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WiscSIMS Workshop - High Resolution Proxies of Paleoclimate Madison Wisconsin June 23-26, 2013

Sun. June 23, 2013

4:00-6:00 PM Open House at WiscSIMS Lab (Weeks Hall, 1215 W. Dayton St.) Upload talks and set-up posters

6:00-9:00 PM Welcoming reception in Weeks Hall Courtyard & WiscSIMS Open House

Mon. June 24 Room A140, Weeks Hall

8:00-9:00AM Continental Breakfast, Upload talks and set-up posters

9:00-9:30	John Valley Welcome and Intro		
9:30-10:30	Noriko Kita (Tutorial): SIMS Basics		
10:30	Reinhard Kozdon (WiscSIMS- Live): watch an analysis- δ^{18} O		
10:45	Break		
11:00-noon	John Valley (Tutorial): Accuracy vs. Precision		

- noon Lunch & group picture
- 1:30-1:45 **Matthew Huber, James Zachos & Reinhard Kozdon** (WiscSIMS- Live): Cenozoic Forams, first data
- 1:45-2:15 Howard Spero (Keynote), Lael Vetter, Claudia Mora, Reinhard Kozdon and John Valley "Resolving Micron Scale δ^{18} O and δ^{13} C Heterogeneity in Cultured Planktic Foraminifera"
- 2:15-2:45 **James Zachos (Keynote):** "Seasonal variability in sea surface temperature, salinity, and carbonate chemistry during Greenhouse Extremes"
- 2:45-3:00 Break
- 3:00 Wolfgang Müller, David Evans, Damiano Della Lunga "UV-LA-(MC-)ICPMS – Principles and Applications to Ice Cores and Foraminifera"
- 3:20 **Reinhard Kozdon**, Clay Kelly, John Valley, Seafloor Diagenesis Attenuates the Carbon Isotope Excursion Marking the PETM
- 3:40 **Ben Linzmeier**, Kozdon, R., Peters, S.E., and Valley, J.W., "Sub-daily depth migration behavior in *Nautilus macromphalus* revealed by δ^{18} O variation in shell measured by ion microprobe"
- 4:00-4:15 **Jan Orland**, **Hai Cheng**, & **Kouki Kitajima** (WiscSIMS- Live): Chinese Speleothem, Asian Monsoon, first data
- 4:15-6:00 **Posters**

POSTERS

- **Richard Casteel** and Jay Banner, "Evaluation of oxygen isotopes of a speleothem as a high resolution temperature proxy"
- Ashley Burkett, Anthony Rathburn, Elena Pérez, Jonathan Martin, Lisa Levin, "The stable isotopic composition of *Cibicidoides wuellerstorfi* (elevated epibenthic foraminifera) from methane seeps in the Pacific"
- Mellissa Cross, David McGee, Wallace Broecker, Jay Quade, and R. Lawrence Edwards, "Developing a high-resolution speleothem record of Great Basin climate and hydrological change for times that correlate with Marine Oxygen Isotope Stages 5 to 7."
- **Reinhard Kozdon,** Ian Orland, John Valley, "Preparation of Carbonates for SIMS: Sample selection, mount preparation, imaging, and pre-selection of suitable domains for analysis"
- Ishfaq Ahmad Mir, "Comparison of late Quaternary productivity variation in two contrasting basins of northern Indian Ocean using geochemical proxies."
- D. Nakashima, N. T. Kita, and T. Ushikubo, "Techniques for ion microprobe analyses of tiny particles: Sample mounts using indium and combination of FIB marking and ¹⁶O⁻ ion imaging"
- **Ian Orland**, Yuval Bursytn, Miryam Bar-Matthews, Reinhard Kozdon, Avner Ayalon, Alan Matthews, John W. Valley, "A high-resolution geochemical record of seasonal climate in a modern Soreq Cave speleothem"
- **Jody Wycech**, D. Clay Kelly, Reinhard Kozdon, "*In Situ* Measurement of Intra-Shell δ^{18} O and Mg/Ca Variability in the Planktic Foraminifer *Globigerinoides sacculifer*. A Case Study from the Pliocene Warm Period"
- Jay Zambito and Kathy Benison, "Extremely high temperatures and paleoclimate trends recorded in Permian ephemeral lake halite"

Tue. June 25

8:30 AM Continental Breakfast

- 9:00- 9:15 **Matthew Huber, James Zachos** and **Reinhard Kozdon**: "What did we learn about Cenozoic forams yesterday?"
- 9:15-9:30 **Ian Orland, Hai Cheng** and **Kouki Kitajima**: "What did we learn about the Asian Monsoon yesterday?"
- 9:30-10:30 Ian Orland (tutorial): "Approaches to Speleothem analysis"

10:30 Break

- 10:45-11:15 **Jay Banner (Keynote)** and Nathan Miller: "Integrating Speleothem Proxies from Temperate Regions: Prospects from Monitoring and Imaging Studies"
- 11:15-11:45 **M. Bar-Matthews (Keynote),** A. Ayalon, Y. Burstyn, I, Orland, A. Matthews, J. Valley: "Significance of High Resolution Proxies in Speleothems for Terrestrial Climate Reconstruction"
- 11:45-12:05 **Julie Retrum**, L. González, R. Edwards, S. Tincher, H. Cheng, F. Urbani: "A Holocene Stalagmite Paleoclimate Record from Northern Venezuela: A Record of Caribbean Climate Change"

12:05 Lunch

- 1:05-1:25 **Jessica Oster**, Katharine Maher, Kouki Kitajima[,] John Valley and Bruce Rogers: "Holocene changes in moisture source and aridity in coastal California recorded by δ^{18} O and U isotopes of opal speleothems"
- 1:25-1:45 **Sarah Truebe**, Julia Cole, Toby Ault, Ali Kimbrough, Gideon Henderson, Stephan Hlohowskyj: "Heterogeneity in speleothem records of North American monsoon rainfall"
- 1:45-2:05 **Birgit Plessen**, Brigitte Richert, Sebastian Breitenbach: "Trace element analysis of speleothems using micro-XRF scanning"
- 2:05-2:25 **D. Keenan-Jones**, A. Foubert, G. Fried, M. Sivaguru, D. Motta, M. Garcia, R. Shosted, M. Perillo, J. Waldsmith, H. Wang and B. Fouke: "High-Resolution Records of Ancient Rainfall, Turbulent Open Channel Flow and Microbial Communities from Travertine Deposits in Roman Aqueducts"
- 2:25-2:45 **Ola Kwiecien**, Sebastian Breitenbach, Mona Stockhecke, Thomas Litt: "Lake Van carbonates – fascinating and challenging"

2:45-3:00 Break

- 3:00-3:20 **Ilya Bindeman**: "Snowball or Slushball glaciations 2.4Ga? Resolving microanalytical evidence in subglacially hydrothermally-altered (down to $-27.3\% \delta^{18}$ O) rocks and coeval supergene materials"
- 3:20-3:50 **John Eiler (Keynote):** "Reconstructing the trace element composition of ancient seawater through SIMS studies of biogenic carbonates"
- 3:50-4:10 **Shannon Davis-Foust**: "Freshwater drum otoliths: the past, present, and future"
- 4:10-4:30 **Craig Kastelle**, Thomas Helser, John Valley, and Ian Orland: "Fish age validation using stable oxygen isotopes (δ^{18} O) signatures in otoliths:

Comparison of secondary ion mass spectrometry and micromilling/ continuous flow isotope ratio mass spectrometry"

- 4:30-4:50 **R. Gannon**, C. Charles, T. Guilderson: "Imaging the 20th century tropical Indian Ocean thermocline through a sclerosponge archive"
- 4:50-5:10 **Anne O'Leary**, Michael Bender, Jaroslaw Stolarski, Jess Adkins, Kate Dennis, Daniel Schrag: "Secondary Ion Mass Spectrometry as a tool for measuring primary geochemistry and characterizing vital effects in fossil corals"
- 5:10-5:30 **Hussein Sayani**, Kim Cobb, Anne Cohen, Brian Monteleone: "Extracting robust Sr/Ca estimates from coral using SIMS"
- 5:30 Break for dinner
- 6:30 **Social hour** at Memorial Union, 2nd floor balcony
- 7:30 **Conference dinner** (Memorial Union, 2nd floor)

Wed. June 26

- 8:30 Continental Breakfast
- 9:00-10:00 Reinhard Kozdon (Tutorial): "Analysis of Biogenic Carbonates"
- 10:00-10:30 Matthew Huber (Keynote): "The Future of Past Climate"
- 10:30 Coffee Break
- 10:45 **Feng He**, Jeremy Shakun, Peter Clark, Anders Carlson, Zhengyu Liu, Bette Otto-Bliesner, John Kutzbach^{, "}Testing mechanisms of the last deglaciation with transient climate simulations and high-resolution proxy data"
- 11:05 **Karen Russ**, Larissa Back, Zhengyu Liu, Kuniaki Inoue, Jiaxu Zhang, and Bette Otto-Bliesner, "The Hydrological Cycle Response to Rapid versus Slow Global Warming"
- 11:25 **Andrew Walters**, Stephen Meyers, Alan Carroll, "Cyclostratigraphic evaluation of repetitive sedimentary microfacies from the Green River Formation via X-ray fluorescence scanning: Evidence for annual, El Niño, and sun-spot cycles?
- 11:45 **Bryan McLean**, "An Isotopic Role for Fossil Small Mammals in Paleoecology and Paleoclimatology"
- 12:05 **Margaret Schoeninger** and Melanie Beasley, "Paleoenvironment and seasonal variation in rainfall at Allia Bay, Kenya 3.97 MA"
- 12:25 Lunch



Integrating Speleothem Proxies from Temperate Regions: Prospects from Monitoring and Imaging Studies

Jay L. Banner and Nathan R. Miller

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Within the temperate and drought-prone Southwest US, Texas occupies a position intermediate between Gulf of Mexico and Pacific Ocean moisture sources and an associated large meridional variation in annual rainfall. Speleothems in the Edwards aquifer karst system in central Texas constitute composite records that span at least the last 70 ky, with 1) first-order growth variations linked to oscillations between glacial and interglacial periods, with higher-order growth variations related to abrupt climate change periods, such as the Bølling-Allerød (BA), and 2) a seasonality of drivers of calcite precipitation that vary by cave setting. Whereas Edwards speleothem proxies on orbital time scales provide insight to climate change in this region, seasonal/annual changes are a key target for understanding changes in seasonality and how abrupt the transitions into climate periods such as the BA were, and for comparisons with other records (marine, lacustrine, dendrochronology, icecore) for a broader understanding of terrestrial climate dynamics. Further prospects include extracting information about storm events from speleothem records. This will require advancement of geochronologic methods and rigorous assessment of proxies by monitoring of the modern cave system.

To advance these prospects requires coupled studies between (1) monitoring of the modern system, to understand the link between seasonality, water geochemistry and calcite geochemistry, and (2) imaging and high-spatial resolution analytical methods, to resolve chemical/isotopic proxies within the speleothem record. The modern Edwards provides clues to how speleothems are forming today, and the extents to which various terrestrial climate proxies are recorded in the isotopic and elemental geochemistry of drip waters and associated modern speleothem calcite. We show examples of seasonality based on multi-year monitoring in several Edwards caves, including one well-ventilated cave setting in which temperature is recorded in both modern substrate calcite and a 20th-21st century speleothem. The slow growth rates of many Edwards speleothems present analytical challenges for obtaining subannual geochemical time series. LA-ICP-MS and SIMS, with small analytical footprints (\leq 10 µm) and high sensitivity, are optimal techniques. Yet, optical systems for determining sampling locations and transect vectors seldom reveal growth bands. Imagery of growth band fabrics is essential to avoid spatial aliasing and fine-scale complexity. UV fluorescence imagery is of significant benefit, as this technique offers resolution over a range of focal depths, and may reveal seasonal variation in the surface-to-subsurface transport of organic compounds. By registering such imagery to the coordinate system of LA-ICP-MS and SIMS, we construct analytical transects where samples are best suited for analysis and interpretation of results. Analytical methods to validate the resolution limits (spatial frequency, signal-to-noise versus amplitudes of chemical gradients in growth band couplets) are in development. The holy trinity for these analytical objectives is to match U-series growth rate estimates with growth band imagery and corresponding geochemical time-series.

Significance of High Resolution Proxies in Speleothems for Terrestrial Climate Reconstruction

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Speleothems in karstic cave environments form by the passage of meteoric water through the overlying soils, where the water dissolves CO_2 to form carbonic acid, which in turn dissolves the host-rock carbonate. Degassing of the supersaturated carbonated meteoric water in the cave, leads to the formation of speleothems, this therefore can be considered as the end product in the much larger sea-atmosphere-land cycle. Their stable isotopic and geochemical composition reflect the environmental conditions above the cave, which depend on larger scale parameters such as isotopic composition of the rainfall source, atmospheric storm patterns, and the regional bedrock temperature.

Our studies in the Eastern Mediterranean (EM) speleothems and marine cores demonstrate that the terrestrial and marine EM records respond to important global and regional climatic events, such as periods of enhanced rainfall over the entire Mediterranean Basin and the Sahara Desert that are associated with the formation of organic rich sediments in the EM Sea (sapropels), Dansgaard-Oeschger (D-O) rapid climate changes, Heinrich events, Bond Cycles and others. Given the ability to accurately date speleothems and to perform high-resolution studies of stable isotopes, trace elements and various other proxies (e.g., fluid inclusions, 'clumped isotopes' thermometry), it has become clear that speleothems enable us more accurately to define the exact timing of important climatic events and to understand the climatic response on land in different parts of the world to rapid climate changes. High resolution studies allow us to address specific questions on the marine-atmosphere interaction, sea surface temperature, rainfall generation and their influence on human habitation and dispersal.

The δ^{18} O and δ^{13} C record of fast growing speleothems in the Soreq cave show frequent sharp δ^{18} O oscillations that last only few years. Together with high-temporal-resolution proxy records using SIMS to measure δ^{18} O (WiscSIMS CAMECA 1280 ion microprobe), laser-ablation (LA-)ICP-MS to measure trace elements, and confocal laser fluorescent microscopy (CLFM) to reveal seasonal variability in organic matter, it becomes possible to understand the seasonal changes in rainfall and how they transmitted into a cave's hydrological system. Such an approach clearly reveals different seasonality patterns during the Holocene between wetter and dryer climatic conditions, and demonstrates different types of seasonal pattern in rainfall and soil productivity between the Holocene, Younger Dryas and the Last Glacial.

Snowball or Slushball glaciations 2.4Ga? Resolving microanalytical evidence in subglacially hydrothermally-altered (down to -27.3% d¹⁸O) rocks and coeval supergene materials

Ilya Bindeman (University of Oregon, Eugene, OR, 97403, Bindeman@uoregon.edu)

Paleoproterozoic is a turning point in Earth's history when oxygen first appeared in the atmosphere and continental weathering became more similar to modern¹. Appearance of oxygen was preceded or accompanied by three to four panglobal glaciations between 2.45Ga (global superplume) and ~2.22Ga (Lomagundi carbon isotope excursion)². The glacial diamictites of this age are abundantly present on all continents. Hard Snowball glaciation restricts hydrologic cycle but the Slushball glaciaton does not, although Slushball is climatically-unstable.

The presentation will report evidence from ultra depleted in d¹⁸O rocks in 10 localities, spanning 200km found in mid-grade metamorphic belt of Russian Karelia, Baltic Shield (described in Refs 3-5). The 2.9-2.55Ga protoliths of these rocks is interpreted to have seen significant exchange with subglacial -27 to -35% meltwaters 2.4Ga. As Karelia was attached to the Superior craton and located near equatorial latitudes at any time during Paleoproterozoic, a panglobal glaciation is required to explain these observations. Our U-Pb zircon geochronology indicates that massive subglacial alteration happened in rift zones during the superplume event, and thus characterize the first 2.4Ga of the four Paleoproterozoic glaciations. We present isotopic countour maps of several of these localities indicating bulls-eve pattern of ¹⁸O isotopic exchange, accompanied by significant (30-50%) hydrothermal dissolution leading to Al, Ti, Zr enrichment, and loss of Si, alkalies and other soluble elements. The best-studied locality has 6x1.5km outcrop with d¹⁸O depletion less than -10‰ and 200x100m of less than -25‰, with world record $d^{18}O$ of -27.3‰, and the dD of amphiboles and micas reaches -235‰. An extended range of d¹⁸O garnets allows precise determination of the exponent in a triple oxygen isotopic system. Studied rocks strictly adhere to mass-dependent fractionation of 17 O vs 18 O with exponent of 0.5278, characteristic of equilibrium (rather than kinetic, with lower exponent) fractionation and denying extraterrestrial origin of these depleted rocks. We discuss alterative ways of depleting d¹⁸O and find no successful explanation other than by protolithic alteration by glacial meltwaters.

Our search for unmetamorphosed 2.4-2.3Ga sedimentary or volcanic rocks and their secondary (subglacial?) alteration products is ongoing. We have analyzed collection of shales (from A. Bekker's) and quartz vugs from Fennoscandia and around the world for deposits spanning 3.2 to 1.4Ga for bulk oxygen and hydrogen isotopes. We found that although the bulk 2.4Ga shales and other materials are more d^{18} O-depleted (down to +3 to +8‰) than younger and older rocks, but temperature uncertainties and the amount of autigenic vs detrital component prevent us from making firm conclusions about these parameters. Using bulk methods we have not found ultra-depleted values (expected <-7-0‰ if altered at 50-100°C by -30‰ water). Investigation of outermost authigenic rims on secondary quartz by microanalytical (SIMS) methods in 2.4Ga materials may serve as a test for d^{18} O value of altering waters. The effort is underway to characterize samples by SEM and BSE and identify authigenic rims.

¹Bekker, A., 2011, Huronian glaciation, In: Encyclopedia of Astrobiology, Springer-Verlag, 1600 p., p. 768-772.
²Hoffman, P.F., 2009. Pan-glacial—a third state in the climate system. Geology Today 25, 100–107.
³Bindeman I.N. (2011) When do we need pan-global freeze to explain 18-O depleted zircons and rocks? Geology 39, 799-800. ⁴Bindeman I.N., Serebryakov N.S. (2011) Geology, Petrology and O and H isotope geochemistry of remarkably ¹⁸O depleted Paleoproterozoic rocks of the Belomorian Belt, Karelia, Russia, attributed to global glaciation 2.4 GaEarth Planet Sci Lett v 306, p. 163-176. ⁵Bindeman I.N., Schmitt A.K., Evans D.A.D. (2010) Limits of hydrosphere-lithosphere interaction: origin of the lowest d18O silicate rock on Earth in the Paleoproterozoic Karelian rift, Geology, v.38, p 631-634.

The stable isotopic composition of Cibicidoides wuellerstorfi (elevated epibenthic foraminifera) from methane seeps in the Pacific

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An understanding of the timing and nature of seafloor methane seepage provides important clues to the study of regional tectonic dynamics, paleoceanography, and global climate change. The manned submersible ALVIN and the remotely operated vehicle JASON were used to sample a variety of methane seepage environments on the Costa Rican and Oregon margins to examine the stable isotopic influences of seeps on benthic foraminifera. Living Cibicidoides wuellerstorfi attached to vestimentiferan tubeworms, from active methane seeps in Costa Rica and experimental substrates in Hydrate Ridge, Oregon, were removed on board and preserved. Comparisons of stable isotopic analyses of these elevated epibenthic specimens were then compared between sites and with the δ^{13} C of living *Cibicidoides* wuellerstorfi inhabiting inactive areas. C. wuellerstorfi from active seep areas in Oregon displayed a slightly wider range (-0.56 to 0.35‰) than those of adjacent non-seep areas (-0.26 to 0.39‰) although averages appear to be similar (seep δ^{13} C=0.08‰, non-seep δ^{13} =0.11‰). Similar patterns are also evident in stable oxygen isotopic composition at seep and adjacent non-seep sites of Hydrate Ridge. δ^{18} O values from seep areas range from 1.99 to 2.70‰, with an average of 2.40‰, while δ^{18} O of non-seep areas range from 2.29 to 2.65‰, with an average of 2.41‰. Carbon isotopic values of carbonate from living, attached C. wuellerstorfi from Costa Rica were more variable (-1.39 to 0.83‰, average 0.05‰) and on average, more negative than isotopic compositions of C. wuellerstorfi from Pacific non-seep samples (-0.2 to 1.12% with an average of 0.40%), reconfirming the idea that foraminiferal carbonate formed in methane seep habitats reflect direct or indirect influences of methane seep fluids. These influences may include food sources and/or variable exposure to intensity of seep fluids. Stable oxygen isotopic compositions of C. wuellerstorfi were statistically different between Mound 11 (ranging from -0.42 to 0.61‰ and an average of 0.26‰), Mound 12 (ranging from -1.39 to 0.42‰ and an average -0.14‰), and Jaco Scar (ranging from -0.76 to 0.83% and an average of 0.08%) on the Costa Rican margin. $\delta^{18}O$ values of foraminiferal calcite are consistent with the presence of highly variable bottom-water temperatures (range of 1.59 to 2.94‰ and an average of 2.33‰), potentially caused by periodic heterogeneous warm seepage that we observed at one location (what Levin et al., 2012 called "hydrothermal seepage"). The variation observed in δ^{13} C and δ^{18} O values of C. wuellerstorfi on the Costa Rican Margin offers a means to assess modern and perhaps ancient variations in seep fluid origin and intensity on continental margins.

Evaluation of oxygen isotopes of a speleothem as a high resolution temperature proxy

Richard Casteel and Jay Banner University of Texas at Austin

Pre-industrial paleoclimate records for Texas and the Southwest US (SW US) demonstrate that severe multi-year droughts are common, but decoupling the roles that temperature and rainfall amount played is poorly understood (Weiss et al., 2009; Banner et al., 2010). Of principle concern for the region is how droughts can be expected to vary with projected future warming. Dendrochronology for the region suggests that droughts more severe and prolonged than the instrumental drought of record in the 1950s have occurred in the region at least once a century since the year 1500 (Cleaveland et al., 2011). What is unknown is the extent to which central Texas temperature variations affected drought variability in the past. If temperature can be accurately extracted from seasonal paleoclimate records, such hindsight may help forecast how global temperature variations will affect regional climate. Integrated monitoring and geochemical studies of speleothems from Westcave preserve (Westcave) in central Texas demonstrate the potential to provide this missing perspective.

In contrast to most cave settings, Westcave is significant in that the δ^{18} O of cave calcite deposits are proxies for temperature (Feng et al., in review). This proxy power derives from Westcave's shallow cliff setting (with small cave volume relative to cave opening), which allows for continuous ventilation and results in cave air that is similar to the surface atmosphere (Casteel and Banner, in prep.). Calcite growth rate is positively correlated with surface air temperatures with greatest growth during warmer months. Calcite collected from glass-plate substrates situated below active drips has δ^{18} O ranging from -6 to -3 % over a corresponding temperature range of 33 to 8°C, with lighter compositions linked to warmer time intervals. Analysis of the top 7-mm of a 20th century stalagmite at Westcave shows similar seasonal trends in δ^{18} O values as the substrate calcite (-4.9 to -2.9‰). Drip water δ^{18} O values are relatively invariant (-4.7 to -4.3‰), eliminating rainfall or drip-water δ^{18} O as a control on calcite δ^{18} O. We infer that the calcite δ^{18} O variations result from the temperature dependent fractionation of oxygen isotopes. This allows the potential use of δ^{18} O values as a temperature proxy (and as a geochronometer) at Westcave (Feng et al., in review). The fast growth rate of stalagmite WC-3 (~1.6 mm/yr) allows for sub-annual micromill δ^{18} O sampling resolution but its young basal age restricts paleotemperature reconstruction to an interval of only ~80 years. To extend the paleotemperature record back further in the Holocene, we propose to evaluate more enduring flowstone records. Basal U-series ages of 2213 (±23) and 2376 (±78) BP for two Westcave flowstone samples demonstrate this possibility, but corresponding growth rates of 85 and 110µm per year are impractical to sample on a sub-annual frequency by micromill. Given these slower growth rates as well as the expected temperature and δ^{18} O seasonality at Westcave, Secondary Ion Mass Spectrometry (SIMS) δ^{18} O analysis, with its high spatial resolution (10 µm), may be applicable. Although accompanied by lower δ^{18} O precision (0.3‰) compared to phosphoric acid IRMS methods (0.1‰), seasonal δ^{18} O variations of ~2-3‰ at Westcave are 7 to 10 times higher than the uncertainty associated with SIMS, thus the potential for obtaining sub-annual paleotemperature resolution by SIMS should be high.

Developing a high-resolution speleothem record of Great Basin climate and hydrological change for times that correlate with Marine Oxygen Isotope Stages 5 to 7.

- Mellissa Cross¹, David McGee², Wallace S. Broecker³, Jay Quade⁴, Hai Cheng¹, and R. Lawrence Edwards¹
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- 2. Department of Earth, Atmosphere, and Planetary Sciences, Massachusetts Institute of Technology, Cambridge, MA, 02142.
- 3. Lamont-Doherty Earth Observatory, Columbia University, Palisades, NY, 10964.
- 4. Department of Geosciences, University of Arizona, Tucson, AZ, 85721.

The repeated rise and fall of paleolake Bonneville is clear evidence that the Great Basin has in the past experienced profound changes in water balance. However, little is known about these climate and hydrological changes prior to the last glacial period. A need still exists for a long-term, continuous, high-resolution, replicated record of Great Basin climate and hydrological change for earlier glacial and interglacial periods. In particular, such a record for the previous interglacial is critical, as this interval may be an analog for future conditions. Located on the southwestern edge of paleolake Bonneville in the Great Basin National Park in Nevada, the highly-decorated Lehman Cave is well-suited to fulfill this need.

Preliminary uranium-thorium dating was performed on 20 speleothems. Nearly eighty 2-10 mg samples with a mean ²³⁸U of 340 ppb were analyzed on the multi-collector inductively-coupled plasma mass spectrometer at the University of Minnesota. Growth phases that correlate with the majority of Marine Oxygen Isotope Stages (MIS) 5, 6, and 7 appear to be represented through a compilation of 8 different stalagmites. Several significant periods are at least partially replicated: 81.5 ka to 103 ka, correlative to the interval between Dansgaard-Oeschger events 21 and 23; 204 ka to 207 ka; and 118 ka to 132 ka, an interval covering the last interglacial period and the end of Termination II and Heinrich Event 11. We have yet to identify growth intervals between 103 ka and 118 ka, 132 ka and 137 ka, and 164 ka and 169 ka. At this point, it is not obvious if growth during interglacial or glacial periods is more common or faster. Growth rates in general for these speleothems are extremely slow, ranging from 3 to 30 microns per year. At the low growth rate end of the spectrum, the conventional stable isotope analyses currently in progress may integrate over a century of climate and hydrological information. Thus, the low growth rate phases may be ideal for SIMS analysis which would integrate oxygen isotope resolution to on the order of a few years.

Freshwater drum otoliths: the past, present, and future Shannon Davis-Foust University of Wisconsin Oshkosh, Biology and Microbiology, 800 Algoma Blvd, Oshkosh, WI 54901

The incremental growth and corresponding elemental compositions of fish otoliths (ear bones) can be analyzed for annual and seasonal variations in relation to environmental factors. In contrast to many other freshwater fish species, freshwater drum (Aplodinotus grunniens) have large otoliths with clear annual increments thereby allowing for precise measurements. Growth chronology indices were constructed from annual increment widths measured from thin-sectioned otoliths for both present-day and pre-European settlement drum populations using dendrochronology techniques and linear mixed models. The modern chronology strongly and positively correlated (r=0.68; p < 0.001) with June-August air temperatures, consistent with drum ecology that the majority of growth occurs during these summer months. There was also a significant increase in increment widths of large drum (>40 cm) that corresponds to the introduction of exotic zebra mussels (Dreissena polymorpha) into the system around 1998. This correlation was supported by diet analysis data, which found that only larger drum were utilizing this new food resource. Modern and archaeological growth-increment widths were pooled and normalized with respect to age of the fish when the otoliths were formed, then averaged with respect to calendar year. The final growth chronology index contained an absolutely dated (1949-2009, 61 years) portion from the modern samples as well as a floating (estimated 1640-1712, 72 years) portion from the archaeological samples. Tree-ring based temperature and drought reconstructions were used to tentatively date the floating portion of the chronology and corroborated anecdotal evidence that the site was occupied by Native Americans for approximately 34 years prior to abandonment in 1712. To date, drum otoliths have been used for growth studies, but elemental compositions have not been published. Given its strong correlation with summer temperatures, it is likely that the oxygen isotope ratios (δ_{180} values) would allow for the reconstruction of historical regional temperature data.

Reconstructing the trace element composition of ancient seawater through SIMS studies of biogenic carbonates

John Eiler California Institute of Technology

The abundances of trace metals (e.g., B, Mg, Sr, Ba, U) in carbonate minerals constrain past ocean chemistry (and thus global weathering cycles) and mineral growth temperatures. However, these constraints are generally useful only when several hurdles are overcome: First, the biogenic carbonates that are the principal target for such applications are often compositionally zoned — complexly and over several scales. Thus, in situ analyses are essential. Second, any such applications must achieve precision and accuracy on the order of %, relative, in order to yield climatically meaningful temperatures; this is routine for some elements and methods but pushes the limits of the highest spatial resolution, in situ analyses of trace elements. Third, even well documented spatial variations in trace elements are useful only when they can be interpreted in the context of a mechanistic understanding of their causes, including vital effects and other non-equilibrium phenomena associated with mineral growth and diagenetic overprinting.

Various forms of SIMS are an important part of the arsenal of analytical tools for addressing these problems because of their in situ capabilities, potential for trace element analyses, and potential for direct comparison with paired in situ stable isotope measurements. Of these, the nanoSIMS seems best suited to the task of documenting trace element variations because of its potential for sub-micron resolution and ability to multi-collect element/element ratios (i.e., potentially improving precision relative to single collector methods). This talk will review the distinctive capabilities and limitations of nanoSIMS measurements for this field, and the relationship of such data to complementary measurements with conventional ion and electron probes and ICPMS. In particular, I will draw on results from several studies conducted in the Caltech labs (by a variety of investigators) to address: limits of precision with this (sometimes peculiar!) instrument; problems of interlab standardization with commonly circulated materials; uses of the nanoSIMS to study products of culturing experiments aimed at understanding vital effects; examples of the constraints nanoSIMS data can provide on extents and mechanisms of diagenetic overprinting; and, finally, I will illustrate the use of this method to estimate the trace element evolution of the Phanerozoic ocean.

Imaging the 20th century tropical Indian Ocean thermocline through a sclerosponge archive

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The ocean's thermocline is typically inaccessible to high-resolution paleoceanographic proxies, and especially little is known about the Indian Ocean thermocline as the instrumental temperature record there is sparse and only extends to 1960. Here we present stable isotope and radiocarbon analyses performed on a novel sclerosponge archive from the western Indian Ocean thermocline region. This collection is comprised of sclerosponges identified as genus Acanthocheatetes which are slow growing (~1mm/year), composed of high-Mg calcite, and precipitate their skeleton in apparent isotopic equilibrium with seawater. The assemblage, dredged off the Seychelles Bank in 2007, spans the better part of the 20th century. Dredges were conducted on a series of drowned reef terraces and are thus vertically well-constrained; the highest concentration of sponges are from three separate dredges that spanned water column depths of 73-92m, 95-119m, and 102-165m. We have combined the sclerosponge data with a proximate surface coral record from St Joseph Island 150km west to create a vertical structure of the upper Indian Ocean throughout the 20th century. These records possess $\delta^{18}O$ variability on average near 0.6‰, a value that would represent swings of nearly 3°C if attributed entirely to temperature. There is a clear signal of interannual variability that appears to pair well with ENSO, though a tighter chronology is necessary to make any accurate comparisons. Radiocarbon data show that a number of sponges span the bomb spike of the early 1960s, yet on account of the sponge's depth of habitat only allows for a chronology accurate to ~5 years. Regardless of chronology, these data provide crucial tests of various hypothesized responses of the Indian Ocean thermocline to anthropogenic forcing.

Testing mechanisms of the last deglaciation with transient climate simulations and high-resolution proxy data

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Transient paleoclimate simulations are climate experiments with the forcing evolving gradually according to reconstructed forcing from past climate changes, such that the time dependent climate responses may be simulated. The comparison between transient paleoclimate simulations and high-resolution proxy data can provide useful clues to understanding past climate changes.

The Milankovitch hypothesis of orbital control on glacial cycles was first firmly established some 40 years ago. One of the most controversial observations against the Milankovitch hypothesis is the relation between a Northern Hemisphere insolation control and a Southern Hemisphere lead of the Northern Hemisphere temperature during the onset of last deglaciation. Here we use transient simulations from NCAR/CCSM to identify the impacts of forcing from changes in orbits, atmospheric CO₂ concentration, ice sheets and the Atlantic meridional overturning circulation (AMOC) on hemispheric temperatures during the first half of the last deglaciation (22–14.3 kyr BP). Our transient simulation with only orbital changes supports the Milankovitch theory in showing that the last deglaciation was initiated by rising insolation during spring and summer in the mid-latitude to high-latitude Northern Hemisphere and by terrestrial snow-albedo feedback. The simulation with all forcings best reproduces the timing and magnitude of surface temperature evolution in the Southern Hemisphere high-resolution deglacial proxy records. AMOC changes associated with an orbitally induced retreat of Northern Hemisphere ice sheets is the most plausible explanation for the early Southern Hemisphere deglacial warming and its lead over Northern Hemisphere temperature; the ensuing rise in atmospheric CO₂ concentration provided the critical feedback on global deglaciation.

"The Future of Past Climate"

Matthew Huber Purdue University

Paleoclimate data play a fundamental role in guiding climate dynamics theory and validating climate models. Here I discuss the importance of proper characterization of random error and systematic biases in paleoclimate sea surface temperature estimates in making these data useful. Examples from the Eocene and Miocene are given and possible ways forward are discussed.

Comparison of late Quaternary productivity variation in two contrasting basins of northern Indian Ocean using geochemical proxies.

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Abstract: A 4.1m long sediment core (SK-117/GC-08) raised from a water depth of 2500 m in the Eastern Arabian Sea (EAS) (Lat: $15^{\circ}29'$ N; Long: $72^{\circ}51'$ E) is studied for variation of productivity during the last 100 ka utilizing geochemical proxies. The temporal variation in element concentration and fluxes of CaCO₃, organic carbon (C_{org}) and Barium excess (Ba_{exc}) together in general indicate a higher productivity during the cold climate and highest during the Last Glacial Maximum in particular. This cold climate-increased productivity coupling may be attributed to the shoaling of nutricline due to enhanced convective mixing resulting from the intensified winter monsoon during cold periods.

A radiocarbon dated sediment core (SK-218/1) covering the past 45 ka is collected from the western Bay of Bengal (Lat: 14° 02'N; Long: 82° 00'E) at a water depth of 3307 m and is studied for variation of productivity utilizing geochemical proxies. The temporal variation in concentration and fluxes of CaCO₃, organic carbon (C_{org}) and Barium excess (Ba_{exc}) together in general indicate a higher productivity during interglacials. This warm climate intensified productivity may be attributed to stronger SW monsoon during interglacial's thereby bringing more fresh water and nutrients from nearby landmass than glacial period.

In both of the basins under same forces of monsoon driving mechanism there doesn't seem similar influence on productivity, EAS productivity is controlled more by local mechanism of convective mixing while as WBOB productivity is more controlled by Indian monsoon forcing mechanism.

Fish age validation using stable oxygen isotopes (δ^{18} O) signatures in otoliths: Comparison of secondary ion mass spectrometry and micromilling/continuous flow isotope ratio mass spectrometry

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Measurements of stable oxygen isotopes (δ^{18} O) were obtained from 7 Pacific cod (*Gadus* macrocephalus) otoliths from which bi-hourly temperature and depth records were stored from electronic archival tags. Two techniques were used to acquire and measure samples for δ^{18} O analysis from full life history traverses (core to edge); micromilling with conventional continuous flow isotope ratio mass spectrometry and microprobe –secondary ion mass spectrometry. Our goals were threefold: 1) evaluate the feasibility of using seasonal signatures of otolith δ^{18} O to validate Pacific cod ageing, 2) corroborate the seasonality of δ^{18} O signatures derived from the two different sampling-mass spectrometry techniques, and 3) verify that temperature is a determinant of otolith δ^{18} O variation using *in situ* archival tag temperatures. Sampling resolution from micromilling yielded an average of 22 (40 ug or more each) discrete δ^{18} O measurements per mm compared to over 50 (~2 ng) per mm from the ion microprobe. Pacific cod otolith δ^{18} O showed the expected cyclical pattern consistent with seasonal variation in temperatures. In some of these, the number of δ^{18} O maxima showed a close correspondence to the estimated age from growth-zone counts, validating standard age determination methods, but overall the results were not completely definitive. The increased spatial resolution from the ion microprobe allowed for finer temporal resolution which corroborated the seasonality of δ^{18} O based on micromilling. As expected, the relationship between Pacific cod otolith aragonite (δ^{18} O) and bottom temperature showed an inverse, statistically significant linear relationship (r^2 =0.75, p<0.001). Mean δ^{18} O declined with temperature at a rate of about 0.25 ‰ /°C, which is approximately consistent with the expected temperaturedriven variation in δ^{18} O of aragonite of $0.2^{\circ}/_{\circ\circ}/^{\circ}$ C from North Atlantic waters. Here, as in the North Atlantic, a 5°C variation should produce a ~1°/ $_{00}$ change in the otolith's δ ¹⁸O composition based on the equilibrium fractionation curves calculated for biogenic aragonite.

High-Resolution Records of Ancient Rainfall, Turbulent Open Channel Flow and Microbial Communities from Travertine Deposits in Roman Aqueducts

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Travertine deposits flooring the Anio Novus, ancient Rome's highest and longest aqueduct, exhibit bedding characteristics on a hierarchy of length scales, which include: (1) cm-scale ripple bedforms with both up- and downstream instability, a feature unknown in analogous ripple-forming systems and (2) mm-scale and smaller, dark-light color variations. Reconstruction of temporal variations in ancient aqueduct water flux should be possible from ultrahigh-resolution measurement and quantitative modeling of the wavelength and instability of these bedforms preserved within the travertine. The fidelity of these calculations require knowledge of the geometry and slope derived from measurement of the original well-preserved stretches of the aqueduct channel such as those at Romavecchia.

Petrographic analyses show that sub-mm darkly colored layers are richer in organic material than surrounding travertine and are associated with sediment deposits. Significant increases of both during rainstorms have been well documented in Aniene river, the source for the Anio Novus aqueduct, in both the ancient and the modern periods. In turn, these variations in seasonal rainfall will have had significant impact on microbial ecology within the aqueduct, which may also be recorded by the submicron travertine layering. Future work will include controlled travertine precipitation experimentation under controlled water chemistry, flow and microbial conditions.

Seafloor Diagenesis Attenuates the Carbon Isotope Excursion Marking the PETM REINHARD KOZDON D. CLAY KELLY JOHN W. VALLEY

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Earth surface temperatures warmed by ~5-8°C during an ancient (~55.5 Ma) global warming event referred to as the Paleocene-Eocene thermal maximum (PETM). This transient (~200 ka) "hyperthermal" climate state is widely touted as an ancient analog for future climate change. A hallmark feature of the PETM is a negative carbon isotope excursion (CIE) that has been documented in various terrestrial and marine substrates from numerous locations around the world. The ubiquity of the CIE signals the rapid release (≤ 30 ka) of massive quantities ($\geq 2000 \times 10^{15}$ g C) of isotopically depleted carbon into the exogenic carbon cycle; however, it has long been recognized that the magnitude of the CIE in terrestrial records is substantially greater than that measured in marine carbonates. For instance, estimates indicate that the average CIE magnitude in terrestrial records is \sim 4.7‰ while the mean CIE magnitude in marine carbonates is only \sim 2.8‰. Resolving this conundrum is paramount for constraining the size and source(s) of carbon input, determining the fate of the released carbon and gauging climate sensitivity to greenhouse gas forcing. Here, the effects of postdepositional diagenesis on planktic foraminiferal records is assessed by *in situ* δ^{13} C measurements of alteration-resistant domains within planktic foraminiferal shells and diagenetic crystallites using secondary ion mass spectrometry with an analytical precision of $\pm 0.7\%$ (7 µm beam). The analyses yielded mean δ^{13} C values of ~2.7‰, ~4.7‰, and 0.0‰ for the crystallites, pre-CIE biogenic, and CIE biogenic calcites, respectively. The δ^{13} C values of the Site 865 PETM crystallites are ~3\% higher than those of biogenic calcite in foraminiferal shells bearing the CIE signal, but ~2% lower than the $\delta^{13}C$ of biogenic calcite in foraminiferal shells bearing the pre-CIE signal. These data indicate that the magnitude of the CIE at the central Pacific ODP Site 865, originally reported as being only $\sim 2.5\%$, is actually ~5‰ and highly congruous with the CIE magnitude seen in terrestrial records. Moreover, a CIE of comparable magnitude (~5‰) has been reproduced in the high-latitude (Weddell Sea) Site 690 PETM record using the same *in situ* analytical approach. These results indicate that the addition of modest amounts of diagenetic carbonate can attenuate the magnitude of the CIE when the whole for a shell is analyzed by conventional analytical approaches. Therefore, we conclude that diagenetic overprinting on foraminiferal shells is a viable explanation for the discrepant magnitudes seen between terrestrial and marine CIE records.

Preparation of carbonates for SIMS: Sample selection, mount preparation, imaging, and preselection of suitable domains for analysis

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The precision of stable isotope analyses by SIMS has improved steadily over the past three decades. Besides new developments in instrumentation and careful tuning of the ion optics, sample preparation and standardization are essential for high precision and accuracy. For measurements of δ^{18} O, WiscSIMS routinely achieves a spot-to-spot reproducibility of $\pm 0.3\%$ (2 SD) from 10-15 µm spots, or $\pm 0.7\%$ (2 SD) for 2-3 µm beam-spot sizes. This allows the extraction of unique paleoclimate information from a variety of proxy-carriers that cannot be assessed by other analytical techniques. For example, sub-annual δ^{18} O gradients were reported in speleothems [1], and daily growth increments were analyzed for δ^{18} O in fish otoliths [2] and foraminiferal shells [3].

Commonly, samples that provide important climate archives – such as speleothems and marine biocarbonates – feature complex internal structures that require careful consideration by the SIMS operator as non-systematic shifts in the measured isotope ratio can occur. Among these features are domains of significant microporosity, growths bands, cavities, cracks, secondary phases, and areas with high organic content. Therefore, both extensive imaging of the sample by SEM as well as preselection of suitable domains for SIMS analysis are essential to obtaining a robust data set.

In this poster, we present the basic steps of sample selection for SIMS, the preparation of the epoxy mount, sample imaging, and criteria to preselect suitable domains for SIMS analysis. We also describe the importance of post-analysis evaluation of SIMS pits at high magnification by SEM in order to identify 'irregular' pit shapes that may bias the data set. Examples from previous and ongoing studies of corals, foraminiferal shells, and speleothems are discussed.

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<u>Tutorial</u>

Carbon and oxygen isotope analyses in biocarbonates by SIMS: Overview of samples analyzed at WiscSIMS, quality control, and latest developments in assessing the potential impact of organics

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Carbonates such as planktic and benthic foraminiferal shells, mollusks, and speleothems are the focus of many paleoclimate investigations, and the data extracted from these marine and terrestrial records are increasingly used to calibrate predictive models of future climate on regional and global scales. *In situ* stable isotope analyses by SIMS provide a powerful tool to extract a whole new set of environmental information from proxy-archives that have previously been inaccessible by conventional analytical techniques. For example, seasonal-scale environmental information was reported from a speleothem that grew during the last deglaciation using 10-µm spot analysis of $\delta^{18}O$ [1], and a paleoclimate record from a tropical Pacific deep-sea core that was re-assessed by targeting alteration-resistant domains within foraminiferal shells indicated that conventional 'whole-shell' measurements from the same core underestimate sea surfaces temperatures by 4° – 8°C [2].

The acquisition of stable isotope data by SIMS with high precision and accuracy – a prerequisite for paleoclimate reconstructions – requires careful sample selection, mount preparation, sample characterization, and the placement of the analysis in well-chosen domains. The WiscSIMS laboratory has now \sim 7 years of experience in analyzing (bio-) carbonates, and a tremendous amount of time and effort has been spent to continuously improve and optimize both sample preparation and data acquisition. In this presentation, we will give an overview of the different types of carbonate samples previously analyzed at WiscSIMS, the selection of suitable domains for *in situ* stable isotope measurements, and the challenges of sample porosity as well as the potential impact of organics.

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Lake Van carbonates – fascinating and challenging

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Lake Van (Eastern Anatolia, Turkey) is a terminal soda lake located in semiarid high plateau. Its geographic setting and unique hydrology (pH ~9.7; salinity ~22‰) make Lake Van an excellent archive of paleoenvironmental changes.

The 220 m long sedimentary profile, covering the lake's entire ca. 500 ka long history, displays an extraordinary complexity. Laminated-, banded-, and graded-clay sections are intercalated with numerous tephra layers. The carbonate fraction is represented by authigenic calcite and aragonite forming either submilimiter-scale annual laminae mixed with clay minerals, and a biogenic fraction, which is represented by low-Mg ostracod valves. Co-occurrence of these two carbonate fractions offers the unique possibility in tracing differences in the elemental and isotopic composition of authigenic/biogenic carbonates, deep/surface water carbonates, and calcite/aragonite mineralization from the same stratigraphic level. Our robust age model and X-ray fluorescence (XRF) profiles indicate that the region and the lake itself responded with high sensitivity to glacial/interglacial changes and D/O oscillations. This sensitivity provides a superb hydrological context for the ongoing comparative study. Instrumental challenges consist in obtaining sufficient amount of material for analysis – ostracod valves are fragile and found at low abundance while submilimiter-scale authigenic carbonate layers are difficult to sample by traditional methods.

Sub-daily depth migration behavior in *Nautilus macromphalus* revealed by $\delta^{18}O$ variation in shell measured by ion microprobe

Linzmeier, B.J., Kozdon, R., Peters, S.E., and Valley, J.W.

Nautilus is and important model organism for the ecology and behavior of extinct externally shelled cephalopods. Individual Nautilus have been tracked migrating across 100 to 400 m depth per day by remote telemetry at Palau and Osprey Reef, Australia. The oxygen isotope ratio in shell aragonite is expected to vary due to depth migration because seawater temperature varies within the migration range (>3°C) and *Nautilus* shell precipitates in oxygen isotope equilibrium with seawater. Growth banding was imaged and within-band ion microprobe oxygen isotope analyses (10 μ m spots, ±0.3‰) were performed to determine if depth migration behavior is recorded in the shell of a wild-caught Nautilus macromphalus from 20 km South of Nouméa, New Caledonia. Daily growth bands (~32 µm thick) in the outer prismatic layer are visible by plain light, ultraviolet light, and confocal laser florescence microscopy (CLFM). Pores in the outer prismatic layer were imaged by scanning electron microscopy. These pores were likely filled by intercrystalline organic matter before the sample was vacuum roasted for one hour at 320 °C. Eighty three ion microprobe analyses (10 µm spot) within 20 growth bands demonstrate that depth migration behavior is recorded in the oxygen isotope ratio of Nautilus shell. Oxygen isotope ratios across all bands vary from 0.2 to -1.6‰ and correspond to a range of ~9°C temperature and ~300 m depth. The average oxygen isotope ratio range within individual bands is 0.7‰ which corresponds to a change of ~3°C temperature across ~100 m depth within a day. These results suggest that sub-daily depth migration behavior in well-preserved ammonoids and nautiloids could be elucidated by using ion microprobe analysis. The range of oxygen isotope ratios measured in sections of shell precipitated in either winter or summer could elucidate seasonal variability in thermohaline stratification.



A) Stitched CLFM images of outer prismatic layer of *Nautilus macromphalus* showing the position of ion microprobe pits and growth banding. B) Oxygen isotope ratios measured by ion microprobe in this *Nautilus macromphalus*. Dashed black lines bracket lower and upper values for instrumental precision around sample measurements. Dashed red vertical lines indicate the darkest portion of growth bands imaged by CLFM. Considerable variation (>1‰) is present both within and between growth bands.

An Isotopic Role for Fossil Small Mammals in Paleoecology and Paleoclimatology

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Fossilized remains of small- and medium-sized (<1kg) mammal species are increasingly utilized as proxies of paleoclimates, paleoenvironments and paleodiets. However, methods vary in their temporal resolution from multiannual or annual (whole teeth/bones) to intraannual (e.g., tooth growth layers). In this paper, I present results from recent analyses of fossil and modern ground-dwelling squirrels (Sciuridae: Marmotini) that span this continuum. The first are whole-tooth enamel carbonate analyses of late Quaternary yellow-bellied marmots (*Marmota flaviventris*) from the Upper Gunnison Basin, Colorado, USA. These have yielded a record of CO₂ response in high-elevation plant communities of the region spanning the past >50ka. Second are results from serial analyses of incisor enamel of modern golden-mantled ground squirrels (*Callospermophilus lateralis*) from the Jemez Mountains, New Mexico, USA. I discuss the influence of both hibernation and seasonal carbon and oxygen variability on these signatures, and applicability of the method for inferring paleoseasonality. Also, I discuss the relevance of SIMS technology for improving and broadening use of the small mammal fossil record.

UV-LA-(MC-)ICPMS – Principles and Applications to Ice Cores and Foraminifera

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Besides SIMS, laser-ablation inductively-coupled-plasma mass spectrometry (LA-(MC-)ICPMS, both single and multi-collector) has revolutionized our ability to analyze trace concentrations and isotope compositions in a wide range of materials at the spatial-resolution of tens of μ m. Overall, both SIMS & LA-ICPMS are complementary techniques for many applications, with their own specific advantages and disadvantages. LA-(MC-)ICPMS has established itself as a high-throughput/ fairly low-cost trace element and high-precision isotope ratio method (for the latter almost on par with TIMS or solution-MC-ICPMS), but on the other hand it lacks routine stable isotope capability, one of the key strengths of SIMS. Owing to the plasma-based high excitation energy ion source following the laser-based in-situ sampling process, resultant mass spectra of LA-(MC-)ICPMS are in many, albeit not all cases significantly simpler that those of SIMS, allowing the use of low mass resolution (m/ Δ m~400) mass spectrometers.

We will briefly review some key relevant developments in LA methodology, specifically the two-volume LA cell concept that enables routine depth-profile analysis for ultimate (sub-)µm scale spatial resolution and reliable continuous track analysis. However, the main part of this presentation will showcase recent novel applications of LA-(MC-)ICPMS in palaeoclimate research, specifically direct analysis of frozen ice cores and development of (shallow-dwelling) large benthic foraminifera (LBF) as proxy archives. In both cases one of the motivations is the understanding of the role of seasonality in the geological past, necessitating spatially-resolved analysis and sufficiently long-lived organisms (i.e. LBFs).

Spatially-resolved analysis of frozen NGRIP ice (GS22, ~86 ka) at >100 μ m resolution is made possible via the recently developed cryo-cell sample holder, uniquely compatible with the two-volume Laurin LA sample cell (1), which allows us to investigate the location of cation impurities in re-crystallizing ice as well as sub-annually-resolved sea ice vs. dust proxies across key rapid climate change events. Recent and cultured LBF (*Operculina*), an underutilized source of (deep-time) palaeoclimate information, are currently being investigated as a new proxy archive for the Paleogene at seasonal resolution (2, 3), given that *Operculina* is the nearest living relative of Eocene *Nummulites*. Here, LA-ICPMS facilitates 1) Mg/Ca (and other ratio) analysis via 2D compositional maps and/or continuous tracks and 2) unequivocal identification of newly formed LBF chambers in culturing experiments, which focus on Mg/Ca_{test}-temperature and Mg/Ca_{test}-Mg/Ca_{seawater} calibrations. In all cases, corresponding results will be presented.

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Techniques for ion microprobe analyses of tiny particles: Sample mounts using indium and combination of FIB marking and ¹⁶O⁻ ion imaging

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Oxygen isotope analyses of tiny extraterrestrial particles ($\leq 100\mu$ m), such as particles returned from comet Wild2 and asteroid Itokawa and interplanetary dust particles, have been successfully made using an IMS-1280 secondary ion mass spectrometer (SIMS) at WiscSIMS laboratory [1-4], in which we applied two techniques for accurate analyses: (1) indium mounting and (2) combination of FIB marking and ¹⁶O⁻ ion imaging. Here we report these two techniques, which are beneficial to high-spatial resolution analysis of terrestrial/extraterrestrial samples which have a few-µm scale fine structure.

Indium mounting [4]: Multiple tiny samples with standards in a flat 25mm disk are desirable to minimize the surface topography effects on high precision isotope analyses [5]. However, preparation (casting and polishing) of a 25mm disk with multiple tiny samples is at risk of consuming a significant portion of samples. To avoid the risk, we prepared a 6mm epoxy disk containing a tiny particle with polished surface, and then epoxy disk was pressed into indium inside of a 25mm diameter Al-disk with standard grains. With this method, we achieved a single flat surface for sample and standard grains with the flatness of the entire disk of better than 40µm. Test analyses with 10µm spots showed that instrumental bias is within 0.3% in δ^{18} O among three San Carlos olivine grains pressed in the Al-disk as long as the tilt of the grains is within 1µm across the 1-2mm diameter.

FIB marking and ¹⁶O⁻ ion imaging [3]: Accuracy of aiming of the analysis locations in tiny particles ($\leq 10\mu$ m) was limited by the optical resolution of the reflected light microscope of SIMS (originally ~3.5µm, which is recently improved to 1.3µm). To improve aiming accuracy, we applied FIB marking and ion imaging. Carbon (or gold) coating of 1×1µm square within a tiny particle is removed by focused ion beam (FIB; Ga⁺). The FIB marking on the particle surface is identified by the 10×10µm ¹⁶O⁻ secondary ion imaging using ~1µm Cs⁺ beam of SIMS. The new aiming technique enabled isotope analysis with 0.4µm aiming accuracy and has an advantage of analyses of particles as small as ~4µm.

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Secondary Ion Mass Spectrometry as a tool for measuring primary geochemistry and characterizing vital effects in fossil corals

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Numerous archives, including brine inclusions in halite, biogenic calcites, and calciumcarbonate veins from mid-ocean ridge flanks, indicate that the major element chemistry of seawater has varied through time^{1,2,3}. Such changes in seawater composition are thought to be linked to continental weathering, seafloor-spreading, and dolomitization. However, robust evidence relating these processes to seawater chemistry remains elusive. Records of seawater chemistry from fossil corals may be able to supplement existing records of seawater chemistry change, but the use of fossil corals as an archive is complicated both by the presence of vital effects and by the tendency of aragonite to alter to calcite.

We used Secondary Ion Mass Spectrometry (SIMS) to measure Mg/Ca and Sr/Ca ratios in ~60 fossil corals ranging in age from Recent to Triassic. All samples were prescreened for diagenetic alteration using XRD and petrographic and SEM microscopy. A subset of samples has also been measured for clumped isotopes.

High-resolution, in-situ SIMS analysis allows us to characterize the presence of vital effects in fossil corals. For most samples (53 out of 62 total) we observed an inverse relationship between Sr/Ca and Mg/Ca ratios, similar to that observed by Gagnon et al. (2007). We were also able to geochemically distinguish between coral fibers and centers of calcification (COCs), which have been previously shown to be compositionally distinct⁴. All data from COCs were excluded from records of Mg/Ca and Sr/Ca through time.

The use of SIMS also permits further characterization of the preservation of our sample set. We measured Mn/Ca ratios together with Mg/Ca and Sr/Ca ratios to test for diagenetic alteration. Mn is a trace element sensitive to diagenesis, and may be enriched in parts of the coral that have been partially altered. We find that in some spots analyzed in fossil corals, Mn/Ca intensity ratios are orders of magnitude higher than in modern corals, and are positively correlated with Mg/Ca ratios and anti-correlated with Sr/Ca ratios, demonstrating the presence of small-scale diagenetic alteration. Spots with high Mn/Ca (> 0.0003 Mn/Ca Intensity Ratio) are excluded from our records of Mg/Ca and Sr/Ca through time. These results suggest that SIMS analysis of fossil corals can yield records of Mg/Ca and Sr/Ca that better reflect primary geochemistry than would bulk measurements.

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A high-resolution geochemical record of seasonal climate in a modern Soreq Cave speleothem

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High-temporal-resolution proxy records of past climate are critical for understanding the dynamics of abrupt climate change. Previous work shows that speleothems (carbonate cave deposits) can record high-resolution geochemical information during their growth, but more work is needed to demonstrate how geochemical data sampled from speleothems with sub-annual resolution can be used as climate proxies. Here, we apply a new analytical approach that reveals how seasonal climate information is transmitted to a modern Soreq Cave (Israel) stalagmite, sample "5-3b", that grew on a drip-collecting device in the cave from 1990-2008.

We use the WiscSIMS CAMECA 1280 ion microprobe to make sub-annual-resolution (10 μ m spots) measurements of: 1) δ^{18} O values with a spot-to-spot precision of ~0.3‰ (2 s.d.), and 2) a suite of trace element concentrations, including Mg, Sr, Ba, Y, P, U, Cu, Na, Mn and Si. In addition, a linear traverse along the 5.4 mm growth axis of sample 5-3b by laser-ablation (LA-)ICP-MS provides a continuous record of trace element variability at 50 μ m resolution. Confocal laser fluorescent microscopy (CLFM) is used to image fluorescent banding in the sample. Instrumental records of rainfall as well as chemical analysis of both dripwater and rainwater from above the cave allow us to compare the meteorological/hydrological signal to the geochemistry of sample 5-3b.

Using a combination of CLFM imaging and geochemical analyses we identify 18 annual growth increments, which match the known duration of growth. Furthermore, diminished fluorescence and a change in trace element variability mark the shift from a relatively wet period between 1990 and 1998 (average annual rainfall = 628 mm) to a drier period between 1999-2008 (433 mm). Prior to this transition, Pearson (r-value) correlation coefficients are highest for ion microprobe analyses of Sr-Y, Y-P, and Mn-Si. After the transition, the best correlations include Mg- δ^{18} O, Mg-Sr, and Sr-Ba. Principal component analysis of trace element data from the LA-ICP-MS traverse indicates that these two sets of correlations reflect two modes of trace element delivery to the cave.

During drier periods, dripwaters are sourced from a reservoir with a decadal residence time that accumulates Mg, Sr, and Ba in the carbonate vadose zone. In wetter periods, dripwaters deliver colloidal material to the cave along more direct pathways, which increases P, Cu, Sr, Na, U, Mn, and Si concentrations in the speleothem. We note that similar patterns of fluorescence intensity, P, and Cu concentrations support the hypothesis that fluorescent bands in Soreq speleothems are caused by organic colloids.

Holocene changes in moisture source and aridity in coastal California recorded by δ^{18} O and U isotopes of opal speleothems.

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The hydrologic cycle in California underwent profound changes over the course of the Holocene. Paleoclimate records from the mountains of eastern California document mid-Holocene mega-droughts that left Sierra Nevada lake levels much lower than present. However, pollen records from the central California coast point to a possible disconnect between the hydrologic balance of coastal and inland sites, suggesting that variations in moisture source and pathway can lead to wet conditions inland while leaving the coast dry. Relatively few terrestrial paleoclimate records have been developed for the California coast that permit evaluation of changes in water balance during the Holocene. We present records of uranium and oxygen isotope variability in an opal speleothem from Pinnacles National Park for 3 to 15.5 ka generated using secondary ion mass spectrometry (SIMS). Uranium isotopes are uniquely sensitive to changes in water balance (precipitation minus evapotranspiration, or P-ET), while oxygen isotopes primarily reflect changes in moisture source. U isotopes document a moderate increase in aridity along the central California coast until ~ 6.5 ka, consistent with the timing of peak aridity in Sierra Nevada lake records. Oxygen isotopes suggest central California precipitation was dominated by subtropical storms during the early- mid Holocene, and North Pacific sourced storms after ~ 5 ka. This record suggests no disconnect in timing but does point to a difference in the magnitude of hydrologic variability between coastal and inland sites in central California, indicating Holocene mega-droughts were more acutely felt in inland mountain ecosystems.

Trace element analysis of speleothems using micro-XRF scanning

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The μ -XRF method is a relatively fast, cheap and nondestructive method for multi element scanning of geological materials. This method has been well established on finely laminated sediments in our laboratory to distinguish e.g. detrital and authigenic layers using an EAGLE III XL.

To apply this method for speleothems, the multi element trace analyses were performed on finely polished speleothems. These samples can reach a maximum surface dimension of up to 30×30 cm. We run at least two different profiles for replication with a spot size of 53 µm, steps of 50 µm and a beam time of 50 s. The routinely used element spectrum comprises Mg, Al, Si, P, S, Cl, K, Ca, Ti, Mn, Fe and Sr and the potential of this method will be discussed on examples of different speleothems from Germany and Kyrgyzstan.

The first example is a speleothem from the recently opened Blessberg Cave in Thuringia, Germany, situated in Triassic marine limestones. The stalagmite is characterized by transparent yellow color with hardly recognizable lamination. From the entire measured element spectrum only Ca, Sr, S, Fe, K and Si are suitable as climatic proxies. Sr seems to increase together with growth rate and may be an indicator for wetter periods. The Ca/Sr ratio shows a good correspondence to the sulfur pattern.

Two further stalagmites from caves, situated in Upper Devonian limestone, near the SE border of the Fergana Basin, Central Asia, have been analyzed. Both speleothems are characterized by immediately alternating light and darker colored laminae, whereas the darker lines are characterized by more soil-derived elements, demonstrated by the good correlation of AI with K, Si, Fe, and Ti. For a better understanding of the environmental factors that influence element variations in speleothems, we install monitoring including microclimatic parameters, analysis of drip water, bulk rock and soil chemistry.

A Holocene Stalagmite Paleoclimate Record from Northern Venezuela: A Record of Caribbean Climate Change

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The dearth of studies and data in the tropics hinders our understanding of atmospheric and oceanic interactions between the low latitudes and the rest of the globe. To understand better the interactions, specifically between the Caribbean and the North Atlantic, three stalagmites were collected from Cueva Zarraga in the Falcón Mountains of northwestern Venezuelan and analyzed to determine local paleoclimatic history. Stalagmites ages were determined by U/Th disequilibrium and show a nearly complete Holocene record. Growth rates of the smallest stalagmite, VCZ-1, averages 30 years/mm and ranges from 8 to 53 years/mm, while the largest stalagmite, VCZ-2, averages 10.8 years/mm and ranges from 2.1 to 62.7 years. Both the carbon and oxygen isotope records preserve quasi-millennial oscillations and show a major depletion shift from the last glacial period into the Holocene, suggesting warmer and wetter conditions during the Holocene. The preservation of quasi-millennial oscillations and of high frequency multi-decadal changes by the δ^{13} C indicates that the soil-vegetation-stalagmite system is acting as an amplifier of the climatic signal produced by climatic events and changes. While tempting to attribute δ^{13} C depletions to decrease of the C4 plant contribution, there is no evidence that the area experienced major vegetation changes. We attribute the δ^{13} C depletion to enhanced recycling of soil CO₂ resulting from canopy effects. In the early Holocene, the δ^{18} O record shows a depletion trend from ~ 11,600, coming out of the Younger Dryas, to 8,000 cal yr BP before reaching the Holocene Thermal Maximum. A prominent δ^{18} O enrichment event is recorded in all the stalagmites that correspond to the 8200 cal yr BP event. Other short-term δ^{18} O enrichment events likely correspond to Bond events 1, 2, 5, and 6. The late Holocene record, like other Caribbean records, indicates that the climate system diverges from insolation and may represent an atmospheric rearrangement that resulted in ENSO increase instability or in reduced seasonal movement of the ITCZ.

Today, Cueva Zarraga is at the northern extent of the Inter-Tropical Convergence Zone (ITCZ) and has two rainy seasons. The cooler and drier conditions of the last glacial period suggest a southern displacement of the ITCZ, also suggested by Brazilian speleothem records that show anticorrelative trends to Cueva Zarraga. The Cariaco Basin and Cueva Zarraga records show very similar trends, except the timing of the Holocene Thermal Maximum. The Cariaco Basin Ti concentration record shows the Holocene Thermal Maximum starts at ~10,000 cal yr BP, while the Cueva Zarraga record suggests a start ~2,000 cal yr BP later, suggesting there is a lag between the erosion leading to the increase in Ti delivery and isotopic composition of precipitation. The close proximity of Cueva Zarraga to Cariaco Basin may allow for a high resolution tropical terrestrial and oceanic climatic response comparison. The late Holocene record in Cueva Zarraga, like other Caribbean records, indicates that the climate system diverges from insolation and may represent an atmospheric rearrangement that resulted in ENSO increase instability or in reduced seasonal movement of the ITCZ.

The Hydrological Cycle Response to Rapid versus Slow Global Warming

Karen Russ, Larissa Back, Zhengyu Liu, Kuniaki Inoue, Jiaxu Zhang, and Bette Otto-Bliesner

Held and Soden (2006) compared climate simulations of the 21st century included in the 4th Assessment Report of the IPCC (2007). All showed an increase of about 7.5% in globally averaged water vapor for each C° increase in globally averaged surface temperature. This result was thought to be explained by plugging a representative surface temperature into the Clausius-Clapeyron relationship. The use of surface temperature was justified by the fact that water vapor is more concentrated in the lower atmosphere.

We find this is not the case for a paleoclimate simulation of the last 22,000 years, where water vapor increases at a rate of only 4.2% per C°. This is not due to relative humidity changes or differences in absolute temperature. Instead, this is due to the geographic pattern of warming during the paleoclimate. Most water vapor resides in the tropics, and an average 1 C° of global surface warming is relatively more concentrated in the tropics for rapid anthropogenic-like warming than for the slow warming of the last deglaciation and Holocene. This is due to thermal inertia of the Southern Ocean, which draws down heat from the atmosphere above it. The rapid warming scenario represents a state of disequilibrium between the atmosphere and ocean in the Southern Hemisphere (S.H.), such that little warming occurs in the higher latitudes of the S.H. atmosphere.

The slower warming of the last deglaciation and Holocene reaches a quasi-equilibrium state, allowing bipolar warming of the atmosphere, with relatively less warming over the tropics. The reduced warming over the tropics translates to a significantly smaller water vapor anomaly over the wet tropics, negatively impacting the global rate of increase in water vapor.

We conclude that the Clausius-Clapeyron relationship applied to *surface* temperature cannot by itself constrain the rate of change in globally averaged water vapor with globally averaged surface temperature. Instead, we propose an alternate formula for predicting water vapor changes that applies more generally to global warming scenarios. Our formula accounts for the three-dimensional spatial variation in the atmospheric temperature anomalies in various warming scenarios.

We also investigate global precipitation and find that it increases at $2\%/C^{\circ}$, a robust response reported by Held and Soden. It should be noted that precipitation anomalies are not constrained by the Clausius-Clapeyron relationship, but rather by the atmospheric energy budget.

Extracting robust Sr/Ca estimates from coral using SIMS

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The ratio of strontium to calcium (Sr/Ca) in coral skeletons provides a highly-resolved archive of past sea-surface temperatures [SST; *Beck et al.*, 1992; *Corrège*, 2006]. However, the accuracy and interpretation of Sr/Ca-based SST reconstructions can be plagued by post-depositional alteration (diagenesis) and coral vital effects. The skeletons of fossil coral, and to some extent modern corals, are highly susceptible to diagenesis in the form of dissolution and/or secondary cements precipitated in skeletal pore spaces. The inclusion of even trace amounts of secondary cements in coral powders milled for conventional mm-scale Sr/Ca analyses via Inductively Coupled Plasma Optical Emission Spectrometry (ICPOES) can create substantial artifacts in paleo-SST reconstructions (e.g. ~1% secondary aragonite results in Sr/Ca offsets equivalent to roughly 0.5°C or more; *Sayani et al.*, 2011). Assuming that diagenetic processes leave the interior of the coral skeleton geochemically intact, as supported by *Cohen and Hart*, 2004 and *Sayani et al.*, 2011, then the high spatial resolution (~20µm) offered by Secondary lon Mass Spectrometry (SIMS) provides a means of extracting the original coral Sr/Ca values from the interior portions of altered fossil coral skeletons. However, the Sr/Ca composition of the coral skeleton at micron-scales is highly variable and may be dominated by biological processes rather than environmental conditions [e.g. *Allison and Finch*, 2004].

Here we assess the accuracy and reproducibility of SIMS analyses of coral Sr/Ca by generating 2-3yr-long, weekly-resolved SIMS Sr/Ca records from three overlapping modern coral cores from Palmyra Island (6°N, 162°W). Bulk Sr/Ca records from the three cores are highly correlated with each other (R=0.6) and with SST (R=-0.74), but exhibit offsets of ± 0.1 mmol/mol from each other (equivalent to $\pm 1^{\circ}$ C). The corresponding SIMS Sr/Ca analyses from each core exhibit relatively large point-to-point variations of ~0.17mmol/mol (1o), compared to ~0.06mmol/mol (1o) in mm-scale Sr/Ca, but their monthly-scale variability resolves the annual SST cycles observed at Palmyra reasonably well. The coralto-coral offsets observed in mm-scale Sr/Ca records are reproduced in the SIMS Sr/Ca records. Uncertainty in SIMS Sr/Ca based on 60 repeat measurements on a single aragonite standard is estimated to be ± 0.026 mmol/mol (1 σ), equivalent to SST errors of $\pm 0.29^{\circ}$ C, more than double the analytical precision of mm-scale Sr/Ca measurements (±0.01mmol/mol, 1o). Error estimates derived from coral SIMS Sr/Ca analyses however suggest that analytical uncertainties may be as low as 0.02mmol/mol (10) or ±0.15°C for coral aragonite, comparable to the ±0.1°C (1o) analytical error for mm-scale Sr/Ca measurements. While our work has demonstrated that coral SIMS Sr/Ca records can approach the fidelity of ICPOES coral Sr/Ca records, in terms of capturing small relative changes in Sr/Ca, the absolute coral Sr/Ca values from overlapping corals differ significantly. Thus, fossil coral Sr/Ca-based SST reconstructions may be associated with uncertainties of ±1°C, unless multiple samples are available from a given time period. In ongoing work, we apply mm-scale and SIMS Sr/Ca analyses to fossil corals from Palmyra Island (Cobb et al., 2003), some of which contain minor to moderate diagenetic overprints (Sayani et al., 2011). As many of these corals overlap in time, we hope to provide robust estimates of paleo-SST through select portions of the last millennium.

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Paleoenvironment and seasonal variation in rainfall at Allia Bay, Kenya 3.97 MA

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This project will reconstruct seasonal patterns of rainfall 3.97 MA at Allia Bay, Kenya using high-resolution serial spot analyses (via SIMS 10 μ m spots in situ) of stable oxygen isotopes in fossil faunal tooth enamel ($\delta^{18}O_{en}$). We expect to reconstruct the local ecology of *Australopithecus anamensis*, the earliest confirmed obligate hominin biped. These first-ever site- and time-specific ecological data are a first step toward understanding the origins of our unique locomotor system.

At tropical latitudes, where Allia Bay is located, seasonal changes in precipitation amounts can result in major shifts in vegetation in open grassland habitats. In contrast, they have limited impact to vegetation in forest ecosystem. The oxygen isotope ratios in enamel of non-drinking species will track intra-annual changes in relative humidity and those of water-dependent species will track variation in precipitation amounts. A comparison between seasonal rainfall patterns and bulk $\delta^{13}C_{en}$ values should distinguish among animals living in closed forest, wooded savanna, open grassland, and mixed habitats.

Resolving Micron Scale δ^{18} O and δ^{13} C Heterogeneity in Cultured Planktic Foraminifera

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Two recent studies by Kozdon et al. (2011; 2009) demonstrated the potential for oxygen isotope analyses by SIMS to quantify depth habitat changes in individual foraminifera shells and to obtain geochemical data from diagenesis-free regions in fossil foraminifera. We have conducted a series of experiments with living foraminifera to quantify the spatial resolving capabilities of coupled SIMS and laser ablation ICP-MS for O and C isotope and Me/Ca analyses. The planktic foraminifera, Orbulina universa, was collected alive and grown in laboratory culture at the Wrigley Marine Science Center on Catalina Island, CA. Specimens were exposed to chemically modified seawater for 12 or 24 hour duration in order to produce bands of isotopic and elementally unique calcite that was embedded within the calcite wall of a shell. Seawater chemical modification included ¹⁸O-enriched seawater + elevated [Ba], ¹³C-enriched seawater + elevated [Ba] and ⁸⁷Sr enriched seawater. SIMS results demonstrate that shell calcite δ^{18} O value shifts of 20% can be fully resolved using a 2x3 µm spot size and that the oxygen isotope data appear to shift synchronously with Ba/Ca changes in shell elemental chemistry, with no discernable spatial offset (Vetter et al., 2013). Although O. universa shells are only 20-25 µm thick, oblique sections through the shell wall allow the SIMS to fully resolve a 50% range in shell δ^{13} C using a 6 µm spot size. Although 8 µm SIMS spots typically improve precision, the larger diameter spot integrates bands of calcite and produces intermediate δ^{13} C values from shell precipitated in both labeled and ambient seawater. SIMS analyses of both C and O isotopes yield data that are consistent with predicted values from previous culture experiments with O. universa (Bemis et al., 1998; Bemis et al., 2000). The coprecipitation of stable isotope and cation tracers in shell calcite highlights the applicability of combining multiple proxies in interpretations of intrashell geochemical heterogeneity in field or fossil samples. These experimental results demonstrate that SIMS analyses of foraminifera shells have the potential to quantify micron scale shell geochemistry as well as paleoenvironmental information from 24 hrs of shell growth. Potential applications for paleoceanographic studies in the fossil record will be discussed.

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Title: Heterogeneity in speleothem records of North American monsoon rainfall

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Abstract: Rainfall in the arid southwestern United States is critical to human occupation of the region. Precipitation occurs via two main mechanisms: winter westerly fronts and the summer monsoon (Adams & Comrie 1997). Climate models and instrumental data predict changes to winter rain (McAfee & Russell 2008, Seager et al. 2007), but summer rain remains unconstrained in models due to its high spatial heterogeneity. Reconstructions of past climate may be one of the only robust ways to understand North American monsoon variability and project it into the future.

Speleothems are excellent sources of past climate information because their calcium carbonate structure retains climate information in many different ways, including oxygen and carbon isotopes (Wagner et al. 2010), trace element composition (Johnson et al. 2006), etc. This climate information is often preserved at high resolution for long periods of time, and can be dated absolutely using uranium-series dating (Edwards et al. 1986). Conveniently, the two rainy seasons in southern Arizona are isotopically distinct: winter rainfall has an average δ^{18} O value of -10‰ VSMOW, whereas summer rainfall averages ~ -5‰ VSMOW. Speleothems in southern Arizona tend to record a seasonal balance of rainfall and can be used to address changes in this balance through time.

We have developed two new speleothem oxygen isotope records covering the last 4000 years from Fort Huachuca Cave and the last 7000 years from Cave of the Bells at 4-5 years resolution each. Both records are well dated and indicate that changes in insolation over the Holocene have affected the balance between monsoon and winter rain, with monsoon rains weakening into the present day. At shorter timescales, however, these two records are not well correlated. There are multiple reasons why this may be true: (1) age model error; (2) cave processes (e.g., cave ventilation or storage in the epikarst); (3) spatial heterogeneity in surface rainfall; and (4) seasonally complicated rainfall isotopic composition patterns (e.g., seasonal balance signal confounding the overall wet vs. dry signal). We are constraining each of these effects via various methods including statistical age-modelling programs (Ault et al. *In Prep.*), extensive modern monitoring/calibration and dripwater modeling (Truebe et al. 2010), modern climate data analysis, and finally high-resolution ion microprobe analyses.

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Cyclostratigraphic evaluation of repetitive sedimentary microfacies from the Green River Formation via X-ray fluorescence scanning: Evidence for Annual, El Niño, and Sunspot Cycles?

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The lacustrine Eocene Green River Formation is well recognized for its extensive sub-millimeter lamination, which has been proposed to express annual, El Niño, and sunspot cycle variability. If validated, these paleoenvironmental signals could provide one of the richest available records of past warm climate behavior during the last major greenhouse climate, potentially spanning yearly to millennial scale resolution. Despite this promise, currently there is surprisingly little understanding of the actual processes behind the generation of these laminae. This is at least partially the result of the small spatial scales involved, usually 100 microns or less, which greatly inhibit traditional means of geochemical investigation. With continuous scanning capabilities down to 100 microns, X-ray fluorescence (XRF) core scanning can help to bridge this gap by providing elemental information at a spatial resolution and degree of continuity not previously possible. Using this powerful tool, 9.96 m of Green River Formation core have been scanned at a 5 mm resolution, and selected intervals have been scanned at a 100 micron resolution, in order to evaluate both large and small scale elemental variability within core material for 16 different elements (Mg, Al, Si, S, K, Ca, Ti, Fe, Cu, Zn, Ga, Pb, Rb, Sr, Zr, Mo). Preliminary results show pronounced antithetic oscillations between siliciclastic (Al, Si, K) and carbonate components (Ca, Sr) at multiple spatial scales, with intervals of highly-enriched redox sensitive elements (S, Mo, Cu, Zn) associated with some siliciclastic-dominated microfacies. Future work will use advanced spectral methods to allow the quantitative evaluation of hypothesized annual, El Niño, and sunspot variability.

In Situ Measurement of Intra-Shell δ^{18} O and Mg/Ca Variability in the Planktic Foraminifer *Globigerinoides sacculifer*: A Case Study from the Pliocene Warm Period

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Paired measurements of oxygen isotope (δ^{18} O) and Mg/Ca ratios in planktic foraminiferal shells are widely used geochemical proxies for reconstructing past sea-surface conditions. However, it is well established that the reproductive stage (gametogenesis) in many Neogene planktic for a miniferal species can add up to $\sim 25\%$ to the total shell mass, and that this gametogenic calcite is grown under different physiological and environmental (water depth) conditions than the pre-gametogenic calcite. Thus, a typical planktic foraminiferal shell is in actuality an aggregate mixture of two phases of biogenic carbonate - ¹⁸O depleted pre-gametogenic calcite and ¹⁸O rich gametogenic calcite. The presence of these two carbonate phases in foraminiferal shells complicates δ^{18} O-based paleoclimate records generated using conventional isotope ratio mass spectrometry that necessitates the analysis of whole shells with the assumption that the shells are well preserved and have a homogenous composition. Here, we use ultra-high resolution techniques such as secondary ion mass spectrometry (SIMS) and electron probe microanalysis (EPMA) to acquire *in situ* δ^{18} O and Mg/Ca ratios, respectively, from minute domains (~10 µm) within individual shells. The *in situ* analyses were performed on fossil shells of the modern species, Globigerinoides sacculifer, preserved in a deep-sea record of the Pliocene Warm Period (circa 3 million years ago) recovered from the West Pacific Warm Pool at ODP Site 806. The SIMS based analyses show that the δ^{18} O of gametogenic calcite is 1-2‰ higher than in the pre-gametogenic calcite of Gs. sacculifer. Furthermore, mass balance calculations using the mean δ^{18} O of the gametogenic and pre-gametogenic calcites predict a whole shell δ^{18} O composition that is ~1.7% lower than the published 'whole shell' δ^{18} O values for Gs. sacculifer at this same location. We tentatively attribute this discrepancy to the addition of ¹⁸O-rich carbonate to the Gs. sacculifer shells by post-depositional diagenesis, but this supposition awaits confirmation. By contrast, in situ EPMA measurements indicate that the Mg/Ca ratios in the pregametogenic and gametogenic calcites are indistinguishable. Moreover, the in situ Mg/Ca ratios yield sea-surface temperatures (~28°C) comparable to those of the published 'whole shell' Gs. sacculifer record. The preliminary findings of this study highlight the potential of in situ, SIMSbased δ^{18} O analyses for enhancing the fidelity of records of past sea-surface conditions, most notably sea-surface salinity as reflected by the δ^{18} O of seawater.

Seasonal variability in sea surface temperature, salinity, and carbonate chemistry during Greenhouse Extremes

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Earth and Planetary Sciences Dept., Univ. of California, Santa Cruz, CA 95064 In theory, given the scale of global carbon emissions and warming, the Paleocene-Eocene Thermal Maximum should have been accompanied by a more energetic hydrologic cycle, manifested by steeper meridional sea surface salinity gradients (E-P), and by increased seasonality of precipitation. Efforts to reconstruct changes in SSS and seasonality of regional SST and SSS are now being aided by recent technical advances (i.e., nanoSIMS; see Kozdon, Kelly et al.) that allow for the characterization of elemental and isotope compositions on the microscale and finer. To date, such work has revealed a high degree of variability in the trace metal and isotopic ratios of individual planktonic foraminifer shells from Eocene pelagic sequences. Though some of the intrashell variability of oxygen isotopes in shells from pelagic sequences appears to be related to a mix of secondary calcite with primary, it is likely that much of the intra- and intershell variability of foraminifera represents signals of subannual to interannual variation in the physiochemical properties of local seawater. If so, this could be tested by measuring trace metal ratios of individual shells in combination with isotopes, particularly in populations of shells from shallow marine, coastal sequences. In theory, by combining metal and isotope ratios it should be possible to reconstruct the seasonal variability of several critical properties of coastal seawater. This could even be achieved with more traditional analytical methods. For example, single shell analysis by LA-ICPMS followed by stable isotope analysis by IRMS of the same shells could be used to reconstruct details of the annual ranges of SST, SSS, and seawater carbon chemistry. The combination of Mg/Ca with δ^{18} O can be used to reconstruct local salinity variations as influenced by E-P and runoff. Similarly, coupling of B/Ca and other metal ratios with δ^{13} C has the potential to supply information on seasonal variability in the carbonate chemistry of surface waters. If successful, such sampling strategies have the potential to yield critical information on how the climate system responded to extremes in greenhouse forcing in Earth's past.

Extremely high temperatures and paleoclimate trends recorded in Permian ephemeral lake halite

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ABSTRACT

Although the late Paleozoic deglaciation is arguably one of the best deep-time analogs for current and predicted climate change, quantitative paleotemperature data from this interval are generally lacking. We reconstruct extreme paleoweather conditions and paleoclimate changes from Permian Nippewalla Group (probably uppermost Leonardian/Kungurian; North America) ephemeral lake halite by using fluid inclusion homogenization temperatures to directly measure the water temperature when the halite precipitated; in these depositional settings, this is an excellent air temperature proxy. Extremely high temperatures, to 73 °C, and large diurnal temperature ranges are evidenced in the lower Nippewalla Group, suggesting conditions more extreme than anywhere on Earth today. In contrast, the upper Nippewalla Group was cooler; maximum temperature was 43 °C and diurnal temperature ranges were smaller, though even these conditions are similar to modern extremely hot environments. Comparison to prior studies suggests that these results may be indicative of regional patterns. This study represents the first pre-Quaternary high-resolution quantitative data set of extreme paleoweather and possible paleoclimate trends from fluid inclusions in halite, and provides new insight into climate change during the late Paleozoic deglaciation.

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