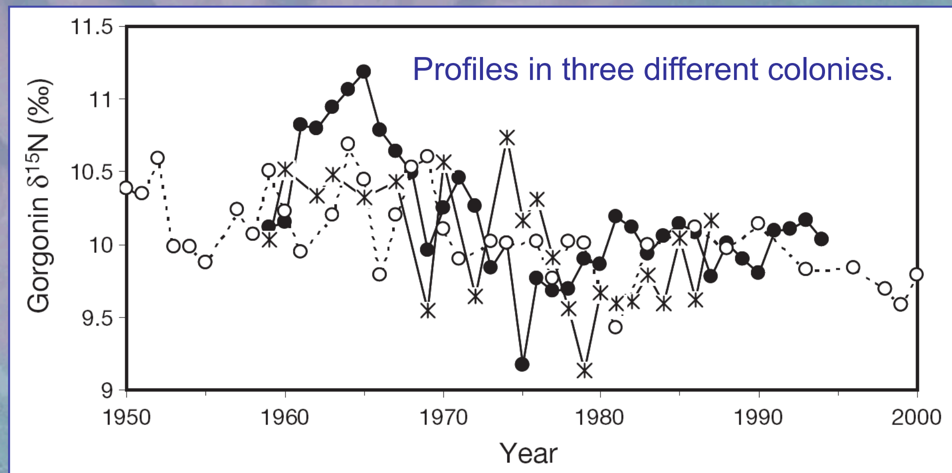

(left) δ$^{15}$N reproduces in different sections from the same Primnoa colony.

Note, however, there are cases where profiles aren't completely reproducible so some internal biological factors may affect δ$^{15}$N. One possibility: different polyps consume different types of POM.

(right) δ$^{15}$N reproduces in different Primnoa colonies from the same location.

From Sherwood et al. MEPS 2005b

Williams et al. 2007 BMS also observe reproducibility in long-term trends between specimens.

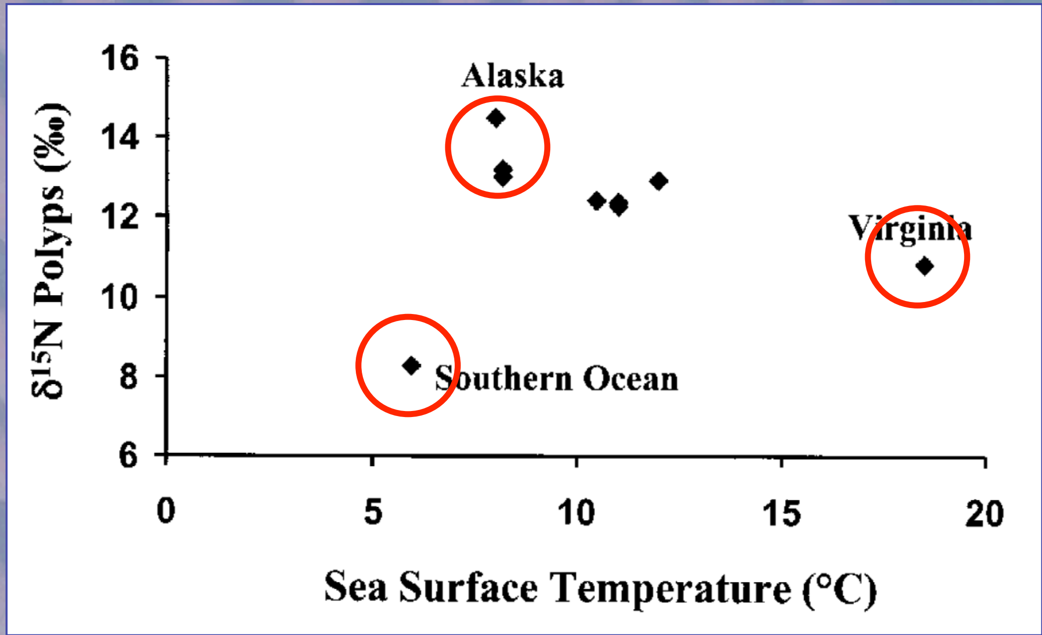


# Reconstructing Surface $\delta^{15}N$

## $\delta^{15}N$ profiles are related to plankton $\delta^{15}N$.

Qualitative correspondence between bulk skeletal $\delta^{15}N$ and average plankton $\delta^{15}N$

- Southern Ocean: low $\delta^{15}N$ (< 2 ‰). High surface nitrate leads to increased phytoplankton fractionation (Altabet & Francois, 1994).
- Alaksa: high $\delta^{15}N$ (12 ‰). High values result from isotopic enrichment of the residual nitrate pool related to more complete utilization of nitrate during phytoplankton blooms.
- Virginia: Low-intermediate $\delta^{15}N$. May represent input of low $\delta^{15}N$ due to dust-fertilised $N_2$-fixation in a LNLC Atlantic.



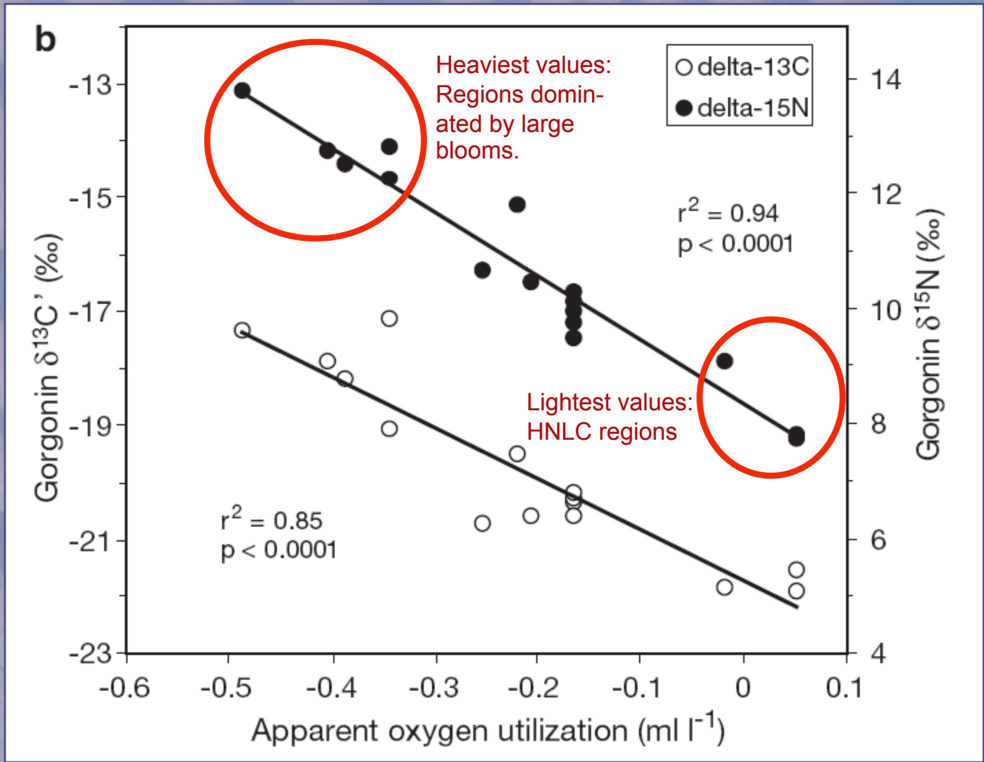

From Heikoop et al. 2002 Hydrobiol.

# Reconstructing Surface δ$^{15}$N

## δ$^{15}$N profiles are correlated with surface productivity.

δ$^{15}$N of individual specimens correlates with apparent oxygen utilization (a measure of productivity).

- Demonstrates coupling between skeletal isotopic ratios and biophysical processes in surface water.




From Sherwood et al. MEPS 2005b

Specimens from

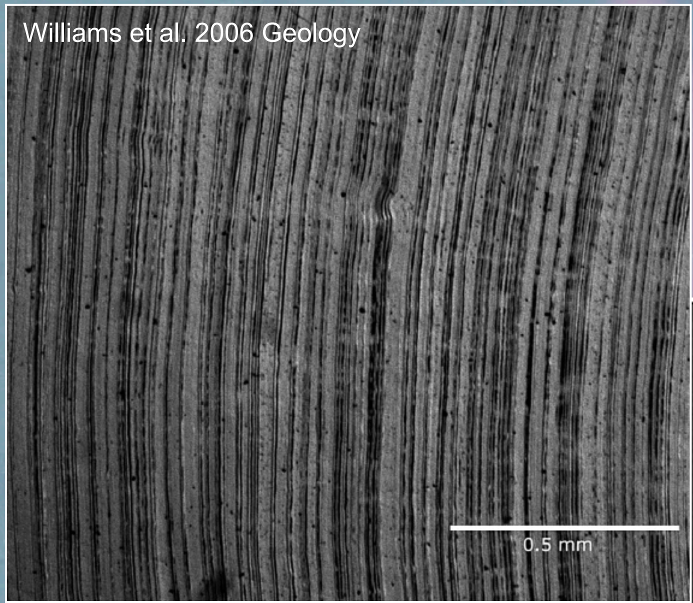
- NE Pacific shelf waters
- NW Atlantic slope waters
- the Sea of Japan
- South Pacific seamount

# To Recap:

1. Organic skeleton corals can be very long lived (thousands of years) with annual banding that allows excellent age control and resolution.
2. Organic skeletons are built from the food consumed by the coral, not dissolved C pools.
3. The food source has to be largely derived from the surface with little modification or time-lag seen in $\Delta^{14}C$ profiles.
4. Nitrogen isotopes suggest a mixed sinking-POM and zooplankton diet.
5. Gorgonin is resistant to diagenesis and $\delta^{15}N$ values are similar in fossil and modern specimens.
6. Bulk colony $\delta^{15}N$ values appear to correlate with surface plankton $\delta^{15}N$ and measures of surface productivity.
7. $\delta^{15}N$ profiles reproduce within specimens and between colonies.

Combined, these observations strongly support the use of organic-skeleton corals for time-series reconstruction of processes controlling POM $\delta^{15}N$ in the surface ocean over millennial-timescales at decadal-resolution.

# Time Series Analysis




(left) Fine banding in Leiopathes. Bands are 5-10 µm wide. Shown to be approx. annual (Williams et al. 2007).

(right) Bands delaminated using KOH.

Note – more recently subsamples have been taken by micromill.

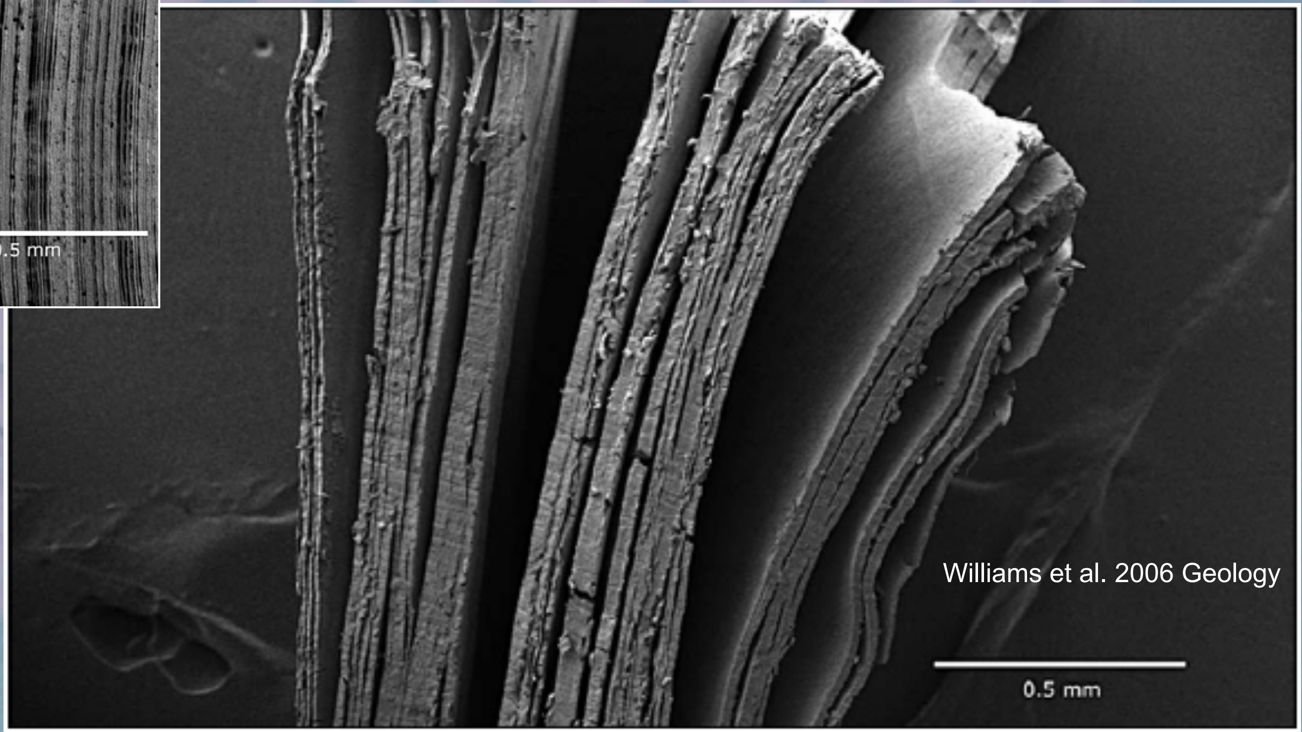
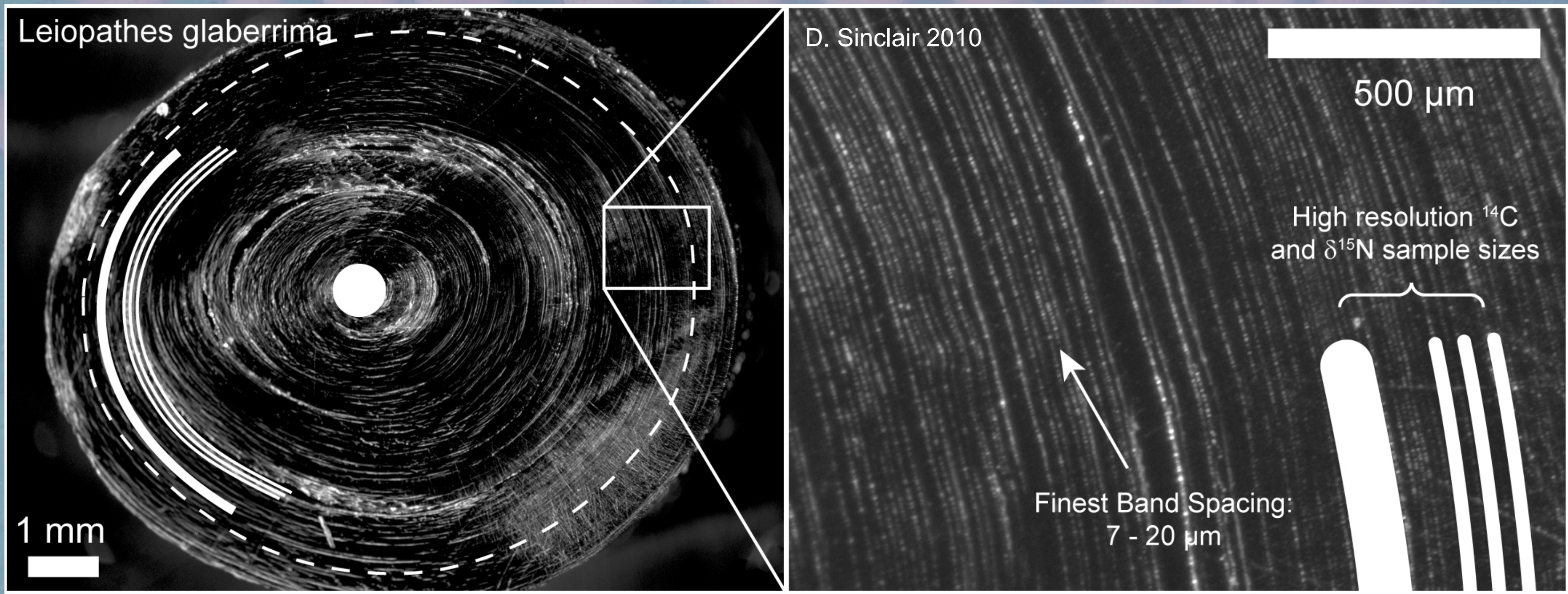



Figure 3. Cross section of specimen A8601 after KOH treatment.

# Time Series Analysis

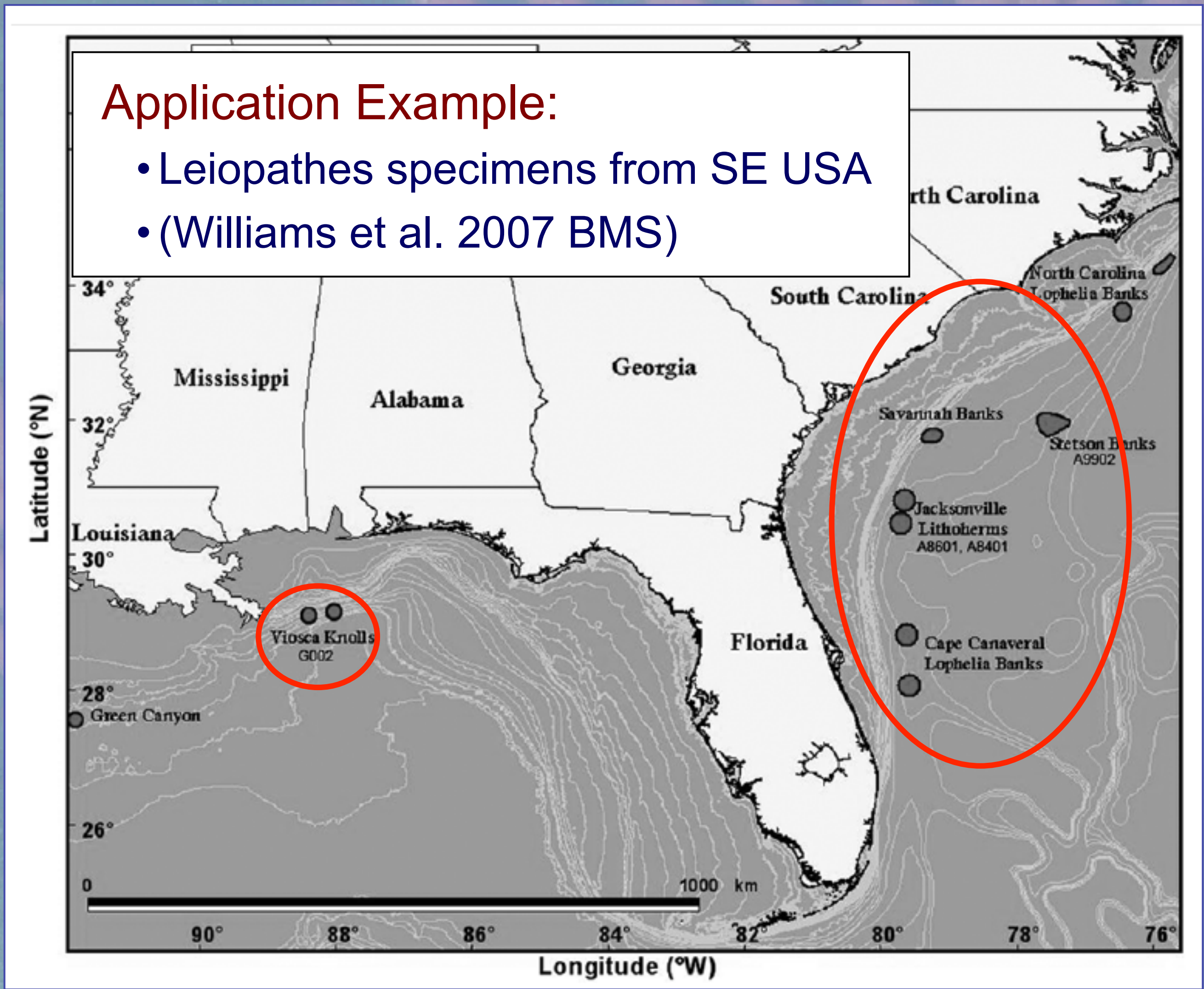
High Resolution Time Series:

- Analysis of $\delta^{15}N$ by Isotope Ratio Mass Spectrometer.
- 0.8 mg subsamples (Williams et al. 2006)
- Micromilling: dimensions 25 µm x 4 mm x 6 mm.
- Resolution approx. 2.5 years per sample.
- Decadal variations resolvable.



# Case Studies

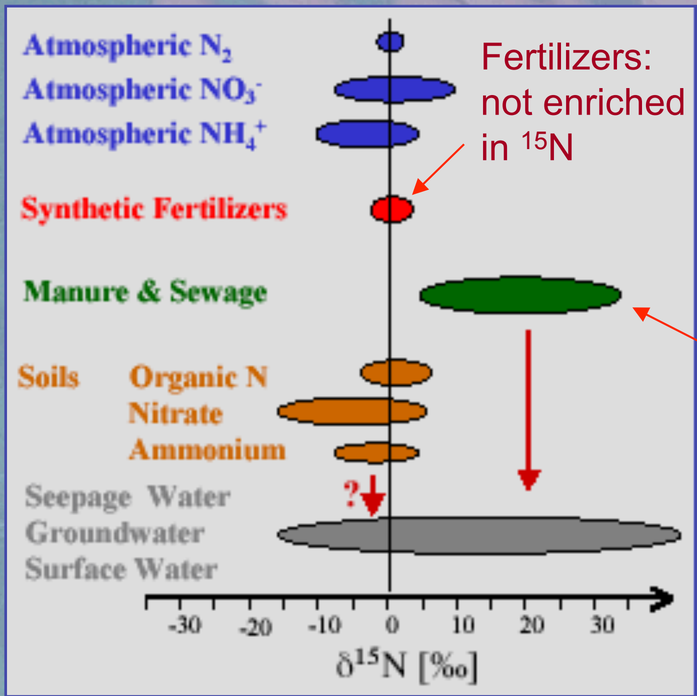
# Case Study 1: SE USA



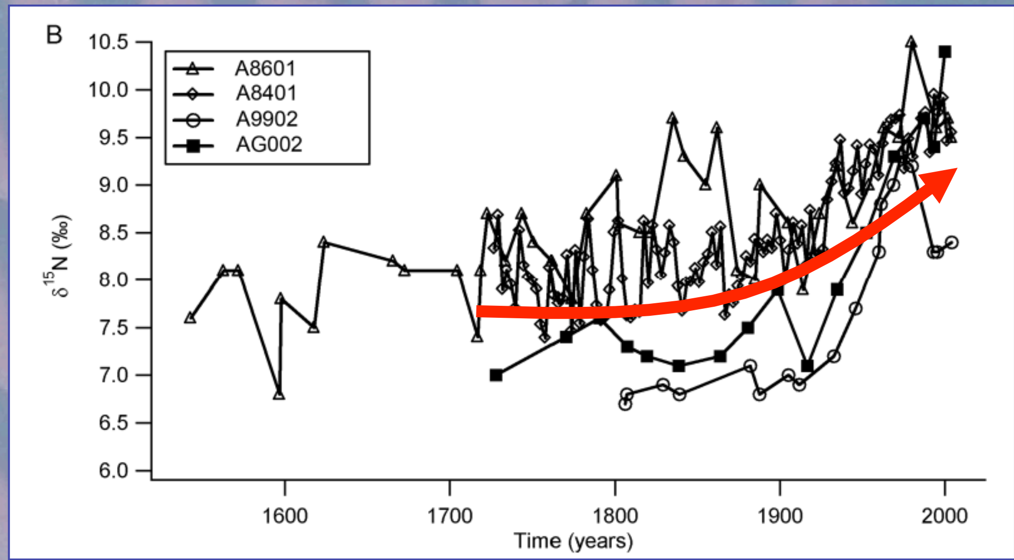
# Case Study 1: SE USA

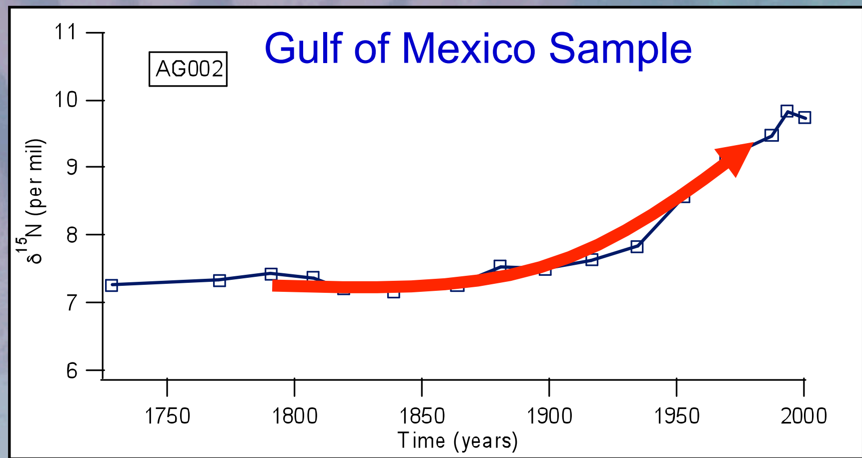
$\delta^{15}N$ in Leiopathes from SE USA:

- All corals show an increasing trend over the last 150 – 200 years.
- Although fertiliser usage has increased, the $\delta^{15}N$ is too low to account for increase.
- Therefore, this increase is attributed to sewerage input.




Sewerage enriched in $^{15}N$



# Similar Studies

Ward-Paige et al. (2005) MEPS

- Studies Plexaura from ‘dirty’ and ‘clean’ sites in the Florida Reef Tract.
- Dirty sites have higher $\delta^{15}N$ which increases with time.
- Suggests ‘dirty’ sites experience a higher overall impact from sewearage with impact increasing.

Risk et al. (2009a) MEPS

- Analysed various Antipatharians from Jeddah.
- The $\delta^{15}N$ of specimens has increased by around 4 ‰ since 1950.
- Suggests progressive decline in water quality through sewearage inputs.

Risk et al. (2009b) Mar. Poll. Bull.

- Shows that the $\delta^{15}N$ of corals (and other organisms) decreases exponentially with distance from points of sewerage stress.

Sherwood et al. (2010) Env. Sci. Tech.

- Various Gorgonians from SE Florida.
- Corals show trend towards elevated $\delta^{15}N$ close to shore.
- Corals show trend towards elevated $\delta^{15}N$ close to the main points of sewerage discharge.
- Suggests corals experience significant sewerage stress.

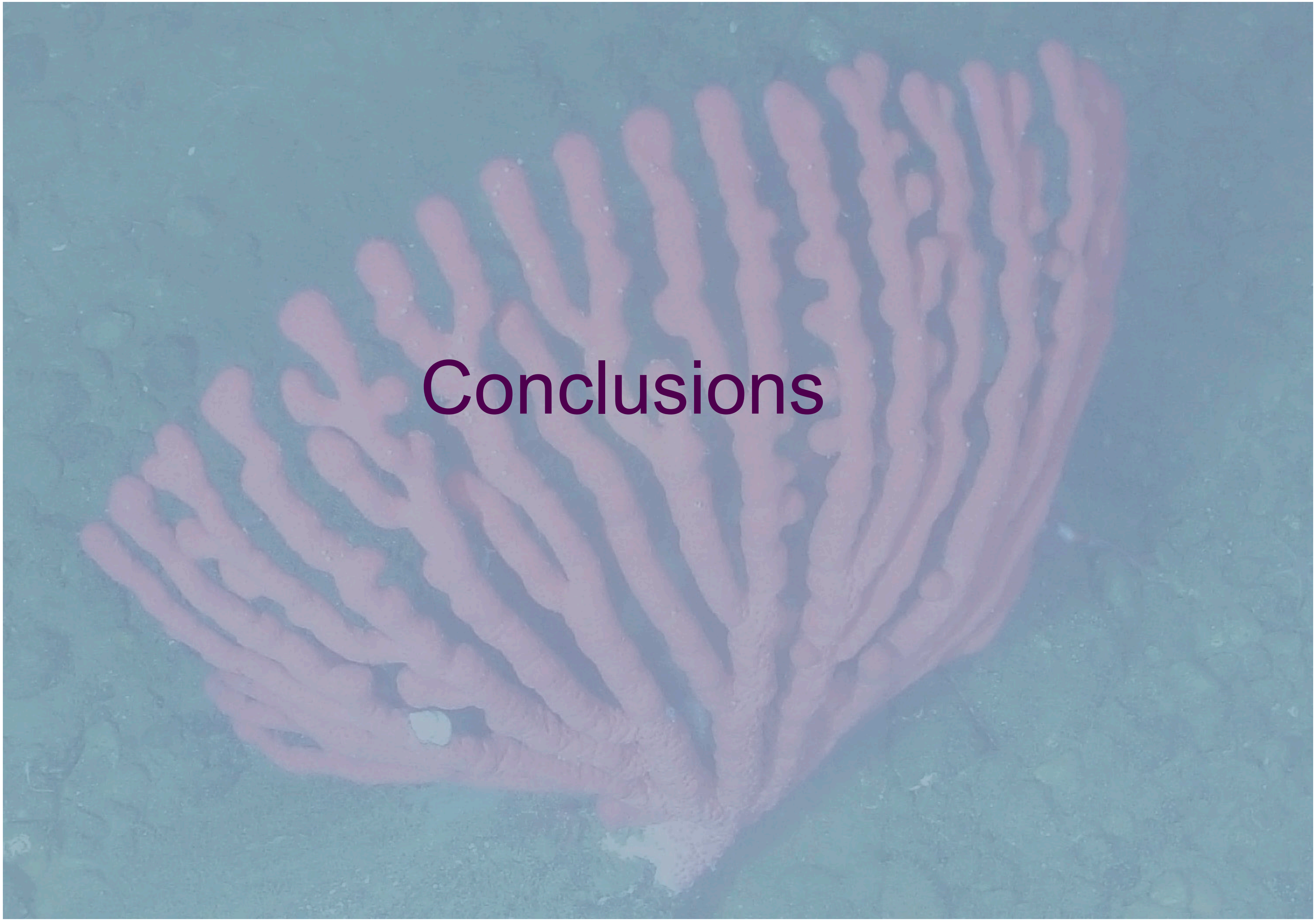
# Case Study 2: Western Pacific

B. Williams and A. Grottoli with samples collected by Pat Colin (nearly submitted)

I am sorry, but this content has been removed from the presentation. This material has not yet been published, and while the authors were happy for me to present this at the meeting, they have requested that it be removed from the archived presentation.

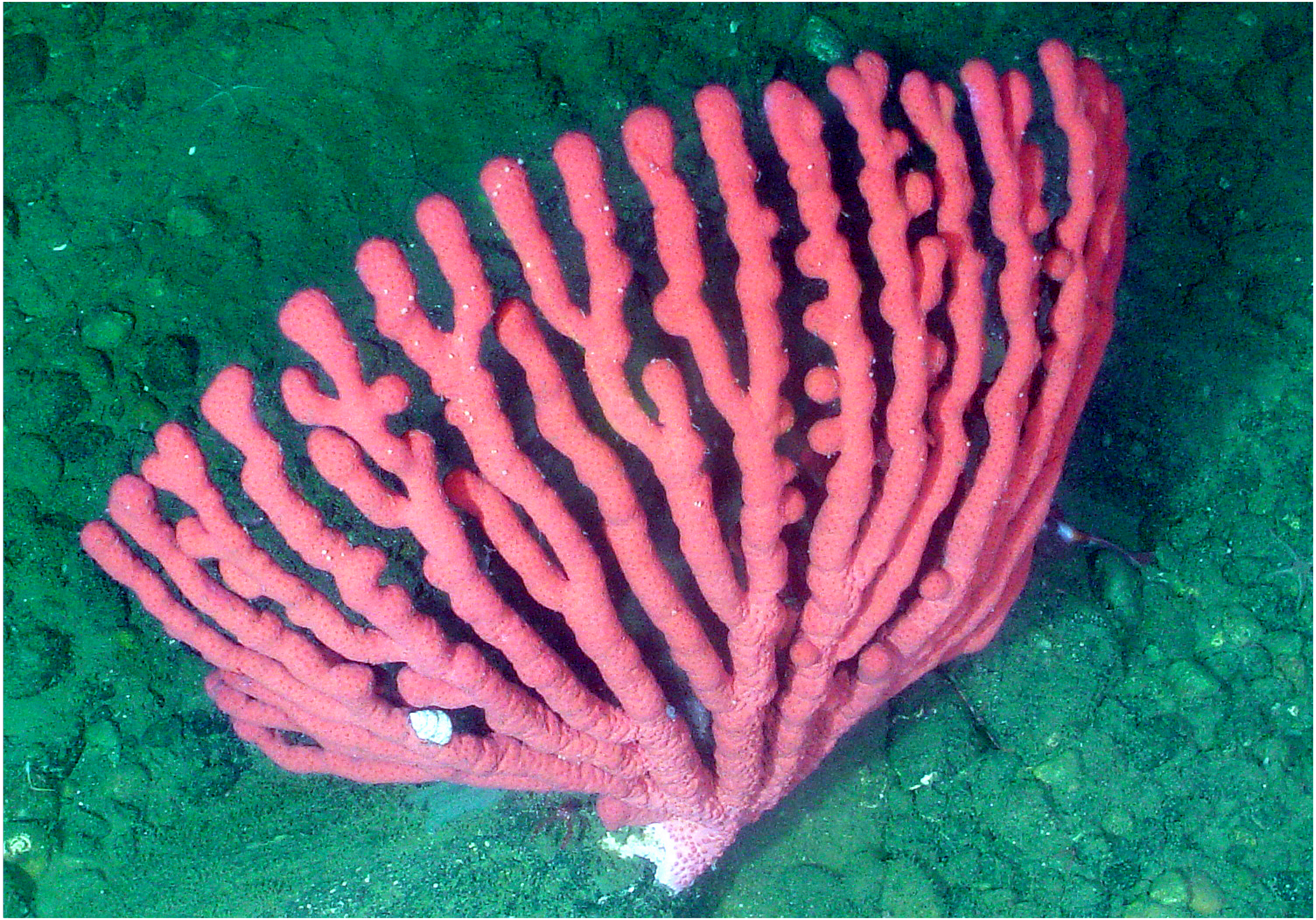
For further information, please contact Dr Branwen Williams (current address (2010): University of Toronto at Mississauga, Ontario, Canada).

# Conclusions

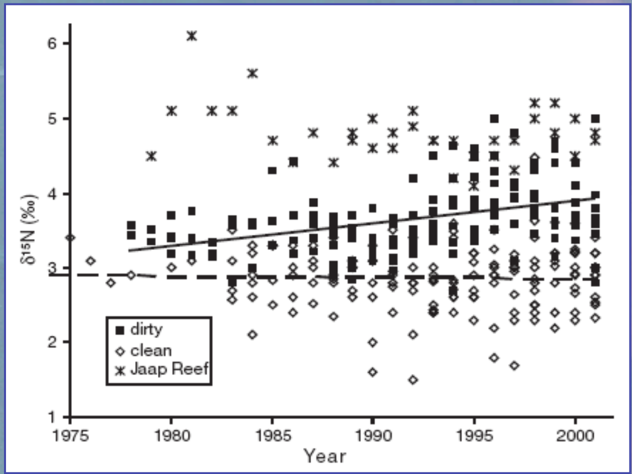


# Conclusions

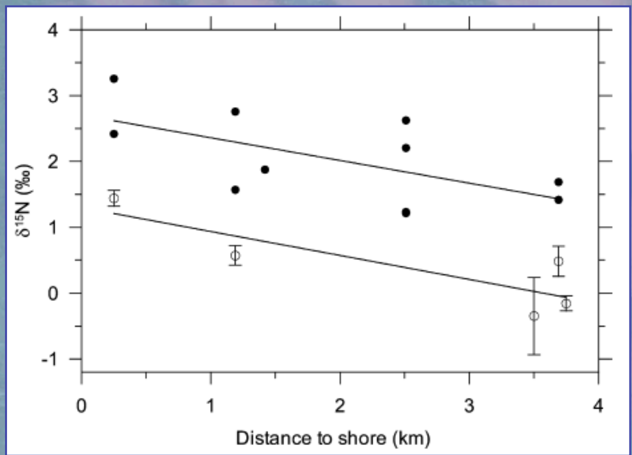
- Organic skeleton corals show great promise for reconstructing processes affecting surface ocean POM.
- This technique is now beginning to be applied to real-world situations.
- The time is ripe for more ‘juicy’ applications, taking advantage of the longevity of some of these corals to reconstruct surface nutrient processes on millennial timescales at decadal resolution.
- Watch this space…

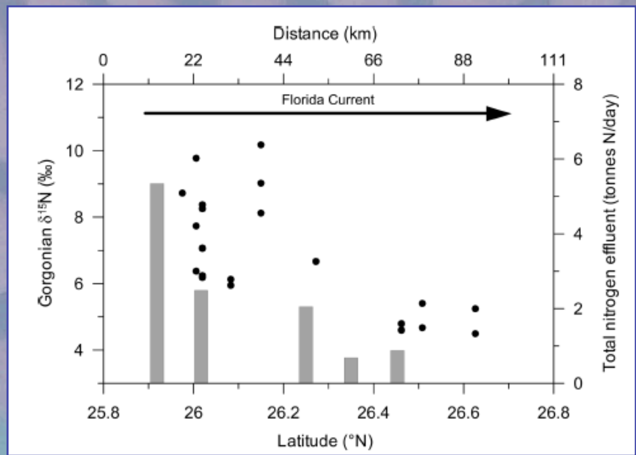


# Similar Studies




From Ward-Paige et al. 2005
Plexaura from ‘dirty’ and ‘clean’ sites in the Florida Reef Tract.
Suggests ‘dirty’ sites experience a higher overall and increasing impact from sewearage.




From Sherwood et al. 2010
Various Gorgonians from SE Florida.
Corals show trend towards elevated $\delta^{15}N$ close to shore, and elevated $\delta^{15}N$ close to the main points of sewerage discharge. Again – suggests corals experiencing significant sewerage stress.