

molecular modeling and biomimetic synthesis, allowed us to probe the determinants of catalytic activity and confirm the identification of the amino acid sidechains required for hydrolysis of the silicon alkoxides. If, as suggested by the data of others, silicic acid is conjugated with organic moieties after its transport into the cell, the catalytic mechanism described here may be important in biosilicification by sponges.

As is often the case, we have been better able to answer mechanistic questions about "how" silica can be formed biologically, than "why" the diversity of structures is elaborated. Studies of spicule formation during cellular regeneration in *Tethya aurantia* reveal that synthesis of the larger silica needles (megascleres) and smaller starburst-shaped microscleres may be independently regulated, presumably at the genetic level. The spatial segregation of these morphologically-distinct spicule types within the sponge further suggests an adaptive significance of the different skeletal elements.

#### B21C-03 1050h INVITED

##### Stable Isotopic Signatures of Microbially Formed Carbonates and Metal Oxides: Temperature Proxies for Biomineralization in Low Temperature Sedimentary Environments

Chuanlun L Zhang (573 884-2677; zhangcl@missouri.edu)

Univ. Missouri, Dept. Geol. Sci., Columbia, MO 65211, United States

Microorganisms exist and mediate geochemical processes in almost all low-temperature sedimentary environments. A variety of authigenic minerals can be formed directly or indirectly by microbial activities. Carbon and oxygen isotopic compositions of these minerals may indicate depositional temperatures at the time of mineral precipitation. A review of isotopic fractionations associated with biogenic magnetite and siderite will be provided. These biogenic minerals show temperature-dependent carbon and oxygen isotopic fractionations under laboratory conditions. However, the temperature-dependent fractionations can be complicated by variation in solution chemistry. An understanding of microbial activity, solution chemistry, mineralogy, and isotope biogeochemistry at the systems level should provide better insight into the mechanisms for biogenic mineral formation in natural environments.

URL: <http://web.missouri.edu/~geoscsc/research.html>

#### B21C-04 1105h INVITED

##### Mg and Sr Incorporation in Foraminifer Shells: Patterns, Controls and Applications.

David W Lea (805-893-8665; lea@geol.ucsb.edu)

University of California, Department of Geological Sciences, Santa Barbara, CA 93106, United States

The incorporation of Mg and Sr in planktonic and benthic foraminifer shells is important for paleoceanographic research because of the potential to record physical and chemical changes in the oceanic environment. Pelagic shells are 99%+ CaCO<sub>3</sub>, and abundances of Mg and Sr are typically ~0.1%, requiring sensitive quantification methods such as ICP-MS or AES.

Mg/Ca values range from 0.5 mmol/mol in cold planktics and benthics to ~5 mmol/mol in tropical planktics, with some species (*Orbulina universa*) having even higher values. The main control on Mg incorporation is temperature, but pH and salinity also exert small influences, presumably through calcification rate. The Mg/Ca content of the primary ontogenetic calcite can be altered by the addition of so-called gametogenic calcite, generally deposited in deep, colder waters. After deposition on the seafloor, dissolution becomes the main influence, with progressively lower Mg/Ca values in more dissolved samples. This loss appears to occur by preferential loss of the more Mg-rich portions of the shell, although the details remain unexplained.

Sr/Ca values range from 0.9 in some benthic species (*Uvigerina* spp.) to 1.6 mmol/mol in some planktics. Culturing results suggest that temperature, salinity and pH all exert a weak control (i.e., 1% per °C) on shell Sr, presumably through a kinetic effect. The main control appears to be related to environmental differences. For example, comparison of Sr/Ca in *Neoglobobulimina pachyderma* from plankton tows and cultures with core-top specimens indicates that the latter have significantly higher values, presumably due to deep crusting, perhaps added with a much higher calcification rate. This observation clearly demonstrates that Sr/Ca is not simply related to a single physical parameter such as temperature.

Downcore records of shell Mg/Ca and Sr/Ca reveal substantial variability that can be correlated with known paleoceanographic change. For Mg/Ca, observed variations can largely be explained by climate-related variations in temperature. For Sr/Ca, it appears that observed variations related to secular

changes in seawater Sr/Ca, but this cannot be fully substantiated without a more complete understanding of primary and post-depositional controls on shell composition.

URL: <http://www.geol.ucsb.edu/~lea/>

#### B21C-05 1120h INVITED

##### Application of Foraminiferal Calcium Carbonate Chemistry to Proxy Past Ocean Conditions: key roles of Biomineral Formation and Dissolution

Henry Elderfield<sup>1</sup> (44-1223-333406;

he101@esc.cam.ac.uk); Stephen Barker; Sally Birse; Stephanie de Villiers; Mervyn Greaves; Pallavi Jha

<sup>1</sup>University of Cambridge, Department of Earth Sciences, Downing Street, Cambridge CB2 3EQ, United Kingdom

The use of the shell chemistry of foraminiferal calcite and aragonite for seawater paleothermometry and paleochemistry rests on confidence in the calibrations established to link metal uptake or isotope fractionation by the marine biogenic calcium carbonate to modern seawater composition. The early pioneering work in this field led to a period of application, principally of the establishment and expansion of stable oxygen and carbon isotope studies. But new work on trace metals in foraminifera has led to an upsurge of interest in, and reappraisal of, what controls metal uptake and the extent to which foraminifera do a good job in recording and revealing the oceans secrets. Two issues are considered: (i) understanding how secretion by the organism takes place and the chemical consequences; (ii) how dissolution changes the initial chemistry. The early work on ultrastructure shows that different, often progressive, layers are formed ranging from anhedral microgranules to euhedral crystallites; and that there is sequential and preferential dissolution of the different textural forms. This forms some basis for understanding, for example, the heterogeneity in foraminiferal Mg/Ca and how this is affected by dissolution. In general, warmer species (higher Mg/Ca) show greatest 104 line broadening and depth (or carbonate ion) related dissolution is accompanied by a decrease both in Mg/Ca and line broadening. Variation in calcification rate has been linked to changes in carbon isotope and Sr/Ca, perhaps through a carbonate ion effect. This is also seen from size fraction data. There is also variability in shell mass both from initial calcification history and from dissolution, and both affect shell chemistry. Shell mass is also associated with changes in normalised size and accompanied by chemical changes. One clear effect of Mg heterogeneity is in its effect on calibrations for thermometry and the extent to which phase differences between temperature (dissolution-corrected Mg/Ca) and ice volume (temperature-corrected oxygen isotopes) can be defined. Most paleoceanographic proxies are complex and are affected by primary and secondary factors which is why multi-proxy approaches are increasingly used. Understanding why and how foraminifera incorporate trace elements through biological mineralization will help aid expansion of this important field.

#### B21C-06 1135h INVITED

##### Understanding the Molecular-Scale Processes of Biomineralization: The Role of Mg<sup>2+</sup> and Sr<sup>2+</sup> in Calcite Growth

Kevin J Davis<sup>1</sup> (540-231-8074; kdavis2@vt.edu)

Patricia M Dove<sup>1</sup> (540-231-2444; dove@vt.edu)

James J De Yoreo<sup>2</sup> (925-423-4240; deyoreo1@lnl.gov)

<sup>1</sup>Dept. of Geological Sciences Virginia Tech, 4044 Derrig Hall, Blacksburg, VA 24061, United States

<sup>2</sup>Dept. of Chemistry and Materials Science Lawrence Livermore National Laboratory, L-350 7000 East Avenue, Livermore, CA 94550, United States

Determining the precise role that common inorganic species assume during the complex processes of biomineralization is central to understanding biomineralization strategies and for the unambiguous use of biogenic minerals as paleoclimate indicators. Inorganic impurities influence the solubility, reactivity, and polymorphic expression of biogenic carbonates leading to a dynamic relationship between the evolution of biomineralizing organisms and the long-term chemistry of the worlds oceans. Biological control over the minor and trace element contents of skeletal materials is therefore a fundamental aspect of the strategies employed by organisms to govern mineral formation. These vital effects, however, impact the use of biogenic minerals as tools for understanding past climates. Resolving the chemical and physical factors that control trace element incorporation during calcite mineralization is critical

to providing the inorganic baseline needed for assessing both paleoclimate signals and biological processes. It is now possible to determine the fundamental thermodynamic and kinetic parameters of calcite growth by making direct quantitative measurements of the microscopic processes occurring at the mineral-water interface. These molecular-scale observations are often able to provide crucial information concerning the actual mechanisms of growth that is otherwise unobtainable through macroscopic techniques.

Here we use in situ fluid-cell atomic force microscopy (AFM) to achieve a physical understanding of the role of magnesium and strontium in governing calcite formation. Despite the biogeochemical importance of this system, macroscopic studies have been unable to discern the actual mechanism by which Mg<sup>2+</sup> mediates calcite growth and morphology. AFM was used to resolve the controversial mechanism of calcite inhibition by magnesium through molecular-scale determination of the thermodynamic and kinetic controls of Mg<sup>2+</sup> on calcite morphology and growth. Comparison of directly observed monomolecular step velocities to standard crystal growth impurity models demonstrated that calcite growth inhibition was due to enhanced mineral solubility through Mg<sup>2+</sup> incorporation. Terrace width measurements on calcite growth spirals confirmed that magnesium thermodynamically inhibits calcite growth by independently demonstrating decreased effective supersaturations in the presence of magnesium.

In contrast, the addition of strontium as an impurity in the growth system caused measured step velocities to decrease by a mechanism that corresponds to the step-pinning model of impurity inhibition. Therefore strontium provides a kinetic barrier to calcite growth by physically blocking the migration of monomolecular steps. The results of this study indicate that impurity size and ability to form solid solutions that are isomorphous with the host crystal play a major role in determining the specific mechanism of inhibition of biogenic calcite crystals. Further, these fundamental empirical observations may explain why Mg/Ca ratios have proved to be a more reliable paleothermometer than Sr/Ca ratios in biogenic calcite.

#### B21D MC: 122 Tuesday 1030h

##### Geomicrobiology and Biogeochemistry of Gas Hydrate Systems II (joint with A, OS)

Presiding: C Zhang, University of Missouri; B D Lanoil, Univ of California

#### B21D-01 1030h

##### Scanning Electron Microscopic Investigations on Natural and Synthetic Gas Hydrates: New Insights into the Formation Process

Kirsten S Techmer<sup>1</sup> (49/551/393931; ktechme1@gwdg.de)

Werner F Kuhs<sup>1</sup> (49/551/393891; wf.kuhs@geo.uni-goettingen.de)

Till Heinrichs<sup>2</sup> (theinri@gwdg.de)

Gerhard Bohrmann<sup>3</sup> (gbohrmann@geomar.de)

<sup>1</sup>Geozentrum, Abt. Kristallographie, Goldschmidtstr.1, Goettingen 37077, Germany

<sup>2</sup>Geozentrum, Abt. Angewandte Geologie, Goldschmidtstrasse 3, Goettingen 37077, Germany

<sup>3</sup>GEOMAR Research Center, Wischhofstr. 1-3, Kiel 241148, Germany

We present results of field-emission scanning electron microscopic investigations of gas hydrates from shallow marine sediments of Cascadia margin as well as from synthesis experiments. The natural hydrates were taken by TV-grab sampling during the TECFLUX project on RV SONNE cruises, SO143 and SO148 on the southern summit of Hydrate Ridge. The samples are dominantly methane hydrates with a low content of H<sub>2</sub>S (1.5-3.0 vol%). The hydrates develop as pure white ice-like layers in otherwise soft sediment deposits. The synthetic gas hydrates were prepared from pure CH<sub>4</sub> gas at variable pressure and temperature including experimental conditions similar to the natural situation. All synthetic hydrates show a porous microstructure with pore diameters of a few hundred nm (see figure) and grain sizes of a few μm[1]. Samples were transferred to a pre-cooled cryo-stage field-emission scanning electron microscope via an interlock. No decomposition was observed during our work, which was carried out below -165° C in a vacuum of <10<sup>-5</sup> mbar by using an electron beam of 1.0-1.5 keV. The microscope is connected with an energy-dispersive X-ray spectrographic analyzer, which can clearly identify methane in the clathrate structure by detecting the carbon peak in the elemental spectrum.

The microstructures of the natural gas hydrates vary greatly with the magnification. In general, large pores between a few to hundreds of  $\mu\text{m}$  in diameter are observed, and these have been also documented in thin sections. These pores are interpreted to originate from gas bubbles that ascend from deeper in the sediment. The pores develop in the pore water as skins of hydrate around the former gas bubbles. We investigated the inner part of the former bubble walls by FE-SEM and could document tiny filaments that often form a network of honeycomb-like structures. EDX-analyses show that these filaments have Cl-peaks, and we think the filaments are remnants of pore water salt that cannot be incorporated into the cage structure of the hydrates. Such ion exclusion may mark the boundaries of the gas hydrate crystal grains. Crystal diameters between 15-40  $\mu\text{m}$  are in accordance with X-ray diffraction results of the same material.

Higher magnifications under the FE-SEM (2000 fold and higher) revealed porous parts of the natural gas hydrates on a sub-micron scale similar to the microstructure observed in synthetic hydrates with a more or less homogeneous three-dimensional sponge-like porosity. The pore size is typically 100-400 nm, again being in close agreement with the synthetic material. The areas with this porosity seem to always be surrounded by dense gas hydrate material. Only isolated pores and channels with diameters of 1-5  $\mu\text{m}$  occur in the dense gas hydrate matrix. They appear to form a system of connected open pores through which water or gas could be transported. A first tentative explanation of the formation of porous hydrates on the basis of a physico-chemical microporification model will be given.

[1] Kuhs, W.-F., Klapproth, A., Gotthardt, F., Techmer, K. and Heinrichs, T. (2000): The formation of meso- and macroporous gas hydrates. - *Geophysical Research Letters* Vol. 27 No 18: 2929 - 2932

## B21D-02 1045h

### Deep-Subsurface Marine Methane Hydrate Microbial Communities: Who's There and What Are They Doing?

Frederick Colwell<sup>1</sup> (208-526-0097; fxc@inel.gov);

David Reed<sup>1</sup> (208-526-7788; reeddw@inel.gov);

Yoshiko Fujita<sup>1</sup> (208-526-1242; fujity@inel.gov);

Mark Delwiche<sup>1</sup> (208-526-1870; mdel1@inel.gov);

David Blackwelder<sup>1</sup> (208-526-3250;

blacdb@inel.gov); Takashi Uchida<sup>2</sup>

(uchida@rc.japex.co.jp); Tetsuya Fujii<sup>3</sup>

(fujii@jnoc.go.jp); Hailong Lu<sup>3</sup>

(hailong@jnoc.go.jp)

<sup>1</sup>Biotechnology Department INEEL, P. O. Box 1625, Idaho Falls, ID 83415-2203, United States

<sup>2</sup>Japan Petroleum Exploration Corporation (JAPEX) Research Center, 1-2-1 Hamada, Mihama, Chiba City 261-0025, Japan

<sup>3</sup>Japan National Oil Corporation (JNOC), 1-2-2 Hamada, Mihama, Chiba City 261-0025, Japan

Natural gas hydrates are crystalline deposits of freshwater and primarily methane. They are estimated to represent a potentially vast reservoir of energy. Relatively little is known regarding microbial communities surrounding deep (>100 meters below sea floor [mbsf]) hydrate-bearing sediments. Deep sediment cores were collected in zones above, within, and below the hydrate bearing strata in an accretionary prism off the coast of Japan. Microorganisms were characterized using cultivation- and non-cultivation-based microbiological techniques to better understand the role that they play in the production and distribution of methane in gas hydrates. Direct counts show cell density at 105 cells/g throughout the hydrate strata. Lipid and 16S rDNA analyses indicate that diverse bacterial and archaeal microorganisms are represented throughout the strata. Acetate and hydrogen were utilized as an energy source for methane-producing microorganisms from each sediment depth. Although the methanogenic biomarker coenzyme M was not present above the detection limit in any of the samples, cloning and characterization of amplified 16S ribosomal RNA genes indicated the presence of methanogenic microorganisms related to the Methanobacteriales and Methanococcales. In addition, archaeal clones closely related to the hyperthermophilic Pyrodictiales were detected. Analysis of eubacterial clones indicated a more diverse eubacterial community compared to the archaea, including members from the groups of cyanobacteria, proteobacteria, gram positive bacteria, and flexibacter-cytophaga-bacteriodes. This study suggests that the diversity of microbial communities associated with the presence of methane in gas hydrate-rich deep marine sediments is greater than previously estimated.

## B21D-03 1100h

### Microbiology of Massive Gas Hydrates from the Gulf of Mexico

Brian D Lanol<sup>1</sup> (909-787-2711; brian.lanol@ucr.edu)

Roger Sassen<sup>2</sup> (sassen@gerg.tamu.edu)

Myron T La Duc<sup>3</sup> (mtladuc@jpl.nasa.gov)

Steven T Sweet<sup>2</sup> (sweet@gerg1.gerg.tamu.edu)

Kenneth H Neelson<sup>3</sup> (kneelson@jpl.nasa.gov)

<sup>1</sup>University of California, Department of Environmental Sciences, Riverside, CA 92521, United States

<sup>2</sup>Geochemical and Environmental Research Group, Texas AM University, College Station, TX 77845, United States

<sup>3</sup>NASA Jet Propulsion Laboratory, 4800 Oak Grove Drive, Pasadena, CA 91109, United States

Although there is significant interest in the potential interactions of microbes with gas hydrate, no direct physical association between them has been demonstrated. We examined several intact samples of naturally occurring gas hydrate from the Gulf of Mexico for evidence of microbes. All samples were collected from an anaerobic hemipelagic mud within the gas hydrate stability zone, at water depths in the ca. 540 to 2000 m range. The  $\delta^{13}\text{C}$  of hydrate bound methane varied from -45.1 to -74.7 parts per mil compared to the Pee-Dee Belemnite standard, reflecting different gas origins. Stable isotope composition data indicated microbial consumption of methane or propane in some of the samples. Evidence of the presence of microbes was initially determined by DAPI total direct counts of hydrate-associated sediments (mean =  $1.5 \times 10^9$  cells  $\text{g}^{-1}$ ) and gas hydrate (mean =  $1.0 \times 10^6$  cells  $\text{g}^{-1}$ ). Small-subunit rRNA phylogenetic characterization was performed to assess the composition of the microbial community in one gas hydrate sample (AT425) that had no detectable associated sediment and showed evidence of microbial methane consumption. *Bacteria* were moderately diverse within AT425, and were dominated by gene sequences related to several groups of Proteobacteria, as well as Actinobacteria and low G+C Firmicutes. In contrast, there was low diversity of *Archaea*, nearly all of which were related to methanogenic *Archaea*, with the majority specifically related to *Methanoseta* spp. The results of this study suggest that there is a direct association between microbes and gas hydrate, a finding that may have significance for hydrocarbon flux into the Gulf of Mexico and for life in extreme environments.

## B21D-04 1115h INVITED

### Anomalous Carbon Isotope Fractionations in Hydrate-Bearing Sediments from the Gulf of Mexico: Are Bacteria to be Blamed?

Paul Aharon<sup>1</sup> (1-205-348-2528; aharon@wgs.geo.ua.edu)

Matthew Hackworth<sup>2</sup> (1-225-388-3413; mhackwo@lsu.edu)

<sup>1</sup>Paul Aharon, Dept. of Geological Sciences, Box 870338, University of Alabama, Tuscaloosa, AL 35487, United States

<sup>2</sup>Matthew Hackworth, Dept. of Geology and Geophysics, Louisiana State University, Baton Rouge, LA 70803, United States

Carbon isotope equilibrium fractionations in the system  $\text{CH}_4\text{-CO}_2\text{-HCO}_3\text{-CaCO}_3$  predict that a solid carbonate phase whose carbon is derived from methane oxidation should yield a  $\delta^{13}\text{C}$  value which is about 5‰ more negative than the methane source. Methane is highly depleted in the  $^{13}\text{C}$  isotope and therefore methane-derived carbonates are expected to yield  $\delta^{13}\text{C}$  values which are at least as negative as the methane source. Here we test the veracity of the empirical isotope fractionations in a study of gas hydrate-bearing sediments from the Gulf of Mexico (GOM) slope where anaerobic methane oxidation is ubiquitous and carbonate products are common.

Push cores through bacterial mats at 560 m water depth were acquired with a manned submersible on the flank of a hydrate mound in the Green Canyon area GC-232. Gas hydrate dissociation at the site is documented by direct visual observations and from the geochemistry of pore fluids which displays an inverse relation between Cl concentrations and  $\delta^{18}\text{O}$  values. The sediments are composed of fine-grained hemipelagic clays and authigenic carbonates comprised of centimeter size, buff-colored high-Mg calcite and aragonite pelletoids. Down-core isotope profiles of the pelletoids and extant pore fluid DICs are uniform ( $\delta^{13}\text{C} = -18.8 \pm 2.7\text{‰}$ , n=84;  $\delta^{13}\text{C}_{\text{DIC}} = -24.9 \pm 5.7\text{‰}$ , n = 14) and yield fractionations of +26.2‰ and +20.1‰, respectively, relative to a thermogenic methane source in the

hydrates ( $\delta^{13}\text{C} = -45 \pm 5\text{‰}$ , n = 26). The large discrepancy observed between the measured and empirical isotope fractionations can be attributed to either one of the following factors (i) dilution of the methane-derived carbonate with allochthonous carbonate sources (e.g., planktonic calcareous tests); (ii) kinetic effects caused by microbial processes, and (iii) molecular fractionation of gases during hydrate dissociation. We provide evidence supporting molecular gas fractionation by bacteria as the principal cause of the anomalously positive  $\delta^{13}\text{C}$  fractionations on the basis of (i) partition of C1/C2-C5 gases between solid hydrates and gases vented into the water column; (ii) known preference of microbial utilization of long-chain hydrocarbons over methane, and (iii) mass balances of  $\delta^{13}\text{C}$  and  $\delta^{14}\text{C}$  distributions between carbon sources and sinks.

## B21D-05 1130h INVITED

### Cold Seep Microbial Communities: How Diverse are They?

Richard D Pancost<sup>1</sup> (+44 (0)1179289178;

R.D.Pancost@bristol.ac.uk); Ioanna Bouloubassi<sup>2</sup>

(iboul@ccr.jussieu.fr); Vanni Aloisi<sup>3</sup>

(galois@mpi-bremen.de); Chuanlun Zhang<sup>5</sup>

(ZhangCL@missouri.edu); Sander Heijs<sup>6</sup>

(S.K.Heijs@biol.rug.nl); Josef Werne<sup>4</sup>

(werne@nioz.nl); Ellen Hopmans<sup>4</sup>

(hopmans@nioz.nl); Jaap Sinninghe Damste<sup>4</sup>

(damste@nioz.nl)

<sup>1</sup>School of Chemistry, University of Bristol, Cantock's Close, Bristol BS8 1TS, United Kingdom

<sup>2</sup>LPCM, Universite P. et M. Curie, Paris, France

<sup>3</sup>LODYC, Universite P. et M. Curie, Paris, France

<sup>4</sup>Netherlands Institute for Sea Research, P.O. Box 59, Den Burg, Netherlands

<sup>5</sup>Department of Geological Sciences, 101 Geological Sciences Building University of Missouri, Columbia, MO 65211, United States

<sup>6</sup>Department of Microbiology, University of Groningen, Haren, Netherlands

For years, the biological role of microorganisms in anaerobic methane oxidation (AMO) has been unclear and the subject of considerable speculation. Recently, both organic geochemical and molecular probing approaches have revealed that AMO is mediated by a consortium of archaea and sulfate reducing bacteria. However, it is unclear if either the archaeal or bacterial components of this consortium are the same in all settings or if multiple populations of related organisms exist. Previous phylogenetic efforts suggest that the populations are diverse, but this approach is limited due to the non-quantitative nature of most phylogenetic surveys. Here, we discuss the variability in lipid distributions amongst cold seeps of the Mediterranean Sea and the Gulf of Mexico and compare those distributions to previously reported lipid distributions for California margin cold seeps (Hinrichs et al., 2000). Previous efforts revealed that the seeps at the California margin are characterised by relatively high hydroxyarchaeol to archaeol ratios, an absence of the sn-3-hydroxyarchaeol isomer, and low abundances of the irregular isoprenoids crocetane and PMI. Similar archaeal lipid distributions were observed in cold seeps in the Gulf of Mexico. In contrast, seeps from the Mediterranean Sea have relatively low hydroxyarchaeol to archaeol ratios, variable mixtures of the sn-3- and sn-2-hydroxyarchaeol isomers, and in some samples high abundances of PMI and crocetane. These results suggest that archaeal populations differ among these areas. Similarly, non-isoprenoidal diether lipids of inferred bacterial origin vary in both distribution and absolute abundance in nearly a dozen Mediterranean cold seep sites. These distributions are generally different than those observed in California margin and Gulf of Mexico cold seeps.

The reasons for this variability in lipid distribution are unclear. Potentially, the same organisms are present at all sites at which AMO occurs, and their lipid distributions vary in response to environmental conditions. In the Mediterranean, pressure and temperature conditions are similar at all sites and seem unlikely causes of lipid variability; instead the growth phase of the archaea which in turn is probably related to methane flux rates could be an important control on archaeal and bacterial lipid distributions. Alternatively, the lipid distributions could reflect a highly heterogeneous distribution of AMO archaea and bacteria.

## B21D-06 1145h INVITED

**Anaerobic Oxidation of Methane Mediated by Microbial Consortia**

Antje Boetius<sup>1,2</sup> (+49-471-4831-1518; aboetius@awi-bremerhaven.de); Marcus Elvert<sup>2</sup> (melvert@mpi-bremen.de); Martin Krueger<sup>2</sup> (mkrueger@mpi-bremen.de); Katja Nauhaus<sup>2</sup> (knauhaus@mpi-bremen.de); Katrin Ravensschlag<sup>2</sup> (kravensc@mpi-bremen.de); Dick Rickert<sup>3</sup> (drickert@geomar.de); Tina Treude<sup>2</sup> (ttreude@mpi-bremen.de)

<sup>1</sup> Alfred Wegener Institute for Polar and Marine Research, Am Handelshafen 12, 27515, Bremerhaven, Germany

<sup>2</sup> Max Planck Institute for Marine Microbiology, Celsiusstr.1, 28359, Bremen, Germany

<sup>3</sup> GEOMAR Research Center for Marine Geosciences, Wischhofstr.1-3, 24148, Kiel, Germany

Stable isotope signatures, radiotracer and modeling techniques have established that most of the methane rising from cold seeps, mud volcanoes and gas hydrates is oxidized microbially under anoxic conditions. However, details of the related biochemical mechanisms and organisms are still largely unknown, although the anaerobic oxidation of methane (AOM) is the major biological sink of methane in marine sediments and thus crucial in balancing the emission of this important greenhouse gas into the atmosphere. The isotopic and genetic signature of the microbial biomass in methane-saturated seep sediments shows that AOM is mediated by different microbial consortia which generally include archaea and sulfate-reducing bacteria. Fluorescence in situ hybridization revealed that both archaea and SRB grow together in symbiotic association. Yet, it cannot be ruled out that single archaea might exist which are capable of anaerobic oxidation of methane. Among the archaea from gassy sediments, rRNA probes target specifically the ANME-2 group, belonging to the Methanosarcinales, and the ANME-1 group. A new cluster of delta-proteobacterial sulfate reducers that is closely related to the Desulfosarcina-Desulfococcus group is also found in most methane rich environments. The consortia are embedded in an organic matrix probably serving as a nucleus for calcification. Field and laboratory data indicate that the process of AOM can support significant cell growth and activity, despite the very low energy yield predicted by thermodynamic models.

**B22A MC: Hall D Tuesday 1330h****Biological Mineralization: Proxies and Processes (joint with OS, PP, MR)**

**Presiding:** P M Dove, Virginia

Polytechnic Institute and State

University; J J DeYoreo, Lawrence

Livermore National Laboratory

**B22A-0124 1330h POSTER****The Mineralogy and Microstructure of Sedimentary Zinc Sulfides Formed by Bacterial Sulfate Reduction.**

John W Moreau<sup>1</sup> (moreau@seismo.berkeley.edu)

Rick I Webb<sup>2</sup> (webb@biosci.uq.edu.au)

Jillian F Banfield<sup>1</sup> (jill@seismo.berkeley.edu)

<sup>1</sup>Department of Geology and Geophysics, University of Wisconsin-Madison, 1215 W Dayton St., Madison, WI 53706, United States

<sup>2</sup>Centre for Microscopy and Microanalysis and Department of Microbiology and Parasitology, University of Queensland, Brisbane, Queensland 4072, Australia

Bacterial sulfate reduction (BSR) is considered to be the predominant mechanism for low-temperature conversion of sulfate to sulfide [1] and is inferred to have existed since the early Proterozoic [2, 3]. Because BSR leads to precipitation of abundant metal sulfide minerals, some ancient, low-temperature sedimentary ore deposits are now hypothesized to have biogenic origins [4]. We have studied zinc sulfide minerals produced by sulfate-reducing bacteria (SRB) living in anoxic, 8 °C waters of a flooded mine near Tenison, Wisconsin [5]. Our objectives were to characterize the morphology, mineralogy, and microstructure of the biominerals and to look for potential biosignatures. Scanning electron microscope images from cryofixed, freeze-fractured samples and transmission electron microscope (TEM) images from ultramicrotomed samples

show a close association between cells and spherical aggregates of ZnS. However, SRB cells are generally not coated by ZnS, implying that the particles form and aggregate in solution after sulfide is expelled from the cell. High-resolution TEM images reveal that the few-micron diameter spheres are comprised of about a billion ZnS particles that are typically 1.5-5 nm in diameter. More coarsely crystalline regions appear to have grown via oriented aggregation of smaller nanoparticles. In some cases, orientation gives rise to twinning on {111} sphalerite. ZnS particles are primarily sphalerite, but domains of wurtzite are not uncommon. Even some of the smallest particles have periodic structure and well-defined morphologies. Reasons for the formation of wurtzite remain unclear, but may be related to the sulfide concentration during aggregation of multinuclear clusters [6] or size-dependent phase stability. In addition, the ZnS spheres are not of uniform density throughout, but contain concentric zones separated from each other by 5-7 nm-wide (average) regions of low particle density. The number of zones per sphere is variable, as is the width of each concentric layer. The existence of these zones implies periodic fluctuations of some form, possibly correlated to nutrient availability, changes in redox conditions within the biofilm, or both. Qualitatively, some spheres located within the same region of the biofilm display similar concentric patterns, indicating that fluctuations are coordinated over micron-scale regions. These results reveal a number of mineralogical and microstructural characteristics of biogenic ZnS that constitute potential biosignatures. These characteristics may be present and recognizable in ancient sedimentary ZnS deposits and would support a nanocrystalline, low-temperature, biogenic origin.

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**B22A-0125 1330h POSTER****Microbes make average 2 nanometer diameter crystalline UO<sub>2</sub> particles.**

Yohey Suzuki<sup>1</sup> (608-262-0915;

yoheys@geology.wisc.edu)

Shelly D Kelly<sup>2</sup>

Ken M Kemner<sup>2</sup>

Jill F Banfield<sup>1</sup>

<sup>1</sup>Geology Geophysics, University of Wisconsin-Madison, 1215 W. Dayton, Madison, WI 53706, United States

<sup>2</sup>Environmental Research Division, Argonne National Laboratory, 9700 S. Cass Ave., Argonne, IL 60439, United States

It is well known that phylogenetically diverse groups of microorganisms are capable of catalyzing the reduction of highly soluble U(VI) to highly insoluble U(IV), which rapidly precipitates as uraninite (UO<sub>2</sub>). Because biological uraninite is highly insoluble, microbial uranyl reduction is being intensively studied as the basis for a cost-effective in-situ bioremediation strategy. Previous studies have described UO<sub>2</sub> biomineralization products as amorphous or poorly crystalline. The objective of this study is to characterize the nanocrystalline uraninite in detail in order to determine the particle size, crystallinity, and size-related structural characteristics, and to examine the implications of these for reoxidation and transport.

In this study, we obtained U-contaminated sediment and water from an inactive U mine and incubated them anaerobically with nutrients to stimulate reductive precipitation of UO<sub>2</sub> by indigenous anaerobic bacteria, mainly Gram-positive spore-forming *Desulfosporosinus* and *Clostridium* spp. as revealed by RNA-based phylogenetic analysis. *Desulfosporosinus* sp. was isolated from the sediment and UO<sub>2</sub> was precipitated by this isolate from a simple solution that contains only U and electron donors. We characterized UO<sub>2</sub> formed in both of the experiments by high resolution-TEM (HRTEM) and X-ray absorption fine structure analysis (XAFS).

The results from HRTEM showed that both the pure and the mixed cultures of microorganisms precipitated around 1.5 - 3 nm crystalline UO<sub>2</sub> particles. Some particles as small as around 1 nm could be imaged. Rare particles around 10 nm in diameter were also present. Particles adhere to cells and form colloidal aggregates with low fractal dimension. In some cases, coarsening by oriented attachment on {111} is evident. Our preliminary results from XAFS for the incubated U-contaminated sample also indicated an average diameter of UO<sub>2</sub> of 2 nm. In nanoparticles, the U-U distance obtained by XAFS was 0.373 nm, 0.012 nm smaller than found in the bulk structure of UO<sub>2</sub> (0.385 nm). This indicates contraction within the nanoparticles due to tensile surface stress. Microbially formed UO<sub>2</sub> is highly reactive, thus will be oxidized quickly as redox conditions change.

Our findings support a growing number of studies that indicate that biominerals formed as the result of enzyme-mediated redox reactions are nanoparticulate.

Preliminary results suggest that these particles will be readily transported through sandy aquifers, especially when conditions prevent high degrees of flocculation. Thus, despite its low (but size-dependent) solubility, UO<sub>2</sub> nanoparticle transport may exert a fundamental control on mobility of U in contaminated environments.

**B22A-0126 1330h POSTER****The Effect of Bacterial Surfaces on Silica Precipitation**

Nathan Yee<sup>1</sup> (44 113 233 5203; nyee@earth.leeds.ac.uk)

Vernon R Phoenix<sup>2</sup> (416 978 0549; vernon@geology.utoronto.ca)

Kurt O Konhauser<sup>1</sup> (44 113 233 5222; k.konhauser@earth.leeds.ac.uk)

Liane G Benning<sup>1</sup> (44 113 233 5222; l.benning@earth.leeds.ac.uk)

<sup>1</sup>University of Leeds, School of Earth Sciences, Leeds LS2 9JT, United Kingdom

<sup>2</sup>University of Toronto, Department of Geology 22 Russell Street, Toronto, ON M5S 3B1, Canada

Bacterial silicification is an important geological process in modern geothermal environments (e.g., New Zealand, Iceland, Japan). The precipitation of silica onto bacterial surfaces can affect microbial fossilization, chemical sediment formation, the porosity and permeability of crustal rocks, and silica transport in geothermal hot springs. Previous studies have suggested that active deposition of silica onto bacterial cells begins with the precipitation of heterogeneously nucleated aggregates of amorphous silica. However, the effect of bacteria on silica precipitation is poorly understood, and it is unclear if bacterial surfaces enhance the kinetics of silica precipitation or if the bacteria act as passive precipitation surfaces.

In this study, we performed silica precipitation experiments with the filamentous cyanobacteria *Calothrix* sp. (strain KC97) to elucidate the rates and mechanisms of silicate biomineralization. Batch experiments were conducted as a function of time, Si saturation states, temperature, pH and Fe concentrations. Experiments at both undersaturated and supersaturated conditions indicate that Si-bacteria interactions are weak, and that minimal bacterial silica sorption/precipitation occurs. In supersaturated solutions, abiotic polymerization rates are rapid and at the times scales of our experiments (1-300 hours) the presence of bacteria does not enhance silica nucleation or monomeric silica polymerization. However, the presence of Fe-coated bacteria significantly increases silica sorption/precipitation rates, and the extent of Si sorption/precipitation increases with increasing Fe concentrations. Fe precipitation experiments performed without Si indicate that iron precipitation onto bacterial surfaces occurs very rapidly and significantly faster than abiotic controls. The experimental data suggest that in the presence of Fe, bacterial silicification occurs as a two step process: 1) Fe precipitates onto bacterial cells via heterogeneous surface nucleation, followed by 2) Si sorption/precipitation onto the Fe-coated bacterial surface. Therefore, Fe may play an important role in the silicification of microbial cells in geothermal environments.

**B22A-0127 1330h POSTER****Manganese Oxide Biomineralization by Spores of the Marine Bacillus sp. Strain SG-1**

John R Bargar<sup>1</sup> (650-926-4949;

bargar@slac.stanford.edu); Brad M Tebo<sup>2</sup>

(858-534-5470); Klaus H Pecher<sup>3</sup> (510-495-2232);

Daniel McCubbery<sup>4</sup> (510-486-8628); Van Chiu<sup>2</sup>,

Brian P Tonner<sup>3</sup> (407-823-2325)

<sup>1</sup>Stanford Synchrotron Radiation Laboratory, PO Box 4349, MS 69, Stanford, CA 94309, United States

<sup>2</sup>Marine Biology Research Division, Scripps Institution of Oceanography, 9500 Gilman Dr., La Jolla, CA 92093-0202, United States

<sup>3</sup>Dept. of Physics, University of Central Florida, Orlando, FL 32816, United States

<sup>4</sup>School of Engineering, Oregon Health Sciences University, 20000 NW Walker Road, Beaverton, OR 97006-8921, United States

Biogenic Mn oxides are ubiquitous in natural waters, have high sorptive capacities for metal ions, and oxidize organic and inorganic substances such as aromatic hydrocarbons, Cr(III), and hydrogen sulfide. In this fashion, Mn(II)-oxidizing bacteria impact the biogeochemical cycling of essential nutrients and toxic trace constituents of natural waters. In spite of their importance, the molecular mechanisms, intermediates, and products of Mn oxide biomineralization are poorly understood. Similarly, the relationship between biotic