# Aqueous Crystal Growth Additional Research Activities

## Abstracts

### By Author

Striegl, R., Dornblaser, M., Schuster, P., Reddy, M., Brabets, T., Aiken, G., 2004, Export of water and carbon from the Yukon River Basin to the Bering Sea. This abstract was presented at the AGU Spring Meeting, Montreal, Canada, May 17-21, 2005.

Shanley, J.B., Marvin-DiPasquale, M., Schuster, P.F., Chalmers, A., Reddy, M.M., 2004, Mercury methylation in forested uplands; how important is it?. Eos Trans. AGU, 85(17), Jt. Assem. Suppl. This abstract was presented at the American Geophysical Union (AGU) Spring Meeting, 2004, Joint Assembly, Montreal, Canada, May 17-21, 2004.

Schuster, P.F., Reddy, M.M., Aiken, G.R., and Shanley, J.B., 2004, Does permafrost have an effect on dissolved organic carbon transport during snowmelt? To be presented at the Water Rock Interaction 11th International Symposium, Saratoga Springs, NY, June 27-July 2, 2004.

Shanley, J.B., Reddy, M.M., and Schuster, P.F., 2005, Mercury and methylmercury dynamics in upland landscapes at Sleepers River, Vermont USA. To be presented at GSA, Cordilleran Section, 101st Annual Meeting, San Jose, CA, April 29-May 1, 2005.

Baedecker, M., Kirshtein, J.D., Wickland, K.P., Metge, D.W., Schuster, P.F., Voytek, M.A., 2006, Microbial diversity in soil cores from the Yukon River Basin, Alaska: EOS Transactions, American Geophysical Union, v. 87, no. 52, AGU Fall Meeting Supplement.

Reddy, M., 2005, Calcite crystal growth inhibition by aquatic humic substances - can humic substances serve as carbonate scale inhibitors? This abstract presented in the Book of Abstracts - Humic Science & Technology VIII Conference, Boston, MA, March 16-18, 2005.

Schuster, P., Aiken, G., Reddy, M., Krabbenhoft, D., Striegl, R., DeWild, J.F., Olson, M.L., Olund, S.D., 2006, Interactions of mercury and organic matter in the Yukon River Basin, abstract presented at the Mercury Conference, Madison, WI, August 6-11, 2006.

**Abstract:** The Yukon River Basin, the fourth largest drainage basin in North America, provides a unique opportunity to study the interaction of mercury (Hg) and organic matter (OM) at a large scale in a relatively undisturbed system. The U.S. Geological Survey recently completed an extensive five-year water-quality study of the Yukon River from its headwaters in Canada to Pilot Station, Alaska near its mouth.  One aspect of that project was to establish a water quality baseline to assess possible future changes from a warming climate.  Two of the key water-quality components we analyzed were Hg and OM in surface water.  It is well known that Hg and OM have strong interactions in aquatic ecosystems.  However, the vast majority of what is known is derived from relatively small streams, lakes and reservoirs at lower latitudes.  The high latitude and vast scale (longitude and flow rate) of the Yukon River, its naturally high suspended sediment loads, and complex geologic terrain make it a unique setting to examine whether Hg-OM interactions hold in these large-scale northern ecosystems.

For water years 2001 through 2004, dissolved organic carbon concentrations in the Yukon River mainstem and two major tributaries ranged from 1 to 15 mg/L and particulate carbon ranged from < 1 to 34 mg/L. Likewise, dissolved total Hg ranged from 0.1 to 4.3 ng/L, and total particulate Hg ranged from <0.1 to 75 ng/L.  These high Hg concentrations in such a remote location are suggestive of contributions from geologically enriched materials.  For both Hg and OM, the highest concentrations were observed during periods of high flow, and both were dominantly in the particulate state (80% for Hg, and 50-80% for OM). The data show a strong positive correlation among dissolved (R2=0.56, p=0.001) and particulate mercury concentrations (R2=0.57, p=0.01) and their respective dissolved and particulate carbon concentrations. This research suggests that Hg-OM interactions described for numerous smaller northern catchments can be scaled up to large undisturbed basins in northern temperate and subarctic climates.  Verification of Hg-OM interactions in large-scale northern ecosystems may prove to be valuable given the vast reservoirs of OM that exist in arctic regions.  Large expanses of permafrost are melting in the arctic and subarctic regions, the soil active layer is deepening, upland soils are drying, the growing season is lengthening, and, as a result, fire frequency is increasing.  Along with these changes, as permafrost melts, the frozen soil is transformed into biogeochemically active zones. The changes in climate affecting the overall transport and reactivity of this carbon pool could have a large impact on the long term fate of the associated OM-bound Hg.

Schuster, P., Aiken, G., Reddy, M., Krabbenhoft, D, Striegl, R., DeWild, J., Olson, M.L., Olund, S.D., Dornblaser, M., and Dawson, A., 2006, Interaction of mercury and organic carbon in the Yukon River Basin, EOS Transactions, American Geophysical Union. Vol. 87, no. 52, Suppl. 26

Redden, G., Tartakovsky, A., Scheibe, T., Fjuita, Y., Smith, R., Reddy, M., Kelly, S., 2006, Coupling between flow and precipitation in heterogeneous subsurface environments and effects on contaminant fate and transport, abstract presented in the Book of Abstracts - ERSP Meeting, April 3-5, 2006, Warrentown, VA.

George D. Redden Yoshiko Fujita Yi-Lin Fang T.D. Scheibe A.M. Tartakovsky Mikala Beig Joanna Taylor Robert W. Smith Michael M. Reddy Shelly Kelly, 2007, Fluid Flow, Solute Mixing and Precipitation In Porous Media, Annual Environmental Remediation Science Program (ERSP) Principal Investigator Meeting, April 16-19, 2007, Lansdowne, VA

Leenheer, J.A., Reddy, M.M., 2007, Characterization of Organic Matter Incorporated in calcium carbonate precipitated in Pyramid Lake, Nevada, American Society of Liminology and Oceanography (ASLO) 2007 Aquatic Sciences Meeting February 4-9, 2007 – Santa Fe, New Mexico.

Schuster, P.F., Striegl, R.G., Aiken, G.R., Brabets, T.P., Hooper, R.P., Krabbenhoft, D.P., Reddy, M.M., Taylor, H.E., Michel, R.L., Shiller, A.M. Eberl, D.D., Voytek, M.A., Kraemer, T.F., Kendall, C., Finlay, J., 2002, An overview and preliminary data of a five-year water quality study of the Yukon River, Eos Trans. American Geophysical Union (AGU), 83(47), Fall Meet. Suppl., Abstract

Schuster, P., Striegl, R., Dornblaser, M. Aiken, G., Krabbenhoft, David, DeWild John, Reddy, M., 2009, Mercury export from the Yukon River, Alaska: Correlations to organic carbon and terrestrial landscape sources, American Geophysical Union (AGU) Meeting, Dec 14-18, 2009, San Francisco, California.

Rosenberry, D.O., Dean, W.E., Duff, J.H., LaBaugh, J.W., Reddy, M.M., Schuster, P.S., Striegl, R.G., Triska, F.J., Winter, T.C., 2003, Advection of water, solutes, and nutrients affects a northern Minnesota watershed at multiple scales, The First Interagency Conference on Research in the Watersheds, 27-30 October 2003, Benson, AZ.

Schuster, P.F., Striegl, R.G., Dornblaser, M., Aiken, G.R., Krabbenhoft, D.P., DeWild, J.F., Reddy, M.M., 2010, Mercury export from the Yukon River Basin: Correlation to organic carbon and potential future response to climate change, abstract for the USGS 2010 Climate Change Conference in Denver, Colorado, March 3, 2010.

Rosenberry, D.O., Dean, W.E., Duff, J.H., LaBaugh, J.W., Reddy, M.M., Schuster, P.S., Striegl, R.G., Triska, F.J., Winter, T.C., 2003, Exchange of water, solutes, and nutrients at the sediment-water interface affects a Northern Minnesota watershed at multiple scales, presented at the First Interagency Conference on Research in the Watersheds, ICRW Program, Maps and Menu, Benzon, AZ, October 2003.

Harris, W.G., Reddy, M.M., Orem, W., 2008, Natural weathering of minerals and potential implications to eutrophication in the Everglades ecosystem, abstract presented at the Greater Everglades Ecosystem Restoration Conference, July 28-August 1, 2008, Naples, Florida.

Reddy, M.M., 2011, Calcite growth-rate inhibition by fulvic acid and magnesium ion at 25 C, ph – 8.5, and calcite supersaturation (IAPKsp) – 4.5 –potenial reduction of calcite formation rate in marine calcifying organisms. The 18th American Conference on Crystal Growth and Epitaxy, July 31 – August5, 2011, Monterey, CA.

Reddy, M.M., 2011, Calcite growth-rate inhibition by fulvic acid and magnesium ion at 25 C, pH – 8.5, and calcite supersaturation (IAPKsp) = 4.5 –potential reduction of calcite formation rate in marine calcifying organisms. 241st National ACS Meeting & Expo, Chemistry of Air, Space & Water, August 28 – September 1, 2011, Denver, CO.

Reddy, M.M., 2012, Calcite growth rate inhibition by polycarboxylate ions, 244th ACS, Fall 2012 National Meeting & Expo., Materials for Health & Medicine, August 19-23, 2012, Philadelphia, PA. (Invited and chairing a session in the Mineral Scales in Biological and Industrial System – Industrial-carbonate, sulfate scales, session Z. Amjad, Organizer).

Koutsoukos, P. and Reddy, M.M., 2014, Calcite growth rate reduction by a low-molecular weight, rigid, cyclic polycarboxylic acid, Abstract appeared in the Goldschmidt Conference, 2014, Sacramento, California June 8-13, 2014.

**Abstract:** Calcium carbonate (calcite) growth-rate modification impacts biogeochemical and industrial processes. Carboxylaterich molecules influence calcification by binding to calcite mineral surfaces, slowing calcite growth rates. Here we show that calcite growth-rates, at calcite supersaturation (Ωc)=4.5, were markedly reduced in the presence of part-per-billion (ppb) concentrations of cyclopentane tetracarboxylic acid (CPETCA)(Figure 1). Calcite growth-rate reduction with increasing CPETCA concentration followed a Langmuir adsorption model over the concentration range of 0 to 50 ppb suggesting that growth-rate reduction occurs by adsorbed CPETCA blocking calcite growth sites, on steps, or on open crystal faces. Growth morphology in the presence of CPETCA (for example, multiple irregular growth steps) was consistent with CPETCA adsorption blockage of growth sites on the calcite surface. At low CPETCA concentrations, a slow CPETCA adsorption step or CPETCA reorientation may cause the brief accelerated calcite-growth rate before the steady-state reduced calcite growth rate.

Reddy, M.M., 2014, The crystal growth of calcite crystals in the presence of a cyclic polycarboxylic acid, 19th International Sumposium on Industrial crystallization, 16-19, September, 2014, Toulouse, France.

### By Title

**Speciation and Fractionation Modeling Studies - Dissolved Organic Carbon (DOC)-Mercury Interaction**

**Abstract:** The chemical form in which mercury exists in water is its speciation. Mercury species are distinguishable from one another, stoichiometrically, and with respect to their bioavailability. In addition, mercury can exist in different phases, for example, as gaseous species, as solid phases, or in adsorbed states. The concept of chemical speciation is central to the equilibrium, kinetic and biogeochemical aspects of mercury in the Everglades Ecosystem.

We have used the computer ionic speciation model "WHAM" (Windermere Humic Aqueous Model) to characterize the mercury-organic species present in Everglades surface water. WHAM focuses on humic and fulvic acid-metal interactions. These calculations indicate that the major mercury species in solution changes from uncharged chloro- and hydroxy- complexes to DOC-bound complexes in the presence of high DOC concentrations (i.e., greater than about 10 milligrams per liter). Inorganic speciation calculated using WHAM has been compared to speciation determined with PHREEQC (pH-redox-equilibrium-equations) with good agreement. WHAM has also been satisfactorily tested using laboratory measurements of calcium ion binding to a soil fulvic acid. The presence of sulfide and sulfur-containing ligands shifts mercury speciation to mercury-sulfur and mercury-organosulfur complexes. Mercury sulfide solid phases appear to be supersaturated in some Everglades' surface and pore waters. Analysis of DOC and sulfide competition for mercury binding is in progress as well as measurement of Everglades fulvic acid mercury interaction, in cooperation with the Department of Civil Engineering, University of Colorado at Boulder.

**Enhanced Dissolution of Cinnabar (Mercuric Sulfide) By Dissolved Organic Matter from The Florida Everglades**

**Abstract:** Organic matter isolated from the Florida Everglades caused a dramatic increase in Hg release (up to 0.35 mM Hgdiss) from cinnabar (HgS), an insoluble solid (log Ksp of -52.4) under most environmental conditions. Hydrophobic (humic and fulvic) acids dissolved more Hg than hydrophilic acids and other non-acid fractions of dissolved organic matter (DOM). Cinnabar dissolution was inhibited by divalent cations such as Ca+2, but was independent of oxygen content in experimental solutions. Dissolution experiments conducted in DI water (pH = 6.0, I = 0.01 M) had no detectable (>2.5 nM) dissolved Hg in solution. The presence of various inorganic (chloride, sulfate, or sulfide) and organic ligands (salicylic acid, acetic acid, EDTA, or cysteine) did not enhance the dissolution of Hg from the mineral.

Aromatic carbon content in DOM (determined by 13C-NMR) correlated positively with enhanced cinnabar dissolution. Zeta potential measurements indicated significant sorption of negatively charged organic matter to the negatively charged cinnabar (pHpzc = 4.0) at pH 6.0. Based on amounts of mercury, sulfide, and sulfate in solution, and the interaction of humic substances with sulfide in solution, the mechanism of cinnabar dissolution seems to be oxidation of sulfide by DOM and subsequent Hg complexation by DOM. Enhanced solubilization of cinnabar by DOM could be an important mechanism for mobilizing Hg in aquatic environments.

The above abstract was submitted to AGU for the 1998 spring meeting, in Boston, MA, May 26-29, 1998.

This paper was publised in the Environmental Science & Technology, 1998, Volume 32, No. 21, pp. 3305-3311. This paper was also cited imder RESEARCH *WATCH* page 510A, "Dissolution of cinnabar by DOM - Dissolved organic matter (DOM) interacts with cations in natural waters and soils and affects solubility, mobility, and toxicity of many trace metals. M. Ravichandran and coworkers found that organic matter isolated from the Florida Everglades caused a dramatic increase in mercury release from cinnabar (HgS). Hydrophobic acids dissolved more mercury than hydrophilic acids and other DOM nonacid fractions. Possible mechanisms of dissolutions include surface complexation of mercury and oxidation of surface sulfur species by the organic matter. DOM enhances mercury release from cinnabar under oxic and anoxic conditions. Enhanced cinnabar solubility has geochemical significance: In mercury-contaminated areas and where conditions favor HgS formation, humic substances could enhance mercury mobilization and affect bioavailability."

**Limestone Characterization to Model Damage from Acidic Precipitation: Effect of Pore Structure on Mass Transfer**

**Abstract:** The pore structure of Salem limestone is investigated, and conclusions regarding the effect of the pore geometry on modeling moisture and contaminant transport are discussed based on thin section petrography, scanning electron microscopy, mercury intrusion porosimetry, and nitrogen adsorption analyses. These investigations are compared to and shown to compliment permeability and capillary pressure measurements for this common building stone. Salem limestone exhibits a bimodal pore size distribution in which the larger pores provide routes for convective mass transfer of contaminants into the material and the smaller pores lead to high surface area adsorption and reaction sites. Relative permeability and capillary pressure measurements of the air/water system indicate that Salem limestone exhibits high capillarity and low effective permeability to water. Based on stone characterization, aqueous diffusion and convection are believed to be the primary transport mechanisms for pollutants in this stone. The extent of contaminant accumulation in the stone depends on the mechanism of partitioning between the aqueous and solid phases. The described characterization techniques and modeling approach can be applied to many systems of interest such as acidic damage to limestone, mass transfer of contaminants in concrete and other porous building materials, and modeling pollutant transport in subsurface moisture zones.

**Modeling Damage to Limestone Exposed to Atmospheric Pollutants**

**Abstract:** Preservation of building and monument stone exposed to acidic environments relies on the understanding of acidic precipitation deposition processes and damage mechanisms. Presented here is a model which predicts sulfur accumulation in porous limestone subjected to dry deposition of SO2. The model assumes deposition and reaction of SO2 to form a thin gypsum crust on the moist surface of the stone, and subsequent sulfur (as aqueous sulfate) transport and accumulation in the stone interior driven by diurnal wetting and drying of the stone surface. Characterization of the limestone pore structure contributes significantly to the evaluation and interpretation of modeled sulfate transport and accumulation in porous building materials. Predicted sulfur accumulation in the stone interior is dependent on the surface boundary conditions, the stone pore geometry and structure, and the rates and mechanisms of aqueous/solid sulfur partitioning (i.e., adsorption, precipitation and dissolution). Model results are compared to moisture content and sulfur accumulation measured in limestone briquettes exposed to a natural dry deposition environment. The model successfully predicts moisture transport in field-exposed limestone, but overestimates the rate of sulfur accumulation. The model may be improved by quantification of the time dependence of the surface sulfate concentration and better understanding of the sulfate partitioning mechanisms.

**Inhibition of Calcite Growth by Natural Organic Material From The Florida Everglades At pH = 8.5 And 25OC**

**Abstract:** The crystallization of calcium carbonate minerals plays an integral role in the water chemistry of terrestrial ecosystems. Natural organic material (NOM) has been shown to reduce or inhibit crystal growth. The purpose of this study is to quantify and understand the kinetic effects of NOM collected from the Florida Everglades on the crystal growth of calcite and other common carbonate minerals such as aragonite and siderite.

Highly reproducible calcite growth experiments were performed in a sealed reactor at constant pH, temperature, supersaturation (Omega = 4.5), PCO2 (10-3.5atm), and ionic strength (0.1 M, KNO3). Metastable supersaturated solutions were prepared by adding CaCl2 solutions dropwise to NaHCO3 solutions, then adjusting pH with KOH. Metastability was verified in all experiments for at least 60 min. by monitoring pH. Crystal growth began immediately upon addition of well-characterized calcite seed crystals. Calcite growth was achieved using a constant composition reactor. Calcium and CO32- ions were replenished stoichiometrically in response to the pH decrease accompanying calcite formation. Crystallization rates were monitored continuously by recording rates of Ca2+ addition.

NOM was added to HCO3- solutions prior to preparation of supersaturated solutions. NOM was in the form of non-volatile hydrophobic acids (primarily fulvic acid) from 3 water samples collected in a North-South transect across the Everglades. NOM from the northern site had a higher molecular weight and was more aromatic in character than that from the south. All NOM samples had similar acid characteristics. Experimental concentrations of NOM ranged from 0.0 to 5.0 mg/l.

Calcite crystallization rates decreases at NOM concentrations as low as 0.2 mg/l. Crystal growth was almost entirely inhibited at the 5 mg/l level using NOM from the northern site. NOM with higher molecular weight and aromaticity was more effective as a growth inhibitor than NOM with lower molecular weight and aromaticity. SEM imaging revealed new growth steps on calcite seed surfaces with no secondary nucleation. Ca-NOM complexation in solution cannot account for decreased growth rates. We attribute calcite growth inhibition to the blockage of surface growth sites by NOM.

**Diel Sulfide and Dissolved Oxygen Concentration Gradients at Two Sites in the Everglades**

**Abstract:** Speciation of mercury in aquatic systems depends, in large part, on the concentrations of dissolved organic carbon (DOC), sulfide and dissolved oxygen (DO) in surface and porewaters. Spatial and temporal monitoring of these constituents, which are critical to the understanding of processes controlling mercury bioavailability, were conducted at an oligotrophic and a eutrophic site in the South Florida Everglades. Close-interval vertical measurements of sulfide and DO concentrations were made using water-quality multi-probes, a DO microprobe, and a portable spectrophotometer. Samples were also collected for DOC, sulfate and chloride determinations which were carried out in the lab by appropriate methods.

Sulfide concentrations in the water column at the eutrophic site were close to detection limit (0.001 mg/l) during the diel study in July 1997. Porewater concentrations were at least three orders of magnitude higher than surface water and reached a maximum level at night (14.2 mg/l). At the oligotrophic site during a diel study in January 1998, the bottom water (5 cm above the sediment/water interface) had roughly the same sulfide concentrations as porewaters during the day (about 0.08 mg/l). At night, however, bottom water sulfide concentrations increased to 0.13 mg/l while porewater concentrations increased only slightly. Based on DO profiles, the oligotrophic site was stratified while the eutrophic site was not. These results demonstrate significant differences between the eutrophic and oligotrophic sites with respect to production and exchange of sulfide and oxygen between the sediments and water column. In most instances, sulfide and oxygen were simultaneously present in the surface- and porewaters indicating a state of disequilibrium. The diel fluctuations of sulfide appear to be influenced by photosynthesis and availability of sulfate.

**Dissolved Organic Carbon in the Everglades, Florida**

**Abstract:** The spatial and temporal variability of dissolved organic carbon (DOC) in surface and pore waters is being studied in the Everglades in an effort to define the effect of DOC on the transport and reactivity of mercury (Hg). It is hypothesized that the organic sulfur content, molecular weight, functional group chemistry, and lability of the organic matter have a controlling influence on Hg cycling processes such as methylation and volatilization. Specific ultraviolet absorbance (SUVA) measurements, in combination with DOC and DOC fractionation analyses, were used to determine both the amount and nature of DOC along a north-south transect (approximately 40 mi.). Samples collected in the northern part of the transect had higher DOC concentrations, were more aromatic, and had a greater amount of hydrophobic acids and hydrophobic neutrals than samples collected further south. In addition, pore waters were found to contain greater DOC concentrations than overlying surface waters. The pore waters in the eutrophic areas to the north were found to contain the highest DOC concentrations. DOC concentrations and SUVA were found to be lower in those areas with higher concentrations of methyl mercury. Nonvolatile hydrophobic and hydrophilic organic acids were found to be the major fractions of the DOC at all locations along the transect. Isolated samples were found to be highly aromatic and to contain greater amounts of organic sulfur compared with similar samples from other environments. Prelimininary results of laboratory studies indicate strong interactions between the isolated samples and Hg+2.

**Characterization of Organic Matter Incorporated in Calcium Carbonate Precipitated in Pyramid lake, Nevada**

**Abstract:** Our previous research demonstrated natural organic matter mediation of carbonate mineral formation in lakes. To better understand this process, we characterized the content and speciation of dissolved organic matter in carbonate minerals formed in Pyramid Lake, Nevada. A 400 grams block of precipitated calcium carbonate from the Pyramid Lake shore was dissolved in 8 liters of 10% acetic acid. Particulate matter was removed by centrifugation and dissolved organic matter was fractionated into nine fractions by a combination of dialysis, resin, adsorption, and selective precipitations to remove inorganic constituents. Coprecipitated dissolved organic matter constituted 0.23% of the calcium carbonate by weight and was depleted in nitrogen and enriched in hydrophilic acids when compared with dissolved organic matter produced by autochthonous processes in lakes. Infrared spectra of the fractions indicated hydroxy-acids as the major structural group that likely forms insoluble complexes with precipitated calcium carbonate in Pyramid Lake.

**Calcite Growth-rate Inhibition by Fulvic Acid and Magnesium Ion at 25 C and Calcite Supersaturatoin of 4.5 -- Potential Calcite Formation Rate Reduction in Marine Calcifying Organisms, Abstract for the 18th American Conference on Crystal Growth and Epitaxy - July 31-August 5, 2011, Monterey, California**

**Abstract:** Field and laboratory studies demonstrate that increasing ocean surface water dissolved carbon dioxide concentration is negatively influencing marine organisms forming calcium carbonate skeletons by reducing the driving force for calcite formation -- calcite supersaturation. In addition to calcite supersaturation changes due to increasing ocean surface water dissolved carbon dioxide concentrations, natural organic acids, a large reactive global carbon reservoir, are implicated in biocalcification processes and may be involved in changes in the rates of calcification (calcite crystal-growth rates are markedly reduced by specific natural organic acids). Moreover, trace metal incorporation during carbonate mineral growth, used for reconstructing past ocean chemistry and paleoclimate (for example, the magnesium-to-calcium ratio of calcifying marine organisms is a proxy for past sea surface temperatures) is strongly growth-rate dependent. Here we report calcite seeded crystallization rates at constant temperature and calcite supersaturation, characterized in the absence and presence of a natural organic acid (a fulvic acid isolated from the Florida Everglades, FA), in the presence and absence of 10-4 M magnesium (Mg) ion and in the presence of both FA and 10-4 M Mg ion. Both FA (0.5 mg/L) and 10-1 M Mg reduce calcite crystal-growth rates at pH=8.5 and calcite supersaturation of 4.5 by 47% and 38%, respectively, compared to control experiments containing no added substances. Organic matter adsorbed from the air onto the seed crystals has no influence on the measured calcite crystal-growth rates; Growth-rate experiments in the presence of both FA and Mg reduce the calcite growth rate to 5% of the control rate; a calcite growth-rate reduction of almost ten times greater reduction than either individual inhibitor. Mg inhibits calcite by substitution of Mg for calcium ion at a growth site. In contrast, polycarboxylate acid anions inhibit calcite growth rates by binding multiple carboxylate groups on the calcite surface. Since both FA and Mg-inhibit calcite growth rates by different adsorption mechanisms involving growth sites on the mineral surface, it seems plausible that adsorbed FA and Mg interact in solution and/or on the growing calcite surface dramatically increasing their combined calcite growth rate inhibition effectiveness. These results suggest that organic acid and Mg concentrations at biocalcification sites in marine calcifying organisms my regulate the calcite crystallization rates and thus the metal ion partitioning impacting use of these organisms as paleoclimate proxies and a global carbon dioxide sink.

**Calcite Growth-rate Inhibition by Fulvic Acid and Magnesium Ion at 25 C and Calcite Supersaturatoin of 4.5 -- Potential Calcite Formation Rate Reduction in Marine Calcifying Organisms, Abstract for the 241st National ACS Meeting Denver, Colorado Fall 2011**

**Abstract:** Calcite seeded crystallization rates, at constant solution composition and calcite supersaturation, are measured in the presence and absence of a natural organic acid (fulvic acid, FA, 0.5 mg/L), in the presence and absence of magnesium ion (Mg, 10-4 M), and in the presence of both FA and Mg. FA and Mg reduce calcite crystal growth rates by 47% and 38%, respectively, compared to control experiments containing no added growth-rate inhibitor. Growth-rate experiments in the presence of both FA and Mg reduce the calcite growth rate to 5% of the control rate. In combination, FA and Mg interactions in solution and/or on the growing calcite surface dramatically decrease calcite growth rates. This result suggests that FA and Mg concentrations at biocalcification sites in marine calcifying organisms mediate calcite crystallization rates. FA and Mg influence rate-dependent metal-ion partitioning and must be considered when using carbonate trace-metal records as paleoclimate proxies.

## Posters

* Ice-Core Evidence Of Rapid Climate Shift During The Termination Of The Little Ice Age.  This poster was presented at the American Geophysical Union (AGU) meeting in December 6-10, 1993, San Francisco, California
* Speciation and Fractionation Modeling Studies -- Dissolved Organic Carbon (DOC)-Mercury Interaction
* Enhanced Dissolution of Cinnabar (Mercuric Sulfide) by Dissolved Organic Matter Isolated from the Everglades, FL
* Rock Disaggregation and Chemical Weathering in the Regolith in a Cold, Alpine Environment
* Diel Sulfide and Dissolved Oxygen Concentration Gradients at Two Sites in the Everglades
* Inhibition of Calcite Growth by Natural Organic Acids from the Florida Everglades at pH 8.5 and 25oC
* Dissolved Organic Carbon Interactions with Mercury in the Everglades
* Aragonite Whiting Events, Pyramid Lake Nevada: What is the Mechanism?
* Inhibition of Precipitation of Metacinnabar (HgS) by Dissolved Organic Matter Isolated from the Everglades, Fl
* Chronological Refinement of an Ice Core Record at Upper Fremont Glacier in South--Central North America
* Reddy, M.M., Calcite growth-rate inhibition by fulvic acid and magnesiums - Potential reduction of calcite formation rate in marine calcifying organisms, abstract presented at the ACS, Denver, Colorado in 2011.

## Lectures

* Reddy, M.M., 2012, Calcite growth=rate inhibition by fulvic acid and magnesium ion - Possible influence on biogenic calcite formation, Florida International University, Southeast Environmental Research Center (SERC), 11200 SW 8th St., Miami, FL 33199, January 11, 2012 (invited and expenses paid, in part, by SERC).
* Reddy, M.M., 2012, Calcite growth rate inhibition by polycarboxylate ions, 244th ACS, Fall 2012 National Meeting & Expo., Materials for Health & Medicine, August 19-23, 2012, Philadelphia, PA (invited).
* Reddy, M.M., 2011, Calcite growth-rate inhibition by fulvic acid and magnesium ion at 25 Cm pH - 8.5, and calcite supersaturation (IAPKsd) - 4.5 - potential reduction of calcite formation rate in marine calcifying organisms. The 18th American Conference on Crystal Growth and Epitaxy, July 31 - August 5, 2011, Monterey, CA.

## Presentations

* Redden, G., Tartakovsky, A., Scheibe, T., Fjuita, Y., Smith, R., Reddy, M., Kelly, S., Coupling between flow and precipitation in heterogeneous subsurface environments and effects on contaminant fate and transport, abstract presented in the Book of Abstracts - ERSP Meeting, April 3-5, 2006, Warrentown, VA.
* George D. Redden Yoshiko Fujita Yi-Lin Fang T.D. Scheibe A.M. Tartakovsky Mikala Beig Joanna Taylor Robert W. Smith Michael M. Reddy Shelly Kelly, 2007, Fluid Flow, Solute Mixing and Precipitation In Porous Media, Annual Environmental Remediation Science Program (ERSP) Principal Investigator Meeting, April 16-19, 2007, Lansdowne, VA.