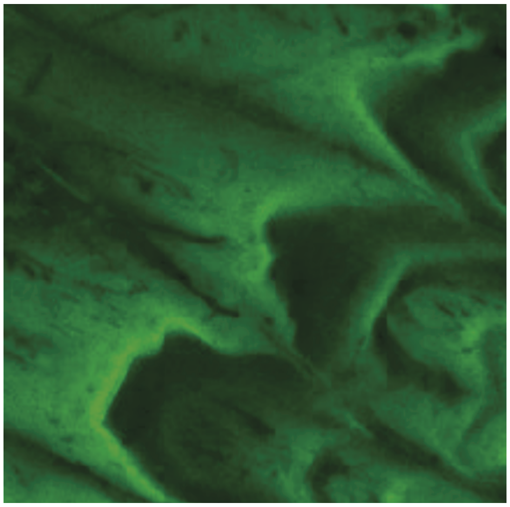

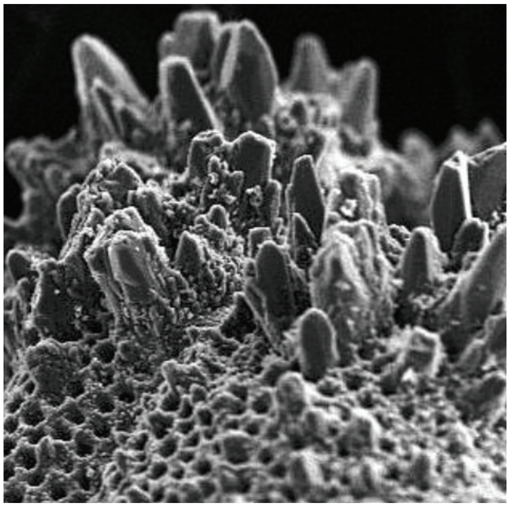

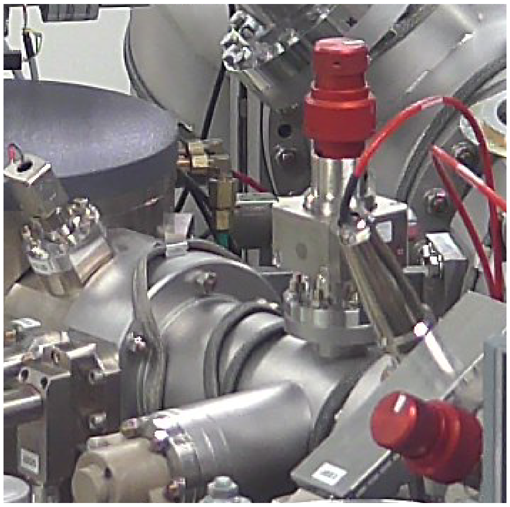

HiRes2015

WiscSIMS

High Resolution Proxies of Paleoclimate

University of Wisconsin-Madison

May 31 - Jun 3, 2015

Sponsored by

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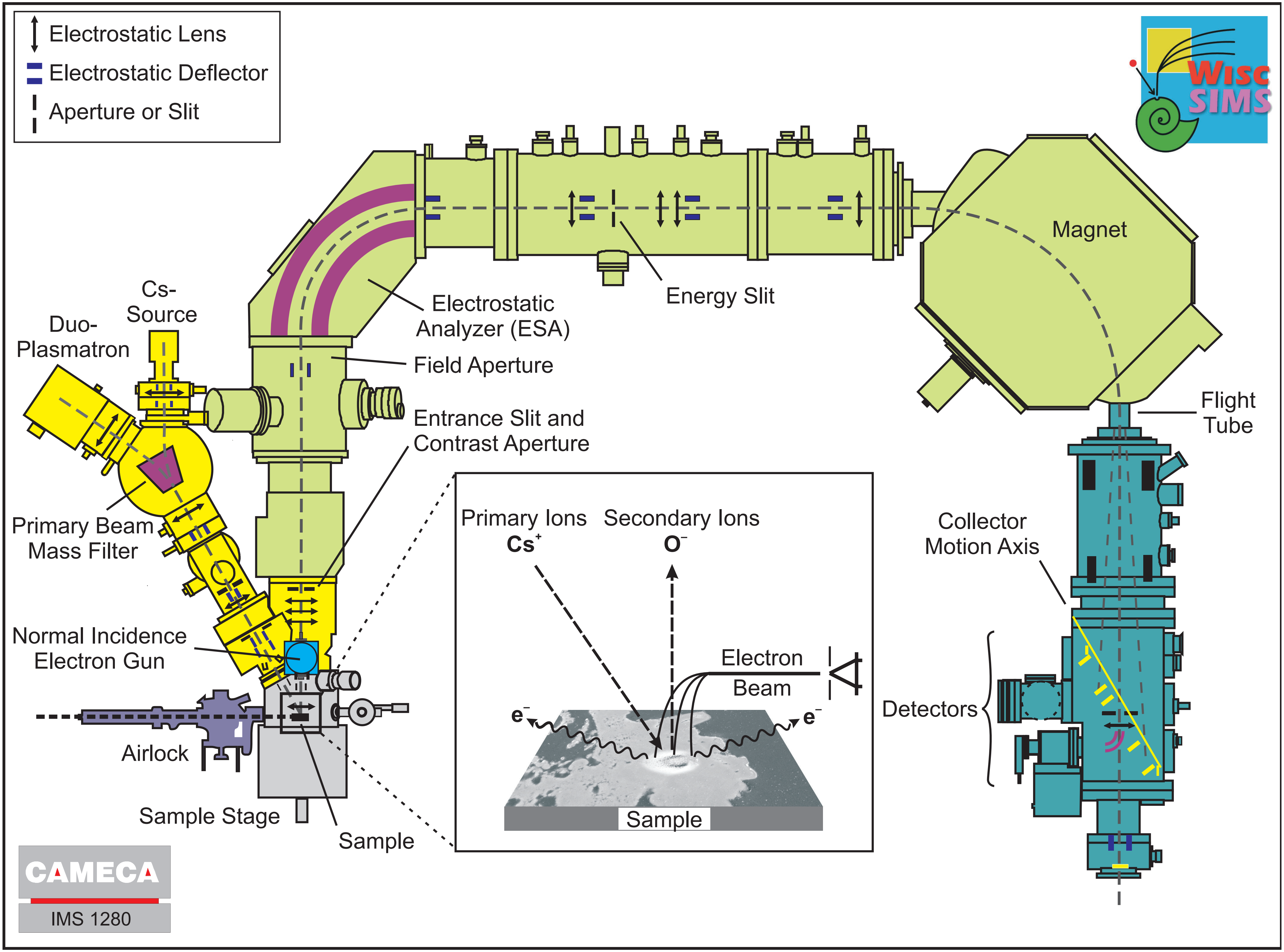
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HiRes2015
WiscSIMS Workshop- High Resolution Proxies of Paleoclimate
Madison Wisconsin May 31-June 3, 2015

Sun. May 31, 2015	
4:00-6:00 PM	Open House at WiscSIMS Lab (Weeks Hall, 1215 W. Dayton St.) Registration, upload talks and set-up posters
6:00-9:00 PM	Barbeque in Weeks Hall Courtyard & WiscSIMS Open House

Mon. June 1	**Room A140, Weeks Hall**
8:00-9:00 AM	**Light Breakfast**, registration, upload talks and set-up posters

Morning Session (Chair: Ian Orland)

9:00-9:20	**John Valley** Welcome and Introduction
9:20-10:20	**Noriko Kita (Tutorial) "**SIMS Basics"
10:20-10:40	**Ian Orland & Kouki Kitajima** WiscSIMS-Live Part 1
10:40-11:00	Break
11:00-12:00	**John Valley (Tutorial)** "In situ isotope geochemistry by SIMS: Accuracy vs. Precision"

Group photo & Lunch (12:00PM-2:00PM)

Group Photo will be taken in Weeks Hall courtyard immediately following the morning session. Lunch will be served at *Steenbock's on Orchard* in the Wisconsin Institute for Discovery (WID).

Afternoon Session (Chair: John Valley)

2:00-3:00	**Richard Alley (Keynote)** "Abrupt climate change: An update, and challenges for high-resolution sampling"
3:00-3:20	**Jack Williams,** Kevin Burke, and Matt McGlone "Extrinsic and intrinsic causes of past abrupt changes in terrestrial ecosystems"
3:20-3:40	Break
3:40-4:10	**Margaret Schoeninger (Keynote)** "Paleoclimate and tooth enamel. Where do we go from here?"
4:10-4:30	**Melanie Beasley**, Ian Orland, John Valley, and Margaret Schoeninger "SIMS reveals diagenesis and seasonal paleoprecipitation at Allia Bay, Kenya 3.97 Ma"
4:30-4:50	**Ian Orland & Kouki Kitajima** WiscSIMS-Live Part 2
4:50-5:10	**Jake Cammack**, Kouki Kitajima, Adam Denny, and Ben Linzmeier "A 5 cm^2 field area: QGIS as a tool for the integration of microanalytical data"

Banquet (Great Hall at Memorial Union)

6:00 PM	Cocktail Hour
7:00-9:00 PM	Dinner

Tue. June 2	**Room A140, Weeks Hall**
8:30-9:00 AM	**Light Breakfast**

Morning Session (Chair: Reinhard Kozdon)

9:00-10:00	**Ian Orland (Tutorial)** “Developments and challenges in ion microprobe studies of speleothems and biocarbonates”
10:00-10:20	**Yongli Gao**, Harry Rowe, Jessica Buckles, Hai Cheng, and Lawrence Edwards “High resolution paleoclimate records from Yucatán speleothems spanning the past 2000 years”
10:20-10:40	**Mellissa Cross**, David McGee, Wallace Broecker, Jay Quade, Jeremy Shakun, Hai Cheng, Yanbin Lu, Lawrence Edwards ”Records of paleoclimate and paleohydrology from slow-growth Great Basin Speleothems”
10:40-11:00	Break
11:00-11:30	**Ronald Amundson (Keynote)**, Erik Oerter, Warren Sharp, Jessica Oster, Angela Ebeling, John Valley, Reinhard Kozdon, Ian Orland, Kenneth Ludwig, John Hellstrom, Jon Woodhead, Janet Herget, Oliver Chadwick “High resolution paleoclimate records from laminated carbonates in soils”
11:30-11:50	**Erik Oerter**, Angela Ebeling, Ronald Amundson “Pedothem carbonates record the aridification of the Atacama Desert”
11:50-12:10	**David Fike** “The environmental importance of microbial sulfate reduction and disproportionation: Insights from SIMS-based δ^{34}S measurements”

Lunch at Steenbock’s on Orchard (12:10PM-1:40PM)

Afternoon Session (Chair: Howard Spero)

1:40-2:10	**Kim Cobb (Keynote),** Luke Chambers, Amelia Longo, Ellery Ingall, Jessica Moerman, Stacy Carolin, Nele Meckler, Jess Adkins, Victoria Smith, Lydia Finney, Syria Lejau, Jenny Malang, Andrew Tuen, Alison Pritchard “The Toba super-eruption: Micro-scale traces of a global-scale climate event?”
2:10-2:40	**Reinhard Kozdon (Keynote)**, Clay Kelly, Howard Spero, and John Valley “Getting the big picture from a small spot: Multi-proxy, multi-instrument *in situ* measurements in foraminifera”
2:40-3:00	**Samantha Bova**, Timothy Herbert, Baylor Fox-Kemper “Assessing the natural variability of the deep ocean using individual benthic foraminifera”
3:00-3:30	**Clay Kelly (Keynote)**, Reinhard Kozdon, Jody Wycech, and John Valley “Forams Forever: use of SIMS δ^{18}O and EPMA Mg/Ca analyses of planktic foraminiferal shells to reconstruct the hydrological cycle during past climate states“

Posters (3:30PM-5:30PM)

Beverages and Refreshments will be provided.

<u>**Wed. June 3**</u>	**Room A140, Weeks Hall**
8:30-9:00 AM	**Light Breakfast**

Morning Session (Chair: Clay Kelly)

9:00-10:00	**Howard Spero (Keynote)** “Quantifying isotopic variations in cultured planktic foraminifera at the micron scale”
10:00-10:20	**Lael Vetter**, Brad Rosenheim, Alvaro Fernández, and Torbjörn Törnqvist “Marsh Madness: An early Holocene sea-level record from peat and paleosols in southeastern Louisiana”
10:20-10:40	**Jody Wycech** Clay Kelly, Reinhard Kozdon, and John Valley “Calibration of in situ SIMS δ^{18}O values to whole shell δ^{18}O compositions using Holocene planktic foraminifera”
10:40-11:00	Break
11:00-11:30	**Alexander Gagnon (Keynote)** “The impact of small-scale heterogeneity on proxies in biomineral archives”
11:30-11:50	**Ann Russell**, Jennifer Fehrenbacher, Howard Spero, Alex Gagnon “Identifying cultured foraminiferal calcite for geochemical paleotemperatures calibrations using ^{87}Sr”
11:50-12:10	**Hussein Sayani**, Kim Cobb, Anne Cohen, Brian Monteleone, Heather Crespo “Reliable Sr/Ca estimates from scleractinian corals using SIMS: Challenges and implications”

Lunch at Steenbock’s on Orchard (12:10PM-1:40PM)

POSTERS

Céline Defouilloy, Noriko Kita, Peter Sobol, Neal Lord, Travis Tenner, and Daisuke Nakashima "New WiscSIMS IMS 1280 100 nm-resolution primary beam deflection system, for accurate aiming of returned samples"

Adam Denny, Reinhard Kozdon, Kouki Kitajima, Maciej Sliwinski, Mike Spicuzza, and John Valley "δ^{18}O and δ^{13}C-zoned carbonate cements as records of porewater temperature and composition in siliciclastics: In-situ SIMS analyses from early Paleozoic sandstones in the Illinois Basin, USA"

Kouki Kitajima, Ariel Strickland, Michael Spicuzza, and John Valley "Improvement in matrix correction of δ^{18}O analysis by SIMS for pyralspite and Cr-pyrope garnets"

Benjamin Linzmeier, Reinhard Kozdon, Shanan Peters, and John Valley "Variability of oxygen isotope ratios on the scale of tens of microns in Nautilus shell aragonite"

Kerry McLeran, Liliana Lefticariu, Matthew Therrell, and Justin Schoof "δ^{18}O analysis in tree rings of Pterocarpus angolensis growing in Zimbabwe"

Ian Orland, Lawrence Edwards, Hai Cheng, Reinhard Kozdon, and John Valley "A spatial gradient of seasonal monsoon signals in East Asian speleothems"

Ian Orland, Reinhard Kozdon, Ben Linzmeier, Jody Wycech, Maciej Sliwinski, Kouki Kitajima, Noriko Kita, and John Valley "Enhancing the accuracy of carbonate δ^{18}O and δ^{13}C measurements at WiscSIMS"

Tamil Selvan "Impact analysis of climate change on the dynamics of glaciers, Garhwal Himalaya"

Maciej Śliwiński, Kouki Kitajima, Reinhard Kozdon, Michael Spicuzza, John Fournelle, Adam Denny, and John Valley "SIMS bias on isotope ratios in dolomite-ankerite: δ^{18}O & δ^{13}C matrix effects"

Richard Smith, Ursula Röhl, Thomas Westerhold, Steve Bohaty, Cédric John, and Paul Wilson "Sub-orbital climate variability in the late Oligocene North Atlantic Ocean"

Hanzhi Zhang, Huayu Lu, Xisheng Xu, Xiaoming Liu, and Tao Yang, Thomas Stevens, Zhiwei Xu, Tian Zhang, Fang Lei, Han Feng "Detrital zircon U-Pb age evidences for provenance of Chinese Loess"

Jiang Zhu, Zhengyu Liu, Xu Zhang, Ian Eisenman, and Wei Liu "Linear weakening of the AMOC in response to lowering ice-sheet topography in CCSM3"

Oral Presentation: We have both PC and Mac desktop computers available for presentations with the latest versions of Powerpoint. Please upload your presentation file using USB on Sunday during the Open House or in the morning prior to your session. If you would like to use your laptop for the presentation, please test your computer for connectivity prior to your session.

Poster Presentation: Poster boards will be located in the hallway outside the meeting room. Please hang your poster on Sunday afternoon or Monday with the provided pins. Posters should be taken down after lunch on Wednesday.

Wireless Internet Access (SSID=UWNet): If you stay at the Wisconsin Union Hotel, they will provide you with a guest NetID that will allow you to logon to UWNet, which you can use inside Weeks Hall (Department of Geoscience) and other areas across campus.
Without a guest NetID, you can also register to use UWNet as a guest for a day.
If you are not staying at the Union Hotel, but need a guest NetID, please see Jim Kern or Noriko Kita.

Abrupt climate change: An update, and challenges for high-resolution sampling

Richard B. Alley
Department of Geosciences, and Earth and Environmental Systems Institute
The Pennsylvania State University
517 Deike Building, University Park, PA 16802
rba6@psu.edu

Abrupt climate changes with a center of action in the North Atlantic are now well-known and reasonably well-characterized from the ice age and deglaciation. Signals propagated to and then across the Southern Ocean. Some of the northern coolings were accompanied by ice-sheet surges triggered by northern subsurface warmings in response to reduced wintertime sinking of chilled surface waters, and these surges may have forced the intertropical convergence zone (ITCZ) far to the south. Details of monsoonal and ITCZ sensitivity are emerging but remain fuzzy. Rates of sea-level rise, and possible implications for future sea-level changes and stability of the West Antarctic ice sheet, remain very fuzzy. Much exciting work remains to be done.

High Resolution Paleoclimate Data from Laminated Carbonates in Soils

Ronald Amundson[1], Erik J. Oerter[1], Warren D. Sharp[2], Jessica L. Oster[3], Angela Ebeling[4], John Valley[5], Reinhard Kozdon[5,8], Ian J. Orland[5,9], Kenneth R. Ludwig[2], John Hellstrom[6], Jon D. Woodhead[6,], Janet M. Hergt[6], Oliver A. Chadwick[7]

[1]Department of Environmental Science, Policy and Management, 145 Mulford Hall, University of California, Berkeley 94720, USA.
[2]Berkeley Geochronology Center, 2455 Ridge Rd., Berkeley, CA 94709, USA.
[3]Department of Earth and Environmental Sciences, Vanderbilt University, Nashville, TN, USA.
[4]Wisconsin Lutheran College, Milwaukee, USA.
[5]WiscSIMS, Department of Geoscience, University of Wisconsin-Madison, WI, USA.
[6]School of Earth Sciences, The University of Melbourne, Melbourne, VIC 3099, Australia.
[7]Department of Geography, University of California, Santa Barbara, CA, USA.
[8]Current address: Department of Marine and Coastal Sciences, Rutgers University, New Brunswick, NJ, USA.
[9]Department of Earth Sciences, University of Minnesota, Minneapolis, MN, USA.

Carbon and oxygen stable isotopes in soil-formed carbonate have provided great insights into continental paleoclimate (Cerling, 1984) and paleoatmospheric chemistry over long expanses of Phanerozoic time. However, the present approach suffers from an inherently coarse time resolution: data from one soil or paleosol is generated, and in the geological record, paleosols may be emplaced in sediments on 10^5 y time intervals or longer. Additionally, soil carbonate commonly represents a time-integrated signal, and century to millennial scale climate episodes are homogenized within a given sample.

While soils are complex and inherently self-homogenizing systems, gravelly soils in arid climates are unique exceptions. Once emplaced by fluvial processes, large gravels or cobbles are both resistant to movement, and maintain varying degrees of porosity within the gravelly matrix. These conditions, in carbonate forming environments, leads to the progressive, and unimpeded, growth of carbonate laminations on gravels. The carbonate coatings on gravels are seldom continuous around the entire clast, and the orientation appears to be driven by thermal gradients in soils that favor the formation of carbonate in warmer and lower carbonate solubility micro-environments (Amundson et al., 1997). Once initiated, laminations can grow continuously, though the history of any given clast may be subject to truncation and overgrowth processes that can complicate the stratigraphic interpretation without adequate microscopic investigation and geochronological analyses. It has long been suspected that these laminations harbor long-term and high resolution information (e.g. Amundson et al., 1996), but only recent advances in U-series dating (e.g. Sharp et al., 2003), and micron scale sampling techniques for both U-series dating (Eggins et al., 2005) and C and O isotope analyses (http://www.geology.wisc.edu/facilities/wiscsims/index.html) have provided the sampling refinement needed to fully realize the potential climatic record embedded in soil carbonate.

We review our recent work on the use of SIMS for (a) millennial scale stable C and O isotope records in the Wind River Basin of Wyoming (over the past 120 Ka) and (b) late Tertiary/early Quaternary climate change in the Atacama Desert, Chile. In Wyoming, the combined high resolution dating and stable isotope records provide a unique understanding of rainfall and atmospheric circulation in the continental interior, one that has significant differences compared to the records found nearer the Pacific coast. In Chile, the stable isotope record documents a steady decline in moisture and plant density in the early Quaternary. However, the samples from Chile exceed the temporal reach of U-series dating, and reveal the opportunity and need for new methods of carbonate dating. In summary, carbonate laminations can rival speleothems or groundwater carbonate records in terms of temporal climate clarity, and excel in terms of their response to short term climate trends and in their ability to be widely applied, since carbonate bearing soils exist on more than 15% of the Earth's surface.

Amundson, R., O. Chadwick, C. Kendall, Y. Wang, M. DeNiro, Isotopic evidence for shifts in atmospheric circulation patterns during the late Quaternary in mid-North America. *Geology* **24**, 23 (Jan, 1996).

Amundson, R., R. C. Graham, and E. Franco-Vizcaino. "Orientation of Carbonate Laminations in Gravelly Soils Along a Winter/Summer Precipitation Gradient in Baja California, Mexico." Soil Science 162, no. 12 (Dec 1997): 940-52.

Cerling, T.E. The Stable Isotopic Composition of Modern Soil Carbonate and Its Relationship to Climate. *Earth and Planetary Science Letters* **71**, 229 (1984).

Eggins, S.M., et al., In situ U-series dating by laser-ablation multi-collector ICPMS: new prospects for Quaternary geochronology. Quaternary Science Reivews 24:2533-2538.

Sharp, W.D., K. R. Ludwig, O. A. Chadwick, R. Amundson, L. L. Glaser, Dating fluvial terraces by 230Th/U on pedogenic carbonate, Wind River Basin, Wyoming. *Quaternary Research* **59**, 139 (2003).

SIMS reveals diagenesis and seasonal paleoprecipitation at Allia Bay, Kenya 3.97 MA

Melanie M. Beasley[1], Ian J. Orland[2], John W. Valley[2], and Margaret J. Schoeninger[1]
[1]Department of Anthropology, University of California, San Diego, CA;
[2]Department of Geoscience, University of Wisconsin, Madison, WI

The ecological niche that early hominins exploited is assumed to have played an essential role in the origins of our lineage and selection for distinguishing characteristics such as bipedalism. Therefore, reconstructing the paleoenvironment is essential for understanding the contributing and motivating factors that resulted in such significant morphological changes. Paleoenvironmental reconstructions in East Africa often rely on surface-collected fossil fauna species lists, carbon isotopes from paleosol carbonates, and bulk carbon and oxygen isotope data from tooth enamel to interpret the past environment. However, these types of data traditionally combine multiple temporal and geographically dispersed components. This project will reconstruct seasonal patterns of rainfall 3.97±0.03 Ma at Allia Bay, Kenya to refine the definition of a mosaic paleoenvironment of *Australopithecus anamensis*, the earliest confirmed obligate hominin biped. Seasonal rainfall patterns are reconstructed using a secondary ion mass spectrometer (SIMS) to generate high-resolution serial spot analyses (13 µm spots) of stable oxygen isotopes in fossil faunal tooth enamel ($\delta^{18}O_{en}$) from a well-characterized excavation. Area 261-1 at Allia Bay represents one of the few excavations in East Africa with *in situ* material recovered with deposition limited to approximately 60 ka of time that ensures relatively high-temporal-resolution paleoenvironment data will be generated.

This presentation will also specifically address the issue of identifying diagenesis (post-depositional alteration) in tooth enamel, a material that has long been assumed to be resistant to diagenesis. Previous research identified mineral structure change in the tooth enamel crystal structure using cathodoluminescence (CL), an imaging method that utilizes photon emissions to identify elements in minerals (Schoeninger et al. 2003). The CL results indicate that portions of the outer layer of enamel have altered crystal structure and ion microprobe data confirm the alteration of the biogenic apatite in tooth enamel (Kohn et al. 1999). Although tooth enamel is assumed to be resistant to diagenesis, it is unclear whether changes identified by CL correspond to altered isotope ratios at the altered/unaltered boundary. It was not until technological advancements with instrumentation, such as the SIMS, that the question of diagenesis of oxygen in enamel could be addressed because oxygen values could not be generated at a high enough resolution to test this question. The SIMS ability to generate serial spot analyses at a scale of 13 µm spots *in situ* ensures the boundary between altered and unaltered tooth enamel can be accurately characterized for changes in the $\delta^{18}O_{en}$ values. The aim of this research project is to identify areas of enamel diagenesis, clarify previous notions about enamel preservation in the fields of paleoanthropology and archaeology, and use the data from unaltered enamel regions to reconstruct the seasonal patterns of rainfall at an early hominin site.

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, seasonality has 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. The fossil enamel analyzed in this study represent fauna occupying the Turkana Basin during a fluvial phase when the Omo River (originating in the Ethiopian Highlands) provided the most important water source, which based on previous work, would have tracked the precipitation changes.

This presentation will highlight the variable seasonality recorded during enamel development for browsers (giraffidae, elephantidae, and deinotheriidae) and grazers (hippopotamidae, suidae and bovidae) indicating the different seasonal impact to $\delta^{18}O_{en}$ within a single mosaic habitat. For mid-sized herbivores, enamel deposition occurs at an approximate daily rate of 10 µm, which is within the SIMS spot analysis capability. Previous serial samples of bulk powder enamel in modern gazelle teeth indicate that the seasonal rainfall at Lake Turkana has an intra-annual variation of approximately $\Delta^{18}O_{en} = 2.5‰$ (Kohn et al. 1998). The fossil samples represent intra-annual variation with the approximate range of amplitude difference in seasonal change in oxygen isotope values being as follows: browsers = 3.0‰; grazers (suidae and bovidae) = 2.5‰; hippopotamidae = 1.5‰. Overall the range of $\delta^{18}O$ values fluctuated for the species by 9‰ for the browsers and by 10‰ for the grazers at the site during the period of enamel development represented by these samples. This snapshot of seasonal rainfall recorded at Allia Bay suggests a great amount of variation in the source oxygen isotope values that *Au. anamensis* would have had to cope with during its occupation at the site.

Phylogenetic analysis suggests that each site-sample associated with *Au. anamensis* and *Au. afarensis* captures a different point along the evolutionary trajectory of early hominins, so it is critical to reconstruct the paleoenvironment of each site to evaluate the interplay between habitat and human evolution. These first-ever site- and time-specific ecological data are a step toward understanding the seasonality of the environment where our unique locomotor system flourished.

Kohn MJ, Schoeninger MJ, Valley JW. 1998. Variability in oxygen isotope compositions of herbivore teeth: reflections of seasonality or developmental physiology? Chem Geol 152:97-112.

Kohn MJ, Schoeninger MJ, Barker WW. 1999. Altered states: Effects of diagenesis on fossil tooth chemistry. Geochim Cosmochim Acta 63:2737-2747.

Schoeninger MJ, Hallin K, Reeser H, Valley JW, Fournelle J. 2003. Isotopic alteration of mammalian tooth enamel. Int J Osteoarchaeol 13:11-19.

Assessing the natural variability of the deep ocean using individual benthic foraminifera

Samantha Bova, Timothy Herbert, Baylor Fox-Kemper
Brown University, Department of Earth, Environmental and Planetary Sciences, Institute at Brown for the Study of Environment and Society, Providence, RI 02912
Email: samantha_bova@brown.edu

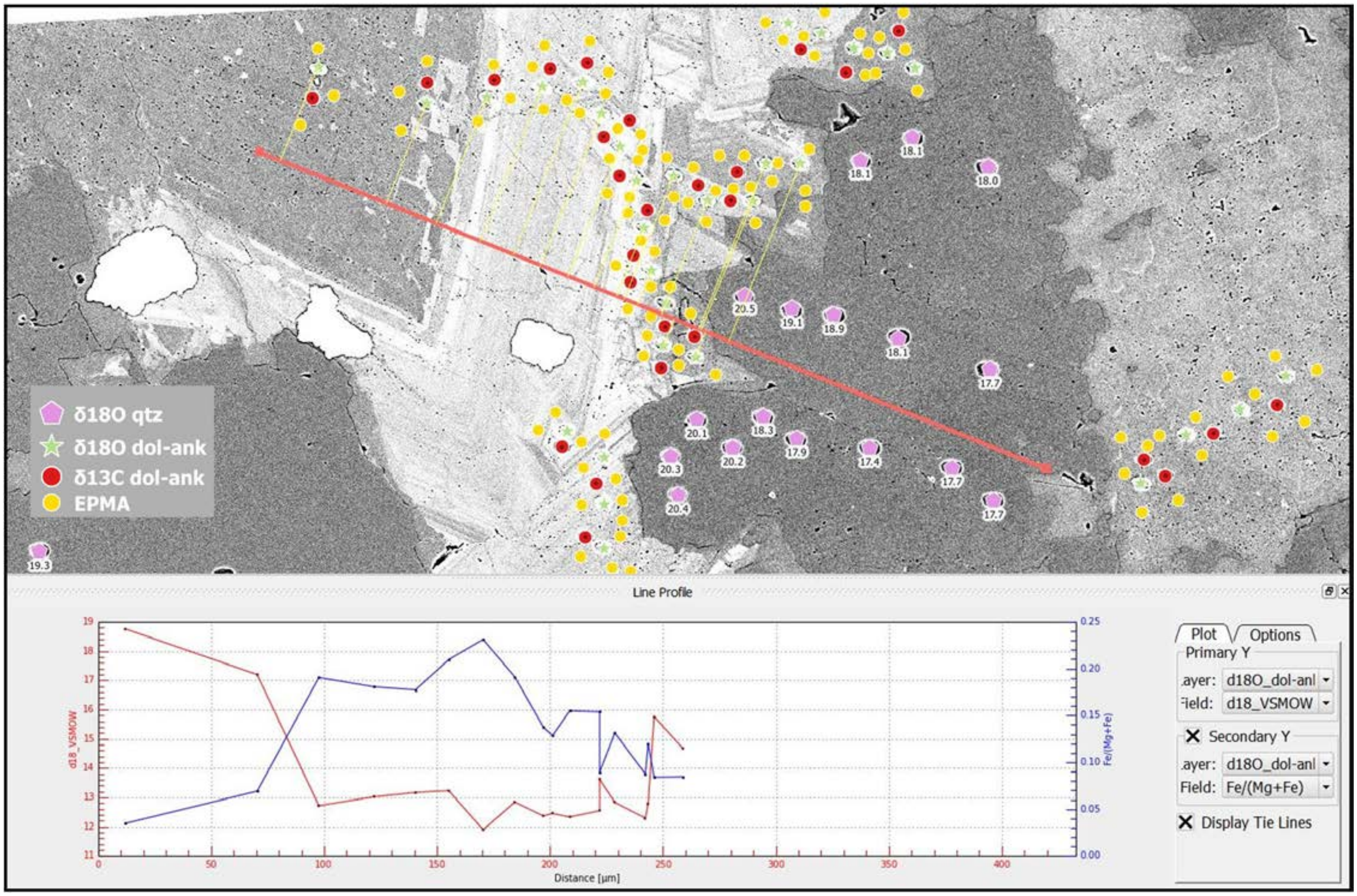
Temperatures in the deep ocean (below 700 m) are rising at historically unprecedented rates, on the order of 0.1°C/decade (Trenberth and Fasullo, 2013; Purkey and Johnson, 2010). When summed globally since 1999, the increase in deep ocean heat content may account for the current hiatus in anthropogenic global warming (Balmaseda et al., 2013). However, attributing the hiatus to deep-ocean warming is not straightforward for two reasons. First, deep ocean water masses are old and have not been at the sea surface where they can exchange heat and gases with the atmosphere since well before industrialization (Gebbie and Huybers, 2012). Second, the historical record is short, spanning just the last 63 years. Therefore, though warming at depth is certainly unprecedented in the historical record, longer records are required to determine if modern rates of deep-ocean warming are truly outside the bounds of natural variability.

Deep-sea sedimentary records provide the opportunity to extend records of deep ocean variability further back in time. We use the oxygen isotopic signature of **individual** *Uvigerina peregrina*, a benthic foraminifer, to assess variability in deep ocean temperature and salinity at 1023 m water depth in the Eastern Equatorial Pacific. We exploit the short life span of individual foraminifera, about 2-4 weeks, to provide approximately month long snapshots of deep ocean properties during five 200-yr intervals during the Holocene (past 10 kyrs). Within each interval we measure 40 individual *Uvigerina*, providing 40 month-long measures of deep ocean properties. Based on these data, we find that two of these 200-year intervals, exhibit larger deep-water variability than that observed during the past two centuries with high confidence. Thus current rates of warming observed in the deep ocean are *not* unprecedented and are well within the background levels of natural deep-water variability. However, though current rates of warming in the deep ocean do not necessitate anthropogenic forcing, our results do require an as yet unknown mechanism for transporting surface anomalies to the intermediate and deep ocean on timescales of centuries to decades.

A 5 cm^2 field area: QGIS as a tool for the integration of microanalytical data

J.N. Cammack, K. Kitajima, A.C. Denny, B.J. Linzmeier
1215 W. Dayton St. Madison, WI 53706
NASA Astrobiology Institute, WiscSIMS

In situ microanalytical techniques have become faster, more precise, and have seen wider use in the geosciences over the last two decades. Individual 2.5 cm diameter samples may have large data sets from *in situ* microanalytical instruments (e.g. SIMS, EPMA, LA-MS) and suites of images from multiple techniques (e.g. cross polarized light, plane polarized light, reflected light, UV, BSE, SE, EBSD, CL, X-ray mapping, confocal microscope, etc.) to answer research questions. A robust data exploration platform is necessary to fully comprehend these large, spatially overlapping datasets and has the potential to elucidate unexpected patterns. QGIS (Quantum Geographic Information Systems) is a free, open source, user-friendly, cross-platform software package created specifically for collecting and processing macroscopic geographic data. While not originally designed for microanalytical techniques, members of the WiscSIMS group at the UW-Madison have started utilizing it to compile *in situ* microanalytical data on individual samples. QGIS has many advantages for microanalytical data exploration and management; there is a growing international community of users and developers that are supporting QGIS, and the software allows for integration of custom scripts and plugins written in Python, C++, or R. Kouki Kitajima recently developed a Python plugin that quickly generates transect plots in the QGIS environment allowing for easy exploration of spatial trends (Figure 1). Importing *in situ* datasets into QGIS requires the *in situ* instrument records an XY stage position for each point or transect. Stage positions from multiple instruments must all be converted to the same units (µm, mm, nm etc.) prior importing into QGIS. Images are georeferenced (scaled and rotated) to the imported XY coordinates for each visible *in situ* analysis. We have been able to georeference SEM images containing multiple SIMS pits using as few as three of the total visible SIMS analysis pits. Pit locations (XY from SIMS) that were not explicitly referenced to the images occur within 3 µm of the center of pits visible in the imported image. SEM generated scale bars are measured to within 1 µm of the length based on using built in measurement tools in QGIS. In a short presentation, we will demonstrate the ease with which QGIS allows users to efficiently integrate microanalytical datasets (e.g., analysis points, user identified sample regions, or images), explore microspatial data, and generate figures, within a single software environment.



Primary Y
ayer: d18O_dol-anl
ield: d18_VSMOW
☒ Secondary Y
ayer: d18O_dol-anl
Field: Fe/(Mg+Fe)
☒ Display Tie Lines

Figure 1: A QGIS screen-capture depicting Kouki Kitajima's transect plot plugin and *in situ* SIMS and EPMA points all acquired during separate instrument sessions. Transect plotting integrates well with existing QGIS selection tools. Notice that only some of the data is included on the transect; those plotted data points are connected by light yellow tie lines perpendicular to the red transect line in the center of the BSE image. Labels can be quickly added or removed from points. QGIS labels are demonstrated by the purple pentagon quartz points labeled with their respective $\delta^{18}O$ VSMOW values. Quartz is represented by the darkest BSE shade in the image. The lighter shades represent increasing iron content on the dolomite (medium shades) - ankerite (lighter shades) solid solution. The brightest white shades on the image are leftover gold coating material required for SIMS analysis. A legend for the different data types is included in the lower left of the BSE image to denote $\delta^{18}O_{qtz}$, $\delta^{18}O_{dol\text{-}ank}$, $\delta^{13}C_{dol\text{-}ank}$, and EPMA points. The legend is not a part of the original screen-capture.

The Toba super-eruption: Micro-scale traces of a global-scale climate event?

Kim M. Cobb[1], Luke R. Chambers[1], Amelia F. Longo[1], Ellery D. Ingall[1], Jessica W. Moerman[1], Stacy A. Carolin[1], Nele Meckler[2], Jess F. Adkins[3], Victoria C. Smith[4], Lydia Finney[5], Syria Lejau[6], Jenny Malang[6], Andrew A. Tuen[7], Alison Pritchard[6]

1. Georgia Institute of Technology
2. ETH Zurich
3. California Institute of Technology
4. University of Oxford
5. Argonne National Laboratory
6. Mulu Cave
7. Universiti Malaysia Sarawak (UNIMAS)

Instrumental climate data, paleoclimate data, and climate models show that large volcanic eruptions cause significant global cooling by injecting reflective aerosols into the upper atmosphere, increasing planetary albedo (see Robock et al., 2000 and references therein). As such, these eruptions provide an empirical constraint on the relationship between radiative forcing and climatic response – a key uncertainty in numerical simulations of future climate change. However, the overall magnitude of a large eruption's climatic effects, and their regional expression, remain highly uncertain, and are the subject of heated debate in the peer-reviewed literature (Robock et al., 2005; Timmreck et al., 2009; Mann et al., 2012a, 2012b, 2013; Anchukaitis et al., 2012). As the largest eruption of the last 2 million years, the Toba eruption ~74 thousand years before present (kybp) on Sumatra presents an opportunity to probe the climatic responses associated with a massive perturbation to the Earth's radiative balance. Here we present trace metal as well as isotopic data from U/Th-dated stalagmites from Gunung Mulu National Park, in northern Borneo, across the Toba depth horizon. Previously published timeseries of stalagmite oxygen isotopes (Carolin et al., 2013) document a significant positive anomaly contemporaneous with the Toba super-eruption (interpreted as dry conditions at the site), but the degree to which Toba contributed to this anomaly has remained uncertain. We present new synchrotron-based micro x-ray fluorescence data showing the presence of distinct horizons in the Toba time interval with elevated concentrations of Fe, Mn, and Co, possibly indicating the presence of Toba ash in the samples. Working with an array of trace elements, we compare the stalagmite geochemistry in these horizons to the geochemistry of 1) distal ash samples from the Younger Toba Tuff (Smith et al., 2011), 2) clays isolated from the Gunung Mulu caves, and 3) depth horizons marked by brown layers and/or known hiatuses. We illustrate the promise of synchrotron-based fluorescence for identifying trace volcanic ash in stalagmites, with potentially broad applications in paleoclimate.

Records of paleoclimate and paleohydrology from slow-growth Great Basin Speleothems

Mellissa Cross, David McGee, Wallace S. Broecker, Jay Quade, Jeremy Shakun, Hai Cheng, Yanbin Lu, R. Lawrence Edwards

We present a record of speleothem trace element (Mg/Ca, Sr/Ca) and stable isotope (δ^{18}O, δ^{13}C) variations from Lehman Caves, NV, in the Great Basin. Our record, anchored by a total of thirty-six uranium-thorium dates, encompasses several periods of time, notably 139 – 129 ka, which includes the penultimate glacial termination; and other growth phases dating to 123 ka, 84 ka, and 82 – 81 ka. We also present new trace element data for stalagmite LC-2, a Lehman Caves stalagmite which has a previously published stable isotope chronology (Shakun et al., 2011). Our δ^{18}O record broadly replicates contemporary Lehman Caves speleothem records (Lachniet et al., 2014, Shakun et al., 2011). Low δ^{18}O values are recorded from 139 to 135 ka, followed by an approximate 3.5‰ rise between 135 to 129 ka. This increase in δ^{18}O values follows the rise in boreal summer insolation and atmospheric CO_2 and is probably due to rising temperatures and potentially increased contributions of summer precipitation. However, our trace element ratios and δ^{13}C values are largely decoupled from δ^{18}O; Mg/Ca and δ^{13}C values show minimal variation between 139 and 130 ka and are followed by a sharp increase between 130 and 129 ka. We interpret this abrupt rise in our δ^{13}C values and Mg/Ca as an increase in prior calcite precipitation driven by a transition from wet to dry conditions. The abrupt drying coincides with the end of Heinrich Stadial 11, within dating uncertainties. Our record demonstrates a link between North Atlantic climate events and Great Basin moisture at this time, which has been previously observed during the last glacial period. The portions of our δ^{18}O record dating to 84 and 82 – 81 ka appear to capture the end of Dansgaard-Oeschger (D-O) event 21 and subsequent cooling, which is consistent with one contemporary record from Goshute Cave, NV (Denniston et al., 2007), but inconsistent with another Great Basin record from Leviathan Cave (Lachniet et al., 2014). Such discrepancies and the general dearth of Great Basin records require additional development of speleothem records in this region. However, the slow growth of some Lehman Caves stalagmites makes this development a challenge. Preliminary dating of a 6 mm long growth phase from one of our speleothems reveals a potentially 35 kyr long record, from 48 to 13 ka. This interval includes Heinrich stadials 1 – 5. The extremely slow growth rate implied necessitates the use of high-resolution techniques like SIMS to resolve Great Basin paleoclimatic and paleohydrologic changes.

NEW WiscSIMS IMS 1280 100 NM-RESOLUTION PRIMARY BEAM DEFLECTION SYSTEM, FOR ACCURATE AIMING OF RETURNED SAMPLES.

C. Defouilloy[1], N. T. Kita[1], P. E. Sobol[1], N. E. Lord[1], T. J. Tenner[1], D. Nakashima[2]. [1]WiscSIMS, Department of Geoscience, University of Wisconsin-Madison, Madison, WI 53706, USA. (defouilloy@wisc.edu) [2]Division of Earth and Planetary Materials Science, Tohoku University, Miyagi 980-8578, Japan.

Introduction: A large radius secondary ion mass spectrometer (SIMS) IMS 1280 at WiscSIMS is capable of high precision oxygen three-isotope analyses using primary beam sizes as small as 1-2 µm. There, accurate positioning of the ion beam on samples becomes critical. However, the accuracy of targeting is limited, due to the ≈ 1 µm step of the stage.

NanoDeflector: To improve positioning accuracy, we modified the IMS1280 scanning capability by adding a microcontroller board with X and Y D/A converters to the instrument's Scan Generator. The X and Y signals are added to the existing signal driving the last deflector of the primary column (DPRIM5). This modification allows for deflection and rastering of the primary beam at a resolution of 0.1 µm with a maxium deflection of ±50 µm.

FIB-marking and aiming: This protocol was first developed by Nakashima et al. [1]. 1 µm squares are traced on targeted grains using a 30 keV focused Ga^+ beam set to 5 pA with a Zeiss FIB-FESEM Auriga. A dose of 0.4 nC/µm² (90 seconds) is applied to remove the 20-nm-thick carbon coating (Fig. 1a). Sample is then placed in the SIMS and we aim as precisely as possible at the FIB marks, which appears as a bright spot, due to the absence of coating (Fig. 1b). The Cs^+ primary beam current intensity is set at 3 pA. At these conditions, the beam spot on the sample surface is < 2 µm in size. The targeted grain is positioned as close as possible to the primary ion beam by moving the stage guided by the optical miscroscope. Using a 10 µm square raster, an ion image is then produced (Fig. 1b) and the beam position is adjusted by moving the stage so that the FIB mark appears as close as possible to the center (Fig. 1c). Then, using the NanoDeflector, the beam position is moved exactly to the center of the ion image (Fig. 1d). Once the FIB mark is properly centered, the raster is stopped and the analysis is initiated. During testing, the "analysis" time was 5 minutes, while actual three-isotope analysis takes 20 minutes.

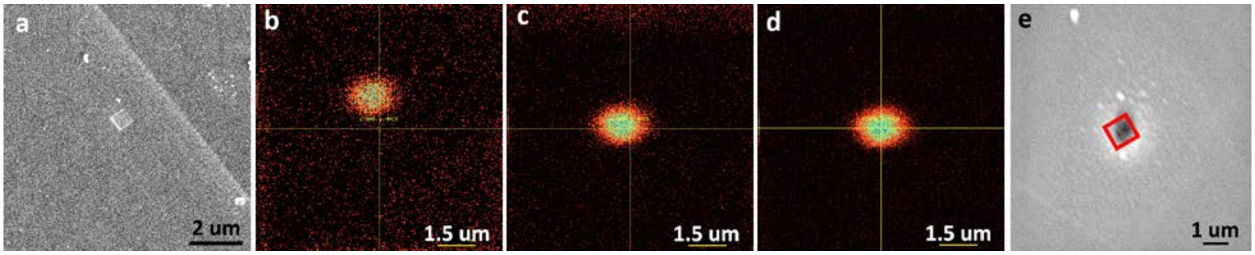


Fig. 1: *(a) SEM SE image of FIB mark #10. (b, c, d) SIMS* $^{16}O^-$ *ion images of the FIB mark with 10 µm rastering, (b) before adjustment, (c) after displacement of the stage, and (d) after adjustment with the Nano Deflector. (e) SE image of the rastered area and the SIMS pit after analysis, compared with the original position of the 1 µm FIB mark.*

After test analyses, SEM imaging of the SIMS pits verified the accuracy of aiming of the SIMS beam relative to the original position of the FIB marks (Fig. 1e). For 20 minute-analysis pits, the distance between the center of the original FIB mark and the center of the SIMS is in average of 0.17 ±0.15 µm (2σ). This is a significant improvement from the aiming tests run by Nakashima et al. [1] where the beam position could only be adjusted by moving the stage.

References: [1] Nakashima D. et al. (2012) *EPSL*, 357-358, p. 355-365.

$\delta^{18}O$ and $\delta^{13}C$-Zoned Carbonate Cements as Records of Porewater Temperature and Composition in Siliciclastics: In-Situ SIMS Analyses From Early Paleozoic Sandstones in the Illinois Basin, USA

Adam C. Denny[1], Reinhard Kozdon[1,2], Kouki Kitajima[1], Maciej G. Sliwinski[1], Mike Spicuzza[1], John W. Valley[1]

[1]Department of Geoscience, University of Wisconsin - Madison, Madison, WI.
[2]Department of Marine and Coastal Sciences, Rutgers University, New Brunswick, NJ.

The collective suite of cementing minerals in a sandstone develops over the course of a sedimentary sequence's diagenetic history. Growth and dissolution patterns, combined with chemical and isotopic zoning within a single mineral overgrowth, can record chemical and morphological evidence of the initial burial conditions as well as a host of chemical and mechanical burial processes, including compaction, mineral alteration, hydrocarbon generation, and pulses of fluid flow—meteoric or otherwise. Previous studies attempting to isolate diagenetic information from carbonate cements have been limited by an inability to resolve the µm-scale isotopic heterogeneity that is commonly present. Recent advances in the analysis of carbonate minerals by Secondary Ion Mass Spectrometry (SIMS) allow in-situ measurements of $\delta^{18}O$ and $\delta^{13}C$ from areas ≤10 µm in diameter. Precision of ±0.3‰ (2SD) is attainable for $\delta^{18}O$ with a 10 µm spot; for $\delta^{13}C$ precision of ±0.7‰ (2SD) is attainable with a 5 µm spot.

We used SIMS analysis of $\delta^{18}O$ in carbonate and silicate cements to test a model wherein slow deposition and burial in the Illinois Basin is recorded in the diagenetic minerals of the middle-Ordovician St. Peter and Cambrian Mt. Simon sandstones (Hyodo et al., 2014 Chem Geol). $\delta^{18}O$ and $\delta^{13}C$-zoned dolomite-ankerite cements in these formations preserve systematic variations consistent with chemical and thermal processes operating on a basin-wide scale.$\delta^{18}O$ in early dolomites range from 23-27‰ VSMOW (-7 to -3‰ VPDB), but later zones show sequentially lower values associated with burial and heating, as was previously observed for $\delta^{18}O$ values in zoned quartz overgrowths (Pollington et al., 2011 Geology). This long period with low fluid fluxes due to burial and compaction was punctuated by a brief period of metal-carrying brine migration, driven through the sandstone aquifers by uplift in the Ouachitas and associated with the Mississippi-Valley Type (MVT) ore deposits (ca. 270 Ma) of the Upper Mississippi Valley. Some late ankerites have $\delta^{18}O$ values of 18‰ VSMOW (-12‰ VPDB) or lower, suggesting that temperatures were elevated above the geotherm by hot brines and/or $\delta^{18}O$ of porewater was lowered. Either way, fluid flow is indicated and we conclude that some of these late periods of diagenetic growth are likely associated with MVT fluids. Values of $\delta^{13}C$ in zoned dolomite-ankerites range from 0 to -7‰ VPDB and frequently vary independently of $\delta^{18}O$, also suggesting open-system behavior.

The Environmental Importance of Microbial Sulfate Reduction and Disproportionation: Insights from SIMS-based $\delta^{34}S$ Measurements

David A. Fike

Department of Earth & Planetary Sciences, Washington University, St. Louis, MO 63130, USA

Sulfur isotope ratio data ($\delta^{34}S$) from sedimentary sulfates and sulfides (predominantly pyrites) have been used to provide a framework for reconstructing biogeochemical cycling, global redox budgets, and microbial metabolic activity. A major feature of the long-term record of sulfur isotopes is a trend toward increased fractionation between sulfate and sulfide over Earth history with particularly large increases around the Archean-Paleoproterozoic transition (~2.5 Ga) and the Neoproterozoic-Phanerozoic transition (~541 Ma). Both of these changes have been interpreted in light of progressively increasing oxygenation with the former attributed to the onset of oxidative weathering and increased marine sulfate concentrations and the latter, to the increased environmental significance of oxidative sulfur cycling and microbial sulfur disproportionation. Microbial sulfur disproportionation, which acts to increase the fractionation between sulfate and sulfide, was originally invoked because the isotopic fractionation during sulfate reduction was thought to have an upper limit of ~46‰, whereas fractionations between coeval sulfate and sulfide of up to ~70‰ were observed both in the modern and in the rock record. However, recent laboratory analyses under more realistic growth conditions have observed fractionations approaching 70‰ solely as the result of sulfate reduction. As such, the relative importance of disproportionation vis-à-vis sulfate reduction in both modern environments and in the rock record remains uncertain. Here we report high-resolution SIMS $\delta^{34}S$ data from a variety of microbial mat systems that show a minimum in isotopic fractionation across the chemocline, the oxic-anoxic transition where disproportionation would be expected to be most abundant. These results suggest that, although disproportionation may be present in these microbial environments, its contribution to the overall isotopic signature is minimal. Instead, isotopic fractionation between sulfate and sulfide appears to be driven primarily by cell-specific rates of sulfate reduction, wherein the long-term trend may be driven by the decreased availability of labile organic matter under progressively more oxygenated conditions over Earth history.

The Impact of Small-Scale Heterogeneity on Proxies in Biomineral Archives.

ALEXANDER GAGNON
School of Oceanography, University of Washington, Seattle, WA.

From the pace of the ice ages to how the carbon cycle has changed through time, much of what we know about earth history and climate dynamics is based on chemical signatures locked within mineral archives. Recorded as trace element anomalies or as isotopic shifts, these chemical signatures reflect how mass and energy move across the planet, as well as the response of biological systems to these changes. When viewed at the sub-micron to nano-scale however, chemical composition rarely follows a simple relationship with environmental conditions. This is especially true for the preserved $CaCO_3$ skeletons of marine organisms, which often exhibit systematic patterns of high magnitude chemical variability at the sub-micron scale. While this biologically-driven variability can complicate the interpretation of climate records, it also represents a rich and largely untapped signal – a window into the mechanisms controlling biomineral growth and the possible basis for new paleoproxies.

Like many processes in the ocean, biomineralization is exceptionally complex. During biomineralization, organisms choreograph the flow of ions, manipulate aqueous speciation, and modulate surface chemistry through organic-mineral interactions. These elementary processes and other steps of biomineralization can affect skeletal chemistry, leaving behind a fingerprint of the biomineralization process. Major advances in our understanding of both biomineralization and paleoproxies hinge on new techniques that can isolate small signals from this complexity.

To probe the mechanisms controlling biomineralization and sub-micron compositional variability, we use a suite of high spatial resolution tools like NanoSIMS, ToF-SIMS, and Atom Probe Tomography (APT) together with stable isotope labels and biomineral culture techniques. In planktonic foraminifera, for example, we conducted modified pulse chase experiments using multiple isotope tracers to measure ion transport rates during biomineralization. By varying elemental concentrations in the surrounding seawater during these pulse chase experiments, we were able to induce systematic shifts in the ion transport rate. The magnitude of these shifts can be inverted to indirectly measure the elemental composition of the calcifying microenvironment, a key and previously unmeasured parameter affecting skeletal chemistry and paleoproxy systematics. Complementary isotope tracer experiments in coral and related experiments applying APT to the organic-mineral interface in foraminifera have uncovered the response of calcification to ocean acidification and aspects of the organic templating process during skeletal nucleation, respectively. Collectively, the mechanistic understanding of biomineralization developed in these experiments can help us explain small-scale proxy heterogeneity, upscale this variability to bulk composition, and more accurately resolve specific environmental signals from the geochemical record.

High Resolution Paleoclimate Records from Yucatán Speleothems Spanning the Past 2000 Years

GAO, Yongli[1], ROWE, Harry[2], BUCKLES, Jessica[1], CHENG, Hai[3], and EDWARDS, R. Lawrence[3],

(1) Geological Sciences, University of Texas at San Antonio, San Antonio, TX 78249, yongli.gao@utsa.edu, (2) Bureau of Economic Geology, The University of Texas at Austin, The Jackson School of Geoscience, University Station, Box X, Austin, TX 78713-8924, (3) Department of Earth Sciences, University of Minnesota, 310 Pillsbury Dr.

Abrupt climate changes including a series of megadrought events have been documented in many terrestrial records in the Mesoamerican region since the late Holocene. Many stalagmites from the western Yucatán region have been dated to establish high-resolution climate proxies spanning the Pre-to-Postclassic Periods of the Maya civilization. These speleothems are fast-growth stalagmites with growth rates ranging from ~0.1 mm/year to >1 mm/year. The relatively fast growth rates of many of the stalagmites allow for high temporal resolution in geochemical analyses. Stable isotope analysis was done with a sampling interval of 0.5 mm and trace metal analysis (Sr concentration) was conducted using a Bruker Artax μ-XRF spectrometer at 0.2 mm interval. The timing of drought events is well-constrained by abrupt increases in $\delta^{18}O$ and $\delta^{13}C$ values along with Sr concentrations since the late Medieval Warm Period. Several multi-decadal drought events are characterized by abrupt increases of Sr concentrations of two speleothem records in the 3rd, 10th, and 11th centuries AD. Additional age dating and high-resolution isotopic analysis are needed to constrain the timing of these megadrought events. The primary goal of this research is to understand the timing and magnitude of climate changes that occurred on the west-central Yucatán peninsula during the time of the Mayan collapse.

Forams Forever: Use of SIMS $\delta^{18}O$ and EPMA Mg/Ca Analyses of Planktic Foraminiferal Shells to Reconstruct the Hydrological Cycle during Past Climate States

[1]Kelly, D.C., [2]Kozdon, R., [1]Wycech, J.B., [1]Valley, J.W.

[1]WiscSIMS, Department of Geoscience, University of Wisconsin-Madison
[2]Department of Marine and Coastal Sciences, Rutgers University, New Brunswick, NJ

A number of abiotic and biotic factors affect the oxygen isotope ($\delta^{18}O$) composition of planktic foraminiferal calcite with calcification temperature and $\delta^{18}O$ of ambient water being the two most influential environmental parameters. From the standpoint of foraminiferal $\delta^{18}O$ paleothermometry, disentangling the signatures of these two variables is crucial as the effect of varying seawater $\delta^{18}O$ composition is often viewed as a poorly constrained liability. To complicate matters, planktic foraminiferal shells typically have heterogeneous $\delta^{18}O$ compositions with as many as three isotopically distinct phases of carbonate (ontogenetic, gametogenic, and diagenetic) being present within an individual shell. This latter complication is particularly troublesome for foraminiferal $\delta^{18}O$ data obtained via conventional gas-source mass spectrometry since this established technique necessitates the analysis of whole shells under the assumption that compositions in foraminiferal shells are homogeneous in $\delta^{18}O$ and well preserved. Here, we demonstrate how the combined usage of such *in situ* analytical techniques as secondary ion mass spectrometry (SIMS) and electron probe microanalysis (EPMA) to acquire "paired" $\delta^{18}O$ and Mg/Ca ratios from the same domain within an individual planktic foraminiferal shell can reduce the deleterious effects of diagenesis which tend to elevate the $\delta^{18}O$ of planktic foraminiferal shells. To this end, we conducted a study that uses *in situ* $\delta^{18}O$ and Mg/Ca data compiled from minute (≤ 10 μm) domains within shells of mixed layer-dwelling planktic foraminifera to reconstruct the response of the hydrologic cycle to an ancient (~56 Ma) global warming event termed the Paleocene-Eocene thermal maximum (PETM). Paleoenvironmental reconstructions suggest that PETM warmth was accompanied by a major perturbation to the hydrologic cycle, which increased poleward transport of atmospheric moisture and reduced sea-surface salinities in the central Arctic Ocean. Still, our knowledge about the hydrologic response and its role in effectuating climate change during the PETM is wanting and often discussed controversially. As a result, we reassessed a well-studied PETM record from the Southern Ocean (ODP Site 690) through the lens of new *in situ* $\delta^{18}O$ and Mg/Ca data acquired from planktic foraminiferal shells. An increase in Mg/Ca ratios equating to ~5ºC warming of sea-surface temperatures (SST) is accompanied by ~2‰ decrease in the $\delta^{18}O$ of planktic foraminiferal calcite during the PETM at this site. The scale of the $\delta^{18}O$ decrease registered by the SIMS-generated record exceeds the ~5ºC warming signaled by the correlative Mg/Ca record, and is nearly twice the magnitude of the decrease seen in the published 'whole shell' $\delta^{18}O$ record for this same PETM section. Hence, we attribute ~1‰ of this $\delta^{18}O$ decrease to a decline in surface-ocean $\delta^{18}O$ driven by increased water vapor transport to this subpolar location, and posit that some combination of sediment mixing and diagenesis conspired to attenuate the magnitude of the decrease seen in the published 'whole shell' $\delta^{18}O$ record.

Tutorial: SIMS Basics

Noriko Kita (WiscSIMS, Department of Geoscience, University of Wisconsin-Madison)

IMS 1280 at WiscSIMS laboratory is a user-friendly instrument and easy to run once it is tuned by a laboratory operator. Even first time users become familiar to routine operation within a few hours after they are on the instrument. However, it takes many visits for most users understand the basic mechanism of how the instrument works. This tutorial talk provides basic knowledge of SIMS techniques to both current and future users, particularly relevant to the high precision stable isotope analyses at WiscSIMS. The following subjects will be covered.

- **Secondary Ion Mass Spectrometer with double focusing ion optics.** Cameca IMS 1280 at WiscSIMS is a large radius double focusing mass spectrometer. Among many areas of research, we are specialized for high precision stable isotope analyses.

- **Sputtering of sample surface by primary ions and secondary ion production.** Our routine high precision analyses use ~10µm diameter spots with Cs^+ ions to produce O^- and C^- secondary ions, which provide typical precisions of 0.2-0.3‰ and 0.7‰, respectively (Kita et al. 2009). Primary beam sizes can be reduced to ≤ 3 µm for higher spatial resolution with compromised analytical precision.

- **Electron gun and charge compensations.** The sputtering process also produces a huge amount of secondary electrons that freely escape from a sample surface. The electron gun sprays a cloud of electrons to compensate charge built-up and protect your sample against electrostatic discharge.

- **Mass spectrum and multi-collection detector system.** Most hydride and molecular interferences are separated by operation at high mass resolving power ($M/\Delta M$) of 2,000-5,000. IMS 1280 has total 10 ion detectors (both Faraday cups and electron multipliers) with five movable trolleys and a fixed axial detector. Multi-collection Faraday cups provide the best possible analytical precision.

- **Hardware and software modifications.** Since the installation in 2005, several upgrades and modifications were made, including UV light optical microscope system and sample viewing software "Badgerscope" that improved sample viewing and aiming performance significantly (Kita et al. 2015).

- **Procedure of oxygen isotope analyses**. Every ~5 min, you move sample stage, aim the location of analyses and press "start" for the analyses, and find your result right away.

Kita N. T., Ushikubo T., Fu B. and Valley J. W. (2009). High precision SIMS oxygen isotope analysis and the effect of sample topography. *Chemical Geology* **264**, 43-57.

Kita N. T., Sobol P. E., Kern J. R., Lord N. E. and Valley J. W. (2015) UV light microscope: Improvements in optical imaging for a secondary ion mass spectrometer. *J. Anal. At. Spectrom.* **30**, 1207-1213.

Improvement in matrix correction of $\delta^{18}O$ analysis by SIMS for pyralspite and Cr-pyrope garnets

Kouki Kitajima[1, 2], Ariel Strickland[1], Michael J. Spicuzza[1] and John W. Valley[1, 2]

[1] *WiscSIMS, Department of Geoscience, University of Wisconsin-Madison, Madison, WI, 53706*
[2] *NASA Astrobiology Institute, Department of Geoscience, University of Wisconsin-Madison, Madison, WI, 53706*

Stable isotope analysis by SIMS requires a large suite of matching standards for minerals that show complex solid-solution. There is no theoretical basis for extrapolating composition and samples are generally bracketed by the cation composition of standards. For oxygen isotope analysis of pyralspite garnets, a matrix correction based on grossular (Ca) component (X_{Grs}) has been proposed (Page et al., 2010). This simple correction scheme has been generally accepted (Ickert and Stern, 2013; Martin et al., 2014; Raimondo et al., 2012) and can be described with a quadratic curve. However, we noticed significant dispersion (>0.5‰) in the low-Ca, near end-member, pyralspite garnets such as pyrope (Mg), almandine (Fe^{2+}) and spessartine (Mn) in recent garnet sessions. While there are some correction schemes that consider these components (Ickert and Stern, 2013; Martin et al., 2014; Vielzeuf et al., 2005), these corrections used a linear fit and/or single component and cannot explain the observed dispersions of low-Ca pyralspite garnets.

In this study, we introduce 22 new garnet standards in addition to the current 27 garnet standards (Page et al., 2010). We report 16 low-Ca pyralspite garnets including intermediate compositions between pyrope and spessartine that were lacking in the composition range of our previous suite of garnet standards. These garnet standards are used to evaluate the quality of the matrix correction for nearly the entire range of pyrope-almandine-spessartine-grossular solid-solutions. We evaluated the homogeneity of chemical composition and $\delta^{18}O$ of all new garnet standards by EPMA and SIMS. The $\delta^{18}O_{True}$ values were calibrated by laser fluorination. For SIMS analysis, normal procedures were followed: 10-µm spot size, 2 Faraday cups, 3.5 min/spot (Kita et al., 2009). We also measured $^{16}O^{1}H$ with the axial Faraday cup to monitor the OH count rate. All analyses were carried out at University of Wisconsin-Madison.

In addition, we also added 6 new Cr-pyrope garnet standards, to evaluate the effect of Cr on the matrix correction. The effect of Cr has not previously been studied systematically for matrix correction For Cr-pyrope garnets, after applying the correction based on grossular content, the calibration curve for Cr-pyrope garnets using new standards reveals that the magnitude of the matrix correction for Cr concentration is ~ 1.9‰ at 13.4 wt.% Cr_2O_3.

For pyralspite and grossular garnets are calibrated with each end-member composition (Ca/Mg+Ca: grossular-pyrope, Mn/Mg+Mn: spessartine-pyrope and $Fe^{2+}/Mg+Fe^{2+}$: almandine-pyrope) instead of X_{Grs}. Each calibration curve was fitted by a quadratic equation with three standards (near both end-members and an intermediate compositions). A pyrope standard (UWPp-1) was used for all calibrations and thus a total of 7 standards were used for this matrix correction (Ca: GrsSE, R-53, UWPp-1; Mn: Sps-3, Sps-4, UWPp-1; Fe: Alm-4, UWG-2, UWPp-1). This correction scheme was evaluated using the measured offset of corrected $\delta^{18}O$ from $\delta^{18}O_{True}$ value for all other garnet standards (excluding the 7 calibration standards). For example, for the SIMS session on 6/24/2014, the 2 standard deviations (2SD) of the residual after Ca correction was 0.81‰. After the Mn correction was performed, the 2SD of the residual was down to 0.76‰; the final residual after the Fe^{2+} correction was 0.33‰. This residual value (0.33‰) is better than the residual if we simply apply the X_{Grs} correction with all standards (0.75‰).

References:

Ickert, R.B., Stern, R.A., 2013. Matrix Corrections and Error Analysis in High-Precision SIMS $^{18}O/^{16}O$ Measurements of Ca–Mg–Fe Garnet. Geostand. Geoanalytical Res. 37, 429–448. doi:10.1111/j.1751-908X.2013.00222.x

Kita, N.T., Ushikubo, T., Fu, B., Valley, J.W., 2009. High precision SIMS oxygen isotope analysis and the effect of sample topography. Chem. Geol. 264, 43–57.

Martin, L.A.J., Rubatto, D., Crépisson, C., Hermann, J., Putlitz, B., Vitale-Brovarone, A., 2014. Garnet oxygen analysis by SHRIMP-SI: Matrix corrections and application to high-pressure metasomatic rocks from Alpine Corsica. Chem. Geol. 374-375, 25–36. doi:10.1016/j.chemgeo.2014.02.010

Page, F.Z., Kita, N.T., Valley, J.W., 2010. Ion microprobe analysis of oxygen isotopes in garnets of complex chemistry. Chem. Geol. 270, 9–19.

Raimondo, T., Clark, C., Hand, M., Cliff, J., Harris, C., 2012. High-resolution geochemical record of fluid-rock interaction in a mid-crustal shear zone: a comparative study of major element and oxygen isotope transport in garnet. J. Metamorph. Geol. 30, 255–280. doi:10.1111/j.1525-1314.2011.00966.x

Vielzeuf, D., Champenois, M., Valley, J.W., Brunet, F., Devidal, J.L., 2005. SIMS analyses of oxygen isotopes: Matrix effects in Fe–Mg–Ca garnets. Chem. Geol. 223, 208–226. doi:http://dx.doi.org/10.1016/j.chemgeo.2005.07.008

Getting the big picture from a small spot: Multi-proxy, multi-instrument *in situ* measurements in foraminifera

R. Kozdon [1, 2], D. C. Kelly [1], H. J. Spero [3], J. W. Valley [1]

[1] WiscSIMS, Department of Geoscience, University of Wisconsin-Madison
[2] Department of Marine and Coastal Sciences, Rutgers University, New Brunswick, NJ
[3] Department of Earth and Planetary Sciences, University of California Davis

The Arctic Ocean has a significant amplification effect on climate change in the high latitudes with impacts within and beyond the Arctic. The early-mid Holocene sea ice minimum and related Arctic water mass stratification is widely regarded as a post-glacial analogue for Arctic conditions that could occur on human timescales[1]. As such, there is a considerable value in reconstructing the state of upper Arctic water column stratification across the Arctic basin during this period. Unfortunately, proxies for water mass stratification such as the comparison of the oxygen isotope composition of several species of planktic foraminifera with different habitat depths[2] cannot be applied in the Arctic as high latitude assemblages are largely monospecific, with *Neogloboquadrina pachyderma* (sinistral) (*Nps*) being the only abundant planktic foraminifera in polar to subpolar water masses.

However, *Nps* forms their first chambers close to the sea surface and secrete its final crust in sub-mixed layer depths of up to about 100 m, thereby providing a record of past water column stratification on micrometer scales that can now be measured by *in situ* approaches with an unprecedented level of detail. I will present a recently initiated study to apply a multi-instrument (SIMS, EPMA and laser-ablation ICP-MS), multi-proxy (δ^{18}O, δ^{13}C, Mg/Ca, Ba/Ca, Na/Ca) *in situ* approach to reconstruct past Arctic water column hydrography from the early to mid-Holocene sea ice minimum, a post-glacial analogue for climate change. Results from this study may lead to better predictions of the future effects of a reduced sea-ice cover on weather systems beyond the Arctic.

Whereas detailed information such as past water column stratification can be reconstructed from the preserved chemical and isotopic heterogeneity in Holocene foraminiferal shells, the degree of diagenesis increases with age and burial depth, and conventional 'whole-shell' measurements of foraminifera that are millions of years old are typically biased to some degree by diagenesis. However, we found that minute (~10 µm diameter) domains within foraminifera are more resistant to diagenetic alteration than the remaining shell, and robust paleorecords can be compiled by *in situ* measurements of this well-persevered biogenic calcite. I will present results from *in situ* δ^{18}O, δ^{13}C, and Mg/Ca analyses of biogenic and diagenetic calcite in tropical planktic foraminiferal shells from an ancient (~56 Ma) global warming event termed the Paleocene-Eocene thermal maximum (PETM) and discuss the different sensitivities of these proxies to diagenetic overprinting. The δ^{18}O and δ^{13}C values of diagenetic calcite are >4‰ and >2‰ higher, respectively, than those of the unaltered planktic foraminiferal calcite, whereas the Mg/Ca ratios of these two generations of calcite are almost indistinguishable. A mass balance reveals that at least 30 weight% of the shells are replaced by diagenetic calcite, which has significant implications on the interpretation of conventional 'whole-shell' measurements.

1 Stranne, C., Jakobsson, M. & Björk, G. Arctic Ocean perennial sea ice breakdown during the Early Holocene Insolation Maximum. *Quaternary Science Reviews* **92**, 123-132, doi: http://dx.doi.org/10.1016/j.quascirev.2013.10.022 (2014).

2 Simstich, J., Sarnthein, M. & Erlenkeuser, H. Paired δ^{18}O signals of *Neogloboquadrina pachyderma* (s) and *Turborotalita quinqueloba* show thermal stratification structure in Nordic Seas. *Mar. Micropaleontol.* **48**, 107-125 (2003).

Variability of oxygen isotope ratios on the scale of tens of microns in Nautilus shell aragonite

Benjamin J. Linzmeier[1*], Reinhard Kozdon[2], Shanan E. Peters[1], John W. Valley[3]
[1]Department of Geoscience, University of Wisconsin-Madison, Madison, Wisconsin, USA
[2]Department of Marine and Coastal Sciences, Rutgers, The State University of New Jersey, New Brunswick, New Jersey, USA
[3]WiscSIMS, Department of Geoscience, University of Wisconsin-Madison, Madison, Wisconsin, USA

Nautilus is often used as an analogue for the ecology and behavior of extinct externally shelled cephalopods. Nautilus shell grows quickly, has internal growth banding that is daily, and precipitates aragonite in oxygen isotope equilibrium with seawater. Tracking of individual wild Nautilus has shown vertical migration of 100 to 400 m water depth per day, crossing a temperature gradient of at least 3°C. Imaging and oxygen isotope analysis of growth banding were undertaken to determine if high spatial resolution oxygen isotope variability exists within growth bands in the shell wall of both a wild-caught *Nautilus macromphalus* from New Caledonia and an aquarium reared *Nautilus belauensis*.

Portions of both shells were vacuum roasted at ~320 ˚C for one hour. Those pieces were then mounted in epoxy, polished, and imaged to visualize growth banding. One centimeter of the wild-caught specimen, corresponding to ~45 days growth, contained growth bands (inclined to the surface at 11 °) that were an average of 34 µm wide. Approximately 3 mm of the aquarium reared specimen, corresponding to ~15 days of growth, contained growth bands that were on average 20 µm wide.

In situ analysis of oxygen isotope ratios using secondary ion mass spectrometry with 10 µm beam-spot size revealed $\delta^{18}O$ variation within and between growth bands. In the wild caught sample, a traverse crosscutting 45 growth bands yielded $\delta^{18}O$ values ranging 2.5‰, from 0.6 to -1.9‰ (VPDB) (0.3‰ average 2SD). The maximum range within a single band was 1.5‰ and 26 out of 39 bands had a larger range than expected given instrumental precision (95% CI, and 22/39 for 99% CI). The average range within bands with 3 or more analyses is 0.84‰ (n=39) in the wild caught individual and 0.63‰ (n=4) in the aquarium reared individual. The $\delta^{18}O$ range within the aquarium reared sample was 1‰ smaller, from –1 to -2.5‰, and the maximum range within an individual band with 3 or more analyses was 1‰. The results from the wild individual suggest depth migration is recorded by the shell. Variation in the aquarium reared sample was likely due to weekly evaporation and the ~8 hour recharge of the aquarium water. Future aquarium rearing with oxygen isotope and temperature control is necessary to characterize possible vital effects or instrument effects (e.g. microtexture) on fine spatial scale oxygen isotope variability $\delta^{18}O$.

δ^{18}O Analysis in Tree Rings of *Pterocarpus angolensis* Growing in Zimbabwe

Kerry E. McLeran
Department of Geography and Environmental Resources, Southern Illinois University, Carbondale

Liliana Lefticariu
Associate Professor, Department of Geology, Southern Illinois University, Carbondale

Matthew D. Therrell
Associate Professor, Department of Geography, University of Alabama

Justin Schoof
Associate Professor, Chair of Geography and Environmental Resources, Southern Illinois University, Carbondale

Instrumental weather records in southern Africa are largely limited to the last 100 years and documentary weather-related data are rare prior to the 1800s, hindering our understanding of the natural and/or anthropogenic factors that influence climate variability over this region. Measuring stable oxygen isotopes (δ^{18}O) in tree rings may provide a good proxy for extending climate data beyond the instrumental record. Our study is designed to identify the relationships between hydroclimate variables and δ^{18}O values ($\delta^{18}O_{tr}$) extracted from annually resolved tree rings of *Pterocarpus angolensis* growing in the arid to semiarid Mzola region of western Zimbabwe. A 90-year (1900-1990) $\delta^{18}O_{tr}$ record using four *P. angolensis* samples is being developed and compared to tree ring width, monthly, seasonal, and annual precipitation totals, meteoric water δ^{18}O values, and mean monthly and seasonal temperature. Preliminary results indicate significant correlations between the average $\delta^{18}O_{tr}$ record and the previous year December precipitation totals ($r=0.41, p<0.0001$), current year January precipitation totals ($r=0.45, p<0.0001$), and combined total precipitation for the previous year November and December and current year January ($r=0.57, p<0.0001$). Unlike ring width data, which often reflect a drought-biased signal to precipitation, our preliminary results suggest that variability in $\delta^{18}O_{tr}$ values primarily reflect wet season precipitation amount. Furthermore, we find that $\delta^{18}O_{tr}$ is

strongly influenced by maximum temperature during the previous year December (*$r=0.39$, $p=0.0001$*) and current year January (*$r=0.40$, $p=0.0001$*), and average maximum temperature during the months of the previous year December and current year January and February (*$r=0.47$, $p<0.001$*). We thus present one of the first oxygen-isotope based studies in southern Africa to correlate variability in $\delta^{18}O_{tr}$ with fluctuations in climatic variables. The results of this study this study will provide the framework for future analysis of climate variability in this region.

Pedothem carbonates record the aridification of the Atacama Desert

Erik Oerter[1], Angela Ebeling[2], Ronald Amundson[1]

[1]Department of Environmental Science, Policy and Management, University of California, Berkeley, USA.
[2]Wisconsin Lutheran College, Milwaukee, WI, USA.

The Atacama Desert of Chile has a fascinatingly arid and stable climate, the formation of which is likely related to the rise of the Andes and associated hemisphere-scale atmospheric circulation changes. An especially promising paleoclimate proxy archive in arid and semi-arid climates are dense, laminated soil carbonate deposits that integrate climate information during the soil's period of sub-aerial exposure, which in the Atacama is especially long as a result of the virtual lack of water-borne erosion. We studied a soil on a late Tertiary to early Quaternary alluvial fan that exhibits evidence of an initial wetter period (secondary clay formation) followed by a period dry enough to form secondary carbonate accumulations, sometimes as dense pedothems (from Greek: πέδον, *pedon*, "soil"; and θέμα, *théma*, "deposit") on soil gravels. Examination of the cut and polished pedothems by reflected light and electron microscopy reveals carbonate laminations that preserve stratigraphic integrity. We used the WiscSIMS CAMECA 1280 ion probe to collect $\delta^{13}C$ and $\delta^{18}O$ values on ~10um spots along transects across the carbonate from inside (adjacent to the clast/coating interface, oldest) to outside (youngest). C stable isotope values show a ~4‰ increase in $\delta^{13}C$ values through time, reflecting a change towards aridification with decreasing plant density and soil respiration. O stable isotope values show a more complex pattern along the same time axis with variability of up to 10‰.

Comparing these data to micro-drilled sampling (~500um dia.) demonstrates the power of the WiscSIMS ion probe to sample regions of high quality carbonate that is dense and pure with coherent lamination stratigraphy and the absence of inclusions or micro-porosity. By avoiding silicate inclusions and sampling the best carbonate, variability in the O stable isotopes of the carbonate becomes apparent, a signal that is not resolvable with coarser sampling methods. The age of the carbonate remains elusive, however because it is older than the 350ka limit of U/Th dating, and initial attempts at applying U/Pb dating by coarse sampling and dissolution has proven unsuccessful. While the timing of the reduction in precipitation from 500-1000 mm y^{-1} in the late Tertiary/early Quaternary to 25 mm y^{-1} that is recorded by this soil remains uncertain, this study adds to the evidence that pedothem carbonates can make distinct contributions to terrestrial paleoclimate records.

Tutorial:
Developments and challenges in ion microprobe studies of speleothems and biocarbonates

Ian J. Orland[1,2]
[1] WiscSIMS, Dept. of Geoscience, University of Wisconsin-Madison
[2] Dept. of Earth Sciences, University of Minnesota-Twin Cities

Speleothems (carbonate cave formations, e.g. stalagmites) and biocarbonates (e.g. foraminifera, *Nautilus*, corals, otoliths, mollusks) provide key proxy records of paleoenvironmental change. In particular, the oxygen and carbon isotope ratios ($\delta^{18}O$, $\delta^{13}C$) of these carbonates preserve invaluable records of past changes in Earth's oceans and atmosphere. *In situ* micro-sampling by ion microprobe offers a means to improve the spatial and temporal resolution of traditional bulk-sampling techniques. Given the urgent need to understand the dynamics of rapid climate change, the ion microprobe represents an important tool for studying abrupt paleoclimate changes as well as seasonal patterns of paleoclimate change. This talk will address analytical developments as well as the accompanying challenges.

Over the last 10 years, the WiscSIMS lab developed methodology that allows for high-precision $\delta^{18}O$ measurements in carbonates. Much of this effort focused on standardization and sample preparation techniques (Kita et al., 2009), but advances were also made in sample viewing, sample targeting, and improved sample holder geometry for accommodating larger target areas (Peres et al., 2013). The average spot-to-spot reproducibility (2 s.d.) for 10 μm diameter spots in calcite is typically ±0.3‰, and is monitored at regular intervals during a session on the calcite standard UWC-3 (Kozdon et al. 2009); for 3 μm diameter spots the 2 s.d. is ±0.6‰ (Vetter et al., 2014). UWC-3 is also used as a $\delta^{13}C$ carbonate standard, 2 s.d. = ±0.7‰ for 6-10 μm spots (Orland, 2012). Recent work explored the utility of UWC-3 as a trace element standard; preliminary results are encouraging, especially given the rarity of carbonate trace element standards (Orland et al., 2014; Müller et al., 2015). To facilitate $\delta^{18}O$ analysis of aragonite samples, an aragonite standard was identified and characterized (UWArg-7; Orland, 2012). Combined with micro-imaging techniques that allow for careful placement of analysis spots in targeted domains, these analytical capabilities have resulted in important new interpretations of traditional carbonate paleoclimate proxies.

As the precision of WiscSIMS measurements improved and the variety of analyzed biocarbonates expanded, some interesting analytical challenges emerged. Most notably, a small offset between $\delta^{18}O$ values measured by SIMS and conventional acid-digestion techniques is sometimes apparent. Multiple potential contributions to the offset have been tested (Orland et al., 2015), including: inter-lab standard (mis)calibration; the possibility that the measured offset is real and a result of water and/or organic inclusions; depth-profiling effects; porosity effects; and the effects of minor element composition.

Kita N. T. et al. (2009) *Chem. Geol.* **264**, 43-57.
Kozdon R. et al. (2009) *Chem. Geol.* **258**, 327-337.
Müller W. et al. (2015) *Geochim. Cosmochim. Acta*. Goldschmidt Conf. abstract
Orland I. J. (2012) PhD dissertation (UW-Madison).
Orland I. J. et al. (2014) *Chem. Geol.* **363**, 322-333.
Orland I. J. et al. (2015) HiRes15 abstract, this volume
Peres P. et al. (2013) *Surf. Interf. Anal.* **45**, 553-556.
Vetter L. et al. (2014) *Geochim. Cosmochim. Acta* **107**, 267-278.

A spatial gradient of seasonal monsoon signals in East Asian speleothems

Ian J. Orland[1,2], R. Lawrence Edwards[1], Hai Cheng[1,3], Reinhard Kozdon[2,4], John W. Valley[2]
[1] Dept. of Earth Sciences, University of Minnesota-Twin Cities
[2] WiscSIMS, Dept. of Geoscience, University of Wisconsin-Madison
[3] Institute of Global Environmental Change, Xi’an Jiaotong University, Xi’an, China
[4] Dept. of Marine and Coastal Sciences, Rutgers University

Over the last decade, ion microprobe analysis of speleothems (cave carbonates) has increased the temporal resolution of their oxygen isotope ($\delta^{18}O$) paleoclimate proxy records. Recent improvements in methodology, standardization, and imaging at the WiscSIMS lab make it possible to examine sub-annual patterns of $\delta^{18}O$ variability at 10-µm-scale, revealing new seasonal paleoenvironmental information. We applied this technique to an important suite of Chinese stalagmites with conventional drill-sampled $\delta^{18}O$ records that reflect changes in Asian Monsoon dynamics across the last deglaciation.

Seasonal-resolution $\delta^{18}O$ analyses in the Chinese stalagmites reveal regular patterns of annual $\delta^{18}O$ variability. Quantitative assessment of the patterns identifies two important components in the $\delta^{18}O$ records. First, the source and rainout histories of water vapors that ultimately yield rainfall over China play a primary role in determining the $\delta^{18}O$ value of speleothem calcite year-round. Second, intra-annual patterns of calcite $\delta^{18}O$ variability indicate that the annual proportion of summer monsoon rainfall changes systematically during the last deglaciation; the annual proportion of monsoon rainfall is greater during the Holocene and Bølling-Allerød than during the Younger Dryas.

This is the first time these components have been characterized in any speleothem $\delta^{18}O$ record of monsoon dynamics because seasonal $\delta^{18}O$ variability is lost by conventional drill-sampling. Ion microprobe analysis of speleothems can also produce year-by-year records of $\delta^{18}O$ across abrupt climate change events. The rapid decrease in calcite $\delta^{18}O$ that marks the Younger Dryas-Holocene transition in a Kulishu Cave (northeastern China) stalagmite spans 16 years at 11.53 ky BP. Across this same time period, patterns of intra-annual $\delta^{18}O$ variability indicate that the annual proportion of summer monsoon rainfall across this transition is stochastic, implying that the Kulishu Cave record can distinguish the regional monsoon response from the hemisphere-wide atmospheric reorganization.

Seasonal $\delta^{18}O$ records were also measured in two other stalagmites from caves that together with Kulishu form a north-south transect of China. These annually-banded Chinese speleothems each record different seasonal $\delta^{18}O_{rain}$ patterns despite all forming during “strong monsoon” intervals (e.g. Holocene). We interpret the distinct seasonal $\delta^{18}O$ patterns from Qingtian (central China) and Dongge (southeastern China) Caves as reflecting subtle regional differences in the relative timing and $\delta^{18}O$ value of monsoon rainfall that are similar to differences observed today. Expanding the spatial network of seasonal speleothem $\delta^{18}O$ records will help determine the mechanisms driving paleomonsoon behavior, and the extent to which the jet stream responds to abrupt climate change.

Orland I. J. et al. (2015) *Geology*, awaiting print publication.

Enhancing the accuracy of carbonate δ^{18}O and δ^{13}C measurements at WiscSIMS

Ian J. Orland[1,2], Reinhard Kozdon[3], Ben Linzmeier[1], Jody Wycech[1], Maciej Sliwinski[1], Kouki Kitajima[1], Noriko T. Kita[1], John W. Valley[1]
[1] WiscSIMS, Dept. of Geoscience, University of Wisconsin-Madison
[2] Dept. of Earth Sciences, University of Minnesota-Twin Cities
[3] Dept. of Marine and Coastal Sciences, Rutgers University

The precision of carbonate δ^{18}O analyses at WiscSIMS is well established and based on the characterization of numerous standard materials and rigorous testing of different sample preparation techniques. As the number of carbonates analyzed at WiscSIMS increased with time, particularly biocarbonates that can include complex internal structures, it has become apparent that SIMS δ^{18}O measurements of some samples have a consistent, sample-dependent offset from bulk δ^{18}O values obtained by phosphoric-acid digestion. The offset is typically <1‰; SIMS δ^{18}O values are always lower than corresponding conventional measurements. Notably, δ^{13}C offsets have not been observed, even in samples where a δ^{18}O offset is apparent. For many research projects, the δ^{18}O offset is of negligible importance because users are interested in relative (not absolute) δ^{18}O values. For the sake of improving accuracy and potentially uncovering new environmental proxies, the WiscSIMS lab has developed multiple diagnostic tools for carbonate analysis and tested numerous hypotheses for the δ^{18}O offset. This poster outlines a number of tests that were conducted in an attempt to characterize the δ^{18}O offset in different carbonate materials (e.g. *Nautilus*, foraminifera, otoliths, speleothems).

The potential causes of the δ^{18}O offset include: inter-lab standard (mis)calibration; the possibility that the measured offset is real and that conventional analyses include material that SIMS methods exclude (and vice versa); depth-profiling effects; porosity effects; and the effects of minor element composition. One explanation for the δ^{18}O offset implicates water and/or organic inclusions in the carbonate that are ionized during primary beam sputtering and affect the δ^{18}O measurement. The lab has developed diagnostic tools, including concurrent measurement of [^{16}O^{1}H] during δ^{18}O analysis and monitoring of ion yield, to help test this hypothesis.

Also tested were pre-treatment techniques (e.g. vacuum roasting, hydrogen peroxide). Their influence on the δ^{18}O value, [^{16}O^{1}H], the concentration of "organic markers" like [^{12}C^{14}N] and [^{31}P], and the mineralogy (in the case of aragonite samples) of *Nautilus*, otoliths, and speleothems were observed in a number of experiments. Other workers have found that for conventional acid-digestion analysis of carbonates, roasting has a varied and confounding effect on different samples. At WiscSIMS, vacuum roasting increased the SIMS-measured δ^{18}O of otolith and *Nautilus* samples by 0.5-1‰ consistently across the sample, while partially converting (determined by *in situ* XRD) the aragonite to calcite. Interestingly, roasting had no effect on the δ^{18}O or [^{16}O^{1}H] values of a speleothem.

Going forward, the WiscSIMS lab will continue to evaluate the δ^{18}O offset observed in some carbonates and develop useful tests to help characterize and/or minimize the effects of water and organic material on SIMS δ^{18}O measurements.

Kozdon R. et al. (2009) *Chem. Geol.* **258**, 327-337.
Matta E. M. et al. (2013) *Rapid Comm. Mass. Spec.* **27**, 691-699.
Orland I. J. (2012) PhD dissertation (UW-Madison).

Identifying cultured foraminiferal calcite for geochemical paleotemperatures calibrations using ^{87}Sr

Ann D. Russell[1], Jennifer Fehrenbacher[1], Howard Spero[1], Alex Gagnon[2]

[1]Department of Earth & Planetary Sciences, University of California, Davis
[2]School of Oceanography, University of Washington

Combining geochemical temperature proxies from foraminiferal species inhabiting distinct portions of the upper ocean (the mixed layer and the thermocline) can provide important information regarding changes in the degree of stratification, with implications for the amount of poleward heat transport and the extent of CO_2 equilibration between the surface ocean and the atmosphere. *Neogloboquadrina dutertrei* is a key species for such reconstructions, as it is associated with the deep chlorophyll maximum. Nevertheless, the few existing temperature relationships based on Mg/Ca or $\delta^{18}O$ in this species come from core tops or sediment trap material, and are poorly constrained, yielding a temperature range of ~5-6°C at a given Mg/Ca ratio.

We are developing a Mg/Ca-temperature relationship for *N. dutertrei* based on laboratory culture experiments. Specimens were collected by plankton tow, measured and photographed; individuals that recovered from collection were placed into seawater spiked with ^{87}Sr to label the calcite grown in culture. We fed the specimens every other day with immobilized *Artemia* nauplii, and took photographs daily to track the addition of chambers. After gametogenesis, specimens were archived and later analyzed for Mg/Ca, $^{87}Sr/^{88}Sr$, and other elemental ratios by laser ablation ICP-MS. Several individuals were also imaged using NanoSIMS to map the cultured calcite.

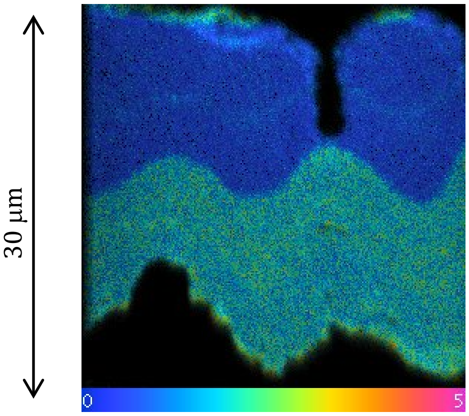


Figure 1. NanoSIMS image of ^{87}Sr in *N. dutertrei* shell (green layer was formed in culture).

The $^{87}Sr/^{88}Sr$ labeling technique clearly showed that many individuals added a calcite "rind" over pre-existing chambers (Figure 1), although relatively few individuals formed new chambers in culture. By incorporating the Mg/Ca data from the rind, we are able to expand the number of data points used in the calibration. The ability to identify the cultured rind using the $^{87}Sr/^{88}Sr$ mapping technique also suggests that it may be possible to obtain a culture-based $\delta^{18}O$-temperature relationship from the same individuals, using the IMS 1280 SIMS at the Wisconsin SIMS laboratory. The greater accuracy of paleotemperatures and paleo-$\delta^{18}O_w$ based on culture calibrations using this approach will improve reconstructions of upper ocean vertical structure, and thus improve estimates of heat transport and atmosphere-ocean CO_2 exchange.

Reliable Sr/Ca Estimates from Scleractinian Corals using SIMS: Challenges and Implications

Hussein R. Sayani[1], Kim M. Cobb[1], Anne L. Cohen[2], Brian Monteleone[2], Heather Crespo[1]
[1] School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, GA, USA
[2] Department of Geology and Geophysics, Woods Hole Oceanographic Institute, Woods Hole, MA, USA

High-resolution records of past sea-surface temperature (SST) variability are now routinely generated using Sr/Ca in fossil corals. However, post-depositional alteration of the coral skeleton (diagenesis), occurring as dissolution and/or precipitation of secondary carbonate cements, can create substantial artifacts in coral-based temperature reconstructions. Commonly used analytical techniques, such as ICP-OES, are unable to selectively sample diagenesis-free regions of fossil corals; as such diagenetic material is often inadvertently measured alongside coral aragonite. The inclusion of even 2% secondary aragonite yields artifacts of ~1°C or more in Sr/Ca-derived temperature [*Sayani et al.*, 2011]. Work by *Cohen and Hart*, 2004 and *Sayani et al.*, 2011 suggests that some alteration phases leave the interior of the coral skeleton geochemically intact, as such µm-scale analytical techniques like secondary ion probe mass spectrometry (SIMS) may allow us to extract reliable Sr/Ca estimates from diagenesis-free regions of altered corals. So far, SIMS has not been heavily used to generate coral-based temperature records [e.g *Allison and Finch*, 2004; *Cohen and Hart*, 2004] due to biologically controlled heterogeneity in coral Sr/Ca at µm-scales [e.g. *Meibom et al.*, 2008].

As a pre-requisite for interpreting SIMS data in fossil corals, we test the accuracy and reproducibility of SIMS Sr/Ca analyses by generating 2-3yr long, weekly-resolved time series from three overlapping modern coral cores collected from Palmyra Atoll (6°N, 162°W). All three modern cores were milled at mm-scales and powders for these “bulk” samples were analyzed via ICP-OES [*Sayani et al, in prep*]. Bulk monthly Sr/Ca from the three modern corals are well correlated with each other (R=0.58 to 0.62) and with Palmyra SST (R=-0.66 to -0.72) between 1980-1998CE, however mean Sr/Ca values between the cores are offset by ±0.1mmol/mol (equivalent to ±1°C). Overlapping SIMS Sr/Ca time series from these cores exhibit relatively large point-to-point variations of ~0.17mmol/mol (1σ), compared to ~0.06mmol/mol (1σ) in bulk Sr/Ca, as is common for coral SIMS analyses. However, their monthly-scale variability resolves annual SST cycles observed at Palmyra reasonably well. For our first fossil coral application, we test the fidelity of ICP-OES Sr/Ca estimates from a moderately altered 70yr old fossil coral by generating weekly-resolved SIMS Sr/Ca time series from the same core. We find that monthly-scale variability in SIMS Sr/Ca resolves annual cycles observed in Palmyra SST fairly well, however SIMS Sr/Ca values from one section are significantly offset from bulk measurements. While our work has demonstrated that coral SIMS Sr/Ca records can approach the fidelity of ICP-OES 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 in both SIMS and bulk ICPOES analyses. Thus, fossil coral Sr/Ca-based SST reconstructions may be limited more by the number of individual colonies that can be analyzed as opposed to any potential diagenetic artifacts.

References

Allison, N., et al. (2004) *Geochem. Geophys. Geosys.* Doi 10.1029/2004gc000696
Cohen, A. L., et al. (2004) *Paleoceanography*. Doi 10.1029/2004pa001084
Meibom, A., et al. (2008) *Geochim. Cosmochim. Acta*. Doi 10.1016/J.Gca.2008.01.009
Sayani, H. R., et al. (2011) *Geochim. Cosmochim. Acta*. Doi 10.1016/J.Gca.2011.08.026

Paleoclimate and tooth enamel. Where do we go from here?

Margaret J. Schoeninger, University of California San Diego, mjschoen@ucsd.edu

Intra-tooth variation in $\delta^{18}O$ values of mammalian dental enamel ($\delta^{18}Oen$) shows great promise as a proxy method for reconstructing paleoclimate. Close to 20 years ago, the oxygen isotope compositions of gazelle tooth enamel from two areas in Kenya, measured using a laser fluorination approach, showed that $\delta^{18}Oen$ values varied with tooth growth patterns, animal physiology, and theoretical models of water use (Kohn 1996; Kohn et al. 1996). More recently, samples of dental enamel, removed sequentially from the gum to the crown of molar teeth of South African domestic animals had $\delta^{18}Oen$ values correlating with birth season (Balasse et al. 2003).

In some mammals, a single tooth may take as long as a year to form so a single tooth monitors a year-long period of the source of oxygen in the tooth enamel, i.e. the animal's body water (Longinelli and Nuti 1973; Longinelli 1984). Animals that must drink water (e.g., humans, goats) show variation in $\delta^{18}Oen$ values that correlate with variation in $\delta^{18}O$ values of local rain across different seasons of the year (usually cold versus warm). In contrast, animals that obtain their body water from their food (e.g., gazelles, deer) have values correlating with relative humidity (Cormie et al. 1994).

In relatively archaeological animal teeth, the technique appears to work extremely well for reconstructing rainfall patterns within single regions and climatic differences across geographic regions (Bocherens et al. 2001; Balasse et al. 2002; Balasse et al. 2003). Pleistocene fossil animals can also produce reliable and accurate values. Adult goats and gazelles from the Neandertal occupied Amud Cave in Israel (53-70 ka), had $\delta^{18}Oen$ values indicating wetter ecological conditions than at anatomically modern human (AMH) occupied Qafzeh Cave, Israel at approximately 92 ka. At Amud Cave, the variation in $\delta^{18}Oen$ values of a nondrinking species (i.e., gazelles) suggested that births occurred in more than once season of the year, which today occurs only under wetter than normal conditions. And, the magnitude and pattern of intra-tooth variation in $\delta^{18}Oen$ values of a species that must drink (i.e., goat) indicated that rain fell throughout the year unlike today when rain occurs only in the winter. AMH occupation of Qafzeh Cave, however, occurred when the region was more open and arid than that during the subsequent Glacial Period or today.

Older teeth may not, however, retain a biological signal in the $\delta^{18}Oen$ values. Sample screening by cathodoluminescence of 3.9 million year old mammalian teeth recovered from a single excavation in northern Kenya identified areas of extensive mineral alteration while other areas appeared minimally altered (Schoeninger et al. 2003a). The outer surface of the enamel, the enamel near dentine, and the enamel along cracks in the tooth luminesced whereas the interior enamel was dark suggestion retention of its biogenic mineral structure. Further investigation via ion micro- probe, electron microprobe, and transmission electron microscope, confirmed that the fossil tooth chemistry included the diagenetic precipitation of secondary minerals and the chemical alteration of the biogenic apatite (Kohn et al. 1999). The authors cautioned extreme care in separating secondary minerals from original biogenic apatite for paleobiological or paleoclimate studies.

Yet, bulk powder removed from enamel areas that appeared minimally altered had $\delta^{18}Oen$ values that matched expectations of wetter conditions in the region 3.9 million years ago compared with today (Schoeninger et al. 2003b). Exotic trees and treedwelling nonhuman primate species recovered locally and in nearby deposits, indicated that woodlands were present in the region 3.9 million years ago unlike today. The difficulty was and remains that using the δ^{18}Oen values for paleoclimate reconstruction as well as for identification of altered and unaltered enamel requires circular reasoning where values accepted as indicators of ecology are also accepted as evidence of a lack of diagenetic alteration. The question posed by this presentation is: where do we go from here? The project described by Melanie Beasley later in this conference was designed to answer the question of whether or not there are regions within these fossil teeth where the δ^{18}Oen values are truly biogenic values.

References Cited:

Balasse M, Ambrose S, Smith A, and Price TD. 2002. The seasonal mobility model for prehistoric herders in the South-western Cape of South Africa assessed by isotopic analysis of sheep tooth enamel. J Archaeol Sci 29:917-932.

Balasse M, Smith A, Ambrose S, and Leigh SR. 2003. Determining sheep birth seasonality by analysis of tooth enamel oxygen isotope ratios: the Late Stone Age site of Kasteelberg (South Africa) J Archaeol Sci 30:205-215.

Bocherens H, Mashkour M, Billiou D, Pellé E, and Mariotti A. 2001. A new approach for studying prehistoric herd management in arid areas: intra-tooth isotopic analyses of archaeological caprine from Iran. Earth and Planetary Sciences 332:67-74.

Cormie AB, Luz B, and Schwarcz HP. 1994. Relationship between the hydrogen and oxygen isotopes of deer bone and their use in the estimation of relative humidity. Geochimica et Cosmochimica Acta 58(16):3439-3449.

Kohn MJ. 1996. A predictive model for animal δ^{18}O: explaining old studies and designing new ones. Geochimica Cosmochimica Acta 60(23):4811-4829.

Kohn MJ, Schoeninger MJ, and Barker WW. 1999. Altered states: effects of diagenesis on fossil tooth chemistry. Geochimica et Cosmochimica Acta 63(18):2737-2747.

Kohn MJ, Schoeninger MJ, and Valley JW. 1996. Herbivore tooth oxygen isotope compositions: effects of diet and physiology. Geochemica et Cosmochemica Acta 60(20):3889-3896.

Longinelli A. 1984. Oxygen isotopes in mammal bone phosphate: A new tool for paleohydrological and paleoclimatological research? Geochimica et Cosmochimica Acta 48:385-390.

Longinelli A, and Nuti S. 1973. Oxygen isotope measurements of phosphate from fish teeth and bones. Earth and Planetary Science Letters 20:337-340.

Schoeninger MJ, Hallin K, Reeser H, Valley JW, and Fournelle J. 2003a. Isotopic alteration of mammalian tooth enamel. International Journal of Osteoarchaeology 13:11-19.

Schoeninger MJ, Reeser H, and Hallin K. 2003b. Paleoenvironment of Australopithecus anamensis at Allia Bay, East Turkana, Kenya: evidence from mammalian herbivore enamel stable isotopes. Journal of Anthropolgical Archaeology 22:200-207.

Impact Analysis of Climate Change on the Dynamics of Glaciers, Garhwal Himalaya

M. TAMIL SELVAN
Remote Sensing and GIS Centre, CSRD,
Jawaharlal Nehru University, New Delhi – 110 067, India
mtselvan@jnu.ac.in

ABSTRACT

Glaciers have been retreating worldwide since the end of the Little Ice Age (1550-1850), but in recent decades they have begun melting at very high rates. The prolonged periods of day and night over the North and South polar regions are not existing in the Himalayan region. But the outflow of cold from the Himalayas produces a steeper temperature gradient due to their extremely high altitude and proximity to the highly energetic tropical environment. Outside the polar region, Himalaya has the maximum concentration of glaciers. 9.04% of the Himalaya is covered with glaciers, with 30-40% additional area being covered with snow.

Natural geomorphological forms are formed by various surface natural agencies and their impact on considering area. Along with surface agencies, the tectonic forces originating deep below the surface of earth also change surface configuration, increase or reduce the rate of surface modification intensity. Hence, analyzing the characteristics of these parameters was utilized to differentiate the different environmental parameters of the rocks in various studies. In this study, the drainage and basin morphometric parameters were obtained from SRTM (Shuttle Radar Topographic Mission) DEM(Digital Elevation Model) data of the Garhwal Himalayan region and analysed. The area is situated north of Main Central Thrust (MCT), which separates the metamorphic from the underlying very low grades of un-metamorphosed sedimentary sequence of the lesser Himalayas. It has been observed that drainage morphometry derived from this Semi-automated technique follows standard rules. The high density of stream frequency and high drainage texture on surface of big glaciers indicate that glacier surface is not uniform in lower altitude and these two parameters can be utilized in automatic mapping of the debris covered glaciers in Garhwal Himalayas. Distribution of the relative relief along the major drainage at some location show asymmetrical distribution, indicate active tectonic at such locations. Dissection index is low at high altitude and increase in downstream direction, it indicate that convex profile at higher altitude and concave at lower altitude. The convex profile does not help in active mobilization of the weathered material at higher altitude, while weathered

material mobilization is quick at lower altitude. The whole of the valley is dominated by low value of Ruggedness index except few places at downstream at junction of the tributaries with main stream especially at lower altitude and main valley.

SIMS bias on isotope ratios in dolomite-ankerite: $\delta^{18}O$ & $\delta^{13}C$ matrix effects

Maciej G. ŚLIWIŃSKI[1*], Kouki KITAJIMA[1,2], Reinhard KOZDON[1,3], Michael J. SPICUZZA[1,4], John H. FOURNELLE[4], Adam DENNY[1,4] and John W. VALLEY[1,2,4]

[1] *WiscSIMS, Department of Geoscience, University of Wisconsin-Madison, Madison, WI, 53706*

[2] *NASA Astrobiology Institute, Department of Geoscience, University of Wisconsin-Madison, Madison, WI, 53706*

[3] *Department of Marine and Coastal Sciences, Rutgers, The State University of New Jersey, New Brunswick, NJ, 08901-8521*

[4] *Department of Geoscience, University of Wisconsin-Madison, Madison, WI, 53706*

This work explores the effects of Fe^{2+} substitution on SIMS $\delta^{13}C$ and $\delta^{18}O$ bias (or 'instrumental mass fractionation') in the analysis of carbonate minerals with compositions that fall along the dolomite-ankerite solid solution [$CaMg(CO_3)_2$-$CaFe(CO_3)_2$]. Bias is the per mil (‰) difference between measured 'raw' and 'true' (*i.e.,* VPDB or VSMOW) values of $\delta^{13}C$ or $\delta^{18}O$. We document the development of a suite of SIMS calibration standards (13 each for C and O isotopes) spanning the chemical compositional range between Fe# = 0.004 and 0.789 [Fe# = molar Fe/(Mg+Fe)].

[Background and motivation] Accurate isotope ratio measurements from sample materials by SIMS require the use of matrix-matched standards to correct for mass fractionation (bias) that occurs: 1) during the production and acceleration of ions from the sample surface (sputtering), 2) during the transmission of secondary ions through the mass spectrometer, and 3) during detection.

For a given configuration of the ion microprobe at WiscSIMS (CAMECA IMS 1280), the influence of instrumental parameters to total bias during an analytical session can be held nearly constant; any instrumental drift that occurs can be monitored and corrected by regularly analyzing a running-standard. For minerals that exhibit solid-solution behavior, this leaves the component of total bias that is a function of variable chemical composition (*i.e.,* the sample matrix effect) in need of calibrating.

There is at present no comprehensive theoretical model for accurately predicting secondary ion yields and thoroughly accounting for the bias imparted to isotope ratios during sputtering. Accurate isotope ratio determinations are thus only possible if a sufficient number of well-characterized standards are employed to empirically characterize, on a session-by-session basis, the total instrumental bias as a function of variable chemical composition.

[Results] Under routine operating conditions, the magnitude of SIMS $\delta^{18}O$ bias *decreases* exponentially with increasing Fe# (by ~10.5‰; Fig. 1, outer right-hand axis). That is, the bias is *greatest* for end-member dolomite (-13.5‰) and *smallest* for the most Fe-rich ankerite (-3‰ for Fe# = 0.789).

In contrast, the magnitude of SIMS $\delta^{13}C$ bias *increases* exponentially with increasing Fe# (by -4.5‰; *i.e.,* values become more negative and hence move further away from true VPDB values; Fig. 1, inner right-hand axis). That is, the bias is *smallest* for end-member dolomite (~ -47.5‰) and *largest* for the most Fe-rich ankerite (~ -52‰ for Fe# = 0.789).

Minor Mn substitution appears to contribute no secondary matrix effects to measurements of SIMS $\delta^{13}C$ and $\delta^{18}O$ bias from the suite of dolomite-ankerite calibration standards [at concentrations < 2.6% molar Mn/(Ca+Mg+Fe+Mn)].

In constructing working calibration curves (Fig. 1), measured values of SIMS $\delta^{13}C$ and $\delta^{18}O$ bias for the suite of calibration standards are normalized to a running standard for drift-monitoring purposes (commonly end-member dolomite standard UW6220; normalized values are thus expressed as 'bias*(STD-UW6220)').

[SIMS $\delta^{18}O$ bias calibration] The compositional dependence of SIMS $\delta^{18}O$ bias (*i.e.* the sample matrix effect) is expressed using the Hill equation, which has wide-ranging applicability in describing empirical relationships of the 'component concentration' *vs*. 'measured effect' type, especially for systems that behave nonlinearly and reach saturation. For calibrations employing either 10- or 3-µm-diameter spot-size measurements, this yields residual values ≤ 0.3-0.4‰ relative to CRM NBS-19 for most standards in the suite (example 10-µm calibration shown in Fig. 1).

Analytical precision for $\delta^{18}O$ is ± 0.3‰ (2SD, standard deviations) for 10-µm spots and ± 0.7‰ (2SD) for 3-µm spots, based on the spot-to-spot reproducibility of a running standard (*n = 8*) that 'brackets' each set of 10 sample measurements. The total analytical uncertainty for individual sample spot analyses is approximated by a combination of precision and calibration residuals (propagated in quadrature), suggesting accuracy of ± 0.5‰ (2SD) for 10-µm spots and ± 1‰ (2SD) for 3-µm spots.

[Results: SIMS δ^{13}C bias calibration] The compositional dependence of SIMS δ^{13}C bias (*i.e.* the sample matrix effect) is again expressed using the Hill equation, although the modeled effect for carbon is the opposite of that observed for oxygen (Fig. 1). For calibrations employing the commonly used 6-µm-diameter spot-size, this yields residual values ≤ 0.3‰ relative to CRM NBS-19 for most standards in the suite.

Analytical precision for δ^{13}C is ± 0.6-1.2‰ (2SD), based on the spot-to-spot reproducibility of a running standard (*n = 8*) that 'brackets' each set of 10 sample measurements. The total analytical uncertainty for individual sample spot analyses of dolomite-ankerite is approximated by combination of precision and the calibration residual (propagated in quadrature), suggesting accuracy of ± 1.0-1.5‰ (2SD).

[Concluding remarks] It is common for the magnitude of SIMS δ^{13}C and δ^{18}O bias measured from calibration standards to vary by several per mil from session-to-session. We find, however, that the overall distribution of standard data points in relation to one another in working calibration plots (*i.e.*, bias*(STD-UW6220) vs. Fe# for either δ^{13}C or δ^{18}O; Fig. 1) remains remarkably consistent from session-to-session. The values of the Hill equation curve shape parameters '*n*' (a sigmodicity factor) and '*k*' (= Fe# at 1/2 bias max) remain unchanged, whereas the best-fit value of the '$bias*_{max}$' parameter behaves as an analytical session-specific scaling factor. Thus while the accuracy and precision of *in situ* stable isotope analyses by SIMS are improved using multiple calibration standards, the constant shape of the Hill function for δ^{13}C and δ^{18}O analyses at WiscSIMS shows that an approximate correction can be made for variable Fe# based on just two standards (dolomite and Fe-rich ankerite).

[References]

Śliwiński *et al., (in review)*. SIMS bias on isotope ratios in dolomite-ankerite, Part I: δ^{18}O matrix effects. *Geostand. Geoanal. Res.*

Śliwiński *et al., (in prep)*. SIMS bias on isotope ratios in dolomite-ankerite, Part II: δ^{13}C matrix effects. *Geostand. Geoanal. Res.*

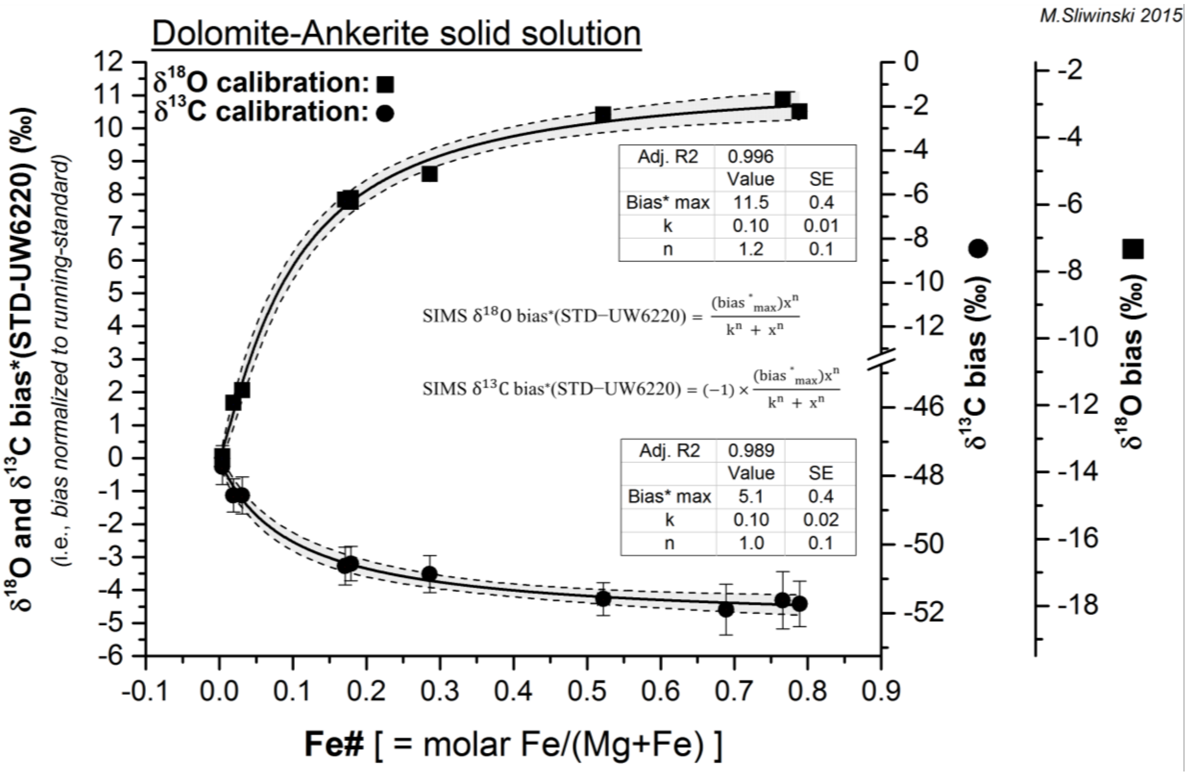


Figure 1. ***(Upper trend)*** *A typical calibration relating SIMS δ^{18}O bias (‰) to the cation composition of the dolomite-ankerite solid solution series [Fe# = Fe / (Mg+Fe)] for measurements employing a 10-µm diameter spot-size.* ***(Lower trend)*** *A typical calibration relating SIMS δ^{13}C bias (‰) to Fe#. In both cases, the matrix effect can be accurately estimated using the Hill equation, which is commonly employed to describe relations of 'concentration' vs. 'effect', especially in systems that behave nonlinearly and reach saturation. Dashed lines represent regression confidence bands (at the 95% level). Error bars represent propagated measurement uncertainties.*

Sub-orbital climate variability in the Late Oligocene North Atlantic Ocean

Richard E. Smith ([a*]), Ursula Röhl ([b]), Thomas Westerhold ([b]),
Steve M. Bohaty ([a]), Cédric M. John ([c]), Paul A. Wilson ([a])-

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([a]) National Oceanography Centre, University of Southampton, Southampton SO14 3ZH, UK. *E-mail: Richard.Smith@noc.soton.ac.uk
([b]) MARUM, University of Bremen, Leobener Strasse, Bremen, Germany
([c]) Department of Earth Science and Engineering, Imperial College London, London, UK.

The beginning and end of the Oligocene were marked by major glaciation events. While the Eocene-Oligocene transition is known to have initiated sustained major ice sheets on Antarctica, the intensification of glaciation associated with the Oligocene-Miocene transition appears to have been ephemeral. The inference of a rapid growth and then retreat of large Antarctic ice sheets on orbital time scales is difficult to reconcile with the strong hysteresis seen in the results of numerical ice sheet model experiments and the modest variability seen in reconstructions of atmospheric CO2 levels. Furthermore, we know very little about the contemporaneous behaviour of the cryosphere in the high northern latitudes and virtually nothing about climate variability at sub-orbital timescales, in sharp contrast to the Pleistocene.

IODP Expedition 342 (Newfoundland Sediment Drifts) recovered a number of highly expanded intervals, including from the Oligocene at Site 1405 (NW Atlantic, 40°N). This presents an exciting opportunity to break new ground and develop an understanding of Oligocene climate dynamics at unparalleled temporal resolution in the North Atlantic Ocean, a key site for ocean circulation. We present data from the latest Oligocene at Site 1405, where sedimentation rates are high (>10cm/kyr) to provide the first indications of sub-orbital ocean climate cyclicity in the Paleogene.

Quantifying Isotopic Variations in Cultured Planktic Foraminifera at the Micron Scale

Howard J. Spero

Department of Earth and Planetary Sciences, University California Davis

Isotope and elemental geochemistry from fossil foraminifera are sources of fundamental environmental information for reconstructing climate and ocean-atmosphere changes throughout the Cenozoic. As such, there is a critical need to develop a mechanistic understanding of the mechanisms by which geochemical signals are incorporated into foraminifera shell calcite as well as calibrating the empirical relationships used to interpret geochemical data for reconstructing oceanographic, climatic and atmospheric change in the fossil record. New geochemical tools such as SIMS, NanoSIMS and laser ablation ICP-MS are providing researchers with an unparalleled view of the foraminifera geochemistry at the micron and submicron level. In this talk, I will present data from laboratory experiments with living planktonic foraminifera that demonstrates SIMS can quantify the oxygen and carbon isotope composition of intrashell foraminifera calcite, relative to VPDB, with spatial resolution between 3-6 μm (Vetter et al., 2013; Vetter et al., 2014). I will also show how NanoSIMS has been used in conjunction with LA-ICP-MS to explain elemental variation (e.g. Mg/Ca) in foraminifera shells as well as demonstrating how NanoSIMS and transmission electron microscopy (TEM) can be used together to explore carbon flow within the cells of a foraminifera-symbiont system (LeKieffre, Meibom and Spero; unpub data). Finally, I will show new results using Atom Probe Tomography (APT) (Branson, Gagnon and Spero, unpub. data) that characterizes the organic matrix/inorganic calcite interface in foraminifera calcite with sub-nm scale resolution. Together, these tools are helping to unravel the fundamental mechanisms of biomineralization and geochemical variation in foraminifera calcite with unprecedented resolution, thereby providing paths to develop new methods to tease out novel information from the fossil record.

Vetter, L., Kozdon, R., Mora, C.I., Eggins, S.M., Valley, J.W., Hönisch, B., Spero, H.J., 2013. Micron-scale intrashell oxygen isotope variation in cultured planktic foraminifers. Geochim. Cosmochim. Acta 107, 267-278.

Vetter, L., Kozdon, R., Valley, J.W., Mora, C.I., Spero, H.J., 2014. SIMS measurements of intrashell $\delta^{13}C$ in the cultured planktic foraminifer *Orbulina universa*. Geochimica et Cosmochimica Acta 139, 527-539.

In Situ Isotope Geochemistry by SIMS: Accuracy vs. Precision

John W. Valley, WiscSIMS, Dept. of Geoscience, University of Wisconsin-Madison

In situ analysis of stable isotope ratios by SIMS (secondary ion mass spectrometer or ion microprobe) has reduced analytical volumes by up to 10^6 compared to conventional bulk techniques. The advent of multicollector SIMS instruments permits measurements at sub-10μm scale with precision improved by $\sim 10^2$ compared to earlier SIMS techniques. Smaller spots, sub-1μm, are possible with a trade-off; precision scales with the number of atoms counted and approaches the theoretical limits imposed by Gaussian counting statistics. For oxygen isotope ratios, spot-to-spot precision of 0.1‰ (1SD) is obtainable for 10-μm spots (~1 μm deep, ~ 1 ng) and degrades to ~1‰ for 1 μm spots (~ 1 pg).

SIMS data are biased by processes during sample sputtering, and transmission and detection of secondary ions. There is no general theory to correct for instrumental bias (or IMF, instrumental mass fractionation). In practice, data are compared to standards that are matched with samples for atomic structure and chemical composition. If standards match samples well, then analytical accuracy can approach precision. However, there are a range of potentially confounding effects that must be carefully controlled to achieve this result, relating to: tuning and operation of the SIMS, sample preparation and characterization, and standardization. This talk will discuss the importance of: homogeneous well-calibrated standards; correlated chemical analysis by electron microprobe if samples are variable in chemistry; proper sample mounting and polishing; sample imaging; and for some minerals, orientation.

In situ analysis permits correlation of isotope data with textures and other analysis. This opens exciting and fundamental new avenues of study for many materials carrying paleoclimate records. Examples will include: foraminifera, mollusks, otoliths, speleothems, soil carbonates, diagenetic cements, and tooth enamel.

Kita NT, Takayuki Ushikubo, Bin Fu and John W. Valley (2009) High Precision SIMS Oxygen Isotope Analyses and the Effect of Sample Topography, Chemical Geology, doi:10.1016/j.chemgeo.2009.02.012. 264: 43-57.

Kita NT, Huberty JM, Kozdon R, Beard BL, and Valley JW (2011) High precision SIMS oxygen, sulfur and iron stable isotope analyses of geological materials: Accuracy, surface topography and crystal orientation. SIMS XVII Proceedings, Surface and Interface Analysis, v 43: 427-431, DOI 10.1002/sia.3424.

Sliwinski MG, Kitajima, K, Kozdon, R, Spicuzza, MJ, Fournelle, JH, Valley, JW (2015) On constraining SIMS matrix effects on $\delta^{18}O$ measured in the dolomite-ankerite solid-solution, Geostandards and Geoanalytical Research, in review.

Valley JW and Kita NT (2009) In situ Oxygen Isotope Geochemistry by Ion Microprobe, In: Fayek M. (ed) MAC Short Course: Secondary Ion Mass Spectrometry in the Earth Sciences, v 41, 19-63.

Marsh Madness: an Early Holocene sea-level record from peat and paleosols in southeastern Louisiana

Lael Vetter[1], Brad E. Rosenheim[1,2], Alvaro Fernández[3], and Torbjörn E. Törnqvist[1]

[1]Department of Earth and Environmental Sciences, Tulane University, New Orleans, LA
[2]College of Marine Science, University of South Florida, St. Petersburg, FL
[3]Geological Institute, ETH Zurich, Zurich, Switzerland

The start of the Holocene interglacial period was a critical time during the transition from glacial to interglacial climate conditions. During the early Holocene, continental ice sheets continued to retreat, causing 50-60 m of sea-level rise. This was punctuated by occasional rapid, short-lived sea-level rise events associated with catastrophic ice sheet collapse. Here we present a record of early Holocene sea-level rise from new sediment cores collected in southeastern Louisiana. Each core captures a transgressive sea-level sequence 14-25 m below present sea-level: an immature paleosol overlain by basal peat that accumulated in an estuarine marsh, overlain by marine lagoonal muds. Radiocarbon dating of basal peat layers yields flooding ages for marine transgression at different depths, from which we reconstruct a regional sea-level history.

Sea-level reconstructions from basal peat records contain several inherent sources of uncertainty, including elevation and depth determination, radiocarbon age errors, constraints on regional subsidence, and interpretations of different depositional facies. For example, during periods of rapid sea-level rise, basal peats may not be preserved in the sedimentary record, and the flooding surface is marked by an organic-rich paleosol overlain by lagoonal deposits. Bulk ^{14}C dates of paleosol organic carbon frequently provide ages older than the time of soil burial, in comparison to plant macrofossils ^{14}C ages. We employ a ramped pyrolysis technique to measure ^{14}C age spectra in cores where basal peat is absent. Surprisingly, we find narrow ^{14}C age spectra across all thermal aliquots from both paleosols and peats, suggesting active layer chemical processing of carbon in these facies during periods of rapid sea-level rise. This suggests that the paleosols can also provide an accurate record of the timing of marine transgression.

Other cores contain a complex record of coastal marsh development during periods of variable sea-level rise. A re-established marsh peat is present 1-4 m above the initial transition to full marine conditions, indicating a sequence of marsh development, rapid sea-level rise, followed by further marsh development as the rate of relative sea-level rise decelerated. Additional paleoenvironmental reconstruction is achieved via stable carbon isotope analyses, foraminiferal and microfaunal analysis, and lignin phenol and other biomarkers. These results have important implications for reconstructing the response of coastal marshes and associated plant communities to variable rates of sea-level rise.

Extrinsic and Intrinsic Causes of Past Abrupt Changes in Terrestrial Ecosystems:

Jack Williams, UW Madison
Kevin Burke, UW Madison
Matt McGlone, Landcare Research, New Zealand

The geological record offers global change ecologists a rich record of abrupt changes in ecological systems, which we can use to understand the processes governing these past regime shifts. These governing processes can be grouped into two broad categories: hammers (strong climatic or other extrinsic forcings to an ecological system) and canoes (tipping points produced by processes intrinsic to ecological systems or via positive biosphere-atmosphere feedbacks). Each produces distinct sets of implications and research questions for ecologists; an overarching research question is to understand the relative contribution and interaction among extrinsic and intrinsic processes. The rapid changes in plant communities in Western Europe during the last deglaciation appears to be an example of a hammer, i.e. direct responses to rapid changes in atmospheric circulation, temperature, and moisture availability. Past rapid climate changes allow us to ask how quickly species and ecosystems can adapt to climate changes at rates as fast or faster than those expected for this century. Abrupt changes terrestrial ecosystems during the Holocene appear to be mostly governed by hydrological variability and, often, intrinsic tipping points within ecological systems. For example, the progressive regional aridification in the US Great Plains and North Africa appears to have caused a series of abrupt local-scale responses, with the timing of abrupt change differing among sites and among taxonomic groups at a site. These variations manifest both as time transgressive sequences and as temporal mosaics of sites varying in timing of response. We can use these past events to identify tipping elements (ecological systems particularly prone to abrupt change) and identify early warning signals of abrupt change.

Calibration of *in situ* SIMS δ^{18}O values to whole shell δ^{18}O compositions using Holocene planktic foraminifera

Wycech, J.B.; Kelly, D.C.; Kozdon, R.; Valley, J.W.
University of Wisconsin-Madison, Department of Geoscience

The use of SIMS to perform high-resolution, *in situ* δ^{18}O analyses on minute domains within individual foraminiferal shells is an emerging field of research that holds great potential for enhancing the fidelity of paleoclimate records (Kozdon et al., 2009, 2011). Relatively high precision (±0.3‰) is now possible by SIMS, but continued tests of the accuracy of such *in situ* δ^{18}O measurements is essential to establish the veracity of this state-of-the-art technique. To this end, a comparative study was conducted using both *in situ* SIMS and conventional gas-source IRMS analyses, to measure the δ^{18}O of the same chamber in an individual foraminiferal shell. The initial experiment was performed on 20 large (~600 µm) *Orbulina universa* shells exhibiting varying states of preservation (4 well-preserved glassy, 1 intermediate, 15 frosty). The shells were handpicked from the uppermost 2 cm (Holocene) of piston core CH15-PC9-00 taken atop Blake Ridge (2,790 meters water depth) in the northwestern Atlantic. The extant planktic foraminiferal species *O. universa* was selected for three reasons: (1) field and culturing studies have established the ecological affinities of this symbiont-bearing, mixed-layer species (e.g. Spero and Parker, 1985; Hemleben et al., 1989), (2) the fractionation of δ^{18}O in *O. universa* calcite vs. water has been empirically calibrated to temperature (e.g., Bemis et al., 1998; Spero, 1998), and (3) adult specimens grow a final chamber that completely envelops the smaller juvenile chambers (Spero, 1988). The latter attribute is particularly advantageous because the final chamber is exceptionally large and eliminates δ^{18}O "contamination" from juvenile chambers. Cultured *O. universa* shells have been measured by SIMS (Vetter et al., 2013), and allow us to compare core top shells to those obtained from culture.

In this study, each shell was manually broken into smaller fragments, the majority of the final chamber fragments were pooled for δ^{18}O analysis by conventional gas-source IRMS, and a remaining fragment was cast in epoxy for SIMS analysis. Thus, the final-chamber δ^{18}O of an individual *O. universa* shell was measured by both SIMS and gas-source IRMS, facilitating direct comparison of two δ^{18}O datasets. SIMS measurements show no systematic δ^{18}O trends across the final shell chamber wall; therefore, the multiple *in situ* δ^{18}O measurements from each final shell chamber were averaged for comparison to the IRMS measurement. Comparison of the SIMS δ^{18}O values to corresponding IRMS δ^{18}O values for the same shell reveals a linear relationship across a 3‰ range with the SIMS values being, on average, ~0.9‰ lower thereby providing a correction of $\delta^{18}O_{SIMS}$ + 0.86‰. The 0.9‰ offset is still evident in *O. universa* shells (1 well-preserved glassy, 3 intermediate, 11 frosty) that have undergone hydrogen peroxide cleaning and sonication. This indicates that the δ^{18}O offset is not caused by SIMS measurement of organic matter or IRMS measurement of diagenetic/coccolith calcite.

The validity of the 0.9‰ correction has been investigated through its application on pre-gametogenic (PREGAM) SIMS $\delta^{18}O$ values acquired from *Globigerinoides sacculifer* shells recovered from an equatorial Pacific sediment trap and Holocene-aged core top sample. The uncorrected PREGAM average SIMS $\delta^{18}O$ values for *Gs. sacculifer* shells from the sediment trap and core top sample fall ~0.6-0.8‰ below the predicted equilibrium $\delta^{18}O_{calcite}$ values of -3.2‰ and -3.1‰ (PDB), respectively. By comparison, the corrected PREGAM SIMS $\delta^{18}O$ values are in agreement with the predicted equilibrium $\delta^{18}O_{calcite}$ value, and reflect realistic calcification temperatures based on the mixed-layer depth habitat of *Gs. sacculifer*. The cause of the offset remains unknown; however, it may be due to the presence of water or organic matter only measured by SIMS and/or a matrix effect of the foraminiferal calcite.

References

Bemis, B.E., Spero, H.J., Bijma, J., and Lea, D.W., 1998, Reevaluation of the oxygen isotopic composition of planktonic foraminifera: Experimental results and revised paleotemperature equations: Paleoceanography, v. 13, no. 2, p. 150–160.

Hemleben, C., Spindler, M., and Anderson, O., 1989, Modern Planktonic Foraminifera: Springer-Verlag New York.

Kozdon, R., Ushikubo, T., Kita, N.T., Spicuzza, M., and Valley, J.W., 2009, Intratest oxygen isotope variability in the planktonic foraminifer N. pachyderma: Real vs. apparent vital effects by ion microprobe: Chemical Geology, v. 258, no. 3-4, p. 327–337.

Kozdon, R., Kelly, D.C., Kita, N.T., Fournelle, J.H., and Valley, J.W., 2011, Planktonic foraminiferal oxygen isotope analysis by ion microprobe technique suggests warm tropical sea surface temperatures during the Early Paleogene: Paleoceanography, v. 26, no. 3.

Spero, H.J., and Parker, S.L., 1985, Photosynthesis in the symbiotic planktonic foraminifer Orbulina universa, and its potential contribution to oceanic primary productivity: Journal of Foraminiferal Research, v. 15, no. 4, p. 273–281.

Spero, H., 1988, Ultrastructural examination of chamber morphogenesis and biomineralization in the planktonic foraminifer Orbulina universa: Marine Biology, v. 99, p. 9–20.

Spero, H.J., 1998, Life History and Stable Isotope Geochemistry of Planktonic Foraminifera: Paleontological Society Papers, v. 4, p. 7–36.

Vetter, L., Kozdon, R., Mora, C.I., Eggins, S.M., Valley, J.W., Hönisch, B., and Spero, H.J., 2013, Micron-scale intrashell oxygen isotope variation in cultured planktic foraminifers: Geochimica et Cosmochimica Acta, v. 107, no. C, p. 267–278.

Detrital zircon U-Pb age evidences for provenance of Chinese Loess

HANZHI ZHANG1*, HUAYU LU1**, XISHENG XU2, XIAOMING LIU3, TAO YANG2, THOMAS STEVENS4, ZHIWEI XU1, TIAN ZHANG5, FANG LEI 1, HAN FENG1

1 *School of Geographic and Oceanographic Sciences, Nanjing University, Nanjing, 210093, China*
2 *State Key Laboratory for Mineral Deposits Research, School of Earth Sciences and Engineering, Nanjing University, Nanjing, 210093, China*
3 *State Key Laboratory of Continent Dynamics, Department of Geology, Northwest University, Xi' an, 710069, China*
4 *Centre for Quaternary Research, Department of Geography, Royal Holloway, University of London, Egham, Surrey TW20 0EX, UK*
5 *School of Astronomy and Space Science, Nanjing University, Nanjing, 210093, China*

Key words: Loess, Provenance, Zircon, LA-ICP-MS

Abstract

The Gobi deserts, deserts and sand fields in northwest China is one of the most important source areas of the world-wide mineral dust. The eolian dust would deposit in China, Northern Pacific Ocean and even Greenland. The emission, transportation, deposition of dust has great influence on earth's system. Besides, the Chinese Loess Plateau (CLP) is the most important late Cenozoic wind -blown dust archives on land. Therefore, investigation on the characteristics of sediment in these source areas could provide essential information for understanding world wide dust cycle and its impact. In spite of lots of work in this issue, great controversy still exists. Detrital zircon age distribution provides a possibility to discriminate potential provenances of loess deposit CLP. 29 samples on the North Tibet Plateau (NTP) plain, Gobi Altay Mountain (GAM) plain, Tengger desert and Mu Us sand field are selected to get the U-Pb ages of detrital zircons using laser ablation–inductively coupled plasma–mass spectrometer (LA-ICP-MS). Multi-Dimensional Scaling (MDS) analysis is applied here to show the similarity of these data and previous ones. The MDS analysis shows that, the Tengger Desert sediments are mainly made of GAM plain materials. While, sediments in the south edge of Tengger Desert are mainly influenced by the NTP plain. On the other hand, sediments in the north Mu Us sand field are largely influenced by the North China Craton and those in the south are basically influenced by the NTP plain. Moreover, materials in the CLP are homogenous and mainly from the NTP plain.

Linear Weakening of the AMOC in Response to Lowering Ice-sheet Topography in CCSM3

Jiang Zhu[1], Zhengyu Liu[1,2], Xu Zhang[3], Ian Eisenman[4], and Wei Liu[4]

[1]Department of Atmospheric and Oceanic Sciences and Center for Climatic Research, University of Wisconsin-Madison, Madison, Wisconsin 53706, USA
[2]Laboratory for Climate and Ocean-Atmosphere Studies, School of Physics, Peking University, Beijing 100871, P. R. China
[3]Alfred Wegener Institute Helmholtz Centre for Polar and Marine Research, Bussestrasse 24, D-27570 Bremerhaven, Germany
[4]Scripps Institution of Oceanography, University of California, San Diego, La Jolla, California 92093, USA

Abstract

The transient response of the Atlantic Meridional Overturning Circulation (AMOC) to a deglacial ice-sheet retreat is studied using the Community Climate System Model version 3 (CCSM3), with a focus on orographic effects rather than meltwater discharge. It is found that the AMOC weakens significantly (41%) in response to the deglacial ice-sheet retreat. The AMOC weakening follows the decrease of the Northern Hemisphere ice-sheet volume linearly, with no evidence of abrupt thresholds. A wind-driven mechanism is proposed to explain the weakening of the AMOC: lowering the Northern Hemisphere ice sheets induces a northward shift of the westerlies, which causes a rapid eastward sea-ice transport and expanded sea-ice cover over the subpolar North Atlantic; this expanded sea ice insulates the ocean from heat loss and leads to suppressed deep convection and a weakened AMOC. A sea ice-ocean positive feedback could be further established between the AMOC decrease and sea-ice expansion.

Participants of WiscSIMS Workshop - High Resolution Proxies of Paleoclimate
(University of Wisconsin-Madison, May 31 - June 3, 2015)

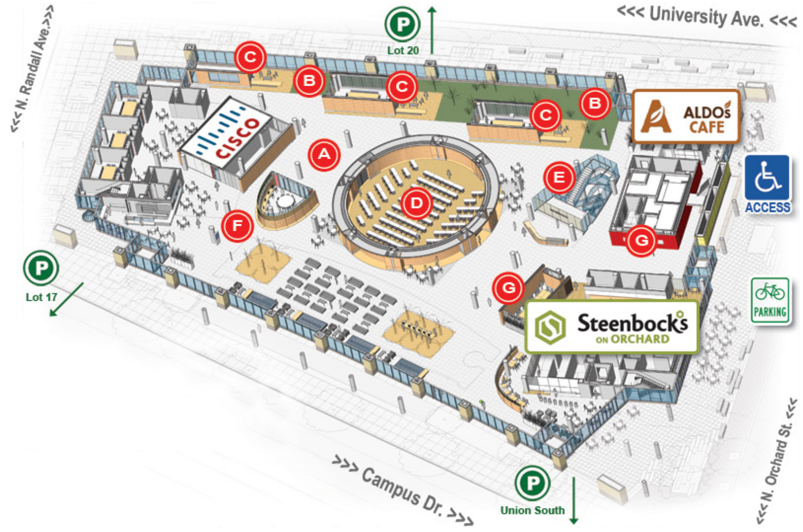
Name	Affiliation	Email
Alley, Richard	Penn State University	rba6@psu.edu
Amundson, Ronald	University of California, Berkeley	earthy@berkeley.edu
Barrett, Kevin	UW-Madison	kdbarrett2@wisc.edu
Baumgartner, Lukas	Université de Lausanne	Lukas.Baumgartner@unil.ch
Beasley, Melanie	University of California, San Diego	mbeasley@ucsd.edu
Blum, Tyler	UW-Madison	tbblum@geology.wisc.edu
Bova, Samantha	Brown University	samantha_bova@brown.edu
Buckles, Jessica	University of Texas at San Antonio	jessica.buckles@utsa.edu
Cammack, Jake	UW-Madison	cammack88@gmail.com
Chiou, Wen-An	University of Maryland	wachiou@umd.edu
Cobb, Kim	Georgia Institute of Technology	kcobb@eas.gatech.edu
Cross, Mellissa	University of Minnesota	cros0324@umn.edu
Defouilloy, Celine	UW-Madison	defouilloy@wisc.edu
Denny, Adam	UW-Madison	adam.c.denny@gmail.com
Fessenden, Julianna	Los Alamos National Laboratory	julianna@lanl.gov
Fike, David	Washington University	dfike@levee.wustl.edu
Gagnon, Alexander	University of Washington	gagnon@uw.edu
Gao, Yongli	University of Texas at San Antonio	yongli.gao@utsa.edu
Green, Robin	Indiana University	robigree@indiana.edu
Jacobson, Dan	CAMECA Instrumets, Inc.	Dan.Jacobson@ametek.com
Jones, Clive	Washington University, St. Louis	clivejones@wustl.edu
Kelly, Clay	UW-Madison	ckelly@geology.wisc.edu
Kern, James	UW-Madison	jkern@geology.wisc.edu
Kim, Soo	UW-Madison	skim448@wisc.edu
Kita, Noriko	UW-Madison	noriko@geology.wisc.edu
Kitajima, Kouki	UW-Madison	saburo@geology.wisc.edu
Kozdon, Reinhard	Rutgers	rkozdon@marine.rutgers.edu
Lefticariu, Liliana	Southern Illinois University	lefticar@siu.edu
Levitt, Nicholas	UW-Madison	nlevitt@wisc.edu
Li, Jingshu	UW-Madison	lijingshu11@mails.ucas.ac.cn
Linzmeier, Ben	UW-Madison	blinzmeier@wisc.edu
Lundberg, Joyce	Carleton University	joyce.lundberg@carleton.ca
Marcott, Shaun	UW-Madison	smarcott@wisc.edu
McKinley, Galen	UW-Madison	gamckinley@wisc.edu
McLeran, Kerry	Southern Illinois University	kmcleran@siu.edu
Oerter, Erik	University of California, Berkeley	erik.oerter@berkeley.edu
Orland, Ian	UW-Madison, University of Minnesota	orland@geology.wisc.edu
Quinn, Ryan	UW-Madison	rquinn2@wisc.edu
Ray, Christopher	University of Texas at San Antonio	cjray971@yahoo.com
Reyes, Alberto	University of Alberta	areyes@ualberta.ca
Russell, Ann	University of California, Davis	adrussell@ucdavis.edu
Sarathi, Akshay	UW-Madison	sarathi@wisc.edu
Sayani, Hussein	Georgia Institute of Technology	hsayani@gatech.edu

Participants of WiscSIMS Workshop - High Resolution Proxies of Paleoclimate
(University of Wisconsin-Madison, May 31 - June 3, 2015)

Name	Affiliation	Email
Schoeninger, Margaret	University of California, San Diego	mjschoen@ucsd.edu
Selvan, M Tamil	Jawaharlal Nehru University	mtselvan@jnu.ac.in
Shakun, Jeremy	Boston College	jeremy.shakun@bc.edu
Sliwinski, Maciej	UW-Madison	mgsliw@gmail.com
Smith, Richard	University of Southampton, UK	richard.smith@noc.soton.ac.uk
Spero, Howard	University of California Davis	hjspero@ucdavis.edu
Spicuzza, Mike	UW-Madison	spicuzza@geology.wisc.edu
Szymanski, Laura	UW-Madison	lszymanski@uwalumni.com
Tenner, Travis	UW-Madison	tenner@wisc.edu
Valley, John	UW-Madison	valley@geology.wisc.edu
Vetter, Lael	Tulane University	lvetter@tulane.edu
Voarintsoa, Ny Riavo	University of Georgia	nv1@uga.edu
Wang, Yue	UW-Madison	ywang327@wisc.edu
Wang, Jianhua	Carnegie Institution of Washington	jwang@ciw.edu
Williams, Jack	UW-Madison	jww@geography.wisc.edu
Wortham, Barbara	Boston College	worthamb@bc.edu
Wycech, Jody	UW-Madison	wycechjody@gmail.com
Wynn, Jonathan	University of South Florida	jgwynn@gmail.com
Zhang, Hanzhi	Nanjing University	ytzhanghanzhi@126.com
Zheng, Yinsui	Brown University	yinsui_zheng@brown.edu
Zhu, Jiang	UW-Madison	jzhu47@wisc.edu

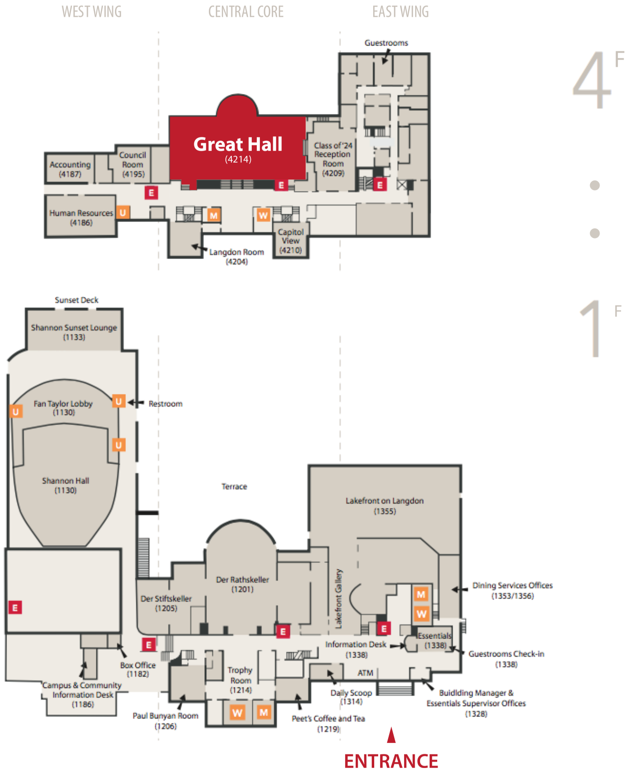
Workshop: Weeks Hall

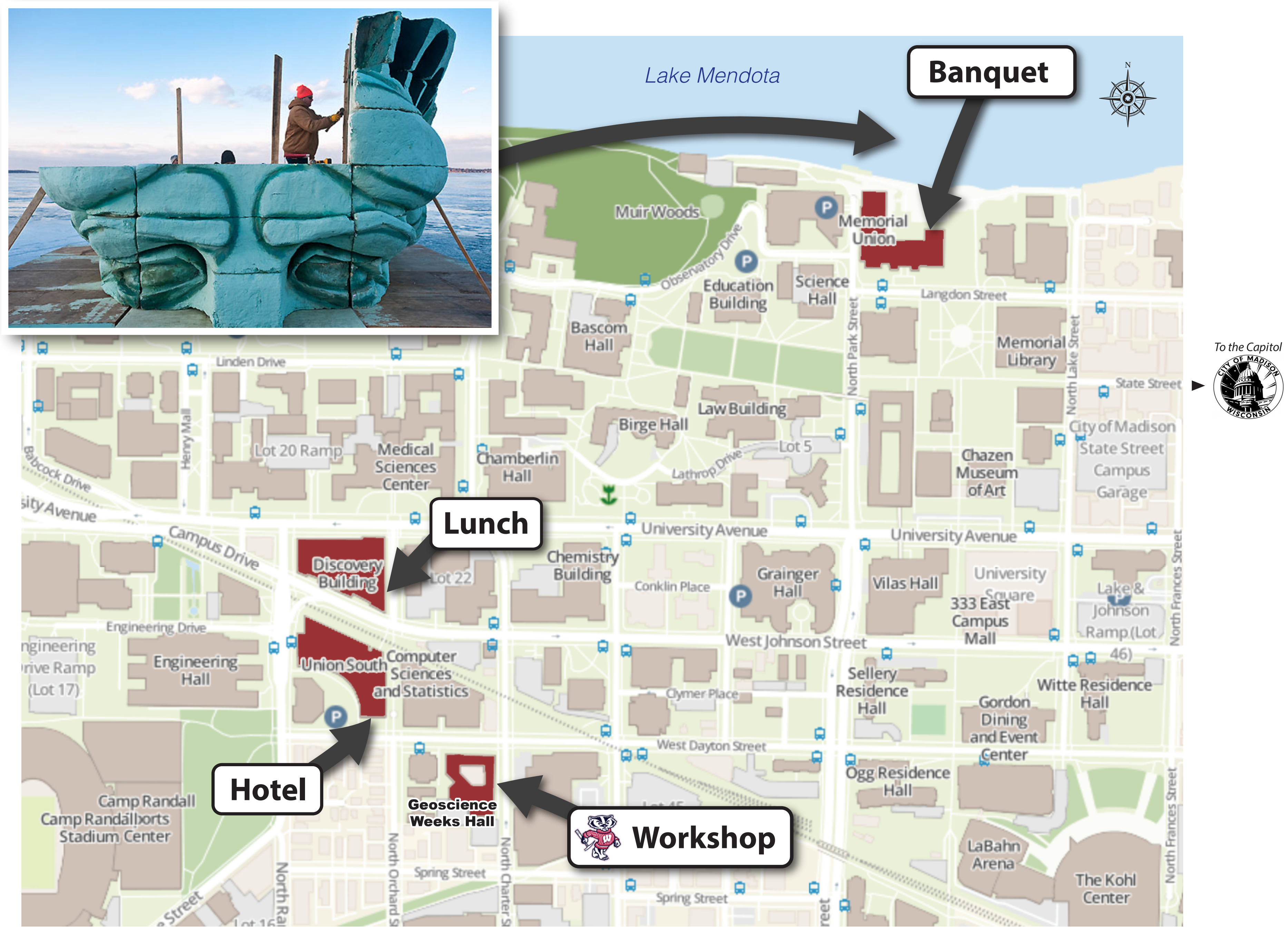
Lunch: Steenbock's on Orchard



Hotel: Wisconsin Union Hotel at Union South

Banquet: Great Hall at Memorial Union





Workshop: **Weeks Hall (1F, Room A140)**
1215 W. Dayton St.
Email: jkern@geology.wisc.edu
(Jim Kern)

Hotel: **Wisconsin Union Hotel**
Union South
1308 W. Dayton St.
Ph: 608.263.2600

Lunch: **Steenbock's on Orchard**
(Mon-Wed)
Discovery Building **(1F)**
300 N. Orchart St.
Ph: 608.204.2733

Banquet: **Great Hall**
(Mon. Evening)
Memorial Union **(4F)**
800 Langdon St.
Ph: 608.262.2511