

## Lecture 1: Introduction to paleoceanographic proxies and insights from the geological record Harry Elderfield

1. What is a proxy
2. Types of proxy: inspection of the marine geological record what processes have occurred in the oceans in the past; inspection of composition of seawater, or processes that have occurred within oceans
3. Testing and evolution of confidence in proxies
4. Use of chemical or isotopic composition of biogenic calcium carbonate as the proxy archive

Fischer, G. & Wefer, eds Use of proxies in paleoceanography Springer (1999)

Elderfield H., ed. The oceans and marine geochemistry, Treatise on geochemistry vol 6 Elsevier (2006)

## Secondary influences on foraminiferal stable isotopes (Babette Hoogakker)

### Summary

Foraminifera are unicellular eukaryotic micro-organisms with reticulating pseudopods. Fossil tests of calcareous foraminifera are widely used to reconstruct marine paleo-environmental conditions.

Foraminiferal  $\delta^{18}\text{O}$ , used to reconstruct past variations in global ice volume/sea-level and salinity, is influenced by primary factors (temperature dependent fractionation of  $^{18}\text{O}$ ) and secondary factors (1-preservation effects related to dissolution and respiration, 2-kinetic fractionation effects during hydration and hydroxylation of  $\text{CO}_2$  related to carbonate chemistry, and 3-metabolic fractionation effects during biomineralization related to species specific vital effects).

Planktonic foraminifera, that live near the sea surface, occupy various depths in the water column (mainly top 200 m) and are subject to a wide range of temperature and nutrient changes (with depth, and seasonally). Furthermore, increased growth rates cause depletion in  $\delta^{18}\text{O}$ , whereas the addition of a gametogenic calcite layer during reproduction causes  $\delta^{18}\text{O}$  enrichment.

Different benthic foraminifera species, that live on (epifaunal) or in (infaunal) the seafloor, from the same location and environment however often show different  $\delta^{18}\text{O}$ , making it unlikely that all species (if any) form their calcite in equilibrium with seawater.

Paleoceanographers got round this by introducing species  $\delta^{18}\text{O}$  offsets, by assuming that one species (often *Uvigerina*) calcifies its calcite closest to equilibrium with seawater, and inferring constant offsets between *Uvigerina* and all other species.

When interpreting mixed benthic foraminiferal species  $\delta^{18}\text{O}$  records it is important to take into account standard deviations of the offsets between various species (generally larger than 0.2‰), as this will limit quantitative interpretation to variations larger than the standard deviation. Furthermore, the sensitivity of different benthic foraminiferal species to changing environmental conditions might be different.

The assumption of constant offset between different benthic foraminiferal species however does not always hold. Locations characterized by seasonal brine formation can show large differences in  $\delta^{18}\text{O}$  between species that are dominant under ice-free and sea-ice conditions.

In addition, in high productivity areas significant variations can be observed in  $\delta^{18}\text{O}$  offsets between infaunal *Uvigerina* and epifaunal *Cibicides*, caused by *Uvigerina* not showing the full glacial-interglacial decrease in  $\delta^{18}\text{O}$ . The deglacial enrichment in *Uvigerina*  $\delta^{18}\text{O}$  can potentially be related to changes in vital effects or kinetic fractionation during intervals of high productivity/ remineralization.

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# Lecture 4. Temperature proxies

Dr. Caroline Dawber

## Outline

- Proxy methods, maturity and confidence levels
- Qualitative & semi-quantitative temperature indices
  - Sediments and geomorphology
  - Temperature sensitive organisms
  - Dendroclimatology
- Paleoecological transfer functions
  - Theory & calibration function
  - Application: CLIMAP LGM SST.
  - Bias and revisions – MARGO
- Carbonate Mg/Ca thermometry
  - Insights from inorganic precipitation experiments
  - Biogenic carbonates
  - Calibrating the foraminifera Mg/Ca thermometers
  - Issues: changes in seawater Mg/Ca
  - Issues: dissolution
  - Issues: diagenetic alteration & secondary inorganic calcite
  - Application: Cenozoic temperature reconstruction and the inception of glaciation
  - 2<sup>nd</sup> generation issues: carbonate ion problem
  - 2<sup>nd</sup> generation issues: salinity influence?
- Clumped isotope thermometry
  - Background & theory
  - Early calibrations
- Organic carbon thermometry
- Alkenone undersaturation index
  - Theory & producers
  - Calibrations
  - Advantages & Disadvantages
- TEX<sub>86</sub>
  - Theory & calibrations
  - Advantages & Disadvantages

## Key References for Lecture 4: Temperature proxies

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## Clumped isotope thermometry

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## Alkenone thermometry

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Conte, M. H., M. Sicre, C. Rühlemann, J. C. Weber, S. Schulte, D. Schulz-Bull, and T. Blanz (2006), Global temperature calibration of the alkenone unsaturation index (UK'37) in surface waters and comparison with surface sediments, [online] Available from: <http://www.agu.org/pubs/crossref/2006/2005GC001054.shtml> (Accessed 5 May 2009)

## TEX<sub>86</sub> thermometry

Schouten, S., E. C. Hopmans, E. Schefuß, and J. S. Sinninghe Damsté (2002), Distributional variations in marine crenarchaeotal membrane lipids: a new tool for reconstructing ancient sea water temperatures?, *Earth and Planetary Science Letters*, 204(1-2), 265–274.

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## EPOCA Lecture 5. Constructing age models

Prof. Nick McCave

0. What is an “age model”: age-depth mapping; time (age) onto space (depth).

1. Actual dating versus correlation to a dated standard.

2. Dating; Direct, Absolute

A. Radiometric methods: long to short half-life.

a. Ar – Ar ( $T_{1/2} = 1.28 \times 10^9$  a) on volcanic ash. [formerly K – Ar].

b.  $^{238}\text{U} - ^{230}\text{Th}$  disequilibrium ( $T_{1/2} = 75,400$  a) on sediment.

c.  $^{14}\text{C}$  ( $T_{1/2} = 5,730$  a) on forams, bulk  $\text{CO}_3$  and organic carbon.

d.  $^{210}\text{Pb}$  disequilibrium ( $T_{1/2} = 22.4$  a) on sediment.

B. Annual Layer counting

a. Varves - lake and sea

b. Tree Rings

c. Ice cores.

3. Dating by correlation to a standard

Standards

a. Biostratigraphic – FAD, LAD, acme, etc.

b. Magnetostratigraphic – reversals and palaeointensity excursions.

c. Tephrochronology (volcanic ash)

d. Ice-core  $\delta^{18}\text{O}$  or  $\delta\text{D}$  or dust records – layer count and flow model

e. Benthic oxygen isotope stacks (old SPECMAP, new LR04).

How are these dated? Mainly by :-

4. Dating by correlation to calculated insolation variations due to periodic orbital variations – ‘Orbital Tuning’

## 5. Standards

- a. Orbital (Milankovitch) fluctuations of insolation.
- b. Biostratigraphic – FAD, LAD, acme, etc.
- d. Magnetostratigraphic – reversals and excursions.
- e. Benthic oxygen isotope stacks (old SPECMAP, new LR04).
- f. Tephrochronology.
- g. Ice-core  $\delta^{18}\text{O}$  or  $\delta\text{D}$  or dust records – layer count and flow model

### C. Properties used to correlate to the standard

- a. Microfossils – forams, coccoliths, diatoms, radiolarians.
- b. Lithology -  $\%\text{CaCO}_3$ , chemical composition – Fe, Ca, etc.
- c. Proxies for lithology – magnetic susceptibility, spectral reflectance.
- d. Magnetic inclination – reversal sequence.
- e. Oxygen isotope ( $\delta^{18}\text{O}$ ) variation in benthic & planktonic forams (& bulk sed.).

## 6. Errors

- a. Errors on dated points.
  - i. Ar-Ar: see dating books.
  - ii. (U – Th);  $\text{Th}_{\text{xs}}$
  - iii. C-14
    - (i) half lives – modern 5730 a and old (Libby) 5568 a.
    - (ii) calibration – INTCAL etc, ages > 25 ka Fairbanks.
    - (iii) marine reservoir age.
  - iv.  $^{210}\text{Pb}$  – CRS and CIC models.
- b. Errors of Interpolation
  - i. Linear versus spline/other curve fit, etc.
  - ii. Using  $^{230}\text{Th}_{\text{xs}}$ , focussing.

## 7. How it's done

Use of 'Analyseries' correlation programme; Sedimentation rate constraints.

## Lecture 4 : Constructing Age models, References

Gradstein, F. M., Ogg, J. G. and Smith, A. G. (Eds.), 2004. *A Geologic Timescale 2004*, Cambridge University Press

### DATING

#### Ar-Ar & K-Ar dating

Villeneuve, M., 2004. Radiogenic isotope chronology, pp. 87-95 in Gradstein, F. M. et al. *A Geologic Timescale 2004*, CUP. (but see Kuiper for FCT age)

Kuiper, K.F. et al., 2008. Synchronizing rock clocks of Earth history. *Science*, **320**: 500-4  
[http://en.wikipedia.org/wiki/Potassium-argon\\_dating](http://en.wikipedia.org/wiki/Potassium-argon_dating)  
[http://en.wikipedia.org/wiki/Argon%E2%80%93argon\\_dating](http://en.wikipedia.org/wiki/Argon%E2%80%93argon_dating)

#### U-Th, <sup>210</sup>Pb dating, Th profiling

Bradley, R.S., 1999. Chapt. 3.2.3, Uranium-series dating, p. 76-80, *Paleoclimatology*, Academic Press,

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#### Radiocarbon

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#### Varves

<http://en.wikipedia.org/wiki/Varve>

#### Tree rings (dendrochronology)

<http://en.wikipedia.org/wiki/Dendrochronology>

#### Ice cores

Bradley, R.S., 1999. Chapt. 5.3, Dating ice cores, p. 142-153, *Paleoclimatology*, Academic Press,

### STANDARDS

#### Orbital fluctuations of Insolation

Hinnov, L.A., 2004. Earth's orbital parameters and cycle stratigraphy, in Gradstein, F. M. et al. *A Geologic Timescale 2004*, CUP, p. 55-62.

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#### Fossil datums

Gradstein F. et al, 2004. Biostratigraphy: time scales from graphic and quantitative methods. In Gradstein, F. M. et al. *A Geologic Timescale 2004*, CUP, pp.49-52 only

Raffi I, et al., 2006. A review of calcareous nannofossil astrobiochronology encompassing the past 25 million years. *Quaternary Science Reviews*, **25**: 3113-3137..

Lourens, L., et al., 2004. The Neogene. In Gradstein, F. M. et al. *A Geologic Timescale 2004*, CUP, p. 409-440. (good e.g. of integrated age model with bio-astro- etc)

#### Magnetostrat.

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Kent, D. V., 1999. Orbital tuning of geomagnetic polarity time-scales. *Phil. Trans. Royal Soc. Lond.*, **357**: 1995-2007.

### **Oxygen Isotope Stack**

Lisiecki L. & Raymo, M.E., 2005. A Pliocene-Pleistocene stack of 57 globally distributed benthic delta O-18 records. *Paleoceanography*, **20**(1) Art. No. PA1003 & **20** (2) Art. No. PA2007

### **Tephrochronology**

Bradley, R.S., 1999. Chapt 4.2.3, Tephrochronology, p. 142-153, *Paleoclimatology*, Academic Press.

Larsen G. & Eiriksson J., 2008. Late Quaternary terrestrial tephrochronology of Iceland - frequency of explosive eruptions, type and volume of tephra deposits. *Journal of Quaternary Science*, **23**, 109-120. (plus other compilations from around the world)

### **Ice-core records.**

EPICA Community Members, 2004. Eight glacial cycles from an Antarctic ice core. *Nature*, **429**, 623-628

### **Properties**

St-Onge, G. et al, 2007. Continuous physical properties of cored marine sediments. In, *Proxies in Late Cenozoic Paleoclimatology*, C. Hillaire-Marcel & A. de Vernal (Eds), Elsevier, p. 63-81.

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### **More detailed stuff**

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Berger, A. and Loutre, M. F., 1994. Astronomical forcing through geological time. In: *Orbital Forcing and Cyclic Sequences*, Eds: de Boer, P. L. and Smith, D. G., *Int. Assoc. Sed. Spec. Pub.* **19**, pp.15-24.

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## Lecture 6: Carbonate system parameters Harry Elderfield

The ocean carbonate system and how it affects CO<sub>2</sub>

How do we estimate carbonate ion

Corrosion of planktonic foraminiferal calcium carbonate

Calcium carbonate accumulation in oceanic sediments

Productivity or preservation

Geochemical solutions

Broecker W.S and Peng T-H Tracers in the Sea Eldigio Press 1982

Zeebe, R. E. and Wolf-Gladrow. CO<sub>2</sub> in Seawater: Equilibrium, Kinetics, Isotopes. Elsevier Oceanography Series, 65, pp. 346, Amsterdam, 2001

## Lecture 7: Biological productivity and export production Harry Elderfield

Biological productivity and nutrients in sea water

HNLC

nutrients as water mass tracers

$\delta^{13}\text{C}$  and Cd/Ca in benthic foraminifera

proxies of export production and nutrient utilisation

Anderson R et al Deep-Sea Research 49, 1909 (2002)

Elderfield H., ed. The oceans and marine geochemistry, Treatise on geochemistry vol 6 Elsevier (2006)

# **Lecture 8. Proxies for tracing patterns and rates of ocean circulation**

Dr. Alexander Piotrowski

- Introduction: Link between ocean circulation and climate
- Deep ocean parameters we would like to reconstruct
  - Water mass flux and/or flowspeed
  - Water mass source (ex. NADW, AABW)
  - Nutrient contents (ex. Concentration of PO<sub>4</sub>, SCO<sub>2</sub>, carbonate speciation)
- Proxies of deep ocean water mass
- Nutrient-based proxies
  - Benthic Foraminiferal carbon isotopes
  - Benthic Foraminiferal Cd/Ca
- Benthic Foraminiferal carbon isotopes
  - Background & theory
  - GEOSEC measurements by Kroopnick, 1985
  - Calibrating to phosphate concentration
  - Issues: other controls on deep water composition
  - Issues: micro-environment (Mackenson Effect)
- Benthic Foraminiferal Cd/Ca
  - Background & theory
  - Relation to carbon isotopes
  - Issues: other controls on proxy reconstructions
- Flow Speed Proxies
- <sup>230</sup>Pa/<sup>231</sup>Th
  - Background & Theory
  - Early calibration by Yu et al., 1996
  - Bermuda Rise record by McManus et al., 2004
  - Productivity control?
- Water mass source/mixing proxies
- Nd isotopes
  - Theory & calibrations
  - Fe-Mn crust and fish teeth records
  - Leaching records, Deep Cape Basin work
  - Advantages & Disadvantages

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## EPOCA: Lecture 9

### The Sedimentary System: Cautionary Tales

Prof. Nick McCave

1. Revision: Sedimentary components and how they arrive at the sea floor - Processes of deep sea sediment transport and deposition
  - Terrigenous material
    - a. Direct from river plumes (little now) – but sea level shifts .....
    - b. Wind-blown dust
    - c. Turbidity currents/ mass movement
    - d. Resuspension on slopes and rises
  - Biogenic components – forams, nannos, diatoms, rads, dinos, POC
    - a. Regional productivity variation; quantity and quality
    - b. Re-entrainment of old material
  - Chemical Scavenging & adsorption
  - Segregation by size/settling velocity in transport: vertical and lateral
2. Coring Artifacts
3. Post-depositional changes; bioturbation
  - Biological mixing: diffusion - diffusivity,  $D_B$
  - Biological mixing: advection – conveyor feeding & pumping
  - effect on C-14 dates
4. Events – effect on age structure, preservation of
5. HOLY GRAIL: High resolution - how to increase S - sedimentation rate: achievement by:
  - Episodic turbidite input
  - ‘Focussing’ e.g. deep downstream of obstacles
  - Drift sedimentation
6. THE GRAIL, laminated sediments, 1 mm/year, but the penalty of bottom anoxia.

## EPOCA: Lecture 9. The Sedimentary System: Cautionary Tales

Problems with records: Coring, bioturbation (mixing & pumping), 'events' and 'excess sedimentation' (focussing). (..... = more important)

General: Sedimentation, transport etc.

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### **Biological pumping of coarse grains upwards.**

McCave, I.N. 1988. Biological pumping upwards of the coarse fraction of deep-sea sediments. *J. Sed. Petrol.*, 58: 148-158.

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### **Impact of lateral supply on age and properties of components**

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## **Practical demonstration P2: Trace elements in biogenic carbonates as proxies for past ocean chemistry**

### **Composition of foraminiferal calcite**

Foraminiferal calcite is composed of extremely pure (~99%) CaCO<sub>3</sub>

Four minor elements Na, Mg, Sr and F comprise most of the remaining ~1% and are present at abundances greater than 10<sup>-3</sup> mol/mol Ca.

Other trace metals are present at extremely low abundances, ~10<sup>-4</sup> to 10<sup>-9</sup> mol/mol Ca.

### **Analytical issues**

Trace elements must be determined in the presence of orders of magnitude greater Ca. Potential for contamination from high concentrations of these elements in sediments and ferro-manganese coatings.

Trace metal clean procedures and sensitive detection methods are essential.

Need precision and accuracy appropriate to the concentration range of trace elements.

Trace element determinations have particular analytical problems - often specific to individual trace metals.

### **Sampling**

Sediment disaggregation, foram picking, weighing, then crushing and splitting for multi-proxy determination.

### **Cleaning**

-Removal of clay materials

-Removal of organic matter

-Removal of Mn-Fe-oxide coatings

-Removal of barite

-Final dilute acid leach before sample dissolution

required for:

Mg/Ca, Sr/Ca, B/Ca, Li/Ca

Cd/Ca, U/Ca, Zn/Ca

Ba/Ca

### **Inductively coupled plasma optical emission spectrophotometry (ICP-OES)**

-preliminary Ca concentration determination

-Mg/Ca & Sr/Ca determined by intensity ratio method

-Al, Fe, Mn, Si, Ti monitored to check cleaning efficiency

Simultaneous determination gives better precision for Mg/Ca, Sr/Ca than ICPMS.

Can determine Fe/Ca - not determined by quadrupole ICPMS

### **Inductively coupled plasma mass-spectrometry (ICP-MS)**

-Samples diluted to constant [Ca] of 100 ug/g

-Element/calcium ratios determined from intensity ratios by sequential scanning.

More sensitive than ICP-OES

Can determine B/Ca, Li/Ca, Cd/Ca, U/Ca - not determined by ICP-OES

### **Precision, Accuracy and Calibration Standards**

Instrumental methods usually limited by the analytical blank or spectral interferences rather than by instrument sensitivity.

Precision is a function of stability of the instrument and sample introduction system.

Calibration standards are prepared gravimetrically from high purity starting materials.

Accuracy depends on the accuracy of the calibration standards.

Cross contamination within mixed standard solutions is determined and corrected.

Interlaboratory calibration determines consistency between laboratories.

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