HiRes2017

High-Resolution Proxies of Paleoclimate

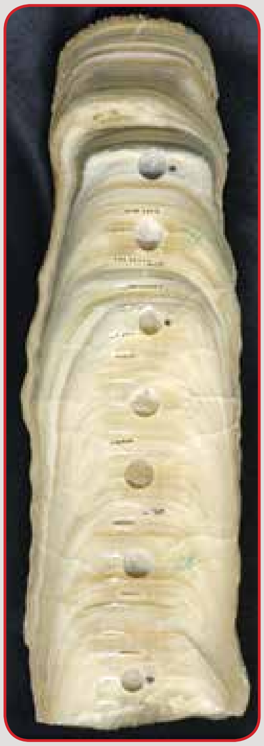
UW-Madison

WiscSIMS

June 18 - 21, 2017


Linzmeier et al, 2016


Foram, Photo credit: Jody Wycech


Stalagmite from Cave of the Mounds, Blue Mounds, WI
Photo credit: Cameron Batchelor

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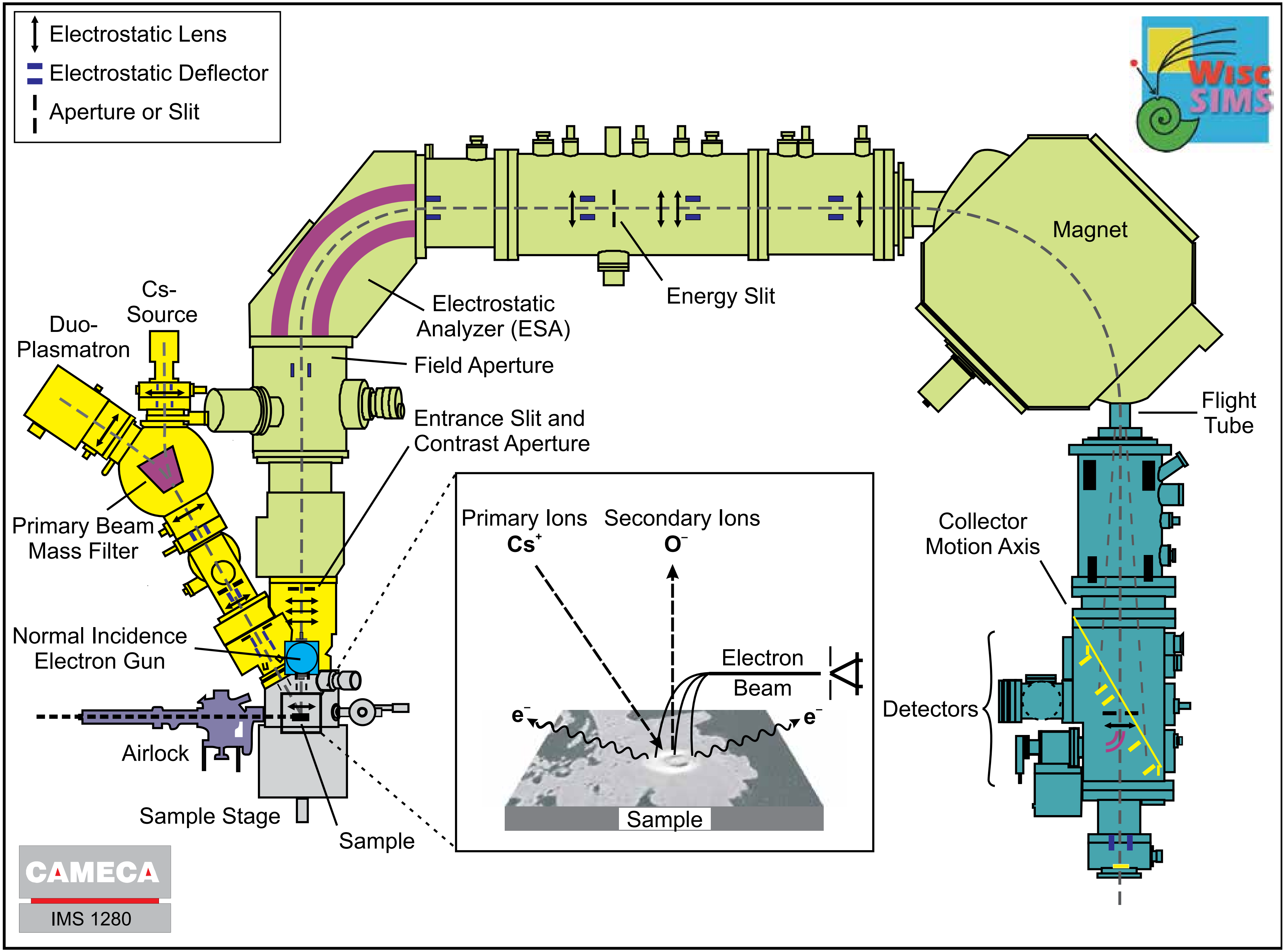
Electrostatic Lens
Electrostatic Deflector
Aperture or Slit
WiscSIMS
Magnet
Energy Slit
Electrostatic Analyzer (ESA)
Field Aperture
Entrance Slit and Contrast Aperture
Cs- Source
Duo- Plasmatron
Primary Beam Mass Filter
Normal Incidence Electron Gun
Airlock
Sample Stage
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Cs+
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Sample
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HiRes2017
High-Resolution Proxies of Paleoclimate
Madison, Wisconsin; June 18-21, 2017

Sunday, June 18, 2017

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

Monday, June 19 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"

Lunch (12:00PM-1:30PM) Union South, 1308 West Dayton St. - room TBD

Afternoon Session (Chair: John Valley)

1:30-1:50 PM **Shaun Marcott (Keynote)** "Heinrich Events, oxygen isotopes, and foraminifera: What can SIMS do for you?"
1:50-2:20 **Zhengyu Liu (Keynote)** "Understanding the temporal slope of the temperature-water isotope relation: The slope equation"
2:20-2:50 **Kathleen Johnson (Keynote)** "Reconstructing seasonal to decadal scale climate variability from speleothems: Potential, strategies, and challenges"
2:50-3:10 **Ian Orland** "Measuring seasonal monsoon signals in Chinese speleothems"
3:10-4:00 **Lightning Poster Talks** (Optional), 3 minutes/poster.
4:00-6:00 **Posters** -- Beverages and Refreshments will be provided.

Dinner -- You are on your own (See restaurant suggestions on page 51)

Tuesday, June 20 Room A140, Weeks Hall

8:30-9:00 AM **Light Breakfast**

Morning Session (Chair: Howard Spero)

9:00-9:30 **Thure Cerling (Keynote)** "Stable Isotope Answers to Problems with Biological and Terrestrial Records"
9:30-10:00 **Melanie Beasley (Keynote)** "Environmental variability in hominin evolution: Moving from geological to biological timescales with SIMS"
10:00-10:20 **Noreen Tuross** "The Need for HiRes in Vertebrate Calcified Tissue Oxygen Isotope Measurements"
10:20-10:40 **Daniel Green** "Mineralization modeling and Bayesian inference reconstruct transient storms from tooth δ^{18}O values"

10:40-11:00	**Break**
11:00-11:30	**Wolfgang Müller (Keynote)** "The Role of Laser-Ablation Plasma Mass Spectrometry (LA-ICPMS) in Palaeoclimate Research: Principles and Applications"
11:30-11:50	**Robert Sherrell** "High-resolution analysis of deep-sea coral skeletons for trace element paleo-proxies of ocean conditions"
11:50-12:10	**Xin-Yuan Zheng** "In situ Fe isotope analysis by femtosecond laser ablation: fundamentals and applications"

Group photo & Lunch 12:10-2:00PM Group Photo will be taken in Weeks Hall courtyard immediately following the morning session. **Lunch**, Union South, 1308 West Dayton St. - room TBD

Afternoon Session (Chair: Reinhard Kozdon)

2:00-2:30	**Jennifer Fehrenbacher (Keynote)** "Light cycle triggers Mg-banding in Neogloboquadrina dutertrei: implications for chamber formation and biomineralization in planktic foraminifers"
2:30-3:00	**Howard Spero (Invited)** " Carbon and nitrogen exchange between a photosynthetic symbiotic dinoflagellate and its planktonic foraminifera host"
3:00-3:20	**Helena Filipsson** "Opening the proxy black box: unravelling biomineralization processes using synchrotron X-ray spectroscopy and plasma analytical methods"
3:20-3:40	**Break**
3:40-4:00	**Alan Wanamaker** "Assessing unexpected isotopic variability in aragonitic biocarbonates through sample replication"
4:00-4:30	**Thomas Helser (Keynote)** "Trace elements, isotopes and growth increments: Paleoclimate and fish otoliths"
4:30-4:50	**Evan Cameron** "Hadean paleoclimate: OH/O ratios as a proxy for water & alteration in zircon"

Banquet (Alumni Lounge at the Pyle Center)
6:00 PM Cocktail Hour 7:00-9:00 PM Dinner

Wednesday, June 21 Room A140, Weeks Hall

8:30-9:00 AM **Light Breakfast**

Morning Session (Chair: Shaun Marcott)

9:00-9:40	**Ian Orland (Tutorial)** "Developments and challenges in ion microprobe studies of speleothems and biocarbonates"
9:40-10:10	**Reinhard Kozdon (Keynote)** "In situ analysis of foraminiferal shells by SIMS, LA-ICPMS and EPMA: What have we learned in the past decade? A résumé and outlook"
10:10-10:30	**Caitlin Livsey** "Reconstructing Holocene Arctic Ocean paleoceanography using SIMS $\delta^{18}O$ and LA-ICP-MS elemental data from single Neogloboquadrina pachyderma shells"
10:30-10:50	**Break**
10:50-11:10	**Jody Wycech "Reconstructing the Oxygen Isotope Composition of the Surface Ocean Using Paired In Situ Micro-Analytical Techniques on Individual Shells of the Planktic Foraminifer Trilobatus sacculifer"**
11:10-11:30	**Ben Linzmeier & Kouki Kitajima** WiscSIMS-Live: Part 2
11:30-12:00	**Ben Linzmeier (Tutorial)** "Integrating in situ geochemical data with QGIS"

Lunch 12:00-1:30 PM Union South, 1308 West Dayton St. - room TBD

POSTERS

Cameron Batchelor "High-precision U-Th chronology of calcite deposition at Cave of the Mounds, Wisconsin and its implications to permafrost and climate"

Kevin Burke "How novel are 21st century climates? A global assessment of future climates and their analogs back through the Eocene"

Huan Cui "Assessing the veracity of deep-time geological records by SIMS: A critical update on paleoclimatic conditions in the wake of the Sturtian Snowball-Earth glaciation"

Adam Denny "δ^{34}S Study of Multiple Generations of Sulfide in the Bakken System by SIMS"

Heather Jones "Extensive Braarudosphaera blooms in the Cretaceous/Paleogene impact crater: why are they there and what do they mean?"

Stanley Ko "Improving proxy calibrations in Desmophyllum dianthus: assessment of elemental abundances and distributions using LA-ICPMS"

Nick Levitt "Application of clumped isotope thermometry to Archean carbonates: Thermal histories and potential for biomarker preservation"

Ben Linzmeier "Using in situ geochemistry to investigate the depth habitat of ammonites"

Rosie Oakes "Using high-resolution imaging techniques to assess the impact of ocean acidification on the condition of pteropod shells"

Susana Salazar Jaramillo "Paleoclimatic Interpretation Using Geochemical Proxies In The Middle Miocene Paleosols Of The Tatacoa Desert, Colombia"

Maciej Śliwiński "SIMS bias on isotope ratios in siderite-magnesite: δ^{18}O & δ^{13}C matrix effects"

Chunhui Zhou "Growth zoning and trace element distribution in freshwater cultured pearls -- and potential study on stable isotope ratios"

Oral Presentations:

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 or The Lowell Center 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 the day. You may need to login every time.

Eduroam is supported on the UW-Madison campus, including Weeks Hall.

We can also create temporary ID numbers, if you are interested. Please see Kouki Kitajima or Ian Orland for questions or help about logging in.

HiRes2017 Conference Participants

HiRes2017
High-Resolution Proxies of Paleoclimate
UW-Madison

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Title: High-precision U-Th chronology of calcite deposition at Cave of the Mounds, Wisconsin and its implications to permafrost and climate

Cameron J. Batchelor, Ian J. Orland, Shaun A. Marcott, Richard Slaughter, and R. Lawrence Edwards

Abstract:

The Laurentide Ice Sheet (LIS) strongly influenced global climate throughout the Quaternary as it underwent cycles of growth and melting. Geomorphological features across Wisconsin provide evidence for the repeated advances and retreats of the LIS, and are the basis for studying the influence of this massive ice sheet on regional climate. However, determining a precise timeline for LIS advances and retreats is difficult since geomorphic features commonly rely on radiocarbon dates that only extend back 40 ka. Here we explore a new approach to this problem in Wisconsin by precisely measuring the timing of active cave carbonate (speleothem) deposition, which indicates the absence of permafrost. Fortuitously, expansive areas of Wisconsin are underlain by karst terrains, which contain speleothems that can be dated using the ^{238}U-^{230}Th radiometric chronometer that is viable to 600 ka with high precision (±1% uncertainty).

Cave of the Mounds National Natural Landmark, located in southwestern Wisconsin, is <20 km from the outermost limit of the LIS during the last glacial period. Because speleothem deposition requires the presence of liquid water, and therefore temperatures above freezing, speleothem deposits inside Cave of the Mounds are relicts from warmer periods when permafrost was not present. Using U-Th dating methods, we generate a detailed history of when there was no local permafrost, and correlate this with local LIS margin advances and retreats to better constrain the glacial history of Wisconsin.

To produce a dataset of ages from speleothems inside Cave of the Mounds, individual trenches were drilled parallel to multiple growth layers from each stalagmite sample, generating 50-100 mg calcite powder per trench. Uranium and Thorium were then isolated using wet chemistry techniques described by Edwards et al. (1987), and analyzed on a Thermo-Scientific Neptune at the University of Minnesota. A total of 72 U-Th dates demonstrate that calcite deposition in the cave spanned several glacial-interglacial cycles, with dates ranging from 250-2 ka. There are two periods of extensive calcite growth occurring at 225-210 ka and 70-60 ka, with a notable deficit in calcite growth occurring around the last interglacial period from ~130-80 ka.

Speleothems can record an extensive history of geochemical and isotopic data through time that can be analyzed using high-resolution methods (e.g. SIMS and laser ablation techniques), including high resolution imaging. To complement our U-Th chronology, samples were imaged using confocal laser fluorescent microscopy (CLFM). Distinct banding can be identified in pairs, as seen by alternating bright (high-organic content/trace element abundance) and dark (low-organic content/trace element abundance) growth layers (Figure 1). Additional samples are being prepared for U-Th dating and high-resolution imaging in order to expand our dataset, diminish sampling bias within the cave, and strengthen our interpretations.

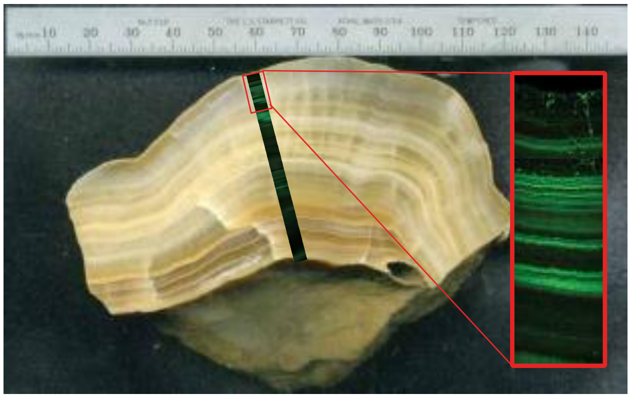

Figure 1: Sample CM5 with a full confocal microscopy transect overlaid, with a zoomed in portion to the right to show distinct banding. The brighter layers are interpreted as organic-rich layers**.**

Environmental variability in hominin evolution:
Moving from geological to biological timescales with SIMS

Melanie M. Beasley
Department of Anthropology, University of California, San Diego, CA

In extant nonhuman primates, seasonal patterns of aridity, day length, temperature, and food availability greatly impact reproduction, social life, life history patterns, and behavioral ecology (Brockman and van Schaik 2005). Seasonality has been implicated as a key factor in the evolution of humans as well. Reed and Fish (2005) suggest that some early *Australopithecus* and *Paranthropus* species may have switched their foraging effort to underground storage organs (USOs) during longer dry seasons because in response to drought, some plants will store energy (higher caloric value) in USOs instead of producing leaves, shoots, and fruits. Therefore, it is critical to determine the full range of variability in the patterns of rainfall at specific fossil localities in order to better understand the ecology and habitat in regions where bipedal hominins flourished. Kingston (2007) highlight that short-term ecological changes (e.g., shifts in seasonal precipitation) might match or even exceed the influence of long-term changes on evolution; assuming this is correct, then it is no longer reasonable to frame human evolution within long-term global or regional trends, but instead the focus must be on smaller, more local sites and time scales.

Paleoenvironmental reconstructions in East Africa often rely on surface-collected fossil fauna that combine multiple temporal and geographically dispersed components that are not *in situ*. Therefore, hypotheses that attempt to explain human evolution in the context of environmental and ecological change focus on large regions and long geologic time scales (thousands to millions of years). This framework lacks the temporal-spatial resolution to develop solid causal links between evolution and the environment (Kingston 2007). Traditional bulk isotopic analysis of tooth enamel distinguishes open from closed ($\delta^{13}C$) and arid from humid ($\delta^{18}O$) habitats of individual animals, but at too large a scale (i.e., aggregates multiple years) to explain the adaptive flexibility of early hominins to ecological variables like seasonality. Recent work has suggested that environmental conditions vary across a wide range of time scales (Potts 2012), including intra-annual seasons. Traditional bulk serial isotopic sampling along the growth axis of larger mammal teeth can aggregate long time periods depending of the tooth size and duration of enamel formation, such sampling requires the destruction of much of a single tooth or multiple teeth for smaller mammals. Unfortunately, much of the enamel material available for destructive isotopic analysis from fossil localities is fragmented material, not complete teeth or tooth rows and it is difficult to serial sample fragments using traditional bulk methods for evaluating seasonal patterns of $\delta^{18}O$. This study is the first to apply secondary ion mass spectrometry (SIMS) analysis to fossil fauna enamel fragments from a hominin locality to generate $\delta^{18}O$ seasonal patterns recorded in enamel at an intra-annual time scale (during the duration of enamel deposition of an individual animal). The high-resolution sampling capability of SIMS, with analysis spots 10 µm *in situ*, provide a new scale of analysis for paleoenvironment reconstructions to address questions about seasonality and hominin evolution.

Currently, *Australopithecus anamensis*, the earliest confirmed obligate hominin biped, has been recovered at three fossil sites in the Omo-Turkana Basin (Allia Bay, Kanapoi, and Fejej) and possibly four sites in the Afar Rift of Ethiopia (Aramis, Asa Issie, Woranso-Mille and Galili). If Kimbel et al. (2006) is correct that each site-sample captures a different point along the evolutionary trajectory of early hominins, then it is important to understand each local paleoenvironment where *Au. anamensis* fossil remains have been recovered to understand the adaptive flexibility of the species. All seven sites have been generally described as mosaic habitats, but variation in canopy cover and moisture regimes (i.e., wet versus dry sites) highlight the idea that *Au. anamensis* was adaptively flexible in a variety of environments and does not appear to be confined to a specific ecological niche. However, within each mosaic habitat the patterns of seasonal rainfall are unknown and are a critical variable to understand the shifting biomass availability (i.e., resources available to early hominins) on the paleolandscape.

This project reconstructed seasonal patterns of rainfall 3.97±0.03 Ma at Allia Bay, Kenya to refine the definition of a mosaic paleoenvironment of *Australopithecus anamensis* at one fossil locality in an attempt to understand the adaptive flexibility of the species. 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 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. The 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. These first-ever site- and time-specific ecological data are a step toward understanding the seasonality of the environment at biological timescales to better understand the adaptive flexibility necessary to flourish within these early mosaic habitats often associated with hominins.

References:
Brockman DK, and van Schaik CP. 2005. Seasonality in primates: studies of living and extinct human and non-human primates: Cambridge University Press.

Kimbel WH, Lockwood CA, Ward CV, Leakey MG, Rak Y, and Johanson DC. 2006. Was *Australopithecus anamensis* ancestral to *A. afarensis*? A case of anagenesis in the hominin fossil record. Journal of Human Evolution 51(2):134-152.

Kingston JD. 2007. Shifting adaptive landscapes: progress and challenges in reconstructing early hominid environments. American Journal of Physical Anthropology 134(S45):20-58.

Potts R. 2012. Evolution and Environmental Change in Early Human Prehistory. Annual Review of Anthropology 41:151-167.

Reed KE, and Fish JL. 2005. Tropical and temperate seasonal influences on human evolution. In: Brockman D, and Van Schaik C, editors. Seasonality in primates: studies of living and extinct human and non-human primates. Cambridge: Cambridge University Press. p 489-518.

Kevin D. Burke
HiRes Abstract
May 1, 2017

How novel are 21st century climates? A global assessment of future climates and their analogs back through the Eocene

Current rates of resource consumption have likely committed our planet to a future whose climate will be warmer than present. Given this knowledge and the fact that environmental change is a multivariate process that leads to a shift in the environmental space of a location (both the mean state as well as the extremes), it is important to assess how much the climate will shift. Yet it is also important to understand when and where analogous climates of the future have occurred in the past. If a future climate has no close analogs, or only weak analogs, is a concern when considering the viability of a species to track and persist in a suitable environment. To quantify how different a future climate will be relative to a baseline period, we calculate the dissimilarity (Standardized Euclidean Distance: SED) between these time periods using a series of one-to-many comparisons. Studies have assessed climate dissimilarity (and novelty) relative to the modern era, however we extend this baseline to quantify how dissimilar projected future climates will be relative to a paleo-baseline as well. Using modeled simulations of past climates (including HadCM3, CCSM, and GISS ModelE-R) we apply this technique to the last interglacial, as well as past earth warm periods including the middle Pliocene (3 Ma) and early Eocene (55 Ma).

These time periods are of interest because various geochemical proxies suggest global climate that was similar, if not warmer, than the present. Modeled climate simulations at the global scale offer the best opportunity to assess how similar these past climates may have been to our projected future. When comparing 21st century climates to individual snapshots of the past, dissimilarity is, on average, higher when compared to past cool periods like the Last Glacial Maximum and the Penultimate Glacial Maximum, and is lower when compared to the last interglacial, the middle Pliocene and the early Eocene. While past earth warm periods like the Eocene may be climatically similar in terms of temperature, their precipitation patterns differ and lead to greater dissimilarity. This suggests that the Pliocene may be a stronger analog for the future than the Eocene. Spatial patterns differ between time periods, and by model, though climate dissimilarity is commonly high in the high latitudes, as well as portions of equatorial Africa and the Tibetan plateau. Regions where climate dissimilarity remains high across all time periods represent locations whose future is more climatically unprecedented than anywhere else on the planet.

HADEAN PALEOCLIMATE: OH/O RATIOS AS A PROXY FOR WATER & ALTERATION IN ZIRCON

E. D. Cameron[1], J. W. Valley[1], D. Ortiz-Cordero[1], K. Kitajima[1], and A. J. Cavosie[2], [1] WiscSIMS, Dept. Geoscience, Univ. Wisconsin, Madison, Wisconsin 53706, USA
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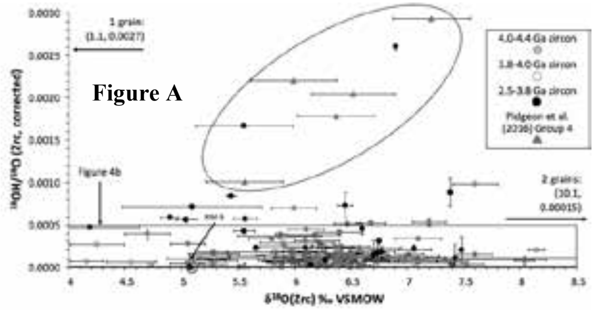

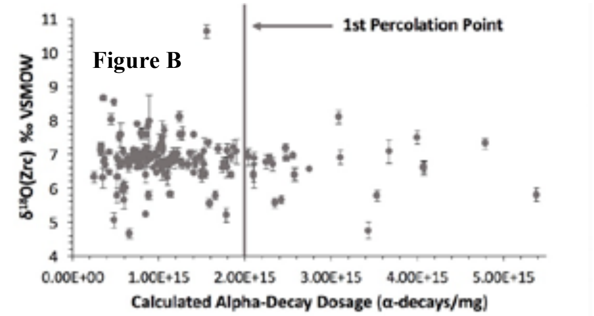

The Jack Hills detrital zircons are notable for being the only "plentiful" source of >4.0 Ga terrestrial material. Such zircons provide the only geochemical information about the Hadean Earth, including its potential atmosphere, climate, and potential for habitability. Values of $\delta^{18}O$ in >4.0 Ga detrital zircons that are slightly elevated above mantle values suggest: that the parent rock of the zircons interacted at low temperature with liquid water before subsequent burial and melting; that Earth cooled quickly after core and Moon formation; and that habitable conditions for life existed 800 Ma before the oldest known microfossils [1].

Interest in the ties between the Jack Hills zircons and the origin of life has increased following the report of two ~4-μm graphite inclusions with $\delta^{13}C = -24 \pm 5‰$ in a 4.1 Ga detrital Jack Hills (JH) zircon that is interpreted to be igneous and unaltered [2]. However, high $\delta^{18}O$ values for some JH zircons are reported to correlate with high OH/O ratios, suggesting cryptic alteration and general unreliability of the high $\delta^{18}O$ JH zircons [3]. OH correlates with radiation damage that is known to open fast pathways for exchange in zircon, which could allow alteration of zircons. Alternatively, some studies have been vigilant to avoid analysis of damaged domains in zircon. We have reanalyzed $\delta^{18}O$ by SIMS in Jack Hills zircons first reported by [1] to be unaltered based on U-Pb concordance, magnetism and CL imaging. Our new data include measurement of ^{16}OH to monitor "water" as a further precaution against radiation damage. When compared against an anhydrous standard, background corrected OH/O is a useful tool for evaluating the fidelity of a single SIMS domain in zircon [4].

Here we present new analyses of 154 detrital Jack Hills zircons of >3.8 Ga age and 36 zircons of <3.8 Ga age for $\delta^{18}O$ and OH/O (fig. A). Each zircon was analyzed by SIMS with 2 to 3 ~10-μm spots on an IMS 1280 at UW-Madison. The spots on the >3.8 Ga zircons were placed close to domains previously recorded as ~>90% concordant in U-Pb ages, and correlated with CL imaging [1]. Spots on the <3.8 Ga zircons were placed on both apparently damaged and pristine domains, guided by CL imaging. OH/O ratios were background corrected by comparing against the KIM-5 bracketing zircon standard. Additionally, using measured [U], [Th] and U-Pb age of the zircons, we calculated the maximum alpha-decay dose each grain could have accumulated, assuming no annealing after regional metamorphism at 2.6 Ga.

Results show that most zircons of [1] have OH/O ratios that are not distinguishable from background. There is no correlation of OH/O to $\delta^{18}O$ in our data for the previously screened, >3.8 Ga zircons. This is notably different from "group 4" zircons from [3] that are dark in CL, apparently altered, and display a correlation between high $\delta^{18}O$ and OH/O (triangles in fig. A). This confirms that mildly elevated $\delta^{18}O$ in zircons that pass the tests of alteration applied by [1,5] are not altered, radiation damaged, or hydrous. There appears to be only a slight correlation between high max. alpha-decay dose and elevated $\delta^{18}O$ for our zircons (fig. B). 14% of the grains analyzed for combined OH/O and $\delta^{18}O$ plot above the first percolation point, suggesting that some annealing could have occurred after 2.6 Ga as proposed by [3]. The lack of correlation between OH/O and $\delta^{18}O$ strengthens the conclusions of [1,5] that $\delta^{18}O$ is preserved in carefully selected zircons providing evidence for Hadean oceans and a Cool Early Earth before 4.3 Ga.

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Stable Isotope Answers to Problems with Biological and Terrestrial Records

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Many records of climate and ecology are attenuated during the “recording” and “sampling” processes. Stable isotopes can provide a proxy for climate and ecology, but the isotope mixing that occurs during recording or sampling must be better understood to interpret biological and terrestrial isotope records. We discuss two examples: isotope mixing during tooth enamel formation and high resolution climate records found in soil carbonates.

Tooth enamel maturation occurs over an extended period of time, during which isotope mixing can occur; however, different portions of enamel have different proportions of “early” and “late” enamel and high resolution isotope sampling can distinguish between these different regions in enamel. The “moving camera” inversion method for untangling the isotope mixing is a promising approach but so far has been little used in practice. Likewise, the SIMS sampling demonstrates that different parts of enamel have different maturation parameters. It, too, is little used so far to reconstruct detailed histories recorded in tooth enamel.

Soil carbonates have been used to reconstruct paleoclimate and paleoecology; most studies have been done using stratigraphic sequences at the outcrop scale. In south-central Utah we have identified regions where pendants of carbonates form below debris-flow emplaced basalt boulders. These have the potential to reconstruct climate on the time scale from the present to the mid-Pleistocene. Micro-mill sampling of such sequence provides a long-term climate history, but attenuation occurs because of the fine scale growth structures within the pendants. We anticipate better resolution of climate and ecological histories using SIMS to study the fine-scale growth structures.

Assessing the veracity of deep-time geological records by SIMS: A critical update on paleoclimatic conditions in the wake of the Sturtian Snowball-Earth glaciation

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Background: The Sturtian glaciation (717–660 million years ago) represents an extreme paleoclimatic anomaly in Earth's history, during which glacial ice extended to equatorial latitude globally, leading to the transformation to a Snowball Earth [1, 2]. Intriguingly, early macro-organisms appeared soon after the Sturtian glaciation [3]. Therefore, paleoclimatic reconstruction of the post-Sturtian period is critical to our understanding of the biogeochemical context of early life evolution. Notably, the post-Sturtian sulfur isotope ($\delta^{34}S$) record is characterized by anomalously high pyrite $\delta^{34}S$ values, many of which are even higher than the contemporaneous sulfate $\delta^{34}S$ values (i.e., $\delta^{34}S_{pyrite} > \delta^{34}S_{sulfate}$). These pyrites are commonly known as "superheavy pyrite", and have been reported globally, including the Datangpo Formation in South China.

Hypotheses: Various models have been proposed to interpret the Datangpo superheavy pyrite, including extremely low concentrations of sulfate in seawater, or the existence of a geographically isolated or geochemically stratified ocean [4-6]. All published models assume a microbial sulfate reduction (MSR) origin for the superheavy pyrite. This assumption hypothesizes that all the pyrites formed in water columns or shallow marine sediments with different degrees of access to seawater sulfate via diffusion. However, it is also possible that the Datangpo superheavy pyrite formed by thermochemical sulfate reduction (TSR) post-deposition during late diagenesis. Similar processes have been widely reported in hydrocarbon reservoirs and lead-zinc deposits [7], but have been largely overlooked in biogeochemical work of the studied formation.

Results: To evaluate these models, detailed petrographic and in situ $\delta^{34}S_{pyrite}$ analyses were conducted by using SEM-SIMS technique for the Cryogenian Tiesi'ao and Datangpo formations (South China) at unprecedented spatial resolution (i.e., 3 μm ion beam diameter). A wide range of $\delta^{34}S_{pyrite}$ values from +11.2‰ to +70.7‰ are reported in this study. Petrographic investigation shows that the isotopically superheavy pyrites in the Datangpo Formation are a late diagenetic product, postdating the mineralization of rhodochrosite and illite, and not an early authigenic phase as previously proposed. Distinct spatial patterns of $\delta^{34}S_{pyrite}$ values at μm scale are found to be coupled with pyrite in different morphologies. Early authigenic framboidal pyrites in the uppermost glacial diamictite show moderate $\delta^{34}S_{pyrite}$ values (from +11.2‰ to +24.5‰, +15.8‰ on average) (Fig. 1A). Late diagenetic superheavy pyrites show homogeneous values (from +56.3‰ to +60.4‰, +57.6‰ on average) in both pyrite framboids and overgrowth phases of one sample (Fig. 1B), and decreasing $\delta^{34}S_{pyrite}$ trend (from +70.7‰ to +60.2‰, +65.0‰ on average) from core to rim of individual pyrite grains in the other studied sample (Fig. 1C–E).

Discussions and conclusions: Based on multiple lines of sedimentological and geochemical evidence at both basinal and μm scales, we argue that the Datangpo superheavy pyrite formed via thermochemical sulfate reduction (TSR), instead of microbial sulfate reduction (MSR). This is the first time that a post-depositional origin is proposed for the Datangpo superheavy pyrite. Both MSR- and TSR-derived framboidal pyrites were found in this study. Our study confirms that framboidal pyrite can be formed in both marine and hydrothermal environments. Previous models invoking a post-Sturtian ocean with extremely low sulfate concentration and geographic restriction [4-6] should be reevaluated.

In contrast to the long-held assumption of a MSR origin for the superheavy pyrite, our results suggest that post-depositional TSR can play an influential role in generating high $\delta^{34}S$ values. Consequently, interpretations of high $\delta^{34}S$ values from the ancient geological record should reconsider the influence that similar post-depositional processes may have in generating superheavy pyrite associated with noteworthy biogeochemical events in the Earth's history. Our study demonstrates that SIMS $\delta^{34}S_{pyrite}$ traverses of individual pyrite grains are a powerful tool for assessing the significance of sedimentary pyrite and can provide new insights for deep-time paleoclimatic studies.

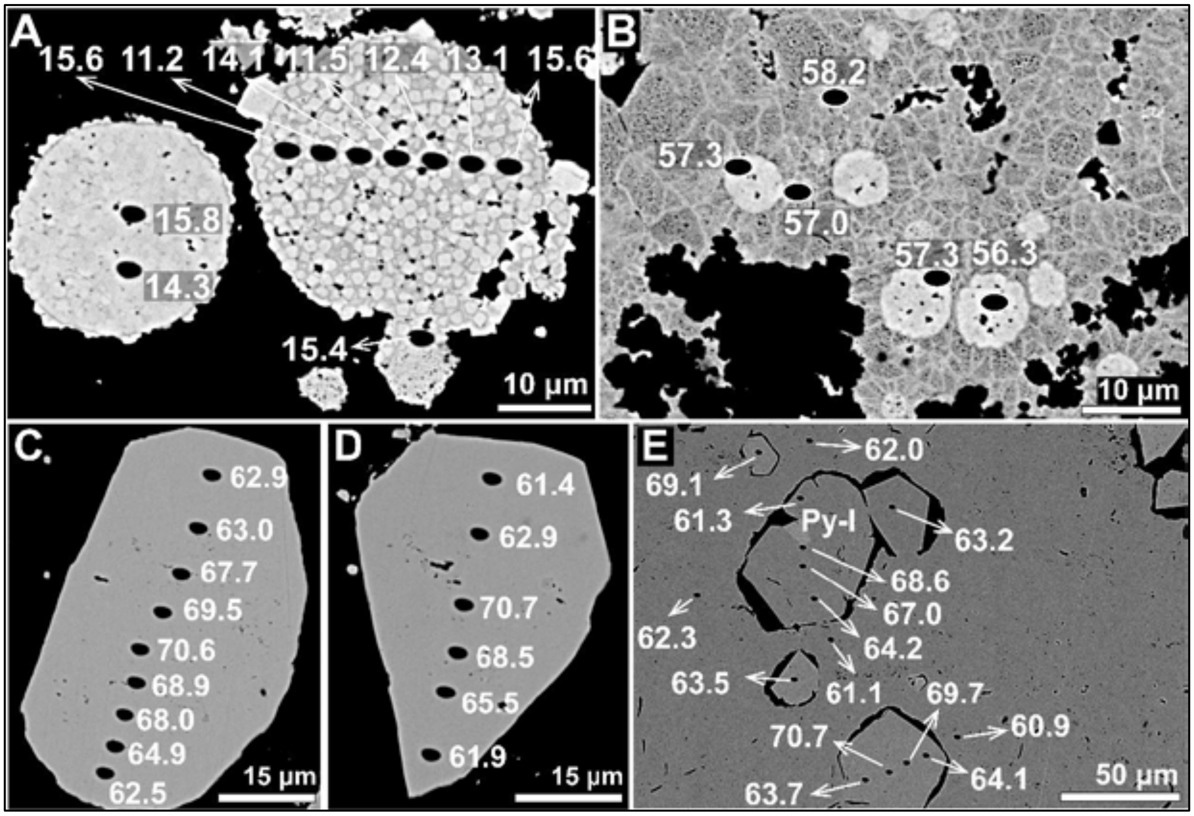

Figure 1. SIMS $\delta^{34}S_{pyrite}$ results measured from the Cryogenian Tiesi'ao Formation (A) and Datangpo Formation (B–E). The $\delta^{34}S_{pyrite}$ transverses from core to rim in individual pyrite in A show either increasing or invariant trends, while the transverses in C and D show opposite trends, suggesting different origins. In this study, we propose that pyrites in A formed by microbial sulfate reduction (MSR), while isotopically superheavy pyrites in B–E formed by thermochemical sulfate reduction (TSR).

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Citation: Cui, H., Kitajima, K., Spicuzza, M.J., Fournelle, J.H., Ishida, A., Denny, A., Zhang, F., Valley, J.W. (2017) Assessing the veracity of deep-time geological records by SIMS: A critical update on paleoclimatic conditions in the wake of the Sturtian Snowball-Earth glaciation. *WiscSIMS workshop HiRes2017: High-Resolution Proxies of Paleoclimate, Madison, WI, USA.*

TITLE: δ^{34}S Study of Multiple Generations of Sulfide in the Bakken System by SIMS

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Sulfur isotope ratios provide insight into both redox conditions during deposition and biological processes in soft sediment. While it is accepted that traditional bulk δ^{34}S analyses often homogenize micron-scale (and larger) variability in sediment, a comprehensive understanding of what information these micron-scale records might contain is still being developed. Petrographic investigations into the Devonian Lower Bakken black shale in North Dakota reveal multiple generations of sulfide growth, including isolated framboids, polyframboids, euhedral pyrite, pyrite pseudomorphing dolomite, and sphalerite. Presented here is a preliminary SIMS δ^{34}S dataset (δ^{34}S values -38 to -10‰, spot size = 3 microns) that, when integrated with petrographic observations, shows multiple lines of evidence of early active biological sulfate reduction. There is also evidence of a sulfate source driven to increasingly heavy δ^{34}S values by partially closed-system fractionation processes, as sulfate supply was depleted in sediments with restricted exchange to external reservoirs. Mass balance calculations on framboid populations are used to estimate rates of sulfate depletion, and possible causes of a bimodal distribution between pyrite framboids (-38 to -32‰ VCDT) and large (> 10 µm) euhedral sulfides (-21 to -10‰) are discussed.

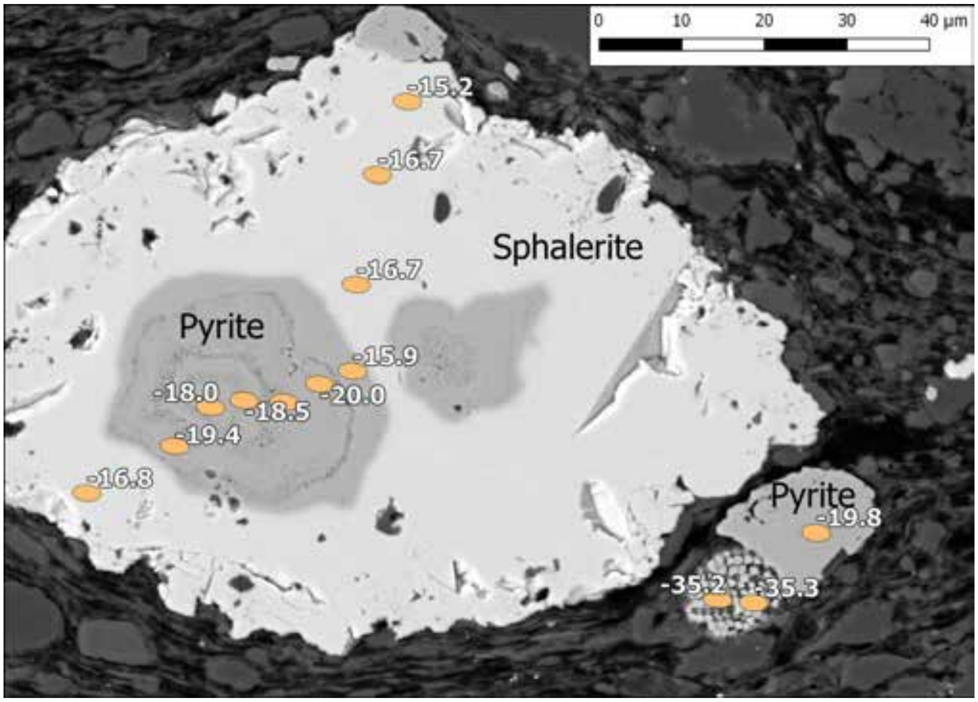

Figure 1. BSE-SEM image of several sulphide growth phases present in the lower Bakken organic-rich shale. The pyrite zonation visible in BSE is due to subsequent bands of mineral inclusions. Sphalerite surrounds some pyrite phases, indicating that it postdates pyrite precipitation. The majority of δ^{34}S SIMS analyses fall in the -20 to -15‰ range. A single pyrite framboid is >15‰ lighter than euhedral sulfides (-35 vs. -20‰), consistent with other framboid analyses in other regions on the sample.

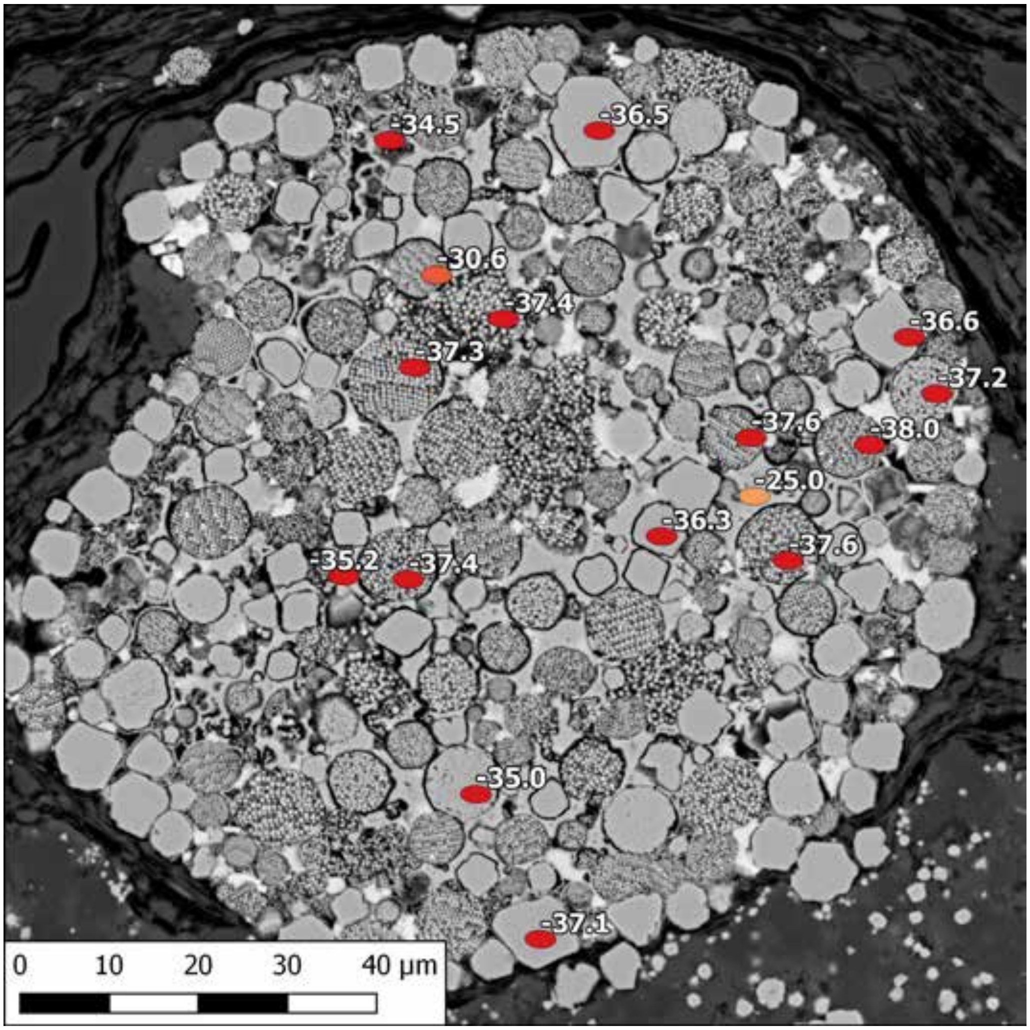

Figure 2. BSE-SEM image of a large pyrite polyframboid. Despite variability in framboid size and degree of ordering, there is a very tight spread in framboid $\delta^{34}S$ values (-38 to -35‰). Small euhedral pyrite grains (< 10 µm) interspersed with the framboids are interpreted to have developed from framboids given satisfactory conditions (perhaps a lack of interstitial organics) to fuse.

Light cycle triggers Mg-banding in *Neogloboquadrina dutertrei*: implications for chamber formation and biomineralization in planktic foraminifers

Jennifer S. Fehrenbacher, Ann D. Russell, Catherine V. Davis, Alexander C. Gagnon, Howard J. Spero, Zihua Zhu, John Cliff, Pamela A. Martin

The relationship between seawater temperature and the average Mg/Ca ratios in planktic foraminifera is well established, providing an essential tool for reconstructing past ocean temperatures. However, many species display alternating high and low Mg-bands within their shell walls that cannot be explained by temperature alone. Recent experiments demonstrate that intrashell Mg variability in *Orbulina universa,* which forms a spherical terminal shell, is paced by the diurnal light/dark cycle. Whether Mg-heterogeneity is also diurnally paced in species with more complex shell morphologies is unknown.

Here we show that high Mg/Ca-calcite forms at night in cultured specimens of the multi-chambered species *Neogloboquadrina dutertrei*. We grew specimens under controlled conditions (constant temperature, pH, and salinity) and transferred the specimens into isotopically modified seawater on a 12h:12h day/night (light/dark) cycle. We also cultured 'control' specimens that were transferred into isotopically modified seawater after collection, but did not undergo day/night transfers. We evaluated the timing of trace element variability in these cultured specimens using the highly spatially resolved analytical techniques Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) and NanoSIMS image mapping. Results demonstrate that *N. dutertrei* adds a significant amount of calcite, and nearly all Mg-bands, after the final chamber forms. The timing and chamber-to-chamber patterns of Mg-banding in *N. dutertrei* is similar to Mg-banding in *O. universa*. We use these results to formulate a new chamber growth and crust addition model for *N. dutertrei* and extend a modified version of this growth model to the planktic foraminifer *O. universa*.

Despite occupying different ecological niches, the timing of Mg/Ca variability in these two species appears to be controlled or triggered by changes in the daily light cycle. These results suggest Mg-banding is an intrinsic component of biomineralization in planktic foraminifers, linked to common physiological processes, that is subsequently modulated by environmental conditions such as temperature and pH.

Opening the proxy black box: unravelling biomineralization processes using synchrotron X-ray spectroscopy and plasma analytical methods

Helena L. Filipsson, Nadine Quintana Krupinski, Per Persson, Marit-Solveig Seidenkrantz, Takashi Toyofuku, and Sam Webb

We are interested in developing proxies for past marine bottom water oxygenation, in particular for low oxygen conditions. Elemental concentration of Manganese (Mn) in biogenic calcite, expressed as Mn/Ca, has the potential to be an indicator of past seawater oxygen levels. Manganese is a redox-sensitive element as well as a micronutrient and it plays an active role in many biogeochemical and biological processes. Mn precipitates in solid form under oxic conditions as Mn oxides (or oxyhydroxides), whereas under reducing conditions, it is dissolved, making dissolved Mn^{2+} available for incorporation into the shells (tests) of foraminifera in low-oxygen conditions. Under hypoxic conditions, dissolved Mn^{2+} is able to diffuse upwards in the sediment and into the overlying water column, and when pore waters become supersaturated with respect to Mn^{2+} and alkalinity is high, Mn can precipitate in carbonates. We collected a set of living benthic foraminifera from Gullmar Fjord, Sweden from varying bottom water oxygen conditions. We analyzed five foraminiferal species from two locations (70 and 116 m water depth) in the fjord from two different dates using solution ICP-MS and a combination of X-ray absorption spectroscopy (XAS) methods and micro X-ray fluorescence (μXRF). We evaluated the speciation and distribution of Mn in foraminifera under these different environmental conditions. The ICP-MS data show that Mn/Ca varied considerably between different foraminiferal species. The spectral data (XAS) indicate that Mn in the foraminiferal tests occurs as a Mn-carbonate species, while small points of external debris with high [Mn] in these uncleaned foraminifera generally have Mn-oxide-type spectra (suggesting these can be removed via cleaning methods). μXRF maps show that in many species, [Mn] is fairly evenly distributed at low or moderate concentration throughout the test, potentially suggesting stable oxygenation conditions. However, other species have specific chambers with elevated [Mn], perhaps suggesting intervals of greater oxygen stress or a response to vital processes that alter the microenvironment. Understanding the process of Mn incorporation in calcite tests is essential to more accurately reconstruct past redox conditions in marine bottom waters, which will help us to predict the evolution and development of modern marine hypoxic events and their effects on marine organisms.

Mineralization modeling and Bayesian inference reconstruct transient storms from tooth δ^{18}O values

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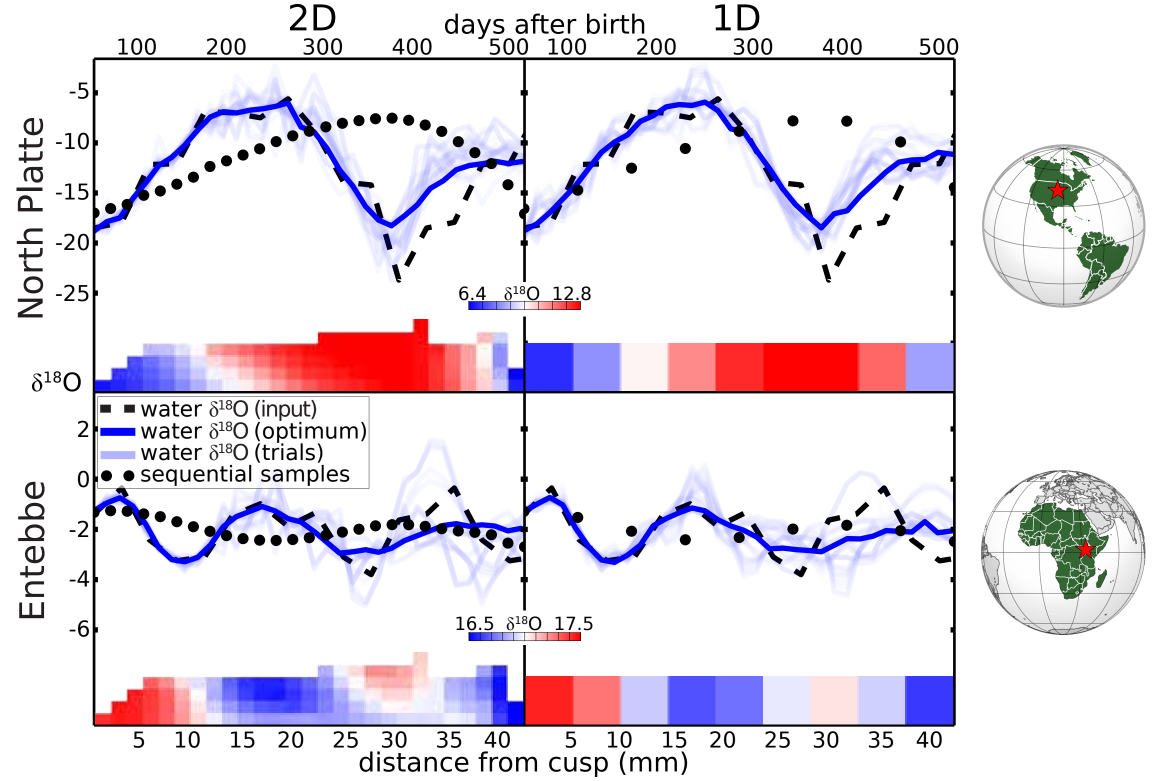
Seasonal rainfall patterns are reflected by oxygen isotope ratios (δ^{18}O values) in tooth enamel, which records environmental chemistry during mineralization. Because temporal variation in precipitation δ^{18}O results in spatial variation in tooth phosphate δ^{18}O, fossilized herbivore molars are commonly used to study seasonality. However, this approach has been hampered by incomplete knowledge of isotope incorporation during mineralization. Here we test a new synchrotron-based mineralization model experimentally in a sheep (*Ovis aries*) subjected to a controlled water switch. This is possible in part due to fine-scaled tooth phosphate δ^{18}O measurements (111 samples per enamel loph, 2-3 replicates per sample). Mineralization, blood oxygen turnover and tooth isotopic measurements show that enamel secretion and maturation waves advance at nonlinear rates with distinct geometries, and include isotopic shifts during enamel maturation from amorphous precursors. We produce a Bayesian inferential system for reconstructing water δ^{18}O inputs from tooth δ^{18}O values. Modeling suggests that with appropriate priors this system can reconstruct precipitation histories at different latitudes with striking fidelity. We validate this system by accurately reconstructing the controlled switch of our experimental animal. Interestingly, reconstruction recovers transient meteorological events that were unplanned, and were subsequently validated by meteorological records, video footage, and measurement of additional samples collected during the experiment. This work demonstrates that with modeling, tooth isotopic measurements have the potential to quantitatively reconstruct seasonal rainfall patterns, aid in paleoclimate research and further explore the relationships between climate, behavior and human evolution.



Reconstructions of drinking water δ^{18}O history (black, dashed) from modeled 2D high-resolution (left) or 1D low-resolution (right) tooth δ^{18}O values, derived from precipitation records in North Platte (United States) and Entebbe (Uganda). Most likely drinking water inputs (blue) and a sample of the most likely 30% of discovered solutions (light blue) are estimated at 14-day intervals. The 2D and 1D tooth δ^{18}O data used for reconstructions are shown at the bottom of each panel. Drinking water estimation from conventional serial sampling (black dots) fails to recover original inputs.

Trace elements, isotopes and growth increments: Paleoclimate and fish otoliths

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Fish otoliths, or ear stones, found in the heads of most teleost fishes help to provide stabilization and orientation in their environment. Otoliths consist of calcium carbonate, in the form of aragonite, which is continuously deposited over a protein matrix throughout the life of the animal. Because otoliths are inert and acellular, isotopes and trace elements can become assimilated, so they can be used as proxies or tracers of past environmental conditions. The recent ability to interpret the information provided by these markers has shown the potential to unlock new insights into fish biogeography, stock structure, climate change, paleoecology, and paleoclimate. Unlike other proxies of marine paleoclimate derived from non-biogenic or sedentary biogenic structures, fish otoliths present a unique challenge because teleost fishes can be highly mobile, traversing numerous water masses over its entire life history, resulting in possible temporal and spatial integration of chemical proxies. This potential to aggregate information is also unique from other proxies because otoliths recovered from archaeological sites can provide evidence, of ecological-scale (< 2 KYP) interactions between climate change, fish population biology, and indigenous human resource use. Our current research aims to reveal these important interactions by considering trace elements, isotopes, and growth increments of otoliths as high-resolution proxies of climate change. The first part of our talk will highlight the use of trace elements to describe water properties, isotopes with respect to paleo-thermography, and the use of otolith growth increments for biological responses as multi-proxy indicators. During the second part of our talk, we will present a case study on the use of SIMS measured δ^{18}O of modern and archaeological Pacific cod (*Gadus macrocephalus*) otoliths recovered from Aialik Bay on the Pacific coast of the Kenai Peninsula, Alaska, an area which has shown evidence of a 2-3 °C rise in coastal marine sea surface temperatures over the last 200 years.

Reconstructing seasonal to decadal scale climate variability from speleothems: Potential, strategies, and challenges

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Recently, an increasing number of researchers have been striving for seasonal to decadal scale speleothem-based records of past climate. This work is motivated by the need to improve our understanding of the natural range and mechanisms of high-frequency climate variability related to coupled climate modes, such as the El Niño-Southern Oscillation (ENSO), the Pacific Decadal Oscillation (PDO), and the Indian Ocean Dipole (IOD), and the interaction between these modes with large-scale climate features such as the seasonal cycle, the Asian monsoon system, and the Intertropical Convergence Zone. This new frontier of speleothem research has been driven by several factors, including improved analytical techniques which allow more precise age control, high-resolution microsampling, and *in situ* chemical analysis at sub-annual scale. Furthermore, long term cave monitoring studies, development of new proxies, incorporation of precipitation $\delta^{18}O$ in isotope enabled general circulation models, and proxy system modeling have contributed to improved understanding of the climatic and non-climatic controls on seasonal to decadal scale geochemical variability in speleothems. In this talk, I will present results from high-resolution speleothem calibration studies and records from Laos, China, and California that utilize multiple proxies, cave monitoring, isotope enabled GCMs, and/or proxy system modeling to generate robust records of past climate and to assess uncertainties introduced by chronological uncertainty, multiple proxy controls, and karst processes. Speleothems potentially represent one of the best archives of terrestrial climate at ultra high-resolution, though proxy interpretation and statistical treatment of data still present major challenges. I will discuss the best strategies for constructing and interpreting seasonal to decadal resolution speleothem time-series, and assess the paleoclimate reconstruction potential of these new records.

Extensive *Braarudosphaera* blooms in the Cretaceous/Paleogene impact crater: why are they there and what do they mean?

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Calcareous nannoplankton, single-celled autotrophs which live in the surface ocean, were decimated at the Cretaceous-Paleogene (K/Pg) boundary with over 93% of species and 85% of genera becoming extinct. The subsequent recovery was hemispherically asynchronous, with Northern Hemisphere nannoplankton populations experiencing delayed recovery compared to the Southern Hemisphere. However, it is uncertain how nannoplankton responded at the impact site itself.

Using a new stratigraphically complete K/Pg section from the Chicxulub Impact Crater (obtained during IODP Expedition 364), it has been possible to document early recovery dynamics of nannoplankton at “ground zero”. Here we present preliminary results which find that samples upwards of 40 cm above the boundary are dominated by dinoflagellate cysts and pentagonal ‘nannoliths’ (calcite plates) of the genus *Braarudosphaera*. Although both of these taxa are commonly observed following the mass extinction event, the persistence and scale of the *Braarudosphaera* blooms in the impact crater (up to 70% of a sample) are highly unusual. The morphology of *Braarudosphaera* pentaliths also varies both within and between samples, which has not been documented at any other K/Pg site. Furthermore, the appearance of typical Paleogene species is severely delayed at “ground zero” perhaps due to competition, detrimental environmental conditions, or a combination of both.

The paleoecological preferences of *Braarudosphaera* are enigmatic. Previous studies have found that *Braarudosphaera* is an indicator of environmental stress with a preference for cold, low salinity, eutrophic waters and restricted competition. However, many of these assumptions have been based on modern assemblages whose ecological affinities may be very different from those in the fossil record. The studies that have focused on the fossil record are mostly qualitative, with quantitative techniques largely restricted to the Oligocene. We are looking to investigate the possibility of using SIMS to determine the isotopic composition of K/Pg *Braarudosphaera* pentaliths. Preliminary work performed on Oligocene-aged samples where *Braarudosphaera* blooms are also abundant, suggest this is possible (Clay Kelly, personal communication). If so, this would enable us to confirm the paleoecological preferences of this genus, and thus the significance of their appearance at the K/Pg boundary.

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 with 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 ~10 μm diameter spots with Cs^+ ions to produce O^- and C^- secondary ions, which provide typical 2SD 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). New upgrade in 2017 for high brightness “RF Plasma” negative oxygen primary ion source and its potential new applications will be mentioned.

- **Procedure of 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.

Improving proxy calibrations in *Desmophyllum dianthus*: assessment of elemental abundances and distributions using LA-ICPMS

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Previous work has shown elemental ratios of P/Ca, Ba/Ca, U/Ca in deep sea coral *Desmophyllum dianthus* to be proxies for seawater nutrient and carbonate concentrations. We seek to refine micromilling-solution-ICPMS and LA-ICPMS sampling methods for these elements, and to improve proxy calibrations by assessing elemental abundances and distributions in fossilized and cultured *D. dianthus*, which grow at ~1mm per year. Preliminary work on fossilized specimens has shown promise in providing quick, reasonable, and reproducible data but the heterogeneous compositions around centers of calcifications (COCs) present challenges. Elements such as Fe, Mn, Zn, and Cu have shown large variations between and within specimens and the effect of such heterogeneity, if any, on the proxies and on age screening methods is largely unknown. Small-scaled systematic variations in chemical composition may reveal unknown aspects about calcification and warrants further investigation. Ongoing incubation experiments at the ICM in Barcelona will provide insight on the composition of cultured *D. dianthus*. Preliminary work using confocal microscopy and laser ablation analyses along traverses as well as depth profiling has demonstrated the capability to distinguish growth before the collection of the coral from Comau Fjord, Chile and from growth during different stages of the experiment.

In situ analysis of foraminiferal shells by SIMS, LA-ICPMS and EPMA: What have we learned in the past decade? A résumé and outlook.

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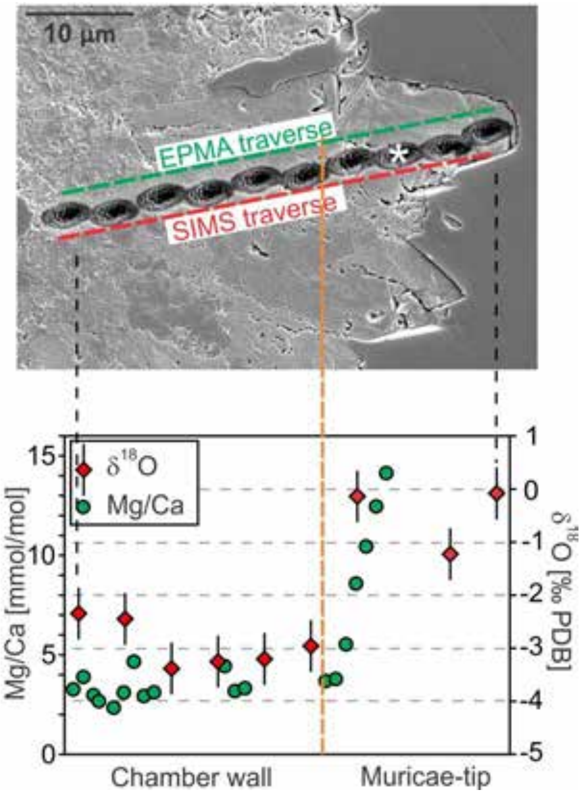
Foraminiferal shells are chemically and isotopically zoned as a result of the complex biologic mechanisms of shell calcification combined with environmental changes such as vertical migration in the water column. After the shell is deposited on the sea floor, this primary compositional heterogeneity may be superimposed by diagenetic alteration, which is an umbrella term for processes such as dissolution, recrystallization, or cementation. Deciphering this biologically- or diagenetically induced isotopic and chemical heterogeneity by new and evolving *in situ* analytical approaches holds great promise to improve our mechanistic understanding of foraminiferal-based proxies and to extract more accurate paleoclimate information from fossil material.

Almost exactly 10 years ago, planktic foraminiferal shells were analyzed for the first time at WiscSIMS for their intrashell $\delta^{18}O$ zonation in <3 µm-sized domains [1]. This study initiated a broad variety of novel and innovative research projects applying *in situ* SIMS analyses of $\delta^{18}O$ and $\delta^{13}C$, combined with trace- and minor-element analyses by LA-ICPMS or EPMA, on foraminiferal shells from laboratory culture, Holocene core-top samples, or fossil shells dating back as far as to the Early Paleogene. For instance: **1.** The $\delta^{18}O$ and $\delta^{13}C$ of shell calcite in the extant planktic foraminifera *O. universa* can be resolved by SIMS for 12 h vs. 24 h calcification periods, respectively [2, 3]. **2.** *In situ* $\delta^{18}O$ measurements by SIMS in well-preserved 10-µm diameter domains discovered within 'frosty' (i.e., moderately preserved) central Pacific planktic shells of the genus *Morozovella* from the Paleocene-Eocene thermal maximum (PETM) are up to 2‰ lower than previously published values based on whole-shell measurements from the same site and approach $\delta^{18}O$ values reported from age-equivalent and extremely rare 'glassy' shells that are considered the 'gold-standard' for paleoclimate reconstructions due to their exceptional preservation [4]. **3.** A hallmark feature of the PETM is a negative carbon isotope excursion (CIE). The average CIE magnitude reported from terrestrial records is ~4.7‰, but only ~2.8‰ is measured, on average, in marine carbonates. *In situ* $\delta^{13}C$ measurements by SIMS in well preserved domain of morozovellid shells indicate that the magnitude of the CIE at the central Pacific ODP Site 865, originally reported as being only ~2.5‰, is actually ~5‰ and highly congruous with the CIE magnitude seen in terrestrial records [5]. Subsequent analysis of $\delta^{13}C$ in diagenetic cements demonstrates that diagenetic alteration has a significant bias on published whole-shell $\delta^{13}C$ data from the PETM. **4.** Paired $\delta^{18}O$:Mg/Ca measurements by SIMS and EPMA in planktic foraminiferal shells from ODP Site 690, Weddell Sea, reveals a salinity decrease of ~5 psu ~40 kyr after peak PETM warming [5]. This negative sea-surface salinity anomaly signals an increase in mean annual precipitation in the Weddell Sea, in agreement with climate model simulations predicating greater poleward migration of storm tracks under a warmer climate regime. **5.** Mg/Ca and Ba/Ca values acquired by LA-ICPMS combined with SIMS $\delta^{18}O$ analyses performed on the same shell of the high latitude planktonic foraminifera *Neogloboquadrina pachyderma* are being used to reconstruct the Arctic water column structure and meltwater signatures since the LGM [6].

Some of the future research directions will include experiments to further improve our understanding of the offset between measurements of δ^{18}O by SIMS and gas-source mass spectrometry observed in foraminiferal shells of Pliocene age and younger, the exploration of new imaging approaches to locate the best domains for analysis, evaluating the 'performance' of different *in situ* approaches to extract robust proxy-data from sites featuring a significant diagenetic overprint such as the Ontong Java Plateau, or the assessment of the potential diagenetic bias on the published benthic δ^{18}O record.



Biogenic and diagenetic phases in foraminiferal shells can be identified and quantified by *in situ* SIMS and EPMA analyses:

Top: Highly magnified SEM image of a polished chamber wall of a planktic foraminiferal shell (*M. velascoensis*) from the PETM-section of ODP Site 865, central Pacific, with ten 3-µm diameter pits for *in situ* δ^{18}O measurements by SIMS. Dashed lines show parallel traverses of δ^{18}O SIMS pits and Mg/Ca ratio measurements by EPMA taken along the major axis of a muricae (= pustular outgrowths from the chamber wall) blade. The volumes sampled for δ^{18}O by SIMS and Mg/Ca by EPMA are comparable in size.

Bottom: Coherent trends in δ^{18}O and Mg/Ca delineated by parallel traverses along the muricae blade. The orange line highlights the transition between biogenic calcite and the diagenetic overgrowth.

References:

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APPLICATION OF CLUMPED ISOTOPE THERMOMETRY TO ARCHEAN CARBONATES: THERMAL HISTORIES AND POTENTIAL FOR BIOMARKER PRESERVATION .

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Introduction: The Campbellrand-Malmani carbonate platform is located on the western margin of the Kaapvaal Craton of South Africa. This sequence has experienced the lowest grade thermal history of any Archean carbonate rocks, and is therefore an archive for records of the early Earth biosphere. However, current understanding of the burial history of these rocks is limited. Clumped isotopes can inform the search for and interpretation of biosignatures in sediments by determining host rock formation temperature and/or thermal history. This approach is especially attractive to studies of (organic) molecular biomarkers where alteration by excessive burial heating can obscure primary information.

Sumner and Beukes [1] have estimated platform burial by thermal subsidence to be from 0.8km/100my to 4.9km/300my between ~2.7 and ~2.5 Ga. The maximum burial temperature of the platform has been estimated by Miyano and Beukes [2] according to metamorphic mineral assemblages in the overlying Kuruman Iron Formation to be ~ 110-170 °C. Estimates of uplift and exhumation rates for the Kaapvaal Craton range from 4.4m/my to 800m/my and the timing of uplift has been recently been estimated between 75 to 30 Ma [3].

The objective of this study is to explore how the burial and exhumation history of the platform affected clumped isotope thermometry using the transient defect/equilibrium defect reording model of Henkes et al. [4] and the solid-state reaction-diffusion based model of Stolper and Eiler [5]. These models present kinetic data for calcite, and recent work indicates that dolomite re-equilibrates more sluggishly [6]. The approach taken here is to compare unique ^{13}C-^{18}O bond reordering kinetics in calcite and dolomite to help constrain the timing and duration of burial, thermal exposure, and exumation of this unique Archean archive.

Investigation: Clumped isotope analyses were performed on micro-drilled powder from hand samples and drill core collected from the Gammohaan Formation of the Campbellrand Subgroup. The majority of samples are from an outcrop from a hill near Kuruman. Samples from three drill core were also taken at depths ranging from ~200 m to ~290 m to test for spatial variability in petrographic textures and geochemical characteristics. Assuming a cratonic geothermal gradient of 20^{o}C/km, the drill core samples would have experienced slightly higher temperatures before sampling of ~ 5 ^{o}C relative to the outcrop samples. Dolomite was not found in sufficient abundance in the drill core samples initially studied.

We explore burial from 2.55 to 2.40 Ga from ambient conditions to a range of peak temperatures from 150-250^{o}C. Under such conditions, calcite quickly attains the maximum temperature for clumped isotopes while dolomite slowly re-orders toward its blocking temperature of 300-350^{o}C [6]. Although some workers have argued for peak metamorphic conditions at ~2 Ga, the rapid equilibration of calcite would not change the results. Exhumation of the platform was modeled as occurring in the range from 200 to 30 Ma.

Results and Conclusions: ^{13}C-^{18}O bonding measurements were converted to temperatures using the calibration curve reported by Lloyd et al. [6]. Specimens where only early carbonate was sampled give apparent temperatures ranging from 114-173°C for calcite and 90-115°C for dolomite. Average values for calcite and dolomite were found to be 137°C (±20) and 99°C (±13), respectively.

Our modeled time-temperature histories below 200 ^{o}C would produce clumped isotope compositions in the observed range. The models further call for a rapid exhumation of the basin of less than 200 million years. This uplift history is broadly consistent with estimates for the Kaapvaal Craton reported by previous investigators. These results indicate that for geologically reasonable exhumation rates, the final calcite clumped isotope temperature is ~20-60 ^{o}C cooler than peak conditions. That these results are in line with the maximum metamorphic temperatures estimated below 200 ^{o}C is encouraging for the reliability of primary biogeochemical signals extracted from the Campbellrand-Malmani carbonate platform.

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Integrating *in situ* geochemical data with QGIS

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Modern in situ geochemical studies cross-correlate measurements from multiple analytical instruments, and integrate them with multiple forms of imagery (optical microscope, SEM, CL, etc.). Because this work fundamentally hinges on the spatial distribution of geochemical information, the spatial location of each analysis is often reported by the instruments as stage coordinates. Compiling and visualizing these data in a single software package that can create high quality figures and useful supplemental data can serve to streamline the workflow of data collection and analysis. Additionally, spatial integration can facilitate collaboration and open new opportunities for statistical analysis of results. Although not originally created for micro-analytical data, we have developed a workflow to use QGIS [1] as a data integration and visualization platform. QGIS is a free, open-source geographic information system software that is supported by a large community of international developers. This software is ideal for research data compilation because it does not rely on proprietary format for data input or export, and custom plugins or analysis scripts can be written in python or R.

In this presentation, we will demonstrate the process of making a QGIS map from WiscSIMS data output, light microscope images, and scanning electron microscopy images. This interactive map will be explored and software features including point labeling, graded coloring of points, logical selection of points, and attribute addition for each point will be demonstrated. We will also exhibit custom-built plugins and other features that enhance the utility of the software by automating repetitive tasks, including import of SEM images, creating line profiles across both point data and images, and exporting data rich supplemental map files. Our newly developed custom plugin, QGIS Pointlogger, can be used to navigate the SIMS stage using spatially referenced sample images. The plugin also populates the QGIS map with data that is imported from the Excel spreadsheet during the session. Future adoption by the microanalytical community holds promise for data integration, collaboration, method development, and sharing data.

[1] QGIS.org

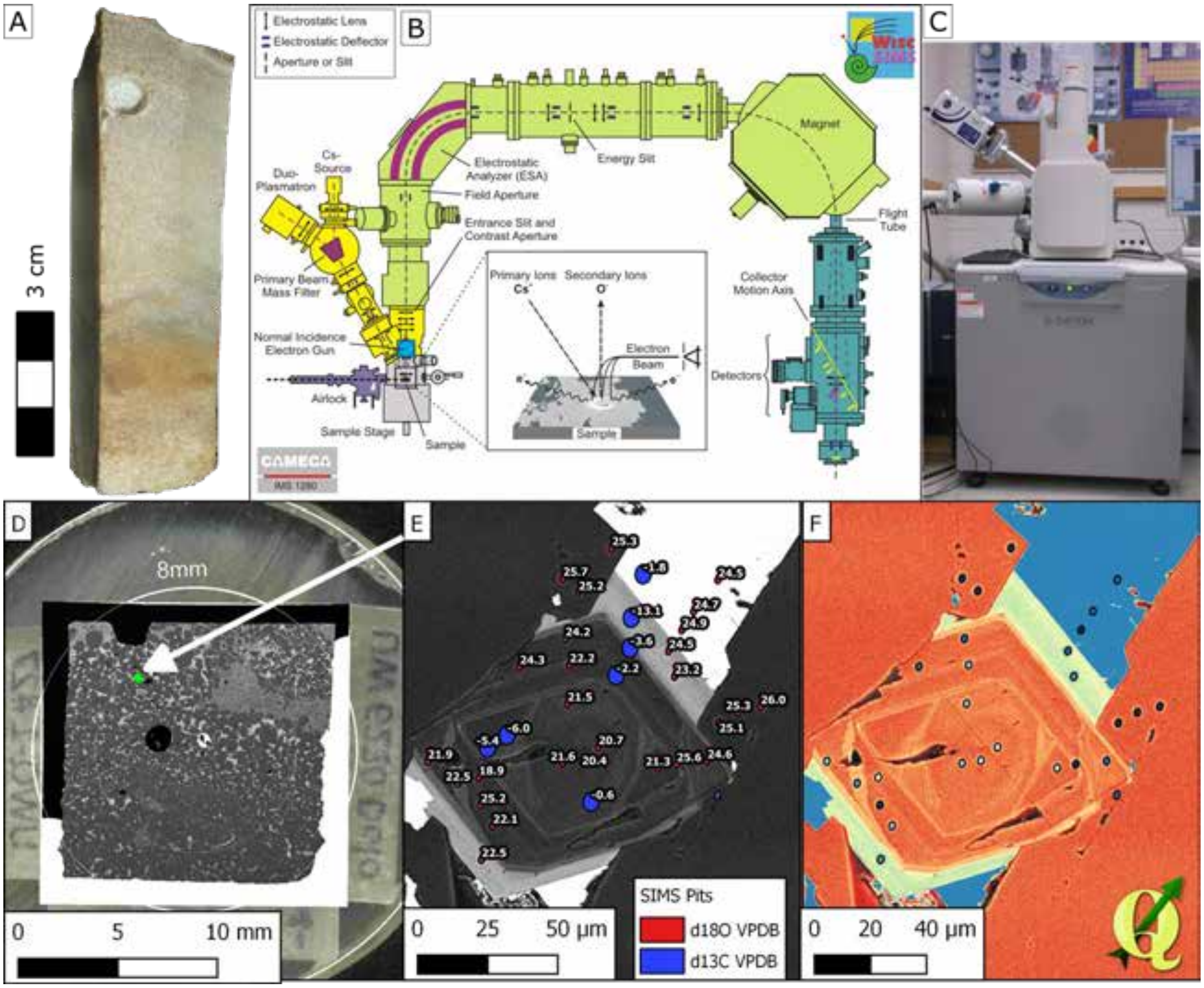

Figure 1. Conceptual workflow from core to QGIS map with some example map images highlighting different visualization options that are built into the QGIS software. A) Image of core sample of quartz sandstone cemented by dolomite and siderite. B) Schematics of Cameca IMS-1280 ion microprobe where *in situ* analyses of both δ^{18}O and δ^{13}C were performed. C) Picture of Hitatchi (S-3400N) scanning electron microscope, where scanning electron, backscattered electron, electron backscatter secondary diffraction, and cathodoluminescence imaging routinely take place. Panels D, E, and F are created solely within QGIS. D) The green spot in panel D shows the location on the SIMS mount where both panels E and F were captured and shows the entire SIMS-mount surface E) SIMS pits are labeled with δ^{18}O or δ^{13}C measurement values and overlain on a BSE image. Positioning of the labels and resizing can be done in a batch setting. Note how the labels have a floating arrangement so they do not overlap. F) The black and white BSE image from E is colorized using a built-in function. SIMS δ^{18}O measurements are colored using a gradient to reflect values and δ^{13}C pits are not shown.

Using *in situ* geochemistry to investigate the depth habitat of ammonites

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Ammonites are among the most iconic of extinct mollusks. Their wide spatial distribution, and biostratigraphic utility make them ideally suited to serve as tools for understanding past climate. Stable isotope analyses to date have focused on adult shells that can be sampled by traditional micro-milling techniques. Such studies have suggested that adults had a benthic mode of life. Eggs and hatchlings are thought to occupy a shallower position in the water column. Stratigraphic occurrence and analogy to modern cephalopods supports this hypothesis, but stable isotope analysis has not previously been applied to this question, primarily because the volume of shell material necessary for traditional techniques precludes sampling of the diminutive embryonic shell (~400 µm diameter). Here we test for the depth ammonite eggs and hatchlings inhabited by using secondary ion mass spectrometry (SIMS) [1] for *in situ* sampling of the shell wall compared to environmental context.

Material from the Maastrichtian (~66 mya) Fox Hills and Owl Creek Formations of North America were sampled in this study. All samples from the Fox Hills Formation were from a single concretion that may have formed in less than 10 years. Samples from the Owl Creek Formation spanned several meters of section, but previously published bulk measurements suggest little or no stratigraphic trends in δ^{18}O within fossil material. Water column stratification was inferred from analysis of other biogenic carbonates produced in surface and bottom waters. Bivalves from the Fox Hills Formation provide benthic water δ^{18}O values, whereas planktic and benthic foraminifera constrain water column δ^{18}O values in the Owl Creek Formation. Diagenetic assessment of material sampled by SIMS was first done using backscattered electron (BSE) and cathodoluminescence (CL) imaging. Original nacreous aragonite microstructure is visible by this imaging technique and is an indication of primary preservation of carbonate. Additionally, electron backscatter diffraction (EBSD) confirmed aragonite mineralogy *in situ.*

Hatchling ammonite δ^{18}O from both sites suggest the scaphites had a planktonic interval immediately after hatching (Fig. 1). This supports the inference that hatching ammonites were planktic derived, analogy to modern and hydrodynamic analogues and models. Surprisingly, shell wall precipitated before hatching in the Fox Hills *Hoploscaphites* suggest a benthic development. This is the first indication of the complexity of the life history of ammonites and it suggests that the relationship between egg size and development depth amongst modern coleoids may not apply to ammonites. Carbon isotope data suggest influence of terrestrial runoff or the egg yolk carbon source at hatching. This study demonstrates the utility of *in situ* geochemistry for sampling original shell material in mollusks to better understand life history and sub-annual water column structure.

Linzmeier, B. J., R. Kozdon, S. E. Peters, and J. W. Valley, 2016, Oxygen Isotope Variability within *Nautilus* Shell Growth Bands, *PLOS ONE* doi:10.1371/journal.pone.0153890.

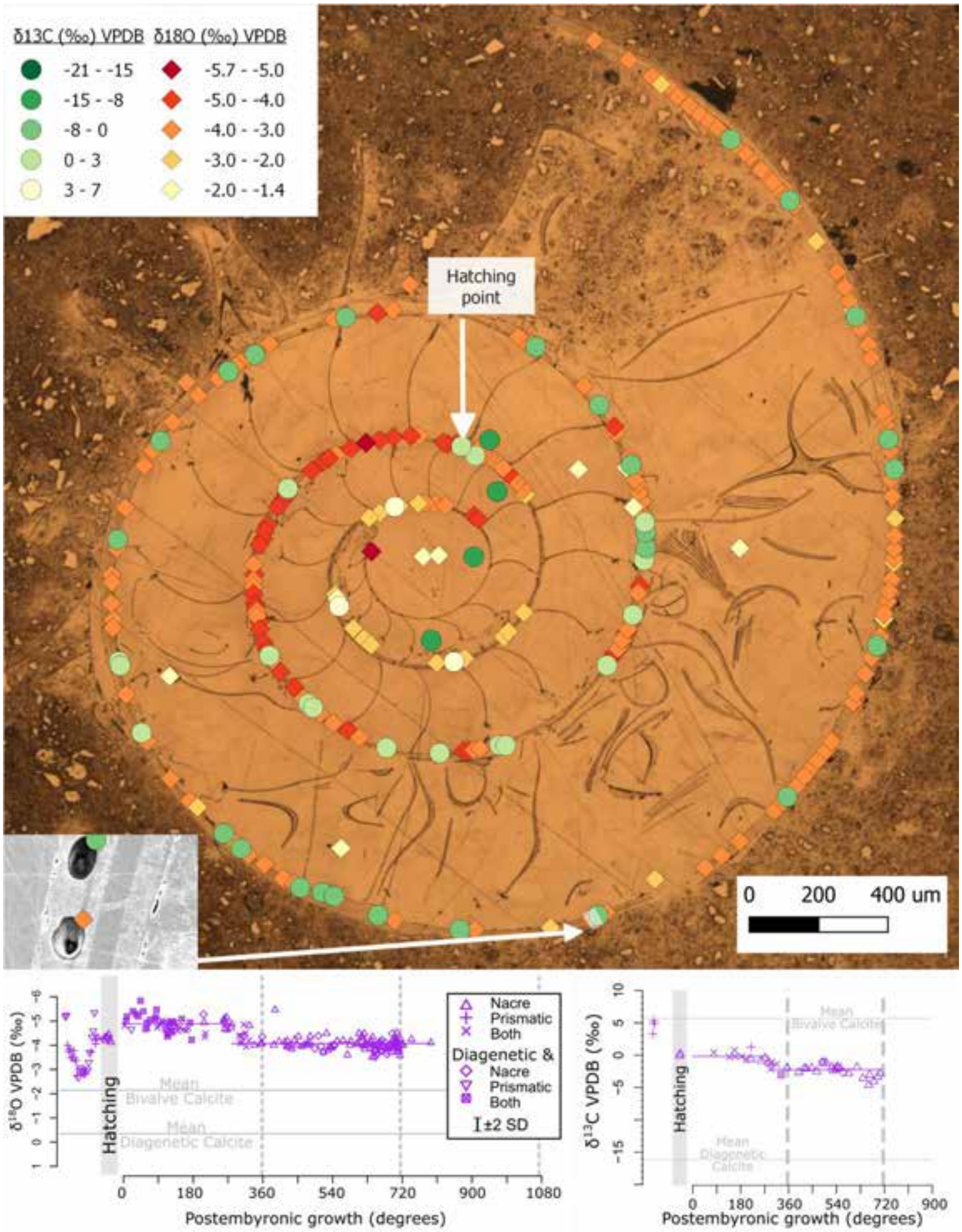

Figure 1. Reflected light image of a gold-coated and SIMS analyzed *Hoploscaphites* from the Fox Hills Formation of South Dakota. Both the $\delta^{18}O$ and $\delta^{13}C$ analysis locations are color coded for measured isotope values using QGIS software. The end of the embryonic shell is noted with a black arrow and is demarcated by the earliest precipitation of nacre and a shell thickening. The outer whorl is filled with broken septa that have been partially delaminated, presumably by authigenic calcite precipitation. The inset image in the top right shows one example each of $\delta^{18}O$ and $\delta^{13}C$ analysis pits imaged by SEM. The panels at the bottom show $\delta^{18}O$ and $\delta^{13}C$ by postembryonic growth in degrees for this sample.

Understanding the temporal slope of the temperature-water isotope relation: The slope equation

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The temporal (Dansgaard) slope relates the temperature in clouds to the δ^{18}O of precipitation δ^{18}O. In paleoclimate, the temporal slope is the critical benchmark to convert precipitation δ^{18}O to surface temperature. Previous studies have used various approaches to approximate the temporal slope, most important are two empirical approaches, one using the present day spatial slope and the other using independent borehole temperature for calibration. In these two approaches, the latter scale gives ~0.3‰°C, about half that of the former. Boyle gave an explanation why the borehole temperature slope is smaller than the spatial slope, but in a loose way. Here, we present a semi-empirical theory that relates the spatial slope with the temporal slope. We studied the relation between temporal and spatial slopes for the middle and high latitudes in a series of simulations in the isotope-enabled atmospheric model isoCAM3 for the last 21,000 years. Our model simulation suggests that both the temporal slope and spatial slope remain largely stable throughout the last deglaciation. The temporal slope can vary substantially across regions. Nevertheless, on average, and most likely, the temporal slope is about 0.3‰°C and is about half of the spatial slope. Furthermore, the relation between temporal and spatial slopes is understood using a semi-theoretical equation that is derived based on two assumptions: the Rayleigh distillation relation and a fixed spatial slope with time. The slope equation quantifies the Boyle's mechanism and suggests that the temporal slope is usually smaller than the spatial slope in the extratropics mainly because of the polar amplification feature in global climate change. Our theory is further supported by tagging experiments in isotope-enabled models.

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Guan, J., J. Zhu, Z. Liu, X. Wen (2017), Confirmation of "slope equation" for the temporal slope of the temperature-water isotope using water tracing experiments. In prep.,

Reconstructing Holocene Arctic Ocean paleoceanography using SIMS $\delta^{18}O$ and LA-ICP-MS elemental data from single *Neogloboquadrina pachyderma* shells

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The Arctic is currently experiencing increasing temperatures twice as fast as regions at lower latitudes. The acceleration of warming, termed Arctic amplification, is primarily driven by positive feedbacks influenced by the loss of Arctic ice cover (Sereze et al., 2009). Changes in air and surface water temperatures as well as fluctuations in rates and volume of deepwater formation in the North Atlantic will have substantial impacts on global climate. Therefore, understanding how the structure of the Arctic water column has changed in response to variations in climate throughout the last 20,000 years will help us to better predict what changes we can expect as the Earth warms over the next century.

The temperature and salinity characteristics with depth in the ocean determine the density profile, and thus the degree of water stratification. The degree of stratification in paleo-oceans is typically estimated by comparing oxygen isotope ratios from foraminifera occupying different depth habitats in the ocean (Simstich et al., 2003). However, this proxy does not work in the Arctic because high latitude polar assemblages are largely composed of only one species, *Neogloboquadrina pachyderma* (Np). Though traditional approaches to determine paleo-stratification are not useful in the Arctic, the distinctive method of calcification of Np allows them to be used in a novel way. Np grows its chambers (ontogenetic calcite) in the surface waters and subsequently descends to below the mixed layer where it quickly adds a thick crust of calcite (Kohfeld et al., 1996). Therefore, geochemical signals from both the surface waters and sub-mixed layer depths are captured within single Np shells. We can target <5 µm – sized domains for $\delta^{18}O$ using secondary ion mass spectrometry (SIMS), therefore capturing signals from both the ontogenetic and crust calcite in single Np shells. These data can be combined with laser ablation-inductively coupled plasma mass spectrometry (LA-ICPMS) profiles of trace elements through the same shells, resulting in a suite of geochemical information from the surface and intermediate depths (Figure 1).

Sample FS-19b

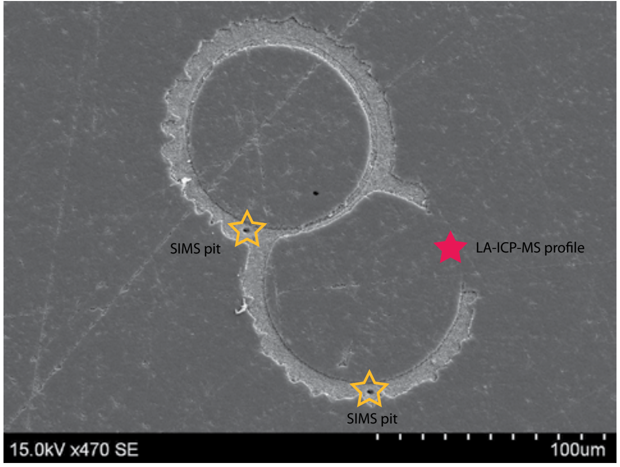

Figure 1. Scanning electron microscope image of an Np fragment with labeled locations of SIMS (<5µm beam diameter) and LA-ICP-MS (square beam, 44 µm x 44 µm)analyses.

$\delta^{18}O$ values in foraminifera shells are controlled by the temperature and the $\delta^{18}O$ signature of the water in which the shell is calcified (Epstein et al., 1951). The $\delta^{18}O$ of seawater itself is controlled by local hydrology, which is reflected in the salinity of the water. Variations are caused by melting ice, river runoff, rainfall, and mixing of different water masses which also control the salinity of the Arctic Ocean. Therefore, it is necessary to use additional proxies in the Arctic to tease apart the relative contributions of each of these processes to the $\delta^{18}O$ of the surface waters. Like salinity, the $\delta^{18}O$ signatures of subsurface waters are more or less conservative, so any changes in $\delta^{18}O$ with depth indicate a shift in water mass (Ravelo and Hillaire-Marcel, 2007).

The ratios of Mg and Ba to Ca in foraminifera shells have been shown to be linked to changes in temperature and riverine input, respectively. Therefore, combining Mg/Ca, Ba/Ca and $\delta^{18}O$ information from discrete layers of calcite allows us to resolve the temperature, salinity and $\delta^{18}O$ of the water in which those layers were grown. Analyzing the crust and ontogenetic calcite layers from single Np shells allow us to determine the hydrographic properties of the surface and the sub-thermocline waters from distinct time intervals. Implementing this method in locations across the Arctic will allow us to reconstruct the structure of the Arctic Ocean through the climatic variations of the last 20,000 years.

Here we present the SIMS $\delta^{18}O$ and LA-ICP-MS Mg/Ca and Ba/Ca results from a suite of live captured shells from the Fram Strait. In this pilot study, we determined what methods are required for the desired combination of analyses, and how to maximize efficiency of both instrument time and material. Using the hydrographic information from the water from which the samples were collected, we were able to define a calibration relationship for Np Mg/Ca-temperature, and resolve which of the published $\delta^{18}O_{calcite}$-$\delta^{18}O_{sw}$ equations works best for Np. These results allow us to apply this method to the Arctic fossil record in order to understand how the structure of the Arctic water column has changed in response to variations in climate throughout the last 20,000 years so that we can better predict what changes we can expect as the Earth warms over the next century.

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Heinrich Events, oxygen isotopes, and foraminifera: What can SIMS do for you?

Shaun Marcott – UW Madison Department of Geoscience

Oxygen isotopes are the iconic paleo-proxy for deriving temperature at the ocean surface and at depth. The utility of the proxy is based on the thermodynamic fractionation between the isotopically light ^{16}O and heavy ^{18}O during calcite precipitation in water. This strong temperature dependent fractionation is commonly described in the form of $\delta^{18}O$ and the systematics were first determined in the 1940s and refined over the last 70 years in both organic and inorganic calcite substances. The underlying assumptions for using $\delta^{18}O$ as a temperature proxy are: **1)** isotopic equilibrium between the oxygen in the water and the biogenic calcium carbonate precipitated in it; **2)** perfect preservation of the isotopic composition of the oxygen in the carbonate shell after deposition in marine sediments; and **3)** the constancy of the isotope composition of the water in the oceans. Here I address the second of these underlying assumptions using secondary-ion-mass-spectrometer (SIMS) to measure the oxygen isotopes on foraminifer shells from sediment core ODP-609 in the North Atlantic across Heinrich event 4 and 1, where large magnitude oxygen isotope excursions occur that have been associated with glacial meltwater events. SIMS is advantageous over traditional gas-source mass spectrometry because the domains of the calcite walls can be precisely targeted (within 5-10 μm), thus avoiding any secondary post-depositional calcite. This talk will discuss our ongoing and preliminary results, and provide an overview of using the Wisc-SIMS facility for new users.

The Role of Laser-Ablation Plasma Mass Spectrometry (LA-ICPMS) in Palaeoclimate Research: Principles and Applications

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Laser-ablation inductively-coupled-plasma mass spectrometry (LA-(MC-)ICPMS has – in conjunction with SIMS - revolutionized our ability to analyze trace concentrations and isotopic compositions in a wide range of materials at the spatial-resolution of tens of µm. LA-(MC-)ICPMS is a fairly low-cost/ high-throughput method for trace element and high-precision isotope ratio analysis (for the latter almost on par with TIMS or solution-MC-ICPMS), but lacks routine stable isotope capability (C, O), one of the key strengths of SIMS. Owing to the plasma-based ion source after laser sampling, resultant mass spectra of LA-ICPMS are in many, albeit not all cases, simpler that those of SIMS, allowing the use of low mass resolution mass spectrometers ($m/\Delta m$~400).

In this presentation I will briefly review some key relevant developments in LA methodology, that allow for example routine depth-profiling analysis for ultimate (sub-)µm scale spatial resolution. The main part, however, will showcase some of our recent applications of LA-(MC-)ICPMS in palaeoenvironmental research. This will include some of the following: direct analysis of deep frozen ice cores, daily resolution in giant clams (Tridacna), tooth enamel or the development of (shallow-dwelling) large benthic foraminifera (LBF) as proxy archives. In all these cases, the overarching motivation is the retrieval of past environmental proxy information at the highest time resolution, in order to, for example, reconstruct past seasonality or identify non-pervasive diagenetic overprint.

Using high-resolution imaging techniques to assess the impact of ocean acidification on the condition of pteropod shells

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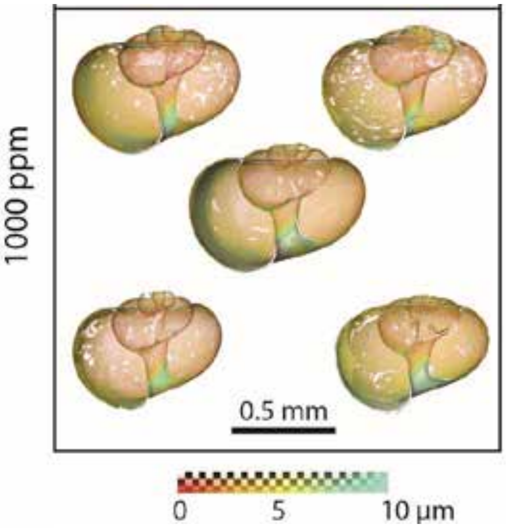
Anthropogenic activities are increasing carbon dioxide levels at an unprecedented rate. These changes affect ocean chemistry, decreasing pH and the concentration of carbonate ions in a process known as ocean acidification. Pteropods are a group of aragonitic molluscs which reach their highest abundances in polar and sub-polar oceans where these chemical changes will be most pronounced. They are therefore predicted to be amongst the first groups to be impacted by ocean acidification. Pteropods play a key role in both the marine food chain, and carbon cycle, and therefore it is with some urgency that we understand how they will be impacted by future changes in ocean chemistry.

Pteropod shells are visibly affected by dissolution and therefore have traditionally been studied using light and scanning electron microscopy. Here we have developed a range of different high-resolution imaging techniques to quantify, and understand, both natural variability, and changes in pteropod shell condition that are likely to occur in the future.



Slices through CT-scanned pteropods incubated at 1000 ppm.

Micro-CT scanning is used to image pteropod shells in three dimensions. This enables the shell thickness and volume to be quantified. We have applied this method to assess inter- and intra- specific variation in pteropod shells from five sites globally, and to investigate pteropod shell damage and repair.

On a finer scale, it's important to understand exactly how the shell degrades under predicted future condition. A pteropod shell is made up of three layers, which could be impacted by different dissolution rates. A combination of nanoSEM and surface profilometry is used to address the breakdown at the microstructure. We find that dissolution first increases surface topography, as dissolution rates vary widely across the shell. At later stages of dissolution, the shell dissolves more evenly across the surface, suggesting that once the surface layer has been breached, the inner layers dissolve at a similar rate.

Finally, pteropods have a thin organic membrane which covers the shell which, due to its thin, and clear nature, is difficult to image. By using a high-resolution light microscope and stacking a large number of images, the organic periostracum has been convincingly imaged for the first time. This enables us to form an integrated view of the organic, and carbonate components of the shell. There has been relatively little isotopic work conducted on pteropods thus far, which may be an informative way to supplement the current findings.

In summary, by combining a range of imaging techniques focused at different scales, we have been able to develop a more holistic understanding of the natural variability, and predicted future response, of pteropods to ocean acidification.

Measuring seasonal monsoon signals in Chinese speleothems

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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 where conventional drill-sampled $\delta^{18}O$ records are interpreted to reflect changes in Asian Monsoon dynamics across the last deglaciation.

Seasonal-resolution $\delta^{18}O$ analyses in three Chinese stalagmites reveal regular patterns of annual $\delta^{18}O$ variability from three caves that form a north-south transect of China. 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 (Orland et al., 2015).

Notably, the seasonal pattern of $\delta^{18}O_{rain}$ variability during "strong monsoon" intervals (e.g. Holocene) is different between the three stalagmites. We interpret the distinct seasonal $\delta^{18}O$ patterns 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 critically, the extent to which the jet stream responds to abrupt climate change.

Orland I. J. et al. (2015) *Geology* **43**, 555-558.

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

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Speleothems (carbonate cave formations, e.g. stalagmites) and biocarbonates (e.g. foraminifera, *Nautilus*, corals, otoliths, mollusks, pteropods) 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 and their accompanying challenges.

Since 2005, the WiscSIMS lab has continued to develop the methodology for attaining high-precision $\delta^{18}O$ measurements in carbonates. Much of this effort focused on instrument tuning, standardization and sample preparation techniques (Kita et al., 2009), but advances were also made in sample viewing (Kita et al., 2015), 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‰ (measured on the calcite running 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 $\delta^{13}C$ standard, 2 s.d. = ±0.7‰ for 6-10 μm spots (Orland, 2012). In the last year, tests of a new Faraday cup amplifier and a shortened analytical cycle confirm further improvement in analytical precision and speed.

Recent work also 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.

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PALEOCLIMATIC INTERPRETATION USING GEOCHEMICAL PROXIES IN THE MIDDLE MIOCENE PALEOSOLS OF THE TATACOA DESERT, COLOMBIA

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An increasingly urgent issue facing the global society is the intensifying warming of the climate in response to continually-increasing anthropogenic CO_2 emissions into the atmosphere. One approach to predicting climate variability over the coming centuries and millennia is through the careful study of past climate analogues. Ancient soil profiles (paleosols) shed light on how terrestrial environments response to climatic shifts and can, in some instances, provide records with sufficient temporal resolution to allow for chemo- and chronostratigraphic correlations with the more extensive and more complete marine proxy records.

The Tatacoa Desert of Colombia, with its extensive paleosol profiles of middle Miocene age (Honda Group), provides an ideal setting for studying the longer-term dynamics of carbon-cycling and climate variability during a time interval of atmospheric CO_2 draw-down to near-modern levels in the aftermath of the climatic warming event that occurred during the Middle Miocene Climate Optimum (MMCO). The objective is to help improve climate change projections. Situated above pale-colored fossil soils at this locality are deeply weathered, red-colored soils rich in pedogenic carbonates (the Upper Red Beds). An erosional discontinuity of *ca.* 13 m.y. separates them. Preliminary estimates of mean annual temperature (MAT) and mean annual precipitation (MAP) derived from the Upper Red Beds indicate appreciably cooler (MAT 20 ± 0.6 °C) and moister conditions (MAP 1300 ± 181 mm) than at present, whereas mass-balance considerations suggests lower atmospheric CO_2 levels at ~11 Ma (~200 ppm). The draw-down is attributed to CO_2 consumption by silicate weathering and transfer of carbon to the lithosphere over a time span of 10^3-10^6 years. This is in agreement with previous studies of high-latitude paleosols, which likewise suggest a decrease in atmospheric CO_2 levels at the end of the middle Miocene.

High-resolution analysis of deep-sea coral skeletons for trace element paleo-proxies of ocean conditions.

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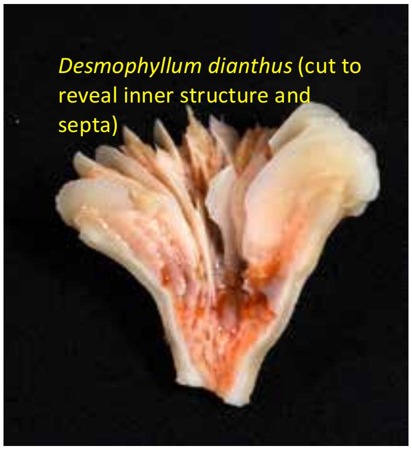
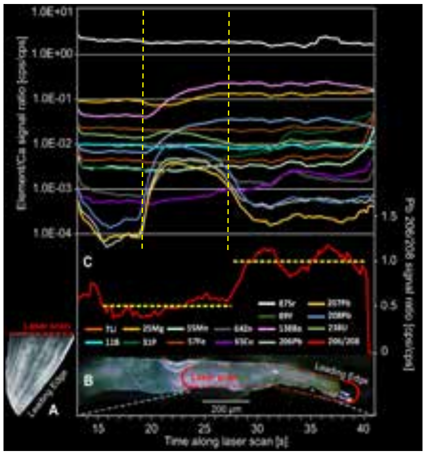
Alive and feeding



Desmophyllum dianthus (cut to reveal inner structure and septa)



Deep-sea or cold-water corals (CWCs) display cosmopolitan distribution over a wide range of depths in the ocean. Similar to their tropical counterparts, they provide continuous, high-resolution records of up to a century or more. Several CWC elemental and isotopic ratios have been proven or suggested as useful paleo-proxies. Our recent work focuses on relatively new and promising proxies for nutrients (P/Ca, Ba/Ca), carbonate system (U/Ca, B/Ca, B isotopes), and temperature (Mg/Li). Understanding the veracity of these proxies in our target archive, the solitary CWC *Desmophyllum dianthus,* requires high-resolution analysis of chemical distributions in the context of the meso-scale structure of the skeleton, on scales of 10's of microns. We are combining optical, LA-ICP-MS and micromilling-solution-ICP-MS approaches in the context of three major efforts: 1) Culturing studies using >150 live *Desmophyllum* currently growing at a range of pH and feeding conditions at the ICM (Barcelona) which we are using to calibrate proxies under a degree of control not possible in the open ocean; 2) Complementary calibration work using live-collected Desmophyllum from various ocean locations, in the context of the global ocean hydrographic database; and 3) exploitation of a new archive of fossil corals from waters around New Zealand, from which we plan to generate a paleo-record of Antarctic Intermediate water composition since the last Glacial period, important for testing hypotheses for mechanisms driving the transition out of the last Glacial period. We will discuss early laser ablation data that address the nature of intra-skeletal elemental variation with implications for efficiently extracting precise and accurate paleo-proxy signals from large archives of fossil corals. To advance rapid fossil coral dating, we have begun experimenting with high-spatial resolution LA-MC-ICP-MS U-Th "speed-dating," which has revealed small-scale variations in U and Th isotope distributions, with potential implications for the accuracy of conventional methods of precise U-Th dating using bulk skeletal samples.

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

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This work explores the effects of Fe^{2+} substitution on SIMS $\delta^{13}C$ and $\delta^{18}O$ bias in the analysis of carbonate minerals with compositions that fall along the siderite-magnesite solid-solution series [$FeCO_3$-$MgCO_3$]. Bias is the per mil (‰) difference between measured 'raw' and 'true' (*i.e.,* VPDB or VSMOW) values of $\delta^{13}C$ or $\delta^{18}O$ (also referred to as 'instrumental mass fractionation'). The component of total bias related specifically to variations in sample chemistry along a solid-solution can be referred to as the sample 'matrix effect'.

[Background and motivation] Carbonates of the siderite-magnesite series are encountered in many different geological environments on Earth[1] as well as in Martian meteorites[2,3]. The isotopic composition of the carbon and oxygen atoms they contain are widely used in the geosciences as proxies for inferring the conditions of carbonate formation. Of interest most commonly is the temperature of precipitation, the source(s) of carbon, and the nature/source of the fluids involved (*e.g.,* marine, meteoric, mixed or hydrothermal waters). Variations in the $\delta^{13}C$ and $\delta^{18}O$ signatures of pedogenic (soil) carbonates, for example, are frequently used as indicators of past ecologic and climatic change on the continents[4-6].

The motivation for this research grew out of a need for standards in the wake of recent technical advances in carbonate $\delta^{13}C$ and $\delta^{18}O$ microanalysis by SIMS, and the potential applicability of this technique in a wide variety of paleoenvironmental and paleoclimatic studies, as well as in the intensifying research efforts concerned with geologic carbon-sequestration[7,8]. Isotope ratios in carbonates can now be routinely measured in-situ from micrometer-scale sample domains with sub-per mil (‰) precision[9]. The accuracy of measurement, however, depends in large-part on the availability and overall quality of matrix-matched standards, as the bias imparted to isotope ratios during sputtering from the sample surface and the subsequent passage of ions through the mass spectrometer cannot be accurately predicted from first principles for naturally-occurring minerals and glasses. For many mineral families wherein the compositional end-members form extensive or complete solid-solutions with one-another – such as the carbonates – proper standardization remains a work in-progress for the community of SIMS laboratories around the world.

[Results] A suite of 13 calibration standards was developed for both isotope systems, spanning the compositional range between Fe# = 0.002 and 0.997 [Fe# = molar Fe/(Mg+Fe)].

The calibration curves of both isotope systems are non-linear and have, over a 2-year period, fallen into one of two distinct and largely self-consistent shape categories (data from 10 analytical sessions) despite adherence to well-established analytical protocols for carbonate $\delta^{13}C$ and $\delta^{18}O$ analyses at WiscSIMS (CAMECA IMS 1280). The cause of this is not well understood at present, and stresses the importance of having available a sufficient number of well-characterized standards so that potential complexities of curvature can be adequately delineated and accounted for on a session-by-session basis. Examples of the more common behavior observed to date are shown in Fig. 1. Note the two different vertical axes. The left-hand axis pertains to the *working calibration curves*, where bias measurements are normalized (or "anchored") to a running standard used for drift-monitoring (in this case end-member magnesite "UWMgs1"). Normalized values are thus expressed as "$\delta^{13}C$ or $\delta^{18}O$ bias*(STD-UWMgs1)"]. The right-hand axis pertains to bias values pre-normalization (in other words, simply the per mil difference between 'raw' and 'true' $\delta^{13}C$ or $\delta^{18}O$ value of each standard). Note also that all bias values for this series are negative. Thus, when describing general trends, the bias is said to *increase* as value become *more negative* (and vice versa).

As with the dolomite-ankerite series[10,11], mass bias for the magnesite-siderite solid-solution is consistently most sensitive to changes in composition near the iron-free end-member. With increasing Fe-content up to ~20 mol% $FeCO_3$ (*i.e.,* Fe# 0-0.2), $\delta^{13}C$ bias *increases* by 3-4.5‰, whereas $\delta^{18}O$ bias *decreases* by up to 13-15‰ (it is normal for bias to vary by 1-2‰ on a session-specific basis). Between the end-members of the series, $\delta^{13}C$ bias *increases* by a total of 10-11‰ (magnesite→siderite), whereas $\delta^{18}O$ bias *decreases* by 13-16‰ (refer to the right-hand *y*-axis of Fig. 1).

As an example, if uncorrected, the presence of 1-2 mol% $FeCO_3$ in a sample material of unknown isotopic composition would produce an accuracy error of ~1‰ for $\delta^{13}C$ and ~2-3‰ for $\delta^{18}O$ measurements.

The compositional dependence of SIMS $\delta^{13}C$ and $\delta^{18}O$ bias*(RM-UWMgs1) (*i.e.* the sample matrix effect) was empirically regressed using a mathematical expression stemming from the family of Hill-type functions (here a modified form of eq. 27 of Goutelle et al., 2008; Fig. 1). The resulting calibrations residuals are ≤ 0.5‰ for $\delta^{18}O$ analyses performed using either a 3- or 10-µm diameter spot-size and for $\delta^{13}C$ analyses performed using a 6-µm spot. This is considered a measure of *analytical accuracy* relative to the *certified reference material* NIST-19. Based on the spot-to-spot reproducibility of running standard values (n = 8) that "bracket" each set of 10 sample measurements, the *analytical precision* associated with 10- and 3-µm $\delta^{18}O$ spots is ±0.3‰ and ±0.7‰ (2SD, standard deviations), respectively, and that associated with 6-µm $\delta^{13}C$ spots is ±0.6-1.2‰ (2SD).

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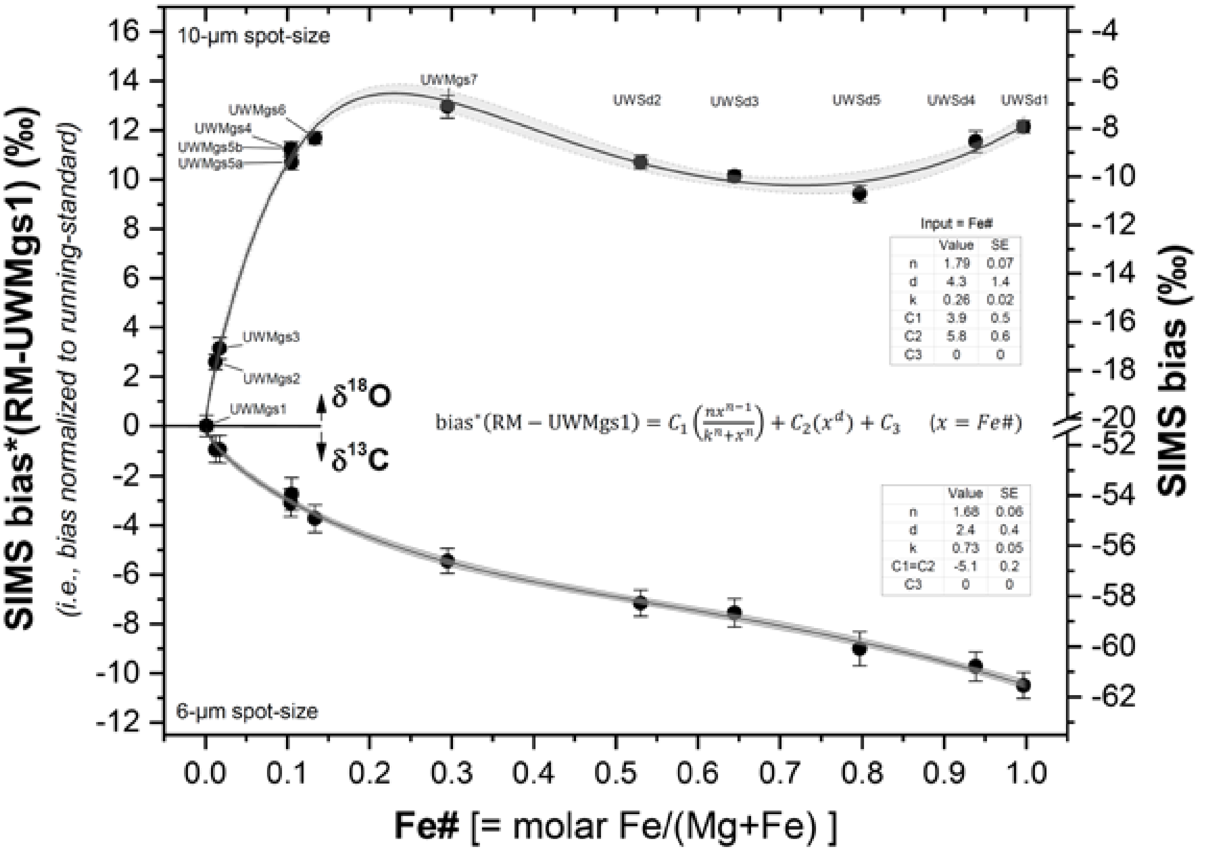

$$\text{bias}^*(\text{RM} - \text{UWMgs1}) = C_1\left(\frac{nx^{n-1}}{k^n + x^n}\right) + C_2(x^d) + C_3 \qquad (x = Fe\#)$$

	Value	SE
n	1.79	0.07
d	4.3	1.4
k	0.26	0.02
C1	3.9	0.5
C2	5.8	0.6
C3	0	0

	Value	SE
n	1.68	0.06
d	2.4	0.4
k	0.73	0.05
C1=C2	-5.1	0.2
C3	0	0

Figure 1. ***(Upper trend)*** *A typical calibration relating SIMS $\delta^{18}O$ bias (‰) to the cation composition of the magnesite-siderite solid solution series [Fe# = Fe / (Mg+Fe)] for measurements employing a 10-µm diameter spot-size.* ***(Lower trend)*** *A typical calibration relating SIMS $\delta^{13}C$ bias (‰) to Fe#. Shading around regressions represents confidence bands (at the 68% level). Error bars represent propagated measurement uncertainties.*

Carbon and nitrogen exchange between a photosynthetic symbiotic dinoflagellate and its planktonic foraminifera host

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The planktonic foraminifera *Orbulina universa* lives in the marine photic zone and possesses photosynthetic dinoflagellate symbionts in its cytoplasm. During the day these dinoflagellates are outside the host cell whereas at night, they migrate inside the foraminiferal cell. These photosynthetic dinoflagellates fix and store carbohydrate during the day. At night, it is thought that the fixed photosynthate carbon is transferred to the host cytoplasm. However, details of carbon translocation from symbiont to host remain unknown. Related to carbon translocation is the question of nitrogen flow through this foraminifera system. Food is thought to provide most of the nitrogen for amino acid synthesis but little is known about NO_3^- and NH_4^+ uptake and retention by the symbionts or foraminifera.

To address these questions, individual *O. universa* were incubated with ^{13}C-bicarbonate, ^{15}N-sources ($^{15}NH_4^+$, $^{15}NO_3^-$) and ^{13}C/^{15}N labeled food following a natural day-night cycle. Specimens were sampled during the 30 hour long pulse-chase experiment, and immediately fixed for TEM imaging to preserve their cellular ultrastructure at different times in the day-night cycle. Following TEM imaging, thin sections were subsequently viewed with a NanoSIMS (nanoscale Secondary-Ion Mass Spectrometry) to visualize the incorporation and transfer of isotopically labeled compounds in the foraminifera and symbionts.

During the light phase, the microalgal symbionts fixed $^{13}CO_2$ into starch that accumulated around the chloroplast pyrenoid and within the cell, initially as starch nodules. Following symbiont migration and incorporation into vacuoles inside the foraminifera host cell at night, ^{13}C labeled photosynthates from the symbionts were observed within the host, primarily in the form of lipid droplets. At the end of the night, the number of ^{13}C-labeled lipids droplets in the foraminifera had increased and the symbiotic microalgae were nearly devoid of starch granules. This is thought to reflect a combination of dinoflagellate respiration and translocation of carbon from the algal symbionts (as lipids). The symbiotic dinoflagellates were also integrating both nitrate and ammonium from the seawater, with ammonium uptake happening at a faster rate. In the case of ammonium, the ^{15}N-signal could also be observed in the foraminiferal cytoplasm, but its pathway of integration (through symbiosis or foraminifera itself) is not yet constrained. The uptake of both $^{15}NH_4^+$ and $^{15}NO_3^-$ by the foraminifera host points to a mechanism that may have evolved in nutrient-poor environments to trap and cycle dissolved inorganic nitrogen within the symbiotic association with minimal loss of N to the surrounding environment.

The Need for HiRes in Vertebrate Calcified Tissue Oxygen Isotope Measurements

Noreen Tuross and Linda Reynard

The need for spatial resolution in the oxygen isotopes analysis of vertebrate bones and teeth is in the literal realm of *res ipsa loquitur*. Many investigators have used drills to ever more finely sample bone, dentin and enamel with varying success in revealing climatic, migratory and/or dietary information. A comparison of BrF_5 phosphate oxygen isotopic values with IR laser ablated data illustrated the comparability of the values at a 250 μm scale (with larger damage halos) (Cerling and Sharp, 1996), and UV laser fluorination of biogenic phosphates at the roughly 100 μm diameter range generally agreed with precipitated silver phosphate data (Jones et al, 1999). We explore the relationship among the oxygen isotopes of precipitated silver phosphate from Pleistocene enamel with carbonate and Secondary Ion Mass Spectrometry data. The SIMs data agrees with the precipitated silver phosphate data and separates primates and grazers on the basis of the oxygen isotopic values: carbonate oxygen does not separate the two groups. The increased resolution of SIMs (10 μm) is of significant value in finely spatially-resolved analysis of oxygen isotopes of primate enamel.

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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 10µm scale with significantly improved precision compared to earlier SIMS techniques. Smaller spots, from 3- to 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. The comparison of biocarbonate samples to inorganic carbonate standards requires special care.

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

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Assessing unexpected isotopic variability in aragonitic biocarbonates through sample replication

Madelyn J. Mette[1], Nina Whitney[1], Jared Ballew[1], Alan Wanamaker[1*]

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* presenting author

Geochemical signatures, particularly oxygen isotopes, from biocarbonates serve as highly important proxy records of past climate and environmental conditions. Assessing signal-to-noise ratios in such records is essential for reconstructing past environmental conditions in a robust manner, yet more often than not isotope records are constructed from single individuals or transects and therefore fail to provide complete/combined estimates of proxy and analytical errors. Recent work has identified oxygen isotopic variability among contemporaneously produced biogenic carbonate outside the range of analytical uncertainty. Such "unexpected" variability may be from natural heterogeneity of the carbonate material or be attributed to sample collection (milling, drilling, etc.), isotopic preparation (acid digestion), and isotopic analysis.

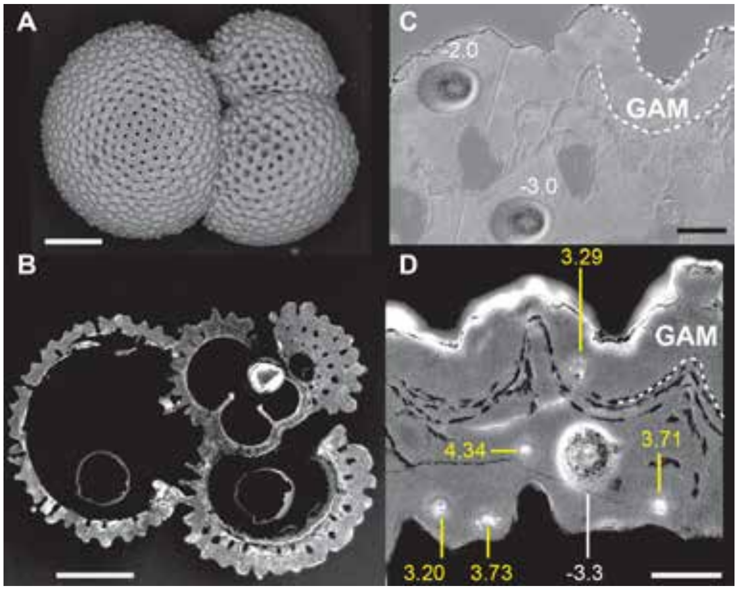
The present study seeks to quantify sources of isotopic variability in the commonly used marine bivalve *Arctica islandica*, with an emphasis on the potential of human-induced variability arising from sampling techniques. Stable carbon ($\delta^{13}C$) and oxygen ($\delta^{18}O$) isotopes were analyzed for replicate samples taken from 36 laboratory-reared juvenile specimens grown at constant temperature and for three individuals from two natural populations (Gulf of Maine at 80m water depth, Northern Norway at 6 m water depth) across two equivalent transects of 10 sequential years. $\delta^{13}C$ variability within a given year among the three clams in field collected samples was near that of analytical uncertainty, while variability in $\delta^{18}O$ was greater than that of both the $\delta^{13}C$ and the instrumental analytical uncertainty. Oxygen isotopic heterogeneity in the biocarbonate rather than human-induced sampling (quality of milling paths) is a likely explanation of "unexpected" isotopic variability in these filed collected samples. Variability among clams in the culture experiment yielded more variable $\delta^{13}C$ values compared to $\delta^{18}O$ and $\delta^{18}O$ variability was less than analytical uncertainty. Statistical analysis (random sampling without replacement for 50,000 iterations) of the samples from the laboratory-reared shells revealed that three to four shells yielded acceptable levels of replication and reduced proxy uncertainty. Because these clams were grown under constant temperature, results from this part of the study represent a "best case scenario," and samples collected from the field with changing seawater temperatures and variable isotopic composition of seawater within a growing season may require additional replication.

This study is intended to provide insight into possible sources of error beyond analytical error involved with measuring stable isotopes in biogenic carbonate. Our findings suggest that replication of oxygen and carbon isotope measurements of contemporaneously produced aragonite is necessary in order to reduce proxy derived noise and to increase the robustness of the environmental signal by including and propagating multiple forms of uncertainty in environmental reconstructions.

Reconstructing the Oxygen Isotope Composition of the Surface Ocean using Paired *In Situ* Micro-Analytical Techniques on Individual Shells of the Planktic Foraminifer *Trilobatus sacculifer*

Wycech, J.B. [1]; Kelly, D.C.[1]
[1]University of Wisconsin-Madison, Department of Geoscience

A critical component of the global climate system is atmospheric water vapor transport, which manifests itself in the marine realm as spatial gradients in the oxygen isotopic composition of the surface ocean ($\delta^{18}O_{sw}$). The traditional approach to reconstructing past $\delta^{18}O_{sw}$ entails techniques that measure the $\delta^{18}O$ and Mg/Ca compositions of whole planktic foraminifer shells. However, such $\delta^{18}O_{sw}$ reconstructions suffer from inaccuracies caused by the heterogeneous geochemical compositions of shells grown by many planktic foraminifer species. This issue is exemplified by the extant planktic foraminifer, *Trilobatus sacculifer*, whose bulk-shell composition is an aggregate mixture of two carbonate phases – pre-gametogenic (PREGAM) and gametogenic (GAM) calcites – grown under different environmental and physiological conditions. The rapid addition of a GAM crust to the exterior of *T. sacculifer* shells poses a major problem to surface-ocean temperature and $\delta^{18}O_{sw}$ reconstructions because it occurs at the end of the life cycle as the shell sinks into deeper, colder waters during reproduction (Bé, 1980); hence, the $\delta^{18}O$ of GAM calcite tends to be ^{18}O-enriched relative to that of the PREGAM calcite (Duplessy et al., 1981). To complicate matters, planktic foraminifer shells typically experience post-mortem alteration as they are incorporated into the sedimentary record via seafloor diagenesis, which tends to further elevate the bulk $\delta^{18}O$ composition by adding secondary carbonate to the shells at cold bottom temperatures (e.g., Pearson et al., 2001; 2007). Isolated measurement of $\delta^{18}O$ in these micrometer-scale carbonate phases using conventional whole-shell analytical techniques is not possible because the various phases are too small.



Scanning electron microscope images of a *T. sacculifer* shell from Caribbean Site A2 (0-2 cm core depth). A. Back-scatter image of whole shell. B. Secondary electron image of shell in cross-section. C, D. Highly magnified views of cross-sectioned shell wall showing 10 µm SIMS $\delta^{18}O$ pits (white values in ‰, PDB) and 3 µm EPMA Mg/Ca pits (yellow values in mmol/mol). GAM calcite outlined with white dashed line. Scale bars are 100 µm in A and B and 10 µm in C and D.

Here, we report the findings of a feasibility study designed to evaluate the accuracy of surface $\delta^{18}O_{sw}$ reconstructions based on paired $\delta^{18}O$ and Mg/Ca ratios measured from homologous, micrometer-scale (3-10 µm) subdomains within individual *T. sacculifer* shells via secondary ion mass spectrometry (SIMS) and electron probe microanalysis (EPMA), respectively (Figure). Shells of *T. sacculifer* were recovered from Holocene-age sediments at four sites spanning a broad spectrum of oceanographic settings: Site 806 (western equatorial Pacific), Site 847 (eastern equatorial Pacific), Site A2 (Caribbean), and Site PC9 (northwestern Atlantic). The ultra-high spatial resolution (3-10 µm) of these *in situ* measurements reveals that the δ^{18}O of GAM calcite is ~1‰ higher than that of PREGAM calcite, while the Mg/Ca ratios of GAM and PREGAM calcite are indistinguishable at all sites. Comparison of SIMS measurements to the predicted $\delta^{18}O_{calcite}$ values for the ocean mixed layer at each site reveals that the PREGAM and GAM δ^{18}O values track the ontogenetic water depth migration of *T. sacculifer*. In addition, mass-balance calculations comparing measured bulk-shell and *in situ* δ^{18}O values to the δ^{18}O value of a hypothetical diagenetic end-member suggest that the *T. sacculifer* shells from the equatorial Pacific and Caribbean sites may be composed of up to 20% diagenetic calcite and the shells from the Northwestern Atlantic site may be composed of up to 30% diagenetic calcite.

In summary, the addition of GAM and diagenetic calcites to *T. sacculifer* shells causes $\delta^{18}O_{sw}$ reconstructions based on bulk-shell chemistries to overestimate observed $\delta^{18}O_{sw}$ by 0.6-1.3‰. By contrast, surface-ocean $\delta^{18}O_{sw}$ reconstructions derived from *in situ* δ^{18}O:Mg/Ca ratios of PREGAM calcite are within 0.3‰ of observed $\delta^{18}O_{sw}$ at each study site. This study serves as a proof-of-concept that *in situ* SIMS δ^{18}O and EPMA Mg/Ca analyses of planktic foraminifer shells can improve both accuracy and precision (0.1-0.3‰, 2SD) of surface $\delta^{18}O_{sw}$ reconstructions by reducing uncertainty related to intra- and inter-shell geochemical variability.

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In situ Fe isotope analysis by femtosecond laser ablation: fundamentals and applications

Xin-Yuan Zheng[1,2*], Brian Beard[1,2], Seungyeol Lee[1,2], Thiruchelvi Reddy[1,2], Huifang Xu[1,2], Weiqiang Li[1,2,3], Clark Johnson[1,2]
[1] Department of Geoscience, University of Wisconsin-Madison, Madison WI 53706, USA
[2] NASA Astrobiology Institute, USA
[3] School of Earth Sciences and Engineering, Nanjing University, Nanjing, China
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Laser ablation coupled to multi-collector ICP-MS (MC-ICP-MS) has emerged as a useful tool to resolve micron-scale variations of many metal and metalloid stable isotope ratios (e.g., Fe, Si, Cu) in various types of samples. Because an analytical precision of ~0.1‰ (2sd) is typically needed for many “non-traditional” stable isotopes due to their limited variability in nature (a few ‰), a thorough understanding of laser ablation induced isotopic fractionations is of fundamental importance to ensure precise and accurate isotope ratio measurements.

We will present results of the first comparison of laser ablation induced Fe isotope fractionations using a 266-nm Ti:Sapphire femtosecond (fs) laser with a pulsewidth of ~150 fs and a 193-nm ArF excimer nanosecond (ns) laser with a pulsewidth of ~4 ns [1]. Aerosols produced by laser ablation of a range of Fe minerals of strong geological interests, including magnetite, siderite, pyrite and pyrrhotite, were aerodynamically sorted by a cascade impactor, and then analyzed for their Fe isotope compositions. The results unambiguously show particle-size dependent Fe isotope fractionations of up to a few per mil in ^{56}Fe/^{54}Fe during both fs- and ns-laser ablation. However, fs-laser ablation is superior to ns-laser ablation, because fs-LA provides stoichiometric total aerosols whose Fe isotope compositions match that of the substrate under all laser operating conditions tested, but ns-laser ablation of magnetite at low fluence (1 J/cm^2) leads to major non-stoichiometric sampling for Fe isotopes (offset by 0.6‰). In addition, fs-LA generates largely similar particle size distributions regardless of mineralogy and fluence, but ns-LA creates mineral-dependent size distributions, where more Fe mass often resides in particles with larger aerodynamic sizes, increasing the risk of incomplete ionization on the ICP.

Our analyses over ~2-years, however, show that the observed advantages of fs-laser ablation do not directly translate into “matrix-free” analysis of stable Fe isotope ratios, contrary to the popular perception. This can be demonstrated by highly inaccurate non-phase-matched LA analyses of magnetite and pyrrhotite using a pyrite as the bracketing standard. Such matrix effects, however, can be largely suppressed by addition of water during fs-LA at a price of reduced sensitivity. Precise and accurate (within 0.1‰) Fe isotope analyses can be achieved under “wet” fs-LA conditions without matrix-matching between sample and bracketing standard. Inaccurate measurements were also observed during non-phase-matched analyses of the same suite of samples by “dry” ns-laser ablation. In contrast, suppression of matrix effects by water addition during ns-laser ablation is obscured by imprecise measurements even under wet conditions, indicative of a less effective influence of water on ns-LA analysis. A matrix-matched bracketing standard, therefore, appears to be always necessary for ns-LA analysis.

With the improved understanding of laser ablation induced isotopic fractionations and matrix effects during fs-LA analysis, we will demonstrate the usefulness of this technique by a case study of reconstructing early environment of the Earth using ~2.5 Ga banded iron formations [2].

[1] Zheng et al., 2017, *Chem. Geol.* 450: 235-247; [2] Li et al., 2015, *PNAS* 27: 8193-8198.

Growth zoning and trace element distribution in freshwater cultured pearls
-- and potential study on stable isotope ratios

Chunhui Zhou
Gemological Institute of America

Poster abstract:

Pearls were one of the earliest natural gems known to humans. Formed within the soft tissues of various freshwater and saltwater mollusks due, for example, to irritations or injuries to their mantle tissues, pearls are mainly composed of concentric layers of aragonite and conchiolin, which are the same substances the animal uses to build its shell.

Gem quality natural pearls are very rare and can command high values. Advances in pearl culturing techniques have provided affordable cultured pearls to enter the market, but have also created challenges to gemological laboratories where conventional gemological tests may be insufficient in separating certain natural and cultured pearls.

Figure 1. Cross section of a Chinese freshwater cultured pearl.

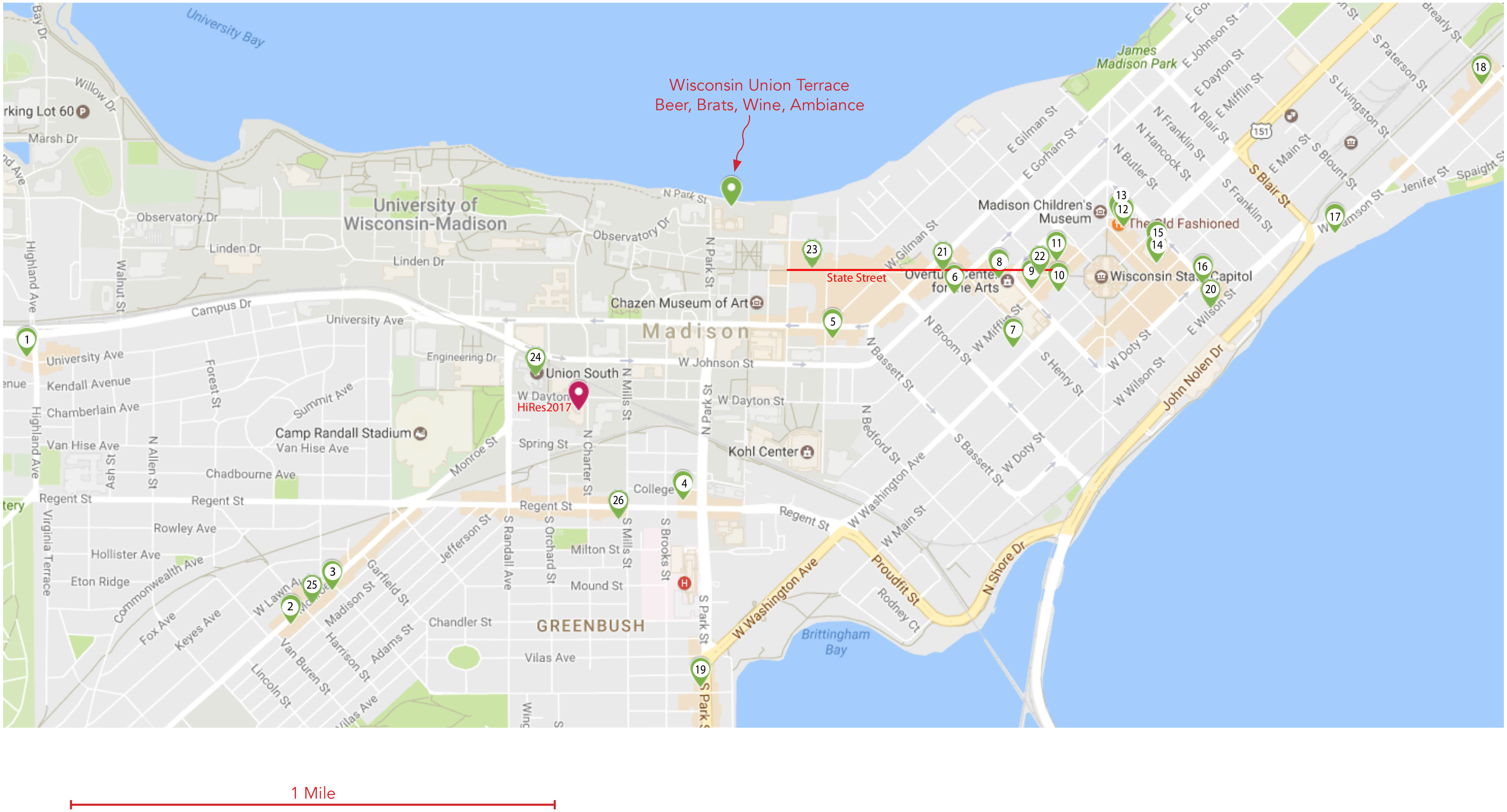
Chinese freshwater non-bead cultured pearls are by far the most abundant and affordable pearls in the market. They are usually grown for periods of 3 to 7 years in natural lakes or rivers, as well as manmade ponds and reservoirs within China's southeastern provinces. Cross sections of Chinese freshwater non-bead cultured pearls have revealed growth zoning similar to tree growth rings (figure 1), which correlate with seasonal and environmental changes in the surrounding water. Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) studies revealed cyclic changes in Mn concentrations from the center to the outer surfaces of the pearls, generally in accordance with their growth rings.

The mineral composition of pearls and their unique growth zonings suggest a study on oxygen and carbon stable isotope ratios may provide important information on the particular growth environments, water temperature fluctuations, and geological origins of different types of pearls, and ultimately may prove to be useful in the identification of certain challenging pearls. In addition, historical and fossil pearls may be used for the identification of paleoclimate conditions of ancient time.

NOTES:

NOTES:

Restaurants within walking distance of Weeks Hall.



Restaurants we like within walking distance of Weeks Hall.
*reservations recommended
Some may be closed on Monday. Many are listed on Open Table.

1. *Lombardino's Restaurant $$ · Italian
2500 University Ave (608) 238-1922
Restaurant & bar serving seasonal Italian cuisine in a space with Roman columns & a mural of Venice.

2. Brasserie V $$ · Belgian Restaurant
1923 Monroe St (608) 255-8500
Elevated throwback offering locally sourced, seasonal French eats & many Belgian beers.

3. Pizza Brutta $$ · Pizza
1805 Monroe St (608) 257-2120
Casual spot for wood-fired, Neapolitan pies created from housemade mozzarella & local ingredients.

4. GreenBush Bar $$ · Bar, Itallian Restaurant
914 Regent St (608) 257-2874
Simple parlor with Christmas lights for Sicilian-style pizza & pasta, plus wine & spirits.

5. Dotty Dumpling's Dowry $$ · Hamburger
317 N Frances St (608) 259-0000
Longtime local institution offering specialty burgers, cheese curds & tap beers in quirky digs.

6. *Estrellon $$$ Gastropub
313 W Johnson St (608) 251-2111
Spanish–style fare is served at this spacious tapas eatery/bar with an elegant, laid-back ambiance.

7. *RED Dine Lounge $$
316 W Washington Ave #100 (608) 294-1234
Sleek eatery serving creative sushi rolls & grilled Japanese fare in modern environs.

8. *Fresco $$$ Fine Dining Restaurant
227 State St (608) 663-7374
Modern New American spot on the Madison Museum of Contemporary Art rooftop offering Downtown views.

9. *Cento $$$ Italian
122 W Mifflin St (608) 284-9378
Farm-to-fork Italian restaurant with housemade pastas & wood-fired pizzas, plus a sizable wine list.

10. *Graft $$+
4.8 (608) 229-8800 Fine Dining Restaurant
Midwestern small plates, wine & local beer in a casually refined restaurant with booth seating.
18 N Carroll St

11. The Coopers Tavern $$ · Bar
20 W Mifflin St (608) 256-1600
Upscale Irish tavern serving pub grub & international beer & wine in a warm, contemporary venue.

12. *Harvest $$$+
21 N Pinckney St (608) 255-6075
Upscale spot overlooking Capitol Square offering farm-to-table New American fare & a long wine list.

13. The Old Fashioned $ American - Wisconsin
23 N Pinckney St (608) 310-4545 Usually a wait
Wisconsin-themed, retro-style tavern offering beers, brats & cheese curds (all sourced in-state).

14. Graze $$ · American
1 S Pinckney St #107 (608) 251-2700 Usually a wait
Lively gastropub plating farm-to-table comfort fare in a modern glass venue with Capitol views.

15. *L'Etoile $$$$ · Fine Dining Restaurant
1 S Pinckney St #107 608) 251-0500
Upscale farm-to-table spot serving French-inspired American fare, wine & cocktails in an airy venue.

16. The Great Dane Pub & Brewing Company $$ · Brewpub
123 E Doty St, Madison, WI (608) 284-0000
A changing roster of craft brews & pub eats served in a lively venue with beer garden & pool tables.

17. *Sardine $$ · Bistro
617 Williamson St (608) 441-1600 Usually a wait
Hip bistro with creative French fare & a lively bar in a former warehouse with Lake Monona views.

18. *A Pig In A Fur Coat $$
940 Williamson St (608) 316-3300
Hip, cozy bistro serving small & large Mediterranean plates, beer & wine at butcher-block tables.

19. Rockhound Brewing Company $
444 S Park St (608) 285-9023
Contemporary setting for house brews on tap paired with burgers, sandwiches & American comfort fare.

20. Ostera Papavero $$
128 E Wilson St +1 608-255-8376
Cozy, laid-back spot serving large portions of seasonal Italian fare & an extensive wine list

21. Himal Chuli Restaurant $+
318 State St +1 (608) 251-9225
Pint-sized spot with an outdoor patio featuring Nepalese cuisine, including many vegetarian dishes

22. Ian's Pizza on State $
100 State St +1 (608) 257-9248
Wisconsin-born chain known for its creative pizzas including its signature mac 'n' cheese pie

23. Sunroom Cafe $
4.1 (608) 255-1555
Hopping cafe serving global fare with lots of vegetarian/vegan options plus house-baked pastries.
638 State St, Madison, WI 53703
sunroomcafe.com

24. Union South $
4.6 Burgers, beer, coffee, pasteries, Ice Cream
1308 W Dayton St

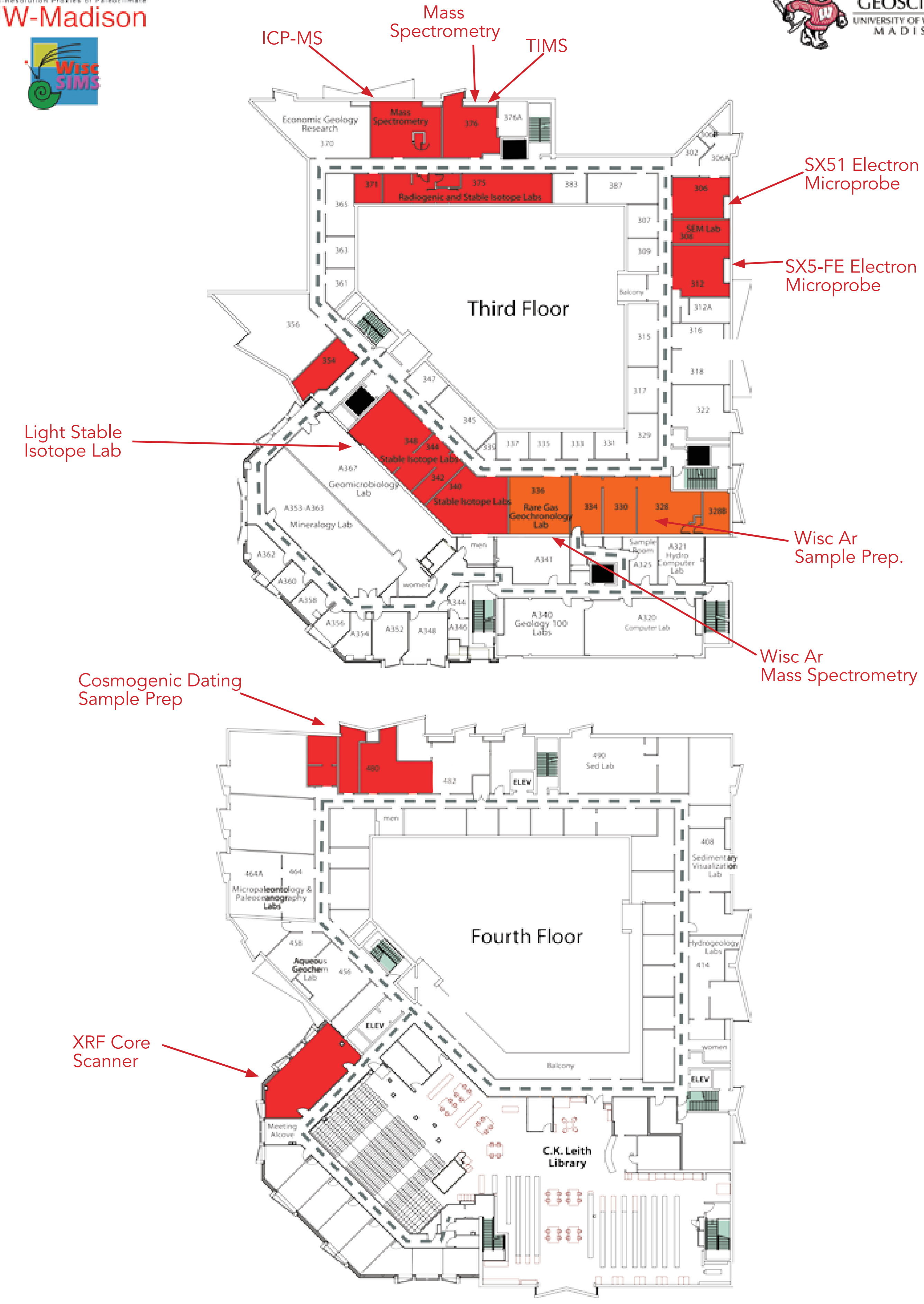
25. Brocach on Monroe Street $$
1843 Monroe St (608) 819-8653
Festive Irish tavern featuring upscale pub grub, Irish & Scotch whiskeys, & live traditional music

26. Hong Hong Cafe $$
2 S Mills St +1 608-259-1668 hongkongcafewi.com
Casual, old-school spot serving Chinese favorites, lunch specials & weekend dim sum

HiRes2017
High-Resolution Proxies of Paleoclimate
UW-Madison

Weeks Hall Lab Location Maps

DEPARTMENT of
GEOSCIENCE
UNIVERSITY OF WISCONSIN
MADISON



HiRes2017
High-Resolution Proxies of Paleoclimate
UW-Madison

Workshop Location:
Weeks Hall
1215 Dayton St.

DEPARTMENT of GEOSCIENCE
UNIVERSITY OF WISCONSIN MADISON

BBQ - Sunday night 5PM
Weeks Hall Courtyard

Weeks Hall - Department of Geoscience

Union South lunch, coffee shop and hotel

Lunch - third floor, room TBD

1308 W. Dayton St.

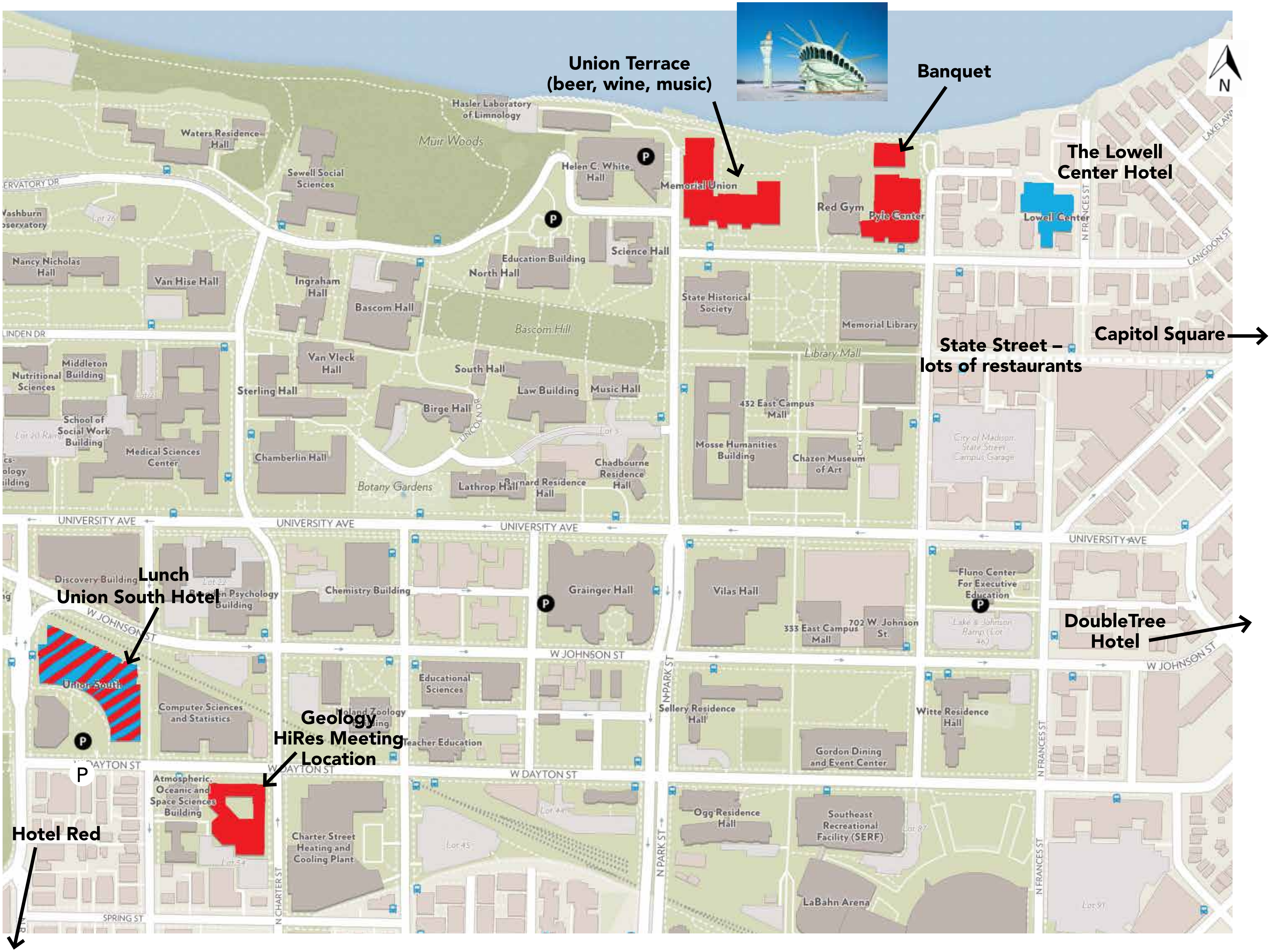
ph: 608-263-2600

Banquet: Pyle Alumni Lounge

Tuesday, June 20 - 6PM

702 Langdon St.

(608) 262-1122


Union Terrace
(beer, wine, music)
Banquet
The Lowell
Center Hotel
Capitol Square
State Street –
lots of restaurants
DoubleTree
Hotel
Lunch
Union South Hotel
Geology
HiRes Meeting
Location
Hotel Red
N
Memorial Union
Pyle Center
Red Gym
Lowell Center
Union South
Hasler Laboratory of Limnology
Muir Woods
Waters Residence Hall
Sewell Social Sciences
Helen C. White Hall
Washburn Observatory
Nancy Nicholas Hall
Van Hise Hall
Ingraham Hall
Bascom Hall
Education Building
North Hall
Science Hall
State Historical Society
Memorial Library
Library Mall
Bascom Hill
Van Vleck Hall
South Hall
Music Hall
Law Building
Birge Hall
Sterling Hall
Middleton Building
Nutritional Sciences
School of Social Work Building
Medical Sciences Center
Chamberlin Hall
Botany Gardens
Lathrop Hall
Barnard Residence Hall
Chadbourne Residence Hall
432 East Campus Mall
Mosse Humanities Building
Chazen Museum of Art
City of Madison State Street Campus Garage
UNIVERSITY AVE
Discovery Building
Psychology Building
Chemistry Building
Grainger Hall
Vilas Hall
333 East Campus Mall
702 W. Johnson St.
Fluno Center For Executive Education
Lake & Johnson Ramp (Lot 46)
W JOHNSON ST
Computer Sciences and Statistics
Educational Sciences
Zoology Building
Teacher Education
Sellery Residence Hall
Witte Residence Hall
Gordon Dining and Event Center
W DAYTON ST
Atmospheric, Oceanic and Space Sciences Building
Charter Street Heating and Cooling Plant
Ogg Residence Hall
Southeast Recreational Facility (SERF)
LaBahn Arena
N PARK ST
N FRANCES ST
N CHARTER ST
SPRING ST
LANGDON ST
LAKELAWN
LINDEN DR
OBSERVATORY DR
LINCOLN DR
Lot 26
Lot 20 Ramp
Lot 22
Lot 5
Lot 44
Lot 45
Lot 54
Lot 87
Lot 91
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A joke fortelling the future?

In February 1979, Pail and Shovel Party leaders Leon Varjian and Jim Mallon constructed Lady Liberty on frozen Lake Mendota, fulfilling a campaign promise to bring wackiness to UW-Madison's Wisconsin Student Association.