THROUGHFLOW

ESR - Meeting at Granada,
24th and 25th November 2011

Overview of Preliminary Results
($^{87}Sr/^{86}Sr$, Trace Element Analysis, XRD),
Outlook on Upcoming Analysis and Intended Aims

Critical look on the Major Obstacle: Diagenesis

Content

1. Preliminary Results of Strontium Isotope Analysis (samples from Bontang and Samarinda – NTA2)

2. Tridacnidae Shells – promising paleoclimatic archives

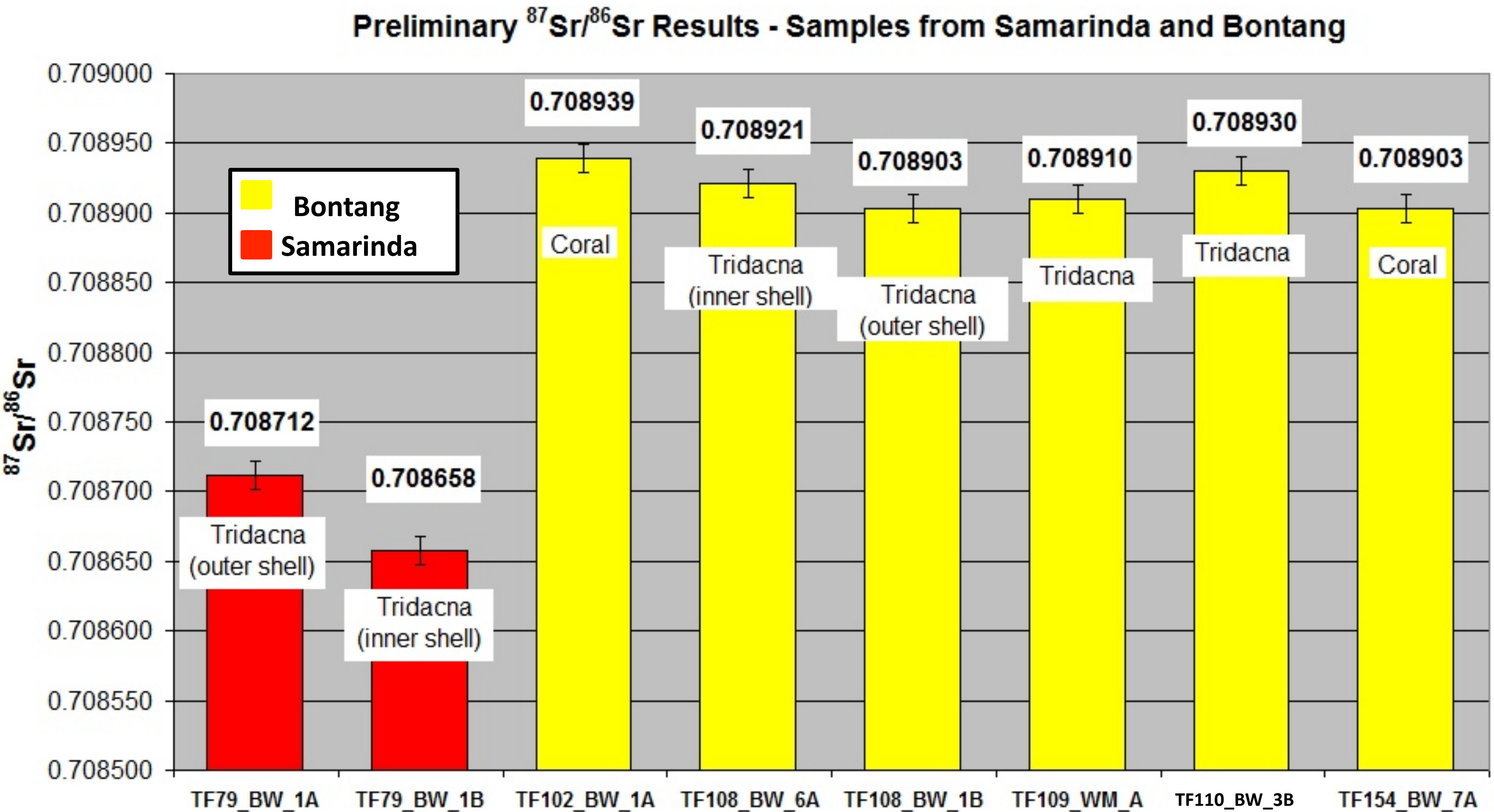
3. Detailed XRD analysis applied on 3 Tridacnidae – Outlook on SEM analysis (Example study of Faylona et al., 2011)

4. Preliminary results of LA-ICPMS
   - Indicators for Diagenesis
   - Paleoclimatic/Paleoenvironmental Proxies

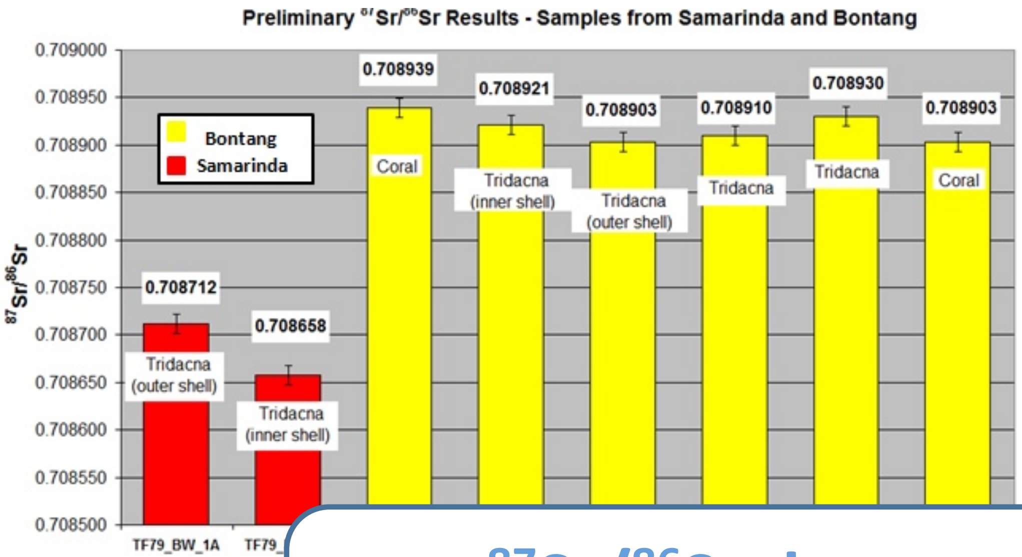
   (Exemplary study of Elliot et al., 2009 & Batenburg et al., 2011)

1. Preliminary Results of Strontium Isotope Analyses

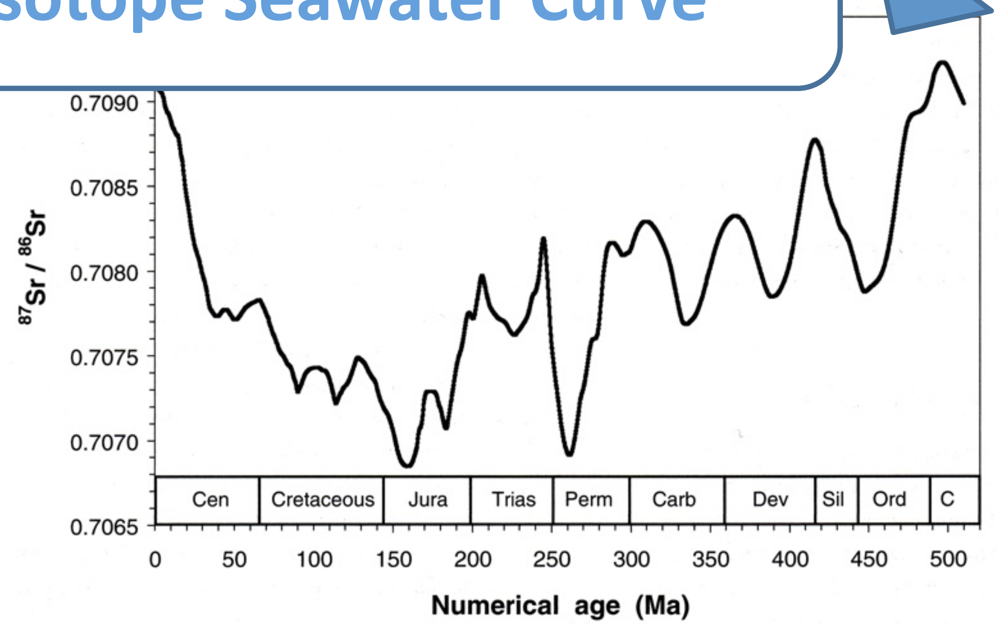
Preliminary Strontium Isotope Results



How can we obtain ages from these data?

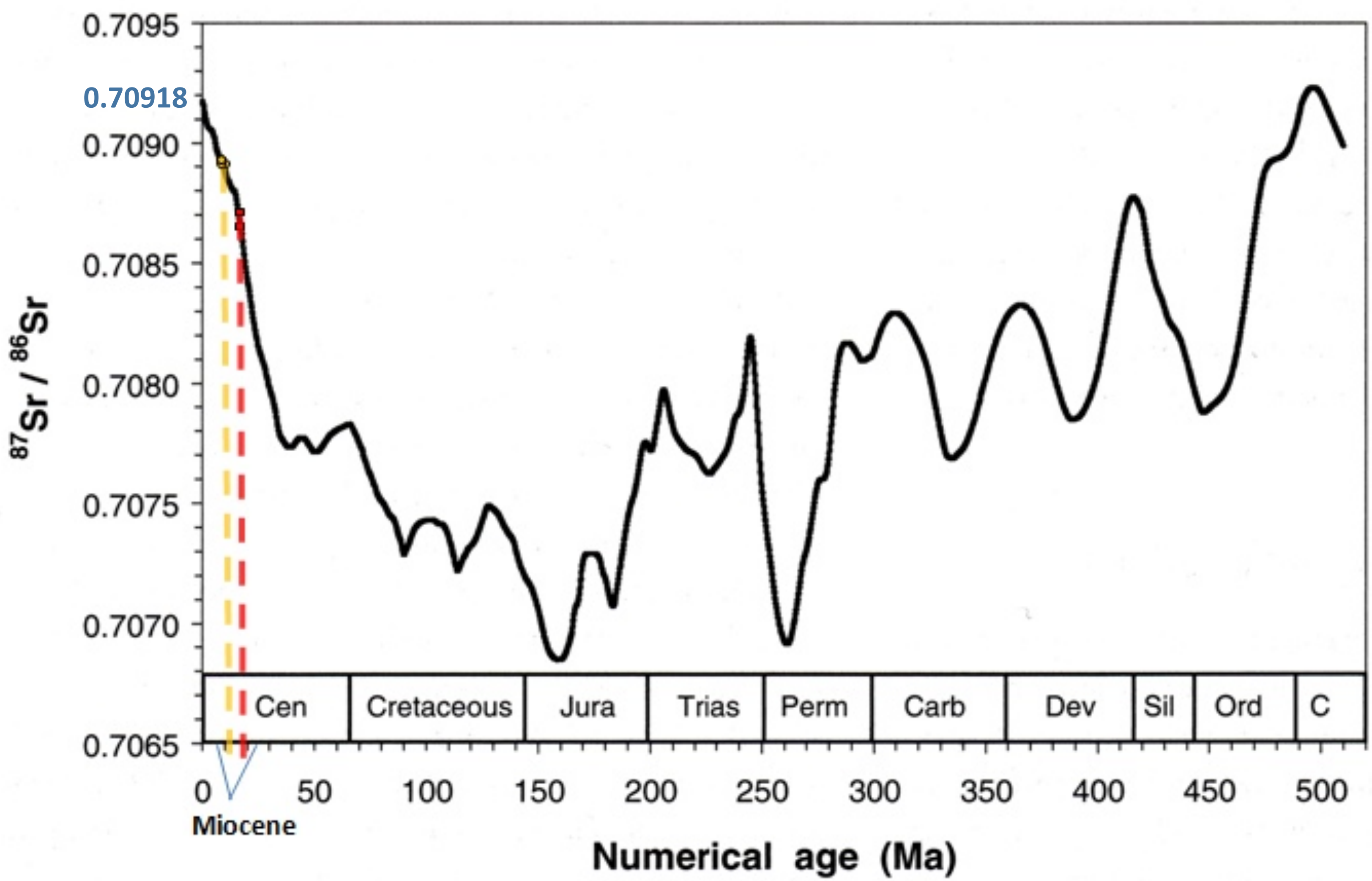


$^{87}Sr/^{86}Sr$ data transferred to Strontium Isotope Seawater Curve



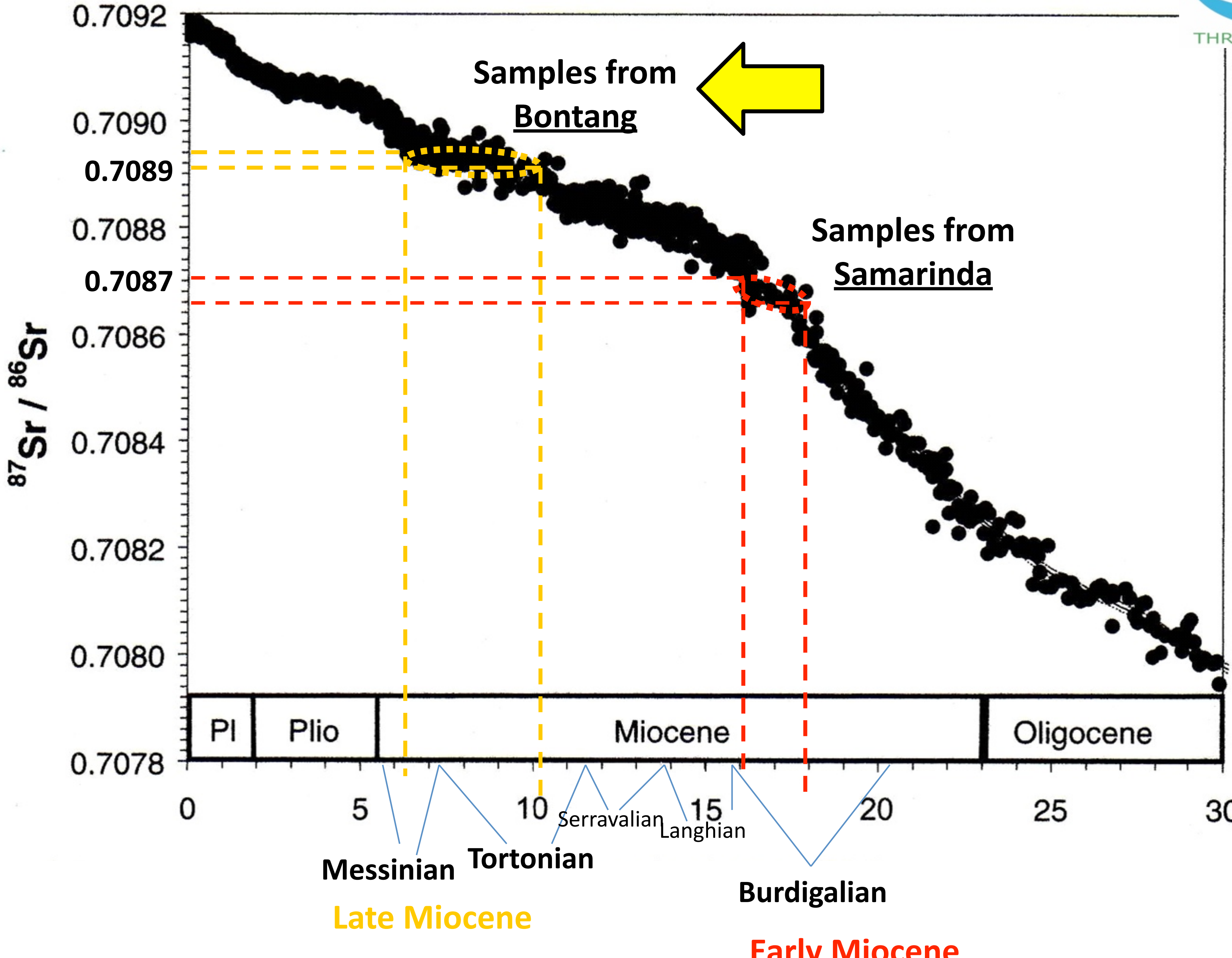
Variation of $^{87}Sr/^{86}Sr$ through the Phanerozoic time after Mc. Arthur and Howarth (2004).

Strontium Isotope Stratigraphy (SIS)



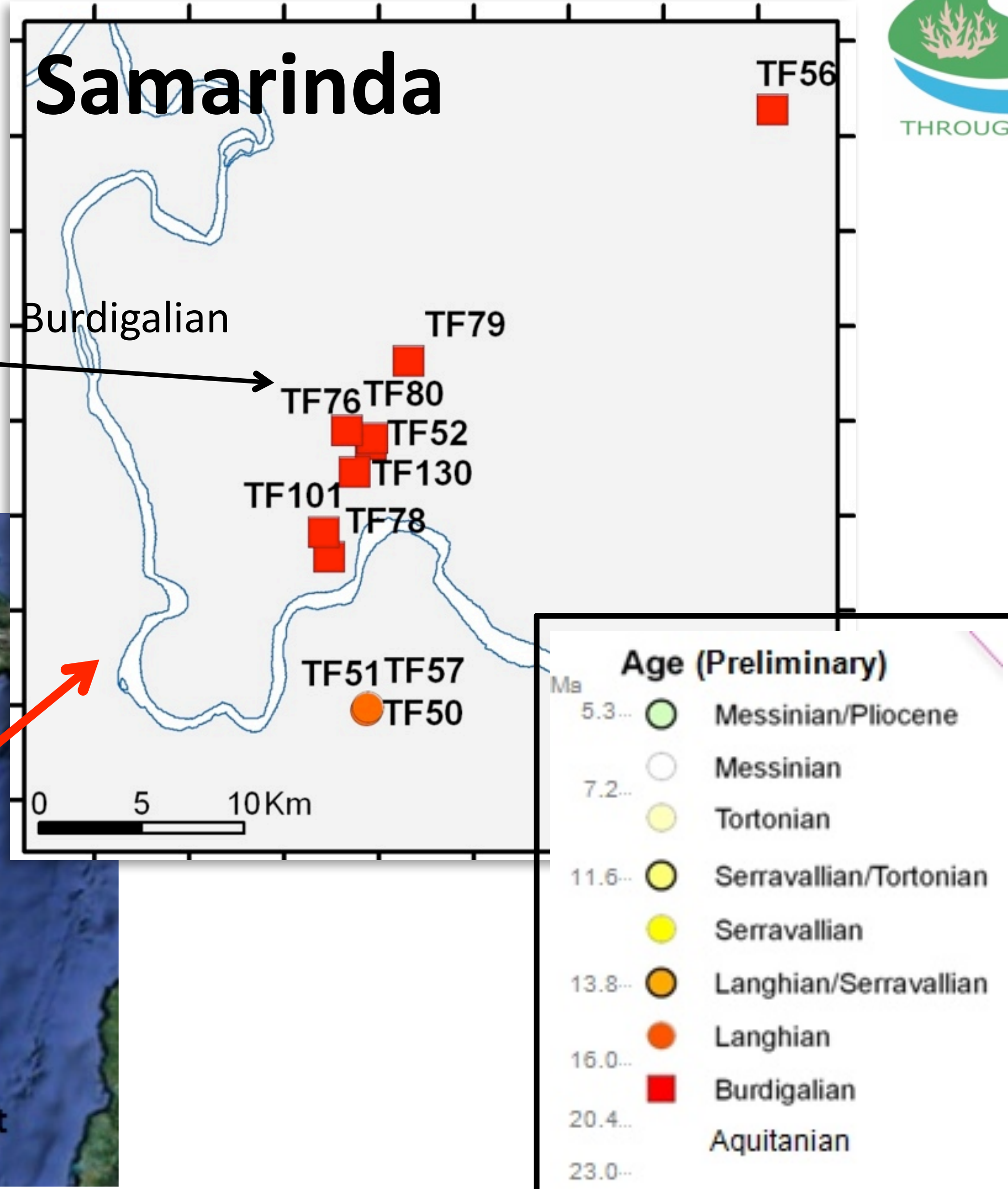
Variation of $^{87}Sr/^{86}Sr$ through the Phanerozoic time after Mc. Arthur and Howarth (2004).

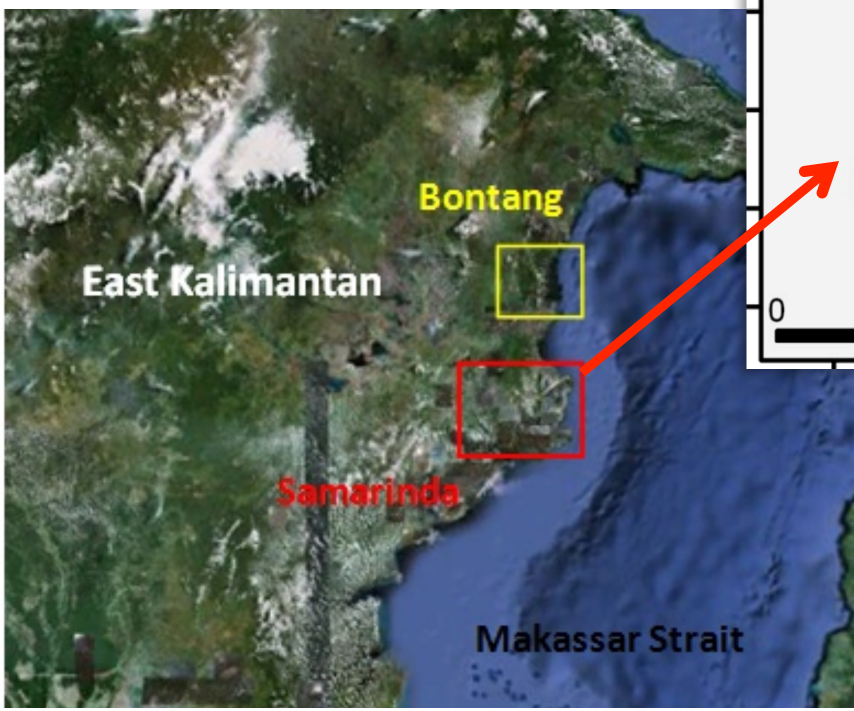
Strontium Isotope Stratigraphy (SIS)



Comparison with estimated ages obtained from Biostratigraphy

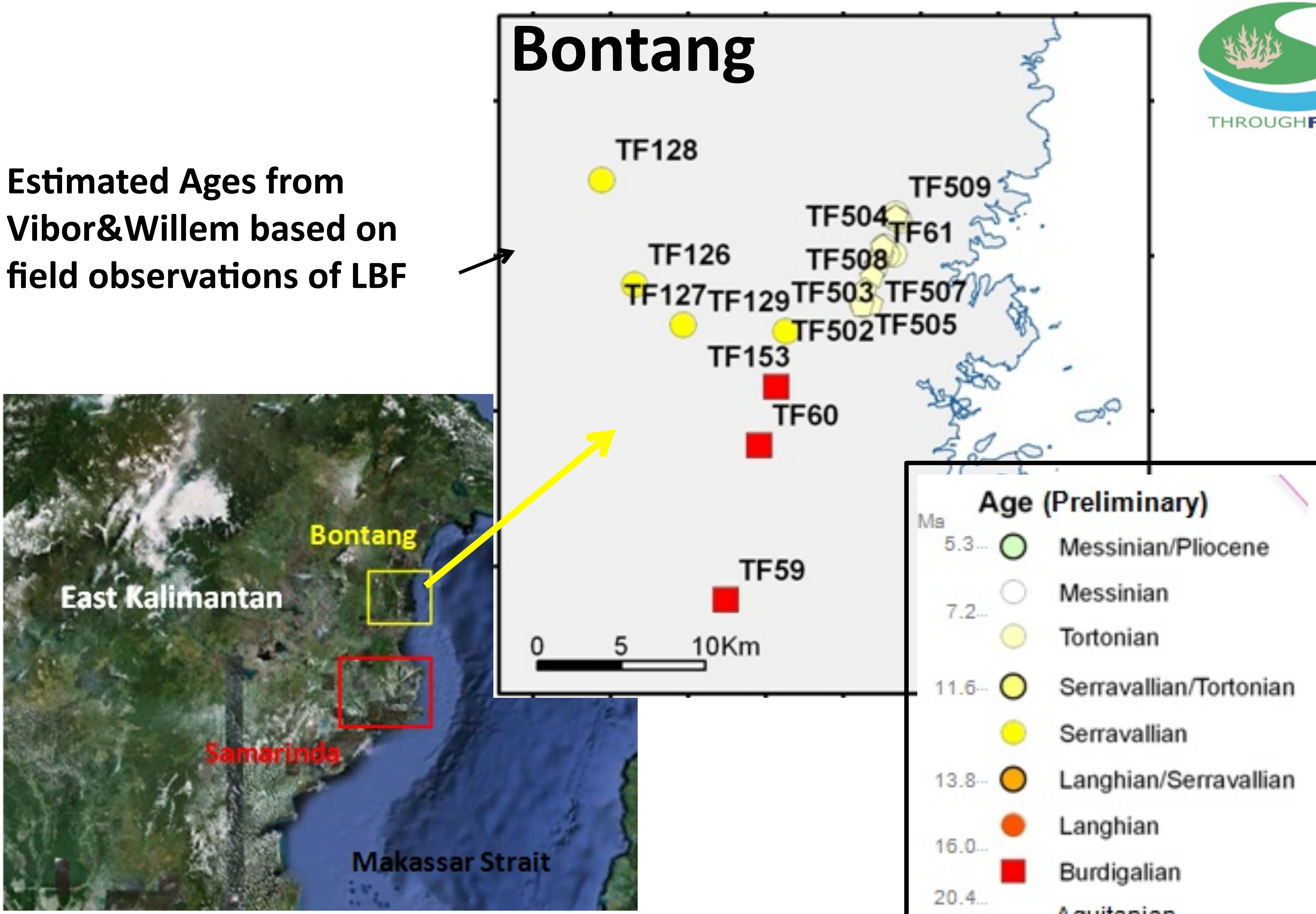
Estimated Ages from Vibor&Willem based on field observations of LBF





Ages SIS: **Burdigalian**

Estimated Ages from Vibor&Willem based on field observations of LBF



Ages SIS: Messinian - Tortonian

2. Tridacnidae shells – promising paleoclimatic archives

Advantages of giant clams:

- **Dense shell structure** (e.g. Aharon & Chappell, 1986) more resistant to diagenetic processes

- **Geochemical composition** of the shell might be **well preserved** through time

- Large shells may provide opportunity for **Paleoenvironmental studies over larger time periods** (*Tridacna gigas* largest bivalve species, believed to live up to 100 years and has very large shells of up to 1 m in length (Rosewater, 1965) – average growth rate: 1cm/a)

- **Visible growth bands** allow high resolution sampling and age control – **Sclerochronology**

2. Results of detailed XRD analysis

THROUGHFLOW

Same slide used for both XRD- and LA-ICPMS analysis

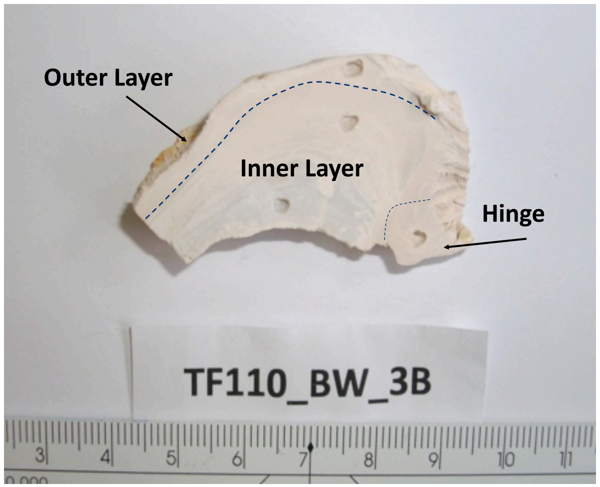
LA-ICPMS

XRD

X-Ray Diffraction (XRD) Analysis

Macroscopically visible - different states of preservation.

Appears to be **best preserved**



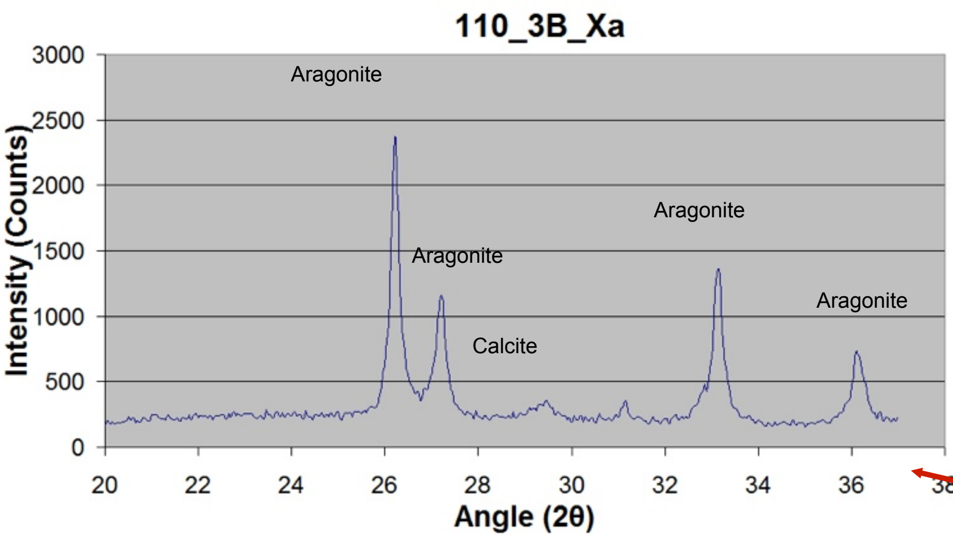
Bioerosion (Micro - boring activity)

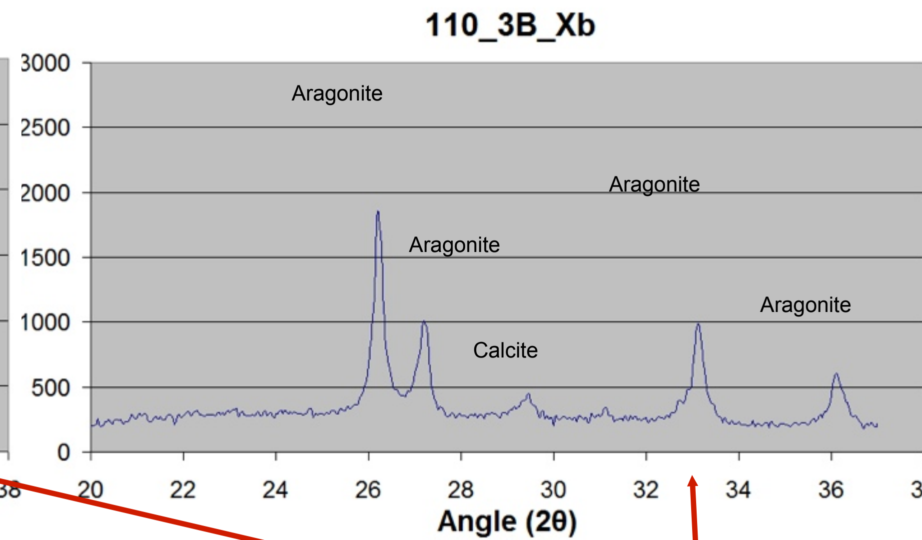
darker colour- expectation **Calcite**

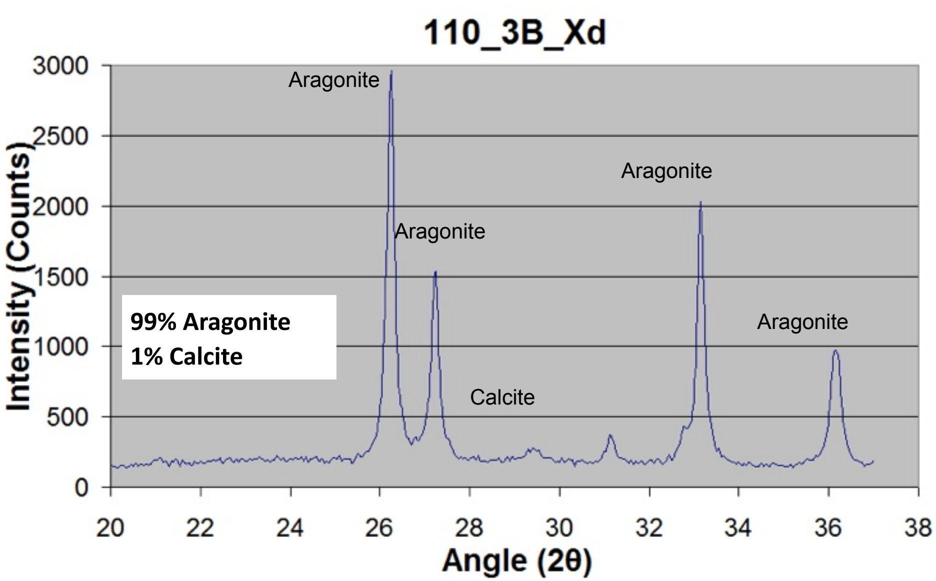
Sample points from different shell areas/distinct growth zones (inner layer, outer layer, hinge)

- **Intrashell deviations of the preservation ?**
- **Areas of best preservation?**

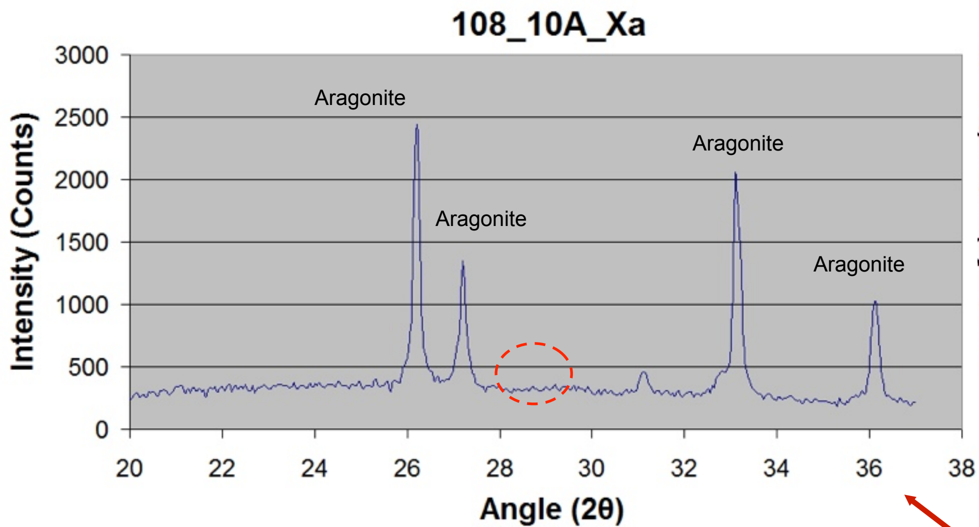
Results of XRD-Analysis

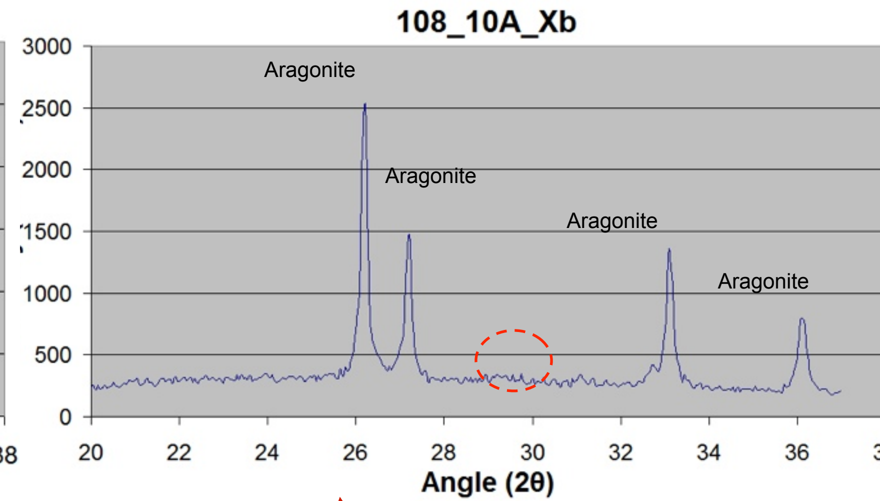


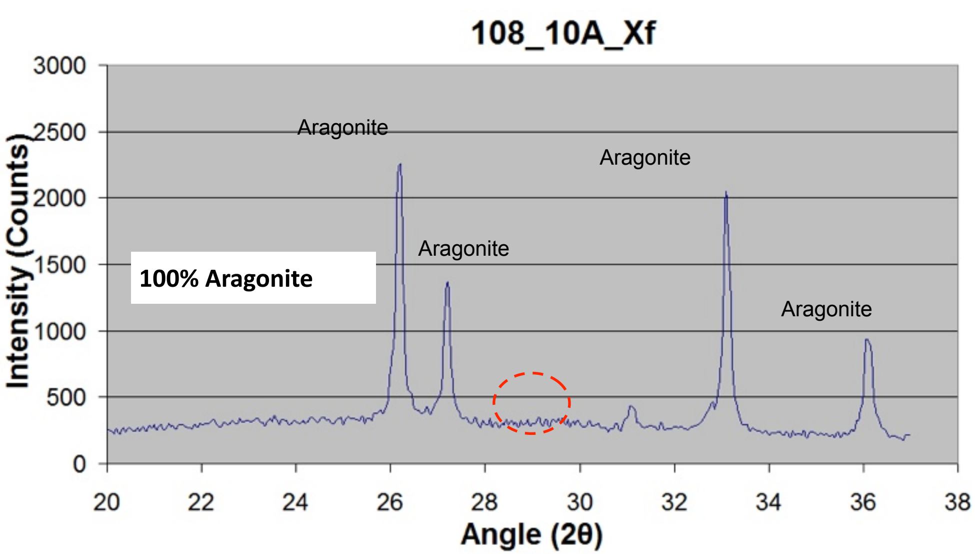


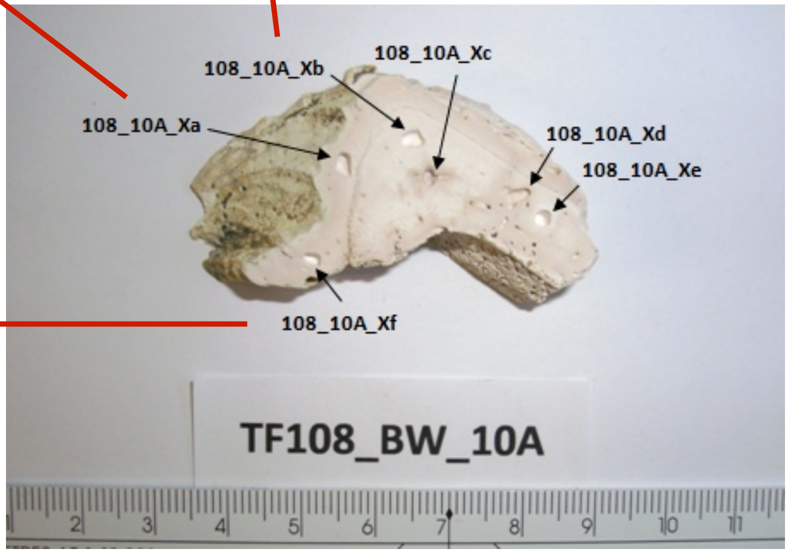


Results of XRD-Analysis

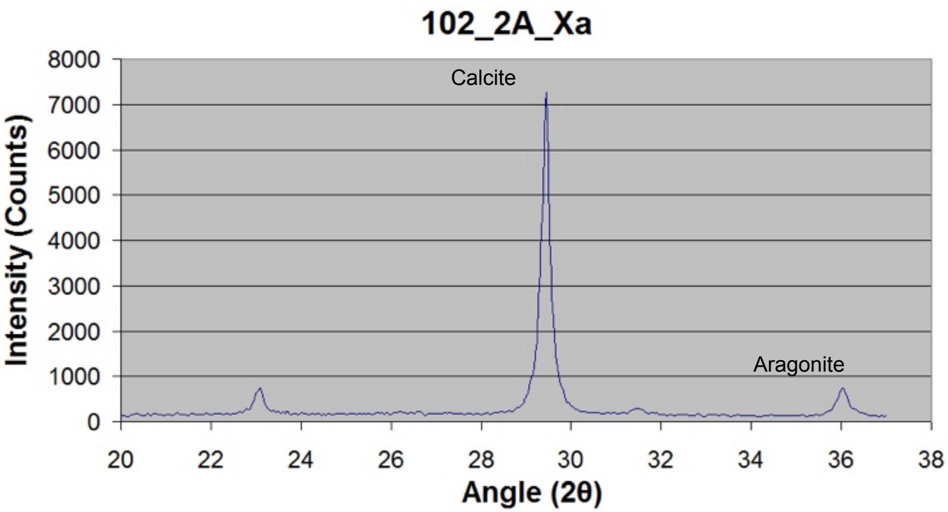


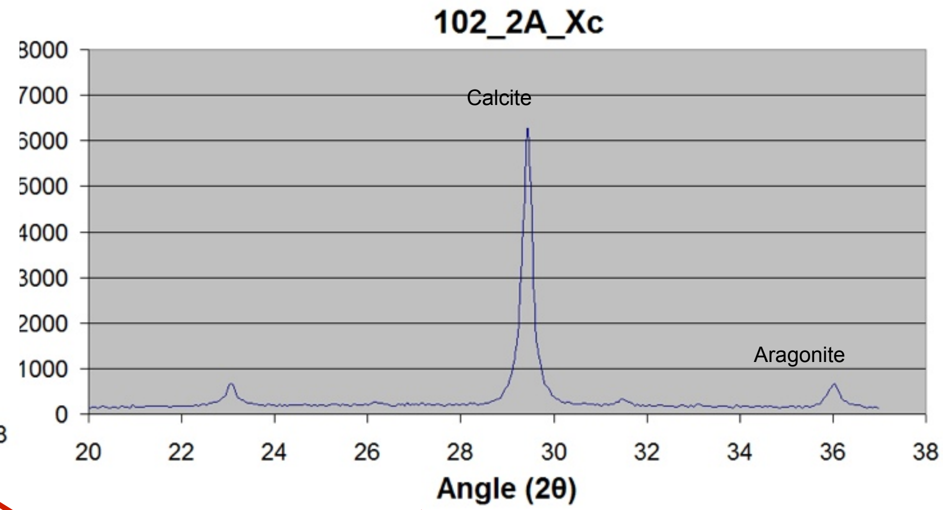


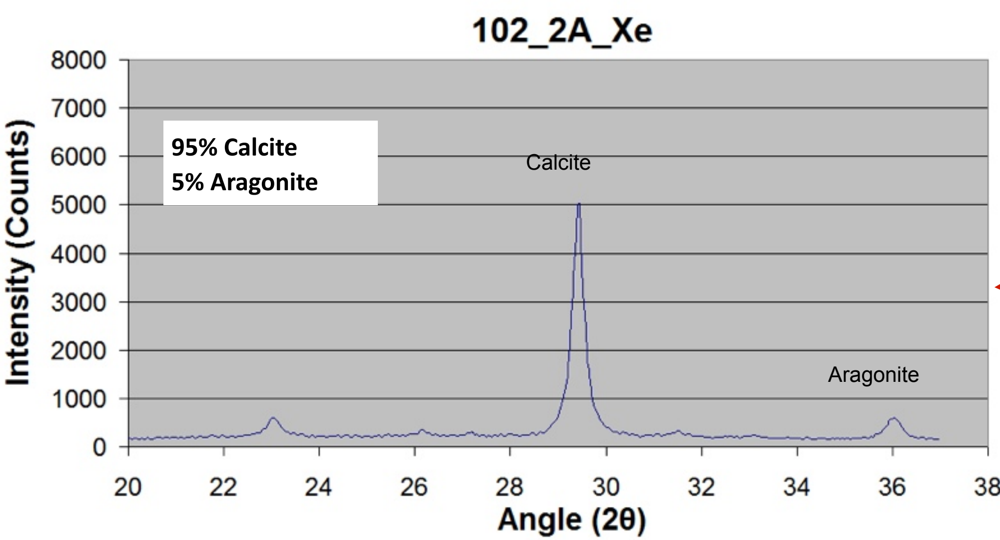


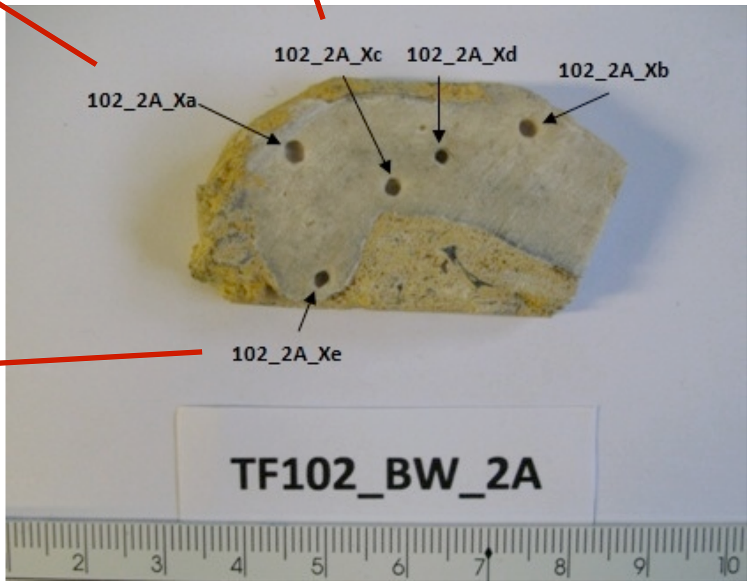


Results of XRD-Analysis



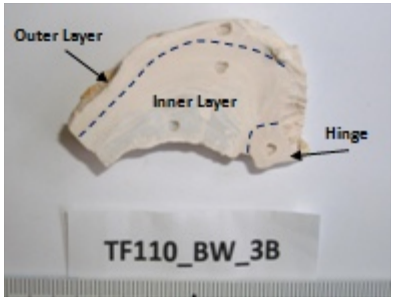






Results:

The apparently best preserved sample is not as good as expected



Sample with bioerosion might partly nevertheless be suitable as paleoclimate archive (microstrustural analysis required)

No significant intrashell variability detectable using XRD

darker coloured sample: XRD confirms first suspicion – strong recrystallization

Calcite

XRD analysis

- **Provides first information about preservation state** of the shell
- Allows **quantitative estimates of aragonite and calcite concentration.**

Enables to make a decision for further preparation strategy

Important selection criteria whether a sample is worth/ suitable for further analysis or not.

But

XRD-analysis are not sufficient to

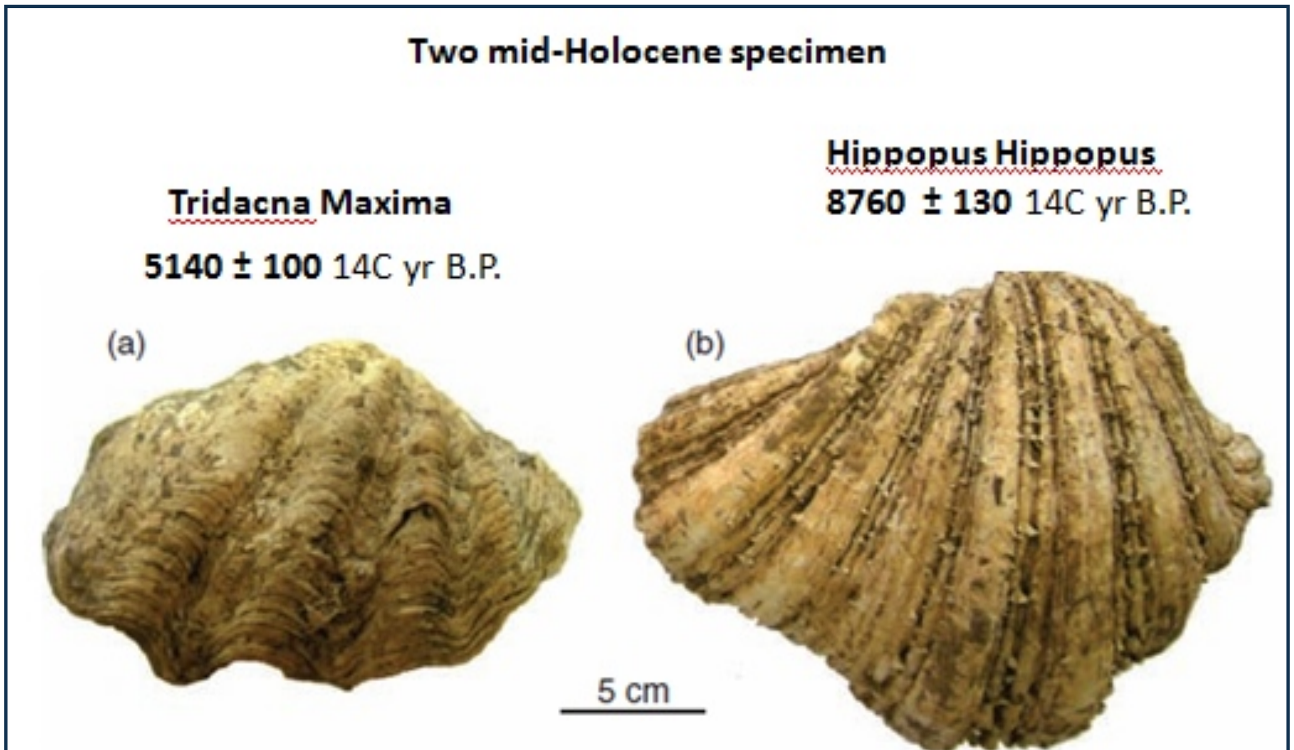
- Distingish between primary aragonite/secondary aragonite
- Resolve mineralogical structure and composition of the shell on a microscopic scale

Supplementary SEM Analysis necessary

Faylona et al., 2011:

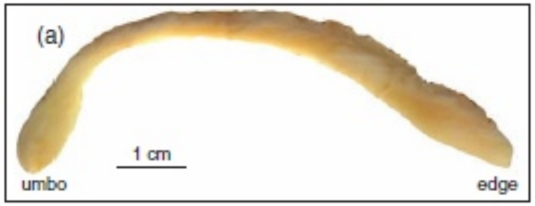
“Preliminary Study on the Preservation of Giant Clam (Tridacnidae) Shells

fromthe Balobok Rockshelter Archaeological Site, South Philippines”



Fourier transform infrared spectroscopy (FTIR)

Tridacna maxima

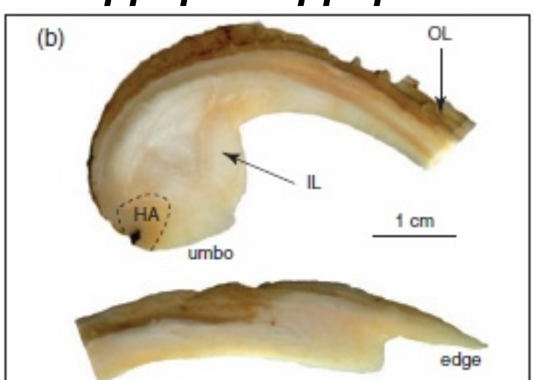


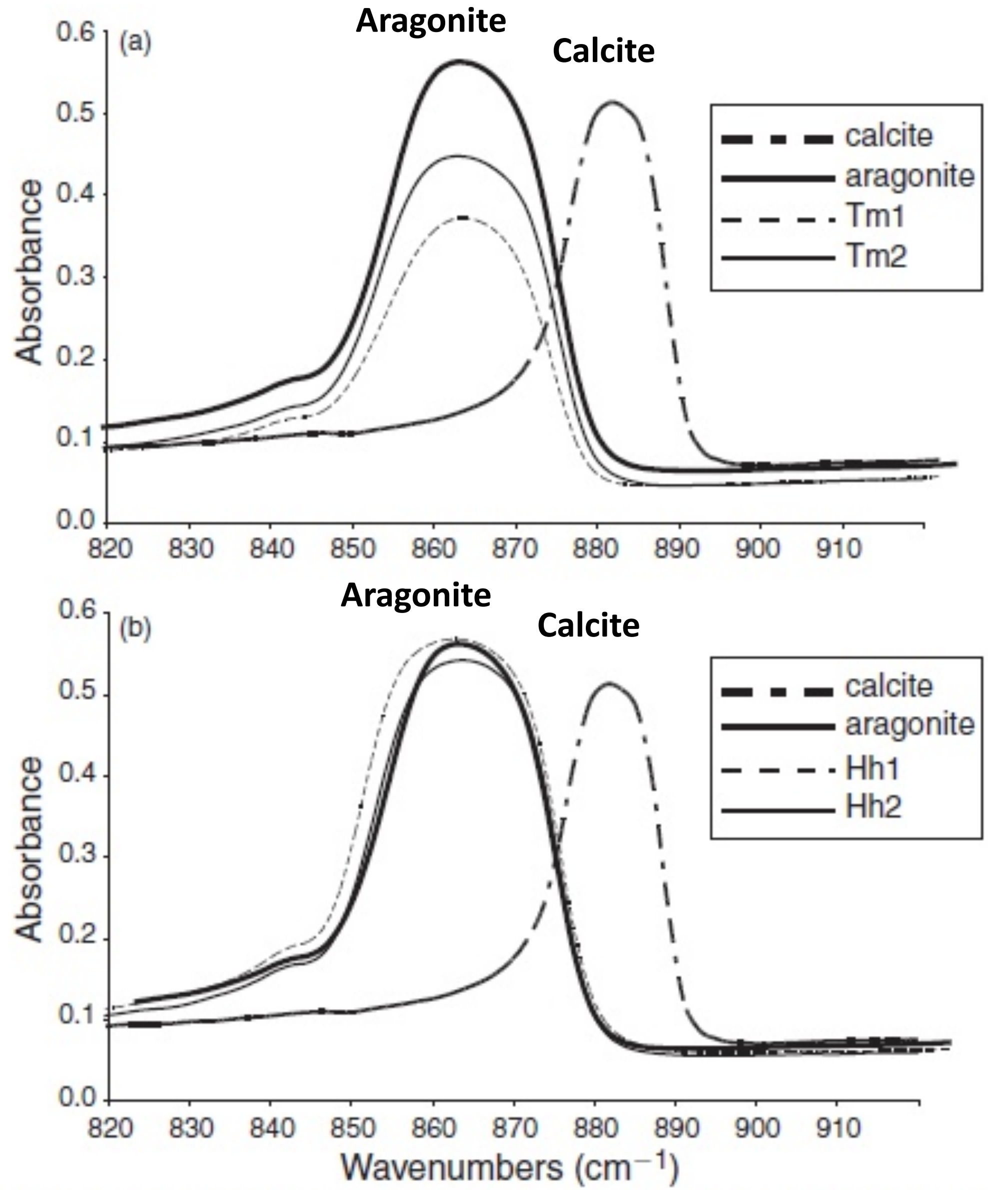
Results:

All spectra obtained on the two shells are **characteristic of aragonite**.

➡**original aragonite mineralogy has been preserved**

Hippopus hippopus





Some basics of the Tridacnidae shell structure:

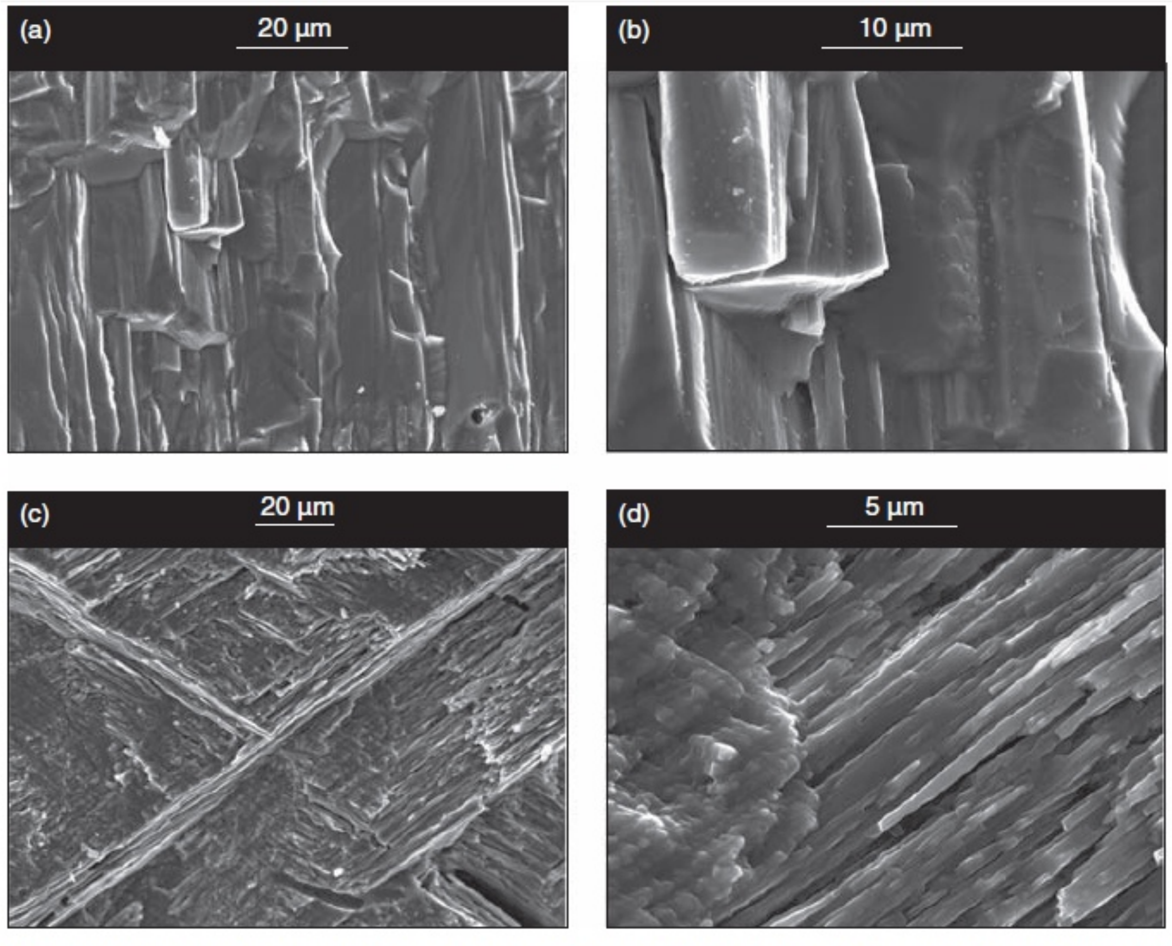
The shell of Tridacnidae is aragonitic with 2 types of microstructures:

Inner Layer : prismatic

Single prisms:
~200 µm long&10µm wide,
well-defined limits,
all oriented in the same direction

Outer Layer & Hinge: crossed-lamellar

elongated crystals, oriented in two main directions, crossing subunits

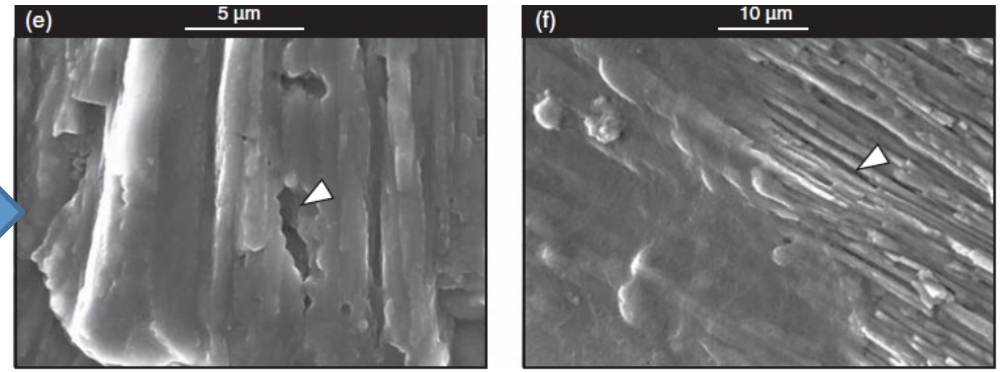


Results of SEM-analysis of a **modern Hippopous hippopus (analysed by Aubert et al., 2007)**

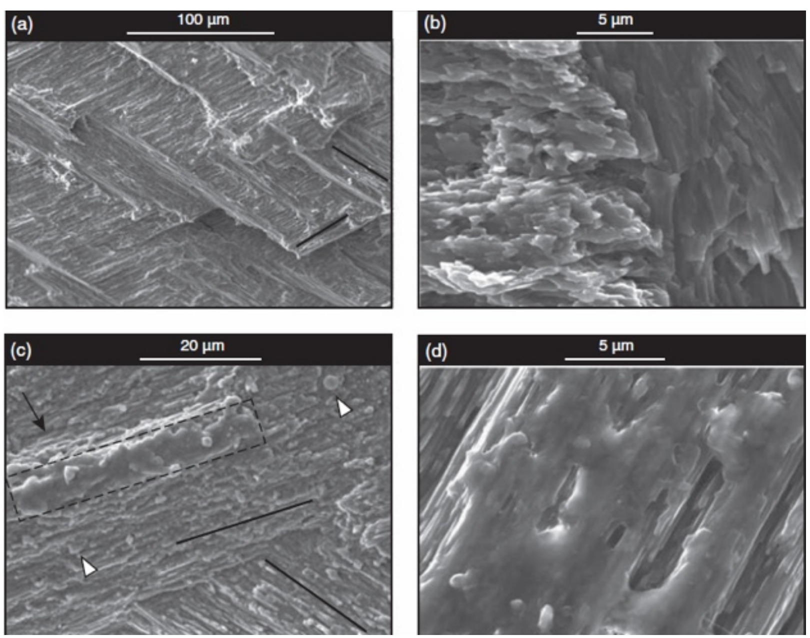
Inner layer (*Hippopus hippopus*)

Prismatic structure of inner layer is strongly transformed.

Dissolution and "melted-like" features.



Outer layer (*Tridacna maxima*)



two directions of the shell's micro-structure still exists
Single laminae not visible
Dissolution patterns
some parts appeared"melted"

Conclusions:

The **aragonitic mineralogy** of the two shells was preserved

But…

SEM analysis have shown clearly dissolution and "melted-like" structures – Start of recrystallization, diagenetic changes already exist

Faylona et al., 2011:

Analysed Tridacnidae not suitable for paleoenvironmental reconstructions,

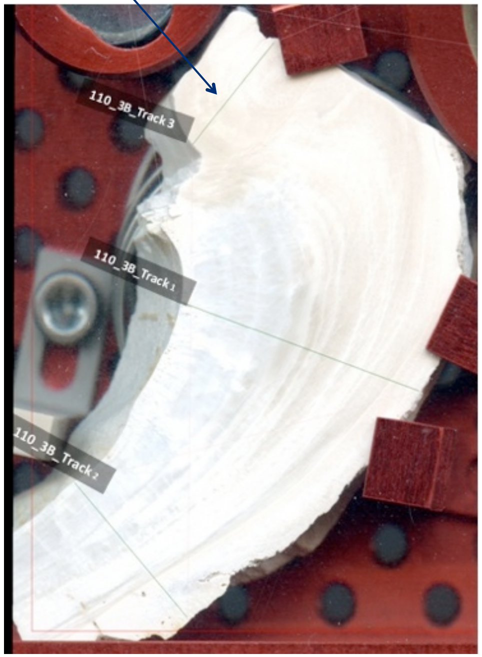
but don't prove the unreliability of the samples

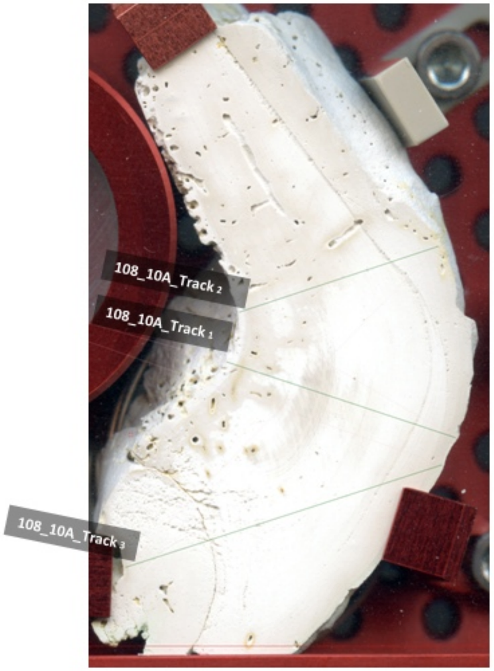
4. Preliminary results of Trace Element Analysis

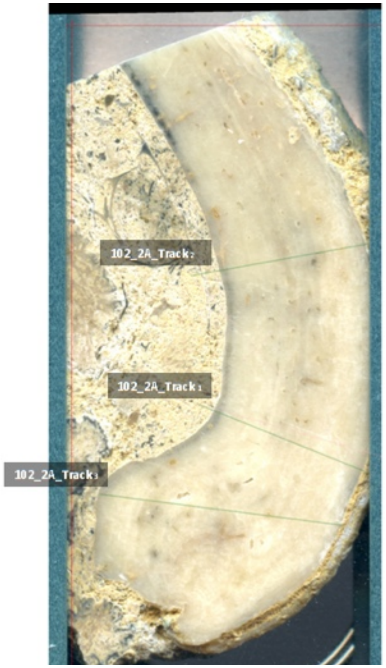
Laser Ablation – Inductively Coupled Plasma Mass Spectrometry (LA-ICPMS)

- 3 Trace element profiles/tracks per sample
- Again: Outer layer, Inner layer and Hinge area were analysed, to decipher areas of best/worst preservation.

Laser ablation track

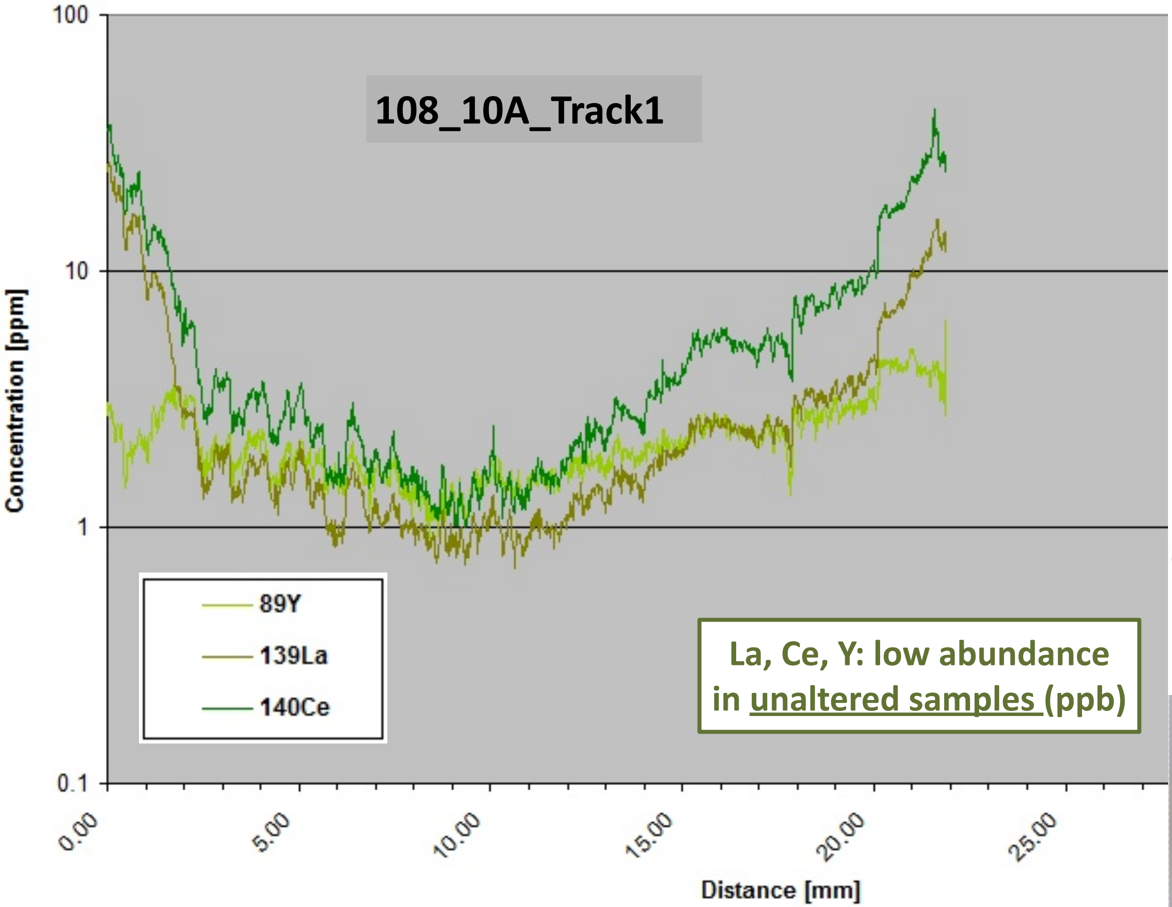


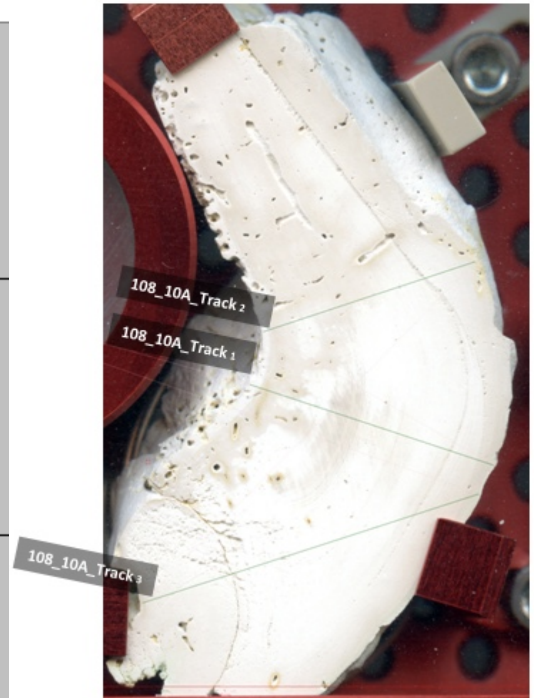


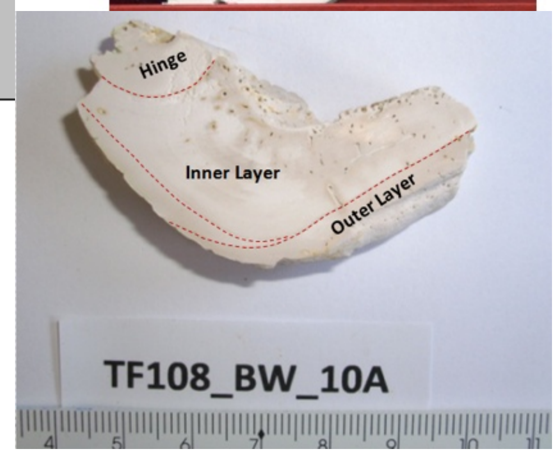


Y, La and Ce as Indicators for diagenesis

XRD: 100% Aragonite

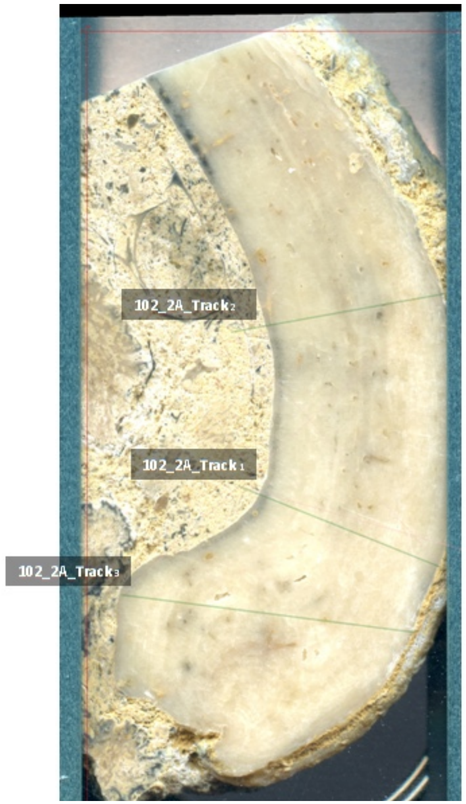


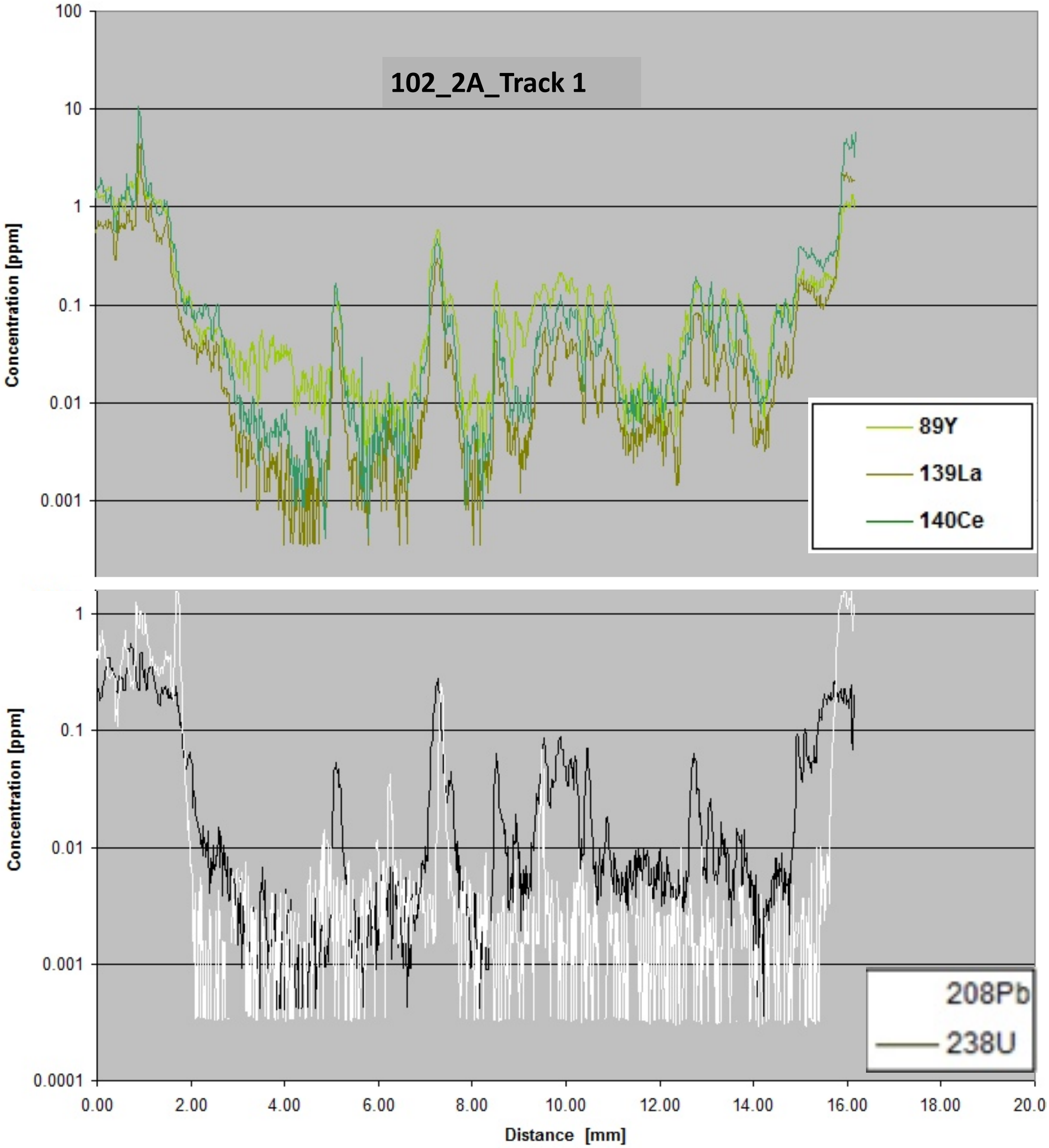




strong deviations between Y and La & Ce (edge area)

XRD: 100% Calcite





Preliminary results of LA-ICPMS
Element/Ca - Important Paleoenvironmental Proxies

Mg/Ca: has been shown to positive correlate with **sea-water temperature (SST)**
Sr/Ca: linked to **shell growth rate**, which is controlled by **seasonal changes**

Ba/Ca: nutrient influxes by river input in coastal areas or upwelling

Exemplary Study of Elliot et al., 2009

strong potential for environmental reconstructions

growth independent incorporation, no biological controls of corporation (e.g symbiotic activity)

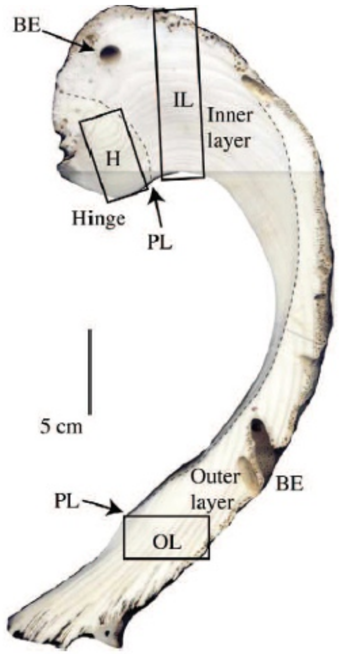
Peaks in shell Ba/Ca correlate positive with peak of surface water chloroform measurements – Ba could be measured as indicator for phytoplankton blooms.

Preliminary results of LA-ICPMS

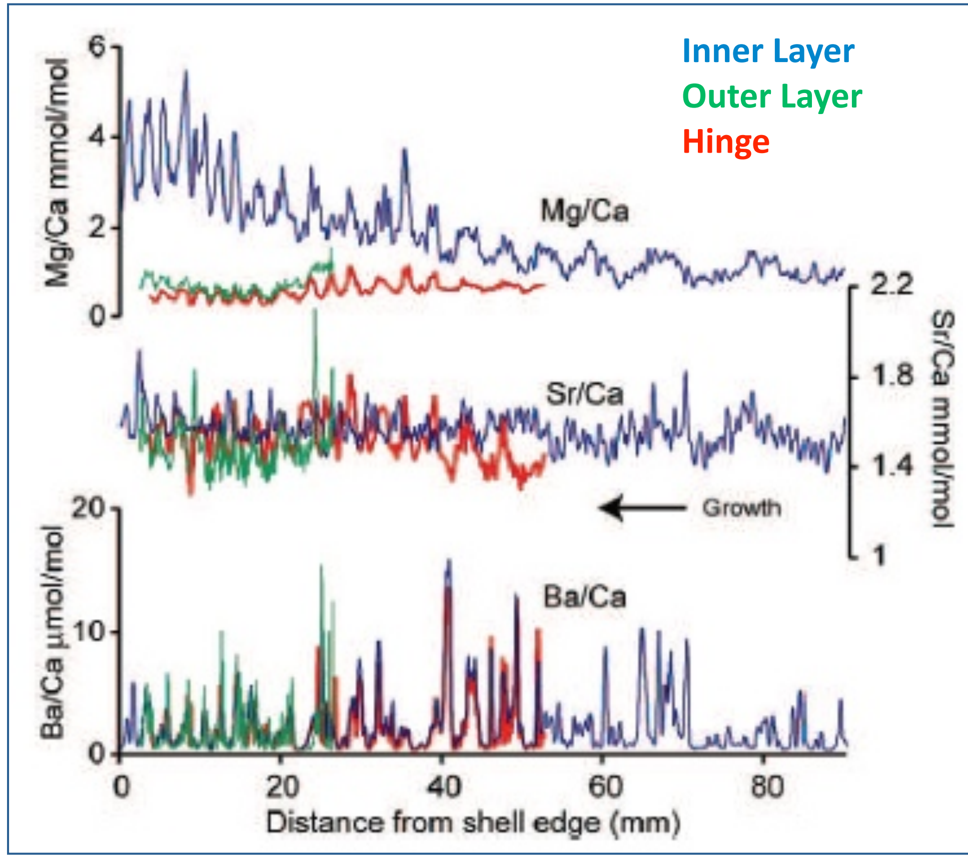
→ **Trace elements as indicators for diagenetic processes**

- The use of trace elements as alteration proxies seems to promising
- More elements must be regarded and intensively studied
- Combination of XRD, SEM, Trace element analysis is required to fully understand variations in the shell carbonate

Comparison of Mg/Ca, Sr/Ca, Ba/Ca between Inner Layer, Outer Layer and Hinge.



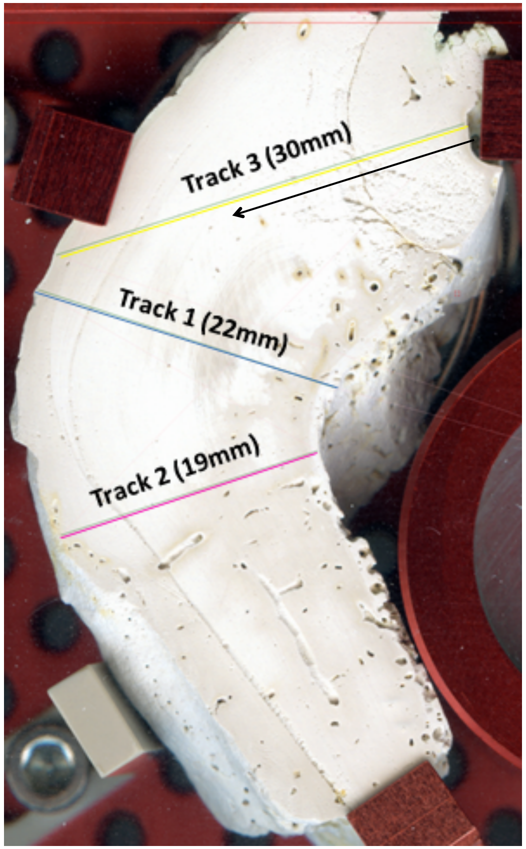
Modern *Tridacna gigas*, Indo-Pacific, Great Palm Island (sampled 1980)

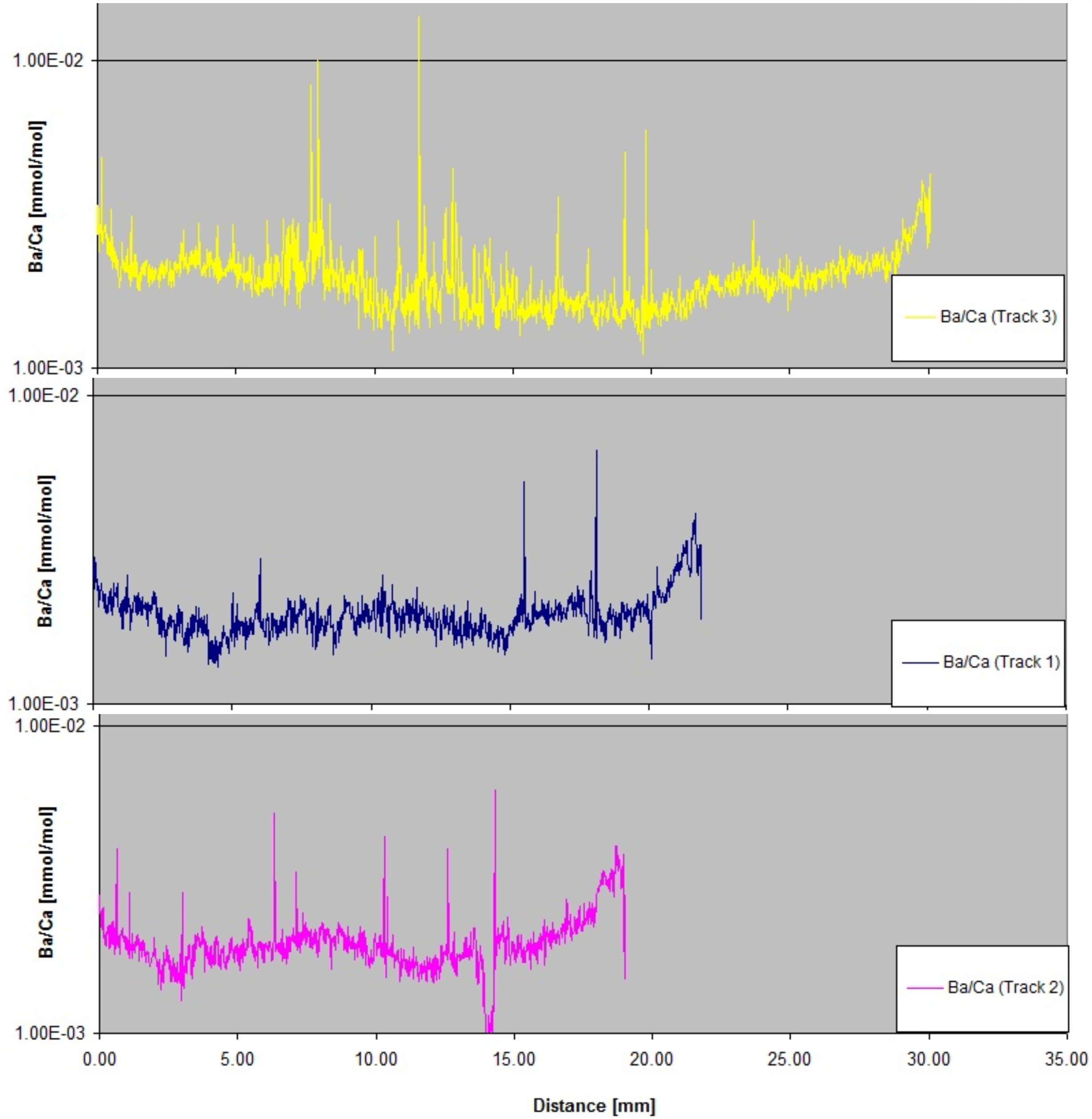


Age equivalent trace element profiles (modified from Elliot et al., 2009)

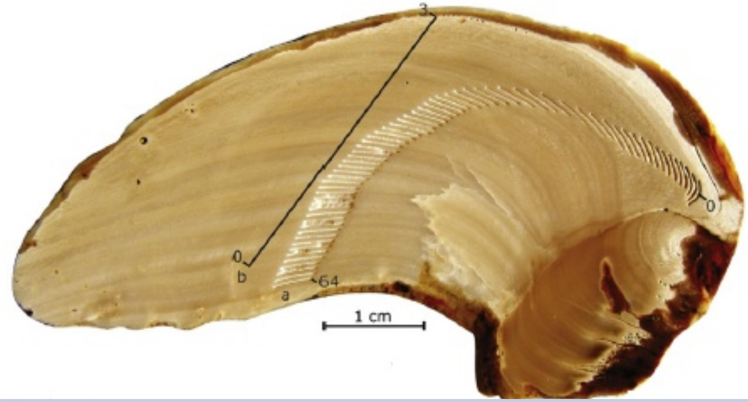
Best agreement show Ba/Ca profiles of the different shell parts – Correlation possible

Comparison of Ba/Ca profiles from the different tracks of sample 108_10A





Batenburg et al., 2011

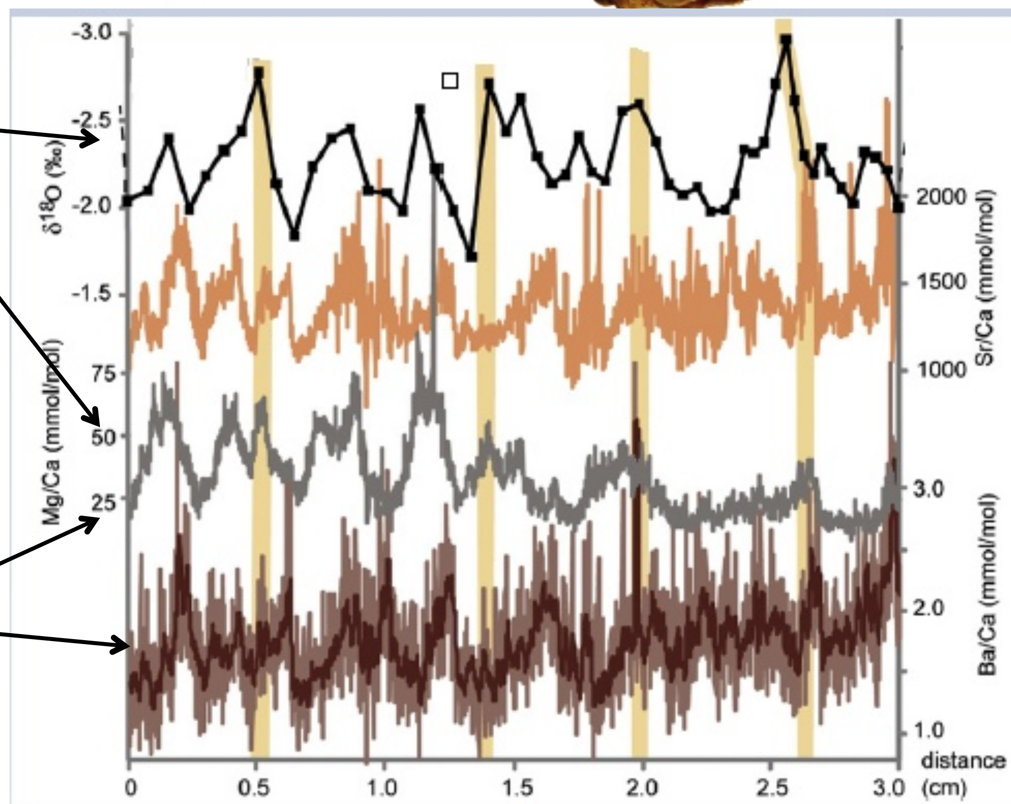


Tridacna Gigas (~ 10-13 Ma)
Serravalian-Tortonian

Negative correlation of Mg/Ca and δ18O

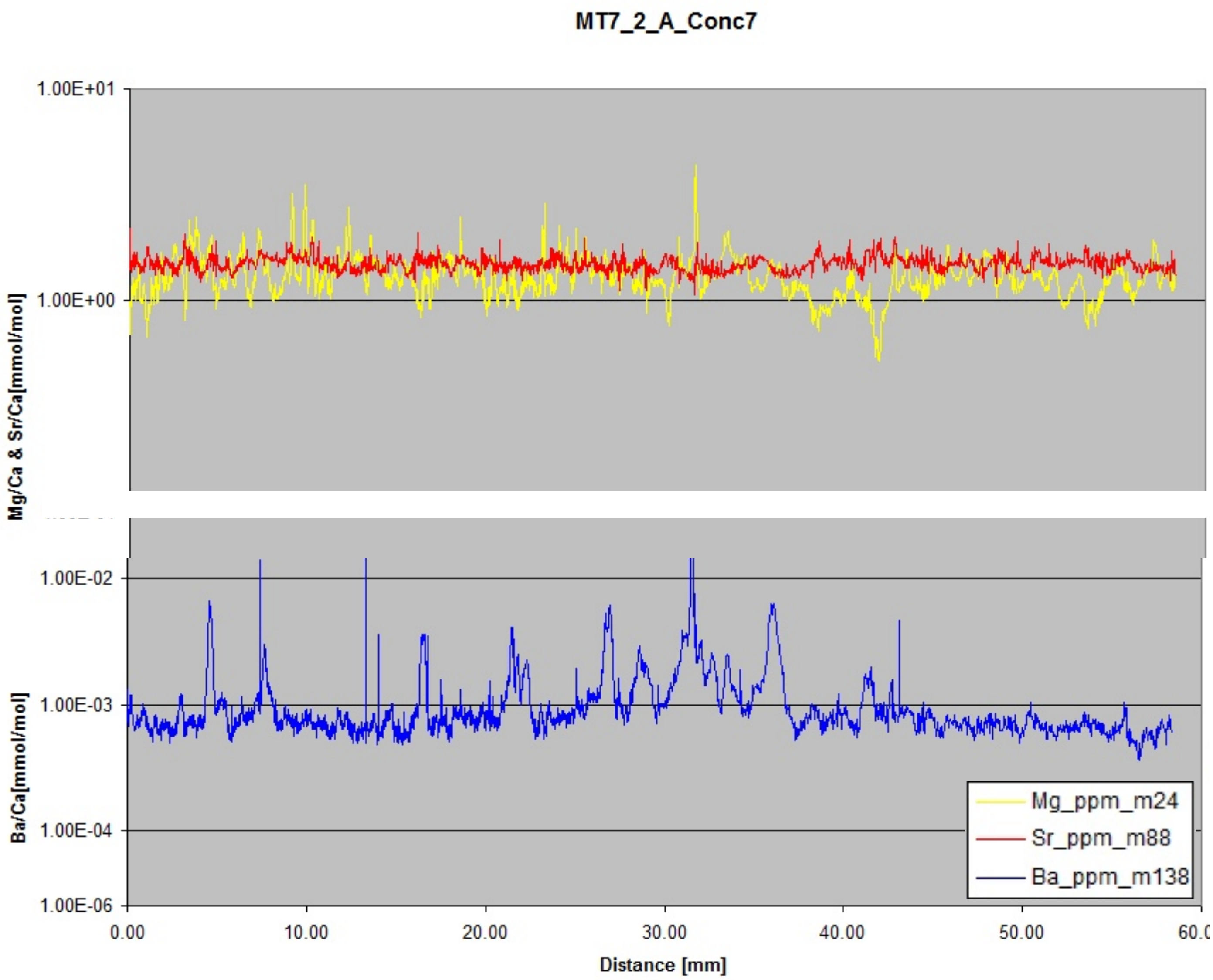
Shell Mg/Ca responds to annual SST cycle
Mg/Ca as SST Proxy

Ba/Ca negatively correlated to Mg/Ca (with a slight phase)

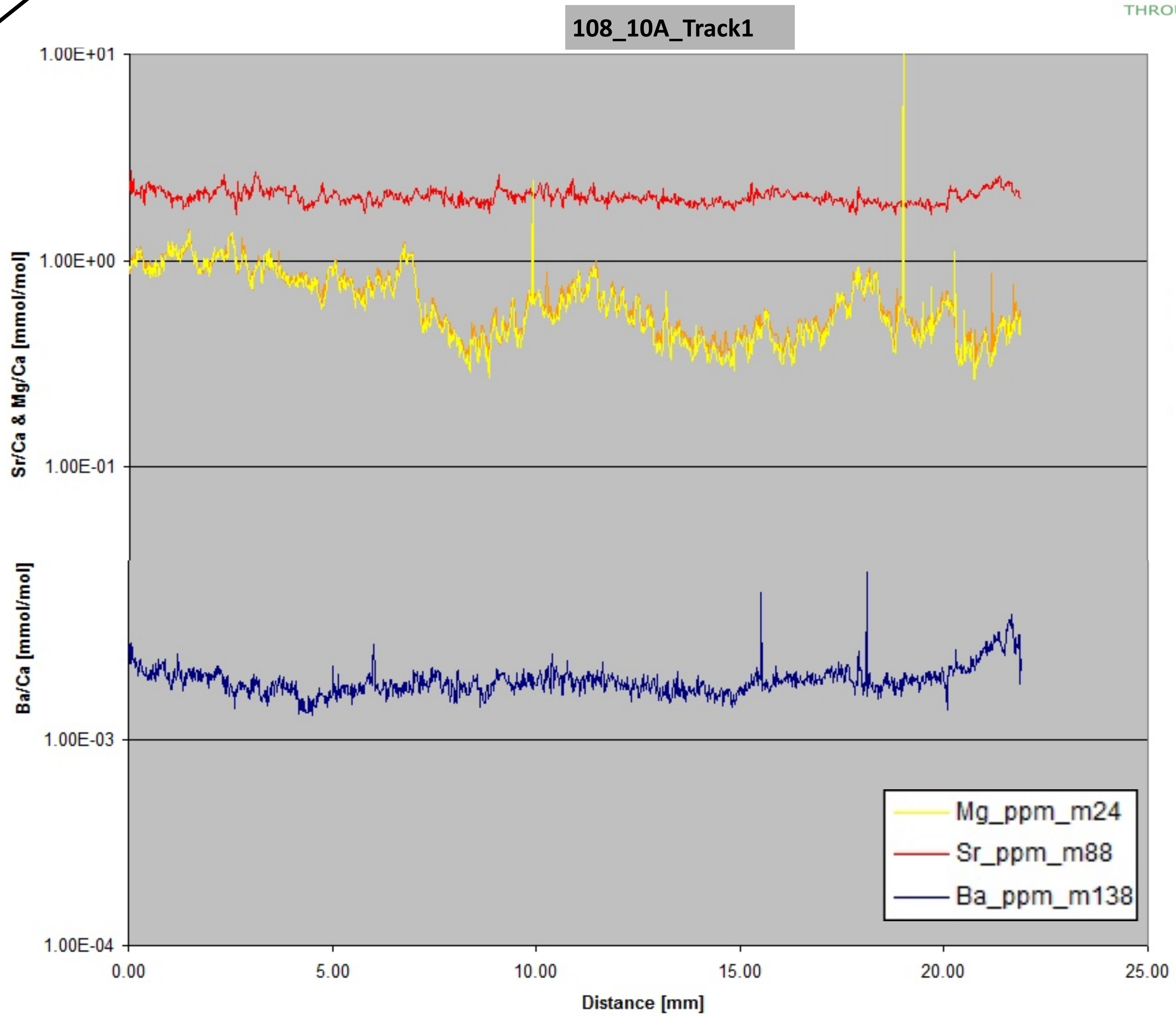


Correlation between $\delta^{18}O$ and Element/Ca ratios (modified from Batenburg et al., 2011).

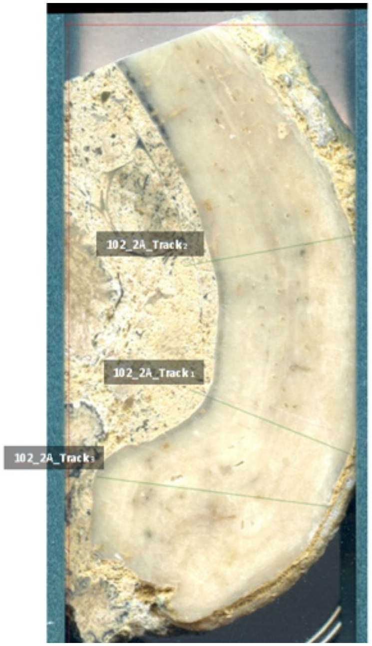
Holocene Tridacna from New Guinea (provided by M. Elliot)

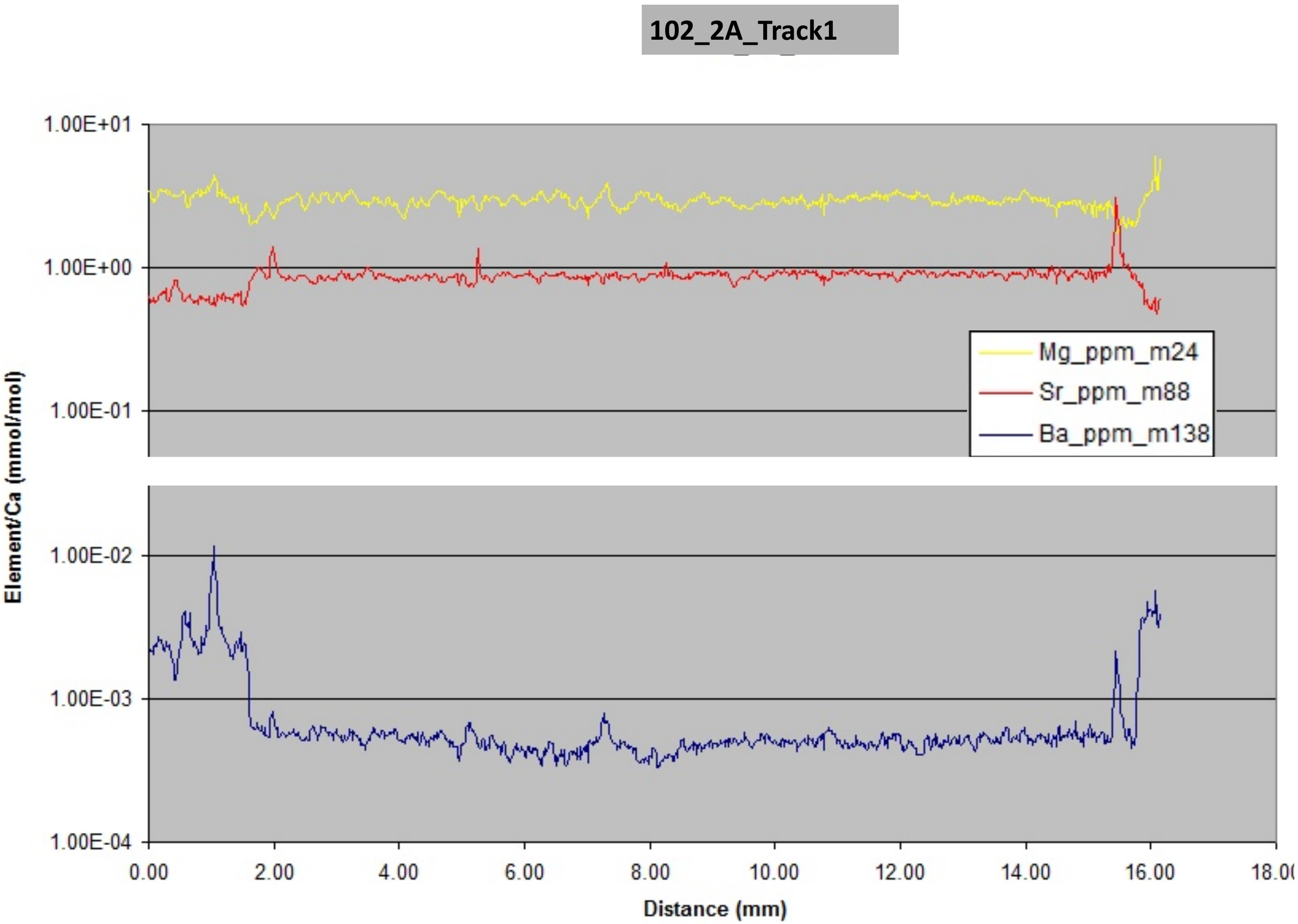


XRD: 100% Aragonite



XRD: 100% Calcite





Sr - loss / Mg - enrichment

Scanning Electron Microscopy

Stable Isotope Analysis

END