

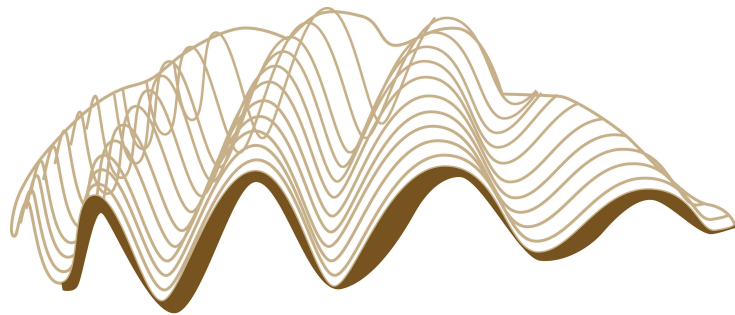
# TERRA NOSTRA

*Schriften der Geo-Union Alfred-Wegener-Stiftung 2010/3*

## 2<sup>nd</sup> International Sclerochronology Conference

24-28<sup>th</sup> July 2010

**Program and Abstracts**



2ND INTERNATIONAL  
**SCLEROCHRONOLOGY**  
CONFERENCE  
2 0 1 0



JOHANNES GUTENBERG  
UNIVERSITÄT MAINZ



**TERRA NOSTRA – Schriften der GeoUnion Alfred-Wegener-Stiftung**

**Publisher**  
*Verlag*



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**Vol. 2010/3**  
*Heft 2010/3*

**2<sup>nd</sup> International Sclerochronology Conference**  
ISC2010, Mainz, Germany, 24-28<sup>th</sup> July 2010

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INCREMENTS

**Printed by**  
*Druck*

University of Mainz

Recommended citation: Schöne, B. R. & Nunn, E. V. (Eds) 2010. 2<sup>nd</sup> International Sclerochronology Conference, 24-28<sup>th</sup> July 2010, Program and Abstracts.

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ISSN 0946-8978

GeoUnion Alfred-Wegener-Stiftung – Berlin, July 2010

Dear Colleague,

On behalf of the conference organization team, I welcome you to the 2<sup>nd</sup> International Sclerochronology Conference (ISC2010) at the University of Mainz.

Three years ago, sclerochronology entered a new era. For the first time, sclerochronologists from all over the world came together in St. Petersburg, FL, USA to exchange thoughts and discuss new research. ISC2007 was overwhelmingly successful and the delegates agreed that this should be the starting point for future, regular meetings of this kind.

Since that time, sclerochronology has gained considerable momentum. Numerous research papers on trace elements, novel isotope techniques and applications attest to the growing interest in this field. However, there is still far more potential to be realized. By addressing key paradigms, envisaging the big picture and providing precisely temporally aligned, robust and quantifiable environmental proxy data, we can attract the attention of the broader scientific community and increase the visibility of sclerochronology. This requires a concerted and holistic approach together with interdisciplinary collaboration. As such, the remit of ISC2010 was to integrate traditional sclerochronological research with the expertise from neighboring disciplines. I am extremely pleased to see that the presentations received for ISC2010 contribute strongly to this purpose.



Aside from the scientific program, the venue offers a broad spectrum of tourist attractions and entertainment. The capital of the federal state of Rhineland-Palatinate looks back over a history of more than two thousand years. The region is famous for its Roman history (Mainz was known as Moguntiacum during Roman times) and, of course, its delicious wines! Mainz is also the place where one of the most groundbreaking machines was invented: the letterpress.

I would like to thank you for taking the time to participate in ISC2010 and contribute both oral and poster presentations. My special thanks to the international and local organization teams as well as to our sponsors and supporters. They facilitated the conference planning and kept things manageable. Ultimately, their help and support made this conference possible.

Conference Chair,

A handwritten signature in black ink, appearing to read 'Bernd R. Schöne'. The signature is stylized and fluid.

Bernd R. Schöne



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## **Organizing committee**

### **Chair**

Bernd R Schöne, University of Mainz, Germany

### **International Team**

Andrew LA Johnson, University of Derby, UK

Claire E Lazareth, LOCEAN – Paleoproxus, Bondy, France

David P Gillikin, Vassar College, Poughkeepsie, NY, USA

Kazushige Tanabe, University of Tokyo, Japan

Meghan Burchell, McMaster University, Hamilton, ON, Canada

Thomas Tütken, University of Bonn, Germany

### **Local Team (University of Mainz)**

#### **- Scientific advisory board**

Elizabeth V Nunn, Kotaro Shirai, Anne-France Maurer

#### **- Organization**

Michael Maus, Jochen Körner, Lars Beierlein, Pascal Radermacher, Dorrit E Jacob

#### **- Workshop**

Nadine Hallmann

#### **- Assistants**

Christoph S Füllenbach, Jessica Zirkel, Hilmar A Holland, Stefanie Thiele, Tobias

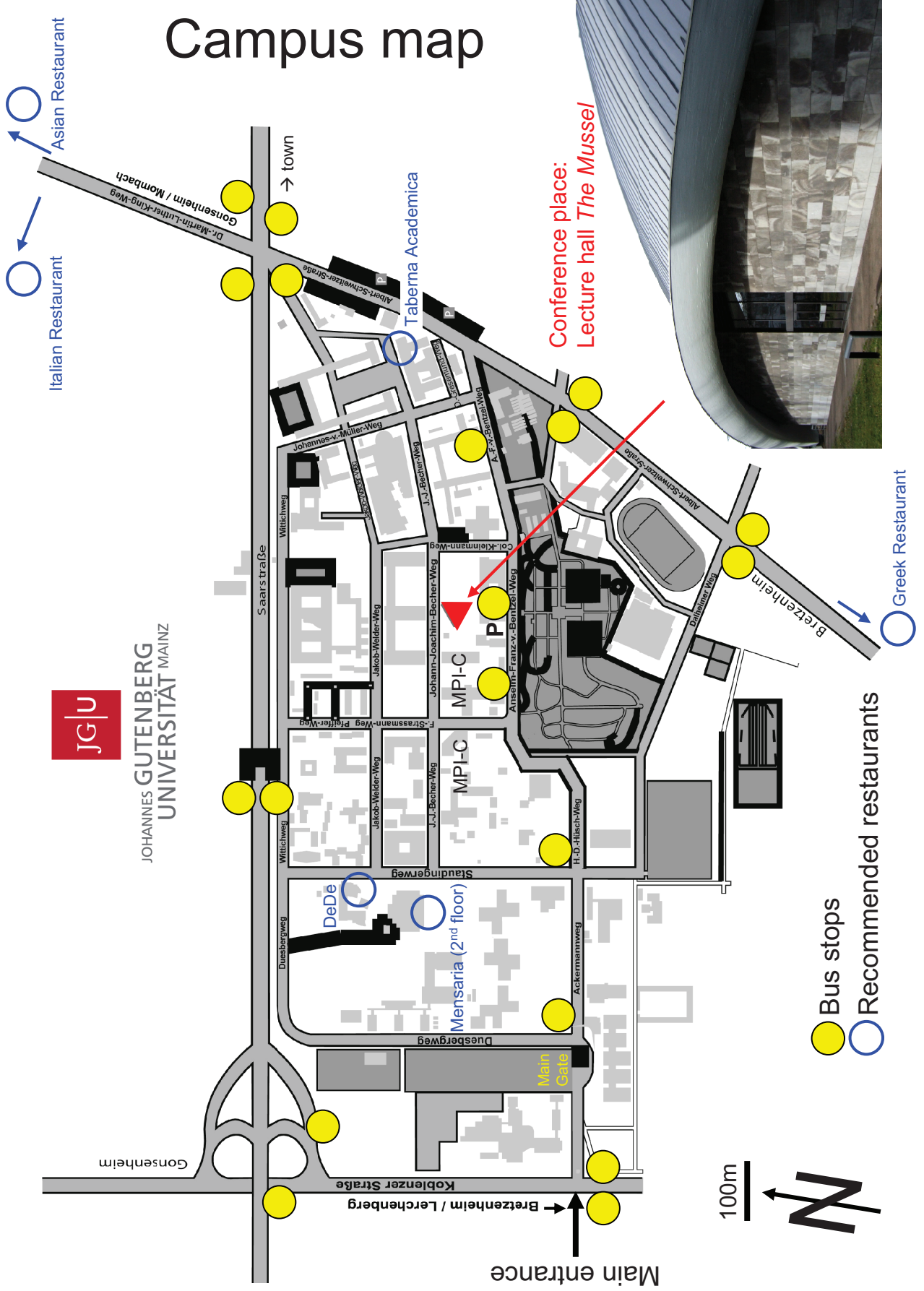
Grützner, Julia Broska, Johannes Gattinger, Lars Heller, Etienne Neuhaus, Magnus

Reutter

#### **- Secretarial team**

Christina Scharhag, Beate Nikoley, Ute Stieffenhofer, Christine Weller

# Campus map



JOHANNES GUTENBERG  
UNIVERSITÄT MAINZ

100m



● Bus stops

○ Recommended restaurants

Italian Restaurant

Asian Restaurant

Greek Restaurant

Conference place:  
Lecture hall *The Mussel*



## General information

### Location and conference address

The Mussel  
University of Mainz  
Johann-Joachim-Becherweg 23  
55128 Mainz  
Tel.: +49 6131 39 24757; Fax: +49 6131 39 24768  
Email: [ISC2010@uni-mainz.de](mailto:ISC2010@uni-mainz.de)  
URL: <http://www.scleroconferences.de>

### Official language

The official language of ISC2010 is English.

### Registration desk

- Open during normal conference hours (see Conference schedule)
- General enquiries and information
- Lost and found
- Messages and special announcement board
- First Aid
- Transport information and taxi phone numbers

### Emergency

- Phone numbers:
  - 110 Police
  - 112 Ambulance, Fire Department
- Fire extinguishers can be found on both levels of the building; please refer to emergency maps

### Refreshments and lunch

Recommendations (see campus map):

- (1) Mensaria, University campus, Staudingerweg, open Mon-Fri (note: the Mensa downstairs from the Mensaria only accepts student cards, but no cash)
- (2) Italian restaurant, Pizzeria Campa Bistorante, An der Allee 120 (keep left on crossing Saarstraße/Albert-Schweitzer-Straße/Dr.-Martin-Luther-King-Weg, follow Saarstraße W, cross bridge heading NNW), open Tue-Sat 17:30 – 23:00, Sun 12:30 – 14:30 and 17:30 – 23:00
- (3) Greek restaurant, ca. 150m S of crossing Dalheimer Weg/Albert-Schweitzer-Straße toward the district of Bretzenheim
- (4) Taberna Academica, University campus, opens Mon-Fri at 10:15, Sat 12:00 – 15:00
- (5) DeDe, Turkish specialities, University campus, Staudingerweg

Note: Complimentary refreshments will be served during the coffee breaks.

**Internet access** (for Windows Firewall configuration see p. 168)

Free internet access is available. EduRoam is accessible to delegates from certain European and Australasian universities. Other delegates will require a guest account and password, which is available from the registration desk. Internet can be accessed through the following options:

- Wireless Internet Access (WLAN)
- Cable-bound internet access (LAN; for cables ask at the registration desk)
- University Computing Center

**Workshop**

Please meet in front of the conference center at 09:00. Workshop runs from 09:00 until ca. 18.00. The additional Friday workshop will follow the same schedule.

**Round-Table Discussions (RTD)**

Currently, four moderated RTDs (Thursday) have been offered for which delegates can sign-up at the registration desk: Shell midden archaeology (Meghan Burchell), Sclerochronology data banks with global coverage and accessibility (Thomas Brey), Proxy development (Thomas Tütken) and Paleoclimate (Andrew Johnson).

**Field Trip**

Please meet in front of the conference center at 08:00 on Friday. We will return at approximately 19:30. Proper walking boots are strongly recommended. A geological hammer and hand lens would also be very useful.

**Conference events (refer to “Mainz City Map” and “Ausgehen in Mainz” leaflets)**

- Icebreaker Party: Conference building, Saturday, 18:00 – 21:00
- Mid-conference dinner: Eisgrub Bräu (Weißliliegasse 1a), Monday, starts at 18:30
- Farewell dinner: Proviantmagazin (Schillerstraße 11a), Wednesday, starts at 18:30 (free drinks until 20:30)

**Posters**

Posters should be put up on Sunday or Monday morning at the latest and should remain until Wednesday. Posters are assigned a poster board number (see list of poster presentations). Attachment materials are available.

**Speaker Ready Room**

Oral presentations can be rehearsed in the Speaker Ready Room.

**Uploading oral presentations**

Oral presentations must be uploaded in the Speaker Ready Room on the morning of your talk before sessions commence (at the latest).

**Rules of conduct**

- Smoking is prohibited throughout the conference center and in the immediate vicinity of the university buildings.
- It is prohibited to copy any oral presentations from the conference computers.
- It is prohibited to take photographs of any scientific material in either oral or poster presentations.

## Conference schedule

### Saturday 24<sup>th</sup> July 2010

15:00 – 18:00 Registration

**18:00 – 21:00 Icebreaker Party (The Mussel, Campus, University of Mainz)**

### Sunday 25<sup>th</sup> July 2010

08:40 – 09:00 Introductory notes

09:00 – 09:10 Official welcome

#### **Session 1A Proxy Development**

**Conveners: David P Gillikin, Christopher S Romanek**

09:10 – 09:40 Christopher S Romanek – **Trace element and stable isotope profiles of accretionary biological tissues** – Keynote

09:40 – 10:00 Cyril Giry, Felis T, Kölling M and Scheffers S – **Geochemistry and skeletal structure of *Diploria strigosa*, implications for coral-based climate reconstruction**

**10:00 – 10:30 Coffee Break (refreshments will be provided)**

#### **Session 1B Proxy Development**

**Conveners: Andrew LA Johnson, Claire E Lazareth, Christopher S Romanek**

10:30 – 10:50 Craig A Grove, Nagtegaal R, Zinke J, Scheufen T, Koster B, Kaper S, McCulloch MT, van den Bergh G and Brummer G-JA – **River runoff reconstructions from novel spectral luminescence scanning of massive coral skeletons**

10:50 – 11:10 Max Wisshak, López Correa M, Marali S and Freiwald A – **A quest for long-lived geochemical archives in the deep sea (Azores)**

- 11:10 – 11:30 Soraya Marali, Wisshak M, López Correa M, Montagna P, McCulloch MT and Freiwald A – **Skeletal and geochemical properties of scleractinian cold-water corals from the Azores**
- 11:30 – 11:50 Matthias López Correa, Sherwood O, Roark B, Montagna P, Edinger E, Rüggeberg A and McCulloch MT – **Patterns of elemental and stable isotopic ( $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$ ) variability in deep-sea bamboo corals of Newfoundland and Labrador**
- 11:50 – 12:10 Dave J Reynolds, Wanamaker AD Jr, Brocas WM, Richardson CA and Butler PG – **The dog cockle, *Glycymeris glycymeris*: a new annually resolved multi-centennial marine palaeoenvironmental archive**
- 12:10 – 12:30 Schwartzmann C, Durrieu G, Sow M, Ciret P, Claire E Lazareth, and Massabuau JC – **One year of giant clam growth: a combined HFNI valvometry and sclerochronology study**
- 12:30 – 14:20 Lunch**

### Session 1C Proxy Development

Conveners: David P Gillikin, Christopher S Romanek

- 14:20 – 14:40 Laurent Chauvaud, Thébault J, Clavier J, Lorrain A and Strand Ø – **What's hiding behind ontogenetic  $\delta^{13}\text{C}$  variations in mollusk shells? New insights from the great scallop (*Pecten maximus*)**
- 14:40 – 15:00 Maite Bauwens, Beelaerts V, Dehairs F and Schoukens J – **Which proxies should be integrated in the multi-proxy model?**
- 15:00 – 15:20 Marco BA Hatch, Schellenberg SA, McGowan JA and Carter M – **Ba/Ca variations in the modern intertidal bean clam *Donax gouldii*: an upwelling proxy?**
- 15:20 – 15:40 David P Gillikin, Haveles AW, Lorrain A, Ivany LC, Versteegh EAA and Dehairs F – **Barium in mollusk shells: a dual proxy of environmental conditions**
- 15:40 – 16:00 Leon J Clarke, Wanamaker Jr AD, Kreutz KJ, Borns Jr HW and Introne DS – **Can calcite bivalve shell B/Ca be used as a palaeosalinity proxy?**
- 16:00 – 16:30 Coffee Break (refreshments will be provided)**

### Session 1D *Proxy Development*

Conveners: Thomas Tütken, Bernd R Schöne, Christopher S Romanek

- 16:30 – 16:50 Julien Thébault, Schöne BR, Chauvaud L, Hallmann N, Richard M, Barth M, Nunn EV and Bassoullet C – **Investigation of Li/Ca ratio temporal variations in shells of two marine bivalves: *Arctica islandica* (Iceland) and *Pecten maximus* (France)**
- 16:50 – 17:10 Poulain C, Anne Lorrain, Thebault J, Gillikin, DP, Munaron JM, Bohn M, Robert R and Paulet Y-M – **The impact of solution chemistry on the incorporation of Mg, Sr and Ba in the aragonite shell of *Ruditapes philippinarum*: results from a laboratory study**
- 17:10 – 17:30 Bernd R Schöne, Zhang Z, Radermacher P, Thébault J, Jacob DE, Nunn EV and Maurer A-F – **Sr/Ca and Mg/Ca ratios of ontogenetically old, long-lived bivalve shells (*Arctica islandica*) and their function as paleotemperature proxies**
- 17:30 – 17:50 Kotaro Shirai and Radermacher P – **Micro scale elemental distribution in shells of *Arctica islandica***
- 17:50 – 18:10 Claire E Lazareth, Le Cornec F, Candaudap F and Freydier R – **Trace element high-resolution distribution in bivalve isochronous growth layers**

## Monday 26<sup>th</sup> July 2010

### Session 2 *Environmental Monitoring and Pollution*

Conveners: Kazushige Tanabe, Christopher A Richardson

- 08:30 – 09:00 Christopher A Richardson – **Mollusc shells: archives of environmental and anthropogenic change** – Keynote
- 09:00 – 09:20 Andrew LA Johnson, Schöne BR and Chenery SRN – **Influences on the trace-element content of freshwater bivalve shells**
- 09:20 – 09:40 Christopher A Richardson, Jones NJE, Butler PG, Scourse JD, Chenery SRN and Hartley JP – **Assessing the history of trace element concentrations in the northern North Sea through Laser Ablation-ICP-MS of *Arctica islandica* shells**
- 09:40 – 10:00 Lisa A Friedrich, Halden NM and Palace VP – **Using otolith microchemistry to delineate environmental effects of mining**
- 10:00 – 10:30 *Coffee Break (refreshments will be provided)*

**Session 3 Invertebrate (Paleo)ecology and Evolution**

**Conveners: Kazushige Tanabe, Christopher A Richardson**

- 10:30 – 11:00     Rob Witbaard – **Sclerochronology and Ecology: They need each other!**  
– Keynote
- 11:00 – 11:20     David H Goodwin, Anderson LC, Roopnarine PD and Kercher PM – **New sclerochronological constraints for ontogenetic patterns in tropical American bivalves: heterochronic evolution associated with the emergence of the Central American Isthmus**
- 11:20 – 11:40     Melita Peharda, Ezgeta-Balić D, Richardson CA, Vrgoč N and Isajlović I – **Sclerochronology and population structure of a commercially important bivalve: the smooth clam *Callista chione* in the eastern Adriatic Sea**
- 11:40 – 12:00     Rob Witbaard and Hippler D – **Following seasonal shell growth in *Arctica islandica***
- 12:00 – 12:20     Silvia Santos, Cardoso JFMF, Nieuwland G, Guimarães F, Witbaard R, Luttikhuisen PC, van der Veer HW and Machado JP – **Validation of the seasonality in growth bands in the bivalve *Macoma balthica* using stable isotope and trace element analysis**
- 12:20 – 12:40     Miyaji T, Kazushige Tanabe, Matsushima Y, Sato S, Yokoyama Y and Matsuzaki H – **Response of daily and annual shell growth patterns of a shallow marine bivalve to Holocene coastal climate change in Japan: a case study on *Phacosoma japonicum* (Veneridae)**
- 12:40 – 13:00     Alexander Arkhipkin and Shcherbich ZN – **A new increment bearing structure for age estimation in jumbo squid *Dosidicus gigas* (Ommastrephidae)**

**13:00 – 14:30     Lunch**

**14:30 – 17:30     Poster Session**

**18:30 onward     Mid-conference Dinner (Eisgrub Bräu, Microbrewery)**

## **Tuesday 27<sup>th</sup> July 2010**

### **Session 4A *Paleoclimate & Paleoenvironmental Reconstructions***

**Conveners: Andrew LA Johnson, Bryan A Black**

- 08:30 – 09:00 Bryan A Black – **Sclerochronology and the potential for multi-species perspectives on past climate and ecological variability** – Keynote
- 09:00 – 09:20 Ulrike Wacker, Munnecke A and Joachimski MM – **Fossil brachiopod shells: reliable archives of seawater temperatures?**
- 09:20 – 09:40 Alexander Nützel, Joachimski MM and López Correa M – **Seasonality in the Late Triassic tropics – High-resolution oxygen and carbon isotope records from aragonitic bivalve shells (Cassian Formation, northern Italy)**
- 09:40 – 10:00 Elizabeth V Nunn and Price GD – **High-latitude seasonality during the Early Cretaceous greenhouse**
- 10:00 – 10:30 Coffee Break (refreshments will be provided)**

### **Session 4B *Paleoclimate & Paleoenvironmental Reconstructions***

**Conveners: Dorrit E Jacob, Kazushige Tanabe, Bryan A Black**

- 10:30 – 10:50 Steffen Hetzinger, Halfar J, Keenlyside N, Mecking J, Kronz A, Steneck R, Adey W and Lebednik PA – **A link between North Pacific and North Atlantic climate on multidecadal time scales: new insights from coralline algae**
- 10:50 – 11:10 Jochen Halfar, Williams B, Hetzinger S, Steneck R and Adey W – **Skeletal density trends in coralline algae suggest ocean acidification impacts in the North Pacific and North Atlantic**
- 11:10 – 11:30 Kristine L DeLong, Quinn TM, Shen C-C and Lin K – **A snapshot of climate variability at Tahiti 9.5 ka using a fossil coral from IODP expedition 310**
- 11:30 – 11:50 David Storz and Gischler E – **Skeletal extension-rate record of a coral from the Maldives tracks ENSO and Indian monsoon variability**
- 11:50 – 12:10 Jens Zinke, Pfeiffer M, Crueger T, Wassenburg J and Hardman E – **Indo-Pacific teleconnections on decadal time-scales assessed by multiple Sr/Ca and oxygen isotope records from the southwestern Indian Ocean**
- 12:10 – 12:30 Miriam Pfeiffer, Zinke J, Dullo W-C, Timm O, Cahyarini SY and Weber ME – **Evaluating twentieth century warming trends with *Porites* corals from the Indian Ocean**
- 12:30 – 14:00 Lunch**

**Session 4C *Paleoclimate & Paleoenvironmental Reconstructions***

**Conveners: Bernd R Schöne, Bryan A Black**

- 14:00 – 14:20 Keziah J Stott, Austin WEN, Sayer MDJ and Wilson RJS – **The investigation of growth rates, environment and climate signals in *Arctica islandica* from NW Scotland**
- 14:20 – 14:40 Paul G Butler, Wanamaker AD Jr, Richardson CA, Scourse JD and Reynolds DJ – **A 1350-year crossdated sclerochronology for the North Icelandic shelf based on growth increments from shells of *Arctica islandica***
- 14:40 – 15:00 James D Scourse, Wanamaker AD Jr, Weidman C, Heinemeier J, Reimer PJ, Butler PG and Richardson CA – **The marine radiocarbon bomb-pulse across the temperate North Atlantic:  $\Delta^{14}\text{C}$  inventories from *Arctica islandica* growth increments**
- 15:00 – 15:20 Michael L Carroll, Ambrose WA Jr, Levin BS, Henkes GA, Hop H, Ryan S, Locke W, Renaud PE, Cottier F and Berge J – **Growth rate and geochemical variability in the Arctic bivalve *Serripes groenlandicus*: a multi-scale Pan-Svalbard proxy**
- 15:20 – 15:40 Emma AA Versteegh, Blicher ME, Troelstra SR and Dehairs F – **The application of bivalve sclerochemistry in reconstructing past Greenland meltwater runoff**
- 15:40 – 16:10 Coffee Break (refreshments will be provided)**

**Session 4D *Paleoclimate & Paleoenvironmental Reconstructions***

**Conveners: C Fred T Andrus, Meghan Burchell, Bryan A Black**

- 16:10 – 16:30 Dorrit E Jacob, Soldati AL, Schöne BR, Bianchi MM and Hajduk A – **Climate signals in shells of *Diplodon chilensis patagonicus* bivalves, Northern Patagonia, Argentina**
- 16:30 – 16:50 Tsuyoshi Watanabe, Komoto Y and Shirai K – **Comparison of daily and seasonal changes in shell microstructures and trace elemental signals for river bivalve *Margaritifera laevis* with in-situ environmental parameters**

**Session 5 *Shell midden archaeology***

**Conveners: Elizabeth V Nunn, C Fred T Andrus, Meghan Burchell**

- 16:50 – 17:20 C Fred T Andrus – **Sclerochronology in archaeology: beyond season of capture analysis** – Keynote



- 17:20 – 17:40 Meghan Burchell, Cannon A, Hallmann N, Schöne BR and Martindale A – **Understanding ancient shellfish use in British Columbia, Canada through high-resolution sclerochronology and oxygen isotope profiles**
- 17:40 – 18:00 Nadine Hallmann, Burchell M, Martindale A, Cannon A and Schwarcz HP – **Holocene climate changes in British Columbia and seasonality estimates reconstructed from the bivalve *Saxidomus gigantea* using high-resolution isotope sclerochronology**

### **Wednesday 28<sup>th</sup> July 2010**

#### **Session 6A *Paleobiology and Life history of vertebrates (skeletochronology)* Conveners: Anne-France Maurer, Thomas Tütken**

- 08:30 – 09:00 Thomas Tütken – **Fossil bones and teeth: geochemical and histological archives for life history and palaeobiology** – Keynote
- 09:00 – 09:20 Daniel Gerdeaux and Dufour E – **Contribution of intra-otolith variations in stable carbon and oxygen isotopes to age validation of pike (*Esox lucius*) scales and otoliths**
- 09:20 – 09:40 Carsten Witzel, Kierdorf U, Frölich K and Kierdorf H – **A study of the periodicity of incremental markings in dental enamel of sheep**
- 09:40 – 10:00 Antoine Zazzo, Balasse M, Passey BH, Moloney AP, Monahan FJ and Schmidt O – **The isotope record of short- and long-term dietary changes in sheep tooth enamel: implications for quantitative reconstruction of paleodiets**
- 10:00 – 10:30 Coffee Break (refreshments will be provided)**

#### **Session 6B *Paleobiology and Life history of vertebrates (skeletochronology)* Conveners: Anne-France Maurer, Thomas Tütken**

- 10:30 – 10:50 ~~Kathlyn M Smith, Fisher DC and Rountrey AN – **Use of tusk growth and stable isotope records to assess an unusual all-female American mastodon (*Mammot americanum*) assemblage**~~
- 10:50 – 11:10 Timothy G Bromage, Juwayeyi YM, Smolyar IV, Gomez S, Hu B and Chisi J – **Incremental lamellar bone rhythms revealed on multi-annual timescales in humans**
- 11:10 – 11:30 Lena Hänsel and Alt KW – **Incremental lines in human teeth: a reliable method for biological age determination?**

**Session 7 *Biom mineralization: Processes & Crystal Fabrics***

**Conveners: Kotaro Shirai, Anders Meibom**

- 11:30 – 12:00 Anders Meibom – **New tools to study paleoenvironmental proxy precision and biological effects** – Keynote
- 12:00 – 12:20 Robin M Cobb, Andrus CFT, Pérez-Huerta A and Olson JB – **Analysis of skeletal growth in stylasterid corals**
- 12:20 – 12:40 Pascal Radermacher, Shirai K and Zhang Z – **Heterogeneity of Sr/Ca and crystal fabrics in the shell of *Arctica islandica*: developing a reliable paleothermometer**
- 12:40 – 14:00 Lunch**

**Session 8 *Cross-links and Visions***

**Conveners: Alan D Wanamaker Jr, Gerrit Lohmann, Bernd R Schöne**

- 14:00 – 14:30 Gerrit Lohmann, Brey T, Lomovasky B and Schöne BR – **Marine-biological proxies and climate circulation: methods and applications** – Keynote
- 14:30 – 14:50 Vasile Ersek, Clark PU, Mix AC, Cheng H and Edwards L – **Response of the Pacific Northwest to Holocene climate forcings**
- 14:50 – 15:10 Denis Scholz, Hoffmann D, Spötl C, Hopcroft P, Mangini A and Richter DK – **Decoupled evolution of temperature and precipitation in western Germany during the Last Interglacial reconstructed from a precisely dated speleothem**
- 15:10 – 15:30 Frank DC, Jan Esper, Raible CC, Büntgen U, Trouet V, Stocker B and Joos F – **Sensitivity of the carbon cycle estimated from ensemble climate reconstructions**
- 15:30 – 16:00 Alan D Wanamaker Jr – **Visions: the future of sclerochronology** – Keynote
- 16:00 – 16:30 Coffee Break (refreshments will be provided)**

**16:30 – 17:15 Ballot: 3<sup>rd</sup> ISC (ISC2013) & Awards**

**18:30 onward Farewell Dinner (Proviantmagazin; free drinks until 20:30)**

## Poster presentations

- | Poster # | Author(s) – Title   |
|----------|---|
| 51       | <u>Konstantina Agiadi</u> and Girone A – <b>Sclerochronological examination, Sr/Ca spectral analysis and signal processing of two <i>Ceratoscopelus</i> otolith morphotypes from the Quaternary Ionian Sea</b>                      |
| 20       | <u>Jessica R Bean</u> and Hill TM – <b>Intermittent growth in gastropod shells: seasonal changes in apertural morphology and shell oxygen isotope records</b>   |
| 21       | <u>Jessica R Bean</u> and Jacobs LM – <b>Seasonal and tidal influences on gastropod shell oxygen isotope records</b>  |
| 52       | <u>Veerle Beelaerts</u> , Bauwens M, Versteegh EAA, Pintelon R and Dehairs F – <b>Periodic time-series modeling with guaranteed positive growth rate estimation for environmental records</b>                                       |
| 54       | <u>Lars Beierlein</u> – <b>Investigating climatic archives from archaeological sites in East Germany: a calibration study on <i>Unio crassus</i></b>  |
| 15       | <u>Erin C Beirne</u> and Wanamaker AD Jr – <b>Experimental calibration of <i>Arctica islandica</i> shell carbonate as a geochemical proxy for environmental dissolved inorganic carbon</b>  |
| 26       | Bellamy E, Mahé K, de Rafélis M and <u>Frank Lartaud</u> – <b>Growth of the common cockle <i>Cerastoderma edule</i>: validation of the periodicity of increment deposition by Calcein marker</b>                                    |
| 42       | <u>Annemarie Bird</u> , Johnson ALA, Leng M and Balson PS – <b>Pliocene climate of the Southern North Sea Basin: a sclerochronological approach</b>   |
| 38       | <u>Peter Bisling</u> , Theopold F, Krause-Nehring J and Brey T – <b>First results on lead in <i>Arctica islandica</i> shells using laser ablation and resonance ionization</b>  |
| 47       | <u>Thomas Brey</u> , Lohmann G, Jenkins K, Ahn IY, Lomovasky B and Voigt M – <b>Does the Antarctic Circumpolar Current isolate high-latitude bivalves from ENSO forcing?</b>  |
| 27       | <u>William M Brocas</u> , Ridgway ID, Reynolds DJ, Butler PG, Richardson CA, Scourse JD and Ramsay K – <b>Developing the use of the dog cockle, <i>Glycymeris glycymeris</i>, shell as a new scleroclimatological proxy species</b> |
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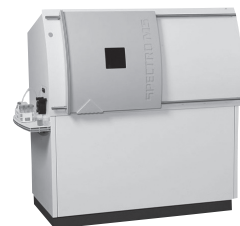
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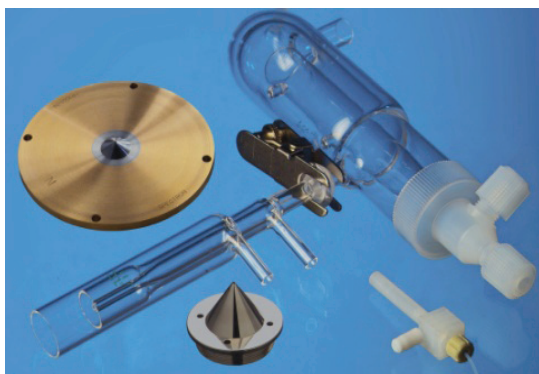
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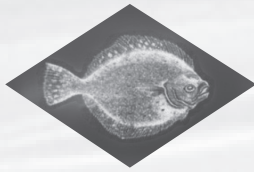
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## **Oral presentation abstracts**



## **Sclerochronology in archaeology: beyond season of capture analysis**

**Andrus CFT\***

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Archaeologists use sclerochronology primarily as a means to assess season of capture in mollusks but are increasingly applying it to achieve other goals. Conversely, non-archaeologists use middens as sources of ancient specimens for purposes such as paleoclimate reconstruction using sclerochronological techniques. As such, archaeologists and sclerochronologists often collaborate, but communication between the two fields is sometimes difficult. I will use examples from my own and my students' research to illustrate what I see as new avenues of collaborative research and discuss some potential sources of miscommunication between the disciplines. The examples will include molluscan paleoclimate and paleoproductivity estimates related to Andean prehistory, evidence for selective habitat exploitation among prehistoric North American Indians, and models of monumental construction patterns and ritual as seen in ring-shaped middens. I will also discuss the development of new archaeologically relevant molluscan proxies in South, Central, and North America. These examples will also illustrate how taphonomic concerns unique to archaeological sites may influence paleoclimate and environmental proxies in mollusks excavated from middens.

## **A new increment bearing structure for age estimation in jumbo squid *Dosidicus gigas* (Ommastrephidae)**

**Arkhipkin AI\*** and Shcherbich ZN

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Age estimation in squid, as in other short-lived animals, is a challenging task. Among a few increment-bearing structures, the calcareous statoliths are the most popular tools to estimate squid age in days. Daily formation of statolith growth increments has been validated in a number of squid species by both chemical marking and comparison of increment number with the known age of squid kept in tanks. However, in large squid the statolith growth decreases with age, often making the growth increments indiscernible near the statolith margin. This is exactly the case for age determination in large specimens of the jumbo squid, *Dosidicus gigas*, whose range expansion to temperate waters in the Eastern Pacific has been impacting local ecosystems and fishermen alike since the last strong El Niño in 1997-98. Age determination using the gladius has also not been possible in this species as growth increments are observed only in the anterior part of its rachis, representing only the last part of squid life. Fortunately, unlike other ommastrephid squid, the gladius of *D. gigas* has a peculiar feature. Its inner part (hypostracum) fills the gladius cone providing the stronger support and rigidity for the mantle tip and fins (Bizikov, 1996). Upon squid growth, external layers of hypostracum are laid periodically to fill in the growing cone. We have sampled statoliths and gladii from six specimens of *D. gigas* (mantle length of 80-88 cm) caught in Coquimbo (Chile) in November 2009. The cone of the gladius was cut longitudinally (according to Bizikov, 1996) and revealed prominent periodical growth increments in the hypostracum layer. Readability of the increments was enhanced with haematoxylin staining. The number of growth increments in the hypostracum varied from 714 (mature female of 87.5 cm ML) to 823 (mature male of 87.5 cm ML). Far fewer growth increments (262-323) were observed in the statoliths taken from the same animals; however the portion near the statolith margin needed extrapolation. Our results showed that the hypostracum layer has a potential to be an alternative tool for age estimations in *D. gigas* in case of partial unreadability of the statoliths especially in large squid. Further investigations are needed to determine the periodicity of increment formation in the hypostracum at various ontogenetic stages of jumbo squid.



## Which proxies should be integrated in the multi-proxy model?

Bauwens M<sup>1,2\*</sup>, Beelaerts V<sup>2</sup>, Dehairs F<sup>1</sup> and Schoukens J<sup>2</sup>

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All potential temperature proxies (e.g.,  $\delta^{18}\text{O}$ , Mg, Sr) suffer of one common problem: the proxy signal is strongly influenced by non-temperature forcers such as salinity, metabolism and shell growth. The use of multi-proxy models offers a solution for that problem. However, the use of classical linear multiple regression models are not always appropriate since some data show substantial non-linear relationships between temperature and elemental ratios. In previous research we demonstrated that the so called Weight Determination by Manifold Regularization (WDMR) approach can be used to develop a non-linear multi-proxy model. Now a new question arises: which proxies should be integrated in the multi-proxy model? We evaluated four trace element records (Mg/Ca, Sr/Ca, Ba/Ca and Pb/Ca ratios) measured in the shell of the common blue mussel *Mytilus edulis*. Different proxy combinations were evaluated over a salinity range between 15 and 32. Our findings highlight Mg/Ca ratios as the most powerful paleothermometers but we indicate that its reconstruction performance is significantly improved by combining it with other elemental ratios into a multi-proxy model. We assume that disturbances on the Mg/Ca profile due to growth and food availability can be explained by variations in the Sr/Ca profile and the Ba/Ca profile, which results in better temperature reconstructions using a Mg/Ca, Sr/Ca and Ba/Ca the WDMR. Although Pb/Ca ratios seem to contribute slightly positively to the final reconstruction performance of a four proxy model, we discourage the use of Pb/Ca in a multi-proxy model for temperature reconstruction since the element is known to be strongly influenced by antropogenetic forcers. Using Mg/Ca, Sr/Ca and Ba/Ca the WDMR model gave a root mean squared error of  $\pm 2.21^\circ\text{C}$  for a temperature reconstruction based on a shell sampled independently in time and location.

## **Sclerochronology and the potential for multi-species perspectives on past climate and ecological variability**

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In terrestrial ecosystems, a global network of tree-ring chronologies serves as a leading indicator of past environmental variability and change, especially over the last 1000 years. Growth increments formed in the hard parts of long-lived animal species have been increasingly recognized for their potential to address analogous issues in marine and freshwater ecosystems. Such archives are of particularly high value considering the scarcity of long-term observational records in aquatic systems. However, to fully realize the data's potential and ensure maximum quality, all time series used to develop chronologies should be exactly dated and sufficiently replicated. When these criteria are fulfilled, "sclerochronologies" may be more directly compared with one another, tree-ring chronologies, and climate records. This potential to combine diverse time series is a particularly strong asset of sclerochronology in that it allows for more holistic assessments of past environmental variability. From an ecological standpoint, combinations of sclerochronologies may be used to compare species of contrasting life histories or evaluate ecosystem processes as they cascade through multiple trophic levels. With respect to climate, combinations of exactly dated sclerochronologies and/or tree-ring chronologies may be used to generate reconstructions in which each species captures climate from its own unique "perspective" of habitat and life history, yielding a more robust estimate than either proxy could provide on its own. Considering the diversity of candidate species and habitats, sclerochronology will undoubtedly grow in coming years given its potential to fill critical gaps in our knowledge of ecological and climatic variability in marine, freshwater, and terrestrial ecosystems. Yet to maximize that potential, every effort must be made to ensure adequate replication and precise dating whenever resources permit.

## Incremental lamellar bone rhythms revealed on multi-annual timescales in humans

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The purpose of our research is to apply novel image analytical methods for characterizing cyclic – or periodic – textures manifest in lamellar bone that belong to the class we refer to as incremental patterns. Moreover, we investigate the midshaft femur histology of sub-Saharan Africans of Bantu origin and known life history with the purpose of characterizing growth rate variability for as many as five years of continuously accreting primary lamellar bone. The lamellar formation rate may be obtained by characterizing the incremental anatomy of an individual's associated dental enamel, well-documented to exhibit a short (ca. 24-hours) and a long period (striae of Retzius), the latter representing a temporary slowing of enamel formation in humans every ca. 8-9 days on average. The number of daily increments between striae is called the repeat interval (RI), which is identical for all teeth of an individual, but which represents the physiological period responsible for the formation of that archetypal fundamental unit of bone called the *lamella* (Bromage et al. 2009 *Calcif. Tiss. Int.* 84, 388-404). Lamellae vary in width, and thus provide time-calibrated measures of growth rate variability.

Midshaft femur sections from ten individuals – six of which have associated teeth and a known RI – were ground to ca. 50  $\mu\text{m}$  thick and imaged by circularly polarized light. Binary images of lamellar bone were rendered and converted to vector format. We employed a discrete model of lamellar bone based upon the parameterization of incremental pattern structure (Smolyar et al. herein). Transects were semi automatically plotted perpendicular to the direction of bone growth and their intersections with lamellae given coordinates. A calculation of entropy and an index of structural anisotropy was performed to assess the impact of anisotropy on the accuracy of growth rate variability measurements. This was done by assigning a label to each intersection and evaluating all alternate possible relationships between lamellae crossed by adjacent transects.

Striking rhythms in lamellar growth rate reveal cycles never before observed in developing bone; in some individuals we observe cycles closely approximating a 28-day rhythm, and in others we visualize rhythms on uni-annual and, in cases, bi-annual cycles. Endogenous biological periodicities, cycles manifest in the external environment, and perturbations to development are all potentially contained within growth rate variability studies of lamellar incremental patterns. Because lamellae are formed within defined periods of time, quantitative measures of widths of individual lamellae provides time-resolved growth rate variability and reveal rhythms in human bone growth heretofore unknown. This study was funded by the USA National Science Foundation.

## Understanding ancient shellfish use in British Columbia, Canada through high-resolution sclerochronology and oxygen isotope profiles

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Archaeological analyses of settlement patterns and subsistence practices at coastal sites often require precise identifications of seasonality to interpret ancient patterns of landscape use. The application of high-resolution sclerochronology and oxygen isotope analysis to archaeological shells can be used as a geo-cultural archive to identify past ecological conditions that influenced settlement patterns and resource procurement strategies. In addition, it can also provide a precise measure of the season of shellfish harvest, and by proxy, site occupation. When coupled with macroscopic growth increment analysis, relative levels of shellfish harvest pressure, shellfish management strategies, and/or resource depression can be identified within a seasonal context.

Historically, both settlement and subsistence in coastal British Columbia, Canada (BC) were influenced by seasonal changes in the abundance and availability of local foods, however, very little is known about regional variability within an archaeological context. This paper presents the results of analysis of the bivalve, *Saxidomus gigantea*, from shell middens from two distinct cultural and environmental regions of the coast of BC. The Dundas Islands Group (7000-1000 BP), in northern BC is considered to be a resource-poor area with marginal food sources, yet it was able to support the development of large village populations. In contrast, the Namu region, on the central coast (6000-1000 BP) shows evidence of a storage-based economy supported by local fisheries. Prior to interpreting seasonality based on  $\delta^{18}\text{O}$  it was necessary to understand the life-history traits of *S.gigantea*. Many occupation sites are located near estuaries therefore the results of the oxygen isotope analysis were aligned with high-resolution sclerochronology to better understand the influence of seasonal influxes of freshwater on  $\delta^{18}\text{O}$ .

The initial results show that people harvested shellfish more intensively, and in a broader seasonal range in the Dundas Islands than in the Namu region. This is likely attributed to a greater need to incorporate shellfish into diets to sustain local village populations. Stratigraphic evidence shows that seasons of shellfish harvest changed over time at the Dundas Islands, which may imply that local clam beds were harvested to depletion, and therefore could not be collected again until the population had regenerated. While there are some similarities in seasonal patterns, for example an emphasis on fall collection, the analysis of shells from both regions have shown distinct differences in the intensity and seasonal range of collection, which is likely related to the role of shellfish in local economies in association with the availability of other foods.

## **A 1350-year crossdated sclerochronology for the North Icelandic shelf based on growth increments from shells of *Arctica islandica***

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The first 1000-year shell-based crossdated chronology has been constructed using growth increments in multiple shells of the bivalve mollusc *Arctica islandica* collected from a site close to the island of Grimsey on the North Icelandic shelf. The chronology extends back to AD 1200 with multiple ( $n \geq 4$ ) series, and the inclusion of two further shells has enabled absolute dating to be extended to AD 655 with a sample depth of one. The sclerochronologically determined calendar dates are consistent with AMS radiocarbon dating of the thirteen subfossil shells included in the chronology. The chronology strength is fully comparable with equivalent tree-ring chronologies, with an expressed population signal (EPS; Wigley et al. 1984 *Jnl. Clim. and App. Meteorology* 23, 201-213) which exceeds ca. 0.85 from AD 1300 to the present day. The chronology includes five shells from animals whose lifetimes exceeded 300 years, and the most long-lived example has now been shown to have lived for ca. 500 years.

The availability of precise calendar dating for shell material which has also been radiocarbon dated has enabled a regional history of changes in the marine radiocarbon reservoir on the North Icelandic shelf to be reconstructed. This indicates that the relative influence of colder (and older) water from Arctic sources has been increasing by comparison with warmer, younger Atlantic-sourced water through most of the period under consideration. During the last ca. 150 years, however, a more complex picture has emerged, and the earlier trend may have reversed.

A strong positive correlation is apparent between the chronology indices and summer (JJA) seawater temperatures at the collection site. While it is not yet possible to hypothesize any causal mechanism, this association may be linked to the strong variability in temperature and salinity that characterized the Great Salinity Anomaly of the late 1960s and early 1970s (Dickson et al. 1988 *Prog. Oceanog.* 20, 103-151).

## **Growth rate and geochemical variability in the Arctic bivalve *Serripes groenlandicus*: a multi-scale Pan-Svalbard proxy**

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Understanding the consequences of climatic change in the Arctic requires linking ecosystem responses to both natural and anthropogenic climatic variations, over a range of temporal and spatial scales. Growth histories and geochemical information contained in the shells of Arctic bivalves provide continuous proxy records of physical and biological information such as temperature, salinity, and food supply over lifetimes spanning decades to centuries. We examined growth rates and interannual growth patterns from 260 individuals of the circumpolar Greenland Cockle (*Serripes groenlandicus*) from 11 sites around the Svalbard archipelago with a wide range of oceanographic and environmental gradients, from Atlantic-influenced waters on the western coast to high-Arctic waters in northeast Svalbard. Absolute growth rates were up to 3 times greater at the most strongly Atlantic-influenced locations compared to the most Arctic-influenced areas. Standardized growth indices (SGI) exhibited interannual patterns with some common features, including a distinctive shift from relatively greater to poorer growth in the mid-1990s. This pattern was consistent with phase-shifts in large-scale climatic drivers. Interannual variability in growth rates was also correlated with regional manifestations of the large-scale drivers including atmospheric pressure, precipitation, and sea ice extent. Shell geochemistry (trace element ratios), calibrated via instrumented moorings from two sites of differing Arctic influence, provides information on seasonal patterns of shell deposition related to temperature and food availability. The Mg/Ca ratio appears to reflect water temperature, while there was a single peak in the shell Ba/Ca ratio which generally matched the temporal pattern of fluorescence in the spring/summer. Annual growth checks were deposited when temperature was relatively warm (above 2°C), but when food supply, measured by fluorescence, was declining. This suggests that a lack of food availability, rather than cold ambient temperature per se, may be the signal that regulates the timing of seasonal dormancy in Arctic bivalves. These results demonstrate that sclerochronological and sclerochemical proxies are useful retrospective analytical tools for establishing baselines of ecosystem variability in Arctic systems and for identifying key ecosystem drivers across spatial and temporal scales.

## What's hiding behind ontogenetic $\delta^{13}\text{C}$ variations in mollusk shells? New insights from the great scallop (*Pecten maximus*)

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Mollusk shells contain geochemical information about environmental conditions that prevailed at the time of formation. We investigated ontogenetic and seasonal variations of  $\delta^{13}\text{C}$  values in calcitic shells of *Pecten maximus*. Ontogenetic variations of  $\delta^{13}\text{C}_{\text{shell}}$  values in three large specimens collected in Norway, France, and Spain exhibited a similar linear decrease with increasing shell height. We removed this linear drift (detrending). These three residual time-series displayed variations that could be linked to environmental fluctuations. To check it, we re-analyzed the isotopic datasets of Lorrain et al. (2002 J. Exp. Mar. Biol. Ecol. 275, 47-61; 2004 Geochim. Cosmochim. Acta 68, 3509-3519) who worked on three scallops harvested in 2000 in the bay of Brest (France), a well-monitored ecosystem. Lowest values of  $\delta^{13}\text{C}_{\text{shell detrended}}$  were recorded in all shells in late spring–early summer, most likely reflecting corresponding variations in food availability. Our results indicate that ontogenetic and seasonal variations of  $\delta^{13}\text{C}_{\text{shell values}}$  cannot be used as a proxy for past  $\delta^{13}\text{C}_{\text{DIC}}$  variations, but should be considered as promising tools for ecophysiological studies.

## Can calcite bivalve shell B/Ca be used as a palaeosalinity proxy?

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Palaeosalinity is an important, yet difficult, parameter to reconstruct in palaeoclimate studies. Previous studies have suggested that sedimentary boron concentrations can be used as a means of reconstructing palaeosalinity in the historical and geological past. This idea is based on a conservative mixing between high boron concentration and high salinity seawater and low boron concentration and low salinity freshwater, e.g., as takes place within estuaries. In this study we have investigated whether B/Ca within the calcite outer layer of laboratory cultured *Mytilus edulis* exhibits a strong relationship with seawater salinity and have also tested whether temperature has any influence on shell B/Ca. Animals were grown under constant salinity and temperature conditions in a three by four factorial design, i.e., salinities of  $32 \pm 0.1$ ,  $28 \pm 0.1$  and  $23 \pm 0.1$  and temperatures of  $4 \pm 0.2$ ,  $8 \pm 0.2$ ,  $12 \pm 0.3$  and  $16 \pm 0.4^\circ\text{C}$ . Quantification of aquaria seawater B/Ca also has allowed direct determination of boron partition coefficients in *M. edulis* shell calcite.



## Analysis of skeletal growth in stylasterid corals

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Corals of the family Stylasteridae have been little studied with respect to fundamental questions of biomineralization, age and growth rate. This presentation focuses on two different species in this hydrocoral family, *Stylaster erubescens* and *Stylaster roseus*. *S. erubescens* is a deep-water species found in the Atlantic. Our specimens were collected on the Blake Plateau off the Charleston Bump in the Gulf Stream. *S. roseus* is a shallow water species often found in the Caribbean. Our specimens were collected near the Cayman Islands. Scanning electron microscope (SEM) imaging on *S. roseus* shows incremental growth in the distal tips, while the base of the colony shows no such incremental growth structures. SEM images of *S. erubescens* show banding only in select portions of the colony and seem less regular than in *S. roseus*. Porous structures can be seen in etched samples under SEM, which may comprise growth increments seen in reflected light. SEM imaging in *S. roseus* shows that growth is delineated by pores in the distal tips that are infilled as the coral skeleton grows from the center of calcification outward. These pores are organic in origin and appear to be a nucleation site for crystal growth. Central canals in the base of the colony also have pore-like structures, such as in the distal tips, however these pores are not as organized; crystal growth does not appear to be directly related to these smaller pores. No center of calcification was found in the deep-water specimens. Basal structures were also studied to assess if the infill of canals is a major factor that inhibits the use of *S. erubescens* as a paleoproxy. The implications of these finds, with respect to skeletal geochemistry and their potential use as a paleoclimate proxy, will be discussed.

## **A snapshot of climate variability at Tahiti 9.5 ka using a fossil coral from IODP Expedition 310**

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The Integrated Ocean Drilling Program (IODP) Expedition 310 recovered drill cores from the drowned reefs around the island of Tahiti (17°40'S, 149°30'W), many of which contained samples of massive corals from the genus *Porites*. Herein we report on one well-preserved fossil coral sample – a 13.6 cm long *Porites* sp. dated by uranium-series techniques at  $9523 \pm 33$  years. Monthly  $\delta^{18}\text{O}$  and Sr/Ca determinations reveal nine clear and robust annual cycles. Coral  $\delta^{18}\text{O}$  and Sr/Ca determinations estimate a mean temperature of ca. 24.3°C (ca. 3.2°C colder than modern) for Tahiti at 9.5 ka; however, this estimate is viewed with caution, since potential sources of cold bias in coral geochemistry remain to be resolved. The interannual variability in coral  $\delta^{18}\text{O}$  is similar between the 9.5 ka coral record and a modern record from nearby Moorea. The seasonal cycle in coral Sr/Ca is approximately the same or greater in the 9.5 ka coral record than in modern coral records from Tahiti. Paired analysis of coral  $\delta^{18}\text{O}$  and Sr/Ca indicates cold/wet (warm/dry) interannual anomalies, opposite from those observed in the modern instrumental record.

## Response of the Pacific Northwest to Holocene climate forcings

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The large-scale Pacific Ocean coupled ocean-atmosphere system has the strongest influence on Pacific Northwest (PNW) climate during winter months. However, the history of Holocene climate during this season is poorly constrained. Here we report the first high-resolution, absolutely-dated record of Holocene winter climate variability in the PNW as captured in a stalagmite from Oregon. The first-order variability of the speleothem  $\delta^{18}\text{O}$  is associated with an increasing trend from the lower early Holocene values to the overall higher  $\delta^{18}\text{O}$  that characterize the late Holocene. We attribute this to a rise in winter insolation through the Holocene and superimposed on the long-term trend is significant millennial to multi-decadal climate variability characterized by both gradual and abrupt shifts. Several prolonged periods of low  $\delta^{18}\text{O}$  values are apparent in the speleothem record for the past 9 kyr with inferred century-scale cooling periods occurring near 6.8, 4.7, and 3.1 kyr. We note that our speleothem does not record a significant decrease of  $\delta^{18}\text{O}$  at the time of the 8.2 kyr event, supporting a reduced response of western North America to the 8.2 kyr cooling in the North Atlantic.

Using multitaper and wavelet techniques we identify significant spectral peaks in the  $\delta^{18}\text{O}$  record at 1600, 650, and 60 years. To obtain a robust evaluation of the correspondence between speleothem  $\delta^{18}\text{O}$  and solar forcing we compare our record with a reconstruction of total solar irradiance and with an estimation of the sunspot number. We conclude that while some centennial and multi-decadal variability in Oregon can be due to direct solar forcing, the millennial and multi-centennial variability, where most of the variance is concentrated, cannot be explained by direct solar forcing as represented in the two reconstructions.

To evaluate the role of changes in ocean and atmospheric circulation in the North Atlantic on PNW winter climate, we compare our speleothem record with measurements of drift ice in the Atlantic Basin. It is apparent that particularly during the early and mid-Holocene increases in the percentage of drift ice are accompanied by increases in  $\delta^{18}\text{O}$  at OCNM, and the cross-wavelet analysis of these two time-series indicate they are highly-coherent and nearly in-phase at periods between ca. 2000 and 1500 years during the early and mid-Holocene. This “see-saw” pattern of cold North Atlantic and warm North Pacific is consistent with teleconnections between the Pacific and Atlantic basins modulated by opposite phases of the North Atlantic Oscillations and the Pacific Decadal Oscillations, as suggested by several climate modeling studies.

## Sensitivity of the carbon cycle estimated from ensemble climate reconstructions

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Carbon flux and storage controlling processes of the atmosphere, ocean, and terrestrial biosphere are temperature sensitive, and by acting as a net positive climate feedback across inter-annual to Milankovitch time-scales are projected to amplify anthropogenic warming. However, the magnitude of the climate sensitivity of the global carbon cycle,  $\gamma$ , is under debate and gives rise to uncertainties in the feedback strength and warming projections. Here we combine in a probabilistic approach an ensemble of proxy-based temperature reconstructions and pre-industrial CO<sub>2</sub> data from three ice cores to constrain  $\gamma$  on the policy-relevant multi-decadal to centennial time-scales. Calibrations that preserve the full amplitude of long-term natural variability, yield a pre-industrial to modern temperature amplitude of 0.7°C exceeding natural variability by 0.3°C. Based upon >200,000 ensemble members, we quantify the median  $\gamma$  to 7.7 ppmv CO<sub>2</sub> increase per °C warming. CO<sub>2</sub> and temperature co-variation between 1050-1549 and 1550-1800 restrict  $\gamma$  to 3.3 to 12.9 ppmv/°C. Estimates of  $\gamma$  computed herein from ten coupled carbon-climate model simulations for the 19th and 20th century are broadly consistent with these constraints, with only two models above and one below this range. However, our results are incompatibly lower ( $p < 0.05$ ) than recent empirical estimates of carbon cycle-climate sensitivities of 40 ppmv/°C and correspondingly suggest ca. 80% less amplification of future warming.

## Using otolith microchemistry to delineate environmental effects of mining

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Otoliths are calcified structures in the inner ear of teleost fish, composed of layers of aragonite in a protein matrix deposited continuously throughout the lifetime of the fish. Both the inorganic portion and the protein matrix have the capacity to incorporate a broad range of trace elements. Periodic changes in trace metal concentrations in the environment may influence the amounts available for incorporation into the otolith through food or ambient water. Otoliths may serve as continuous recorders of exposure to trace elements owing to their metabolic stability, continuous growth throughout the life of the fish, and annular structure that provides a corresponding time-scale. However, the relationship between fish otoliths and the chemical environment is complex, and is complicated by fish physiology as well as differences in habitat.

We have examined otolith microchemistry from a variety of settings to determine if a chemical signature related to mining activity and local geology of an area can be detected in otolith microchemistry. Otoliths were taken from geologically distinct areas that have been influenced by metal or coal mining activity. In each case, a suite of elements indicative of the surrounding geology or mining activity was chosen for LA-ICP-MS analyses across the annular growth zones. Otoliths from fish captured near and downstream from a rare element pegmatite mine contain signatures of Li, Cs, and elevated Rb, whereas those from lakes distant to or upstream from the pegmatite do not have such concentrations of those elements. Otoliths taken from lakes adjacent to Cu, Pb, and Zn mining contain single peaks of the three metals that are interpreted to indicate when the fish came into contact with the tailings. Fish stocked in a closed open-pit Ni-Cu-Cr mine contain constant levels of these base metals throughout their life history. Anomalously high peaks of Se detected in otoliths from fish collected in coal mine end pits indicated that fish from the mine-impacted system migrated from nearby reference streams that do not receive Se-bearing runoff. These cases indicate that otolith microchemistry can be used to evaluate the extent of mining activity affects in an environment, as well as provide information on fish movement into and out of affected areas.

## Contribution of intra-otolith variations in stable carbon and oxygen isotopes to age validation of pike (*Esox lucius*) scales and otoliths

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Pike (*Esox lucius*) is the largest predator in fish communities of freshwater systems in Europe. Usually, pike age is determined from the observation of growth annuli of scales. However, false checks can lead to erroneous determinations. Lake Annecy (France) presents seasonal variations in temperature and a large thermal vertical stratification during summer. Variations in stable isotope ratios measured in fish otoliths can record fish life history, in particular thermal habitats. It is then possible to count the number of winters experienced by a fish.

Eleven pike specimens were caught from Lake Annecy in February and June 2008. Fish Total Length ranged from 520 mm to 960 mm. We generated monthly resolution profiles in stable carbon and oxygen isotope values ( $\delta^{13}\text{C}_{\text{oto}}$  and  $\delta^{18}\text{O}_{\text{oto}}$ ) of sagittal otoliths. Profiles show regular, seasonal variations.  $\delta^{13}\text{C}_{\text{oto}}$  and  $\delta^{18}\text{O}_{\text{oto}}$  values ranged from -15 to -10.5‰ and from -9.5 to -6.5‰, respectively. Fish from 520 to 570 mm were two years old (2+) and the largest fish (960 mm) was five years old (5+).

Isotopic results were compared to otolith and scale growth marks. Isotopic variations match alternations of otolith dark and light growth marks. There is also a good match with scale annuli. The first mark observed in scales cannot be interpreted as a winter mark. This suggests that a habitat and/or diet change occurred during the first summer of life.

## Barium in mollusk shells: a dual proxy of environmental conditions

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Many trace element signals in mollusk shells are not robust proxies of environmental conditions. Reports on Mg/Ca, Sr/Ca, U/Ca and Mn/Ca have shown that these proxies can be complicated by vital or kinetic effects. Ba/Ca profiles on the other hand have been shown to be similar in several different species of bivalves and highly reproducible between shells growing in the same region. The typical signal is a flat 'background' signal episodically interrupted by sharp peaks. The background signal records ambient dissolved Ba/Ca of the water in which the mollusk grew. There is typically an inverse relationship between Ba/Ca in water and salinity, making the background Ba/Ca proxy in mollusk shells a potential salinity proxy. The driving mechanism of the peak has yet to be understood; the main hypothesis is that the peaks are related to ingestion of Ba rich phytoplankton or direct ingestion of barite. Developing the Ba/Ca peak proxy further could possibly lead to a paleo-productivity proxy. In this paper we give examples of Ba/Ca profiles from several different groups of marine and freshwater modern bivalves as well as from Eocene *Venericardia* from the Gosport Sand (Alabama, USA) and Pliocene *Mercenaria* from the Duplin Formation in South Carolina. The Eocene fossil specimens show profiles similar to modern bivalves, with low background Ba/Ca indicating full marine salinities. However, the much younger fossil specimen (*Mercenaria* sp. from the Pliocene) showed clear signs of 'elemental diagenesis', with background Ba/Ca levels about 10 times higher than modern specimens (despite original mineralogy of aragonite and typical isotope profiles). This highlights the potential and problems of using this developing proxy on fossil specimens.

## Geochemistry and skeletal structure of *Diploria strigosa*, implications for coral-based climate reconstruction

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Geochemical tracers incorporated into the skeleton of reef-building corals are ideal proxies for reconstructing environmental parameters of ambient seawater such as temperature and salinity at subseasonal resolution. However, validation concerns of these environmental proxies due to the complex skeleton of some tropical Atlantic corals have hindered coral-based environmental reconstructions in contrast to the tropical Pacific. In order to identify complications associated with the complex skeletal architecture of the coral *Diploria strigosa*, we performed microsampling experiments along and across individual skeletal elements. Here we demonstrate that the geochemical Sr/Ca,  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  heterogeneity at millimetre scale observed between skeletal elements is a systematic feature of *D. strigosa* where the theca wall is depleted in Sr,  $^{18}\text{O}$  and  $^{13}\text{C}$  compared to adjacent septa and columella. This finding has important implications for coral paleoclimatology because such geochemical heterogeneity related to the so-called vital effect can lead, for Sr/Ca and  $\delta^{18}\text{O}$ , to apparent temperature biases of several degrees that are induced by the mixing of different macroskeletal elements during sampling. We found that differences between apparent temperature signature inferred from the septal and thecal materials are greater for Sr/Ca suggesting that this temperature proxy is more sensitive to macroskeletal mixing than  $\delta^{18}\text{O}$ . Subseasonal sampling experiments performed along individual skeletal elements of a single corallite reveal that microdrilling the centre of the theca wall is the microsampling method that best resolves the seasonal pattern of both Sr/Ca and  $\delta^{18}\text{O}$ . Furthermore, we propose that samples which deviate from the initial/optimal sampling axis along the centre of the theca of *D. strigosa* are very likely characterized by higher Sr/Ca,  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  values that are not environmentally-dependent. Therefore, anomalous trends towards higher Sr/Ca,  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  values and disturbance or loss of Sr/Ca and/or  $\delta^{18}\text{O}$  seasonality are potential manifestations of this sampling artifact.



## **New sclerochronological constraints for ontogenetic patterns in tropical American bivalves: heterochronic evolution associated with the emergence of the Central American Isthmus**

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Oceanographic conditions in tropical American oceans changed dramatically following the closure of the Panama Seaway. Prior to the emergence of the Central American Isthmus (CAI), equatorial Atlantic and Pacific water mixed freely. Today, however, seasonal upwelling of cold, nutrient-rich water characterizes the tropical Eastern Pacific, whereas warm, nutrient-poor water dominates the Caribbean. Here we document growth patterns from presumed cognate species found on either side of the CAI: *Corbula dietziana* (Western Atlantic) and *C. speciosa* (Eastern Pacific). Despite diverging ca. 3.5 million years ago, these species are geometrically identical differing only in size. Our results suggest this size difference is a function of heterochrony.

Corbulids are small, sturdy-shelled clams that range from the Late Jurassic through the recent. Despite their long geologic range, corbulid morphology remains relatively unchanged. In general, corbulids possess ovate to trigonal inequivalve shells: the right valve tending to be larger than the left. Their conservative morphology notwithstanding, corbulids employ various growth strategies to achieve their adult shape. Previous sclerochronologic and stable oxygen isotope ( $\delta^{18}\text{O}$ ) analysis indicate that some species grow isometrically, while others display allometric patterns of growth. *C. dietziana* and *C. speciosa* grow allometrically by producing a well-defined nepioconch followed by a marked change in the primary growth direction.

To understand observed size differences, we documented growth rates by measuring size at specific ages, which were established using  $\delta^{18}\text{O}$  profiles. Because oxygen isotope variation in biogenic carbonates is a function of temperature and the isotopic composition of water, both of which show strong annual cyclicity in tropical American oceans, patterns of within-shell  $\delta^{18}\text{O}$  variation can be used to establish ontogenetic age. Next, the sizes and ages of the nepioconchs were compared to establish differences in growth rates between the juvenile and adult shells of both species. Our data indicate diverging growth patterns following development of the nepioconch: *C. speciosa* lives longer than *C. dietziana*. If the ancestral ontogenetic pattern is comparable to that of *C. dietziana*, then *C. speciosa* experienced peramorphosis through hypermorphosis. In contrast, if the ancestral growth rate is similar to that of *C. speciosa*, then *C. dietziana* experienced pedomorphosis through progenesis.

## River runoff reconstructions from novel spectral luminescence scanning of massive coral skeletons

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Inshore massive corals often display bright luminescent lines that have been linked to river flood plumes from coastal catchments and hence have the potential to provide a long-term record of hinterland precipitation. Coral luminescence is thought to result from the incorporation of soil-derived humic acids transported to the reef during major flood events. Corals far from terrestrial sources generally only exhibit dull, relatively broad luminescence bands, which are attributed to seasonal changes in coral density. We therefore tested the hypothesis that spectral ratios rather than conventional luminescence intensity provides a quantitative proxy record of river runoff without the confounding effects of seasonal density changes. For this purpose we have developed a new, rapid spectral luminescence scanning (SLS) technique that splits emission intensities into Red, Green and Blue domains (RGB) for entire cores with an unprecedented linear resolution of 71.4  $\mu\text{m}$ . Since humic acids have longer emission wavelength than the coral aragonite, normalisation of spectral emissions should yield a sensitive optical humic acid/aragonite ratio for humic acid runoff, i.e., G/B ratio. Indeed G/B-ratios rather than intensities are well correlated with Ba/Ca, a geochemical coral proxy for sediment runoff, and with rainfall data, as exemplified for coral records from Madagascar. Coral cores also display recent declining trends in luminescence intensity, which are also reported in corals elsewhere. Such trends appear to be associated with a modern decline in skeletal densities. By contrast, G/B spectral ratios not only mark the impact of individual cyclones but also imply that humic acid runoff increased in Madagascar over the past few decades while coral skeletal densities decreased. Consequently, the SLS technique deconvolves the long-term interplay between humic acid incorporation and coral density that have confounded earlier attempts to use luminescence intensities as a proxy for river runoff.

## **Skeletal density trends in coralline algae suggest ocean acidification impacts in the North Pacific and North Atlantic**

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Ocean acidification can seriously impact calcifying marine plants and animals. In fact, it has recently been suggested that tropical corals and other marine calcifiers are already suffering from declining calcification rates. Greater oceanic CO<sub>2</sub> uptake at mid-to-high latitudes means calcium carbonate organisms in the subarctic are more susceptible to increasing ocean acidification than at lower latitudes. This is particularly true for the metabolically expensive high Mg-calcite skeletons of the shallow-water, habitat-forming coralline algae. Here we present the first century-scale record of declining skeletal densities in the coralline algae *Clathromorphum* sp. indicating ongoing ocean acidification is occurring in the Bering Sea and the subarctic NW Atlantic. *Clathromorphum* forms annual growth increments in its massive calcitic skeleton and is known to have a lifespan of up to several centuries. Time-series of skeletal density were generated at submonthly resolution using Micro Computer Tomography yielding a century-long time series of density variations in subarctic coralline algae from two ocean basins. Results indicate a decline in calcification since 1990 as well as positive departures from 1940-1990. These patterns give a first indication of the influence of rising atmospheric CO<sub>2</sub> on mid- and high-latitude shallow marine ecosystems. Furthermore, the similarity between the records from subarctic high-Mg coralline alga and the tropical corals is striking, and demonstrates not only the potential of coralline algae as archives of ocean acidification, but also the possible global-scale decline in calcification of some important marine biota.

## Holocene climate changes in British Columbia and seasonality estimates reconstructed from the bivalve *Saxidomus gigantea* using high-resolution isotope sclerochronology

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Bivalve mollusk shells are ideally suited for worldwide, high-resolution environmental reconstructions. In order to analyze climate variability and environmental changes in British Columbia during the Holocene, oxygen isotopes were measured in the butter clam *Saxidomus gigantea*. Stable isotopes and daily growth increments were analyzed in both modern and Holocene shells. Fossil shells were collected from archaeological sites in northern (Dundas Islands) and central (Namu and Hunter Island) British Columbia. The oxygen isotope data reveal clear annual profiles, with the most positive  $\delta^{18}\text{O}$  values occurring during winter and the most negative  $\delta^{18}\text{O}$  values during summer. In addition, the negative  $\delta^{18}\text{O}$  summer values observed in the early and late Holocene become considerably more negative during the mid Holocene (around 3000 to 5000 BP). The  $\delta^{18}\text{O}$  summer values are far more variable than the positive winter values, which remain relatively constant throughout the Holocene. This implies a much fresher interval during the mid Holocene.

The shell record was also compared with other proxy archives, such as trees (ring formation and tree line position), lake sediments, pollen records, plants and chironomid communities. The climate changes observed in the  $\delta^{18}\text{O}$  shell record match well with environmental changes reported for British Columbia. A number of studies have revealed a warm and dry early Holocene on the Pacific Northwest coast, which is followed by an episode of cooling and moistening into the mid Holocene. In particular, most coastal locations experienced an increase in precipitation during the mid Holocene, although overall, the mid Holocene of the Northwest coast was warmer and drier than present. The mid Holocene transition is also characterized by a number of cultural changes. Finally, a cooling trend is observed in the mid to late Holocene.

In addition to the climate information outline above, details about the season of shell collection can also be obtained from the oxygen isotope and sclerochronological analyses of shells. This allows a precise measurement of seasonality. The oxygen isotope profiles and daily growth increment widths reveal that the archaeological shells from northern and central British Columbia were collected during the spring and autumn. This could be due to the paralytic shellfish poisoning, which mostly occurs during the summer months. Such seasonality studies provide valuable information about the seasonal pattern of site occupation and local subsistence strategies because shellfish is a seasonally important food source.

## **Ba/Ca variations in the modern intertidal bean clam *Donax gouldii*: an upwelling proxy?**

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The discovery and calibration of high resolution paleoceanographic proxies are key to extending historical climate records and understanding regional climate variability. Skeletal remains have emerged as an often reliable recorder of environmental conditions. For the aragonitic bivalve *Donax gouldii*, we have determined that  $\delta^{18}\text{O}$  records seawater temperature and Sr/Ca is biologically controlled (Hatch and Schellenberg in prep.), and now explore Ba/Ca as a paleoproductivity proxy. Ba/Ca ratios in calcium carbonate have been attributed to diatom blooms and the Ba/Ca ratio of seawater (Lea and Spero 1994 *Paleoceanog.* 9, 445-452; Thebault et al. 2009 *Limnol. Oceanogr.* 54, 1002-1014.). To assess the Ba/Ca variability at approximately sub-weekly resolution, thin-sectioned shells were analyzed via Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry and tidally-induced growth bands were cross-dated to validate daily chronology. The timing of Ba/Ca peaks were compared to a suite of locally measured physical and biological factors including seawater temperature, nitrate, silicate, wave height, chlorophyll, diatom abundance and phytoplankton community composition. Cross-dating validated the chronology of shells collected over a six month period and revealed a single, simultaneous, large, short lived (> 1.5 week) Ba/Ca peak in all shells coinciding with peaks in nitrate concentration and a diatom abundance. While Thebault et al. (2009) attribute Ba/Ca peaks to ingestion of diatoms, a second larger diatom bloom does not coincide with any Ba/Ca peak in *Donax*. Unlike the diatom bloom that occurred when the shell recorded a Ba/Ca peak, this diatom bloom was not associated with a large nitrate spike. Alternate hypotheses for these observations include (1) diatom blooms increase Ba/Ca, but sampling failed to resolve the second Ba/Ca peak or (2) increased dissolved nutrients from upwelling increase Ba/Ca, evidenced by the lack of Ba/Ca peak for second diatom bloom which was not associated with a nitrate peak. These alternate hypotheses are being further evaluated in light of cross-dated *Donax* shell chemistry records and physico-chemical oceanographic data.

## **Incremental lines in human teeth: a reliable method for biological age determination?**

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Individual age determination plays a significant role in the reconstruction of pre-historical populations as well as in forensic science. In addition to morphological age determination on skeletons, histological and chemical techniques are also applicable. The measurement of accuracy in age determination decreases significantly from infancy and adolescence, which provides comparatively good results with insignificant errors, to adulthood. Comparatively good results with low variations can be expected from the tooth cementum annulation (TCA). Tooth cementum is built periodically throughout life by mineralisation. On the histological cross-sections these appositions appear as incremental lines running parallel to the surface of the cementum. They are visible as dark and light lines and one pair is formed annually. Therefore, the phenomenon of TCA is compared to the concentric annual rings of trees in dendrochronology as well as to the periodical growth lines of shells.

By the mid-1980s, incremental lines had been identified on 24 mammalian species. A method for age determination of human teeth based on the number of incremental lines was first tested for its applicability in 1982 by Stott et al. (Stott et al. 1982 J. Dent. Res. 61, 814-817). Several further studies followed, which increased the prevalence of the TCA method. In the last few years controversial discussions about the reliability and validity of TCA have emerged (Großkopf 1990 Z. Rechtsmed. 103, 351-359; Kagerer et al. Anthropol. Anz. 59, 331-342; Wittwer-Backofen et al. 2004 Am. J. Phys. Anthropol. 123, 119-129). Age variable changes on the tooth, structural changes due to nutritional and alimential influences, nonaccretion or doubling of individual lines as well as intra- and interobserver error create problems.

A study about the applicability of TCA on recent material is presently being performed at the Institute of Anthropology, University of Mainz. Photographs of microscopic cross-sections of the tooth root are prepared and incremental lines are enumerated. In addition, further age determinative dental methods are used as a basis for comparison.

## **A link between North Pacific and North Atlantic climate on multidecadal time scales: new insights from coralline algae**

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Observations of North Pacific (NP) sea surface temperatures (SSTs) are only available for the past century and become relatively sparse before the 1940s – too short to statistically assess low-frequency variability in climate and the surface ocean. Variability in the decadal to multidecadal bands, the characteristic time scales of Pacific Decadal Variability (PDV, 20 and 60 years) and Atlantic Multidecadal Variability (AMV, 60-80 years), has been detected in growth-based proxy reconstructions derived from tree rings and bivalves from the Northern Hemisphere. However, high-resolution geochemical marine proxy records of multi-centennial length are currently not available for the NP, preventing the recognition of multidecadal SST variations and regime shifts in the distant past. Recently, coralline algae have received increased attention as archives of paleoclimate information as they display incremental growth patterns in a high Mg-calcite skeleton that can be targeted for high-resolution geochemical sampling. We present a seasonally-resolved record of coralline algal Mg/Ca variations compiled from two *Clathromorphum nereostratum* specimens from the NP/Bering Sea region (Aleutian Islands, Alaska). Mg/Ca ratios of individual growth increments were analyzed by measuring single-point electron microprobe transects, yielding a 186-year record (1818-2003). This represents the longest seasonally-resolved marine proxy record to date from the subarctic NP encompassing several multidecadal cycles of climate and ocean variability. On interannual to interdecadal scales algal Mg/Ca ratios are strongly related to regional gridded-SST data. Both instrumental SSTs as well as algal Mg/Ca ratios in the western Aleutian region suggest a strong AMV influence on our study sites, but no significant correlation to the leading mode of PDV. A comparison of our NP record to tree ring-derived proxy reconstructions of AMV, that extend well beyond the instrumental period, yields a high correlation on multidecadal time scales. These proxy-based findings suggest a strong low-frequency linkage between NP and NA climate modes as proposed earlier by studies based on observational SSTs and climate models. This is the first evidence for a direct link between NA and NP SST patterns on multidecadal time scales based on annually resolved continuous marine proxy data that extend back to the early 19<sup>th</sup> century. Hence our results raise new possibilities to study important low-frequency teleconnections between the NA and NP ocean basins and their long-term persistence by using marine paleo-proxy data.

## Climate signals in shells of *Diplodon chilensis patagonicus* bivalves, Northern Patagonia, Argentina

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Sclerochronological as well as oxygen and carbon stable isotope data of *Diplodon chilensis patagonicus* shells from three lakes in the Nahuel Huapi National Park, Northern Patagonia, Argentina are presented. The data are complemented with results from a one year lake monitoring project on Laguna El Trébol yielding temperature, oxygen and carbon isotopic data for the lake water. The bivalve shells grow throughout most of the year, mainly controlled by water temperature, except for a growth break in austral spring, coinciding with the bivalves' reproduction period. Oxygen isotope values of the water reconstructed from shell values and instrumental records agree qualitatively with the shell growth curves. Carbon isotope values in the shells are consistent with the majority of the carbonate in the shell being derived from dissolved inorganic carbon in the water body.

About 58% of shell growth variability can be explained by SST variations in the South Pacific between ca. 40 and 55°S. Atmospheric forcing on shell growth via the Antarctic Oscillation is prominent for approximately the last 30 years ( $R = 0.4$ ) with strongest common spectral power for the 10-16 year period. It dominates the ENSO influence which was the strongest climatic factor during the years before ca. 1980 ( $R = 0.3$ ). The bivalve shells record most prominently the recent trend of the Antarctic Oscillation towards its positive polarity which caused regional warming in northern Patagonia.



## Influences on the trace element content of freshwater bivalve shells

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Ontogenetic profiles of shell  $\delta^{18}\text{O}$  from bivalves generally afford an accurate picture of ambient temperature variation. Equivalent profiles of trace element variation might be expected to reflect fluctuations in environmental concentrations. Bivalve shell is, however, a complex material, including organic components within (intra-) and between (inter-) the crystalline calcium carbonate. At least some trace elements are likely to have an affinity for the organic matter. Hence inclusion of variable amounts of this in samples will distort the results. Analysing shells of the freshwater bivalves *Dreissena*, *Unio* and *Anodonta* by Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS) and Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES), we investigated whether trace elements are indeed concentrated in organic material and whether chemical removal of the majority of this leads to more meaningful results (reflecting environmental concentrations) on analysis of the remainder. We found that certain elements are strongly concentrated in organic material, implying the need for very tight spatial control on sampling or prior removal of organics. However, we also found strong inter-taxic differences in the trace element content of cleaned shell material. These show that biological controls may overprint any signature of environmental variation in trace element concentration.

## Trace element high-resolution distribution in bivalve isochronous growth layers

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Trace element content variations along successive growth layers of bivalve shells have been used to provide records of environmental changes. However, the link between the shell chemistry and the environment is not straightforward because of vital effects. To better understand what is recorded in the shell, trace element distribution within shell material deposited at the same time has been studied (e.g., Foster et al. 2008 Chem. Geol. 254, 113-119). To accurately reconstruct environmental changes, the shell layer analyzed must indeed represent the environment at the time of deposition, whatever the position of the analyzed loci along an isochronously deposited growth line. Using Laser Ablation-ICP-MS, we evaluated the geochemical spatial homogeneity along single growth layers of five *Protothaca thaca* bivalve shells from two South America sites. Two growths layers, close to and far from the ventral margin, were analyzed.

We show that the trace element spatial distribution (Mg/Ca, Sr/Ca, Ba/Ca) along shell layers is not homogeneous. All shells display similar trace element isochronous distributions; different between young and adult biomaterial. In the more juvenile (i.e., old biomaterial) isochronous profiles, all trace element contents decrease toward the internal part of the external shell layer. Secondary electronic microscope study shows slight dissolution in shell parts close to the umbo. Very early diagenesis, animal still alive, might have modified the trace element distributions in the "old" secreted shell parts and/or equilibration with the surrounding seawater (favored by shell alteration?) might have changed the chemistry of the shell. Close to the ventral margin (fresh biomaterial), significant, reproducible Mg/Ca heterogeneities are observed along isochronous profiles for all individuals. We hypothesize that this might be due to a zonation of the outer epithelium of the mantle. Using LA-ICP-MS, two time-series for the same growth period, but at various distances from the external part of the shell, were conducted. The profiles obtained are highly similar for Sr/Ca and Ba/Ca. For Mg/Ca, time-series changes are similar but Mg/Ca ratios differ. The resulting calculated SST difference is of 4°C.

Our study shows that the location of high-resolution analyses points in shell cross-section must be precisely defined and followed with consistency all along the section to provide accurate environmental records. Shell diagenesis can occur in living bivalves, potentially modifying the shell composition. In *Protothaca thaca* shells, Sr and Ba seem the most promising elements to study as potential high-resolution environmental proxies. This study was financed and conducted in the frame of the French PNEDC CONCHAS project and also benefited from the support of the EU-project CENSOR (contract 511071).

## **Marine-biological proxies and climate circulation: methods and applications**

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A serious problem which has become very popular in the discussion on how future environmental conditions will affect mankind is whether increasing human population and industrialisation has already caused or will have the potential to induce a significant impact on the Earth's climate. To properly address this question requires detailed knowledge about amplitude and rapidness in the natural variations of environmental properties in the ocean, over the continents, and in the cryosphere – particularly for warm climate periods. The best way to gain this knowledge would be the inspection of historical time-series of direct measurements as well as the combination of such environmental observations. Unfortunately, historical records for environmental data, which would allow consideration of changing climate on a global scale, are too short and already fall within the period of strong human impact on natural conditions. Information on earlier times can be obtained either from proxies that record past climate and environmental conditions or by simulating climate, using comprehensive models of the climate system under appropriate external forcing. The models are clearly unrivalled in their ability to simulate a broad suite of variables across the entire world but their reliability on long time scales requires additional evaluation. Only climate records derived from environmental proxy-parameters enable the test of these models because they provide records of climate variations that have actually occurred in the past.

Several attempts to reconstruct climate patterns over the last centuries have been made. Proxy records obtained from ice cores, tree rings and corals, as well as historical data and long instrumental records have been used to reconstruct large-scale climate patterns for the last millenium. E.g., one stable mode of climate oscillations is on millennial time scale which is possibly linked to alternating warm and cold periods of which the Medieval Warm Period and Little Ice Age are the most recent manifestations of such an oscillation. Only a few marine records exist. We will show that robust statistical methods are essential in order to understand and interpret precisely temporally aligned data derived from biogenic skeletons. Several applications for Northern and Southern Hemisphere data (e.g., Iceland, South America) and their link to circulation are discussed. It is shown that the concept of stable teleconnections is a useful concept for climate reconstructions.

## Patterns of elemental and stable isotopic ( $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ ) variability in deep-sea bamboo corals of Newfoundland and Labrador

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Deep-sea gorgonian octocorals of the families *Primnoidae* and *Isididae* exhibit centennial-scale lifespans and, in some species, annually-secreted growth rings. Because of these attributes they have outstanding potential as long term paleoceanographic archives. Previous work has focused on characterization of growth rates (e.g., increments,  $^{14}\text{C}_{\text{AMS}}$ ) and isotopic and elemental composition of skeletal calcite (e.g.,  $\Delta^{14}\text{C}$ ,  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$ ) and in organic fractions (e.g.,  $\delta^{15}\text{N}$ ). However, imprecise skeletal chronologies and scarcity of long-term oceanographic data for calibration purposes have presented major impediments to the development of reliable proxies. We examined trace element and stable carbon ( $\delta^{13}\text{C}$ ) and oxygen ( $\delta^{18}\text{O}$ ) isotope variability in a live-collected, 140 year old specimen of *Keratoisis ornata* (Isididae) from -700 m on the southern Grand Banks (Newfoundland). Hydrographic records from this region extend back to the early 20<sup>th</sup> century, overlapping with the coral record almost continuously over a period of 96 years. Skeletal chronology was established through a combination of  $^{210}\text{Pb}$  and bomb- $^{14}\text{C}$  dating. Focusing on the skeletal calcite fraction, trace elements ( $^7\text{Li}$ ,  $^{11}\text{B}$ ,  $^{25}\text{Mg}$ ,  $^{31}\text{P}$ ,  $^{55}\text{Mn}$ ,  $^{84}\text{Sr}$ ,  $^{138}\text{Ba}$ ,  $^{238}\text{U}$ ; normalized to  $^{43}\text{Ca}$ ) were measured along parallel radii of an axial section using Laser Ablation-ICP-MS (10  $\mu\text{m}$  resolution), while  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values were measured on MicroMill samples (100  $\mu\text{m}$  resolution). Annually-averaged element profile replicates were aligned using peaks and troughs in Ba/Ca, which correlated remarkably well along parallel radii ( $R = 0.62$  to  $0.85$ ). Reproducibility of other elements ranged from medium (B/Ca,  $R = 0.49$  to  $0.65$ ; Mg/Ca,  $R = 0.21$  to  $0.39$ ) to poor or inconsistent (Sr/Ca,  $R = 0.06$  to  $0.31$ ; U/Ca,  $R = -0.01$  to  $0.79$ ). For all elements, temperature and salinity explained <10% of the interannual variability. Mean adult calcite Mg/Ca-concentrations instead are temperature driven, which extended the range of the existing Mg/Ca-temperature calibration (Sherwood et al., 2005; 6 to 10°C) down to 3°C. Stable isotope data exhibited classic kinetic isotope effects (KIE), with  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  correlated (slope = 0.33,  $R^2 = 0.4$ ) along a line extending from expected equilibrium to more depleted values. Temperature reconstructions using the 'lines technique' (Smith et al. 2000 Palaios 15, 25-32) may be feasible in deep-sea gorgonians. Similar geochemical patterns were replicated with a ca. 140 year old specimen of *K. ornata* from the Northern Labrador Sea dating back to ca. 1000 yrs BP.

## Skeletal and geochemical properties of scleractinian cold-water corals from the Azores

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In recent years cold-water corals have become an object of intense geochemical research. It has been suggested that their aragonitic skeleton holds valuable information about past and present oceanographic parameters, such as nutrient abundance and temperature. However, the extraction of environmental information from trace elements and stable isotopes is complicated by vital effects.

In our study three Recent cold-water scleractinian species – *Desmophyllum cristagalli*, *Caryophyllia cyathus* and *Stenocyathus vermiformis* – were collected alive with a submersible at 500 m water depth in the Azores. In addition, ambient seawater samples were taken for oxygen isotope ( $\delta^{18}\text{O}_{\text{sw}}$ ) and stable carbon isotope ( $\delta^{13}\text{C}_{\text{DIC}}$ ) analysis. Data loggers deployed for one year offered a high-resolution temperature data set, reflecting a very stable bathyal temperature regime with an annual mean of  $12.3 \pm 0.25^\circ\text{C}$ . These environmental data were compared with proxy-based reconstructions to test the suitability of cold-water corals as geochemical archives, and to elucidate the role of vital effects. Optical and scanning electron microscopy were used to examine the skeletal architecture. Carbonate powders for oxygen isotope ( $\delta^{18}\text{O}_{\text{ar}}$ ) and stable carbon isotope ( $\delta^{13}\text{C}_{\text{ar}}$ ) analysis were extracted from longitudinal and transversal skeletal transects with a MicroMill (100  $\mu\text{m}$  track-spacing). The spatial distribution of trace and minor elements (Mg, Sr, Ca) was mapped with an Electron Microprobe and quantified with Laser-Ablation-ICP-MS (Li, B, Mg, P, Mn, Sr, Ba, U).

The aragonitic microstructure of all three coral species is essentially equal. It consists of microgranular aragonite at the centres of calcification and of increments composed of semispherulitic fibrous crystal bundles in the theca and the septa. Stable isotope and trace element variations are coupled to this incrementation and microstructure types. Mg for instance, is enriched in the centres of calcification and depleted in the surrounding fibres. Oxygen isotopes as a common temperature proxy show large variations of up to 4‰ (VPDB) that would correspond to an apparent temperature range of  $\approx 16^\circ\text{C}$ , contrasting with the stable bathyal temperature (ca.  $0.5^\circ\text{C}$  range). This highlights a dominant kinetic vital effect, which is also expressed in a strong linear correlation of  $\delta^{13}\text{C}$  vs.  $\delta^{18}\text{O}$ . Nevertheless, this linear regression can be used to deduce the ambient temperature with the “lines technique” (Smith et al. 2000 *Palaios* 15, 25-32) yielding temperatures that deviate by about  $2^\circ\text{C}$  from measured values.

## **New tools to study paleoenvironmental proxy precision and biological effects**

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The extent and causes of recent environmental variations represent a vitally important problem for scientists, lawmakers and society in general. Essential to the ongoing scientific debate is the development of proxies that can reconstruct environmental change on both short (10-1000 years) and long (i.e., geologic) timescales. However, for every such proxy, a fundamental question exists that is rarely addressed: To what *precision* can the proxy reconstruct environmental variation? Only by answering this question quantitatively is it possible to decide if a given proxy is precise enough to be applicable and useful. An easily applicable and general method to quantify the precision of linear environmental proxies will be presented together with a new analytical development to study the origin of biological effects on the composition of biominerals.

## **Response of daily and annual shell growth patterns of a shallow marine bivalve to Holocene coastal climate change in Japan: a case study on *Phacosoma japonicum* (Veneridae)**

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It is well known that the distribution patterns of shallow-marine mollusk faunas around the Japanese Islands have changed episodically during the Holocene in response to the latitudinal displacement and relative strength of oceanic currents (Matsushima 1984 Bull. Kanagawa Pref. Mus. 15, 37-109). However, little is known about the biotic response of individual species to Holocene climate change at daily to annual scales of temporal resolution.

The venerid bivalve *Phacosoma japonicum* used in our study is regarded as an ideal species to investigate this subject for the following reasons. Firstly, lunar daily and annual growth increments are well-preserved in the outer shell layer, thereby enabling calculation of the age and growth rate of individual specimens (Tanabe 1980 Lethaia 21, 231-241; Schöne et al. 2003 Mar. Biol. 142, 473-485; Miyaji et al. 2007 Mar. Ecol. Prog. Ser. 336, 141-150). Secondly, previous studies have extensively investigated latitudinal variations in patterns of shell microgrowth and the ecological, genetic, and environmental background of the species (e.g., Tanabe and Oba 1988 Mar. Ecol. Prog. Ser. 47, 75-82; Sato 1994 Mar. Biol. 118, 663-672; Schöne et al. 2003 Mar. Biol. 142, 473-485). Thirdly, fossil shells of this species are abundant in Holocene shallow-marine deposits and archeological sites throughout the Japanese Islands.

Holocene shells of this species recovered from various sites in Japan preserve lunar daily and annual growth increments in the outer shell layer and hinge plate, as is also observed in modern shells. Sclerochronological analyses of 29 shells with known <sup>14</sup>C ages revealed that the life history traits (e.g., length of the growth period and the mean lunar daily growth rate at a given age) have changed markedly over the past 8000 years (Miyaji et al. 2010 Palaeogeogr. Palaeoclimatol. Palaeocol. 286, 107-120). The intra-annual patterns of lunar daily increments and shell oxygen isotope records of the fossil shells can be compared with those of modern specimens from various locations, which are constrained by annual patterns of seawater temperature and summer-autumn precipitation rates. Furthermore, the temporal trend recorded in the fossil shells show a strong correlation with climate change in mid-latitude parts of East Asia over the last 8000 years, indicating that *P. japonicum* has changed its life history traits in response to Holocene terrestrial and coastal climate change.

## High-latitude seasonality during the Early Cretaceous greenhouse

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The investigation of high-latitude seasonality during the Cretaceous greenhouse is fundamental for addressing key palaeoclimatic debates such as the nature of the equator-to-pole temperature gradient and the presence or absence of polar ice sheets at this time. However to date, Cretaceous sea surface temperatures have predominantly been reconstructed using biological materials such as foraminifera ( $\delta^{18}\text{O}$ ), fish teeth ( $\delta^{18}\text{O}$ ) and membrane lipids (TEX<sub>86</sub>), which do not provide information on sub-annual time scales. This study presents new stable isotope data from two Boreal Realm belemnite genera, *Acroteuthis* and *Pachyteuthis*, which were collected from the Ryazanian–Hauterivian succession of the Pechora Basin in Arctic Russia. Long-term palaeotemperature profiles were constructed for this succession using both  $\delta^{18}\text{O}$  and Mg/Ca data. The profiles showed warm temperatures in the Ryazanian, a cooling event, which culminated in the Late Valanginian and finally a return to much warmer values in the Hauterivian. Suitable belemnite specimens were therefore selected from three distinct horizons (one Ryazanian, one Valanginian and one Hauterivian), in order to investigate the seasonal differences between warm and cold phase belemnites. Well-preserved belemnite rostra were milled along transects perpendicular to the visible growth lines in order to generate carbonate powder for high-resolution  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  analysis. The data showed that during the Ryazanian and Hauterivian warm intervals, belemnite  $\delta^{18}\text{O}$  ratios fluctuated by as much as 3‰ over the course of one year. Conversely, belemnites from the Valanginian cool interval showed a  $\delta^{18}\text{O}$  variability of typically less than 1‰. These trends are consistent in both *Acroteuthis* and *Pachyteuthis*, strongly suggesting that the observed variability is environmental in origin. If the  $\delta^{18}\text{O}$  data are interpreted as being primarily influenced by temperature (with only minor fluctuations in  $\delta^{18}\text{O}_{\text{seawater}}$  values), then this equates to seasonal palaeotemperature fluctuations of over 10°C in the warm phases and of just 4°C in the cool phase. A possible explanation is that during the cool phase, temperatures remained consistently low throughout the year, whilst in the warm phases, high latitude summer temperatures increased significantly.



## **Seasonality in the Late Triassic tropics: high-resolution oxygen and carbon isotope records from aragonitic bivalve shells (Cassian Formation, Northern Italy)**

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The Late Triassic Cassian Formation (N Italy, Dolomites) is one of the very few occurrences with original aragonite preservation. This important Early Mesozoic fossil lagerstätte has produced more than 1000 described invertebrate species. Mollusk shells are commonly preserved as primary aragonite. Three pristine aragonitic megalodontoid bivalves were sampled for  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  sclerochronology ( $n = 270$ ). The presence of aragonite and crossed lamellar shell microstructure (first record for Triassic megalodontoids) suggests an absence or minimal impact of diagenetic alteration. To our knowledge, this is the first high resolution sclerochronological study from unaltered aragonite shells from the Triassic. The  $\delta^{13}\text{C}$  values range from 3.6 to 5.8‰ VPDB and show a distinct cyclicity, likewise  $\delta^{18}\text{O}$  values exhibit a pronounced cyclicity varying from -3.6 to -1.4‰ VPDB. These variations in  $\delta^{18}\text{O}$  suggest a pronounced seasonality in Late Triassic tropical shallow waters, with inferred seasonal temperature changes ranging from 24 to 32°C. Influx of fresh water during the rainy seasons (mega-monsoon) or upwelling might also explain part of the variation in  $\delta^{18}\text{O}$  values. The presented data suggest that the diverse Cassian fauna lived under conditions characterized by warm sea surface waters with a pronounced seasonality. Similar conditions were reported for modern tropical settings. Ongoing studies focus on other organisms (e.g., corals and sponges) and on other geochemical temperature proxies (e.g., Sr/Ca). This facilitates a better understanding of the Late Triassic climate in the tropical Tethys.

## **Sclerochronology and population structure of a commercially important bivalve: the smooth clam *Callista chione* in the eastern Adriatic Sea**

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The age, growth and population structure of the commercially important smooth clam *Callista chione* in the eastern Adriatic Sea were reconstructed from annually-resolved growth lines in the shell. Clams were collected during 2007 and 2008 using either a hydraulic dredge or commercial SCUBA diving at four locations (Rab Island, Pag Bay, Cetina Estuary and Kaštela Bay) in Croatian coastal waters. The age of 436 clam shells was determined from the internal growth lines present in shell cross-sections and the timing of growth line formation was ascertained from monthly collections of clams to occur between August and September during the period when sea water temperatures were maximal. Differences were apparent in the age structure and growth rates of clams collected from the four locations. Von Bertalanffy growth (VBG) curves obtained for clams from these locations were  $L_t = 72.4 (1 - e^{-0.25 (t-2.68)})$  (Rab Island),  $L_t = 74.5 (1 - e^{-0.15 (t+0.57)})$  (Pag Bay),  $L_t = 79.3 (1 - e^{-0.34 (t-0.97)})$  (Cetina estuary) and  $L_t = 82.5 (1 - e^{-0.11 (t+2.88)})$  (Kaštela Bay). The age of the smooth clams ranged between 3 and 44 years whilst median clam ages were similar at three of the four locations i.e., 14, 12, 4 and 12 years respectively. The VBG growth constants recorded from clams in this study are within the range of values obtained by previous authors for the species. The observed differences in population structure between locations indicate different levels of exploitation and illustrate the need for establishing long-term strategies for the sustainable exploitation of smooth clams in the Croatian Adriatic.

## Evaluating twentieth century warming trends with *Porites* corals from the Indian Ocean

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Instrumental records of sea surface temperature (SST) are unreliable prior to 1960 due to changes in the measurement procedures. Recently, it has been shown that an abrupt drop of 0.3°C in global mean SST after 1945 merely results from uncorrected instrumental biases in the sea surface temperature record (Thompson et al. 2008, Nature 453, 646-649). This cool bias has a profound impact on the historical record of 20<sup>th</sup> century surface temperatures. Thus, the development of independent SST records is needed in order to validate the historical SST database. Here, we present a temperature reconstruction developed using a set of *Porites* coral geochemical records from the western tropical Indian Ocean, a region that is tightly coupled to global mean temperatures. Our temperature reconstruction shows the pronounced warming of the Indian Ocean over the course of the 20<sup>th</sup> century that has been attributed to anthropogenic warming. Moreover, we find that the coral index closely follows global mean surface air temperatures that are free of systematic biases due to changes in the measurement procedures. The distinct temperature drop after 1945 that is evident in Indian Ocean and global mean SST series neither appears in the coral record nor in the global mean surface air temperature series. We conclude that multi-core coral temperature reconstructions may provide unbiased records of 20<sup>th</sup> century SST throughout the tropical oceans.

## The impact of solution chemistry on the incorporation of Mg, Sr and Ba in the aragonite shell of *Ruditapes philippinarum*: results from a laboratory study

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Individuals of *Ruditapes philippinarum* were reared at constant temperature (20°C) under different controlled conditions of salinity and water chemistry, commonly encountered in their natural habitat. Clams were exposed to a constant salinity of 35 PSU for the first 35 days and then three salinity conditions were tested (20, 28 and 35 PSU) until 64 days. The main objectives of this study were: (1) to test if Sr/Ca, Mg/Ca and Ba/Ca shell ratios were stable when clams were reared under stable environmental conditions, (2) to study the effect of salinity and water chemistry on elemental uptake and the response time necessary to induce a modification in the shell chemistry and (3) to improve our understanding on pathways and incorporation of elements into the shell. Both laser analyses (Ba/Ca, Sr/Ca, Mg/Ca) and 2D-mapping WDS microprobe analyses (S, Sr and Mg) were performed. While we found a positive relation between salinity and shell Mg/Ca and Ba/Ca ratios, Sr/Ca ratios showed an inverse relationship, i.e., shell Sr/Ca ratios higher at low water Sr/Ca while growth was not significantly different between treatments. Interestingly, despite stable conditions of water Mg/Ca ratios for clams reared at salinity 35 PSU during the whole experiment, shell Mg/Ca ratios increased through time, possibly due to an incorporation of particulate Mg. The Partition coefficient of Mg ( $D_{Mg}$ ), significantly different between the three salinity treatments, was very low (mean value of 0.00054). This low  $D_{Mg}$  suggests that incorporation of magnesium into shell carbonate is highly regulated by the organism. As already observed in previous studies, shell Ba/Ca ratios showed the strongest positive relationship with seawater chemistry, and this after a very short response time (one day). Finally, a high positive correlation between Ba/Ca and Sr/Ca was observed in each salinity treatment but with different slopes. This result suggests that pathways of Sr<sup>2+</sup> and Ba<sup>2+</sup> through mantle membranes are similar and probably via the Ca<sup>2+</sup> channel. This implies that, in this experiment, incorporation of Sr<sup>2+</sup> and Ba<sup>2+</sup> may be influenced by several factors: (1) the concentration of Ca in the surrounding water, (2) the density of Ca<sup>2+</sup> channels in mantle membrane and (3) the Sr/Ca and Ba/Ca ratios of the surrounding water.

## **Heterogeneity of Sr/Ca and crystal fabrics in the shell of *Arctica islandica*: developing a reliable paleothermometer**

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Quantifiable paleotemperature proxy data from biogenic carbonates can help to improve our understanding of past climate dynamics. It has recently been suggested, that Sr/Ca values derived from the outer shell layer (along the axis of maximum growth) of the ocean quahog, *Arctica islandica*, could potentially function as a paleothermometer. However, Sr/Ca ratios are known to show heterogeneity across contemporaneously deposited shell material, i.e., within the outer shell layer. It is likely that either physiological or syndepositional biomineralization processes probably control the Sr incorporation into the biomineral. Sr is significantly enriched near the annual growth lines (though not necessarily associated with organic molecules), whereas carbonate-rich shell portions exhibit reduced levels of Sr. Here, we document that the distribution of Sr in the outer layer of the *A. islandica* shell is also associated with differences in crystal fabrics.

Sr/Ca heterogeneity in contemporaneously deposited shell portions was measured (in the ventral margin) by LA-ICP-MS and ICP-OES. The ICP-OES data, covering the distance from the outermost to the innermost shell surface, showed a hammock-type distribution of Sr with a variability of at least 30%. LA-ICP-MS analyses of two parallel line-scans (conducted in the same shell portion as the ICP-OES analyses) showed a very different pattern of variability. Sr values in the outer shell layer were higher near the outer sublayer than near the inner sublayer. This may be linked to slight differences in the crossed-acicular crystal fabrics between the two sublayers. Furthermore, Sr/Ca ratios were higher near the annual growth lines, which largely consist of irregular simple prisms.

The heterogeneity of Sr in *A. islandica* shells is strongly related to differences in shell fabrics (and growth structures). Furthermore, the observed variability in Sr concentration appears to be maintained by differences in biomineralization mechanisms. Establishing Sr/Ca as a reliable paleothermometer therefore requires a comprehensive understanding of the physiological controls on shell biomineralization.

## The dog cockle, *Glycymeris glycymeris*: a new annually resolved multi-centennial marine palaeoenvironmental archive

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The dog cockle, *Glycymeris glycymeris* is a long-lived marine bivalve mollusc that inhabits coarse sands to sandy gravel substrates of the continental shelf seas of Europe and North Western Africa at water depths up to ca. 100 m. Previous studies have shown *G. glycymeris* to contain >100 growth increments (Ramsay et al. 2000 J. Sea Res. 43, 167-176), however provide no evidence for the periodicity at which these growth lines are formed. We examine the internal growth lines of live and dead *G. glycymeris* collected from the Tiree Passage (West Scotland, UK) to assess the potential of *G. glycymeris* for becoming a long-term annually resolved marine palaeoenvironmental archive. The internal growth lines from four live and fifty of the largest (>40 mm) dead collected valves were embedded into epoxy resin and sectioned along the axis of maximum growth from the umbone to the ventral margin. The cut surfaces were ground and polished using methods as described by Scourse et al. (2006 Holocene 16, 967-974). The polished surfaces were etched using 0.1M HCl for 120s, bathed in distilled water and left to air dry. Acetate peel replicas were constructed using methods described by Richardson (2001 Ocean. and Mar. Bio. 39, 103-164). The growth series were measured from digital photomosaics of the acetate peel replicas using transmitted light microscopy under 2.5x, 4x and 10x magnifications. Calcium carbonate (CaCO<sub>3</sub>) samples were milled from the ventral margin and umbone regions from the two longest lived *G. glycymeris* for radiocarbon analysis; further CaCO<sub>3</sub> samples were micro-milled at sub-incremental resolution from the widest growth lines of the two smaller live-collected shells for stable isotopic analysis. The maximum longevity of *G. glycymeris* within the Tiree Passage population determined sclerochronologically and verified by radiocarbon analysis (<sup>14</sup>C) is ca. 200 years. The growth series from nine of the dead collected and the two relatively long-lived live collected *G. glycymeris* statistically cross-match using techniques described by Scourse et al. (2006), forming the first multi-centennial absolute dated master sclerochronology from this species. The <sup>14</sup>C determinations independently validate the nature of the cross-matching, dating the years of death of both shells to have occurred during the post-bomb period of AD 1960 – AD 1985. Comparison of the <sup>14</sup>C determinations and the sclerochronologically derived longevities provides evidence that the growth lines within *G. glycymeris* are formed on an annual basis. Comparison between the master chronology and instrumental environmental observations suggests that the growth of *G. glycymeris* is strongly coupled to environmental forcing supporting the use of this species as a scleroclimatological palaeoenvironmental proxy.

## **Mollusc shells: archives of environmental and anthropogenic change**

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Tidally deposited and annual growth lines present in sections of the shells of bivalves have been shown to record changes in the environmental conditions experienced throughout their life. Recent refinements in methodologies for revealing these patterns, together with advancements in analytical techniques, have opened up the possibility for evaluating the rolls of natural environmental changes as well as anthropogenic impacts in regulating the chemistry of the shell. Using selected examples of the shells of bivalves from different environmental scenarios the value of the various growth line series as an environmental archive will be demonstrated. Intertidal and shallow water dwelling bivalves have been shown to provide information on historical changes in heavy metal contamination in the coastal marine environment, whilst species living in areas of upwelling events record changes in seawater chemistry related to these events. The shells of long-lived subtidal dwelling species have the potential to reveal long-term trends in seawater chemistry over centuries, providing a relationship between seawater concentrations and incorporation in the shell is known.

## **Assessing the history of trace element concentrations in the northern North Sea through Laser Ablation-ICP-MS of *Arctica islandica* shells**

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Live-collected shells of the long-lived clam *Arctica islandica* were obtained by trawling at three stations in the Fladen Ground, northern North Sea, UK. Annual growth lines in acetate peel replicas of polished and etched shell sections were dated by increment counting and crossmatching and the width of the growth series measured. The elemental composition (lead, copper, zinc, iron, manganese, barium, and magnesium) of dated annual growth increments was determined using Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS). Correlations in composition of the dated increments were observed between years and between shells from similar areas within and between stations, although there were differences both in the timing and magnitude of the concentrations of these elements. Discrete peaks in element concentrations within years were observed with little evidence of sustained levels of element incorporation.

*Arctica islandica* shells recorded historically the annual and sub-annual elemental composition of the shell over periods of up to 50 years. The chemical composition and annual growth series of clams collected ca. 68 km apart showed similarities both in the concentration and timing of the peaks of elements in the shell. The peaks in shell concentrations were unrelated to anthropogenic activity and more likely reflected changes in the bio-availability of elements released from the sediment. It is speculated that an increase in biological oxygen demand in the near sediment surface waters or the natural burrowing activities of the clams may increase availability of certain elements.



## Trace element and stable isotope profiles of accretionary biological tissues

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Oxygen isotope sclerochronology has a rich history that emerged from theoretical calculations performed by Harold Urey on the temperature dependence of oxygen isotope fractionation in carbonates and experimental investigations conducted by Samuel Epstein. These early works were followed by M.L. Keith, who demonstrated that seasonal water temperature variations may be preserved within the shell of a single mollusk as periodic oscillations in carbon and oxygen isotope profiles. In 1983, Douglas Jones related these profiles to periodic structural features (growth increments) in the shell, thus firmly cementing the foundation for sclerochronology as a fundamental tool in paleoenvironmental studies.

Our perspective of paleoclimate is constantly reshaped by new proxies and techniques that are focused on a better understanding of past environmental conditions and processes. As the minimum sample mass for analysis has decreased and the spatial control over physical sampling has increased, the temporal resolution of geochemical profiles has evolved to the point that weekly events may be recognized in shell material. Emerging technologies such as laser ablation-element (LA-ICP-MS) and -isotope ratio mass spectrometry (LA-IRMS), and secondary ion mass spectrometry (SIMS) permit 5 micron (dia.) spots (or smaller) to be analyzed for trace element or isotope composition. New systematics for non-traditional stable isotopes (e.g., Mg and Ca isotopes) provide novel insights into element dynamics and reservoirs that were previously thought to have stochastic isotope distributions, and high intensity spectroscopic techniques (e.g., synchrotron x-ray microprobe) uncover fine scale elemental zonation patterns in biomineralized materials that were not known to exist previously. Finally, whole new tools have emerged, such as clumped isotope paleothermometry, that provide paleoenvironmental information without having to measure or assume fluid compositions. Geochemical profiles provide a powerful chronometer once proxy information is converted to the time domain. This task is aided by physical attributes of the shell such as growth increments and shell density properties, but additional advances are needed to take full advantage of the time series offered by environmental proxies. This talk summarizes some recent advances in analytical capabilities and it outlines future directions in sclerochronology research investigations.

## **Validation of the seasonality in growth bands in the bivalve *Macoma balthica* using stable isotope and trace element analysis**

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The growth of bivalve shells occurs through the deposition of successive layers of carbonate material. This calcification process in the shell is usually a seasonal event mainly related to temperature, with the highest calcification rates during spring-summer and the lowest rates in autumn-winter. Some species can be aged by macroscopic analysis of the shell growth bands. However, since the deposition of carbonate depends on the environmental conditions, the use of shell growth bands for ageing needs to be validated. In the present study, we have analyzed the formation of growth bands in the bivalve *Macoma balthica*, a dominant species in many estuaries and coastal areas along the Atlantic coast. During a 1.5 year period, individual growth and environmental conditions were monitored every month. Stable oxygen and carbon isotopes as well as trace elements were analysed in the new area grown and compared to the formation of growth bands. A clear seasonal pattern in stable oxygen isotope ratios was observed in *M. balthica*, which was related to the formation of growth bands. We will further relate the incorporation of isotopes in the shell with their amount in the water and with water temperature. Trace element analysis in the chondrophore revealed that Sr was associated to the formation of growth bands.

## **Decoupled evolution of temperature and precipitation in western Germany during the Last Interglacial reconstructed from a precisely dated speleothem**

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We present high-resolution stable oxygen and carbon isotope ( $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$ ) as well as trace element profiles for stalagmite HBSH-1 from Hüttenblärschachthöhle, western Germany. The chronology was established by MC-ICP-MS  $^{230}\text{Th}/\text{U}$ -dating, and the high U-content of the stalagmite allowed determination of very precise  $^{230}\text{Th}/\text{U}$ -ages although using very small sample sizes. The beginning and end of individual growth phases of the stalagmite could, thus, be determined very accurately. Stalagmite HBSH-1 grew during the penultimate interglacial (MIS 7), the Last Interglacial (MIS 5) and the Holocene. The major part of the sample (40 cm) grew between 130 and 80 ka providing a climate record with decadal to centennial resolution for this period. The record shows three growth interruptions during MIS 5 coinciding with Greenland Stadials 25, 24 and 22, as recorded in the NGRIP ice core. The end of the MIS 5 growth phase coincides with GS 21. This shows that stalagmite growth in this area is a very sensitive proxy for Northern Hemisphere cooling. Correlation of the absolutely dated stalagmite record with Greenland ice cores may provide a tool to improve the chronology of the Greenland Stadials.

The  $\delta^{18}\text{O}$  profile of stalagmite HBSH-1 shows a distinct similarity during MIS 5 with the NGRIP ice core and a sea surface temperature record from the Iberian Margin. This suggests that stalagmite  $\delta^{18}\text{O}$  mainly reflects past temperature variability. Stalagmite HBSH-1 consists of aragonite rather than calcite, which is probably a result of pronounced prior calcite precipitation in the epikarst above the cave. In this case, the  $\delta^{13}\text{C}$  signal rather reflects changes in past precipitation than temperature. The  $\delta^{13}\text{C}$  record of HBSH-1 shows three pronounced negative peaks during MIS 5, in agreement with the three MIS 5 warm phases, MIS 5e, 5c and 5a. During the Last Interglacial, however, the evolution of  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$ , and thus temperature and precipitation, is opposite. Whereas the  $\delta^{18}\text{O}$  signal suggests the warmest temperatures around 125 ka followed by a gradual decrease, the  $\delta^{13}\text{C}$  signal indicates wetter conditions towards the end of the Last Interglacial.

The decoupling of temperature and precipitation during this time period is also seen in a series of snapshot simulations performed using a fast coupled ocean-atmosphere general circulation model. This behaviour can be explained by the influence of varying solar insolation patterns (in response to changing orbital configuration) on atmospheric dynamics and the resulting influence on storm activity in the region.

## **Sr/Ca and Mg/Ca ratios of ontogenetically old, long-lived bivalve shells (*Arctica islandica*) and their function as paleotemperature proxies**

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The Sr/Ca and Mg/Ca ratios of many biogenic skeletons provide useful paleotemperature estimates. As yet however, it has remained largely impossible to obtain such information from bivalve shells. In the present study, metal-to-calcium values in the hinge plate (aragonite, outer shell layer) of four ontogenetically old (85 to 374 year-old) specimens of the long-lived bivalve, *Arctica islandica*, were measured on a LA-ICP-MS. The shells were collected alive in 1868, 1986 and 2003 from three different localities around Iceland. With increasing ontogenetic age and decreasing growth rate, a distinct trend toward increasing Sr/Ca (max. 5.17 mmol/mol) and Mg/Ca values (max. 0.89 mmol/mol) and greater variance were observed. Three potential explanations for these trends include a reduced capacity for element selection due to cell ageing, changing metabolism and/or a relative increase in the number of organic-rich (= Mg-rich) and organic-poor (= Sr-rich) shell portions through ontogeny. Partition coefficients however, remained far below 1, indicating that physiology exerted a strong control over the element partitioning between the shells and the ambient water. After mathematical elimination of these vital effects, residuals exhibited a highly significant negative correlation (e.g., age-detrended Sr/Ca data:  $R = -0.64$ ,  $R^2 = 0.41$ ,  $p < 0.0001$ , growth rate-detrended Mg/Ca data:  $R = -0.52$ ,  $R^2 = 0.27$ ,  $p < 0.0001$ ) with sea surface temperature. These results are in good agreement with results obtained from the precipitation of abiogenic aragonite. The results of the present study can help to develop new techniques to extract environmental signals from the metal-to-calcium ratios of bivalve shells.

## One year of giant clam growth: a combined HFNI valvometry and sclerochronology study

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Growth increment thickness changes in mollusc shells are used as a proxy of environmental changes, in particular for sea-surface temperature (SST) variations. Long-lived (50-100 yr) giant clam sclerochronology records are highly valuable in this prospect. Aubert et al. (2009 Coral Reef, 24) reported that growth increment thickness changes of the *Hippopus hippopus* species are seasonal, governed for 50% by SST, and able to record exceptional upwelling events.

To better understand the relationship between shell growth, the environment, and other potential forcing in these clams, their shell growth was studied in situ by combining two techniques. First, 16 living clams were placed on a New-Caledonian reef for one year (depth 3-4 m), with their shells equipped with lightweight electrodes to measure the shell gaping activity by High Frequency Non Invasive (HFNI) valvometry technique (Tran et al. 2003 *Envir. Tox. Chem.* 22, 914-920). HFNI allows recording valve movements at 0.6 Hz for each clam, without interfering with the normal behaviour, and also measuring growth rate. The rationale is that if daily growth layers are produced, when valves close every day, the minimal distance between electrodes increases daily. We recorded, for the very first time, an online growth rate index based on this principle by mathematically isolating these minimal daily distances and plotting them as a function of time. Data were published automatically online: [http://www.domino.u-bordeaux.fr/molluscan\\_eye](http://www.domino.u-bordeaux.fr/molluscan_eye). After one year of recording, five specimens out of sixteen were studied by sclerochronology. The daily growth increment thickness was dated and measured. Results were analysed as a function of time, SST, irradiance and pluviometry.

The comparison between the two techniques highlights several important aspects of the shell growth. For all clams the minimum distance between the electrodes increased regularly, demonstrating a continuous growth (no annual growth cessation). The combined data set demonstrates that annual growth pattern is significantly controlled by SST but also by the combination of SST and irradiance. The relationship is not linear. Specifically, when SST reached its annual maximum (27-28°C) with solar irradiance still at its maximum (March), the mean shell growth rate decreased and became highly variable and erratic compared to the other periods. Over the same time period, strong behavioural stress symptoms recorded by valvometry progressively appeared in the whole group. This could be related to oxidative stress (excess of free radicals associated to SST and zooxanthellae activity). It strongly suggest that at 27-28°C, *Hippopus* from New Caledonia could be already living close to their upper SST limit, an important finding in the present global warming context. We are grateful to the South Province of New Caledonia, Aquitaine Valo Association and the Aquitaine Region (France) for granting that project.

## The marine radiocarbon bomb-pulse across the temperate North Atlantic: $\Delta^{14}\text{C}$ inventories from *Arctica islandica* growth increments

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Marine radiocarbon bomb-pulse inventories from annually-resolved archives from temperate regions have been under-exploited. We present series of  $\Delta^{14}\text{C}$  excess from known-age annual increments of the long-lived bivalve mollusc *Arctica islandica* from four sites across the coastal North Atlantic (German Bight, North Sea; Tromsø, north Norway; Siglufjordur, north Icelandic shelf; Grimsey, north Icelandic shelf) combined with a published series from Georges Bank (NW Atlantic). The atmospheric bomb-pulse is shown to be a step-function whose response in the marine environment is immediate but of smaller amplitude and with a longer decay time as a result of the much larger marine carbon reservoir. Attenuation is determined by the regional hydrographic setting of the sites, processes controlling the isotopic exchange of  $^{14}\text{C}$  at the air-sea boundary, and salinity as a function of the freshwater flux. The inventories form a sequence from high magnitude-early peak (German Bight) to low magnitude-late peak (Grimsey). All series show rapid response to increase in atmospheric  $\Delta^{14}\text{C}$  excess but slow response to decline resulting from a combination of rapid isotopic air-sea exchange and continued entrainment of older water masses. An inflection in the rise of the marine bomb-pulse in the German Bight and at Grimsey between 1960 and 1962 correlates with the temporary decline in atmospheric  $\Delta^{14}\text{C}$  excess series resulting from the moratorium in atmospheric weapons testing. Most of the records are characterised by bimodal distributions in  $\Delta^{14}\text{C}$  excess. The inventories constitute calibration series for the use of the bomb-pulse as a high-resolution dating tool in the marine environment and as a tracer of coastal ocean water masses.

## Micro-scale elemental distribution in shells of *Arctica islandica*.

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Chemical variations of biogenic calcium carbonates have been used as proxies for past environmental conditions. In particular, Sr/Ca ratios in aragonitic coral skeletons and Mg/Ca ratios in calcitic foraminifera tests are considered as reliable temperature proxies. However, the relationship between metal/calcium ratios of bivalve shells and environmental factors is still largely unclear, mainly due to vital effects. This is even true for the long-lived bivalve mollusk, *Arctica islandica*, which is one of the most intensively examined species. However, the relationship between micro-scale elemental distribution and growth patterns may provide unique information about biological effects on the incorporation of trace elements, because shell growth is biologically controlled. Respective studies have been published for corals and foraminifera, but little is known for bivalve shells.

In this study, we analyzed the Sr, Mg and S concentration in shells of *A. islandica* with 1 micrometer spatial resolution along the axis of maximum growth and compared these data with the growth patterns of the shell. High concentrations of Sr, Mg and S were found near growth lines. Seasonal variations of Sr and S were more significant than Mg. In ontogenetically younger portions of the shell, strong enrichment of Sr and S was also frequently observed near daily growth lines. In the hinge portion, annual growth lines were also positively correlated with S and Sr. High S contents near organic-rich growth lines may suggest the presence of sulfated polysaccharides. Strong correlation of Sr (and perhaps also Mg) with S may indicate that Sr and Mg are strongly affected by growth rate.

## Use of tusk growth and stable isotope records to assess an unusual all-female American mastodon (*Mammot americanum*) assemblage

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The Bothwell site in northwestern Indiana (Great Lakes region, USA) produced an assemblage of late Pleistocene ( $11,440 \pm 60$  BP) faunal remains, including thirteen American mastodon tusks. Analyses of tusk dimensions and growth increments in dentin indicate that all tusks belong to reproductive-age females. Sites with remains of multiple female mastodons are extremely rare, and the tusks are analyzed here to determine what might have led to the formation of such an assemblage. Age and sex demographics of the mastodons are similar to those expected for a matriarchal family unit, raising the possibility of a single catastrophic mortality event. However, seasonal variation in the oxygen isotope composition of carbonate in tusk dentin allowed determination of season of death for four individuals, and these analyses indicate that there were two or more distinct mastodon mortality events at the Bothwell site. Patterns in sub-annual variation in the carbon isotope composition of carbonate in tusk dentin suggest that the mastodons experienced similar seasonal changes in diet for the years just prior to their deaths. Carbon isotope analyses of dentin collagen indicate that the mastodons consumed a diet of mainly C<sub>3</sub> plants. Causes of death are unresolved, but the absence of evidence for declining growth rates prior to death suggests nutritional stress was not a factor. Entrapment is also judged to be unlikely. The fossils may have accumulated at this site because the depositional environment offered high preservation potential. Alternatively, the site could represent a Paleoindian meat cache. Further studies on bone modification and duration of fossil accumulation will aid in evaluation of these hypotheses.



## **The skeletal extension-rate record of a coral from the Maldives tracks ENSO and Indian monsoon variability**

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Until now, only a few coral proxy studies investigated coral growth as a proxy for climate variability. The first such coral record from the massive coral species *Porites lutea* is presented from the NW Indian Ocean. The time-series derives from the lagoon of Rasdhoo Atoll (4°N, 73°W), situated in the central area of the Maldives Archipelago, which is located in the vicinity of the Indian monsoon forcing. The record spans 90 yrs and covers the period 1917-2007. The mean annual extension increases throughout the 20<sup>th</sup> century as a consequence of the rise of sea surface temperatures (SST) in this region. The extension rates exhibit a distinct interannual variability, which is driven by SST variations linked to El Niño-Southern Oscillation forcing. It can be demonstrated that decadal variations of the extension-rates are linked to similar variations in the strength of the summer monsoon currents. Interannual and decadal variability in monsoon current activity and rainfall over India are an expression of the summer monsoon strength. This is the reason why a statistical link between coral extension rates and precipitation over India can be established. This implies that annual extension rates in corals can be used as a new marine proxy for Indian monsoon variability on decadal resolution. It is suggested that the geomorphology of the atoll influenced the potential of this new coral archive to track climate variability.

## **The investigation of growth rates, environment and climate signals in *Arctica islandica* from NW Scotland**

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On the NW coast of Scotland there are multiple sites where *Arctica islandica*, the longest-lived marine bivalve recorded to date, can be found. Our research focuses on living populations from two sea lochs (fjords): Creran and Etive. In total six sites have been studied. All are shallow water environments, from which shells have been collected by the Natural Environmental Research Council (NERC) National Facility for Scientific Diving (NFSD).

Results from a shallow water site (11-17 m deep) outside Loch Creran indicate shells with a relatively low inter-series correlation of 0.37. The master chronology from the site has been compared to gridded sea surface temperature data. The correlation between the two series is not time stable, suggesting that shells from this region may not be ideal climate proxies. However, it does appear, that from the late 1980s onwards some external factors have had a marked influence on growth rates, causing a noticeable increase in growth rates from the late 1980s to the present. It is hypothesised that this growth increase is a direct response to the introduction of marine aquaculture in the region. The results have prompted the investigation of the other sites from which shells have been collected and we present a regional synthesis of this anthropogenic trigger to shell growth.

This paper brings together biometric data (shell weight, length and age) collected from all sites under investigation, and reviews a national (UK) dataset, which has been established from museum shell collections. In addition, results gained from a master chronology, which have been compared to the available instrumental data will be presented, together with a review of the potential problems and benefits associated with investigating *Arctica islandica* growth rates from shallow water environments.

## Investigation of Li/Ca ratio temporal variations in shells of two marine bivalves: *Arctica islandica* (Iceland) and *Pecten maximus* (France)

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In the past decade, the elemental composition of bivalve shells has been increasingly used for paleoenvironmental reconstructions. With few exceptions, most investigations have only dealt with a few elements (mainly Sr, Mg, Ba, and some trace metals including Mn, Pb, Zn, and Cd). Here we present the first studies on inter- and intra-annual variations of Li/Ca ratio in the outer shell layer of two marine bivalve species: *Arctica islandica* (Arcticidae; aragonitic shell) collected off northeast Iceland and *Pecten maximus* (Pectinidae; calcitic shell) collected in Brittany (France). Surprisingly, this element has never been analyzed in bivalve shells despite its interesting potential as a paleoceanographic proxy in other marine biogenic carbonates (foraminifera, corals, brachiopods).

Li/Ca in juvenile *A. islandica* presented well-marked seasonal variations (range: ca. 7-11  $\mu\text{mol mol}^{-1}$ ) over the period 2001-2006, with minimum values recorded at the annual growth lines, and without large inter-annual differences. These seasonal variations were significantly, but weakly, correlated with seawater temperature. On the other hand, Li/Ca covaried significantly with daily growth rates (slope = 0.098;  $R^2 = 0.53$ ) and with the discharge from one of the closest rivers. This suggests that seasonal variations of Li/Ca in *A. islandica* may most likely be explained (1) by shell growth rate and/or (2) by significant river inputs of Li-rich silicate particles flowing to the sea as soon as snow melts (potential proxy for mechanical weathering of Icelandic basalts, and consequently, for frequency and intensity of past jökulhlaups). The same kind of pattern was observed in 2001 and 2007 in shells of juvenile *P. maximus* from the Bay of Brest (range: ca. 15-45  $\mu\text{mol mol}^{-1}$ ). As in *A. islandica*, Li/Ca covaried only slightly with seawater temperature, but was strongly correlated with daily shell growth rate (slope = 0.090;  $R^2 = 0.54$ ). For some years (1999, 2004), this pattern, although still discernable, was punctuated with sharp episodic peaks up to 250  $\mu\text{mol mol}^{-1}$ . We suggest that these peaks might be linked to the occurrence of phytoplankton species producing a toxin (domoic acid) known to be a powerful chelating agent tying up various materials such as Li.

Given the strong and similar relationships between Li/Ca and shell growth rate in both species, we conclude that the incorporation of Li in bivalve shells may be mainly controlled by physiology. Li/Ca may therefore be a useful proxy for addressing seasonal variations of growth rate in bivalves that lack discernable microgrowth patterns. Abrupt decreases of Li/Ca may in turn help identify growth retardations due to harsh environmental conditions. An influence of Li-rich silicate particles (in Iceland) and harmful algal blooms (in Brittany) cannot be excluded. Further works, including experimental studies, are needed to test these hypotheses.

## **Fossil bones and teeth: geochemical and histological archives for life history and palaeobiology**

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The element (Sr/Ca, Ba/Ca) and isotope compositions ( $\delta D$ ,  $\delta^{13}C$ ,  $\delta^{15}N$ ,  $\delta^{34}S$ ,  $\delta^{18}O$ ,  $\delta^{44}Ca$ ,  $^{87}Sr/^{86}Sr$ ) of fossil bones and teeth are increasingly used in palaeontology, palaeoanthropology and archaeology for the reconstruction of diet, climate, migration, and thermophysiology of animals and humans. The isotopic composition of the food and drinking water ingested by vertebrates during their ontogeny are recorded in skeletal tissues and reflect the diet as well as environmental conditions (e.g., climate, seasonality, vegetation, geology). Phosphatic hard tissues such as bones and teeth are therefore important archives for the reconstruction of life-histories and the palaeobiology of extinct vertebrates because these skeletal components integrate histological and chemical information during the period of tissue formation and growth. This enables the reconstruction of the palaeobiology, palaeoecology and palaeoenvironment of extinct vertebrates. Furthermore, incrementally-developed tissues may preserve a multi-year proxy record of ingested isotope compositions. Bone and tooth microstructure is usually not taphonomically altered thus forming an important archive of the growth and life history. However, diagenetic changes in the biogenic apatite itself could bias original chemical compositions and must always be considered and closely regulated.

Skeletochronology based on histological growth marks in skeletal tissues such as lines of arrested growth (LAGs) is used for age and growth rate determination of extant and extinct vertebrates. LAGs occur in skeletal tissues of many vertebrate species predominantly in ectothermic reptiles and amphibians, however, they also occur in endothermic birds and mammals as well as in many dinosaurs. LAGs are routinely used as annual time markers for the determination of ontogenetic age and growth rates of extinct vertebrates such as dinosaurs. Growth marks such as lines of Ebner or striae of Retzius in dental tissues are used to infer the tooth formation and replacement rates of reptiles and mammals, including early humans.

Microanalytical and microsampling techniques (SIMS, LA-ICP-MS, LA-MC-ICP-MS, Micromill) are increasingly applied for high-spatial resolution in situ element and isotope analysis and serial microsampling of skeletal tissue growth increments. The combination of geochemical and histological techniques allows a refined, quantitative reconstruction of the life history, diet and mobility of extant and extinct vertebrates. Some case studies will be discussed to illustrate the application potential of histological and geochemical analysis of vertebrate skeletal remains.

## The application of bivalve sclerochemistry in reconstructing past Greenland meltwater runoff

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Ongoing global warming causes accelerated melting of the Greenland ice sheet. Increased amounts of runoff have been observed since the early 1990s. As complete loss of this ice sheet would result in a global sea level rise of ca. 7 m, it is crucial to gain insight in its dynamics through time. Instrumental data for Greenland cover the last few decades only. Modelling studies investigate both the natural variability in ice cap mass balance, and the influence of future global warming. Proxy data are crucial for the validation of these models. Along the Greenland west coast during summer, glacial meltwater results in a layer of cool and fresh water on top of slightly warmer and more saline water. This layer varies in thickness with the amount of meltwater. As glacial meltwater has very low oxygen isotope ( $\delta^{18}\text{O}$ ) values of -30 to -20‰, these can be discerned in bivalve shell  $\delta^{18}\text{O}$  records.

We investigate the utility in reconstructing meltwater amounts of two bivalve species: the intertidal to subtidal bay mussel (*Mytilus trossulus*, lifespan > 22 y) collected at Disko Bay (W Greenland) and the Iceland scallop (*Chlamys islandica*, lifespan > 21 y), which occurs at 10-100 m depth, and was kept in a suspended culture at 15 m depth in Kobbefjord near Nuuk (SW Greenland). For *M. trossulus* it is known that shell  $\delta^{18}\text{O}$  is influenced by both temperature and water  $\delta^{18}\text{O}$  values, whereas Mg/Ca composition records temperature and Sr/Ca traces salinity (Klein et al. 1996 GCA 60, 4207-4221; Klein et al. 1996 Geology 24, 415-418). For *C. islandica* such relationships have not yet been investigated. We present high-resolution  $\delta^{18}\text{O}$  and trace element records of *C. islandica* for the monitoring period of 17 months, and compare these with records of shell growth, temperature, water composition and chlorophyll *a*. We link *M. trossulus* sclerochemical records to available temperature measurements and modelled local runoff for the time intervals 1996-2008 and 1921-1933.

*M. trossulus* is abundant in Greenland archaeological finds from different settlement periods, and *C. islandica* occurs in fossil shell assemblages. The developed proxy can give insight in decadal aspects of the behaviour of the Greenland ice sheet during different Holocene climate intervals and in the climatic circumstances and seasonality accompanying the rise and demise of Greenland cultures, such as the Norse settlement period during the Medieval Warm Period.

## **Fossil brachiopod shells: reliable archives of seawater temperatures?**

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One hundred Silurian brachiopod shells from tropical shallow water carbonate of the Baltic Sea (Gotland/Sweden) were screened by cathodoluminescence and scanning electron microscope analyses. Investigations indicate that they were influenced by diagenesis. Every shell shows luminescence in parts and most SEM-sections show a mosaic of well preserved and altered fibres. The four best preserved brachiopod valves were chosen for high-resolution stable isotope measurements (300  $\mu\text{m}$ ) and element analysis (Mn, Fe, Sr, Mg) along the ontogenetic transects. SEM analyses were performed in transverse sections. From every sampled brachiopod shell, seven to five SEM-sections were prepared perpendicular to growth direction in order to get a better overview on the preservation state of the entire shell. Additionally, isotope samples were taken from the surrounding rock matrix and the filling.

$\delta^{18}\text{O}$  variations of 1 to 1.8‰ along the ontogenetic transects of the single specimen are recorded. By the use of the equation published by Anderson and Arthur (1983 SEPM Short Course 10, 1-151) temperature changes of about 9°C could be calculated during the life of a single specimen. Assuming that signals are preserved, the explanation that the  $\delta^{18}\text{O}$  curves might indicate a fluctuation during one year representing the lifetime of the organisms, seems more plausible than a cause by influences of vital effects during shell precipitation. The  $\delta^{18}\text{O}$  changes might additionally be caused by changes of salinity. However, strong evidence exists that the curves do not reflect primary signals, especially in the most anterior parts of the shells. The preservation state mostly tends to decrease along the shell transects with increasing distance to the hinge. Thus stable isotope measurements and SEM investigations indicate that the posterior part is probably more resistant against diagenetic alteration. However, preservation state analyses are not always unequivocal and especially cathodoluminescence observations do not correlate with stable isotope developments along the ontogenetic transects. Looking at element concentrations does not offer definite proof either.

More studies on Silurian brachiopod shells from Gotland will be needed to confirm the assumptions made here. In addition, high-resolution isotope analyses and detailed preservation state investigations of fossil brachiopods from different locations could show whether Paleozoic shells have preserved their primary isotope signals.

## **Visions: the future of sclerochronology**

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A major challenge many of us face in the rapidly growing field of sclerochronology is demonstrating that our relatively “young” discipline is developed enough to help address major environmental issues, such as global climate change, pollution, land-use changes, ocean acidification, and past changes in ocean and terrestrial ecosystems. Although sclerochronology is not a new field (e.g., Coutts 1970 *Nature* 226, 874; Hudson et al. 1976 *Geology* 4, 361-364), its utility in environmental sciences has not yet been fully realized. However, recent activity and interest within the sclerochronology community, along with a substantial increase in the number of high-quality, peer-reviewed studies utilizing sclerochronological techniques, are strong indicators that sclerochronology can and will contribute significantly in addressing important issues related to environmental change.

The vitality and future efficacy of sclerochronology is promising, yet progress during the next years and decades may be slow and at times frustrating. As many of our colleagues in the field of dendrochronology faced “growing pains” some forty years ago, we too will face similar issues and encounter roadblocks as we move forward with our emerging discipline. Fortunately for the field of sclerochronology, our dendrochronology and dendroclimatology colleagues have provided a tremendous foundation (concepts and methods for constructing absolutely-dated chronologies with an application to climate studies) from which we may further develop and refine our aquatic-based discipline.

Although the visibility of our discipline is increasing, many of us still need to educate our colleagues and funding agencies about the scope, utility, and ultimate pursuits of sclerochronology. A major goal of this paper is to highlight some recent sclerochronological contributions that have successfully addressed specific environmental change questions, and research that has significantly advanced our understanding of natural systems by providing key proxy data beyond the scope of instrumental records. Additionally, this paper will discuss future possibilities and potential priorities within the discipline of sclerochronology in the context of developing a more “mature” field for studying environmental change issues.

## **Comparison of daily and seasonal changes in shell microstructures and trace elemental signals for river bivalve *Margaritifera laevis* with in-situ environmental parameters**

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*Margaritifera laevis* is known as a long living freshwater bivalve. Their aragonite shells could be useful and unique materials for reconstructing the past changes in river environments (e.g., Schöne et al. 2004 Quat. Sci. Rev. 23, 1803-1816). Here we present sclerochronological and geochemical results from *Margaritifera* shells collected in the Shiribetsu River, central part of Hokkaido, Japan. A combined approach of SEM and optical microscope observations, and trace elemental analysis using LA-ICP-MS has been used and compared with the in situ hourly environmental data of temperature, pH and dissolved oxygen and monthly meteorological records. The number of fine (daily) growth lines corresponds with days when the average daily temperature was higher than 10°C and the daily growth width patterns were correlated with daily temperature changes. Annual extension rates have a negative correlation to annual volume of water charges and the concentrations of several trace elements were high in the shell part during spring. These results indicate that the *Margaritifera* shells could be a powerful tool for reconstructing the river environments and air conditions during winter around central Hokkaido. Our future work will apply this strategy to the modern long living and fossil shells which we have recently found in different river and archaeological midden sites.



## A quest for long-lived geochemical archives in the deep sea (Azores)

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The rugged bathymetry of the Azores supports a diverse heterozoan association resulting in intense biotically-controlled carbonate production that classifies this setting as a typical cold-water carbonate factory. Below the seasonal thermocline and below a deep mixed layer, environmental conditions are very stable in terms of salinity and temperature, providing an ideal frame to test potential long-lived geochemical archives in the upper bathyal. Target species in this respect are the cold-water corals *Caryophyllia cyathus* and *Desmophyllum cristagalli*, the stylasterid *Errina dabneyi*, and the newly described deep-sea oyster species *Neopycnodonte zibrowii*, that thrive protected under overhangs or along steep cliff faces in close to 500 m depth in the Faial Channel. Investigations include their microstructure, growth rate, stable isotope signature ( $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$ ) and elemental composition (Mg, Sr, S, etc.).

Radiocarbon dating of *N. zibrowii* reveals an impressive lifespan of several centuries, placing them among the longest-lived molluscs known to date. This longevity and a distinct incremental growth with a proposed reproductive cyclicality of few years (conchiolin-rich growth breaks) and an annual cyclicality potentially triggered by seasonally varying nutrient flux (Mg and S fluctuations), identify *N. zibrowii* as a promising environmental archive. However, isotope investigations indicate complex vital effects leading to a  $\delta^{18}\text{O}$  spread of 1.8‰ and an unexpected positive offset from expected equilibrium conditions of ca. 0.5‰ on average (deduced via the annual mean temperature of  $12.3 \pm 0.3^\circ\text{C}$  and ambient seawater  $\delta^{18}\text{O}_{\text{sw}}$  of  $0.55 \pm 0.07\text{‰}$  V-SMOW). Likewise, strong Mg/Ca fluctuations indicate a physiological control related to metabolism and biomineralisation, prohibiting its use as a temperature proxy. The  $\delta^{13}\text{C}$  shows an ontogenetic decrease, but may bear an environmental signal in adult portions as indicated by a strong peak-resemblance in contemporaneous shells.

Etched vacuum-epoxy-casts of *E. dabneyi* skeletons, studied by SEM, reveal that the internal architecture with its coenosarc canal meshwork, dactylo- and gastropores is modified during growth involving dissolution and re-precipitation of skeletal material. This internal rebuilding process inevitably alters initial geochemical signatures and the distribution of radiogenic isotopes, and has to be taken into account when applying radiometric dating techniques and when using stylasterids as geochemical archives. Research is currently focusing on the solitary scleractinians *C. cyathus* and *D. cristagalli*, which exhibit the largest  $\delta^{18}\text{O}$  spread of up to 4‰, strongly contrasting with the stable bathyal temperatures. Nevertheless, the close linear correlation with  $\delta^{13}\text{C}$  enables the extraction of meaningful temperature signals via a modified lines technique, despite vital effects.

## **Sclerochronology and ecology: They need each other!**

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Hard skeletal parts of marine and freshwater bivalves and gastropods are often being used for environmental reconstructions. The attractiveness of using shells from both phyla lies in their long geological history, which makes it possible to "calibrate" geological circumstances to present day ones. Applications vary from the use of internal growth lines with annual and sub annual rhythms. The high-resolution analyses of the chemical-elemental composition of carbonate shell material has added an extra dimension to the application. For a valid interpretation of the results however, a detailed knowledge of the ecology of the species is indispensable. In different environments, the same species might respond differently. At the same time, one may ask whether we have enough insight into the ecological aspects to disclose the environmental history from shell material.

Based on examples, I hope to illustrate how "ecology" is incorporated within shell growth patterns and how important the incorporation of ecological knowledge is for the sclerochronological interpretation of fossil, sub fossil and present day shell material. Looking at bivalves from tidal flats, the tidal elevation of their habitat determines immersion time and the length of the feeding period. For species which occur over wide geographical areas the seasonal timing of growth and spawning might differ. For sub-tidally living species, oceanographic processes like stratification, mixing or wind and wave action can be important modifiers of shell growth. Human activities like fishing can also significantly impact shell growth and populations.

It is a challenge to use shell growth patterns for environmental and climate reconstructions. There is an abundance of studies which have successfully applied the methods. However we should be aware of the wide variety of conditions that can modify shell growth. Where possible I would make a plea for more detailed auto-ecological studies of present day species in order to understand potential modifiers of shell growth.

## Following seasonal shell growth in *Arctica islandica*

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For environmental and climatological reconstruction, *Arctica islandica* (Bivalvia) has become an increasingly important species. Critical to its use as an environmental recorder, is a detailed knowledge on how the animals behave and when they grow. To answer the latter question we perform long-term growth experiments with 15 to 50 mm high *Arctica islandica* shells since 2006. All animals are individually marked. Once a month the shell sizes of the animals are measured.

So far, the results show that most of the shell growth takes place in spring. Between March and the end of May, approximately 50% of the annual increase in shell size is achieved. During summer conditions, shell growth is retarded. In late summer and early autumn the growth rate picks up for a short period. Based on these temporally varying growth rates it might become easier to translate observed shell growth patterns or the chemical composition of growth increments to the field conditions under which the growth increments have been formed.

## **A study of the periodicity of incremental markings in the dental enamel of sheep**

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The sequence of tooth formation is frequently used as a means of age determination and life history reconstruction in mammals. The stage of dental development can be assessed radiologically based on crown and root formation in developing dentitions. Age-at-death determination in juvenile individuals and reconstruction of growth processes is based on the presence of incremental markings in dental hard tissues, especially enamel. The growth marks in enamel are considered to reflect rhythmic changes in the activity of the enamel-forming cells, the ameloblasts. In humans and several other primate species these growth marks have been subdivided into short-period incremental markings (prism cross striations, laminations) reflecting a circadian activity rhythm, and long period incremental markings (striae of Retzius) with a periodicity of several days. Striae of Retzius are reported to occur with a constant periodicity in all teeth of an individual. Moreover, several studies reported additional markings with a narrower spacing than normally occurs between prism cross striations. These additional markings were termed intradian or infradian lines.

In humans and non-human primates, the formative periods of tooth crowns have been determined by counting either prism cross striations directly or the striae of Retzius, and multiplying their number by the individual periodicity. Combining overlapping tooth chronologies enables the reconstruction of the formative period of the complete dentition. The neonatal line, an especially prominent stria caused by physiological stress during birth, can be taken as a starting line allowing precise age-at-death determination in juvenile individuals. Especially prominent striae can also be used to reconstruct the timing of stress events during dental development.

Striae of Retzius and prism cross striations can also be identified in the enamel of sheep and pigs. However, reconstruction of the timing of dental development based on the assumption that prism cross striations in these species reflect a circadian rhythm leads to results that far exceed the formative periods established based on radiological studies. This leads us to hypothesize that in sheep and pigs prism cross striations actually reflect an infradian rhythm. To establish the periodicity (repeat interval) of incremental markings in enamel we performed a fluorochrome labelling study with Soay sheep. First results of this study are presented.

## The isotope record of short- and long-term dietary changes in sheep tooth enamel: implications for quantitative reconstruction of paleodiets

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Quantitative reconstruction of paleodiet by means of sequential sampling and carbon isotope analysis in hypsodont tooth enamel requires a precise knowledge of the isotopic enrichment between dietary carbon and carbon from enamel apatite ( $\epsilon^*_{D-E}$ ), as well as of the timing and duration of the enamel mineralization process (amelogenesis). To better constrain these parameters, we performed a series of controlled feeding experiments on sheep ranging in age from 6 to 24 months old. Twenty eight lambs and fourteen ewes were fed isotopically distinct diets for different periods of time, and then slaughtered, allowing the timing and rate of molar growth to be determined. High resolution sampling and stable carbon isotope analysis of breath CO<sub>2</sub> performed on six individuals following a diet-switch showed that 70-90% of dietary carbon had turned over in less than 24 hours. Sequential sampling and carbon isotopic analysis was performed on the first (M<sub>1</sub>) and second (M<sub>2</sub>) lower molars of four lambs as well as on the third lower molar (M<sub>3</sub>) of eleven ewes. The changes in diet were recorded in all molars. We found that the length of enamel matrix apposition is approximately one-quarter of the final tooth length during crown extension, and that enamel maturation spans slightly less than 3 months in M<sub>1</sub>, and 4 months in M<sub>2</sub> and M<sub>3</sub>. Portions of enamel in equilibrium with dietary carbon were used to calculate  $\epsilon^*_{D-E}$  values. Animals on grass silage diets had values similar to previous observations, whereas animal switched to pelleted corn diets had values ca. 4‰ lower, a pattern consistent with lower methane production observed for animals fed concentrate diets. The tooth enamel forward model of Passey and Cerling (2002 *Geochim. Cosmochim. Acta* 66, 3225-3234) closely predicted the amplitude of isotope changes recorded in tooth enamel, but slightly underestimated the rate of isotope change, suggesting that the rate of accumulation of carbonate during maturation may not be constant over time. Although stable isotope profiles in tooth enamel represent underdetermined systems, our results demonstrate that they can provide useful information about dietary variability if the mineralization process is taken into account.

## **Indo-Pacific teleconnections on decadal time-scales assessed by multiple Sr/Ca and oxygen isotope records from the southwestern Indian Ocean**

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Atmospheric and oceanic teleconnections between the Indian Ocean and the Pacific are thought to vary on interannual to multidecadal time scales. A better knowledge of past SST and salinity variability over the Indian Ocean and their interaction with the tropical Pacific is needed to characterize natural climate variability. We produced several 50-350 year long climate records from the southwestern Indian Ocean with sufficient temporal resolution in order to unravel natural changes in the teleconnectivity with the tropical Pacific. We obtained two monthly resolved Sr/Ca and  $\delta^{18}\text{O}$  records from Rodrigues island (Mauritius), three Sr/Ca and  $\delta^{18}\text{O}$  records from Reunion and three Sr/Ca and  $\delta^{18}\text{O}$  records from southwestern Madagascar, all key regions affected by the southern Hemisphere trade winds and southern Indian Ocean gyres. We find strong evidence for teleconnections in Sr/Ca and  $\delta^{18}\text{O}$  records to the Pacific Decadal Oscillation and ENSO. The oxygen isotope records from the Mascarenes are affected by decadal salinity variations and show a strong freshening trend after the late 1970s. The freshening trend is probably related to advection of low salinity waters with the South Equatorial Current and/or increased cyclonicity. We conclude that the use of multiple coral time series significantly improves the climatic interpretation of proxy records, above all for Sr/Ca.

## **Poster presentation abstracts**





## **Sclerochronological examination, Sr/Ca spectral analysis and signal processing of two *Ceratoscopelus* otolith morphotypes from the Quaternary Ionian Sea**

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The thorough study of the abundant *Ceratoscopelus* otoliths found in the Lower–Middle Quaternary (Gelasian–Ionian) sediments of SW Kephallonia and SE Zakynthos Islands revealed the presence of two co-existent morphotypes, *Ceratoscopelus maderensis* and *Ceratoscopelus* sp.1. *Ceratoscopelus* sp.1 exhibits a sharp postero – ventral angle, a larger postero – dorsal area and an almost linear ventral rim, in comparison with the common *C. maderensis* (Agiadi et al. 2010 Riv. It. Pal. Str. 116, 63-78). Here, we present the results of the sclerochronological examination performed on selected specimens from this material, with respect to the growth structures observed on thin sections of these otoliths. Furthermore, we performed a preliminary analysis of the strontium and calcium content within specific parts of selected specimens, in order to detect any differences and/or similarities between the inner morphology and environmental chemical imprint within the otoliths of the two morphotypes.

Transverse polished otolith samples were examined with a scanning electron microscope (SEM), as a first measure to exclude the effect of diagenesis. Continuing, the strontium and calcium content, along specified growth lines of each otolith, was obtained, by means of energy – dispersive X-ray microanalysis (EDS) coupled on the SEM. The Sr/Ca ratio and the otolith growth pattern, as reflected by the greyscale variation under the polarizing microscope, along the same otolith growth line, for each otolith specimen, was compared with cross-spectral analysis, so as to (a) detect significant periodic components in the variability of the two parameters, (b) calculate the coherency between them, at each frequency component, and (c) estimate their phase lag for each significant periodicity.

The studied otolith specimens contained no sign of diagenetic alterations, when examined under the SEM, which is a good indicator, and allows the further analysis for strontium and calcium content. All the analysis yielded more than 0.1% strontium content, which is considered sufficient for a reliable quantitative ED microanalysis. Examination under polarizing light, showed that the fossil specimens exhibit the same strong daily increment formation observed in modern representatives of *C. maderensis*. Based on the spectral analysis, a strong and significant periodic component (95% confidence level) appears consistently in all the specimens, both for the greyscale and the Sr/Ca. Comparison with the polarizing microscopy observations indicates a correspondence with the daily periodicity. In addition, the two parameters exhibit high coherency, more than 0.8, and phase lag close to zero, for this frequency.

## **Intermittent growth in gastropod shells: seasonal changes in apertural morphology and shell oxygen isotope records**

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Many gastropods intermittently form features such as growth bands and denticles as spiral shell growth occurs. Changes in apertural morphology are thought to indicate the periodic or final cessation of spiral shell growth, yet this hypothesis has not been tested in most clades. Seasonal monitoring of shell growth patterns in natural populations and under laboratory conditions combined with oxygen isotope records reflecting seasonal water temperature changes indicate that spiral shell growth in the muricid gastropod *Acanthinucella spirata* occurs intermittently.

*Acanthinucella spirata* were collected from Tomales Bay and Duxbury Reef, Bolinas in northern California and grown in flow-through tanks at Bodega Marine Laboratory for 12 months. When spiral shell growth occurred, the outer apertural lip thinned. Accretion of external growth bands and internal denticles indicated cessation of spiral growth. Spiral shell growth occurred in the laboratory from fall through spring, and similar seasonal growth periods were observed at both field sites. When spiral growth ceased in spring, denticles formed and the outer apertural lip thickened. Snails were rarely observed growing in summer and early fall, and *A. spirata* is likely an intermittent grower as was also reflected in shell oxygen isotope patterns.

The external calcite shell layers of *A. spirata* were sampled parallel to the aperture on the body whorl for oxygen isotopic analyses, thus providing a sequential record of growth. Results demonstrated seasonal oxygen isotopic variability that would be expected given local intertidal temperature records. However, while oxygen isotope patterns indicated spiral shell growth during periods of decreasing water temperatures, as would be expected in fall and winter, record of growth during times when water temperatures are increasing were limited or absent. As a result, it is likely that shell oxygen isotope records from this species are not complete records of annual temperature changes. Field and laboratory observations of seasonal morphological changes and spiral growth, in combination with oxygen isotope analyses are necessary to interpret growth patterns and age of individuals in species with intermittent shell growth.

## Seasonal and tidal influences on gastropod shell oxygen isotope records

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The ratio of  $^{18}\text{O}/^{16}\text{O}$  in the calcium carbonate of mollusk shells reflects both the calcification temperature and the  $\delta^{18}\text{O}$  of the ambient waters. Oxygen isotope records in mollusks have been used to reconstruct past water chemistry including temperature and salinity, and to determine life-history traits such as shell growth rates and minimum ages of individuals based on annual oxygen isotope curves. However,  $\delta^{18}\text{O}_{\text{water}}$  in the intertidal may vary significantly with daily tidal cycles, seasonal salinity variations and location in an estuarine environment. As a result, carbonate records from intertidal organisms may indicate the time and place of shell accretion rather than large-scale seasonal temperature patterns in marine and estuarine systems.

To understand oxygen isotope variability along the northern California coast, we collected water samples at two sites in Tomales Bay and an exposed reef in Bolinas at varying tidal heights over the spring and summer months. Water was collected from the lowermost intertidal zone inhabited by the muricid gastropod *Nucella ostrina*. Calcite samples were collected from *N. ostrina* parallel to the apertural margin to compare  $\delta^{18}\text{O}_{\text{shell}}$  with  $\delta^{18}\text{O}_{\text{water}}$ . Preliminary results indicate  $\delta^{18}\text{O}_{\text{water}}$  site variability may be greater than seasonal  $\delta^{18}\text{O}_{\text{water}}$  variation and may obscure annual  $\delta^{18}\text{O}_{\text{shell}}$  signals.

## Periodic time-series modeling with guaranteed positive growth rate estimation for environmental records

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Proxies are measured on a distance scale, mostly along the maximum growth axis. Since all environmental archives grow at different speeds, and since the growth rate varies during the life-time, the different proxy records need a common axis, for example a time axis on which they can be compared. A number of methods which estimate a time axis are described in literature (Martinson et al. 1982 *J. Geophys. Res.* 87, 4807-4818; Paillard et al. 1996 *EOS Trans.* 77, 379; Yu and Ding 1998 *Geophys. Res. Lett.* 25, 4525-4528; Lisiecki and Lisiecki 2002 *Paleoceanog.* 17, doi: 10.1029/2001PA000733; Goodwin et al. 2009 *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 276, 47-55; Brüggeman 1992 *Paleoceanog.* 7, 476-487; Wilckinson and Ivany 2002 *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 185, 95-114; De Ridder et al. 2004 *Geochem. Geophys. Geosyst.* 5, doi: 10.1029/2004GC000771; de Brauwere et al. 2008 *Computer Geosci.* 34, 1781-1790; Beelaerts et al. 2010 *Math. Geosci.*, in press). The methods described in de Brauwere et al. (2008 *Computer Geosci.* 34, 1781-1790) and Beelaerts et al. (2010 *Math. Geosci.*, in press) are parametric signal model methods, which assume that the signal on a time scale is harmonic. In these methods, the unconstrained identification of the proposed signal model chooses the best parameters irrespective of the order of the data observations. In other words, subsequent observations can be inversed on the time axis. Both methods are especially vulnerable to this artifact when the number of phase distortion parameters is relatively high and thus when the noise sensitivity is larger. In de Brauwere et al. (2008 *Computer Geosci.* 34, 1781-1790) a method, the time inversion constraint method, is described which corrects these time inversions by including inequality constraints on the phase distortion parameters (Fletcher 1991 *Practical Methods of Optimization*, Wiley). For large violations against the order of the time instances, the number of constraints becomes larger than the number of parameters, and consequently, the method becomes unfeasible.

The aim of this work is to impose the positivity of the growth rate with a reduced number of linear constraints on the signal model parameters. The new method is compared to the time inversion constraint method and its noise sensitivity is tested on by means of a Monte-Carlo simulation. The usefulness of the method is demonstrated on the measurement of the vessel density, in a mangrove tree, *Rhizophora mucronata*, and the measurements of the Mg/Ca ratio, in a bivalve, *Mytilus trossulus*.

## Investigating climatic archives from archaeological sites in East Germany: a calibration study on *Unio crassus*

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In order to understand the environmental and climatic circumstances under which the Central European Neolithic Revolution occurred, high-resolution climatic archives are essential. Such information is often preserved in the form of archaeological middens, containing bivalve shells. However, the full potential of such shell midden material has rarely been utilized. Freshwater shells of the genus *Unio* sp. (Philipsson 1788) are frequently found as grave goods in archaeological sites of the Saale-Unstrut area (East Germany). The sites range in age from the Neolithic (6000BP) to the Bronze Age (2800BP) and the shells are typically well-preserved, which suggests that they were collected alive.

To fully understand the archaeological archives, a calibration against recent shell records is required. For this purpose, high-resolution sclerochronological isotope analyses ( $\delta^{18}\text{O}$ ) were conducted on modern *Unio crassus* shells, collected from river banks of the Helme and Kleine Helme Rivers. Two cross-sections from each specimen were prepared, one for sclerochronological purposes (Mutvei's Solution) and the other for stable isotope measurements. The results from these recent shells were then compared to an archaeological shell of *U. crassus* from the Neolithic.

The  $\delta^{18}\text{O}$  values of *U. crassus* from the Helme River varied between -7.87‰ and -4.23‰, whereas those of the shell from the Kleine Helme River ranged from -7.72‰ to -5.41‰. Both records showed distinct seasonal variations, mainly related to ambient temperature. According to monitoring experiments, the shell aragonite was precipitated in environmental equilibrium with the surrounding water. Major growth lines coincided with the most positive values in the  $\delta^{18}\text{O}$  record and were therefore formed during the coldest months of the year. The main growing season ranges from April to November. In contrast to the modern shells, the archaeological specimen showed lower  $\delta^{18}\text{O}$  values (-8.56‰ to -5.83‰). The results of this study strongly suggest that temperatures can be reconstructed from unionid  $\delta^{18}\text{O}$  values. If the isotopic signature remains unchanged, then the Neolithic shells must have experienced warmer temperatures or increased precipitation than their modern counterparts.

## **Experimental calibration of *Arctica islandica* shell carbonate as a geochemical proxy for environmental dissolved inorganic carbon**

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The extratropical oceans are the primary regions of carbon removal from the atmosphere, yet proxy records of past marine dissolved inorganic carbon (DIC) values from these regions are scarce. Development of robust proxies for marine carbon cycling is of critical importance in forecasting the oceanic response to human-induced increases in atmospheric carbon dioxide concentrations. Recent studies from the North Atlantic region have documented the response of shell carbonate from the long-lived molluscan species, *Arctica islandica* L. to the changing carbon composition of the atmosphere over recent centuries (i.e., the Suess effect) (Butler et al. 2009 Earth Planet.Sci. Lett. 279, 230-241; Schöne et al. 2010 Palaeogeogr. Palaeoclimatol. Palaeoecol., in press). However,  $\delta^{13}\text{C}$  values of shell carbonate reflects both the DIC pool from ambient, environmental conditions, and from metabolic carbon (McConnaughey et al. 1997 Geochim. Cosmochim. Acta 61, 611-622). If there is a consistent percentage of metabolic carbon incorporated into the shell, a correction can be made for this contribution in order to reconstruct  $\delta^{13}\text{C}$  of seawater DIC at the time of shell formation (e.g., Poulain et al. 2010 Chem. Geol. 272, 75-82). This study aims to examine the relationship between shell carbonate of *A. islandica* (adults and juveniles) and environmental  $\delta^{13}\text{C}_{\text{DIC}}$ , through a growth experiment in the Gulf of Maine. We hypothesize that this species, in its mature phase, deposits its shell with a consistent offset from isotopic equilibrium with ambient seawater due to a metabolic effect. Over 300 animals are being cultured in laboratory and in situ conditions in Walpole, Maine, USA, for a period of approximately nine months. Several environmental parameters are being continuously monitored in order to quantify the degree to which *A. islandica* shell carbonate reflects environmental conditions during biomineralization. Results from tissue, hemolymph, DIC, environmental monitoring and shell carbonate analyses will be presented for the preliminary stages of the growth experiment.

## **Growth of the common cockle *Cerastoderma edule*: validation of the periodicity of increment deposition by Calcein marker**

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Cockle (*Cerastoderma edule*) growth has not been studied a lot yet and the current approach of counting external ridges in order to make an age estimation is limited. Nevertheless, growth is a key parameter for monitoring bivalve populations, which are heavily exploited in French estuaries. The Bay of Somme, which is located in the eastern Channel in the north of France, is the first French field of cockles (*Cerastoderma edule*). In order to improve stock management, it is necessary to increase our knowledge of this species. This study is looking at the growth of the common cockle.

In this way, the recapture of shells previously marked under calcein marker and then breed in natural conditions in the Bay of Somme, was performed in order to determine the shell growth patterns. From a methodological point of view, calcein marking has showed a fluorescent increment in shells subjected to only 30 minutes immersion time at 150 mg.L<sup>-1</sup> but also for shells immersed for three hours at 50 mg.L<sup>-1</sup>.

High-resolution picture analysis with the TNPC software (Digital Processing for Calcified Structures) dedicated by Noesis Society and Ifremer, performed on several marked cockles, permitted us to count 23 increments on average between the mark and the ventral edge of the valves, corresponding to the 12 days interval during which 23 tides happened. The periodicity of increment formation is validated for a tidal frequency. This preliminary study gives a clue to the understanding of cockle growth and could be completed by cockle age monitoring, but also by chemical analysis to learn more about the biomineralization process of this species.

## Pliocene climate of the Southern North Sea Basin: a sclerochronological approach

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General Circulation Models (GCMs) investigating future climate changes predict a rise in global temperatures by 2-3°C. The Pliocene is reflective of a generally warmer world, when compared to present. This global temperature increase coupled with elevated CO<sub>2</sub> levels, and a comparable palaeogeography to present, means that the Pliocene provides a suitable test-bed for assessment of future climate model outcomes. However, GCMs and proxy data sets produce contradictory conclusions in prediction of North Atlantic Pliocene climate. Therefore supplementary proxy datasets that provide high-resolution seasonal data could assist in mitigating these inconsistencies. A reliable approach is oxygen-isotope sclerochronology of Pliocene *Aequipecten opercularis* bivalves. Results from this current investigation from the Pliocene Southern North Sea Basin (SNSB), in part contradict previous views that the Pliocene climate of the area SNSB was predominantly warm-temperate to subtropical, with cooling episodes. The oxygen isotope thermometry datasets obtained from a wide-ranging temporal context of Pliocene deposits from the UK (Coralline Crag) and Belgium (Lillo formation) have indicated that winter and summer temperatures are similar to present-day cool temperate seasonal temperature ranges (6-17°C) of the area, results also demonstrate seasonal ranges increased through the Lillo Formation. These results indicate more prevalent cool intervals within the Pliocene, than had previously been recognised that may relate to overall global signatures associated with Milankovich cycles, or changes in ocean heat supply linked to reduction of Gulf Stream strength. Further investigations into other Pliocene deposits, specifically in North America, will address this idea. Additionally, within the majority of Pliocene *A. opercularis* shells there is a large variation in amplitude of increment size during growth. Furthermore, an anti-phase relationship between increment size and temperature is recorded; this pattern appears to be rare within modern or Holocene specimens (excluding some Mediterranean specimens). This indicates that the overall control on increment size may not be temperature. One possibility is that it relates to resuspension of benthic detritus (food) created by enhanced winter storm activity, within the context of a globally warmed world.



## First results on lead in *Arctica islandica* shells using laser ablation and resonance ionization

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The reconstruction of past environmental conditions facilitates to recognize future impacts of long-term trends or extreme events. Often, it is difficult to assess chronological and historical records of adequate data from remote areas such as the hydrosphere. However, sclerochronologic studies of mussel shells may contribute a solution to this problem. The toxic element lead has been dispersed into the environment for a long time, mostly because it was added to the gasoline until the introduction of unleaded gasoline during the 1980s. The gasoline related annual lead deposition over the North Sea between 1958 and 1995 has been modeled in a comprehensive ‘lead study’ at GKSS (von Storch et al. 2003 Sci. Total Environ. 311, 151-176). However, lead concentrations in tissues of the mussel *Mytilus edulis* from the German North Sea coast do not correlate with model predictions (Ministry of the Environment of Niedersachsen 1999 “Data source of lead concentration of blue mussels in the North Sea”).

The concentration of trace metals in bivalve shells may reflect the concentration of these metals in the environment, as shown for Pb, Cu, Zn in the mussel *Modiolus modiolus* (Richardson et al. 2001 Mar. Ecol. Prog. Ser. 211, 157-167). Here, we intend to reconstruct the long-term (decades to century) trends in lead contamination of the German Bight by measuring lead profiles in the shell of the long-lived bivalve *Arctica islandica*. We apply a novel combination of laser ablation and laser ionization techniques with a Time-of-Flight mass spectrometer (ToF). Narrow shell slices cut along the line of strongest growth are mounted on a three-axis positioner at the focus of the beam for laser ablation. The laser beam produces a sample plume expanding into a supersonic jet of helium carrier gas for the transport of the plume into the ion source of the ToF. Intense tunable laser radiation at the wavelength corresponding to an excited energy level in lead produces lead ions by resonant laser ionization. Here, we discuss the present state of the instrumental development and present preliminary measurements of transects of lead.

## Does the Antarctic Circumpolar Current isolate high-latitude bivalves from ENSO forcing?

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The Antarctic Circumpolar Current (ACC) is called the “mightiest current in the oceans” ( $\pm 125$  Sverdrup) and represents a distinct barrier between sub-Antarctic (no winter sea ice, summer SST  $> 5^{\circ}\text{C}$ ) and truly Antarctic environments (winter sea ice, summer SST  $< 5^{\circ}\text{C}$ ). We present data on decadal shell growth patterns over the last 50 years in shallow water bivalve species from either side of the ACC, i.e., *Eurhomalea exalbida* from the Beagle Channel, Tierra del Fuego, South America ( $54^{\circ}50'\text{S}$ ,  $68^{\circ}16'\text{W}$ ), and *Laternula elliptica* from King George Island, South Shetland Islands, Antarctica ( $62^{\circ}14'\text{S}$   $58^{\circ}31'\text{W}$ ). In both species, shell growth is coupled to El Niño – Southern Oscillation (ENSO). ENSO forcing differs between the two species in its dominant frequency mode and in sign and may even change over time. We discuss ENSO signal transmission pathways and forcing mechanisms with particular reference to ongoing climate change in the Antarctic Peninsula region.

## Developing the use of the dog cockle, *Glycymeris glycymeris*, shell as a new scleroclimatological proxy species

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Growth series contained in the shell of the long-lived (> 100 years) dog cockle, *Glycymeris glycymeris*, can potentially be used as a scleroclimatological proxy. Inhabiting predominantly coarse sand and gravels this species is widely distributed in the coastal waters of the European continental shelf. The patterns of growth lines in shells of *G. glycymeris* collected in 2009 from two sites around the Isle of Man have been studied.

Annually-resolved growth increments were measured in photomicrograph mosaics obtained from acetate peel replicas of multiple shells and cross-matched to construct a growth series chronology for each site. A common growth signal ( $R = 0.557$  and  $p < 0.0001$ ) was apparent amongst the shells from the two sites despite their location ca. 15 miles apart. Comparison of the growth series with local instrumental data from the Isle of Man Cypris station indicated a close correlation ( $R = 0.771$ ,  $p < 0.0001$ ) between annual shell growth and seawater temperature.

Independent verification of an annual periodicity of growth line formation was obtained by comparing the growth series in shells collected close to one of the sites twelve years previously with the growth series in shells collected in 2009; an exact correspondence indicated an annual periodicity of formation. The growth series in the shell of *G. glycymeris* offers considerable opportunity and warrants the further development of the shell as a scleroclimatological archive.

## Is the Alaska Coastal Current becoming less saline? An example using coralline algal Ba/Ca ratios

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The Alaska Coastal Current (ACC) plays an important role in the transport of heat and freshwater from the North Pacific into the Bering Sea. Changes in the properties and strength of the ACC, which is fed by glacial meltwaters and coastal runoff into the Gulf of Alaska, ultimately affect Bering Strait throughflow into the Arctic Ocean. While a drastic freshening of the ACC has prompted detailed oceanographic monitoring efforts, long-term oceanographic observations from this area are sparse and paleoclimate data non-existent.

Here we present a multidecadal oceanographic history of the ACC within the Aleutian Island region using proxy records obtained from the coralline alga *Clathromorphum nereostratum*. This calcareous alga is a dominant component of the Aleutian Islands shallow marine ecosystem, and well suited for paleoclimate reconstructions because it is: (1) Long-lived on the timescale of decades to centuries, and (2) has a high-Mg calcite skeleton which produces annual growth increments, similar to tree rings. Living algal samples were collected off the Aleutian Island Akun, along the western border of Unimak Pass – the main conduit for ACC flow into the Bering Sea.

Annually-resolved Magnesium/Calcium and Barium/Calcium time series were generated using Laser Ablation Inductively Coupled Plasma Mass Spectrometry. While Mg/Ca time series indicate a positive relationship with instrumental temperatures, algal Ba/Ca is negatively correlated to a station-based salinity record. This indicates that the algal Ba content is sensitive to salinity changes in the ACC. The algal Ba/Ca reconstruction indicates that the recently observed freshening of the ACC is unprecedented in at least the past 65 years, and possibly the result of accelerated glacial melting in mainland Alaska.

## **Stable isotopic profiles of meagre (*Argyrosomus regius*): reconstruction of environment and fishing practises at Cansado, Mauritania**

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Thousands of otoliths were recovered from the Epipaleolithic site of Cansado (radiocarbon dated to 6730 BP) located near Cap Blanc (Baie du Lévrier, Africa, 20°50' N). Meagre (*Argyrosomus regius*, Asso, 1801) is the dominant species. This is a migrating benthopelagic species, inhabiting coastal temperate waters from Western Europe to Northwest Africa, moving along shore or offshore-onshore in response to temperature change. Its predominance is likely to indicate fresh oceanic conditions and relatively strong upwelling activity at 6730 BP along Mauritanian coasts.

High-resolution stable isotope profiles were generated for eight archaeological otoliths and seven otoliths from modern specimens collected in Nouadhibou (19°N) to gain more insights into environmental conditions at the seasonal scale as well as into fishing activities. Modern and archaeological specimens exhibited similar ontogenetic and sinusoidal isotopic variations. The  $\delta^{13}\text{C}_{\text{oto}}$  and  $\delta^{18}\text{O}_{\text{oto}}$  values ranged from ca. -5 to +1 ‰ and from ca. -2 to +1.5 ‰, respectively. Intra-otolith isotopic variations were compared to light intensity profiles to determine individual age and the timing of growth mark deposition. When observed in reflected light, translucent zones corresponded to minimum intra-annual  $\delta^{18}\text{O}_{\text{oto}}$  values, and were therefore deposited during the warm season. Life history patterns and reconstructed thermal histories based on cyclic variations in  $\delta^{18}\text{O}_{\text{oto}}$  values during 'adult' life confirmed the presence of coastal upwelling at 6730 BP. Moreover, fishing occurred seasonally during the fresh season, suggesting that human groups exploiting marine resources had a good knowledge of fish population behavior.

## The giant clam *Tridacna maxima*, a high-resolution proxy for past climate reconstruction in the South-West Pacific: first stages of the calibration

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Analysis of climatic variability during the climatic optimum (ca. 6000 yr BP) and the period of the first human populations (ca. 3000 yr BP) in New Caledonia and Vanuatu (South-West Pacific) requires studies of paleoceanographic time-records over several tens of years. Although corals are typically used for such purposes, interpretation of paleoceanographic records can be disturbed by diagenetic modifications affecting the very porous skeleton. As a result, the use of an additional biocarbonated archive – the giant clams which are less affected by diagenesis – has been developed recently. Nevertheless, the use of fossils of giant clams as archives of the past requires to improve the calibration of geochemical and sclerochronological proxies.

*Tridacna maxima*, currently living in the tropical waters of New Caledonia, were selected for these calibration experiments, because they can be found in the Holocene (the last 10,000 years) fossil environments including archaeological sites. In November 2008, the monitoring of environmental parameters started comprising analyses of photosynthetic pigments, nutrients, stable isotopes in water, trace elements concentrations of suspended particulate matter (SPM) and in water, salinity (SSS), temperature (SST), and pH. Here, we present the sclerochronological analysis of one of the *T. maxima* used in our experiment. This one was collected in November 2009 following the death of the animal in the tank. Daily growth increments were analyzed to perform an accurate chronology to calibrate both shell geochemistry and growth increment width changes in relation to the environmental records. After testing several preparation techniques (from the thin-section to etching methods), it appears that the growth increment width changes of the external shell layer show an annual periodicity characterized by higher growth rate from November to March (summer) and lower growth rate from June to September (winter). This sclerochronology shows that either scaled folds or interdigitating sections can be used for daily increment width measurements. The joint comparison with environmental recorded data points out some correlation between growth increment width, NO<sub>x</sub> (NO<sub>2</sub> + NO<sub>3</sub>), pheophytin concentrations and SST. This highlights that *T. maxima* would probably be a reliable archive of past environmental factors. Shell growth variations on the external shell layer of *T. maxima*, however, need to be better constrained before this species can be used for past environmental reconstructions. Nevertheless, daily growth measurements could be used for studies of seasonality patterns through time.

This study is supported jointly by the French INSU-EC2CO program and the IRD. We thank the Province Sud of New Caledonia for having given us the authorizations to make this experiment.

## **Coastal hunter-gatherers in northern Chile: archaeological and paleoecological approach**

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The Chinchorro culture dated between 7000 and 3500 years ago had its economy strongly oriented to maritime resources. This culture is known for its mortuary patterns, characterized by the well-preserved and oldest artificial human mummies, which reveal early funerary practices. The funerary objects, like fishhooks and nets, are also very well-preserved, giving deep insight into the material cultural (Rivera 1991 *J. World Prehist.* 5, 1-47; Arriaza 1994 *Chungara* 26, 11-48; Santoro et al. 2004 In Veth et al. *Desert Peoples. Archaeological Perspectives*, 243-260). Despite the excellent preservation of material objects, the way of life of the Chinchorro people is not well understood, and we do not know yet how they articulated their culture in association with the management of the fragile environment of the desert coast and surrounding areas in order to developed their complex and long-lasting culture. Thus, a dissertation project has been developed in two Chinchorro sites located in the Camarones Valley in the Atacama Desert in northern Chile. This project analyzes data gathered during archaeological excavations at the sites of Camarones 14 and Camarones Sur.

The excavations focused on the recovery of data that will help determine if the Chinchorro people were living in the same area during the whole year or if they were moving seasonally around in search of food and water and of social interactions with other people living along the coast or in the mountains.

Thus, in order to examine sedentism, this project studies faunal remains. The analyses have a focus on species identification and their seasonal occurrence. Marine mollusk shells of *Concholepas concholepas* have been studied through shell growth-line and stable isotope analyses. Both techniques will give information about the period of the year in which mollusks were collected and, consequently, when the Chinchorro people were living in individual sites. Detecting the season during which people were exploiting the surrounding environment will contribute to our understanding of Chinchorro mobility and its relation to economic strategies, mobility/sedentism, and early cultural complexity.

## **Establishing a chemical baseline for a mining-impacted area using otolith microchemistry**

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Assessing environmental change relies on monitoring physical, chemical, and biological parameters over extended periods of time. However, detecting change is difficult in areas where base-line data is sparse or non-existent. Biominerals, which may archive chemical information, are becoming important tools for monitoring environmental change. In particular, otoliths have been referred to as continuous recorders of exposure to the environment. They are metabolically inert, unlikely to be resorbed, and grow throughout the life of the fish, and their annular structure adds a chronology to the record. As such, otoliths can provide a detailed chemical history of the environments in which the fish have lived over the lifespan of the individuals. Combining this data with archived samples can expand the time frame back several decades, providing an historical perspective to trace element levels in an environment.

In this study, recent and archived samples were collected from sites adjacent to a rare-element pegmatite mine, as well as reference sites. LA-ICP-MS analyses of the otoliths across the annular structure provided a year-by-year reconstruction of trace element fluctuations in otolith microchemistry from this area. Average trace element concentrations were calculated per year and per species to construct preliminary temporal chemical trends for an affected site and a reference site. The chemical trends can be used to determine baseline chemistries for the area in order to monitor changes within the environment, establish what affects mining has had on the area, and to determine the success of tailings impoundment strategies.



## Distribution patterns of *Arctica islandica* shells in the North Sea: ontogenetic and radiometric ages

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Shells of the bivalve mollusk, *Arctica islandica*, yield important data on environmental and climatic changes in high-latitude marine settings. The extraordinary longevity of this species makes it an ideal recorder of lower-frequency climate variability and also permits the construction of long master chronologies from individual specimens with overlapping lifespans. However, current sclerochronological research using this species is predominantly based on accidental findings of fossil shells. In this study, we investigated whether *A. islandica* shells from the North Sea exhibit a preferential spatial distribution of maximum lifespans and radiometric ages. In total, 52 of the largest and thickest specimens selected from an extensive collection of shells, dredged from below 55 m of water depth, were examined. Of the 52 specimens, 32 were collected as single shells (dead-collected) during July and August 2002, whilst the living bivalves were dredged from the sea floor in 1848, 1868, 1985, 1998, 2002 and 2003. All specimens were extremely well preserved and were processed following routine sclerochronological methods, including immersion in Mutvei's solution. Ontogenetic ages were measured by counting the annual growth increments under a stereo microscope. In addition, the absolute ages of the dead individuals were determined by means of <sup>14</sup>C<sub>AMS</sub>. The ontogenetic (137 years) and radiometrically oldest individuals (9239 cal year BP) came from the east coast of England, whereas the Norwegian west coast predominantly yielded younger individuals (109 years, 4641 cal year BP). Strikingly, specimens collected alive were much younger than the specimens that died prior to the 19<sup>th</sup> century (non-parametric *t*-test:  $p < 0.001$ ). Given the excellent preservation, it seems unlikely that the accumulation of older shells along the British east coast is the result of extensive transport and redeposition by currents. It is hypothesized that the stable habitat at some sites supported longevity, whilst at other localities, predation or other detrimental effects prevailed. Differences in sedimentation and erosion rates may account for the observed differences in the spatial distribution of radiometrically older and younger shells. At sites with lower sedimentation or higher erosion rates, radiometrically old shells are more common in the upper 30 cm of sediment than they are at sites with higher sedimentation and/or lower erosion rates. The finding that modern shells were significantly younger than their fossil counterparts is most likely to the result of extensive fishing in the North Sea, especially by ground-trawling. The current study demonstrated that *A. islandica* shells in the North Sea show characteristic age distribution patterns that are related to anthropogenic factors, sediment accumulation rates and specific habitat conditions. Further research is necessary to study potential links between food supply, longevity and absolute shell growth rates.

## Stable isotope ratios in *Pinna nobilis* shells record ecological information and water mass properties in the Mediterranean

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Sclerochronologic and stable isotope records in *Pinna nobilis* shells potentially record ecological and oceanographic information. *P. nobilis* is a subtidal bivalve adapted to live in a variety of environments from shallow coastal lagoons to >50 m depth in the Mediterranean. We hypothesize that stable isotope ratios ( $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$ ) and growth increment patterns from individuals living in different environments serve as ecological indicators. Our objectives were to (1) establish whether nacre tongues observed across the posterior adductor muscle scar (PAMS) in cross-sectioned shells formed annually; and (2) compare monthly resolved variations in  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  values recorded in animals from two populations located above and below the thermocline (17 m and 30 m depth, respectively).

Our results demonstrate that nacre tongues are deposited annually. Previous studies have reported that temperature stress is the dominant factor controlling annual growth increments. Our initial findings, however, suggest that annually formed nacre tongues are independent of temperature. Oxygen isotope ratios in all three shells follow a sinusoidal pattern reflecting seasonal variability. Specimens from 17 m form nacre tongues during decreasing  $\delta^{18}\text{O}$  values (i.e., early to late spring), whereas the specimen from 30 m formed nacre tongues near or at the most positive  $\delta^{18}\text{O}$  values (i.e., winter). This observation is consistent with delayed water heating at 30 m by advection from warmer surface waters and a fixed timing unrelated to temperature for nacre tongue formation. Carbon isotope ratios provide additional information on environmental factors that may govern nacre tongue formation. Like  $\delta^{18}\text{O}$ ,  $\delta^{13}\text{C}$  values follow a sinusoidal pattern. In specimens from 17 m,  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values are in phase with each other; however, they are out of phase in the specimen from 30 m depth. We hypothesize that these phase relationships can be used as a depth indicator. The timing of nacre tongue formation with respect to carbon occurs at relatively low values in the sinusoidal time series of all three shells irrespective of depth. If  $\delta^{13}\text{C}$  values serve as a proxy for primary productivity, perhaps food availability rather than temperature controls nacre tongue formation. Alternatively, gonad maturation is a possible factor influencing nacre tongue formation because it starts in spring. Reproduction probably does not influence nacre tongue formation because reproduction occurs only once a year around September for the western Mediterranean, which does not agree with our isotopic results. Such information will allow reconstruction of ecosystem and oceanographic conditions.

## **Periodicity of growth lines in freshwater mussels: a stable isotope study**

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Freshwater mussels are some of the most threatened species in North America: approximately 70% of them are extinct, endangered, or in need of special protection. Despite their precarious status, fundamental aspects of their biology remain largely unknown, such as intra- and inter-annual growth rates and longevity. A better understanding of their basic biology and ecology can help resource managers understand population dynamics and develop effective management strategies. Oxygen isotope sclerochronology provides a simple technique to address these gaps in our knowledge. In this study we assess the periodicity of growth lines in freshwater mussel species from the Wolf River in Tennessee. The periodicity of growth lines in the majority of freshwater mussel species has not been investigated. Of the 26 species found on the Wolf River, only a handful at the most have had the periodicity of their growth lines rigorously investigated. Once the periodicity of these lines is determined, growth rate and longevity can be determined. Additional information about the environment the mussels grew in can also be obtained from the isotopic data archived in these shells. Stable oxygen isotopes provide information about precipitation and water temperature while stable carbon isotopes can give insight into food sources and carbon biogeochemistry of the stream when metabolic carbon is accounted for.

## **Assessing shell growth records from *Arctica islandica* in the Gulf of Maine as indicators of environmental change**

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The current array of instrumental records for monitoring ocean circulation dynamics and long-term trends in productivity and/or seawater temperature in the Gulf of Maine (GoM) is spatially and temporally limited. Documenting and understanding the past and present changes in ocean circulation and marine climate are critical to gaining an understanding of the natural variability within this ecosystem. Previous work has shown that GoM productivity, measured by *Calanus finmarchicus* abundance, is strongly influenced by minor shifts in slope water currents (Gulf Stream [GS]; Labrador Current [LC]) (MERCINA 2001 Oceanography 14, 76-82). Further, the relative position and strength of the GS and LC appear to be in part modulated by the North Atlantic Oscillation. However, it is unclear if the modern relationships among the North Atlantic Oscillation, LC, and GS impacted the oceanography in the GoM in a similar way in the past. We therefore propose to use proxy records to refine and extend our knowledge of this system. The long-lived ocean quahog, *Arctica islandica*, has been extremely useful in documenting past environmental variability in marine ecosystems (e.g., Weidman et al. 1994 J. Geophys. Res. - Oceans 99, 18305-18314; Wanamaker et al. 2008 Clim. Dyn. 31, 183-194). A previous study (Wanamaker et al. 2009 Int. J. Earth Sci. 98, 19-29) showed that *A. islandica* shell growth was positively correlated with *C. finmarchicus* abundance levels. This study aims to develop the first multi-site master shell chronologies in the GoM to explore the use of shell growth records derived from *A. islandica* as an environmental change proxy.

## Sectorial dark field: the best lightning technique for etched thick-sections?

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There are several different reflected-light techniques that can be used for sclerochronological examinations of etched thick-sections under the microscope. This raises the obvious question of which technique is the best to minimize inaccuracy when measuring increments and defining the distances in between?

The techniques evaluated in this study were compared on two different microscopes. The Olympus SZX 16 is equipped with a Nikon Coolpix 995-camera and comes with both bright field lightning and dark field lightning for incident light. For dark field, the Light Emitting Diodes (LED) are arranged in a circle and generate a light entering the field of view at an angle of 60° (Schott VisiLED MC1000). The Zeiss Axio Imager A1m is equipped with an AxioCam MRC 5-camera and in addition to axial bright and dark field lighting techniques, this system also offers differential interference contrast (DIC). A polished cross-section of an *Arctica islandica* shell, treated with Mutvei's solution, was examined under both microscopes.

The camera with the DIC setup had no apparent positive effect on the image quality. The bright field was arranged so that lighting was generated at an inclined angle with two opposite spotlights on the thick-section. This minimized the size of the shadows and highlighted the relief. Overall however, the sectorial dark field lightning is the most suitable. Images are not as blurry as those taken using DIC. Furthermore, the contours are highlighted and the disturbing glossy effect, produced by conventional lighting, is reduced. The best ratio of shadow reduction and relief highlighting is achieved by using one quarter of the LED circle.

## How well is *Patella vulgata* Linnaeus 1758 reflecting changes in sea surface temperatures (SST)? First results using living and archaeological samples from Northern Spain

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Human populations have been exploiting coastal regions in different parts of the planet, at least since the Middle Palaeolithic. In Cantabrian Spain, the study of the exploitation of molluscs and shell middens formation during the late Pleistocene and early Holocene has shown the importance of these resources in human diets, being one of the most commonly collected species the limpet *Patella vulgata* which is present from the upper Palaeolithic to the Neolithic (ca. 40,000-5700 cal BP).

In recent years, the application of geochemical techniques on carbonate materials has yielded significant results in palaeoclimate and archaeological research. Variations in stable oxygen isotopes in seawater can be recorded in shell carbonates of many gastropod and bivalve molluscs and can be used as useful indicators of temperature fluctuations. Moreover, as marine molluscs form their shells daily by precipitating carbonate along different line growths, they are also used to determine the season of death. In this study, we performed stable oxygen and carbon isotope analyses on *P. vulgata* shells from archaeological sites of Northern Spain with two main objectives: (1) the reconstruction of the evolution of sea surface palaeotemperatures from before the last glacial maximum to the mid-Holocene (ca. 40,000-5700 cal BP) and (2) the study of subsistence strategies and mobility and settlement patterns of the hunter-gatherers. Thus, thanks to the seasonal climatic variations that *P. vulgata* reflects, information can be obtained about the times when the molluscs were gathered. It is equally possible to determine whether the climate changes have influenced the subsistence and social strategies used by human groups over time.

This work presents preliminary results of the palaeoclimate reconstruction. For this purpose, we took a total of 174 powdered samples from the inner surface of the marginal part of *P. vulgata* shells (where the last growth lines precipitate) recovered in 36 stratigraphic units from archaeological sites of different ages in Northern Spain. Samples were then analysed in a Finnigan MAT 251 mass-spectrometer to obtain the stable carbon and oxygen isotope values. For comparison, we also analysed 48 samples of living specimens collected monthly along two years (2005 and 2006) in order to identify seasonal variations in sea surface temperature. Results show that archaeological *P. vulgata* specimens reflect important temperature differences (ca. 30,000-5700 cal BP) between Palaeolithic samples (colder conditions) and Mesolithic and Neolithic ones (warmer). They also show a good correspondence with global palaeoclimate curves obtained in Greenland ice cores (GRIP and GISP2).

## **Possible ocean acidification during the PETM: analogue for future ocean acidification?**

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The aim of this subproject of the BMBF-sponsored national research initiative BioAcid is to assess the impact of future ocean acidification on the biomineralization performance of calcitic and aragonitic bivalves. The predicted changes in the CO<sub>2</sub> concentrations, caused by anthropogenic burning of fossil hydrocarbons, will lead to a drop in seawater pH that reaches a critical level in 2100 and is combined with an increase in the surface water temperatures. Similar changes in the ocean-atmosphere systems took place some 55 million years ago during the PETM (Paleocene–Eocene Thermal Maximum). Arguably, the PETM is the best analogue of Earth's history for future. It represents an interval of global warming and ocean acidification. In order to add the geological (time) perspective to the otherwise mainly biological approaches of BioAcid, we intend to investigate fossil bivalves sampled across shoal-water deposits of the PETM. First attempts to sample the PETM in Oman have not lead to the expected results as the critical interval is probably not well exposed. An alternative working area is SW Slovenia. There, the critical boundary interval is exposed. In addition, modern bivalve samples from Ischia, characterized by degassing CO<sub>2</sub> vents are presently under investigation. Finally, cultured bivalves, kept under artificial acidic conditions, from experiments developed in aquaria will be investigated. Two main tools for the quantification of bivalve calcification under acidic seawater conditions: (1) geochemistry and here mainly non-traditional isotope systems that are affected by metabolims (C, O, Mg, Ca isotopes, trace elements) and (2) shell ultrastructure analysis focussing in textural differences between shell material precipitated under 'normal' with such precipitated under acidic seawater conditions. The later approach is undertaken in collaboration with the University of Munich.

## Reconstruction of North Pacific Holocene climate using marine bivalve shell midden deposits

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Bivalve mollusk shells are useful tools for multi-species and multi-proxy paleoenvironmental reconstructions with a high temporal and spatial resolution. In order to reconstruct Holocene climate variability and environmental changes, stable oxygen and carbon isotopes were measured in modern and fossil marine bivalve shells of the hard clam *Meretrix lusoria* from Japan (Tokyo Bay and Seto Inland Sea) and the butter clam *Saxidomus gigantea* from Alaska (Mink Island and Little Takli Island) and British Columbia (Dundas Islands, Namu and Hunter Island). All specimens were <sup>14</sup>C<sub>AMS</sub> dated. Both species reveal clear seasonal cycles in  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  values. Paleotemperatures and freshwater flux can be reconstructed from stable isotope ratios. The shell isotope records presented here reveal environmental and climatic changes in the coastal region during the Holocene. Modern shells from Japan record more positive  $\delta^{18}\text{O}$  values than shells from the past 2000 years, which indicates a warmer and wetter period compared to the present. Modern Alaskan shells have more negative  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  values than shells from about 900 to 1400 BP. This coincides with the freshening and warming trend observed in several published studies. The butter clam could therefore be used to reconstruct the Alaska Coastal Current, which is driven by freshwater influx. *S. gigantea* shells from northern British Columbia have more negative  $\delta^{18}\text{O}$  summer values between 3000 and 5000 BP and so they reveal a fresher mid Holocene than early and late Holocene. High-resolution proxy data for the marine realm of the high latitudes are still sparse. These environmental shell records therefore provide a valuable contribution to such studies. The data were compared with other proxy archives, such as tree rings, pollen, corals, lake sediments and chironomids, in order to investigate teleconnections and the development of North Pacific climate in space and time. Ultimately, the aim of this work is to create a network of proxy data based on bivalve shells to examine Holocene large-scale climate variability, and to improve the understanding of major pressure and circulation systems, as well as natural climate oscillations such as PDO and ENSO.



## The influence of increased $p\text{CO}_2$ on the calcification of *Mytilus edulis*

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One of the most important and abundant calcifying organisms in several marine ecosystems is the blue mussel, *Mytilus edulis*. It has a wide geographic distribution (Gosling 1992 Developm. Aquacult. Fish. Sci. 25, 1-20) and tolerates a broad range of environmental conditions (Seed and Suchanek 1992 Developm. Aquacult. Fish. Sci. 25, 87-170). Blue mussel beds are also common features in the Kiel Fjord (Baltic Sea), a habitat dominated by low salinity (10-20 PSU), low alkalinity (1900-2150  $\mu\text{mol kg}^{-1}$ ), low pH (minimum values  $< 7.5$ ) and high  $p\text{CO}_2$  (maximum value of 2340 ppm). The resulting calcium carbonate saturation state (min. values:  $\Omega_{\text{arag}} = 0.34$  and  $\Omega_{\text{calc}} = 0.58$ ) is significantly lower than in the open ocean (Thomsen et al. submitted). Therefore,  $p\text{CO}_2$  in Kiel Fjord during summer is already higher than what is predicted for the future (e.g., Caldeira and Wickett 2003 Nature 425, 365). Additionally, Meier (2006 Clim. Dyn. 27, 39-68) projected an increase of temperature (2.6 to 5.0 °C) in the next 100 years for the Baltic Sea.

To contribute to the understanding of the ability of calcifying organisms to live under ocean acidification conditions and of biomineralization mechanisms, *M. edulis* from this naturally  $\text{CO}_2$ -enriched habitat were cultured in a flow-through system. Experiments were conducted using  $\text{CO}_2$  concentrations ranging from 380 ppm to 4000 ppm and temperatures ranging from 5° to 25°C. At the end of the experiments, hemolymph and extrapallial fluid (EPF) were taken and analyzed for pH,  $p\text{CO}_2$ , bicarbonate and elemental ratios. Fluids showed decreased pH and increased  $\text{CO}_2$  with increasing water  $p\text{CO}_2$ . Elemental ratios (Mg/Ca and Sr/Ca) in the fluids did not show  $p\text{CO}_2$  or temperature-related systematic changes.

Furthermore, boron isotopes ( $\delta^{11}\text{B}$ ), used in isotope geochemistry as a pH proxy, were investigated by LA-MC-ICP-MS in shell portions precipitated during the experimental treatment. We observed high  $\delta^{11}\text{B}$  variability between different individuals, but also within single shells. Average  $\delta^{11}\text{B}$  values showed a weak positive correlation with pH. When comparing our results to published studies, boron isotopes appeared to represent internal pH conditions (EPF) instead of ambient water pH (Kasemann et al. 2009 Chem. Geol. 260, 138-147; Reynaud et al. 2004 Coral Reefs 23, 539-546; Sanyal et al. 2000 Geochim. Cosmochim. Acta 64, 1551-1555).

## **Estimating periods of extended shell closure from bivalve growth patterns: a potential new proxy for seasonally hostile environmental conditions**

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When exposed to environmental stress (e.g., seasonal anoxia or highly variable salinity) bivalve mollusks tend to keep their valves closed until the ambient conditions have improved (i.e., when the conditions are within the physiological tolerance of the animal). During extended periods of shell closure, the animal switches to an anaerobic metabolism as the oxygen levels in the soft parts drop. As a result of this process, acidic metabolites start to dissolve the inner shell surface, while the outer shell surface largely remains intact. Consequently, the shells of these specimens are typically very thin. This observation leads to the question of whether the hostility of the environment, and the resultant temporal changes, can be estimated from the relative difference between the shell material deposited each year in the outer and inner shell layers ( $\Delta$ SGI values). For this purpose, annual increment width chronologies of 10 specimens of the ocean quahog, *Arctica islandia* from the Baltic Sea (a restricted environment) were compared to those of eight specimens from offshore Iceland. Shell cross-sections were cut and polished before being immersed in Mutvei's solution. Sclerochronological analyses were conducted in the inner shell layer of the hinge plate and in the outer shell layer along the axis of maximum growth (i.e. near the outer shell surface). The specimens from the Baltic Sea were typically younger (20-25 years on average) and thinner (average shell thickness at 1.5 cm from the hinge was 0.5-1 mm) than those from Iceland (over 100 years old, 2 mm shell thickness).  $\Delta$ SGI chronologies of specimens from the Baltic Sea exhibited significantly more variability than the specimens from Iceland. In some years, the contemporaneously deposited growth increments of the inner shell layer were much narrower than those of the outer shell layer. In some years, the annual increments of the inner shell layer were difficult to identify or even missing. This study strongly suggests that extended periods of shell closure can be estimated from the difference in relative growth increment widths between the two shell layers of this species. A combined analysis of the inner and outer shell layer may therefore be useful as a proxy for detrimental environmental conditions.

## **Tobago coral record as a high-resolution archive of Amazon and Orinoco River outflow and tropical climate variability**

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We have investigated the trace elemental composition in the skeleton of a massive growing Tobago coral (*Colpophyllia natans*) retrieved from the northwest side of Tobago in February 2008. Tobago reefs and surface ocean conditions around the island are influenced by seasonal pulses of discharge from South American rivers, in particular the Orinoco River, that delivers low-salinity, sediment- and nutrient-enriched waters to the tropical North Atlantic during the wet season.

Here we present a century-long (1892-2007) high-resolution record of coral trace elemental variations analyzed by Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS). The analysis yields continuous individual trace elemental records (Sr/Ca, U/Ca, Ba/Ca, B/Ca) with up to bi-weekly resolution for the 20<sup>th</sup> century. By comparing geochemical coral proxy data to observations of local sea surface conditions (e.g., sea surface temperature, salinity) and historical stream-flow data, we assess the influence of variability in Orinoco and also Amazon River runoff on the study site. Our findings show that a link exists between Tobago coral Ba/Ca and distinct episodes of South American river-runoff. In addition, we examine whether the impact of large-scale tropical climate variability (e.g., El Niño - Southern Oscillation events) on local climate and ocean variability is detectable in coral trace elemental proxies. Annual banding patterns, the occurrence of stress bands and potential changes in skeletal linear extension rate of the coral core is also investigated. A slowdown in coral growth during the last 20 years of the Tobago coral record is observed.

## **Validation of growth increment periodicity and the position of the first annulus in Blackspot Seabream (*Pagellus bogaraveo*) otoliths**

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Blackspot seabream (*Pagellus bogaraveo*) is an important commercially exploited fish species in the Azores archipelago. Previous sclerochronological research has shown that this species produces a single set of opaque and hyaline rings throughout the year (Krug 1989 *Cybium* 13, 347-355) indicating that otoliths can be reliably used for aging. Several initiatives exist to age this species, counting annuli of whole or sectioned otoliths for routine fisheries assessments in the Azores. To date, however, there has been no endeavour to explore the periodicity of daily rings or to verify the location of the first annual increment.

Considering fish from the Central Island Group of the Azores archipelago, otoliths were extracted and prepared for reading. Individuals spanned a size range of 13-52 cm and were determined to be 1-20 years old. Using macrostructural observation, regression analysis of size at age was used to predict the position of the first annulus. Specimens were then mounted in resin blocks, cut, ground and polished in preparation for microstructural analysis following a method similar to that of Secor et al. (1992 *Spec. Pub. Can. J. Fish. Aquat. Sci.* 117, 19-57). Daily rings were counted in order to corroborate correspondence of the first annual increment to a period equivalent to one year.

Confirming the periodicity of otolith sclerochronological features is vital to the development of a reliable aging protocol since misinterpretation of fish age can have grave consequences for stock assessment and subsequently fisheries management.

## **Is it possible to construct long master chronologies from the fossil shells of *Margaritifera falcata* (British Columbia, Canada)?**

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Variations in annual shell growth have been observed in the freshwater bivalves, *Margaritifera falcata*, from British Columbia. These variations are strongly linked to local precipitation patterns and ENSO (Schöne et al. 2007 Int. J. Earth Sci. 96, 525-540). The aforementioned study was based on a 50-year master chronology that had been constructed from live-collected shells. The current study tested whether the annual increment time-series of subfossil individuals could be combined with, and thereby temporally extend, the existing master chronology. For this purpose, 68 single valves were excavated from river bank deposits along the Little Campbell River, British Columbia. Shell remains were only recovered from the upper 50 cm of the soil. Polished cross-sections, immersed in Mutvei's solution, were digitized and the annual increment widths measured using the software Panopea©. Some specimens attained life-spans of around 100 years. Age-detrended and standardized growth increment time-series were then cross-dated with the existing master chronology. Using this approach, it has been possible to extend the master chronology back to 1898 AD. According to the cross-dating, all of the "fossil" shells died within the three years prior to collection. An EPS (estimated population strength) value of 0.95 suggests a high intercorrelation among the time-series. The new time-series exhibited a stronger correlation with local precipitation and ENSO indices. This study clearly demonstrates that subfossil shells, with unknown dates of death can potentially be used to extend master chronologies backwards. However, the limiting factor for constructing longer master chronologies is the limited preservation potential of the shells at this locality (humid environment, low pH value of the soil) and likely of many other freshwater habitats as well. The shell carbonate was typically dissolved within about three years. Subsequent studies of this kind should therefore focus on localities at which the potential for the preservation of calcium carbonate is much higher.

## **Reconstructing the variability of shelf water bottom temperatures in the Middle Atlantic Bight from annual growth increments**

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Many physical oceanographic studies in the Middle Atlantic Bight (MAB) indicate large interannual variability in shelf water temperature. This variability is mostly due to changes in the rate of volume transport along the large-scale coastal current system extending from Labrador to Cape Hatteras. Transport along the western Atlantic coastal currents is directly related to large-scale changes in climate mechanisms. Previous work assumed that during the Neogene variations and interactions of cool boreal waters that flowed equatorially and warm tropical waters that penetrated northward have influenced the marine lithology and biological assemblages along the MAB shelf. Our overarching hypothesis is that oceanographic processes along the MAB operating today were also present during the Neogene. Previous work has shown that variations in annual growth increment widths of bivalve shells correlate with climate conditions. Therefore, to test our hypothesis, we will compare annual increment records from living and Pliocene bivalve shells. Here, we present the first step in testing our hypothesis: comparing interannual variability between growth increment records from living *Spisula solidissima* (Dilwyn, 1817) shells and instrument measurement data. Our future work will compare sclerochronologic records between living and Pliocene shells.

Modern shells, collected live by NOAA Fisheries Service: Northeast Regional Fishery Science Center, from across the MAB between 1992 and 2002. The increment width data series from the modern shells represent a modern MAB analog data set that will be compared to fossil shells of the same genus. Over 500 shells were sectioned, polished, photographed and measured. Individual growth increment records were cross-dated and compared to all other shell records across the MAB using a measure of index dissimilarity. The same dissimilarity measures were used to determine the closeness of modern increment-width patterns to instrumental data series. Preliminary results indicate that shell patterns reflect the same large interannual availabilities as the closest instrumental records. Our future comparison of modern analog shell increment records to the Pliocene series will provide information on processes governing change and stability in the MAB region at spatial and temporal scales not attainable with conventional oceanographic techniques.

## **Molecular mechanisms of cellular differentiation in teleost fish scales**

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The teleost fish scale is a dermal skeleton having circular ridges on its surface, and is rich in hydroxyapatite crystals. The distance between the ridges largely depends on growth speed of the fish body. Therefore, annual fluctuations in fish growth speed form annual rings in the scale. Moreover, the crystals in the scale include trace elements that are useful for the reconstruction of the environment that the fish have experienced. The formation of ridges as well as crystals is under regulation of scleroblasts (Sbs), and thus, the molecular understanding on the functions of Sbs is important for sclerochronological studies using fish scales.

The scale under regeneration is a good biological model to study Sb functions, because Sb differentiation and scale growth occur actively. During scale regeneration in the goldfish, Sbs first arise as cell cluster in the scale pocket at Day 2 of regeneration, and start to secrete external-layer matrix. After the beginning of the external-layer calcification (Day 3), they differentiate into three types; episquamal scleroblast (ESb), hyposquamal scleroblast (HSb) and marginal scleroblast (MSb). The MSbs located at the scale margin continue to produce the external layer, and thus, the scale increases its area. The ESbs produce the ridge at close to the scale margin, and thereafter gradually become flat with decreasing activity. The HSbs add the basal plate under the external layer, and thus, the scale increases its thickness.

In this study, in order to understand the molecular mechanism of Sb differentiation, we cloned the cDNAs of osteoblastic differentiation factor (Runx2) and bone matrix proteins (SPARC, BGP) in the goldfish, and analyzed their mRNA expression patterns during scale regeneration by quantitative RT-PCR and in-situ hybridization. Runx2 expression became maximum at day 3 of scale regeneration, when active differentiation of Sbs into ESbs, HSbs and MSbs initiated. SPARC and BGP expression became maximum at days 7 and 14, respectively. Expression of these genes was observed in the cells of Sb-cluster and the flat cells around the cluster at day 2. As the regeneration progressed, the expressions were restricted in the Esbs, HSbs, MSbs, and the cells around the MSbs. These results strongly suggest that Runx2, SPARC and BGP have important roles in Sb differentiation like in the case in osteoblastic differentiation. It is also suggested that Sb progenitors are localized around the MSbs.

## Freshwater mussel shells (*Hyriopsis* sp.) as archives of environmental information

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Bivalves occur in various environments of low and high latitudes, in freshwater and marine settings, and have carbonate shells which are formed by accretionary growth. Therefore, they can potentially paleoenvironmental information in their shells in the form of isotope ratios and elemental composition. Freshwater environments not only react sensitively to climatic changes, but also play a major role in the transportation of material weathered by chemical and physical factors. So, freshwater bivalves are useful as paleoenvironmental archives. While there are many reports about marine bivalves, papers on freshwater bivalves are rare. We present results of Sr/Ca ratios and growth history of shells of the cultured freshwater pearl mussel, *Hyriopsis* sp. (Unionidae).

Three specimens which have same growth history were analyzed for shell structure and the elemental composition by means of ICP-MS. We compared Sr/Ca ratios of shells and water temperature, Sr/Ca ratio of water and annual growth rates.

The profile of first-order fluctuations of Sr/Ca ratios of the outer shell layer along the maximum growth axis was consistent with the profile of oxygen isotope ratios of the shell, which is known as a proxy of temperature ( $R = 0.58$ ,  $p < 0.01$ ). However, the Sr/Ca ratios of three specimens were also influenced by ontogenetic aging. On the other hand, Sr/Ca ratios of the ambient water showed almost no fluctuations. So, the dominant factor controlling Sr/Ca ratios of shell fluctuations was water temperature.



## **Distribution, age and growth of the fan mussel *Atrina fragilis* from around the UK and Ireland**

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In the 19<sup>th</sup> century, specimens of the fan mussel *Atrina fragilis* (Pennant, 1777) were recorded in considerable numbers in the fishing gears of scientific researchers and commercial fishers. The species is now reported as being scarce within UK waters largely as a consequence of damage to these populations from inshore fishing activities and the species is now protected. The distribution of live-collected *A. fragilis* from around the coast of the UK and Ireland was established using historical data from both museums and private collections and from recent reports of live animals from within the scientific community. *Atrina fragilis* has two distinct centres of abundance, in southwest England and northeast Scotland and is largely absent on eastern coasts. The outer shell surface of *A. fragilis* bears few marks such as rings, other than shell margin damage, to indicate its age. However the inner surface of the adductor muscle scar exhibits a series of growth rings. Similar adductor muscle scar rings in the Mediterranean fan mussel *Pinna nobilis* have been shown to be annual in origin. The annual periodicity of the adductor muscle scars, and therefore the positions of the shell surface rings, was validated by analysing the stable isotopic composition of samples of calcium carbonate drilled sequentially along the shell surface along the direction of growth from the umbo to the shell margin. Estimated seawater temperatures from the isotopic analyses of *A. fragilis* shells from the SE Haddock Bank and “The Smalls” (Bristol Channel) demonstrated that the deposition of the surface growth rings generally coincided with the minimum seawater temperatures, although occasionally some rings, presumably formed as a result of a disturbance event, were produced at other times of the year, e.g., when seawater temperatures were maximal. On the basis of the finding that the rings were annually formed when seawater temperatures were lowest, the numbers of rings on the adductor muscle scars were counted. From this the oldest of the 68 fan mussels examined was estimated to be 15 years of age. Population growth curves for *A. fragilis* from three localities (Falmouth-Torbay, Scilly Isles, Haddock Bank) were constructed from the adductor muscle scars and showed that fan mussels in the shallow Falmouth-Torbay populations contained the fastest growing individuals while those in the deeper water Haddock Bank and Scilly Isles populations attained the greatest size, although the latter populations of fan mussels grew at a slower rate than the shallower depth Falmouth-Torbay fan mussels.

## **Bleaching of biogenic carbonates: beware of changes in trace element concentrations!**

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Why is it often difficult to establish reliable trace element proxies in biogenic carbonates? The organic matrix may be one reason for these inconsistencies. Proxy analyses imply that physical processes control trace element incorporation into biogenic carbonates. Incorporation of trace elements into the organic matrix, however, is also controlled by physiological processes. These may distort the physically determined correlation between environmental parameter and the examined proxy. One approach to avoid this distortion would be to chemically remove the organic matrix prior to trace element measurements.

We treated bivalve shell powder (*Arctica islandica*) and inorganic carbonate with 12 different chemicals/cocktails and analyzed for effects on: (1) organic matter (N) content, (2) trace element ratios (Sr/Ca, Mg/Ca, Ba/Ca, Mn/Ca; ICP-MS), and (3) structure and composition of the carbonate (XRD).

The different treatments (1) vary in their efficiency to remove organic matter, (2) cause treatment and element specific changes in trace element ratios, and (3) can even alter the structure and composition of the carbonate (e.g., NaOH treatment: conversion of CaCO<sub>3</sub> into Ca(OH)<sub>2</sub>). Among all examined methods, there was no treatment without any side effects. NaOCl treatment, however, can be applied prior to Sr/Ca measurements to efficiently remove the organic matrix without altering Sr/Ca ratios and/or the carbonate structure.

## Test of Marine Protected Area source-sink hypothesis on fishes using otolith microchemistry<sup>#</sup>

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Ecosystem-based fishery management (EBFM) is a new approach which promotes the protection of essential habitats for fish and other ecosystems' components against destructive fishing effects and promotes the increase in fish diversity and abundance. In such context, the use of Marine Protected Areas (MPA) and particularly no-take marine reserves is highly recommended. Many investigations addressing the impacts of MPA in fish communities and ecosystems function have been realized in the last two decades, so it is now well established that marine reserves enhance the density, biomass and size of organisms inside their boundaries. MPA also contribute to the regeneration of habitat and the re-building of fish stock heavily impacted by a long history of exploitation. One question remains: are MPA playing a role as sources or sinks for fish?

The aim of this study is to characterize the chemical signatures of otoliths from fish sampled in/out of the creek and to reconstruct their environmental history. The final goal is to define indicators to test the MPA source-sink hypothesis and to determine their efficiency as fisheries management tools.

Three fish species *Galeoides decadactylus* (migratory fish), *Sarotherodon melanotheron* and *Tilapia guineensis* (sedentary fish) living in and out the Bamboung creek and waters (2 seasons) were sampled. We used ICP-MS and LA-ICP-MS to determine the trace element concentrations (Li, Rb, Ba, Mg, Mn, Sr). Multivariate analyses showed that the elemental composition of the water enabled very good discrimination of sites and seasons (70-100% correct classification). Elemental signatures in otoliths are specific to discriminate sites with an excellent precision (90-100% correct classification). Greatest contributors to the discriminating function were Sr, Rb, Mn and Ca. We also analyzed transects from the core to the edge of the otolith with a 50 µm laser spot, allowing a very high resolution, to determine the migration of each species.

## **Trace elements and stable isotopes from unionid bivalve shells: proxy records of environmental conditions and pollution events. Experimental approach in situ (Ile-de-France) and in laboratory**

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The application of stable isotope and carbonate trace elements geochemistry to freshwater bivalves has mainly been used to infer riverine hydrology. Living unionids were collected from the Magny-les-Aubigny pool (Burgundy, France) and 20 mussels were transplanted into plexiglass cages and deployed along the Seine River, two locations upstream before Paris and two downstream. Living shells were marked monthly with MnCl or calcein. By the same time, water samples and temperatures were collected more frequently. Before the analysis, thick-sections were viewed under an optical microscope with UV light or cathodoluminescence and manganese or calcein marks were mapped for each shell. All shell samples were cleaned using Milli-Q water and bleached with NaOCl(aq). Isotope samples were milled parallel to the growth increments, along a transect from the most recently formed shell portion (growing tip) to the oldest (umbo) in the aragonite outer layer of the shell. An average of 250 samples per shell were collected and analyzed on mass spectrometer GV Instruments Isoprime for the determination of stable oxygen and carbon isotope ratios. For trace elements, the laser ablation ICP-MS was used with spot size of 90  $\mu\text{m}$  in diameter on the thick-section from the interior to exterior shell.

Each shell exhibits an excellent linear relationship between  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  values. The most negative values fall in the spring or summer. The isotope analyses also showed differences between sites (Seine) and the origin of the juvenile growth environment (Burgundy). A metabolic control is also seen for the youngest part of the shells with a consistent pattern of decreasing  $\delta^{13}\text{C}$ . This trend reflects an increasing contribution of metabolic  $\text{CO}_2$  to skeletal carbonate throughout ontogeny. For trace elements, the flood events of the Seine correspond to geochemical shifts in the shells (Cr, Ni, Cu, Zn etc.) whereas shells from laboratory show constant trends.

## Microstructure, trace elements and stable isotopes of Recent and Holocene bathyal Mediterranean *Corallium rubrum* (Strait of Sicily)

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The gorgonian *Corallium rubrum* (Scleraxonia), or precious red coral, is being exploited in Mediterranean shallow waters for jewelry production. Its dense calcitic skeleton with clear annual bands (0.6 mm/yr) witnesses a decadal longevity. Their Mg/Ca-cycles are microstructure related (Vieulzeuf et al. 2008; Am. Mineral. 93, 1799-1815) and potentially track intra-annual temperature shifts of ca. 10°C variability. During the ship expeditions M70/1 (*RV METEOR*) and MARCOS (*RV Urania*) within the EU-projects HERMES and HERMIONE, bathyal living colonies of *C. rubrum* were found at ca. 650 m in the Strait of Sicily. QUEST-ROV video-surveys documented dense colonies underneath overhangs associated with living scleractinian deep-water corals (e.g., *Lophelia pertusa* and *Madrepora oculata*). ROV-technique allowed for a minimal impact sampling. A small *C. rubrum* colony and a *L. pertusa* colony were collected alive at the same site, as well as a large fossil *C. rubrum* skeleton, to compare their geochemical compositions and banding patterns. Water samples and CTD casts provide solid environmental background data, exhibiting minimal seasonal variability of 13.74° to 13.9°C and 38.69 to 38.72 PSU. Seawater oxygen isotope and stable carbon isotope measurements provide a background for skeletal carbonate isotopic composition. Our research in this stable-conditioned “natural laboratory” aims to unravel the degree of biological fractionation and of microstructure on the primary isotope and trace element signature, which is important for decadal-scale paleoceanographic reconstructions from shallow-water *C. rubrum*. Like their shallow-water cousins bathyal *C. rubrum* specimens have a conspicuous incremental banding. Micromill sampling at ca. 100 µm spacing provided carbonate powder for stable isotope analyses ( $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$ ) on a Finnigan MAT252. Elemental maps (10 x 10 µm resolution) were acquired with a JEOL Superprobe JXA-8200 to resolve spatial Mg, Ca, S and Sr distributions. Quantitative element compositions were measured with a laser ablation ICP-MS (10 µm spacing) for <sup>7</sup>Li, <sup>11</sup>B, <sup>25</sup>Mg, <sup>31</sup>P, <sup>55</sup>Mn, <sup>84</sup>Sr, <sup>111</sup>Cd, <sup>138</sup>Ba and <sup>238</sup>U. Stable isotopes show strong disequilibrium precipitation with the known linear  $\delta^{18}\text{O}/\delta^{13}\text{C}$  correlation in *L. pertusa*. Isotopic and elemental patterns in *C. rubrum* are much more confined, but clearly related to the microstructure. Their variability exceeds the expected levels in this stable environment. Juvenile parts are Mg/Ca-enriched and isotopically depleted from expected equilibrium. Adult parts are more homogenous and possibly more reliable for environmental reconstructions.

## **Strontium isotope ratios of bivalve shells and tree cores in past migration studies**

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The isotope ratios of biologically available strontium in ecosystems primarily depend on their geological substratum. Strontium reference maps are therefore needed to provide the basis to trace the movement of people and animals in modern times and in the past. Strontium isoscapes are generated through the analysis of modern geological and biological samples collected within a variety of geological units in a study area. For the reconstruction of mobility in the past, however, data from modern environmental samples must be handled with caution. The exponential industrial development in the 20<sup>th</sup> century could have modified the isotope ratios of the biomass. Modern fertilizers or acidic rain could have altered the bioavailable strontium, which makes the comparison of modern and fossil samples difficult. Therefore, it is essential to control, whenever possible, potential drifts of the strontium isotope ratios of an ecosystem throughout time.

Here we present strontium isotope ratios of modern and archaeological freshwater bivalve shells and tree cores collected in the vicinity of Lombards' cemeteries in central Germany. The investigation tests whether the delimitation of the regional variability of the strontium isotopic composition deduced from environmental samples is reliable enough to infer new insights about the mobility of the Lombards in this area during the 5<sup>th</sup> and 6<sup>th</sup> century AD.

## Extraction of sea surface salinity proxy by means of high resolution minor trace element analysis in venerid bivalve shells

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Elemental profiles in biogenic carbonates such as corals and foraminifers are well-known proxies of climate change and past environmental conditions. For example, Sr/Ca ratios in coral skeletons were used for reconstruction of oxygen isotope ratio of seawater (= salinity) by combination with oxygen isotopes of the skeletons. Mg/Ca ratios in foraminiferal tests were regarded as important as proxies of seawater temperatures. However, the factors controlling the element/Ca ratios of bivalve shells are generally much less understood than those governing stable oxygen isotope ratios. For this reason, there is no consensus to widely use bivalve shell element/Ca ratios for detailed environmental reconstruction.

Ba/Ca ratios have been proposed as a proxy of dissolved seawater Ba/Ca in coral skeletons and foraminiferal tests, providing information on salinity, nutrient and alkalinity distributions in past oceans (e.g., Sinclair and McCulloch 2004 *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 214, 155-174). Ba/Ca peaks found in calcitic bivalve shells are related to phytoplankton blooms (Lazareth et al. 2003 *Estuar. Coastal Mar. Sci.* 57, 1103-1114), salinity (Gillikin et al. 2006 *Geochim. Cosmochim. Acta* 70, 395-407), but they are apparently strongly species-specific.

This study aimed to determine the proxy of environmental conditions of Ba/Ca profiles in an aragonite bivalve shell. We examined minor and trace element compositions using LA-ICP-MS in some live-caught shells of a venerid bivalve *Phacosoma japonicum* from Tokyo Bay, central Japan, and also monthly collected seawater samples from the same location in 2009. This species secretes lunar day-based microincrements (LDI) in the outer shell layer, so that we can mark calendar dates in the LDI sequence (Miyaji et al. 2007 *Mar. Ecol. Prog. Ser.* 336, 141-150). The obtained results were compared with the environmental data of the nearby seawater during which the shells grew. Some peaks showing high Ba/Ca ratios were recognized in the LDI portions formed during the monsoon (June/July) and typhoon seasons, which can be compared with the high Ba/Ca ratios in the seawater samples collected during the same seasons. These results suggest that the Ba/Ca profile in modern and fossil aragonitic bivalve shells can be used as a proxy of past and present seawater salinity.

## Environmental vs. physiological control of the Mg/Ca and Sr/Ca distribution in oyster shells

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Trace metal compositions of bivalve shells are commonly used for high-resolution reconstructions of past and present environments. However, these proxies are affected by intrinsic and extrinsic factors which greatly differ among species. Because (1) they present a wide stratigraphic range through geological times and (2) their shells made of calcite (most stable CaCO<sub>3</sub> phase – in comparison to aragonite – in respect to diagenetic alterations) should provide primary geochemical signatures, oysters were chosen as a potential paleoenvironmental archive.

This study focuses on the use of Mg/Ca and Sr/Ca ratios of oyster shells as environmental and/or physiological proxies. To test the ontogenic and inter-specific impact on the geochemical records, juvenile (< 2 years-old) and adult (> 2 years-old) *Crassostrea gigas* and *Ostrea edulis* specimens were bred during two years at two distinct locations along the French coasts: Baie des Veys (Normandy, open marine) and Marennes-Oléron Bay (Charente-Maritime, protected area). During this period, environmental parameters were recorded on an infra-daily basis using an IFREMER YSI probe fixed to the oyster tables. Additionally, the shells were monthly labelled in Mn-doped seawater to establish a chronological time-scale in the growth record. Water temperatures are quite variable (5 to 23°C), while the salinity is almost constant (32 to 34 PSU).

Geochemical analyses (400 spots per specimen, equally spaced) were performed using a Cameca SX50 microprobe on the foliated calcite of the hinge section. Sclerochronological profiles and age models were obtained using optical-CL observation of the hinge section of the shells, where Mn marks are easily revealed. Results show high variability, both between individuals from the same species and among sites. Non-univocal relationship exists between Mg/Ca (or Sr/Ca) and temperature despite apparent similarities between the curves, except for adult shells where metabolic activity (growth rate) seems to erase part of the environmental record.



## High-resolution *Porites* coral proxy records as indicators of climatic and environmental change in East Kalimantan, Indonesia

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Environmentally unsound developments of coastal areas are placing many reefs across the world under threat. On many locations soil erosion due to land degradation, mining activities, coastal development and deforestation is now supplying large quantities of sediment to local river systems. In many cases, those sediments are being discharged directly on to reefs systems which commonly exist in close proximity of the river mouth.

The degradation of many coral reefs around the world is linked to injudicious land-based activities. The Berau delta/barrier reef system, located offshore the north eastern coast of Kalimantan, Indonesia is characterized by a unique and pristine reef system. Complex fringing reefs as well as numerous patch reefs have developed within close proximity of the river mouth. Although anthropogenic influence in the region has long been rather small, the region is slowly being exposed to increasing rates of mining activities, deforestation and land use changes. However, the scale and impact of soil erosion and sediment supply to the delta/barrier reef system is scarcely documented and not well understood due to the absence of long, high-resolution time-series. Coral skeletons archive historical sedimentation records as they entrap terrigenous sediments into their skeleton. The advantage using corals as climate and environmental archives is that they provide long time series of several decades exceeding the period of instrumental data. In this study we aim to establish quantitative measures of changes in sediment supply to the reef system and its relation to natural and/or anthropogenic induced climate and environmental changes. To meet this goal several proxy parameters will be examined, i.e., (1) Sr/Ca ratios as an indicator for sea surface temperature changes, (2) Ba/Ca ratios and luminescence as a measure for terrestrial sediment input, (3) combined Sr/Ca and  $\delta^{18}\text{O}$  values to establish a hydrological balance for the region, and (4) coral growth rate and calcification rates as an indicator of reef health in response to thermal and sedimentation stress.

Our results show that the year-to-year variability of sediment supply to the reef system is regulated by the El Niño - Southern Oscillation (ENSO) climate system. During positive phases of the Niño 3.4 index (El Niño) sediment supply is reduced due to draughts in the region. During negative phases of the Niño 3.4 index (La Niña) the sediment supply increases drastically due to enhanced rainfall in the region. Since the mid 1980s a clear trend toward higher levels of sediment discharge is superimposed on the year to year variability. This observed trend in sediment discharge is much higher than can be expected from the reconstructed hydrological balance (Sr/Ca and  $\delta^{18}\text{O}$  values) and must be attributed to increasing land based activities. Our results show that by integrating multiple coral proxies, it is possible to distinguish between climatic and/or anthropogenic induced changes in sediment discharge.

## Shell microstructural changes in shell layers of the chemosynthetic bivalve, *Conchocele bisecta*

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*Conchocele bisecta* (Thyasiridae, Bivalvia) is known as a chemosynthetic bivalve endemic to reducing environments such as seep sites, and bears symbiotic sulfur-oxidizing bacteria in its gill tissue. Though several anatomical and ecological studies of *Conchocele* have been carried out, shell growth patterns have not been studied before. Therefore, we attempted to reveal the shell growth pattern of *C. bisecta* focusing on the microstructural changes in shell layers and shell isotope data. We used Holocene specimens collected at four sites: Okhotsk Sea (400-450 m in depth); off Wakkanai, Japan Sea (100-120m); off Niigata, Japan Sea (420-450 m); Sagami Bay on the Pacific coast of Japan (1100-1200 m). In addition, we collected specimens from the middle Pleistocene (Kakinokidai Formation, Kazusa group, central Japan; 100-150 m in paleobathymetry). The shell structure was examined by using SEM, acetate peel method, and XRD analysis.

Each specimen at the five sites showed outer, middle and inner layers as well as a myostracum that consisted of aragonite. Thick disturbance rings were observed in the outer and middle layers. The outer layer showed spherulites of various sizes and shapes (spherulitic, planar spherulitic, spherulitic prismatic structures) and spindles in each specimen. The middle layer was divided into the outer (cone complex crossed-lamellar structure) and inner parts (crossed-lamellar structure) with a transitional boundary. The inner layer had three types of sublayers (cone complex crossed-lamellar structure, IL1; alternation of irregular prismatic and fine complex crossed-lamellar structures, IL2; irregular complex crossed-lamellar structure, IL3). Two regional groups (group 1: Okhotsk Sea, off Wakkanai, off Niigata and group 2: Sagami Bay, Kakinokidai Formation) were identified by the shell morphological characteristics, the position of the thick disturbance rings, and the characteristics of the microstructures in the inner layer (IL1 and IL2, mainly IL3). The oxygen and carbon isotope ratios were measured in the outer layer of the Okhotsk specimen along the axis of maximum growth (distance from umbo: 0-110 mm). There were two growth stages divided by spherulite sizes (small and large) and isotope fluctuations. In the early growth stage (0-70 mm), the growth phases showed three cycles and high-amplitude variations ( $\delta^{18}\text{O} = 3.8\text{‰}$  to  $4.5\text{‰}$  and  $\delta^{13}\text{C} = -3.1\text{‰}$  to  $1.2\text{‰}$ ), and, in the late growth stage (70-115 mm), five cycles and low-amplitude variations ( $\delta^{18}\text{O} = 3.6\text{‰}$  to  $4.1\text{‰}$  and  $\delta^{13}\text{C} = -2.5\text{‰}$  to  $-0.1\text{‰}$ ). The boundary between the two stages showed a rapid increase in the spherulite size and the first appearance of disturbance rings. These characteristics may be affected by changes in shell growth rate caused by sexual maturity or rapid environmental change. Disturbance rings observed in the outer shell surface coincided with the positions strongly depleted in  $^{13}\text{C}$  and  $^{18}\text{O}$  and the increase of spherulite sized crystals.

## **Sclerochronological analysis of the Early Cretaceous Boreal Realm belemnite *Arcroteuthis lateralis***

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Since the earliest days of oxygen isotope analysis in biogenic carbonates, belemnite rostra have been used to reconstruct palaeoclimatic and palaeoenvironmental conditions. This has been done however, with no true understanding of belemnite ontogeny or ecology. How long did belemnites live for? Where did they live (shallow/deep waters; benthic/pelagic)? Were they active swimmers? Did they migrate extensively (vertically and/or laterally) during their lives? Preliminary investigations into some of these questions have been undertaken, however definitive answers remain elusive. This presents a major problem because both ontogenetic and ecological factors significantly influence the fractionation of certain isotopes and trace elements into biogenic calcite, and as long as these factors remain unknown in belemnites, it will remain impossible to accurately reconstruct past environments and climates from belemnite-derived geochemical data. *Arcroteuthis lateralis* (Phillips, 1835) was endemic to the Late Jurassic–Early Cretaceous Boreal Realm. It is one of the largest and most robust belemnite species known. The adult rostra typically exceed 50 mm diameter in the stem region, and the apex, apical canal and phragmocone are all strongly ventrally displaced. Together, these features result in a belemnite that is ideal for sclerochronological analysis because the section of the rostrum between the apical canal and dorsal margin is significantly expanded. This provides an excellent opportunity to investigate growth-increment, stable isotope and trace element variability in the rostrum at an extremely high resolution. This contribution presents preliminary sclerochronological data from an *Arcroteuthis lateralis* specimen collected from a Lower Cretaceous shallow marine succession in Russia. Ultimately, this study will provide vital, new information that will considerably improve our understanding of the belemnite mode of life and consequently, will significantly advance and refine future palaeoclimatic and palaeoenvironmental investigations.

## Pb concentration and isotopes in Pacific sclerosponge

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During 20<sup>th</sup> century, most lead (Pb) contamination in the environment was derived from anthropogenic aerosols, e.g., the combustion of leaded gasoline. We can identify the sources of Pb pollution by using Pb isotopes ( $^{206}\text{Pb}/^{207}\text{Pb}$ ,  $^{208}\text{Pb}/^{207}\text{Pb}$ ), because their isotopic ratios are region-specific (Bollhofer et al. 2000 *Geochim. Cosmochim. Acta* 65, 1727-1740). Pb contents in biogenic carbonates (e.g., corals and bivalves) have been used to reconstruct the historical changes of ambient Pb composition (e.g., Shen and Boyle 1987 *Earth Planet. Sci. Lett.* 82, 289-304; Lazareth et al. 2000 *Geol.* 28, 515-518). Sclerosponges (coralline sponges) are also potential recorders of Pb change in the ocean surface because their skeletons contain > 10 times more Pb than corals. In addition, sclerosponge skeletons grow slowly (0.01-1.34 mm/year), live up to several hundred years, can be found throughout the geological record and occur in various water depths (< 500 m; Druffel et al. 1986 *Nature* 321, 58-61; Rosenheim et al. 2005 *Palaeogeogr., Palaeoclimatol., Palaeoecol.* 228, 109-129). In this study, we measured Pb concentrations and Pb isotopes in high-Mg calcite skeletons of the sclerosponge, *Acanthochaetetes wellsi*, collected from Kume Island, Japan (East China Sea), to assess the usefulness of this species as a proxy for historical lead pollution and atmospheric circulation. High-resolution Pb contents in the skeletons were obtained using Laser Ablation-ICP-MS (LA-ICP-MS). Pb isotope ratios of the skeletons were analyzed with a Multiple Collector-Inductively Coupled Plasma-Mass Spectrometry (MC-ICP-MS; Tanimizu and Ishikawa 2006 *Geochem J.* 40, 121-133).

The Pb contents reached 2-11 ppm, i.e., 20 times higher than those reported for corals. Skeletal Pb concentrations increased gradually from 1970 to 1980 and increased more rapidly until the late 1990s. Thereafter, Pb values decreased suddenly. This trend indicated that the emission of Pb from anthropogenic aerosols has changed dynamically near the sampling site. The  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio increased from 1970 to the late 1990s, and then decreased. Also, the  $^{208}\text{Pb}/^{207}\text{Pb}$  ratio was higher between 1970 and 1980, and then decreased afterward. These isotope profiles indicate that the Pb pollution source has shifted from Japan to China at around 1980.

## **Sclerochronology: a highly versatile tool for mariculture and reconstruction of life history traits of the queen conch, *Strombus gigas* (Gastropoda)**

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The shell of the queen conch *Strombus gigas* provides a rapidly growing palaeoenvironmental proxy archive, allowing the detailed reconstruction of important life-history traits such as ontogeny, growth rate and growth seasonality. In this study, modern sclerochronological methods are used to cross-date the palaeotemperatures derived from the shell with local sea surface temperature (SST) records. The growth history of the shell suggests a bimodal seasonality in growth, with the growing season confined to the interval between April and November. In Glovers Reef, offshore Belize, the queen conch accreted shell carbonate at rates of up to 6 mm day<sup>-1</sup> during the spring (April-June) and autumn (September-November). However a reduced period of growth occurred during the mid-summer months (July-August). The shell growth patterns indicate a positive response to annual seasonality with regards to precipitation. It seems likely that when precipitation levels are high, food availability is increased as the result of nutrient input to the ecosystem in correspondence with an increase in coastal runoff. Slow growth rates occur when precipitation, and as a consequence riverine runoff, is low. The SST however appears to influence growth only on a secondary level. Despite the bimodal growing season and the winter cessation in growth, the growth rates reconstructed here from two *S. gigas* shells are among the fastest yet reported for this species. The *S. gigas* specimens from Belize reached their final shell height (of 22.7 and 23.5 cm in distance between the apex and the siphonal notch) at the transition to adulthood in just 2 years. The extremely rapid growth as observed in this species permits detailed, high-resolution reconstructions of life history traits where sub-daily resolutions can be achieved with ease. The potential for future studies has yet to be further explored. Queen conch sclerochronology provides an opportunity to recover extremely high-resolution palaeotemperature records, which could be used to improve numeric climate models, where the shells essentially function as mineralized buoys. The shell recorder may also help to reveal changes in biogeochemical dynamics in benthic ecosystems on intra-seasonal time scales in the fossil record. Furthermore, sclerochronology provides a rapid, effective and highly versatile investigative strategy when compared to time- and cost-consuming fieldwork for improving fisheries management and maricultural pursuits.

## **Generating growth and calcification in freshwater mollusks in closed-system tank ecosystems: a starting point for climatic and ecological proxy calibration**

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In order to test and calibrate climatic and ecological proxy data from bivalve shells it is essential to conduct tank experiments where the environmental parameters are known. Although it is easy to keep bivalves alive, it is currently extremely difficult to generate shell growth *in vitro*. In this study we investigated potential methods for generating shell growth using two bivalve genera, *Anodonta* sp. and *Unio*. sp. We connected three 120 liter tanks to each other using a shared filter system to ensure that conditions were constant in each tank. Specimens were introduced to the tank environment in December 2008, and the bivalves were monitored for a 17-month period. In addition, in an attempt to maintain a stable ecosystem, several plants (*Elodea* sp., *Ceratophyllum* sp.) and gastropods of the genus *Limnea* sp. were also introduced. Water temperatures ranged between 18.5°C in the winter and 26.0°C in the summer, with pH values typically fluctuating around 8.4. After the experimental period was over, some of the shells were removed from the tanks and then prepared using standard sclerochronological techniques. The bivalves showed very little shell growth, whereas the gastropods grew by up to 3 cm in height. Further research is needed in order to optimize the conditions for shell growth in tank experiments and to identify the physical and chemical requirements of the animals.

## Variations in stable isotopic composition of unionid shells from Lake Balaton (Hungary): recent and archaeological studies

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Carbonate samples were taken from *Unio* shells and were measured for stable oxygen and carbon isotope compositions in order to understand how climate conditions are reflected by the isotopic composition of *Unio* shell material from Lake Balaton (Hungary). The physical and oxygen isotope monitoring of the lake water was conducted between 1999 and 2005 and between 2007 and 2009 and data were compared with the stable isotopic composition of *Unio* shell specimens grown in the same period. Using sampling conducted at high-resolution, variations in seasonal fluctuation can be observed. The period studied contain wet and extremely dry periods beyond the normal years and, therefore, the isotopic variation detected in ambient water and shell isotopic profile can be related directly to the amount of precipitation, inflow and evaporation and studied more detailed. According to the recent examinations *Unio* shells are reflect the environmental variations and the processes in the past can be better understand.

The past climate reconstruction based isotopic variation of shell carbonate can be demonstrated through two archaeological study. Within the Late Copper Age subphases covered by the excavation sites in Balatonkeresztúr (southern part of Lake Balaton). Based on stable isotopic composition of shell material from archaeological periods, the period of Boleraz subphase of Baden (5460-5310 cal yr BP) can be characterized with warm/dry climatic condition. Around 5310 cal yr BP (between Boleraz and Early Classical Baden) the climate turns into a variable condition and becomes wet/cold in agreement with archaeological and palynological studies. The positive shift in isotopic compositions of shells from the subphase of Early Classical Baden (5310-5060 cal yr BP) suggests an increasingly arid condition, which is not shown in archaeological studies. This observation may suggest that short term dry to wet changes can influence more the settlement structure and agronomy in this area, than increasing drought. The isotopic composition of bivalve samples from the Bronze Age from Ordacsehi (southern part of Lake Balaton) suggests that the Early Bronze Age (3960 cal BP) can be characterized with stable conditions, while shells measured from the Middle to the Late Bronze Age (3690 cal yr BP) indicate variable, wet climatic conditions.

Our study demonstrates that the stable isotopic composition of bivalve shells can be used as a powerful tool to detect past climate variations.

## **“Neither fish nor fowl?” Significant increase of animal protein in human diet during the Neolithic in Central Germany**

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The most significant historic change in human diet was probably the transition from hunting and gathering to sedentary farming, which started in Central Germany at about 5500 BC. Many studies have focused on this specific Meso-Neolithic change in diet in various geographical areas, but only few took a closer look on the developments within the Neolithic. Acting on the assumption that the adoption of this completely novel lifestyle was a long and laborious path of experimentation phases, rebounds and learning processes, one must expect that husbandry and farming strategies were subjected to a specific development dependent on experience and ecological resources of the Neolithic populations. Even if corn is regarded to be the major basis of Neolithic foodstuff supply, the influence of animal products in human diet should not be underestimated. Our study focuses on the impact of animal protein, whether from meat or dairy products, in human diet during 3500 years of agricultural history. Stable carbon and nitrogen isotope analyses of bone collagen has been carried out on 258 human bone samples from all over Saxony-Anhalt, covering archaeological sites of the early, middle and late Neolithic periods. The results of the  $\delta^{15}\text{N}$  investigation show a significant increase of animal protein in human food consumption, which correlates with a chronological sequence of archaeological cultures. While animal products did not seem to play a major role in human diet in the Early Neolithic, the importance of meat and dairy products increases during the Middle Neolithic and reaches its highest level in populations of the Late Neolithic and Early Bronze Age. These developments may be a result of various factors, e.g., a growing stabilization of the supply of animal products due to sophisticated husbandry practices, a shift of farming focuses as well as climatic factors or sociocultural developments. Our aim is to provide further insight into human food consumption and husbandry strategies and to determine when and for what reasons people started to intensify livestock breeding and dairy farming.



## Incremental patterns in nature: a model of 2D cyclic structure

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Cyclic or periodic textures manifest in nature belong to the class we refer to as incremental patterns, which reflect formation/life history attributes and potentially details about the mechanisms of pattern formation. The present work is concerned with incremental patterns formed in hard tissues. Incremental patterns are layered, the widths of layers being a reflection of growth rate. The significance of such layers for biological research is that changes in their widths reflect internal and external events in the life history of an organism, being a primary source of information about the duration and amplitude of periodic phenomena as well as about other natural history events occurring during formation: Information about cyclicality, interactions between environmental and/or physiological cycles, and perturbations to the responding system are all inherently contained within incremental patterns, providing a means of appreciating aspects of organismal life history or accretion rates in the recent and historical past that could not be examined otherwise.

To formalize incremental patterns a discrete model is described that is based upon the parameterization of incremental pattern structure. Analysis contains two principal steps. First, an incremental pattern is quantified; i.e., a plot of “Growth rate vs. Time” is constructed. The second step is to use this plot to parameterize the incremental pattern. The possibility of developing a unified formal framework for the processing of incremental patterns is based upon features common to most incremental patterns: (a) Incremental patterns have a layered structure; (b) Each layer is developed during one cycle of growth  $\Delta T_i$ , and the width of a layer is the measure of growth rate during  $\Delta T_i$ ; (c) Due to numerous breaks and confluences of layers, incremental patterns are anisotropic; the size and number of layers is a function of the direction in which the measurements are taken. Presently, there is no method for the quantification of incremental patterns that takes anisotropy into account. It follows from “c” that to quantify the growth rate of a 2D incremental pattern, it is necessary to connect events that occur at different time scales. The impact of anisotropy on the accuracy of the quantification of growth rate variability is assessed by a calculation of entropy and an index of structural anisotropy; i.e., the notion of entropy is introduced as a measure of uncertainty in the quantification of growth rate, or the degree to which the model adequately represents the pattern.

The performance of the described method is illustrated on images of fish scales, dental enamel, and incremental primary lamellar bone of iguana, monkey, and human. We visualize striking periodicities in growth rate of all images. Incremental analysis has thus revealed cycles never before observed, which occur at various frequencies.

## **A new method for estimating calcification rate of coral skeletons using a transparent X-ray 2D-imaging scanner (TATSCAN-X1) in conjunction with geochemical analyses**

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Calcification rate of coral skeletons is one of the crucial parameters for estimating climate change such as global warming and ocean acidification related which are both related to CO<sub>2</sub> fluctuations. Annual calcification rate (g cm<sup>-2</sup> year<sup>-1</sup>) is the product of annual extension rate (cm year<sup>-1</sup>) and average annual bulk-density (mainly depending on porosity; g cm<sup>-3</sup>) of coral skeletal growth relating to the global and local climate/ocean changes. We have developed a new analytical method estimating the calcification rate from coral skeletons, which enables rapid and precise analyses of larger coral slabs.

For analyzing the coral calcification rate, it is necessary to develop (1) a non-destructive 2D digital imaging method, (2) appropriate sample preparation methods, and (3) analyses software. We used a newly developed non-destructive transparent X-ray 2D imaging scanner called “TATSCAN-X1” at JAMSTEC (Sakamoto et al. 2008 EGU A09065). It measures a 2D intensity of transparent X-ray through coral samples by using digital imaging intensifier X-ray camera. It is possible to scan the materials up to 1500 mm-long and 150 mm-wide. Spatial resolution of X-Y stage is set up within 0.1 mm. Conventional spatial resolution of digitized X-ray image will be < 50 μm. In order to minimize the errors of coral skeletal density, the coral slab should be cut with thickness errors of ± ca. 50 μm. In addition, we developed a software (“CoreCal”) for 2D-correction X-ray irradiation by 3D X-ray hallow and made the calculation theory of skeletal density precisions estimated from the density precisions of giant clam standards and thickness precisions of it and coral slab samples.

In this study, we will introduce the relationship between coral skeletal growth and seawater physical and chemical properties. The new methods with geochemical analyses applied to massive corals (10 to 15 cm in diameter) of the *Porites* spp. collected from Ishigaki Island, Japan in August 2009. Seven corals were collected 50 m interval from coast with depth transect of between 150 and 400 m (inner reef) and of 700 m (outer reef). For chronology of coral density band, we analyzed stable oxygen isotope of coral skeleton along the coral growth direction using a GV IsoPrime mass spectrometer with an automated carbonate system (IsoPrime Multiprep) at JAMSTEC. As a result, skeletal density varies from 1.41 to 1.84 (g cm<sup>-3</sup>). The precisions of skeletal density were ca. 2.4% (1σ). Our method with geochemical analyses should provide the precise data acquisition of coral calcification rate in the point of that the estimation of the precisions and precise chronology.

## Isotopic approach to assess dissolved Mo and Ba uptake in scallop shells: new insights into the use of Mo/Ca and Ba/Ca ratios as proxies in temperate coastal environments

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The understanding of climate and anthropogenic signals in the global climate change and the disturbances of coastal ecosystems is of principal concern in the scientific community. The investigation of fluctuations on short time-scales requires well-dated climate or environmental archives with a high temporal resolution. The successive calcareous layers of bivalve shells, able to trap and store elements from the surrounding environment, and abiding improvement of microanalytical techniques such as LA-ICP-MS, were shown to provide a reliable tool to investigate the high frequency variability of climate and primary productivity (Vander Putten et al. 2000 *Geochim. Cosmochim. Acta* 64, 997-1011).

Recent investigations using laser ablation on scallop shells (*Comptopallium radula*, *Pecten maximus*) showed that the variability of Mo and Ba concentrations in shells could serve as a potential high-resolution tracer of the phytoplankton dynamics in coastal environments (Thébault et al. 2009 *Limnol. Oceanogr.* 54, 1002-1014; Barats et al. 2010 *Biogeosciences* 7, 233-245). The extent of spring Mo/Ca<sub>shell</sub> enrichments was explained by the net uptake of silicate and nitrate by phytoplankton, suggesting a connection with diatoms' spring-time productivity (Barats et al. 2010 *Biogeosciences* 7, 233-245). However, Barats et al. (2009 *Biogeosciences* 6, 157-170) demonstrated that Ba/Ca<sub>shell</sub> ratio cannot be used directly as a relevant paleoproductivity tracer and that complex processes occur in the pelagic/benthic Ba cycle and are responsible for significant Ba inputs at the sediment-water interface.

Here, we propose a new experimental approach in order to better constrain the processes controlling the Mo and Ba enrichments in scallop shells and to better assess their potential as proxies. The influence of dissolved Mo and Ba on the formation of shell elemental peaks was assessed on juvenile *Pecten maximus* using successive isotopic enrichments of the surrounding water. Experiment took place during May corresponding to shell growth period of the scallops. The uptake and kinetics of <sup>95</sup>Mo, <sup>97</sup>Mo, <sup>135</sup>Ba and <sup>137</sup>Ba were followed during two weeks in scallop soft tissues using ICP-MS and in shells using femtosecond laser ablation coupled to an ICP-MS.

## **Do freshwater gobies move along the river system? Investigations of freshwater habitat use of two Sicydiine species *Sicydium punctatum* (Caribbean) and *Sicyopterus lagocephalus* (Indo-Pacific)**

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Tropical insular river systems are colonised by Sicydiinae, which are amphidromous fish. After hatching in freshwater, free embryos drift downstream towards the sea where larval development occurs. After larval growth, pelagic post-larvae recruit back to rivers where they undergo an extensive metamorphosis; they become benthic and herbivorous. Although more than 110 Sicydiine species exhibit this life pattern, little is known about it. It is, however, essential to understand each step of this cycle for conservation issues as recruiting post-larvae support fisheries, which are declining.

The pelvic suction cup allows Sicydiinae to colonize habitats far upstream in the river system. However, recent studies showed that early-hatched larvae have less than three days to reach the estuary while prolonged exposure to freshwater increases mortality (Bell 2009 Am. Fish. Soc. Symp. 69, 321-341; Valade et al. 2009 Cybium 33, 309-319). Consequently, the closer the spawning grounds are to the river mouth the higher the larval survival rate is. Why do adults colonise elevated habitats if the larval survival rate decreases with the distance from the estuary? Do adult individuals move along the river system?

In order to assess the freshwater habitat use, we investigated otolith elemental fingerprint for two Sicydiinae species: *Sicydium punctatum* from Guadeloupe and *Sicyopterus lagocephalus* from Vanuatu and New Caledonia. Sr/Ca and Ba/Ca ratios in otoliths are known to be potential tracers of freshwater and marine habitats. Elemental variations were analysed using femtosecond laser ablation coupled with an ICP-MS. All specimens of both species showed evidence of a marine larval stage, confirming amphidromy. Based on Sr/Ca ratios, adult migratory behaviour was observed for *S. lagocephalus* with movements between freshwater and brackish habitats but not for *S. punctatum*. However, significant peaks of Ba/Ca ratios in some *S. punctatum* individuals do indicate a change in environmental conditions within the freshwater system. Based on these results, several hypotheses about the change in environmental conditions during both *Sicyopterus* and *Sicydium* adult life are discussed: reproductive migrations, search of territory, flooding events etc. The consequences of these observations in terms of species management and conservation are also discussed. In addition, this work shows the importance of conjointly using several environmental elemental markers to study migratory behaviour.

## **Proteomic and mRNA expression analyses in the teleost fish otolith and scale suggest organic control of rhythmic growth and biomineralization**

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Two important age determinants of teleost fishes, the otolith and scale, are the biominerals that contain calcium carbonate (aragonite) and calcium phosphate (hydroxyapatite) crystals, respectively. Here, we review our recent data of proteomic analyses of organic matrices and mRNA expression analyses of selected matrix proteins in these tissues.

**Otolith.** Using MS/MS analysis, N-terminal sequencing and immunoscreening of a cDNA library, we have identified 17 proteins in the otolith matrix and endolymph (the mother solution of otolith crystallization) of the rainbow trout. The otolith matrix mainly contained a putative framework molecule, otolin-1, and some calcium-binding proteins such as OMP-1 and OMM-64. The endolymph contained no detectable otolith matrix proteins. These data suggest that otolith matrix molecules, which are produced by inner ear epithelial cells and secreted into the endolymph, deposit onto the otolith quickly and selectively. In the in-vitro crystallization system, the aggregate complex that included otolin-1 and OMM-64 induced the aragonite crystals. Moreover, expression of otolin-1 mRNA had apparent diel variations with high levels at night. Taken these data together with previous reports, we present here a hypothesis that diel variations in otolin-1 production lead to diel deposition of aggregate complex that includes OMM-64 and other matrix proteins, which regulates diel deposition of aragonite crystals. Such rhythmic growth may finally result in formation of daily growth increments.

**Scale.** Using MS/MS analysis, we have identified 5 putative mineralization-related proteins from goldfish scales. The apolipoprotein A-I (Apo A-I) is one of the candidate proteins that induce mineralization of the scale. The protein constructed high density lipoprotein (HDL) in the scale. The scale HDL was more acidic than that in the blood, had an ability of self-aggregation, and interacted with calcium phosphate crystals. The Apo A-I mRNA was expressed not in the scale cells, but in the hepatocytes. Therefore, the HDL was suggested to be produced in the liver, introduced to the scale through the blood, changed its charge more acidic, and might regulate the growth of apatite crystals.

## Temperature and pH proxies in cultured scleractinian corals

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Corals are well-established proxy recorders for climate reconstructions. They have been applied successfully in many studies, in spite of their strong vital effects with respect to stable isotopes and trace element incorporation. The impact of temperature on several proxies has been studied extensively, whereas the effect of pH and concomitant variations in biogenic calcification has been examined to a lesser extent. To investigate the effect of both environmental parameters, a branching scleractinian coral of the genus *Pocillopora* sp. was grown under controlled laboratory conditions in natural seawater at (1) a temperature range from 22 to 28°C at constant pH; and (2) a pH range from 7.8 to 8.3 at constant temperature.

The temperature exerts a weak control on  $\delta^{18}\text{O}$  in *Pocillopora* sp. with  $-0.14\text{‰}/^\circ\text{C}$ , which is in good agreement with sensitivity of  $-0.13\text{‰}/^\circ\text{C}$  determined for *Pavona clavus* (Wellington et al. 1996 Paleceanog. 11, 467-480). The temperature response of Sr/Ca in *Pocillopora* sp. is significant ( $-0.07\text{ mmol/mol}/^\circ\text{C}$ ) and compares well with the range of observed sensitivities of coral Sr/Ca ( $-0.03$  to  $-0.09$ , Reynaud et al. 2007 GCA 71, 354-362) and inorganic aragonite ( $-0.045$ , Dietzel et al. 2004 Chem. Geol. 203, 139-151). Although absolute values of Mg/Ca differ, the slope of  $+0.15\text{ mmol/mol}/^\circ\text{C}$  agrees with the one determined in *Porites lutea* ( $+0.13$ , Mitsuguchi et al. 1996 Science 274, 961-963) and *Acropora* sp. ( $+0.14$ , Reynaud et al. 2007 GCA 71, 354-362).

The pH shows a clear control on  $\delta^{11}\text{B}$  in *Pocillopora* sp.  $\delta^{11}\text{B}$  systematically increases with pH by about  $+10\text{‰}/\text{pH-unit}$ . Data comply with isotopic signatures of other branching corals of *Acropora* sp. (Hönisch et al. 2004 GCA 68, 3675-3685). However, they are still systematically enriched in  $^{11}\text{B}$  relative to the empirical value for aqueous  $\text{B}(\text{OH})_4^-$  (Klochko et al. 2006 EPSL 248, 261-270).  $\delta^{18}\text{O}$  also demonstrates a weak response to pH with  $-0.7\text{‰}/\text{pH-unit}$ . Spero et al. (1997 Nature 390, 497-500) observed a similar trend demonstrating that foraminiferal oxygen isotopes inversely correlate with seawater carbonate concentrations. Unlike responses of stable isotopes, Sr/Ca is not affected by pH. This appears to be in contrast to findings in *Favia fragum* recruits by Cohen et al. (2009 Geochem. Geophys. Geosys. 10, Q07005, 12p.), showing that Sr/Ca increases at low pH. The pH also exerts a control on Mg/Ca in *Pocillopora* sp., with  $0.52\text{ mmol/mol}/\text{pH-unit}$ . A similar trend was found in *Favia fragum* (Cohen et al. 2009 Geochem. Geophys. Geosys. 10, Q07005, 12p).

## Polar coralline red algae as potential environmental recorder

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During the past decades, the investigation of cool-water carbonate factories has gained momentum within carbonate geology. The least known cool-water carbonate factories are those of the polar regions. Prominent primary producers in marine carbonate factories are coralline red algae, which secrete cell wall compartments of cryptocrystalline Mg-calcites. Almost all coralline algae start to grow from settled spores on a hard substrate to form a crust. They add cell filaments laterally and subsequently on top of existing ones. With time, several centimetres thick crusts with a layered arrangement of calcified filaments may result. Additionally, many species form branches with an ultrastructural composition showing distinct banding patterns, which differ in filament and cell wall thickness and Mg content. Examination of these potentially annual bands may be applicable to detect environmental variables such as variations and trends in temperature fluctuations and possibly changes in the nutritional regime.

In 2006, the northernmost coralline algal grounds were discovered at 80°30'N off Nordaustlandet (Svalbard) during RV Merian cruise MSM2/3. This site and several others around Svalbard were thoroughly documented and sampled with the manned submarine Jago (IFM Geomar, Kiel). Additional data concerning the physical environment were achieved by multibeam mapping surveys, CTD- and light-measurements. The video footage obtained during the Jago-dives was complemented by using a photographic probe (Photosea 70D) to achieve high-resolution still images of the seabed.

These recent findings show that polar coralline algae are much more widespread than previously thought, thus representing a unique polar carbonate factory. The value of these coralline algae to reconstruct historic environmental changes will be evaluated using radiometric dating, geochemical methods and a sclerochronological approach. The coralline algal grounds off Svalbard will be compared with those sampled off northern Norway (Freiwald and Henrich 1994 Sedimentol. 41, 963-984), still beyond the Polar Circle. This comparison may help to elucidate the influence of poleward increasing seasonality on calcifying organisms. The ultrastructure of skeletal banding patterns will be assessed with SEM and transmitted light microscopy, which together with a photographic documentation will serve for a statistical examination of the banding patterns. The non-destructive element mapping for quantification and detection of shifts and sites of calcite and major trace elements such as Mg will be carried out using electron microprobe and laser ablation. Individual growth increments will be microdrilled to collect samples for stable isotopes ( $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$ ) and for  $^{14}\text{C}$  dating methods. This study may provide hard data to the debate on the ongoing environmental change in the Arctic.

## **Barium and molybdenum records in shells of *Comptopallium radula* (Bivalvia; Pectinidae): high-resolution proxies for phytoplankton dynamics in the coral reef lagoon of New Caledonia**

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Ba/Ca and Mo/Ca ratios were investigated in shells of the tropical scallop *Comptopallium radula*. Three juvenile specimens were harvested alive in the southwest lagoon of New Caledonia (southwest Pacific Ocean) after a 1-year weekly hydrological survey. Calcite samples representing a few hours of biomineralization were laser-ablated along the maximal growth axis and analyzed for Ba/Ca and Mo/Ca ratios using an ICP-MS. Absolute dates of shell precipitation assigned on the basis of periodic formation of shell growth patterns led to the accurate reconstruction of ontogenetic variations of elemental ratios with subweekly resolution.

Inter-individual variability of Ba/Ca and Mo/Ca time series was low, indicating an environmental control on the incorporation of these elements within shells. Both profiles were characterized by a background level punctuated by sharp peaks. The ingestion of diatoms enriched in Ba (adsorbed on iron oxyhydroxides associated with the frustules) is the most likely cause of the formation of Ba/Ca peaks in this bivalve species. Some contribution of diatom-associated barite crystals is also possible. In every instance, Ba/Ca would possibly be a proxy for the timing and magnitude of diatom blooms in New Caledonia. Among all the theories that could be advanced to explain the occurrence of Mo/Ca peaks, the most plausible ones appear to be (1) the ingestion of phytoplankton cells grown upon nitrate and therefore containing high levels of Mo required for the activity of nitrate reductase, and (2) the release of Mo out of the sediment during the development of anoxic conditions at the sediment-water interface. If so, then Mo/Ca could be a new proxy either (1) for nitrate uptake by phytoplankton in coastal ecosystems, which would contribute to our understanding of the historical balance between new and regenerated production, or (2) for hypoxia/anoxia events at SWI.

We conclude with confirmation that Ba/Ca is an interesting tool, albeit still poorly understood, for describing historical phytoplankton dynamics in New Caledonia, and the introduction of Mo/Ca as a promising addition to the arsenal of proxies. Further work, such as experiments under semi-controlled conditions, is necessary to confirm these two elements as proxies.



## **A novel approach for the determination of growth increments of *Arctica islandica***

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The outer border of transects along the line of strongest growth of *Arctica islandica* can be well described by a logarithmic spiral with its origin in the vicinity of the ligament. A logarithmic spiral is usually given in polar coordinates as  $R = A \cdot \exp [B \cdot \varphi(t)]$  (1) where R is the distance from the origin of the spiral, A is the amplitude, B is a constant and  $\varphi(t)$  is the time-dependent growth angle function. Fitting this spiral to several transects of *A. islandica* reveals – at least for specimens found near the island of Helgoland, Germany – a nearly constant factor B in (1). The growth angle function  $\varphi(t)$  itself can be approximated in a good way by an exponential decay function with obvious deviations which may be assigned to several factors to be discussed.

Two practical aspects of this method should be mentioned here. Firstly, discontinuities in the growth angle plot (i.e.,  $\varphi$  vs. index of stria) may indicate unresolved stria which in turn may be discovered by closer investigation of the region theoretically expected. Secondly, for one bivalve the line of growth in the umbo region is described by (1) with the same parameter set except the amplitude A. Finding the umbo amplitude  $A_u$  is easily accomplished by drawing chords from the origin of the spiral to at least two consecutive stria in the mantle. Then  $A_u$  is varied until two consecutive striae in the umbo region strike the intersection points of chords with the spiral function. In this manner, measurements from the umbo are uniquely mapped to those from the mantle.

## High-frequency oscillations in annual shell growth of bivalves: physiological rather than climatic control?

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Variations of annual shell growth can provide valuable information about past climates. To generate such information, growth increment widths are typically measured in the outer shell layer near to the outer shell surface (OSS), i.e., along the axis of height, or in the hinge plate (HP). However, it remains untested whether the relative increase in shell height and the growth of the hinge plate are actually similar. In this study, annual increment width chronologies (OSS and HP) of five *Arctica islandica* specimens, collected alive from offshore Iceland, were compared with each other. Measurements were generated using digitized images of cross-sections immersed in Mutvei's solution. Inherent age-trends were removed from the time-series and the data standardized (SGI values). Despite a highly significant linear correlation ( $R = 0.58-0.75$ ;  $p < 0.0001$ ), the two records from each specimen were not exactly the same. On the contrary, residual chronologies computed from the OSS and HP records ( $\Delta$ SGI) showed significant (tested by white noise spectra) periodic fluctuations on time-scales of two to three years. Furthermore, continuous wavelet spectra of the  $\Delta$ SGI chronologies demonstrated that the spectral densities do not occur contemporaneously among the five specimens. These findings strongly suggest that growth in shell height (= shell size) and the hinge plate alternates periodically. In addition, these variations do not seem to be controlled by external forcings, but by the individual physiological state. It is hypothesized that functional morphological demands or biomechanical needs control these variations in shell growth rather than climate. In conclusion, high-frequency periodic oscillations in annual increment width chronologies obtained from bivalve shells should be interpreted with great care in the future.

## Longevity and growth rates of *Desmophyllum dianthus* in the Marmara Sea and its potential as high-resolution geochemical deep-sea archive

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Living framework building cold-water corals have been observed at ambient temperatures of ca. 13.9°C in the Ionian Sea, the Adriatic Sea, the Aegean Sea, as well as late Holocene solitary corals in the Eastern Mediterranean. These foreshadowed the discovery of living cold-water corals in 2007 in the Marmara Sea, where during submersible-dives (Le Nautile / RV Atalante / MARNAUT-expedition) large and abundant occurrences of the solitary deep-sea coral *Desmophyllum dianthus* were filmed and sampled along steep cliffs. These recently dead corals have been documented at depths of ca. 900 to 1200 m, where temperatures of ca. 14.5°C and fairly low dissolved oxygen concentrations of < 1.27 ml/l prevail. Framework building cold-water corals like *Lophelia pertusa* and *Madrepora oculata* have not been observed in this low-oxygen environment. The individual solitary coral cones reach 15 cm in height with a calyx diameter of 7 cm. Their size rivals that of their recent Atlantic cousins in the Northwest Atlantic (e.g., New England Seamounts), while most Recent *D. dianthus* in the Western and Eastern Mediterranean comprise much smaller corallites.

The age and growth rate of a 10 cm high *D. dianthus* specimen has been constrained by six U-series ages along the growth axis. The base of the coral dates back to ca. 100 years, while the subsequently younger ages are evenly spaced, approaching present-day (ca. 25 years). The calculated growth rate of ca. 1 mm/yr resembles those obtained from North Atlantic corals, varying between 0.5 and 2.0 mm/yr. This quick growth rate allows us to test these corals as a potential high-resolution archive (sub-annual) for a wide variety of environmental and geochemical parameters. We are using these age constraints to track changes through time. Using the 'lines technique', that is, applying a function of the linear regression of  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  values of the skeletal aragonite, temperature reconstructions at six characteristic time slices across the last century are being attempted. Radiocarbon is being measured along the growth axes, to reveal past seawater concentrations of  $\Delta^{14}\text{C}$  and the pattern of change of the anthropogenic bomb-spike. Likewise, boron isotopes ( $\delta^{11}\text{B}$ ), at known age intervals from the U-series based growth rate model, has been measured to track changes of pH. In addition, neodymium ( $^{143}\text{Nd}/^{144}\text{Nd}$ ) and strontium ( $^{87}\text{Sr}/^{86}\text{Sr}$ ) isotopes are being measured to track any changes in the Marmara watermasses.

## **A molluscan perspective on hydrological cycle dynamics in northwestern Europe**

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We present the application of unionid freshwater mussel  $\delta^{18}\text{O}$  values as a proxy for past river conditions in the Rhine and Meuse (The Netherlands). We used a set of nine shells from selected climatic intervals during the late Holocene. One Meuse river shell lived during the Subboreal and its  $\delta^{18}\text{O}_{\text{ar}}$  values are similar to modern values. The Rhine specimens represent the Subboreal, the Roman Warm Period and the Medieval Warm Period. These shells also show averages and ranges of aragonite  $\delta^{18}\text{O}$  values similar to modern specimens. This indicates that environmental conditions such as Rhine river dynamics, Alpine meltwater input and drought severity during these climatic intervals were similar to those of the 20<sup>th</sup> century. Subtle centennial to millennial climatic variations during the late Holocene cannot be discerned in these shells. This is due to their relatively short lifespan and the large inter-annual and intra-seasonal variation in environmental conditions. However, these shells appear suitable for studying seasonal to decadal scale climate variability. The two shells with the longest lifespan appear to show decadal scale variability in reconstructed water  $\delta^{18}\text{O}$  values during the Medieval Warm Period, possibly forced by the North Atlantic Oscillation, which is the dominant mode of variability influencing precipitation regimes over Western Europe.

## Small metabolic carbon contribution to shell carbonates of cultured freshwater pearl mussel *Hyriopsis* sp.

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The stable carbon isotope ratios of dissolved inorganic carbon (DIC) can reveal carbon dynamics in terrestrial water systems. Many researchers have analyzed stable carbon isotope ratios of freshwater bivalve shells in order to evaluate their potential as a proxy of stable carbon isotope values of DIC ( $\delta^{13}\text{C}_{\text{DIC}}$ ). The two major sources of inorganic carbon of bivalve shells are DIC of the ambient water and metabolic carbon derived from consumed organic matter (e.g., McConaughy et al. 1997 *Geochim. Cosmochim. Acta* 61, 611-622). The amount of metabolic carbon is typically less than 10% in bivalve carbonates, while the contribution of each carbon source changes with ontogeny (Lorrain et al. 2004 *Geochim. Cosmochim. Acta* 68, 3509-3519; Gillikin et al. 2009 *J. Geophys. Res.* 114, G01007).

We present stable carbon isotope ratios of shells of the commercially cultured freshwater pearl mussel, *Hyriopsis* sp., (Unionidae) and  $\delta^{13}\text{C}_{\text{DIC}}$  values of ambient water from Lake Kasumigaura, Japan. Three  $\delta^{13}\text{C}$  profiles of the outer shell layer ( $\delta^{13}\text{C}_{\text{SHELL}}$ ) along the axis of maximum shell growth were correlated with each other using shell  $\delta^{18}\text{O}$  values. The numbers of  $\delta^{18}\text{O}$  cycles in the outer shell layer was five or six. This is consistent with the age indicated by the pearl culture records. The  $\delta^{13}\text{C}_{\text{SHELL}}$  values varied mainly from ca. -12 ‰ to ca. -9 ‰, and, unlike the water temperature profile, its pattern was not symmetric and sinusoidal. Amplitudes of each isotope cycle exhibited neither a clear annual periodicity nor an ontogenic trend. All water samples were collected between February 2008 and September 2009 near the aquaculture facilities. The concentration of carbon and the  $\delta^{13}\text{C}_{\text{DIC}}$  values varied greatly from 2.5 mM and -8 ‰ in winter to 1.5 mM and -13.6 ‰ in summer.

Taking the  $\delta^{13}\text{C}$  values of organic materials in Lake Kasumigaura into account and the typical amount of metabolic carbon incorporation of ca. 10%, the metabolic carbon likely causes a > -2.5‰ decrease in  $\delta^{13}\text{C}_{\text{SHELL}}$  values. However  $\delta^{13}\text{C}_{\text{SHELL}}$  values compare well to the  $\delta^{13}\text{C}_{\text{DIC}}$  values of the surrounding water during the growth period of the shells. The contributions of metabolic carbon to  $\delta^{13}\text{C}_{\text{SHELL}}$  values are assumed to be minor in this specimen. The absence of secular  $\delta^{13}\text{C}$  trends with increasing ontogenetic age suggests that the contributions of body size to  $\delta^{13}\text{C}_{\text{SHELL}}$  values are also minor. Despite missing data of temperature dependence on carbon isotope fractionation, large  $\delta^{13}\text{C}$  fluctuations of ambient water suggest that  $\delta^{13}\text{C}_{\text{SHELL}}$  values may serve as a proxy of past freshwater DIC dynamics.

## Controls of ontogenetic age and growth rate on trace elements in marine aragonitic bivalve shells: implications for the development of trace elemental proxies

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Trace element concentrations of bivalve shells contain a wealth of environmental and climatic information of the past (special issues by Schöne and Surge 2005, *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, Gröcke and Gillikin 2008 *Geo-Mar. Lett.*, Oschman 2009 *Int. J. Earth Sci.*). However, after more than half a century of study, most of the trace elemental variations are still not well understood, largely because of lacking data on the specific biological controls on the trace elemental distributions in the shells.

The present study aims to identify the mechanisms of two major biological factors (ontogenetic age and growth rate) controlling the trace elemental incorporation into bivalve shells. 21 trace elements in shells of the long-lived bivalve mollusk, *Arctica islandica*, were studied over the entire lifespan of the shells, and their relations with age and growth rate were explored. Results showed that the 21 trace elements fall into four categories further subdivided by ontogenetic age and growth rate. Through ontogeny and with decreasing growth rate, the concentrations of elements B, Mg, Ga, Sr, Ba, Pb and U (“B group”) increase, while concentrations of elements of the “Li group” (Li, Na, Mn, Cu and Sn) decrease. V, Cr, Co, Ni, and Rb (“V group”) remain nearly unchanged. The concentration of the elements Si, P, Fe and Zn (“Si group”) vary inconsistently from specimen to specimen, showing no common trends. In addition, six elements (B, Na, Mg, Mn, Sr, and Ba) are significantly correlated (exponential functions) with ontogenetic age and shell growth rates (logarithmic equations). The effects of ontogenetic age and growth rate on bivalve shell elemental concentrations and a potential means to extract environmental and climatic information from these trace elements are discussed.

## Seasonal to decadal climate variability during the Late Oligocene ('Kasseler Meeressand' unit, Germany)

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The Oligocene was the last time in the Earth's history when a unipolar glaciation was followed by a significant reduction in polar ice-sheets as a consequence of increasing temperatures. In order to investigate the climate variability during the Late Oligocene, variations in shell growth, together with oxygen isotope and Sr/Ca ratios of the long-lived bivalve mollusks *Arctica islandica rotundata* and *Glycymeris obovata* were measured. The bivalves were collected from the 'Kasseler Meeressand' unit in the lower part of the Kassel Formation (Chattian Stage) in Kassel, Germany. At this time, the ancient North Sea was connected to the Tethys in the south by the Central European Epicontinental Seaway (CEES). The shallow water sediments of the Kassel Basin yielded a well-preserved bivalve mollusk fauna, dominated by *G. obovata*. The specimens were mostly unaltered by diagenesis (based on X-ray diffraction and cathodoluminescence). Sclerochronological studies of the growth patterns and the oxygen isotope ratios clearly exhibited annual cycles with distinct seasonal oscillations confirming periodic formation of the shell material. Several specimens of *G. obovata* reached ontogenetic ages of more than 100 years and as such, they can open century-long windows into the climatic past. The  $\delta^{18}\text{O}_{\text{aragonite}}$  values range from 1.36‰ during the winter to -1.14‰ in the summer and furthermore are positively correlated with Sr/Ca ratios. Major growth lines, i.e., periods of slow growth, occurred between the most negative and most positive  $\delta^{18}\text{O}_{\text{shell}}$  values. The bivalve shells investigated here provide highly resolved data on seasonal to decadal climate. These fossils may therefore serve as an unique ancient analogue for predicted climate shifts in Central Europe because future climatic conditions will likely be characterized by the loss of polar ice-sheets in the Northern Hemisphere.





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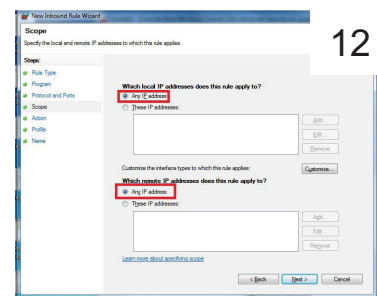
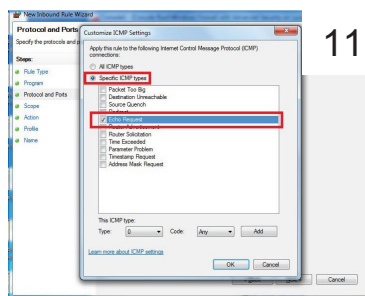
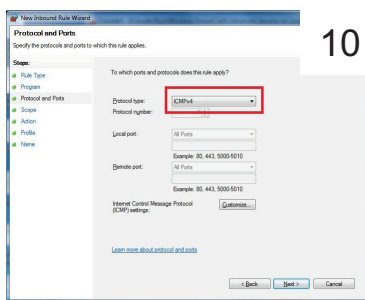
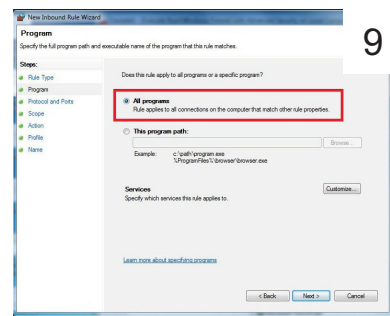
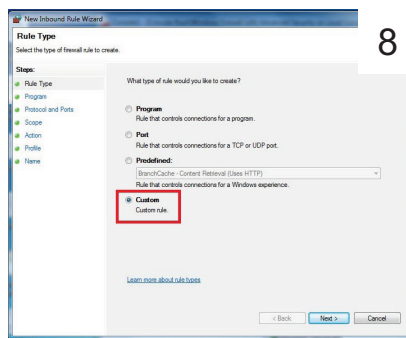
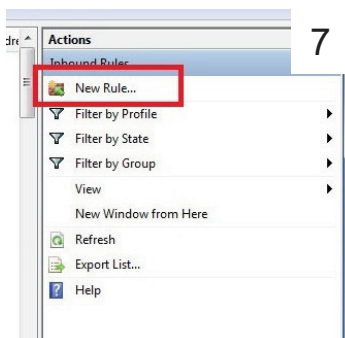
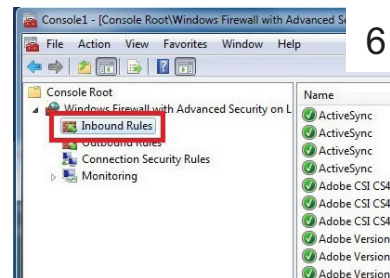
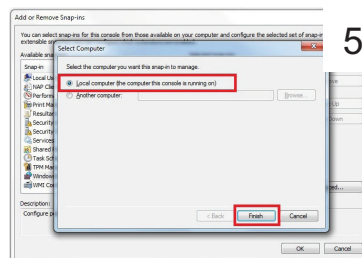
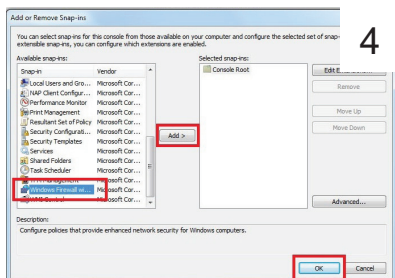
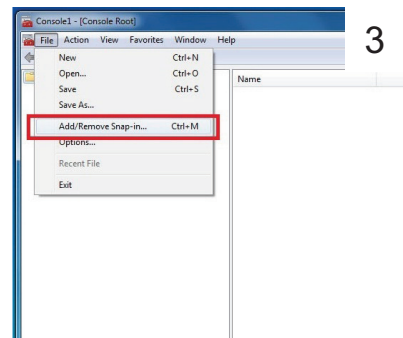
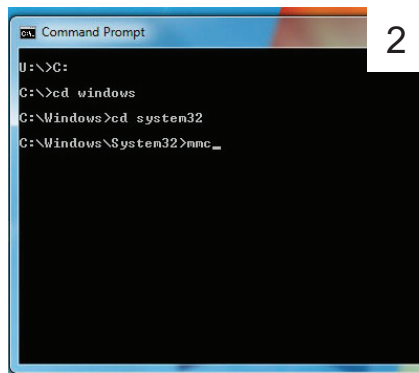
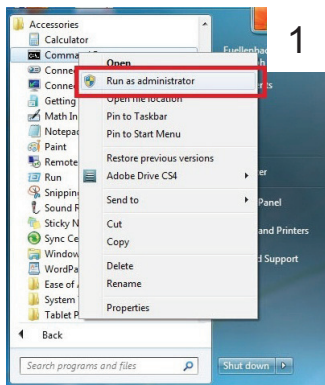
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# WLAN access: Firewall configuration for Windows Vista / 7

- (1) Start: right-click on "Command Prompt", select "Run as administrator"
- (2) Command Prompt opens... at C:\ type "mmc" [without quotation marks] and hit Return
- (3) Hit "Add/Remove Snap-in" – (4) Select "Windows Firewall" and hit "Add >", then "OK"
- (5) Choose "Local computer" and hit "Finish"
- (6) Click "Windows Firewall" and choose "Inbound Rules"
- (7) Choose "New Rule" in selection menu – (8) Select "Custom", "Next"
- (9) Check "All programs", "Next" – (10) Select protocol type "ICMPv4", "Next"
- (11) Specify ICMP types: tick "Echo Request", "OK"
- (12) Select "Any IP\_address" for local AND remote IP addresses, "Next"



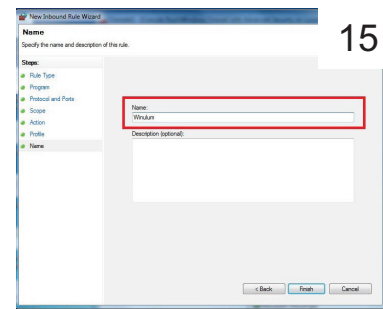
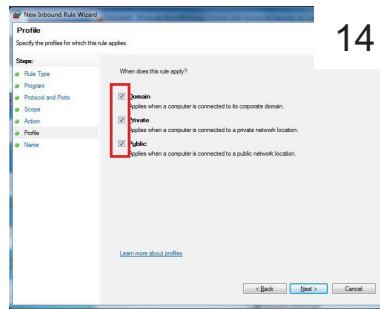
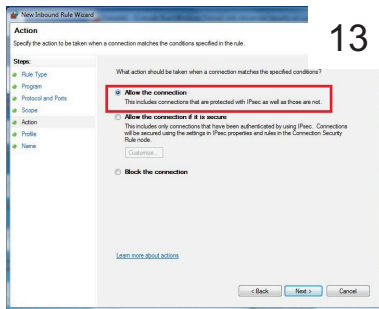
## WLAN access: Firewall configuration for Windows Vista / 7 cont'd

(13) Tick "Allow the connection", "Next"

(14) Select "Domain", "Private" and "Public", "Next"

(15) Type "Winulum" for name, "Finish"

... Once completed, please do the same for the "Outbound Rules" (start all over at 6).

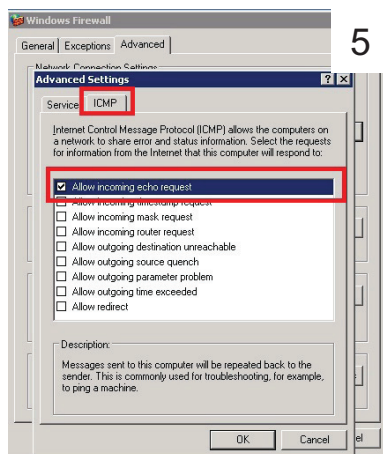
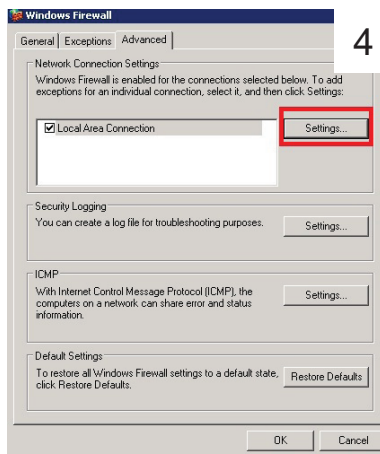
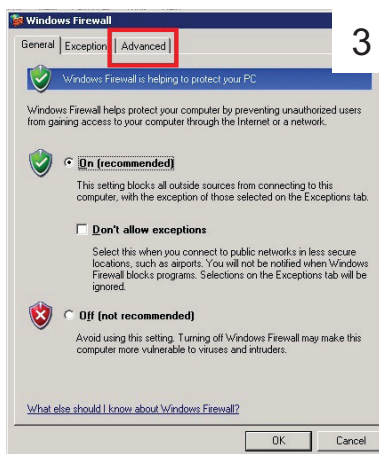
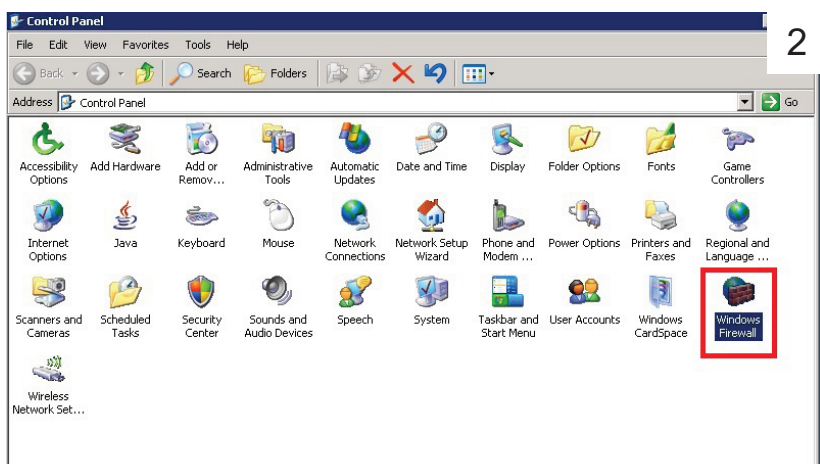
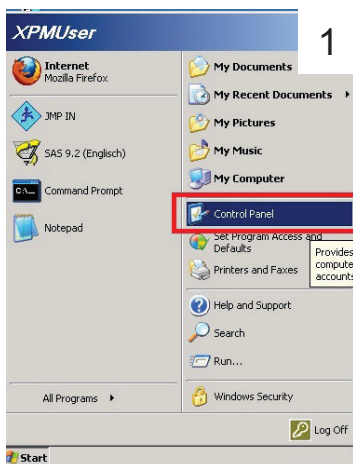


## WLAN access: Firewall configuration for Windows XP SP3

(1) Start - Control Panel – (2) Windows Firewall – (3) Advanced Features...

(4) Open "Settings" for "Local Area Connection"

(5) ICMP: check box "Allow incoming echo request" - OK



Notes

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Supplement: Wednesday 28<sup>th</sup> July 2010, 10:30, oral presentation (substitutes Smith et al.)

## **A Chilean bivalve as potential recorder of environmental changes: Sclerochronological and geochemical calibration of *Eurhomalea rufa***

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Along the south-eastern pacific coasts, the major cause of climate variability is the El Niño phenomenon (EN) that occurs every few years. During a few months, positive SST anomalies, reaching several degrees, severely affect the near shore ecosystems. Largely widespread on these coasts, molluscs, the shell of which records environment at a high resolution, are favourable archives to measure such environmental variability.

*Eurhomalea rufa* is a Veneridae living in meso or infra-littoral sandy bottoms along the South-eastern Pacific coasts, at a depth of less than 10 cm below the sediment surface. Even though little is known about the biology of this burrowing species, in particular about its growth modalities, *E. rufa* shell might provide a potential pluri-annual recorder of environmental parameters. A sclerochronological and geochemical study has thus been conducted on the shell of this species to access both its growth increment parameters and its ability to record the surrounding environment. A living specimen of *E. rufa* has been sampled at the end of December 2005 at Hornitos, a fine sandy beach located north of the Mejillones peninsula (Antofagasta, Northern Chile). Sea-surface temperature (SST) was recorded at Antofagasta harbor by the Cendhoc (Centro Nacional de Datos Oceanográficos de Chile) at an hourly resolution.

The sclerochronological work, performed on both the external layer and the umbo region of the shell, indicates that the daily growth rhythm is linked to the tidal range periodicity; semi-diurnal with diurnal inequalities at the studied location. From this temporal framework, we inferred an age of about 30 month for our 64 mm-long specimen. The mean daily growth, for a period of 15 months, is 42+/-22  $\mu\text{m}$ . Oxygen isotope variations were measured on the same growth period at a biweekly resolution. Those shell parameters have been then compared to SST data. Shell growth and  $\delta^{18}\text{O}_{\text{shell}}$  are significantly correlated to daily SST with  $R^2= 0.63 / P<0.001$  and  $R^2= 0.25 / P< 0.05$  respectively. The low SST vs.  $\delta^{18}\text{O}_{\text{shell}}$  correlation could be due to high daily SST variations during the warm season. This SST heterogeneity might disturb the quality of the chemical signal because the mollusc is submitted to a wide range of punctual temperature extrema. *Eurhomalea rufa* increments, used as a direct recorder of SST, open thus promising perspectives for paleo-thermometry reconstructions. Study supported by the EU-project CENSOR (Climate variability and El Nino Southern Oscillation: Impacts for natural resources and management, contract 511071) and PALEOTROPIQUE-IRD (now PALEOPROXUS, IPSL/LOCEAN).