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The Atlantis Massif is an oceanic core complex situated on 1.5-Ma-old crust at 30°N on the Mid-Atlantic Ridge. Its domed, corrugated upper surface is interpreted as a major detachment fault. The steep, mass-wasted south wall of the massif provides a window into the architecture of the footwall of this detachment fault and underlying rocks. *Alvin* and *Argo II* were used to collect outcrop-scale geological data in the context of fine-scale bathymetry from ABE surveys. Variably serpentinized peridotite and lesser gabbroic rock form the bulk of the massif. Outcrops below ~1800 m b.s.l. are generally massive, grading upward into a region cut by an array of shear zones, faults, and joints. The uppermost ~50 m of basement rock show a pervasive anastomosing foliation dipping gently west and cropping out for about 3 km. Samples from this interval include mylonitic material wrapping around less deformed phacoids of basement rock. The mylonites are unconformably overlain by a thin (1-3 m) cap of breccia, grading upward into pelagic limestone. The breccia is massive to crudely bedded with both clast- and matrix-supported textures. It includes subangular clasts of basalt and serpentinite in a limestone matrix. Small normal faults offset all of these units and the unconformity. The Lost City Hydrothermal Vent Field sits on top of the breccia unit. We interpret the mylonites as a detachment fault responsible for exhumation of the upper mantle material that forms the core of the massif. The overlying sedimentary rocks represent debris shed onto the detachment fault surface when it defined the median valley wall. As the detachment fault surface moved off axis and flattened into its present orientation, the sedimentary material changed progressively from clastic to pelagic and became consolidated. This assemblage may cover the rest of the Atlantis Massif and occur on other oceanic core complexes.

B12A-0775 1330h POSTER

Long-Lived Serpentinization and Carbonate Precipitation at the Lost City Hydrothermal Vent Field

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The discovery of spectacular, actively venting carbonate chimneys at the Lost City hydrothermal vent field (LCHF) on the Atlantis Massif (MAR 30°N) has stimulated great interest in the role of serpentinization in driving hydrothermal circulation in peridotite-hosted systems and in the biological communities that may be supported in these environments. The top of this fault-bounded, dome-like massif consists of variably deformed, talc-bearing serpentinites and gabbroic rocks (~1.5 Ma), unconformably overlain by polymictic sedimentary breccias and bedded pelagic limestones or chalks that form a flat-lying carbonate cap. The limestones and matrix of the breccias consist of highly indurated foraminiferal sand with a well-preserved sub-tropical fauna, which were at least locally deposited before the last glacial maximum. Calcite and/or aragonite veins are abundant; fractures in the basement are filled by carbonate sediments and lithic fragments. Veining generally pre-dates sedimentary fracture-infilling. The youngest hydrothermal phases include the LCHF chimneys and carbonate precipitates on outcrop surfaces, in cavities, and as growths protruding from fissures that are locally venting fluids. Sr-, C- and O-isotope analyses and radiocarbon age-dating indicate that this system is the integrated effect of tectonic activity, serpentinization, and hydrothermal flow that has lasted at least 30,000 years. C- and O-isotope compositions indicate a range of precipitation temperatures from ambient conditions up to ~250°C at depth and reflect mixing of seawater and serpentinization-derived hydrothermal fluids. Analyses of separated fractions of sedimentary and hydrothermal components define a sedimentary end-member composition of $\delta^{13}C = 1.3 \pm 0.3$ and $\delta^{18}O = 1.5 \pm 0.5$ ‰ (VPDB) and a hydrothermal end-member composition of $\delta^{13}C = 3.3$ and $\delta^{18}O = 5$ ‰. Based on the

present-day degree of serpentinization, the geophysical structure and age of the lithosphere at the Atlantis Massif, and the radiocarbon ages, we estimate a minimum rate of serpentinization of $1.2 \cdot 10^{-4} km^3/y$. Our field observations together with available gravity and seismic data indicate that a considerable proportion of the massif is relatively unaltered peridotite. The access of seawater to relatively cool, fresh peridotite, coupled with faulting, volumetric expansion and mass wasting processes are crucial to sustain such systems. In addition, diffusely percolating, high pH fluids emanating from the underlying serpentinites promote rapid sediment lithification, which offers an efficient mechanism for slowing heat loss and maintaining higher temperatures in the basement. Collectively these processes have the potential to prolong hydrothermal activity for tens of thousands of years.

B12A-0776 1330h POSTER

Chemistry of a serpentinization-controlled hydrothermal system at the Lost City hydrothermal vent field

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The Lost City Hydrothermal Field (LCHF), at 30°N near the Mid-Atlantic Ridge, is an off-axis, low temperature, high-pH, ultramafic-hosted vent system. Within the field, carbonate chimneys tower up to 60 m above the seafloor, making them the tallest vent structures known. The chemistry of the vent structures and fluids at the LCHF is controlled by reactions between seawater and ultramafic rocks beneath the Atlantis Massif. Mixing of warm alkaline vent fluids with seawater causes precipitation of calcium carbonate and growth of the edifices, which range from tall, graceful pinnacles to fragile flanges and colloform deposits. Geochemical and petrological analyses of the carbonate rocks reveal distinct differences between the active and extinct structures. Actively venting chimneys and flanges are extremely porous, friable formations composed predominantly of aragonite and brucite. These structures provide important niches for well-developed microbial communities that thrive on and within the chimney walls. Some of the active chimneys may also contain the mineral ikaite, an unstable, hydrated form of calcium carbonate. TIMS and ICP-MS analyses of the carbonate chimneys show that the most active chimneys have low Sr isotope values and that they are low in trace metals (e.g., Mn, Ti, Pb). Active structures emit high-pH, low-Mg fluids at 40-90°C. The fluids also have low Sr values, indicating circulation of hydrothermal solutions through the serpentinite bedrock beneath the field. In contrast to the active structures, extinct chimneys are less porous, are well lithified, and they are composed predominantly of calcite that yields Sr isotope values near seawater values. Prolonged lower temperature seawater-hydrothermal fluid interaction within the chimneys results in the conversion of aragonite to calcite and in the enrichment of some trace metals (e.g., Mn, Ti, Co, Zn). It also promotes the incorporation of foraminifera within the outer, cemented walls of the carbonate structures. The Lost City system represents a novel natural laboratory for observing hydrothermal and biological activity in a system controlled by moderate temperature serpentinization reactions. The LCHF is the only vent field of its kind known to date; however, it is likely not unique along the global mid-ocean ridge spreading network.

URL: <http://www.lostcity.washington.edu>

B12A-0777 1330h POSTER

Serpentinization and Heat Generation at Slow Spreading Ridges

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The discovery of ultramafic hosted hydrothermal systems at Rainbow on the Mid Atlantic Ridge and Lost City, a vent site approximately 15km west of the MAR, provides unique perspectives on chemical and heat generating processes associated with serpentinization at a range of chemical and physical conditions. Vent fluid chemistry associated with alteration of ultramafic rocks at an axial and an off axis site on the MAR provides important constraints on heat and mass transport in subseafloor reaction zones. Low pH, high temperature fluids issuing from vents at the Rainbow site indicate slow rates of olivine hydrolysis and the near proximity of an intermittent magmatic heat source, which is needed to account for the high temperatures and flow rates observed at this site. Based on geochemical constraints, the Lost City vent fluids suggest higher temperatures than actually measured at vents. Therefore, the relatively low measured temperature of the Lost City vent fluid, likely reflects the effects of conductive cooling during transit from the site of alteration to the seafloor. Heat balance models suggest that heat production during serpentinization is ineffective, especially at relatively low and high temperatures due to kinetic constraints. Even at intermediate temperatures, however, where the olivine to serpentine conversion rate is more rapid, relatively low fluid to rock mass ratios are needed for exothermic heat generation to have even a minor influence on alteration temperature. Vent fluid chemistry reported for Lost City, however, suggests relatively high fluid to rock mass ratios as indicated by near seawater concentrations of dissolved Cl, K and Na. Although it can be argued that Cl is taken up during alteration in amounts that exactly balance hydration effects, the same would have to be true of K and Na, which is an unlikely scenario. The combination of vent fluid chemistry and heat balance models indicate that Lost City vent fluids may be associated with tectonically driven circulation where long lived faults allow fluid to access deep crustal sections at relatively high temperatures. Alternatively, vent fluids at Lost City may be produced by off axis gabbroic intrusions or near axis locations where magmatic heat sources are available and then transported to the current off axis location.

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B12B MCC: Level 2 Monday 1330h

Impacts of Biomineralization on Earth Environments I Posters (joint with A, OS, PP, V, GC, MR)

Presiding: L Wasylenko, Virginia

Polytechnic Institute and State

University; P Dove, Virginia

Polytechnic Institute and State

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B12B-0778 1330h POSTER

Microbial Biosignatures in High Iron Thermal Springs

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The emerging anoxic source waters at Chocolate Pots hot springs in Yellowstone National Park contain 2.6 to 11.2 mg/L Fe(II) and are 51-54°C and pH 5.5-6.0. These waters flow down the accumulating iron deposits and over three major phototrophic mat communities: *Synechococcus/Chloroflexus* at 51-54°C, *Pseudanabaena* at 51-54°C, and a narrow *Oscillatoria* at 36-45°C. We are assessing the contribution of the phototrophs to biosignature formation in this high iron system. These biosignatures can be used to assess the biological contribution to ancient iron deposits on Earth (e.g. Precambrian Banded Iron Formations) and, potentially, to those found on Mars. Most studies to date have focused on chemotrophic iron-oxidizing communities; however, recent research has demonstrated that phototrophs have a significant physiological impact on these iron thermal springs (Pierson et al. 1999, Pierson and Parenteau 2000, and Trouwborst et al., 2003).

We completed a survey of the microfossils, biominerals, biofabrics, and lipid biomarkers in the phototrophic mats and stromatolitic iron deposits using scanning and transmission electron microscopy (SEM and TEM), energy dispersive spectrometry (EDS), powder X-ray diffraction (XRD), and gas chromatography-mass spectrometry (GC-MS). The *Synechococcus/Chloroflexus* mat was heavily encrusted with iron silicates while the narrow *Oscillatoria* mat was encrusted primarily with iron oxides. Encrustation of the cells increased with depth in the mats. Amorphous 2-line ferrihydrite is the primary precipitate in the spring and the only iron oxide mineral associated with the mats. Goethite, hematite, and siderite were detected in dry sediment samples on the face of the main iron deposit. Analysis of polar lipid fatty acid methyl esters (FAME) generated a suite of lipid biomarkers. The *Synechococcus/Chloroflexus* mat contained two mono-unsaturated isomers of n-C_{18:1} with smaller amounts of polyunsaturated n-C_{18:2}, characteristic of cyanobacteria. The mat also contained abundant n,n-wax esters of C₃₂ to C₃₇, characteristic of *Chloroflexus*. 10-Methyl-C₁₆ was also detected, indicative of sulfate reducing bacteria (SRB). The narrow *Oscillatoria* mat was dominated by the aforementioned cyanobacterial biomarkers as well as iso-C_{17:1}, a biomarker for some groups of SRB. Unusual dimethyl fatty acids were also detected. The goal of this research is to provide an initial dataset that will illustrate the maximum amount of paleobiological and paleoenvironmental information expected to form in these types of iron deposits. Insights from our research may help elucidate the role of phototrophs in the deposition of BIFs on Earth, and may assist in the search for evidence of fossilized microbial life in iron deposits on Mars. Pierson, B.K., M.N. Parenteau, and B.M. Griffin, Phototrophs in high-iron-concentration microbial mats: Ecology of phototrophs in an iron-depositing hot spring, *Appl. Environ. Microbiol.*, 65, 5474-5483, 1999. Pierson, B.K., and M.N. Parenteau, Phototrophs in high iron microbial mats: Microstructure of mats in iron-depositing hot springs, *FEMS Microbiology Ecology* 32, 181-196, 2000. Trouwborst, R., G. Koch, G. Luther, and B.K. Pierson, Photosynthesis and iron in hot spring microbial mats (abstract), NAI General Meeting, *Astrobiology* 2(4), 206, 2003.

B12B-0779 1330h POSTER

The MICROBE (Microcosm Investigation of Carbonate Reef/Ocean Microbial Biogeochemistry & Ecology) Project

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We present a methodology to manipulate carbonate reef sediments in order to study the geochemical and microbiological response of reef systems to perturbations. We specifically plan to study the effects of changes in the atmospheric partial pressure of CO₂. Our laboratory set-up will consist of cores containing carbonate reef sediments and overlying water. These microcosms are designed to replicate the gross hydraulic and geochemical characteristics of sediments in a natural tropical reef patch. This is achieved by reproducing the advective transport of water and particulates in and out of the sediments induced by tides and surface waves. Seawater from nearby reefs is to be introduced into the cores with reversible peristaltic pumps. The pumps will vary the overlying water column and simulate the changes in hydrostatic head that accompany waves and tides. The parameters characterizing these oscillations will be set at values reflecting those at nearby natural settings. Sediment column characteristics will be determined non-destructively through openings at various depths down the sediment cores. These openings are fitted with rubber septa and shut-off valves, which allow gas-tight sampling of porewaters. An additional set of openings allows for the removal of small amounts of sediments using augers. Our porewater analyses will include dissolved O₂, CO₂, CH₄ and alkalinity, ammonium, sulfide, and iron and manganese ions. Our solid phase analyses will include carbonate composition and framework structure, and iron and manganese abundances in the carbonate phases. We will measure microbial abundance in porewater and the sediment particles by DAPI cell counts and will assay community composition using Denaturing Gradient Gel Electrophoresis (DGGE). Our goal is to use this methodology to observe and record carbonate precipitation and dissolution by microbiota under varying carbon dioxide regimes. pCO₂ concentrations will be manipulated by bubbling a N₂/CO₂ mixture through the overlying water column and will be regulated by a CO₂ detector connected to the column's

head space. Settings will reflect a range of concentrations between pre-industrial (280 ppmv) and predicted future (700 ppmv) levels. Analyses and observations in microcosms exposed to different carbon dioxide levels will be crucial in elucidating the impact of the ongoing carbon dioxide increase in the atmosphere on carbonate dissolution and precipitation in coral reef sediments during early diagenesis. Our prediction is that increased pCO₂ will lead to a decreased efficiency of recycling of organic matter and nutrients in a reef, lower productivity and, potentially, attenuated reef biodiversity.

B12B-0780 1330h POSTER

Influence of Mn Ion on the Iron Biomineralization by an Iron-reducing Bacterium

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Manganese ion is known to be easily sorbed to iron oxide surface or co-precipitated into iron oxides structure, but the effect of manganese ion on iron biomineralization is not sufficiently understood. The objectives of this study were to examine the influence of Mn substitution and sorption on iron biomineralization and to identify biogeochemical factors determining phase distribution of Mn ion during iron biomineralization. The reductive biomineralization of Mn-substituted (Fe_{1-x}Mn_xOOH) or Mn-sorbed (FeOOH plus MnCl₂) akaganite by an iron-reducing bacterium (*Shewanella* alga, PV-4) was investigated under anaerobic conditions at circumneutral pH (pH = 7 - 8) and at 25 deg.C. The influence of Mn ion on the iron biomineralization was explored along with effects of bicarbonate (30 - 210 mM) on biomineralization using lactate (10 mM) as an electron donor. No exogenous electron carrier substance (i.e., anthraquinone disulfonate) or reducing agent (i.e., cysteine) was added to the anaerobic medium. Solid phases and aqueous chemistry were characterized after incubations with both of the iron-reducing bacterium and Mn-substituted or Mn-sorbed akaganite for 30 days. The iron reducing bacterium, *S. alga*, mainly formed siderite (FeCO₃), green rust [Fe₂+Fe₃+(OH)₁₆CO₃·4H₂O], and magnetite (Fe₃O₄) using Mn-substituted akaganite, while rhodochrosite (MnCO₃), siderite, and magnetite were dominant phases using Mn-sorbed akaganite in the bicarbonate buffered medium. Scanning electron microscopy and transmission electron microscopy with energy dispersive X-ray analysis of iron minerals formed by *S. alga* showed that Mn was preferentially concentrated in the siderite and green rust. This research indicates that microorganisms may affect the cyclings of Fe, Mn and C and the fate of metal contaminants in subsurface environments.

B12B-0781 1330h POSTER

Modeling Zinc Isotope Fractionations

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In this study quantum mechanical models are used to estimate equilibrium zinc-isotope fractionations between zinc oxide and sulfide minerals, as well as aqueous complexes. A major goal in stable isotope geochemistry and biogeochemistry is the determination of equilibrium fractionations between different phases present in typical geochemical systems. The search for reliable biosignatures, in particular, will rely on careful studies contrasting biological fractionation processes, abiological kinetic fractionations, and equilibrium isotope effects. For many stable isotope systems, however, the determination of equilibrium fractionations is hampered by the difficulty of achieving isotopic equilibrium in a reasonable laboratory timescale, particularly at the low temperatures relevant to biogeochemistry. The equilibrium stable isotope geochemistry of heavy, biologically important elements like zinc and iron is particularly poorly known, because accurate measurements of their isotopic compositions have only recently become possible. Theoretical estimates of equilibrium stable isotope fractionations can provide a useful framework for understanding natural fractionation processes, and for extrapolating sparse experimental results to lower temperatures. Equilibrium stable isotope fractionations are mainly caused by isotopic effects on vibrational energies, so it is necessary to measure or model

isotopic effects on vibrational frequencies before fractionations can be estimated. Quantum mechanical modeling using density functional theory (DFT) is a powerful technique for determining unknown properties of minerals, molecules, and aqueous complexes. Here DFT is used to estimate vibrational frequencies and zinc-isotope (⁶⁸Zn/⁶⁶Zn) fractionations in isotopically substituted ZnO (zincite) and two polymorphs of ZnS (sphalerite and wurtzite), as well as aqueous complexes like [Zn(H₂O)₆]²⁺ and [ZnCl₄]²⁻. The results predict that sulfide minerals will have lower ⁶⁸Zn/⁶⁶Zn ratios than coexisting ZnO, by 10⁰/00 at room temperature, while fractionations between coexisting wurtzite and sphalerite are very small. ⁶⁸Zn/⁶⁶Zn in aqueous [Zn(H₂O)₆]²⁺ will be intermediate between ZnO and sulfides, while [ZnCl₄]²⁻ is similar to sulfides. A general depletion of heavy isotopes in sulfides equilibrated with oxide minerals and aqueous solutions is consistent with Fe-isotope measurements of pyrite in banded iron formations (Johnson et al., 2003, Contrib. Mineral. Petrol., v. 144, p. 523-547). The geochemistries of stable zinc, chromium, and iron isotope fractionations are in qualitative agreement, and suggest 1) that chloro-complexes will tend to concentrate the light isotopes of metallic elements, and 2) that complexes and minerals with 4-fold metal ion coordination (i.e., ZnO-zincite, [FeCl₄]⁻) will tend to concentrate heavy isotopes relative to analogous materials with 6-fold coordination ([Zn(H₂O)₆]²⁺, [FeCl₆]³⁻).

B12B-0782 1330h POSTER

Ground-Truthing the Boron Isotope - Paleo-pH Proxy in Planktonic Foraminifera Shells: Partial Dissolution and Shell Size Effects

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Empirical calibration studies have shown that seawater pH controls the boron isotope composition ($\delta^{11}\text{B}$) of planktonic foraminifera shells. First applications of this new tool revealed promising parallels between reconstructed surface seawater pH and past pCO₂ levels as measured in ice cores. However, little attention has been paid to secondary parameters that might affect the $\delta^{11}\text{B}$ -pH record of marine calcium carbonate. Here we investigate $\delta^{11}\text{B}$ of different size fractions of the symbiont-bearing planktonic foraminifer *Globigerinoides sacculifer*, ranging from 250 to 865 μm in shell diameter. Sediment samples from the Ontong Java Plateau in the Pacific and the 90° East Ridge in the Indian Ocean reveal a systematic size pattern with up to +2.4‰ heavier $\delta^{11}\text{B}$ values in larger individuals. This pattern is most likely due to differences in symbiont photosynthetic activity and its integrated effect on the pH of the foraminiferal microenvironment. Smaller individuals must either live deeper in the water column where light intensities are lower or the symbiont density in smaller individuals is lower as compared to large specimens. Sediment samples from different water depths were studied to investigate dissolution effects on foraminiferal $\delta^{11}\text{B}$ by looking at shell weight. Because *in situ* dissolution studies have shown that smaller individuals of a certain foraminifera species are more susceptible to dissolution than larger ones, we expected partial shell dissolution to have a more significant affect on the chemical composition of smaller foraminifera shells relative to larger shells. Between sediment cores of various depths we observe decreases in $\delta^{11}\text{B}$ on the order of -0.7 to -1.6‰ that are associated with lower shell weights. Analyses of Mg/Ca ratios and shell surface microstructure will test our interpretation of the shell size and depth transect $\delta^{11}\text{B}$ data.

B12B-0783 1330h POSTER

Climate Change and Planktic Foraminiferal size Evolution

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Planktic foraminifers are a major producer for pelagic carbonate since the late Cretaceous. The production of foraminiferal carbonate is related to the size, shape, and distribution of individual species. We have analysed size and shape of planktic foraminifers in relation to global environmental changes during the Neogene. Morphological changes may be a response to either geographical or temporal environmental changes. Alternatively, species might avoid climatic stress by shifting their distribution area. We have analysed the morphological response on two different time-scales (entire Neogene, late Quaternary) and at two taxonomic levels (species, family). On short time-scales (140 kys) Globorotalia truncatulinoides at three different locations in the South Atlantic had stable environmental preferences and reacted to the climatic changes by habitat tracking. This process of habitat tracking allows a species continued exploitation of its ecological niche despite environmental changes. During the Neogene, in contrast, a growth to gigantism from mid-Miocene to Recent was identified in tropical and subtropical foraminiferal assemblages, whereas in polar areas the size of foraminifers stayed rather stable over the entire time interval. The higher calcification rates leading to larger final size may have resulted in an increased export production of inorganic carbonates to the sea floor. The dominant environmental change throughout the Neogene is high latitude cooling. Despite the ecological and physiological evidence for a positive correlation of planktic foraminiferal test size with temperature today, we identify a more intricate mechanism of environmental forcing of foraminiferal size evolution in the geological record. We can demonstrate, that changes in surface water stratification, rather than temperature per se, had likely determined growth rates and test sizes of planktic foraminifers. Increases in size have occurred during times of strong vertical water stratification in low latitudes during polar cooling phases. Vertical surface water heterogeneity increases the number of ecological niches and thus allows for specific adaptations and, evidently, growth towards larger size. The onset of the dramatic size increase in planktic foraminifers falls within the Monterey event, a rapid extraction of carbon from the Ocean-Atmosphere system through a massive deposition of organic carbon. Whether these two events are related and have a common cause is highly speculative at the moment, but it appears that global climatic changes certainly have influenced growth of planktic foraminifer tests and therefore carbonate deposition.

B12B-0784 1330h POSTER

Where In The Coral Is The Magnesium (and other trace elements) ?

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Coral record information on reef health, historical ocean temperatures, flood events, and global climate change. In the scientific literature, time-series geochemical analyses of coral data (stable isotopes, trace elements, rare earth elements) have been based on sampling intervals greater than 1 millimeter. Within the last decade, new technologies have emerged that allow collection of time-series geochemical data on a micrometer scale. The laser ablation ICP/MS is an instrument that analyzes solid samples on a micrometer scale and simultaneously measures numerous trace elements. Using laser ablation ICP/MS in conjunction with the Scanning Electron Microscope (SEM) we have examined the sites and potential problems of geochemical sampling within the coral skeletal structure. Spot sampling (50 micrometer sampling size (spot size) with 85 micrometer spacing between samples) was conducted on parallel, longitudinal endothelial, exothelial and coralite wall structures. The locations were chosen based on SEM mosaic images of Montastrea faveolata. The analysis revealed values and intervals of data for trace elements including Mg, Al, Ba, Cu, and U that varied downcore between the three separate coral structures. Depth (age) intervals that showed an abundance of Mg (and other elements) within the exothelial area may be absent or substantially lower in either or both the endothelial and wall areas within the same intervals and vice versa. In addition, some areas that exhibit particularly high Mg peaks can be correlated with the location of hexagonal crystals identified with the SEM. These crystals are forming adjacent to "normal" acicular aragonite crystals, but have only been found within the exothelial areas of the coral. These results suggest that biomineralization of aragonite and the existence and location of trace elements within the skeleton are controlled separately by: 1) the coral polyp that lives in the endothelial portion of the skeleton, 2) the colonial tissue within the exothelial portion of the skeleton, and 3) the wall that separates these two areas. The micro-architecture of these three areas also differs and may

explain the variations of trace element amounts found at different depths. It is well known that corals allow insight to the historical record of our oceans and global climate, however, this study shows that care must be taken to during sampling to ensure consistent data reporting

B12B-0785 1330h POSTER

Sr/Ca and Mg/Ca in Aragonitic Bivalves: Do They Record Temperature?

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The chemical or isotopic composition of calcareous skeletons have long been recognized as archives of past and present environmental conditions. Oxygen isotopes ($\delta^{18}O$) of biogenic carbonates are a powerful proxy of SST, however, although usually dominated by SST, salinity (SSS) also significantly effects the oxygen isotopic signal recorded in the carbonate. This has led researchers to explore new proxies, which are independent of SSS. Generally, Sr/Ca and Mg/Ca of seawater remains unchanged above salinities of 10 and marine animals will commonly live in habitats that do not fluctuate below this salinity. To solve the issue of SSS complicating paleotemperature records, these "new" proxies must be at least as reliable as $\delta^{18}O$. If an environmental control is dominant, the proxies should be reproducible between specimens growing under the same field conditions. Both Sr and Mg have been used as paleotemperature proxies in corals and foraminifera, whereas a fewer attempts have been made to use these proxies in bivalves. Some report a clear seasonal periodicity in Sr/Ca profiles of bivalves, which covaries with $\delta^{18}O$ (i.e., temperature), whereas others have found no clear periodicity. We test the robustness of these proxies by analyzing the shell material from three species of aragonitic clams from around the world using a LA-ICP-MS. Three individuals of *M. mercenaria* from North Carolina, USA, three individuals of *Saxidomus giganteus* from Washington, USA and one Arctic *islandica* from Norway have been analyzed. As expected, there is excellent reproducibility of $\delta^{18}O$ between specimens (both *M. mercenaria* and *S. giganteus*) indicating external environmental conditions control this proxy (i.e. SST and SSS). Preliminary data analysis show that Sr and Mg are not reproducible between specimens from the same site nor do they exhibit a clear seasonal cyclicity, indicating individual metabolic effects (i.e., vital effects) dominate the incorporation of these elements. *A. islandica* on the other hand, also does not have an easily discernable periodicity in the Sr signal, but Mg does seem to be more in sync with $\delta^{18}O$. Also, both Sr and Mg are higher in the more recently formed shell section (when the clam is older) indicating that this may be due to the ontogenetic change in physiology and hence, again, suggests a physiological control on the incorporation of both these elements. If there is an effect of temperature on the incorporation of these elements in these three species, the signal is masked by the larger signal produced by vital effects.

B12B-0786 1330h POSTER

Trace Elements in Diatom Frustules as a Paleoclimatic Proxy

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The calibration in modern environments of the different proxies used in any paleoenvironmental study is a critical aspect leading to more realistic reconstructions of past conditions. Diatoms are among the main contributors to phytoplankton blooms in both lakes and oceans. They have been widely used as ecological and biogeochemical indicators of present and former

environmental conditions. During the formation of highly ornamented cell walls or frustules, these algae take up dissolved silicic acid from the water to precipitate it as opaline silica that is further preserved in the sediments. Recent investigations have shown that diatoms can also incorporate trace elements in the opal. The causes and mechanisms of this incorporation, however, remain elusive. Thus, understanding the processes leading and regulating the uptake of different trace elements by diatoms will potentially furnish a new proxy for past water conditions. This indicator would be independent of the mobility of the elements and/or of diagenetic effects within the sediments. We tested the potential of this approach by determining the elemental composition of recent diatom frustules from Lake Geneva (Switzerland). The studied samples were further placed in a well defined chronological framework and compared with the most recent environmental history of the lake. Our preliminary results imply that the incorporation of different trace elements into the frustule has substantially changed throughout the studied time interval. A similar trend characterizes most of the analyzed metals (Al, Ca, Ti, V, Cr, Mn, Fe, Ga, Rb, Sr, Ba, Pb) with comparatively higher concentrations for the last half of the twentieth century. Some other elements such as Sc seems to follow a rather opposite trend whereas Zn concentrations show a more scatter distribution. The calibration of these results with the well-known environmental history of Lake Geneva and its catchment area will allow us to evaluate the use of this technique as proxy for former environmental conditions. Furthermore, the combination of ongoing laboratory and field studies will provide crucial information concerning the interaction of known concentrations of dissolved trace elements in the water and diatoms, as well as the mechanism leading to their incorporation in the frustule.

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B12C MCC: Level 2 Monday 1330h

Biomineralization Processes and Mechanisms I Posters (joint with H, OS, V, MR)

Presiding: L Wasylenki, Virginia Polytechnic Institute and State University; S Weiner, Weizmann Institute of Science

B12C-0787 1330h POSTER

Sulfated Macromolecules as Templates for Calcite Nucleation and Growth

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Mineralization of egg and seashells is controlled by an intimate association of inorganic materials with organic macromolecules. Among them, particular polyanionic sulfated macromolecules referred to as proteoglycans have been described to be involved in the calcification of these biominerals. The sulfated moieties of the proteoglycans are part of polymer chains constituted of building-blocks of disaccharide units, referred to as sulfated glycosaminoglycans (GAGs), which are covalently attached to a protein core. By using a sitting drop crystallization assay under controlled conditions of time, pH and reactants concentration, we have tested several sulfated and non-sulfated GAGs (i.e.: dermatan and keratan sulfate, hyaluronic acid and heparin), differing in their sulfonate and carboxylate degree and pattern, in their ability to modify calcium carbonate crystal morphology as observed under scanning electron microscopy. Without the addition of GAGs, regular {104} rhombohedral calcite crystals were obtained. When hyaluronic acid (HA), a non-sulfated but carboxylated GAG, was added, 20 nm long piles of unmodified calcite crystals were observed. When desulfated dermatan, which is an epimeric form of HA but shorter polymer, having their carboxylate groups in an inverted configuration, was added, isolated rhombohedral {104} calcite crystals showing rounded corners with planes oriented parallel to the c axis were observed. When dermatan sulfated was added, isolated calcite crystals exhibit a columnar morphology as a {hk0} cylinder with three {104} faces forming a cap at both ends. Heparin activity depends on the fraction added. Fast-moving heparin fraction (FM), is an undersulfated, low-molecular-weight heterogeneous polymer, while slow-moving heparin fraction (SM) is a high-molecular-weight homogeneous