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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 kyrs) 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 Monterrey 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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Corals 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 endothecal, exothecal and corallite 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 exothecal area may be absent or substantially lower in either or both the endothecal 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 exothecal 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 endothecal portion of the skeleton, 2) the colonial tissue within the exothecal portion of the skeleton, and 3) the wall that separates these two areas. The microarchitecture 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 (d18O) 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 d18O. 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 d18O (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 Arctica islandica from Norway have been analyzed. As expected, there is excellent reproducibility of d18O 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 d18O. 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 ontogenic 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 Paleochemical 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 characterize 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 mm 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 an high-molecular-weight homogeneous

polymer rich in trisulfated-disaccharide units. When FM was added, isolated calcite crystals displayed rhombohedrical {104} faces but flat corners of {111} faces. The addition of the hypersulfated heparin SM induce the formation of large rosette-like aggregated calcite crystals, where the majority of the {104} faces appeared not to be lost, although aggregation is done by different kind of faces. It is concluded that, the variation of the sulfate and carboxylate content and configuration drastically changed the morphology of the calcite crystals. The production of calcite particles with defined morphologies could be interesting for the design of novel materials with desirable shape- and texture-depending properties. Granted by FONDAP 11980002.

B12C-0788 1330h POSTER

New Observations on Seawater Vacuoles, pH Distribution, and Their Role in the Biomineralization Process in Foraminifera

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We suggest that biomineralization in radial foraminifera is based mainly on seawater vacuolation. During calcification the benthic foraminifer Amphistegina lobifera showed large, static, intra-shell seawater vacuoles, with residence time of an hour in their last chamber. Mobile, intra-shell, smaller vacuoles were initially observed in the periphery of the last chamber and later within the endoplasm of internal chambers. The residence time of water in the mobile vacuoles was up to 12 hr in calcifying individuals and more then 2 days in non-calcifying ones. Experiments with fluorescent dyes showed that labeled seawater entered the large vacuoles first and later appeared in the smaller mobile ones. Fluorescence pH imaging showed that the pH in these vacuoles increased with time by about 0.5 pH unit relative to seawater reaching 8.7. Prior to secondary calcification, the organism generated a thin pseudopodial sheet, which delineates the biomineralization zone. It contained many extra-shell seawater vacuoles with short residence time of about 10 min that were highly abundant during the calcification process. The pH in these vacuoles was 8.5 to 8.7. In the vicinity of the growing crystals, we observed intensive cytoplasmic streams, which are loaded with dark granules that are also alkaline (8.2-8.5), well above the cytosol pH (7.2-7.5). Use of specific probe, showed that about 50% of these alkaline granules are mitochondria while the other ones were vesicles containing fibrillar material (based on TEM). Both were more abundant in the pseudopodial sheet then in the endoplasm. We propose that during secondary calcification, the organism separates itself from the environment using the pseudopodial sheet. The alkaline seawater vacuoles (of both intra and extra-shell origin) are transferred via the pseudopodial sheet and are exocytosed into the biomineralization space between the inner membrane of the sheet and the existing skeleton. Inorganic carbon is concentrated in the vacuoles relative to seawater by diffusion of CO_2 from the mitochondria and from the cytosol into the alkaline vacuoles. Therefore the seawater vacuoles provide both Calcium and carbonate to the biomineralization site.

B12C-0789 1330h POSTER

An investigation of di-peptide modulation of calcite growth

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The central role(s) of the organic component in biologically controlled mineralization is widely recognized. These proteins are characterized by a high proportion of acidic amino acids, especially aspartate, Asp. Knowledge of the relationship between the structure of the organic components that give specialized functionality and their effect on crystallization is essential for understanding mineralization mechanisms. However, our current understanding of mechanisms by which these complex compounds promote, direct, and inhibit growth is very limited. As a step toward building a comprehensive model for protein controls on the directed growth of calcite, we are investigating the interactions of five di-peptides with the calcite surface during near-equilibrium growth. Using in situ Fluid Cell AFM, the effects of these Asp-Amino acid peptides on growth rate and hillock morphology were determined at near equilibrium conditions and 23.5C. Calcium and carbonate activity ratios are held to approximately 1.0 for all solutions, pH is 8.5, and ionic strength is 0.10 molal. Each of the peptides induces strong changes in growth morphology by changing the step edge morphology but each has a structure-specific effect on hillock morphology. Their impacts on the growth kinetics fall into two groups determined by functional group properties. Our findings for these simple compounds suggest predictable relations between the functional group chemistry of different peptides and indicate the cooperative nature of multiple groups in causing a suite of specialized effects on growth. This reiterates the site-specific nature of organic interactions with the kink-sites at calcite step edges.

B12C-0790 1330h POSTER

Effect of Calcite Surfaces on Chiral Separtion of Amino Acids

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Studies have suggested that mineral surfaces break chirality of biomolecules by selective adsorption of amino acids to mineral surfaces and mineral surfaces catalyze amino acid polymerization. Recently, a plausible chiral-separation of amino acids was proposed by showing aspartic acids adsorb selectively on chiral calcite surfaces (Hazen et al., 2001, P NATL ACAD SCI USA). However, the selective adsorption is still phenomenal observation without a theoretical model. We have applied molecular modeling tools to explain the selective adsorption in terms of structures and energetics of interactions between aspartic acids and calcite surfaces. Molecular dynamics (MD) simulations were used to obtain structures of L- and D-aspartic acids and calcite surfaces. The Universal Force Field with Ewald sum and canonical ensemble at 300K were used. Simulations were run with a time step of 1 fs for 100,000 steps. The charges of each atom were calculated every 300 steps using the charge equilibration method (QEq). The interactions between one type of aspartic acid (D or L) and a calcite surface ((21$\bar{3}$1) or (3$\bar{1}$21)) were simulated in a 3-D periodic box model. Gas-phase MD simulations predicted that D-aspartic acid has stronger binding energy (averaged internal energy of a system) than L-aspartic acid to calcite (21$\bar{3}$1) surface, while L-aspartic acid has stronger binding energy than D-aspartic acid to calcite (3$\bar{1}$21) surface. The gas-phase simulations are in a good agreement with the experimental observation of aspartic acids' preferential adsorption in that lager binding energy corresponds to more adsorption. Because the adsorption occurs in solution, we simulated the interactions in solution by adding 451 water molecules in the lowest-energy configurations obtained from gas phase simulations. The solution simulations predicted a similar trend to the gas phase simulations, but the averaged binding-energy differences between D/L amino acids with calcite surfaces were within the range of energy deviation of each simulation. Therefore, molecular orbital calculations were carried out using the program GAMESS to calculate more accurate interaction-energies from minimum-energy configurations of solution-phase MD simulations. Molecular orbital calculations combined with MD simulations are expected to give a theoretical basis to understand the selective adsorption.

B12C-0791 1330h POSTER

Partitioning of Mg Into Calcite: Direct Measurement of the Relative Influences of Temperature, Growth Rate, and Solution Chemistry

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Magnesium contents of biogenic carbonates are recognized as potential paleotemperature proxies. However, the extents to which temperature, salinity, growth rates, fluid [Mg], and biological factors govern Mg contents in calcite are as yet unresolved. An ongoing source of uncertainty is that the crystal growth mechanism(s) in most past studies was inferred or unknown. Here we present two sets of complementary experiments on abiotic calcite growth in which nanoscale observation and measurement of layer-mechanism growth rates are linked with solid crystal Mg contents. Systematic variations in solution chemistry and temperature enable us to evaluate the relative influences of the inorganic controls on Mg incorporation. We directly measured monomolecular step velocities on calcite using fluid cell atomic force microscopy. Temperature varied from 15 to 30°C, supersaturation (ln [aCa^{2+} x a$CO_3{}^{2-}$/K_{sp}]) from 0.3 to 1.0, and fluid [Mg] from 0 to 10^{-4}m. The resulting data relate temperature, growth rates, and fluid [Mg], yielding thermodynamic and kinetic information, including activation energies for calcite precipitation. Long-term experiments at corresponding conditions produced growth hillocks large enough for electron microprobe analysis of Mg concentrations and distributions. These results illustrate relationships between the parameters above and Mg contents of calcite. Our work shows unequivocally that degree of supersaturation, and thus growth rate, exerts a key influence on Mg partitioning. For example, at 23.5°C, despite decreasing Mg/Ca in solutions with increasing supersaturation, Mg contents in calcite increase several fold. Mg also displays a distinct preference for the obtuse (positive) steps on growth hillocks over acute (negative) steps, despite more pronounced morphological effects on acute steps as observed at the nanoscale. This finding contrasts with that of Paquette and Reeder (1995; GCA 59:735), who grew calcite in high ionic strength solutions with multiple impurities. This study advances our understanding of how inorganic factors control Mg signatures in calcite. Quantifying these effects is a critical step toward accurately interpreting the information recorded as trace element signatures in biogenic calcite.

B12C-0792 1330h POSTER

Interaction of Magnesium and Inorganic Carbon Species with the Dissolving Calcite Surface

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Much of the current focus of biomineralization studies involves investigation of the processes by which calcifying organisms orchestrate various nucleation and growth reaction mechanisms to bring about a selective result. These strategies must include the ability to incorporate or exclude impurities, calibrate saturation index, and organize other aspects of interfacial chemistry that in turn control the overall reactivity and behavior of the surface. In nearshore marine or terrestrial environments, the stress imposed by variations in salinity, saturation state, ratios of major and minor solution components, temperature, and other environmental variables may have selected for effective chemical strategies by which calcifiers can maintain skeletal integrity even in marginally saturated or undersaturated conditions. This notion is the motivation for developing an understanding of the mechanistic role of Mg^{2+} and other components in undersaturated solutions, and it is our goal to use these observations to build a general model for the interaction of lattice and impurity components in dissolution reactions. The inhibition imposed by dissolved Mg and inorganic carbon species is selective and complex, but can be understood in terms of changes in etch pit morphology, step speeds, double kink nucleation and single kink propagation rates. By independently varying pH, CO_2, and Mg^{2+} concentrations in otherwise simple $NaHCO_3$ solutions, we have used a suite of AFM and scanning interferometry experiments to selectively elucidate the action of dissolved species at specific surface sites. In CO_2-free solutions, pH > 8, dissolved Mg generates relatively little inhibition even at concentrations of $\sim$1 mM. In carbonated solutions of fixed alkalinity (pH 8.5 – 9), inhibition at concentrations of Mg^{2+} less than $\sim$ 50 μM appear to result from attachment at obtuse (+) step edges. Higher total Mg^{2+} concentrations ($\sim$1 mM) appear to retard (+) kink propagation along (−) step edges, resulting in unique etch pit profiles. The change in etch pit morphology may be linked to changes in the relative rates of double kink nucleation versus single kink propagation rates, mediated by competitive adsorption of ion pairs of magnesium with either carbonate or bicarbonate.

B12C-0793 1330h POSTER

The Role of Ca^{2+}/CO_3^{2-} Ratio in Calcite Dissolution and Growth: Implications for Mechanistic Control of Biomineralization

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The hypothesis that secular variations in the Mg/Ca ratio of seawater have exerted a fundamental control over the mineralogy and abundance of both skeletal and nonskeletal carbonates has received substantial support from both experimental and field data. In this context, ongoing efforts directed at understanding the mechanistic basis for interaction of Mg and Sr with carbonate mineral surfaces during growth (e.g., Davis et al. 2000) are of obvious importance. However, a growing body of experimental dissolution data records additional site-specific interactions between the surface and dissolved free carbon species and carbonate complexes. We suggest these data may provide additional insight into mechanisms by which organisms maintain skeletal integrity under variable conditions, including the possible development of surface precursors of mixed carbonate phases. For example, recent data have shown that kink dynamics along the fast, obtuse (+) step directions are highly sensitive to the ratio of magnesium to carbonate ion. We have used these observations as the basis for exploration of the relationship between the simple ratio of dissolved calcium to carbonate ion and surface dynamics. In sets of carefully designed experiments, we sought to maintain (1) a constant distance from equilibrium by varying Ca^{2+}/CO_3^{2-} ratio at constant IAP, (2) constant Ca^{2+}/CO_3^{2-} at variable IAP, (3) all under conditions of both over- and undersaturation ranging from far to close to equilibrium. Using an integrated approach, observations were made over a wide range of space and time scales using both AFM and VSI (vertical scanning interferometry). These coupled observations provide resolution of the relationship between the overall rate of reaction (total change in surface topography) and detailed observations of characteristic step dynamics developed during both dissolution and growth. Our preliminary results confirm a strong sensitivity of the conventional fast step direction to changes in Ca^{2+}/CO_3^{2-} ratio; the conventional slow step is relatively insensitive by comparison. These results imply additional complexity in the relationship between step morphology, impurity incorporation, and saturation state at Ca^{2+}/CO_3^{2-} activity ratios of ~ 1 (Teng et al. 1999), and invite more extensive treatment of differential roles of cation and anion during attachment and detachment. Davis et al. (2000) Science 290, 1134-1137. Teng et al. (1999) Geochimica et Cosmochimica Acta 63, 2507-2512.

B12C-0794 1330h POSTER

The Effect of Oxygen on Siderite and Rhodochrosite Dissolution

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Siderite ($FeCO_3$) and rhodochrosite ($MnCO_3$) affect the cycling of metals in aqueous environments. $FeCO_3$ and $MnCO_3$ dissolution is investigated under oxic and anoxic conditions. Under anoxic conditions, dissolution rates for both minerals are consistent with parallel proton and hydrolysis dissolution pathways. For siderite under oxic conditions the dissolution rate is below the detection limit for $6.0 < pH < 10.3$, and $Fe(OH)_3$ hillock formation preferential to steps is observed in concurrent AFM micrographs. At $pH > 10.3$, the oxic dissolution rate is greater than under the corresponding anoxic conditions, possibly due to electron transfer reaction between $[Fe^{3+}(OH)_4]^-$(aq) and $>Fe^{II}OH$. For rhodochrosite at $5.8 < pH < 7.7$ under oxic conditions, the macroscopic dissolution rate equals the anoxic dissolution rate though micrographs show the formation of a Mn_2O_3 tabular precipitate. For $pH > 7.7$ under oxic conditions, the dissolution rate decreases, and an MnOOH hillock film grows across the surface. These (hydr)oxide films affect the properties of mineral surfaces.

B12C-0795 1330h POSTER

The Coral and the Moon: A Biological Effect Possibly Affecting the Precision of the Sr/Ca Paleotemperature Proxy

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In thermodynamic equilibrium with sea water the Sr/Ca ratio of aragonite varies predictably with temperature and the Sr/Ca ratio in coral have thus become a frequently used proxy for past Sea Surface Temperature (SST). However, biological effects can offset the Sr/Ca ratio from its equilibrium value. We present high spatial resolution ion microprobe analyses of Sr/Ca variation in well defined skeletal elements in the reef-building coral Porites lutea from Watamu, Kenya. Our data reveal distinct monthly oscillations in the Sr/Ca ratio, with an amplitude in excess of ten percent of the average Sr/Ca ratio. Such large variations, which we speculate can be the result of metabolic changes synchronous with the lunar cycle, will introduce variability in Sr/Ca measurements based on conventional sampling techniques (e.g. dentist drill) well beyond the analytical precision. Monte Carlo simulations show that under such conditions the precision of the Sr/Ca paleo-thermometer can be limited to about two degrees. Aragonite precipitated during periods of reduced growth rate have smaller biological effects than aragonite precipitated during periods of accelerated growth. Thus, Sr/Ca-based temperature reconstructions from massive scleractinian corals, such as Porites, would potentially become more precise if the corals are preferentially sampled in low growth-rate regions of the skeleton. We therefore recommend a reanalysis of existing Sr/Ca records based on knowledge of temperature impacts on growth rates. If the biological effects observed in the Porites coral studied by us are also observed in other Porites specimens from which long SST records have been derived on the basis of the Sr/Ca paleothermometer using conventional sampling techniques, it may invalidate conclusions based on inferred SST variations of less than about two degrees. Our results also may help explain the notorious difficulties involved in obtaining an accurate and consistent calibration of the Sr/Ca vs. SST relationship. In general, our results point to a strong biological control on the Sr/Ca ratio in coralline aragonite and emphasize the importance of investigating and understanding the Sr/Ca micro-distribution.

B12C-0796 1330h POSTER

Strontium Partitioning in Calcite Precipitated by Ureolysis

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Strontium incorporation into calcite generated by ureolysis is being investigated as part of an assessment of a proposed in situ containment and stabilization approach for ^{90}Sr contamination in groundwater. The remediation approach relies on the ability of indigenous urea hydrolyzing bacteria to, upon the addition of urea create conditions that accelerate calcite precipitation, and associated co-precipitation of metal and radionuclide contaminants. Urea hydrolysis produces ammonium carbonate and result in elevated pH, causing an increase in the saturation index for calcite. In our experiments both urea hydrolyzing bacteria and extracellular urease are used to promote urea hydrolysis and subsequent calcite precipitation in a medium designed to mimic the chemistry of the Snake River Plain Aquifer in Idaho. Measured distribution coefficients for Sr in calcite produced by ureolysis are significantly higher ($D > 0.5$) than values reported in the literature for natural and synthetic calcites ($D \sim 0.1$). They were also higher than values for calcite produced non-ureolytically in this study ($D \sim 0.3$). The extent of Sr incorporation appeared to be driven primarily by the overall rate of calcite precipitation, where faster precipitation was associated with greater Sr uptake into the solid. Because bacterial ureolysis can generate high rates of calcite precipitation, this approach is promising for remediation of ^{90}Sr contamination in environments where calcite is stable over the long term.

B12C-0797 1330h POSTER

Temperature Dependent Sr-Isotope ($\delta^{88}Sr$) and Ca-Isotope ($\delta^{44}Ca$) Fractionation in Carbonate Precipitates and Corals

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The knowledge of the influence of temperature and other environmental factors on isotope fractionation of divalent cations like Ca^{2+} and Sr^{2+} during inorganic and biogenic controlled precipitation of calcium carbonate is crucial for their interpretation as paleo proxies. In order to extend our earlier studies on Ca-isotope fractionation (e.g. Gussone et al., 2003), we determined $\delta^{88}Sr$ isotope ratios on seawater and on corals. We define the stable Sr isotope ratio as $\delta^{88}Sr=((^{88}Sr/^{86}Sr)_{Sample}/(^{88}Sr/^{86}Sr)_{Standard}-1)*1000$; Sr Standard is NBS 987. First measurements of the IAPSO seawater standard result in $\delta^{88}Sr$ of 0.38 ± 0.02 $^{o}/_{oo}$. Coral $CaCO_3$ precipitated from seawater in a temperature range from about 22°C to about 27°C correspond to $\delta^{88}Sr$-values ranging from 0.17 $^{o}/_{oo}$ to about 0.32 $^{o}/_{oo}$ indicating that carbonate precipitated from seawater is isotopically lighter than seawater itself. The slope of 0.027 $^{o}/_{oo}$/°C for the temperature-$\delta^{88}Sr$ relationship in corals is about a factor of 1.7 larger than the slope of $\delta^{44}Ca$ ratios in inorganically precipitated aragonite. However, the fractionation $\alpha(T)=((^{88}Sr/^{86}Sr)_{CaCO3})/(^{88}Sr/^{86}Sr)_{Seawater})$ at a given temperature is about one order of magnitude less for Sr-isotopes relative to Ca-isotopes. The larger temperature-$\delta^{88}Sr$ gradient in comparison to the Ca-isotopes is interpreted to reflect the smaller ion potential and the correspondingly smaller mass of the associated Sr^{2+}-aquocomplex. The observation that $\delta^{88}Sr$ and $\delta^{44}Ca$ are positively correlated with temperature points to the likelihood that kinetic or equilibrium fractionation effects and the mass of the associated acquocomplex control the degree of divalent cation isotope fractionation during $CaCO_3$-precipitation. Reference: Gussone N., Eisenhauer A., Heuser A., Dietzel M., Bock B., Böhm F., Spero H., Lea D. W., Bijma J., and Nägler T. F. (2003) Model for Kinetic Effects on Calcium Isotope Fractionation ($\delta^{44}Ca$) in Inorganic Aragonite and Cultured Planktonic Foraminifera. Geochim Cosmochim Acta 67(7), 1375-1382.

B12C-0798 1330h POSTER

Calcium Isotope Systematics During Development of the Domestic Chicken (*Gallus gallus*)

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Calcium isotope distributions have been recognized as showing systematic and predictable fractionation in nature. However, most of the observed calcium isotope fractionation to date is due to biological processes. The presence of abundant amounts of calcium in mineralized tissues makes the isotopic system of calcium particularly valuable in biological and paleobiological questions involving biomineralization. In order to apply calcium isotope systematics to paleobiological questions the changes in the calcium isotope signatures of mineralized tissue in modern animals should be studied. My study observed the domestic chicken (*Gallus gallus*) through embryologic ontogeny. This was accomplished by obtaining fertilized eggs staged in a growth series from day 12 to day 20. The eggs were dissected

and shell, embryonic bone, albumen, and yolk were analyzed in order to characterize the calcium isotopic composition of the individual components over the course of the growth series. Several systematic changes in the isotopic signatures of various tissues were observed during the course of the development of the embryos. In general, mineralization in biological systems preferentially partitions the lighter isotopes of calcium into hard parts. As a result of this fractionation during mineralization, partitioning of light isotopes of calcium into the mineralized tissues may result in residual tissues being enriched in the heavier isotopes as ontogeny progresses. Better understanding of the behavior of calcium in modern biological systems will improve its application to fossils and expand the number of paleobiological and evolutionary questions that can be addressed using calcium isotopic data.

B12C-0799 1330h POSTER

Cyanobacterial Calcite Precipitation - Laboratory Study on Different Spatial Scales

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Lacustrine calcite precipitation with sedimentation rates up to 1 mm per year can result in large carbonate deposits. Varved lake sediments high in calcite content are now intensively studied as high-resolution continental archives for environmental change. Especially in oligotrophic hardwater lakes, eukaryotic and prokaryotic picoplankton was found to be important in the overall process of calcite precipitation. Rates and mechanisms of bacteria-surface mediated precipitation reactions, however, remain poorly understood. For interpreting geochemical and isotopic information stored in sediments, it is essential to know the carbonate precipitation mechanisms and the governing environmental factors. Thus, laboratory experiments with picoplankton under controlled conditions were combined with electron and atomic force microscopy in order to obtain insights into the details of the calcite precipitation mechanisms of cyanobacteria. This study aimed at evaluating the potential of such laboratory studies and investigating the influence of environmental parameters as a first step. Under carefully controlled chemical and physical conditions, precipitation of calcite was induced by adding cultures of picocyanobacteria to supersaturated solutions of $CaCO_3$ at different $CaCl_2/NaHCO_3$ ratios. The cell suspensions were purged with an artificial atmosphere at constant CO_2 concentration. Abiotic solutions were used as reference systems. Chemical conditions such as pH, calcium and carbonate concentrations were continuously monitored by ion selective electrodes. The influence of supersaturation in the range of Ω = 2 - 20 on biogenic precipitation was quantified at different ratios of calcium (0.7 - 48 mM) /carbonate (6 μM - 35 μM). In a series of bulk experiments it was possible to detect critical values of supersaturation for the onset of precipitation both with and without cells, both in the range of Ω = 5 - 10. The morphology of the precipitates was analyzed by scanning electron microscopy. Both, initial crystals (<500 nm) and larger grown crystals (>10 μm) showed rhombohedral and hexagonal-prism shapes characteristic for calcite. Ultrathin-sections (~100nm) of the cyanobacteria cells and the attached calcite crystals were prepared by Focused Ion Beam. This technique allowed us to preserve the cell wall - crystal interface as intact as possible in order to perform Transmission Electron Microscopy (TEM) analysis of the sections. Using TEM-Electron Energy Loss Spectroscopy, carbon bonds in both calcite crystals and cyanobacteria cells were detected and identified. The carbon absorption spectra are significantly different to discriminate the organic and inorganic carbon. Thus, the absorption peaks are the fingerprints of the analyzed material and can be used to analyze the transition zone between the cell and the particle.

B12C-0800 1330h POSTER

Precipitation of Dolomite in Aerobic Culture Experiments Using Halophilic Bacteria

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The study of carbonate biomineralization in hypersaline environments provides information about the key role microorganisms have played in global carbon cycling, especially in the Precambrian. Recently, a microbial dolomite model was proposed based on the study of a hypersaline coastal lagoon, Lagoa Vermelha, Rio de Janeiro (Brazil). This model suggests that sulfate-reducing bacteria mediate dolomite precipitation by increasing pH and removing the sulfate inhibitor. The anoxic conditions of this system may not, however, apply to all ancient dolomite formation. Dolomite is an abundant carbonate mineral found widespread in the geological record in a variety of environmental settings. Thus, a single microbial dolomite model probably cannot explain its widespread distribution and a broad spectrum of conditions may be linked with its formation. In contrast to Lagoa Vermelha, Brejo do Espinho, a shallow hypersaline lagoon located in the same region, is a dolomite-forming environment with oxic bottom conditions. The sediment comprises primarily high Mg-calcite and Ca-dolomite. Heterotrophic microorganisms have been isolated from algal mats growing in Brejo do Espinho, and biomineralization experiments have been conducted at variable temperatures (15, 20, 25, 30, 35 and 40°C) and salinities (sea water and 2x seawater) to simulate the natural environmental conditions. After a 20-day incubation period, several aerobic culture experiments have crystal growth of Ca-dolomite and high Mg-calcite. Our study demonstrates that, under aerobic conditions, heterotrophic microorganisms can mediate dolomite precipitation. These results indicate that microbial dolomite precipitation is not necessarily linked to any particular group of organisms or specific metabolic processes or even a specific environment, i.e., it is not exclusively an anoxic mineral but can be precipitated in the presence of oxygen. This has implications for the distribution of dolomite in the geologic record.

B12C-0801 1330h POSTER

Microbial Mediation of Ca-Mg-Carbonates and Mg-Phosphates: Linking the Carbon and Phosphorous Cycles

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An extensive literature exists on the involvement of microbes in mineral precipitation, including in situ studies performed in natural environments where a specific mineral occurs, as well as laboratory experiments. In order to understand the mechanism of biomineralization, bacteria culture experiments must be conducted to evaluate the involvement of microorganisms, which can act as geochemical agents promoting mineral formation by affecting local geochemical conditions. To date, much research on the biomineralization of carbonate minerals has been performed, but little attention has been given to phosphate mineral formation, in spite of its importance in sustaining life and its intrinsic relation with the carbon cycle. We report the results of 25 bacteria culture experiments that were designed to precipitate carbonate and phosphate minerals, using bacteria strains isolated from saline soils in Spain and a hypersaline lagoon, Brejo do Espinho, near Rio de Janeiro, Brazil. In these environments, there is a predominance of carbonate mineral precipitation, such as calcite, high Mg-calcite and dolomite. Of the 25 strains that produced dolomite and calcite, 14 contained, in addition, struvite, while 6 of these produced large amounts of struvite crystals. For any given microorganism, a slight increase in the amount of crystal formation was observed when less calcium acetate was added to the culture media, and a transformation from struvite to monohydrocalcite and dolomite was observed in these experiments. This study provides information to understand the relationship between the phosphorus and carbon cycle during mineral precipitation. Although struvite is not abundant in the geological record, defining its mechanism of precipitation may provide information to better interpret the contribution of microbes in the recycling of phosphorus, as well as the diagenetic processes involving carbonate and phosphate minerals.

B12C-0802 1330h POSTER

Formation and Stabilization of Mixed Valence Ferrihydrite on Bacterial Surfaces From Hydrothermal Vents

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The dynamics of iron oxidation and reduction at hydrothermal sites is an important biogeochemical process which involves major biomineralization of iron oxides. In this study, we have studied biomineralization by the Rimicaris exoculata shrimp collected at a Mid Atlantic Ridge hydrothermal vent. The structure, morphology and impurities distributions of the minerals were analyzed by Transmission electron microscopy and electron energy loss spectroscopy. The main minerals observed are clusters of two-lines ferrihydrite, found attached to the bacterial cells present in the organ scaphognatite of the shrimp. EELS measurements at the Fe 2p excitation demonstrate that the ferrihydrite is bearing a mixed valence iron distribution. The stability of this uncommon phase is then discussed based on work previously reported in literature for analogous poorly ordered iron oxides. The specific biomineralization mechanism might be a key to the stabilization of this phase.

B12C-0803 1330h POSTER

Nanometer-Size Iron Sulfides Biomineralized by a Deep-Sea Hydrothermal Vent Gastropod in Cooperation with Endosymbiotic Sulfate-Reducing Bacteria

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The scaly-foot gastropod has been discovered only from a deep-sea hydrothermal field in the Central Indian Ridge among the global Mid Ocean Ridges (MOR) and found to be peculiar, because it has scale-shaped sclerites composed of hard proteins and iron sulfides that covered the sides of the foot. As the product and mechanism of the iron sulfide biomineralization have not been elucidated in any details, yet, we conducted crystallographic and molecular phylogenetic characterizations of the sclerites. It was revealed that nanometer-scale (1) mackinawite (FeS) + greigite (Fe3S4), (2) pyrite (FeS2) and (3) mackinawite formed in distinct strata from the outer to inner parts of the sclerites, respectively. This study demonstrated for the first time that pyrite occurred in nature as exceedingly small crystalline nanoparticles (around 3 nm in diameter) and to grow via the aggregation-based pathway. Phylogenetic analyses based on 16S rRNA and dissimilatory sulfite reductase (DSR) genes detected predominant occurrence of bacteria that have the sequences of both genes closely related to sulfate-reducing Desulfobulbus spp. Fluorescence in-situ hybridization analysis using a probe specific to the retrieved 16S rRNA gene sequences of the Desulfobulbus-related bacteria revealed the localized occurrence of the bacteria in the most inner part of the sclerites, which represents a novel structural integration between bacteria and metazoans. The results strongly suggested the potential contribution of endosymbiotic SRB to formation of stratified nanometer-scale iron sulfides inside the gastropod's scaly. As mackinawite that is easily oxidized under slightly oxic conditions and persisted, pyrite seems

to have formed via the strictly anoxic pathway. The results presented here may provide aid in deciphering important, but still partially understood formation mechanisms and biochemical and geochemical roles of iron sulfides.

B12C-0804 1330h POSTER

The Effects of Microbial Fe(III) reduction on Clay Sediment Flocculation and Mineral Transformation

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This study was undertaken to investigate physicochemical properties of smectite associated with microbial reduction of structural Fe(III). Iron reducing bacterium, Shewanella oneidensis were inoculated with formate as the electron donor and smectite as the sole electron acceptor for the intervals of 3, 12, 24, and 48 hours in anaerobic chamber. The extent of Fe(III) reduction was observed to reach up to 9%. The control, containing microwave radiation heat-killed bacterial cells and M1 media plus formate, was prepared from the same smectite sample. Settling experiments were performed in anaerobic chamber for 1) the bioreduced nontronite samples which contain viable cells and biopolymers secreted by bacteria, with variable incubation time points, and 2) abiotic nonreduced controls having dead cells (no biopolymers). Furthermore, the separate set of incubation was prepared in aerobic condition where the microbial Fe-respiration does not prevail, but viable bacteria produced the biopolymers, and then suspended in a settling column in aerobic condition. Compared with abiotic nonreduced control, Micromeritics Sedigraph measured 2.3- m increase of mean aggregate size and a 30-times faster average settling velocity in the bioreduced nontronite suspensions. In addition, the aerobically inoculated nontronite (no Fe-respiration) shows a similar aggregate size distribution to that of an abiotic nonreduced control. Significant changes in physical properties of smectite induced by microbial Fe(III) reduction were directly observed using Environmental Cell Transmission Electron Microscope (EC-TEM). Particularly, neoformation of minerals in bioreduced smectite sample indicate that environmental factor such as bacterial activity should be considered as a geological variable for the mineral transformation studies. Neoformed Illite phase was identified in bioreduced smectite sample that challenge the conventional concept of smectite-to-illite transformation with far-reaching implications. In floc architecture, several domains of smectite packets are glued by biopolymers secreted by bacteria, and the aspect ratio (thickness/length) of individual smectite particle increases from 0.11 to 0.18. We suggest that surface chemistry changes (more negatively charged on smectite surface) induced by microbial Fe(III) reduction more likely to promote the flocculation by absorbing the cations which bridge the smectite particles and the biopolymers resulting in the increase of mean aggregate size.

B12C-0805 1330h POSTER

Investigations of Fe and Mn Bioreduction in Unconsolidated Clastic Sediments

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We studied the microbial reduction of Mn and Fe in sediments from Oak Ridge, TN, and the Hanford Site, WA. Bioreduction was by incubation of 1 g sediment in 10 ml of 30 mM pH 7 bicarbonate buffer with 7-9 x 107 cells/ml it S. putrefaciens CN32 and 10 mM sodium lactate as electron donor. Solution chemistry was monitored during incubation and sediments were pasteurized before characterization. For the unconsolidated clay-rich saprolite from Oak Ridge, Fe reduction occurred after Mn reduction was essentially complete. In sediments from the Pliocene Ringold Fm. (Hanford), incubated under the same conditions, Fe reduction was inhibited, and Mn(III/IV) was incompletely reduced. When Ringold sediments were incubated under conditions with greater available electron donor, more Fe was reduced after reduction of almost all of the available Mn(IV). Transmission and scanning electron microscopy and X-ray microprobe and XANES analysis of Ringold sediments were used to determine the spatial and temporal distribution of Mn. Initially, Mn(III/IV) was present as fragments of phyllomanganate minerals and as interlammelar precipitates with Fe oxides in micas and on silicate clast surfaces. The precipitates were botryoidal and chemically heterogeneous at the sub-micron scale. Precipitates within micas had expanded and deformed the sheet structure of each flake. With the lesser available donor, Mn reduction essentially ceased after 43 days of incubation, and the bulk Mn XANES spectrum indicated residual Mn(III/IV). X-ray microprobe mapping indicated all of the remaining Mn was associated with interlamellar and grain-surface iron oxides, and microXANES showed that the Mn valence within a single mica clast was heterogeneously distributed, and varied from Mn(III/IV) to Mn(II). At longer incubation times, the Mn nearer to the clast exterior tended to be more uniformly reduced than Mn in the interior. The Mn in clast interiors was apparently not readily bioavailable, but could act to buffer the sediment's redox capacity and re-oxidize Fe(II) produced during incubation. Re-oxidation was confirmed by dilute-acid extraction of poorly crystalline Fe(III) oxides.

B12D MCC: 3002 Monday 1340h

Molecular Biogeochemical Processes of Terrestrial Environments III *(joint with H, V, MR)*

Presiding: **J Cervini-Silva,** University of California, Berkeley**; J Chorover,** University of Arizona

B12D-01 1340h

The Link Between Microbial Community Composition and Organic Matter Transformations in a Laboratory System

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The carbon cycle in aquifer systems is poorly understood. In particular, the role of prokaryotic and eukaryotic microbes in the cycling of organic matter (OM) has not been well documented. The goal of this work was to utilize stable isotopes in combination with geochemical and microbial methods to study microbially-mediated OM transformations in aquifers and aquifer sediments. A laboratory flow-through column experiment was conducted with sediment collected from a pristine, shallow, coastal plain aquifer. The groundwater medium was amended with low levels of isotopically labeled nutrients, 13C-acetate and 15N-ammonium. At pre-determined time points, DNA, RNA, and relevant biomarkers were isolated from the sediment and groundwater. The labeled nucleic acids were separated from non-labeled nucleic acids by ultracentrifugation and then sequenced to determine the composition of the actively-respiring microbial consortia. In parallel, the organic matter was analyzed by GC-MS and ESI-FT-ICR-MS. The incorporation of 13C and 15N was examined for both the aqueous phase and sediment bound microbial communities along with the dissolved and adsorbed OM. Analyzing both dissolved and adsorbed fractions enabled us to determine the relative importance of each on microbial activity and OM transformations. The incorporation of 13C and 15N allowed us to estimate residence times of different organic matter fractions and to answer fundamental questions about organic matter lability and microbial community dynamics in the subsurface environment.

B12D-02 1355h

Photochemistry of Dissolved Organic Matter in Arctic Surface Waters

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It has been shown that persistent organic pollutants (POPs), transported to the Arctic by long-range processes, can potentially contaminate Arctic surface waters and affect both local ecosystems and human health. Once deposited, the behavior of these pollutants is poorly understood; particularly the processes that govern their lifetime and concentrations within the water column. Here, we discuss the photochemical degradation of several halogenated organic pollutants (e.g., lindane, hexachlorobenzene) as mediated by natural dissolved organic matter (DOM). These experiments were conducted both in a controlled laboratory setting using an artificial sunlight simulator, as well as in situ in Alaskan surface waters near Toolik Lake. Our findings to date show high variability in the photodegradation rates of the target POPs and can be correlated to both their structure and the type of DOM present.

B12D-03 1410h

Molecular Simulation of Electron Exchange Between Ferrous and Ferric Iron in Hydrolyzing Aqueous Solutions

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We have constructed a molecular model for ferrous-ferric electron transfer in hydrolyzing aqueous solutions. The model is explored at two pH values, where the pH is defined by the influence of added protons on the ratios of the hydrolysis species of ferric iron. We find two important effects on electron transfer rates as a funciton of pH. First, it is shown that the barrier to electron transfer at any given ion separation increases with increasing pH due to the stabilization of ferric iron. A similar increase in the transfer barrier would result, for example, from increasing the dielectric constant, effectively pinning the electron on the ferrous ion. The second effect, which acts opposite to the first, is the decrease in the potential of mean force between the ferrous and ferric ions as the pH increases. These two contributions, of opposite sign, are of approximately equal magnitudes. Electron transfer reorganization energies for the hydrolysis species show a surprising degree of overlap, indicating that fluctuations in hydrolysis state can be viewed on a continuum with other solvent contributions to the reorganization energy. This continuum picture is odds with current interpretations of the pH dependence of the transfer rate, which ascribe the observed increase in rate with increasing pH to hydrogen atom transfer involving Fe^{2+}-$FeOH^{2+}$, where the $FeOH^{2+}$ species present at vanishingly small concentrations.

B12D-04 1425h

The Effects of Microbial Surface Attachment on the Dissolution Kinetics of Plagioclase Feldspar

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The rate of mineral dissolution can be influenced by the attachment of microbes to a mineral surface. We have previously reported the effect of Shewanella oneidensis (MR-1) biofilm formation on the dissolution kinetics of calcite, dolomite and rhodochrosite, where the organisms completely control dissolution kinetics by recognizing high-energy surface sites overlying screw dislocations and attaching to those sites, inhibiting the opening of etch pits and significantly retarding dissolution. Note that calcite and dolomite are not known to possess nutritional significance for MR-1; and while this facultative anaerobe can reduce both Mn and Fe, our experiments were all conducted with aerobic organisms. In recent experiments, we have observed that this inhibitory effect requires the cells to be alive; dead cells do not prevent the opening of etch pits and subsequent dissolution of the carbonate crystals under conditions in which they would otherwise dissolve. Now