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MORE EFFECTIVE TIME GRID RECONSTRUCTION IN THE CALIBRATION OF GEOCHEMICAL PROXIES FROM CORAL SKELETONS

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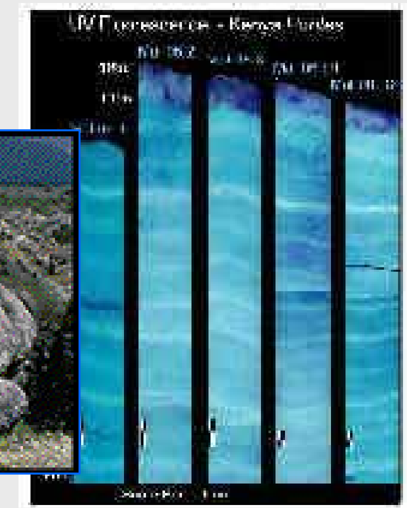
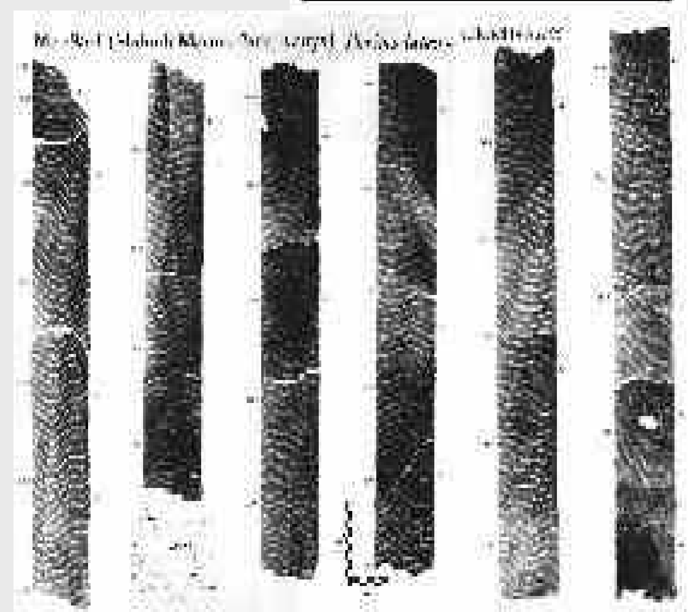
Corals as marine archives for paleoclimate reconstructions





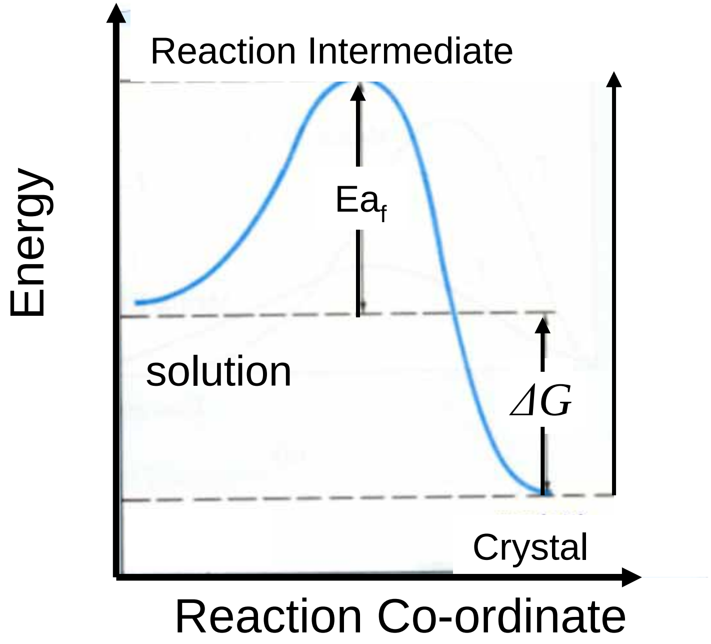
In the last years, in the Mediterranean Sea we have been looking for new high-resolution climate archives, such as the non-tropical coral *Cladocora caespitosa*.

The aim of this study was to develop a new method of calibration between the Sea Temperature data and geochemical data.

Temperature Dependence

$$D_{Thermodynamic} = a_T \cdot e^{\frac{\Delta G_{Sr} - \Delta G_{Ca}}{RT}} \cdot \left(\frac{\gamma_{Sr^{2+}} \cdot f_{Ca^{2+}_{(aragonite)}}}{\gamma_{Ca^{2+}} \cdot f_{Sr^{2+}_{(aragonite)}}} \right)$$

$$D_{Kinetic} = a_K \cdot e^{\frac{Ea_{fSr} - Ea_{fCa}}{RT}} \cdot \left(\frac{\gamma_{Sr^{2+}}}{\gamma_{Ca^{2+}}} \right)$$



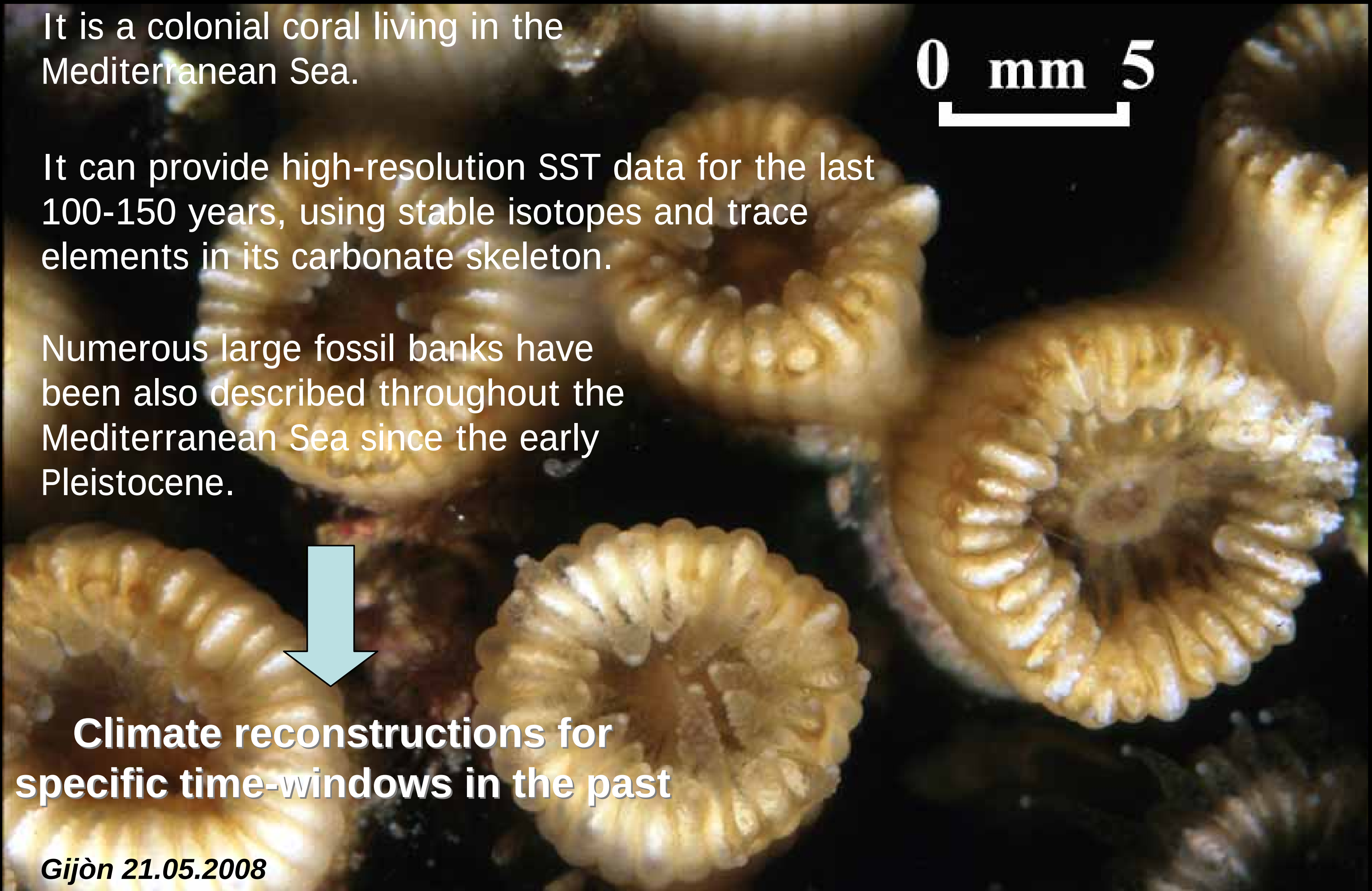
Where a_T and a_k = pre-exponential costants for thermodynamic and kinetic reactions

$Ea_{Sr,Ca}$= activation energies for Sr and Ca forward reactions

$\Delta G_{Sr,Ca}$ = free energy change for Sr and Ca precipitation reactions

<u>Both thermodynamic and kinetic distribution coefficients are clearly temperature dependent</u>

The Mediterranean coral Cladocora caespitosa



It is a colonial coral living in the Mediterranean Sea.

It can provide high-resolution SST data for the last 100-150 years, using stable isotopes and trace elements in its carbonate skeleton.

Numerous large fossil banks have been also described throughout the Mediterranean Sea since the early Pleistocene.

↓

Climate reconstructions for specific time-windows in the past

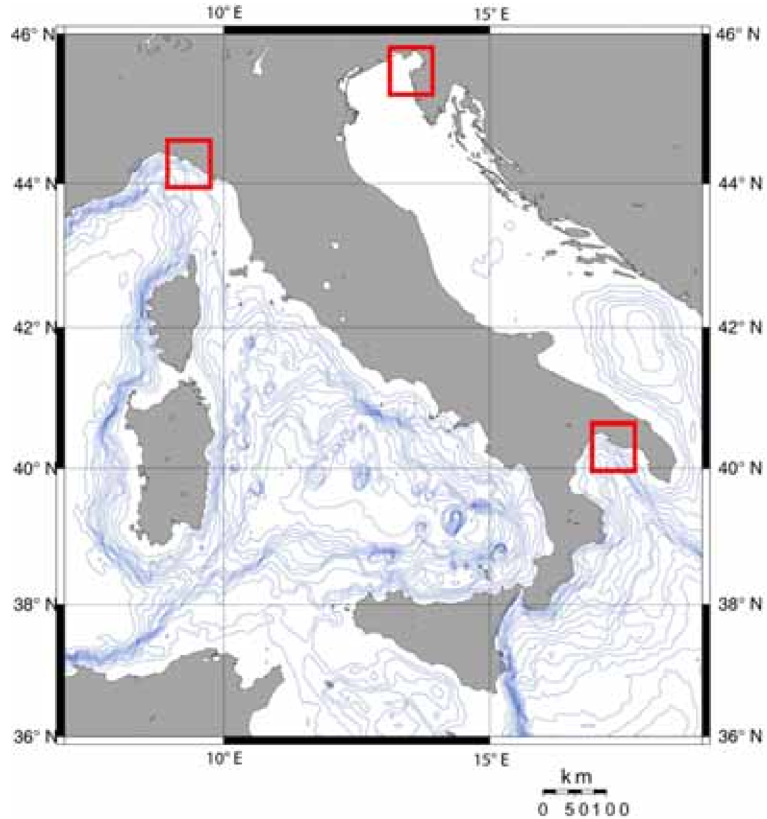
Sampling sites

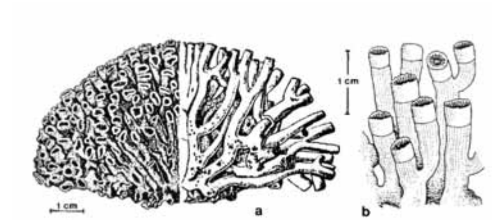
The coral samples were collected in 3 Italian sites with different SST ranges:

• Miramare in the North Adriatic Sea (temperature between 7 and 25°C)

• Portofino in the North Tyrrhenian Sea (temperature between 13 and 27 °C)

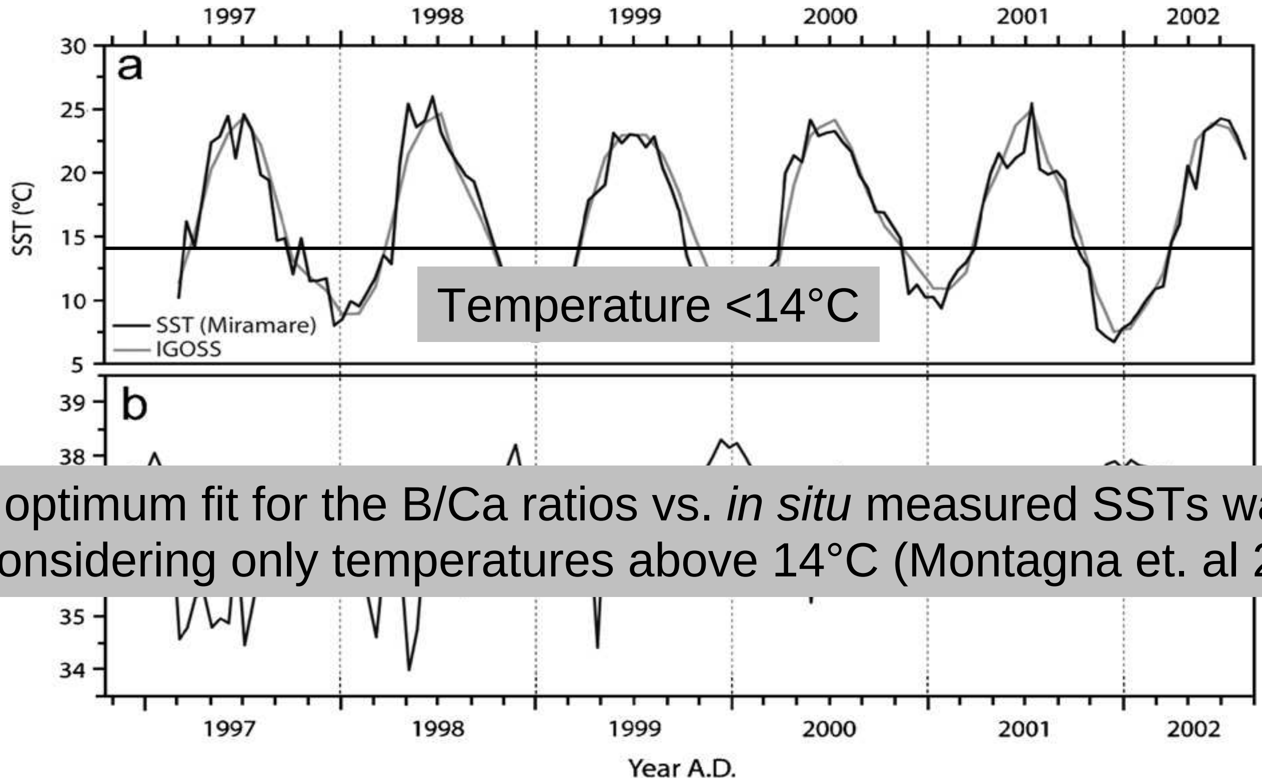
• Taranto in the Ionian Sea (temperature between 11 and 28 °C)





SST and SSS 'In situ' Measurements (Miramare)

(a)In situ weekly/fortnightly SST record from MRM and monthly IGOSS SSTs.
(b) In situ weekly/fortnightly SSS record from MRM.



Temperature <14°C

The optimum fit for the B/Ca ratios vs. *in situ* measured SSTs was obtained by considering only temperatures above 14°C (Montagna et. al 2007)

Montagna, P., Malcolm, Mc., Mazzoli, C., Silenzi, S., Odorico, R., The non-tropical Cladocora caespitosa as the new climate archive for the Mediterranean: high-resolution (weekly) trace elements systematics. Quaternary science Reviews 26 (2007) 441-462.

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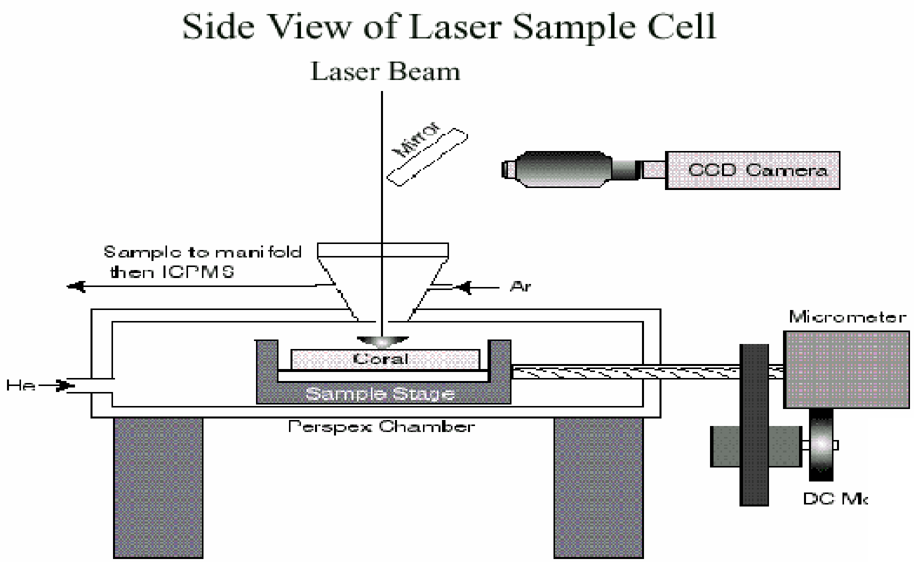
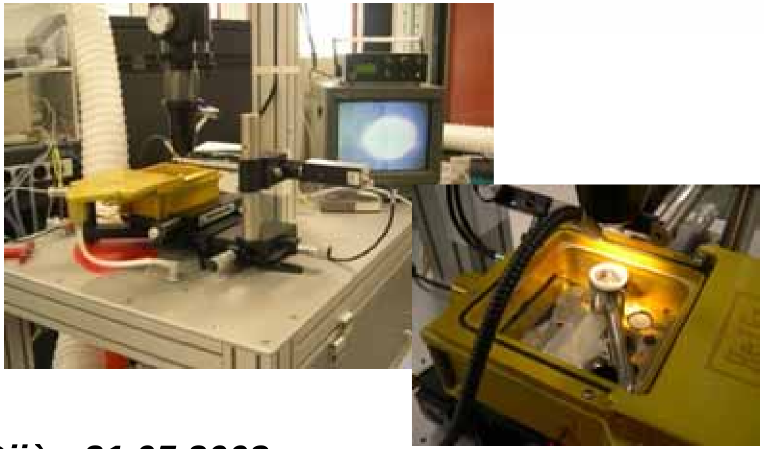
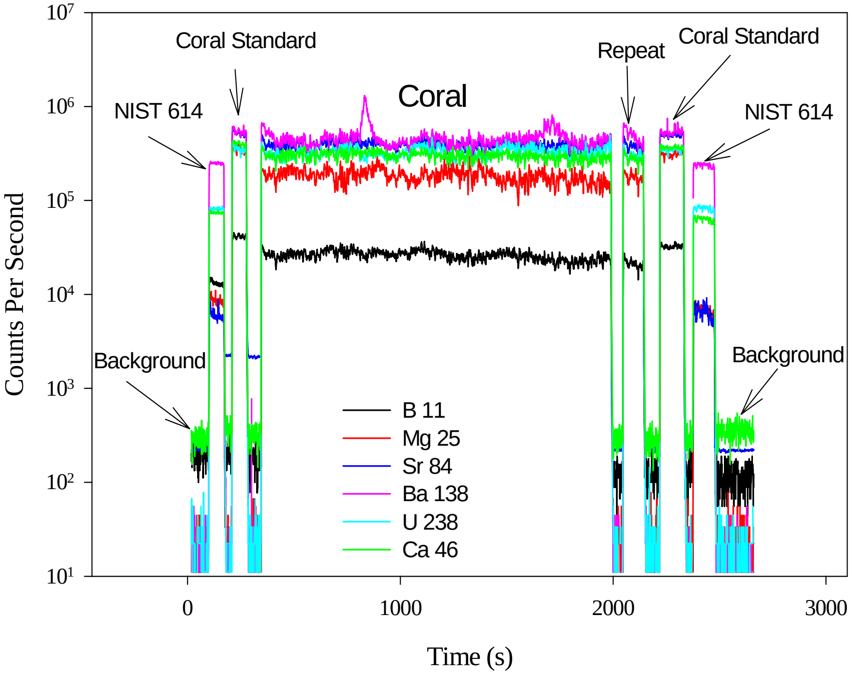
Laser Ablation-ICP-MS







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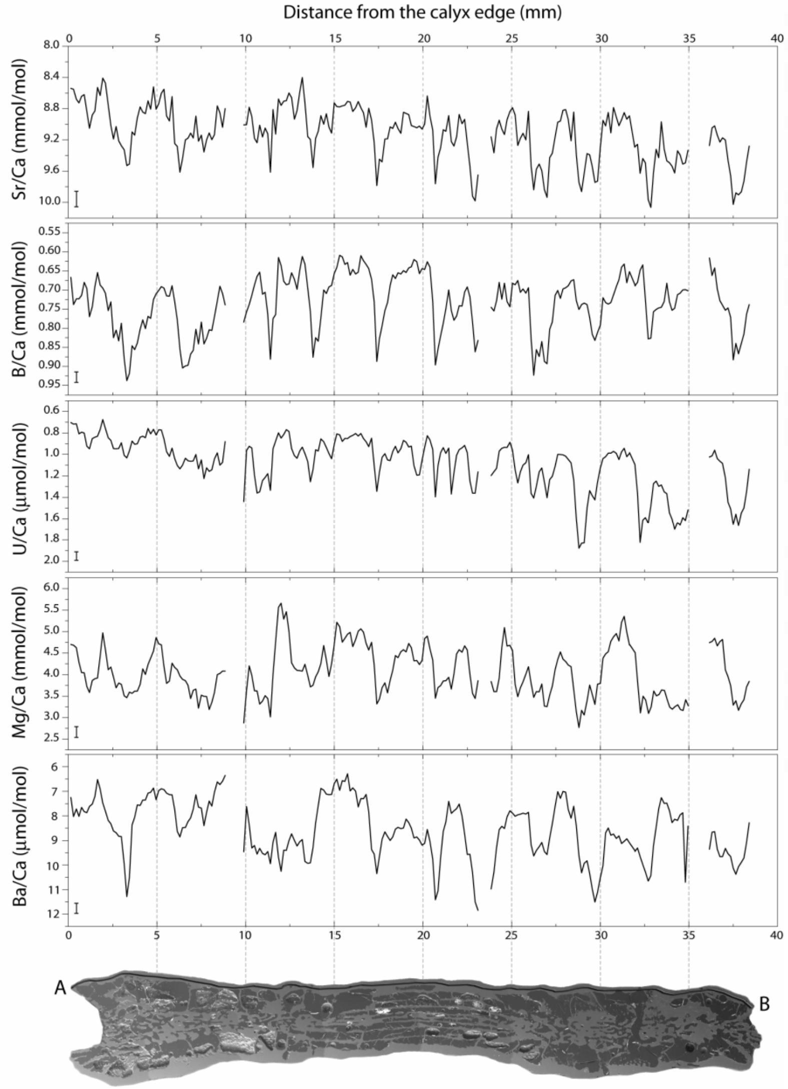
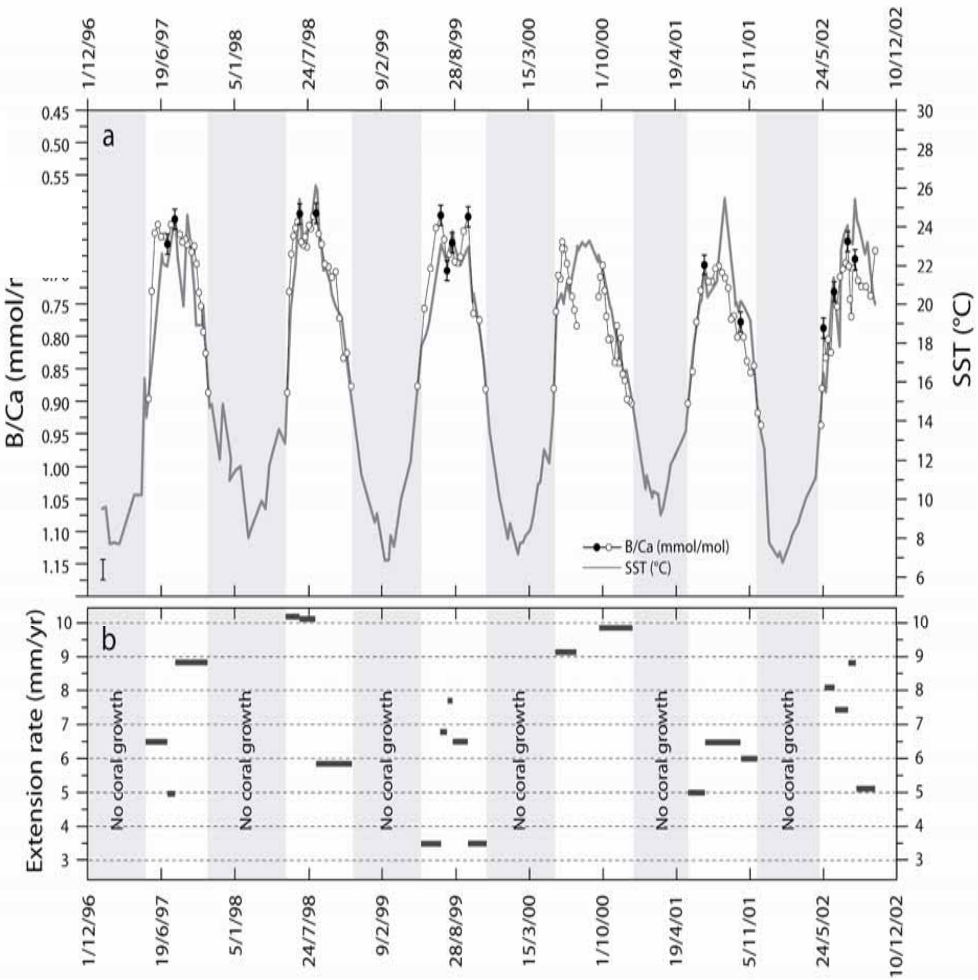
Trace elements

^{11}B, ^{25}Mg, ^{43}Ca, ^{84}Sr, ^{138}Ba, ^{238}U





B/Ca (mmol/mol) = 1.239 (±0.026) - 0.024 (± 0.001) SST (°C)

Pearson's r, 95% confidence interval –0.876 [-0.911; -0.819]

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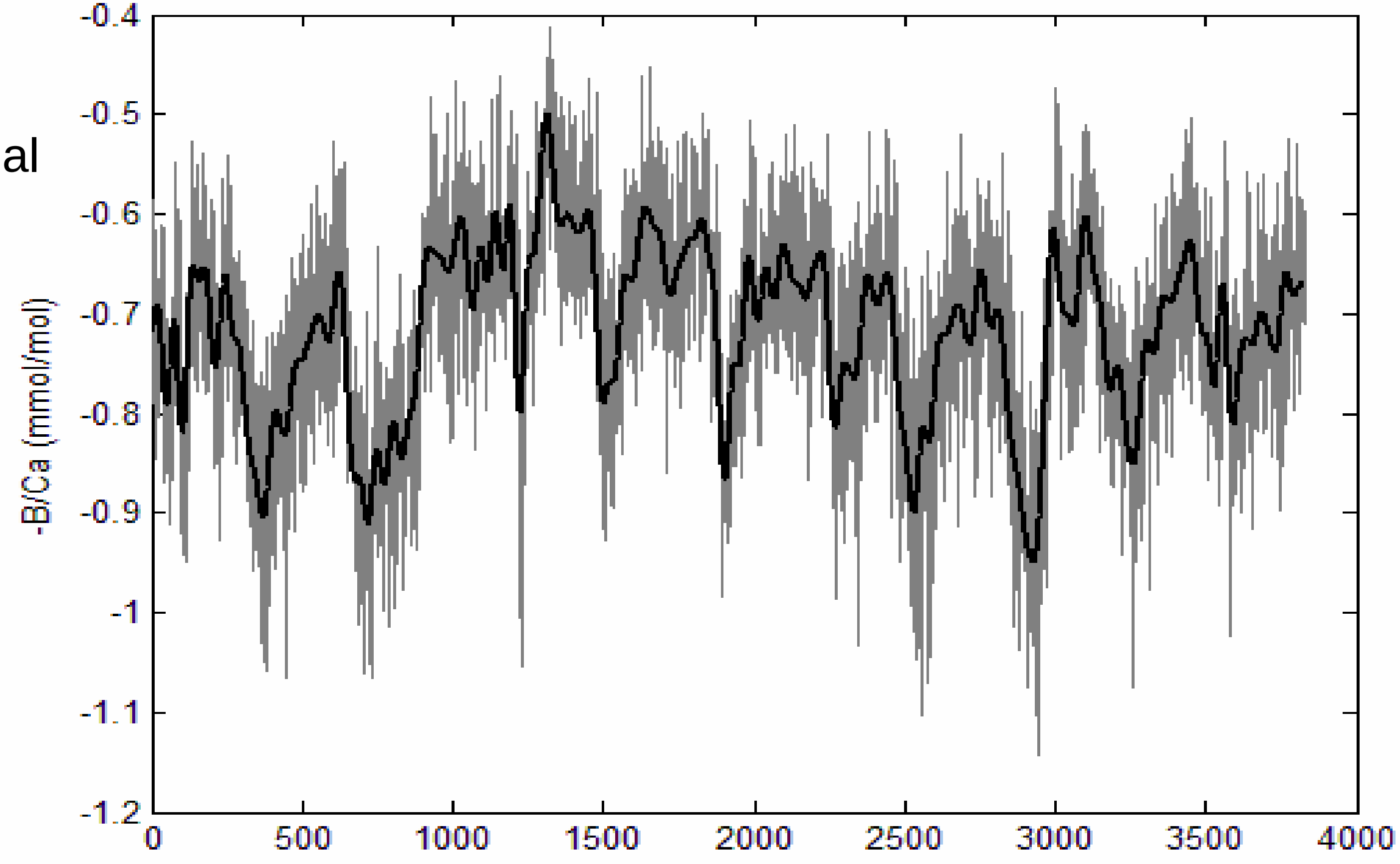
Data Filtering and Calibration

-Signal
-Smoothed signal
(Mann, 2004)



Mann, M. E. (2004), On smoothing potentially non stationary climate time series Geophys. Res. Lett. Vol.31,L07214, doi:10.1029/2004GL019569.

Johnson standardized signal B/Ca

$$z = \gamma + \delta \cdot g(\frac{x - \xi}{\lambda})$$

$$z = -0.533 + 0.6280 \cdot \log(\frac{y}{1 - y})$$

$$y = \frac{(-B / Ca + 0.918)}{0.329}$$

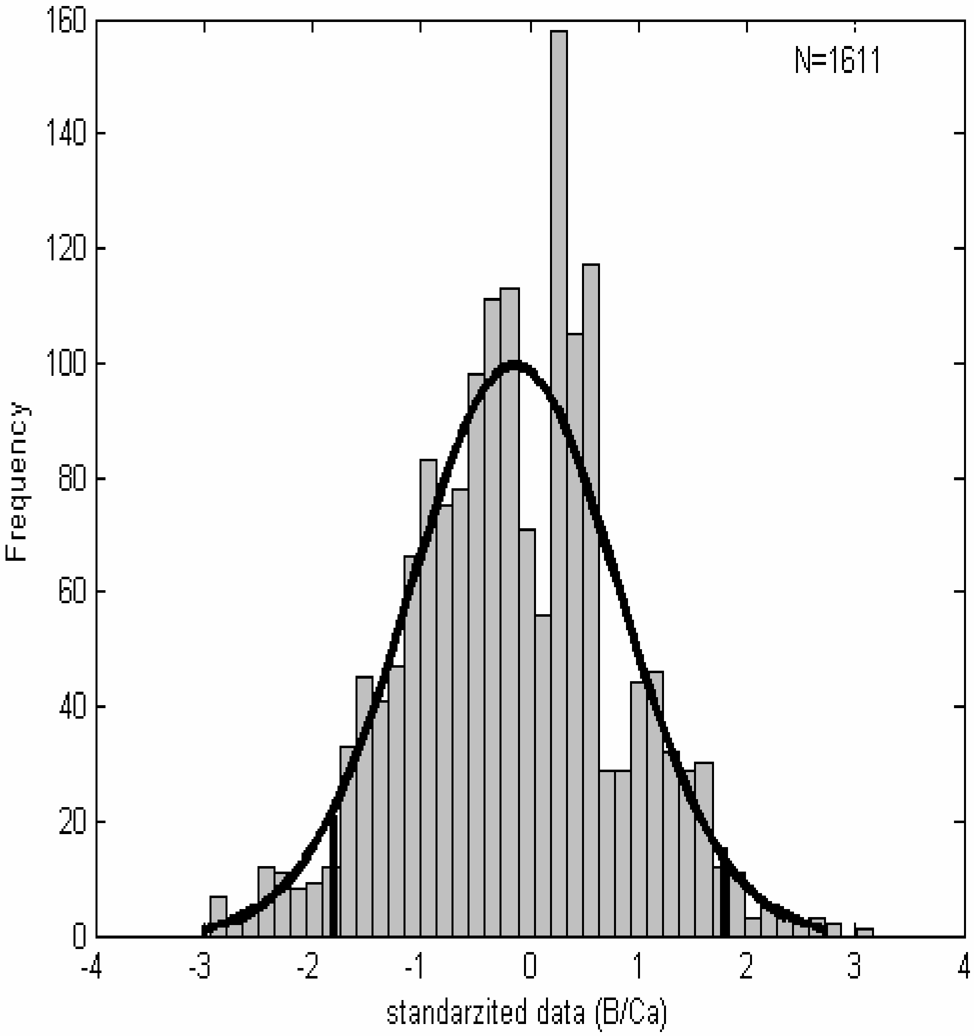
Johnson's Functions (*Giovanardi et.al.* 2006)

S_N (*normal family*) $g(y) = y;$

S_L (log−*normal family*) $g(y) = \ln(y);$

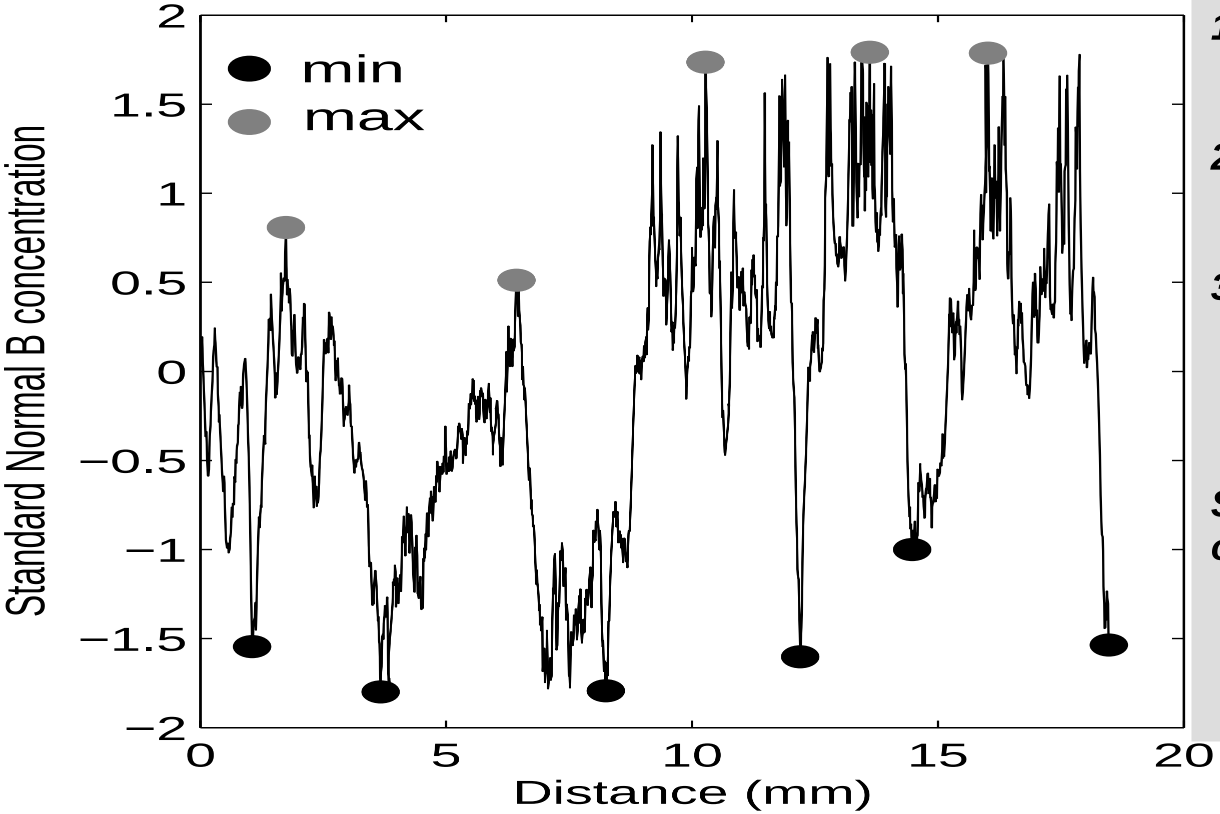
S_U (*unbounded family*) $g(y) = \ln[y + \sqrt{y^2 + 1}];$

S_B (*bounded family*) $g(y) = \ln\left(\frac{y}{1 - y}\right);$



Maximum, Minimun and Time Instances

To estimate the time instances, we start considering an average constant growth rate, where the time instances between the observations are constant.



1. ***dx=distance between two subsequent***
2. ***gr= is an average costant growth rate***
3. ***Ts=dx/gr is the time istances between these observations***

So the time istance at which the nth observation was formed is given by:

$$t_n = nT_s \qquad (T_s = 0.003 \text{ year})$$

Standard normal values for -[B] the 'o' indicate the maximum and minimum of the data series.

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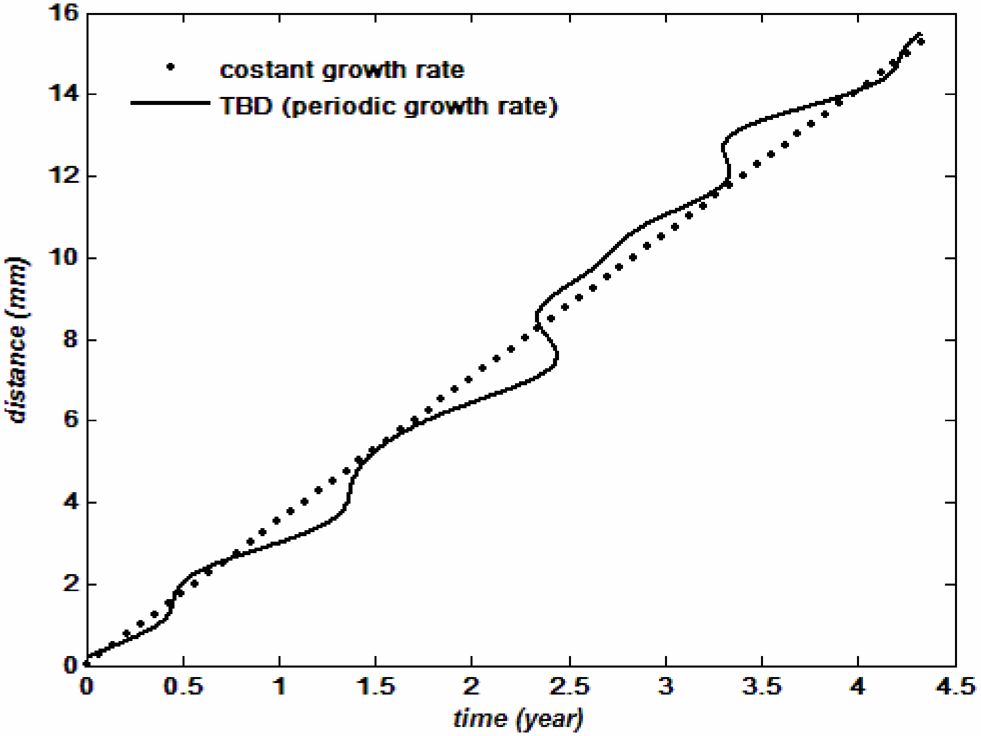
Conceptual Approach of the Time Base Distortion (TBD) Method

The time instance at which the n[th] observation was formed is given by:

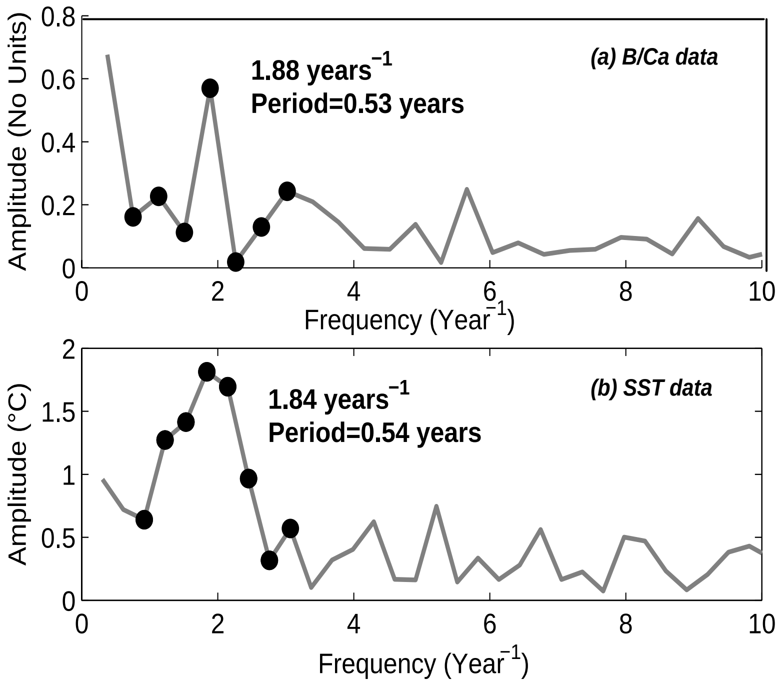
$t_n = nT_s$ **[*T_s=0.003 is the sample period (dimension is time)*]**

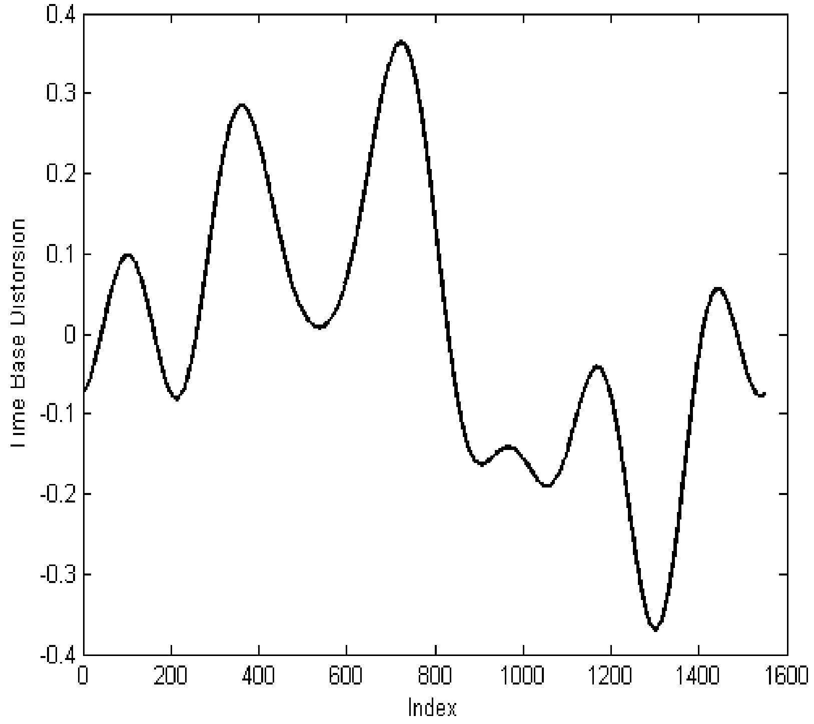
$t_n = nT_s + g(n)T_s$

where the first term is the constant time step and g(n) represents the time base distortion (TBD) at the observation position n (scalar quantity).



Spectrum in the frequency Domain



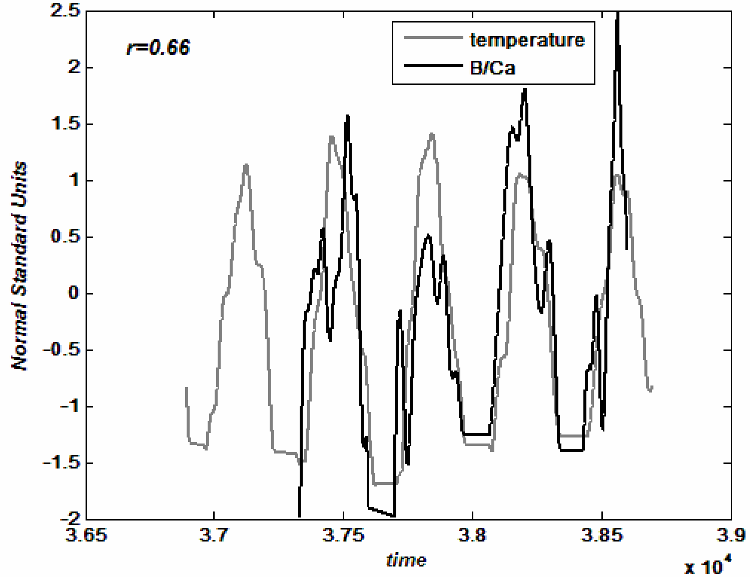


(a) Fourier spectrum of the B signal on the improved time grid;
(b) Fourier spectrum of the instrumental SST data

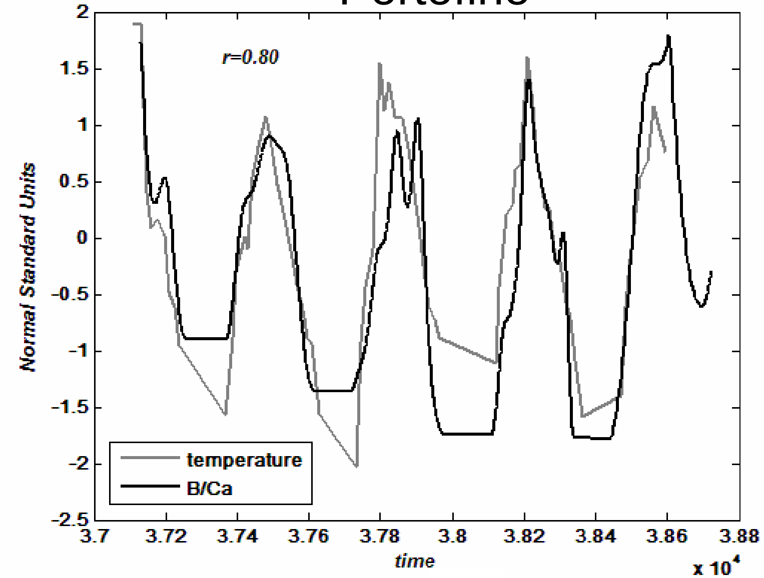
Time Base Distortion Function

Correlation coefficients (SST vs. B/Ca)

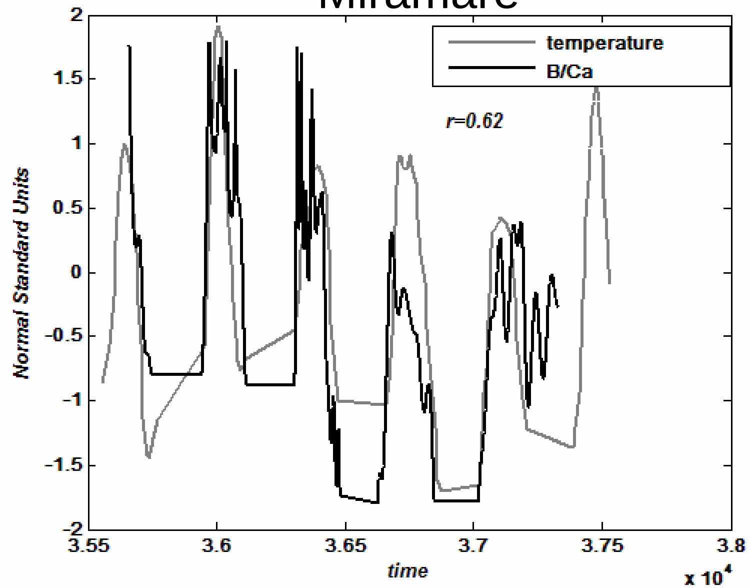
Taranto



Portofino



Miramare



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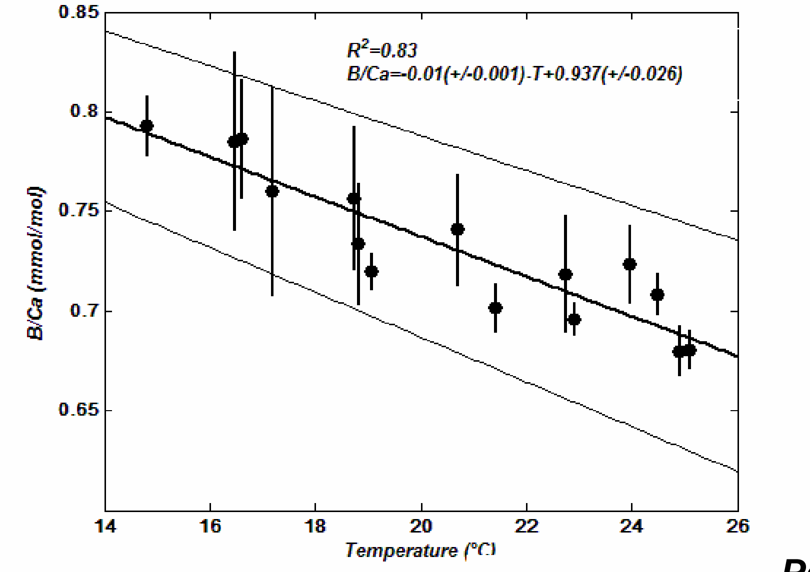
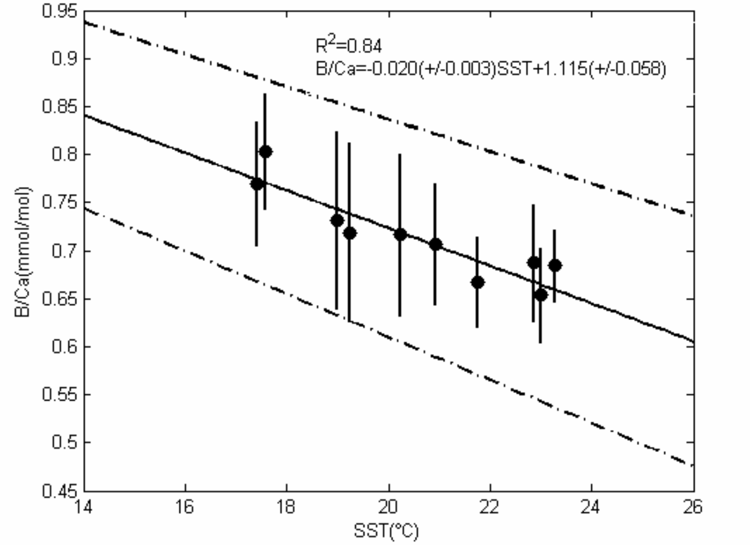
Calibration equations (B/Ca vs SST)

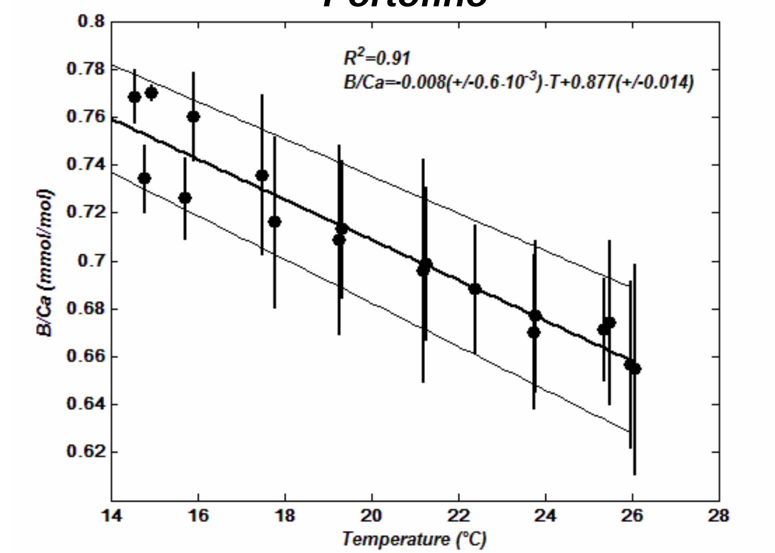
Taranto



Miramare

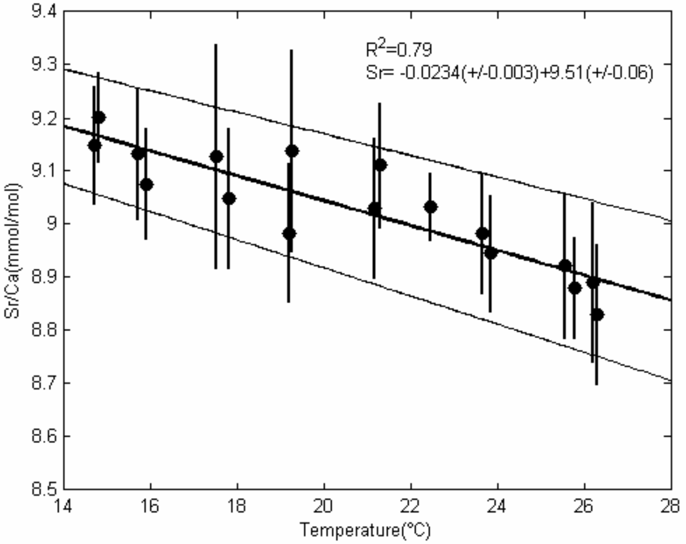


Portofino

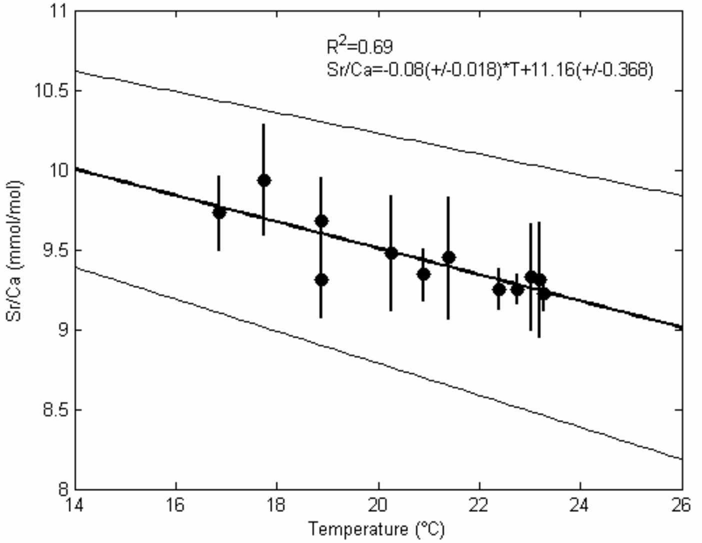


Calibration equations (Sr/Ca vs SST)

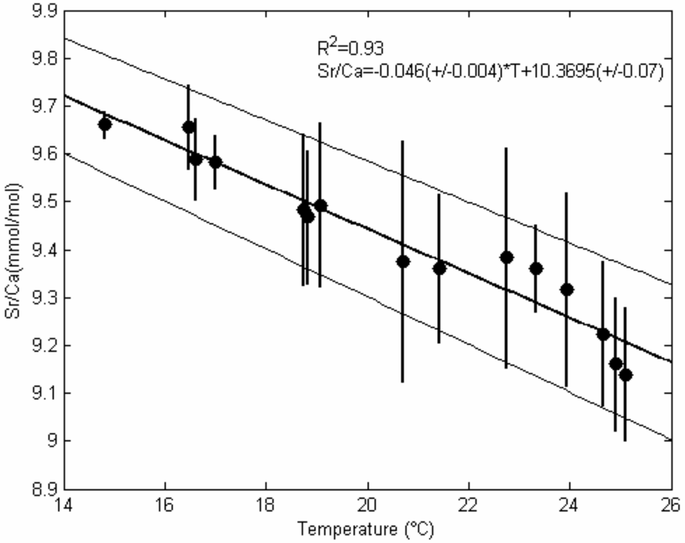
Taranto



Miramare



Portofino



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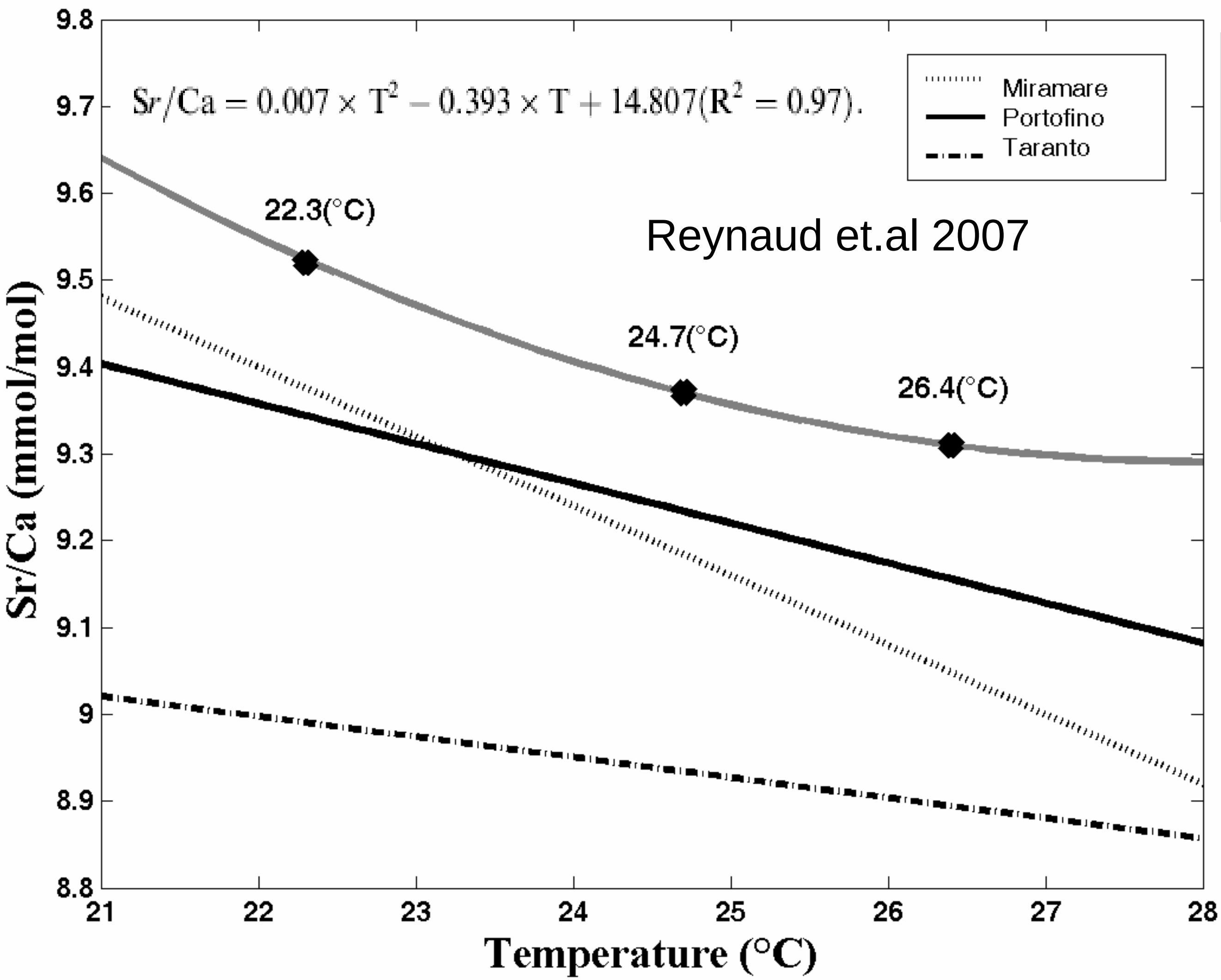
Comparison: Cladocora and Cultured Tropical Coral (Acropora)

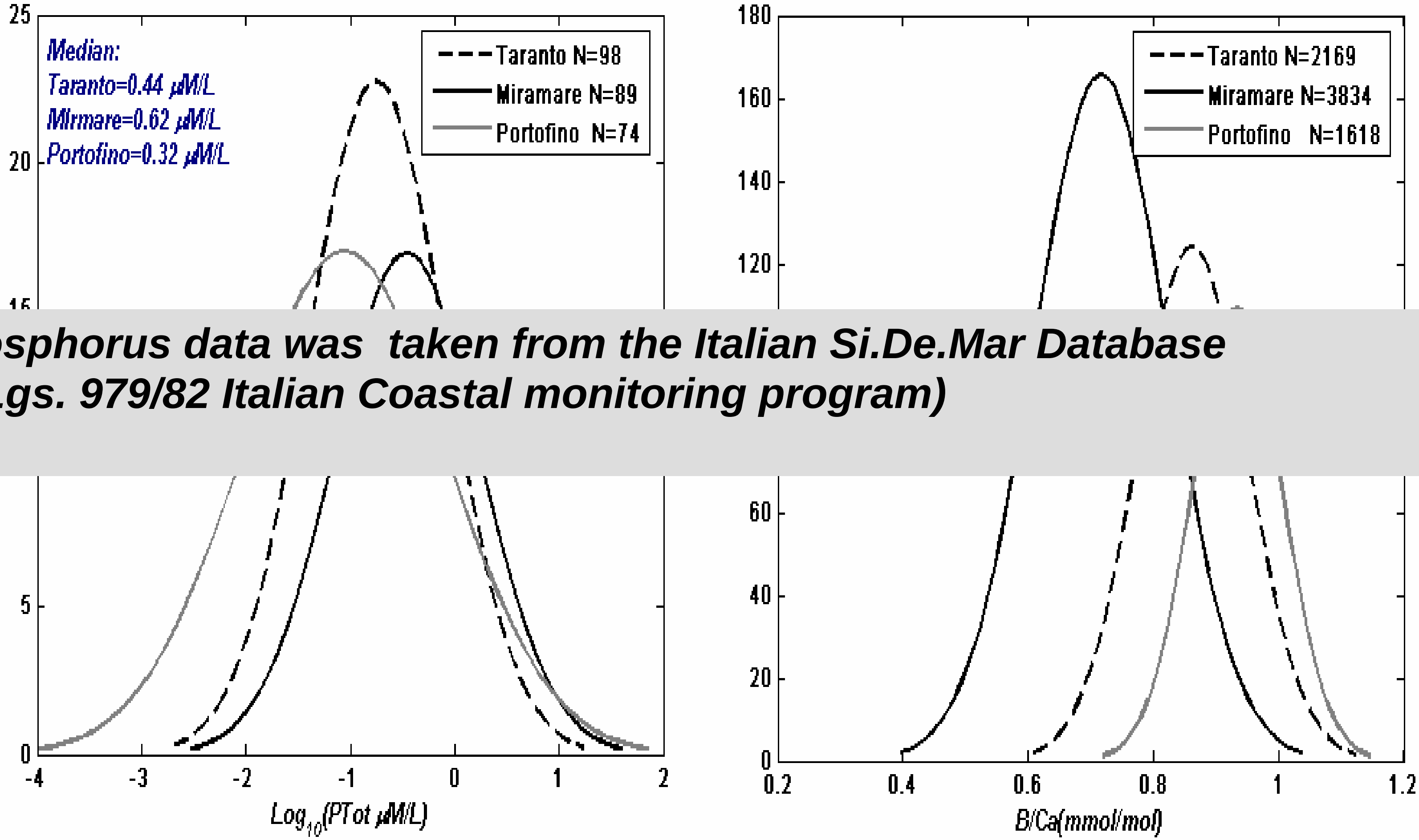


- Miramare (Tmax=25°C)
- Portofino (Tmax=27 °C)
- Taranto (Tmax=28 °C)

Thank you

Phophate and Growth Rate Inhibition

A number of phosfate compounds have been found to inhibit crystal growth (Morse, 1983; SimKiss, 1964)



Phosphorus data was taken from the Italian Si.De.Mar Database (D.Lgs. 979/82 Italian Coastal monitoring program)

MorseJ. W. (1983) The Kinetics of Calcium Carbonate Dissolution and Precipitation. In Carbonates : Mineralogy and Chemistry, Vol. 11, pp 227-264. Mineralogical Society of America.

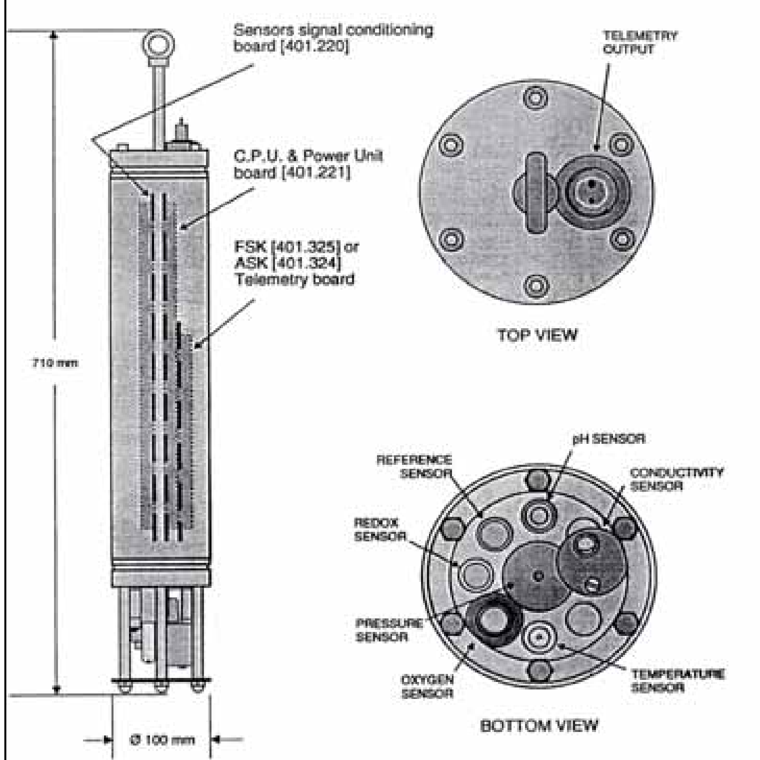
Simkiss K. 1964 Phosphates as crystal poison of calcification. Biological Rewiew 39, 487-505

In situ measurements: CTD Probe

Real Time data acquisition

CTD scheme

Conducticity (Salinity)
Temperature
Pressure(Depth)



Buoy system

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Summary

- *Why study corals in the Mediterranean Sea?*
- *The non-Tropical coral Cladocora caespitosa*
- *Sampling and Methods*
- *Data filtering and Calibration*
- *Comparison and Results*
- *Conclusions and Future Work*

Corals as Paleoclimate archives

- Coral Calcification

$$Ca^{2+} + CO_3^{2-} \underset{k2}{\overset{k1}{\rightleftharpoons}} CaCO_3$$

$$Sr^{2+} + CO_3^{2-} \underset{k4}{\overset{k3}{\rightleftharpoons}} SrCO_3$$

Equilibrium

$-daCa^{2+}/dt = daCaCO_3/dt$

$-daSr^{2+}/dt = daSrCO_3/dt$

If the crystal growth is very slow, then the trace element partitioning in the crystal approximates that of equilibrium

Equilibrium Distribution Coefficient:

$$D = \left(\frac{K3 \cdot K2}{K4 \cdot K1}\right) \cdot \left(\frac{\gamma_{Sr^{2+}} \cdot f_{Ca^{2+}_{(aragonite)}}}{\gamma_{Ca^{2+}} \cdot f_{Sr^{2+}_{(aragonite)}}}\right)$$