Guyot Science 2006
A Summary of the Research Progress and Accomplishments
Made by the Faculty Members of the
Department of Geosciences During the Year 2006

The year January – December 2006 witnessed some important events and transitions for the Princeton Department of Geosciences. Tony Dahlen stepped down after five years as department chair and was succeeded by Bess Ward, a marine microbiologist and biogeochemist who has been a member of the faculty since 1998. George Philander accepted a Research Chair in Climate Studies at the University of Cape Town, where his mission is to raise the quality and visibility of South African climate and ocean science on the national and international stage. He remains an essential member of our faculty for half the year and is spending his spring semesters in South Africa. Guust Nolet was inducted into the American Academy of Arts and Sciences and was awarded the Bownocker Medal from Ohio State University. Previous recipients include several NAS members in the Geosciences, as well as Al Gore (2004). Jorge Sarmiento published a Chemical Oceanography textbook that was very well received and seems set to become the new standard in the field. Daniel Sigman, an isotope biogeochemist, and Thomas Duffy, a mineral physicist, were both promoted to full professor. Gerta Keller and T.C. Onstott continued to attract media and national attention, Gerta for her high visibility work on the controversy over the impact theory of mass extinction, and T.C. for his innovative biogeochemistry work in exotic environments such as deep gold mines and the Arctic Tundra. We were joined by two assistant professors, Adam Maloof, a geologist who applies paleomagnetism and other tools to the study of the ancient earth, and Frederik Simons, a geophysicist who is developing a variety of innovative new tools to study the structure and evolution of planetary lithospheres as well as pioneering in the development of a freely drifting submersible vehicle to increase telesismic coverage in the world’s oceans. Adam and Frederik participated in the Freshman seminar with Emeritus Professor Robert Phinney, continuing the tradition of serious field work for beginning students, which is so important in our undergraduate program. The recent research accomplishments of each member of the Geosciences faculty are described in the individual reports that follow. A list of faculty publications during the past two years, 2005-2006, is appended to each narrative report.

Geosciences Faculty: Back row, left to right: Allan Rubin (s), Bill Bonini (r), Jason Morgan (r; s), George Philander, Michael Oppenheimer (s), Kenneth Deffeyes (r), Tony Dahlen (s), Guust Nolet, John Suppe, Gregory van der Vink (s), Michael Bender, Jorge Sarmiento, Tullis Onstott, Lincoln Hollister, François Morel, Robert Phinney (r; s); Front row: Franklyn van Houten (r; s), Daniel Sigman, Gerta Keller, Adam Maloof, Bess Ward, Chairman, Frederik Simons, Nadine McQuarrie, Satish Myneni, Tom Duffy. (r) = emeritus; (s) = photo scanned. Photo by Bill Bonini with additions by Laurie Wanat.
The activities of my laboratory focus largely on studies of the geochemistry of O$_2$, with applications to understanding the global carbon cycle and glacial-interglacial climate change. The geochemical properties we study are the concentration of O$_2$ in air (which we measure to very high precision), and the relative abundance of the three stable O isotopes ($^{16}$O, $^{17}$O, and $^{18}$O) in O$_2$. There are two subjects for the isotopic studies: O$_2$ in fossil air extracted from ice cores, and dissolved O$_2$ in seawater.

The results inform us about a range of topics. Studies of the O$_2$ concentration (or ratio of O$_2$/N$_2$) in air constrain the fate of fossil fuel CO$_2$ that does not remain in the atmosphere. These measurements allow us to partition the “missing” CO$_2$ between the oceans and the land biosphere. They also constrain rates of seasonal biological production by the oceans. Finally, they provide a test of models describing the global interaction of ocean circulation and biogeochemistry.

The isotopic measurements of O$_2$ in ice-core trapped gases reflect the relative fertility of Earth’s biosphere, averaged over about 1,000 years.

The triple isotope composition of O$_2$ in seawater reflects the fraction of dissolved O$_2$ from photosynthesis. O$_2$ supersaturation reflects net production (photosynthesis in excess of respiration); by combining measurements of O$_2$ concentrations and isotopes, we can determine rates of photosynthesis, respiration, net production, and organic carbon export in aquatic ecosystems. Of course rate determinations of these processes in seawater have been made for many years; what makes our work new is that our approach does not require labor-intensive bottle incubations at sea, and our measurements can be made on large numbers of samples collected by colleagues on cruises of opportunity, and returned to the lab.

A second focus involves the geochemistry of Ar and will expand to include other noble gases. In seawater samples, Ar gives a measure of physical supersaturation due to warming of waters and bubble entrainment. In air samples, the Ar/N$_2$ ratio reflects seasonal outgassing and ingassing due to temperature-driven solubility changes, and also to atmospheric mixing. In the past atmosphere, the isotopic abundance of $^{40}$Ar, produced by radioactive decay of potassium in the solid Earth, has progressively risen with time. The recent rise rate reflects the outgassing rate of the contemporary Earth, and it also provides a means of dating trapped gases in ancient ice (the older the ice, the lower its $^{40}$Ar abundance).

During the past year, we continued two long-term programs: measuring the O$_2$/N$_2$ and Ar/N$_2$ ratio of air at the 8 remote sampling sites of our observing network, and measuring the O$_2$/Ar ratio and triple isotope composition of O$_2$ (hence net community production and gross primary production on a cruises transiting the Southern Ocean).

Highlights of our research during the past year:

1. Developing a method for measuring the $^{40}$Ar/$^{38}$Ar ratio of air to high precision (± 0.01 ‰), and using it to determine, by analyzing gases from the Vostok and EPICA Dome C ice cores, the current rise rate. The results constrain the degassing rate of $^{40}$Ar from the solid Earth, providing a target for models of Earth degassing and also providing a tool to date very old ice samples by dating trapped gases from the Dry Valleys and elsewhere (to an uncertainty of about ± 200 kyr).

2. Participating in an expedition to Mullins Valley, Antarctica, led by Dave Marchant (Boston University) to sample ice that underlies millions-year-old volcanic ashes. We successfully drilled cores out to ash ages of 1.5 Ma, and will date these samples and begin reconstructing greenhouse gas concentration histories further back in time than heretofore possible.

3. Completing a study of the O$_2$/N$_2$ ratio of the Vostok ice core and using the data, which vary with local summertime solar insolation, to date the core by an orbital tuning approach (one aligns the O$_2$/N$_2$ variations with insolation variations). This work provides the most accurate chronology for the Vostok ice core prior to about 140 ka, and allows direct comparison of the timing of climate changes with the timing of changes in insolation induced by variations in Earth’s orbit about the sun.

4. Developing a greatly improved and simplified method for continuously measuring the O$_2$/Ar ratio of surface seawater dissolved gases during ships’ transits. The data allow us to continually calculate the air-sea flux of O$_2$, derived from mixed layer photosynthesis in excess of respiration, hence net community production.

5. Integrating Southern Ocean data and models to demonstrate a strong link between the observed spatial distribution of net community production and modeled dissolution of iron in the surface waters, with a ratio of Fe deposition to NCP close to the estimated Fe/C ratio of phytoplankton. This correlation is arguably the strongest evidence for close regulation of carbon export by iron deposition throughout most of the Southern Ocean. This is Nicolas Cassar’s post-doctoral research.

6. Analyzing our atmospheric O$_2$/N$_2$ records, which date back to 1991, to determine the rate of change in ocean carbon uptake during this period. The data show that ocean uptake of CO$_2$ is accelerating as the CO$_2$ concentration of air rises. This result is widely assumed, but has not previously been demonstrated experimentally. We need to collect data for at least one more year before we nail this down.
In 2006 I wrapped up my collaboration with Guust Nolet and postdoctoral fellow Raffaella Montelli, to account for finite-frequency waveform fronting healing effects in global seismic traveltomeography. In this project, Raffa used 3-D finite-frequency sensitivity kernels to invert long-period, cross-correlation P-wave and S-wave traveltimes measured by Guy Masters at Scripps Institution of Oceanography, together with short-period ISC traveltimes edited by Bob Engdahl at the University of Colorado. The results, published in Science (2004) and Geochemistry, Geophysics, Geosystems (2006) provide persuasive evidence for the presence of a number of well-resolved convection plumes—including Ascension, Azores, Canary, Cape Verde, Cook Island, Easter Island, Samoa and Tahiti—that originate in the vicinity of the core-mantle boundary, as originally proposed by Jason Morgan more than thirty years ago. All of the observed plumes have a diameter of several hundred kilometers, indicating that plumes convey a substantial fraction of the internal heat escaping from the earth. Starting plumes that have not yet risen all the way to the earth’s surface beneath the Coral Sea, east of Solomon and south of Java are also evident in Raffa’s P-wave and S-wave tomographic images. These will be the last results from the Princeton tomography group that rely on measurements made by other investigators. In future work, we will use our newly developed finite-frequency tomographic theory to invert a suite of P-wave and S-wave traveltimes and amplitudes, currently being measured in ten overlapping passbands by graduate students Karin Sigloch and Yue Tian, under the supervision of Guust Nolet.

Fifth-year graduate student Tarje Nissen-Meyer made substantial progress during 2006 on his dissertation project, to compute exact 3-D waveform and traveltome sensitivity kernels in a background spherical earth model, using an axially symmetric spectral element method (SEM). Once the 2-D SEM is fully developed, it will be capable of computing the response of a spherical earth to a moment tensor or point force source up to 1-Hz frequency, substantially better than can be achieved with normal-mode summation codes. Individual 2-D computations are required for the monopole, dipole and quadrupole components of the source. At the present time, these three source types have been successfully implemented and fully benchmarked against both mode summation and an exact analytical solution in the simple case of an earth model lacking a fluid outer core. These results will be published in two back-to-back papers in the next issue of Geophysical Journal International. During the past several months, Tarje has optimized the mesher to deal with a realistic spherical earth model such as PREM, and implemented a displacement potential representation to account for the presence of the earth’s fluid core. The next steps are to fully parallelize the code for implementation on a small cluster, and to implement the rotations of the displacement
and strain fields and the temporal convolutions needed to compute the sensitivity kernels. This work is being conducted in collaboration with Alex Fournier, who defended his Princeton Ph.D. dissertation in December 2003, and who is now a member of the faculty at the University of Toulouse.

Guust Nolet and I are both very excited about a recently launched collaboration with Ingrid Daubechies in the Princeton Department of Mathematics, to use wavelets and possibly curvelets as a basis for finite-frequency tomographic inversions. In 2006 we obtained our first results, which have been submitted for publication in Geophysical Journal International. In this paper, postdoctoral scholar Ignace Loris combined an \( \ell_1 \)-norm regularization method with a wavelet basis to solve a toy 2-D tomographic problem of the canonical linear form \( \mathbf{Am} = \mathbf{d} \), allowing for the possibility of sharp discontinuities superimposed on a smoothly varying background; an iterative method is used to find a sparse solution \( \mathbf{m} \) that contains no more fine-scale structure than is necessary to fit the data \( \mathbf{d} \) within the assigned errors. Ignace has now returned to a permanent faculty position at the Vrije Universiteit in Brussels, and a new postdoc, Huub Douma, who received his Ph.D. from the Colorado School of Mines, has joined the project. Huub has begun to investigate whether seismic reciprocity can be used to speed up a number of currently challenging or even prohibitive numerical computations in complex media.

Finally, in 2006, I was pleased to be able to continue my collaboration with Frederik Simons, who just joined the Geosciences Department as our newest assistant professor in September 2006, following two years as a faculty member at University College London. Frederik and I extended our spherical generalization of the one-dimensional time-frequency multitapers of Slepian and Thomson to the case of a double polar cap, for application to the so-called “polar gap” problem in satellite geodesy (Geophysical Journal International 2006), and will shortly submit a new paper to the same journal, comparing periodogram, maximum likelihood and multitaper methods of estimating spherical harmonic power spectra from noisy data on a spatially localized portion of a sphere. These results are applicable to geodetic, planetary and cosmological data. Finally, we have begun to think about the extension of our theoretical results to noise-cognizant multitapers, for application to data collected by the GRACE space mission. These new tapers should be applicable to a variety of hydrological and climate problems, including the estimation of water balances in drainage basins, and the determination of contemporary icesheet melting rates in Greenland and Antarctica.

Two-Year Bibliography
Referred articles:

Our research program focuses broadly on the physical and chemical properties of minerals relevant for understanding large-scale geophysical properties of the Earth and planets. Currently, we are emphasizing study of elastic properties to pressures of the Earth’s upper mantle and examination of crystal structures and phase transitions at conditions of the Earth’s deep lower mantle and outer core.

There has been considerable interest in recent years in the potential role of hydrogen in the Earth’s interior. Even if present in small quantities, hydrogen can strongly affect phase relations, rheological and transport properties, and even seismic velocities. Wadsleyite (\( \text{Mg}_2\text{SiO}_4 \)) is the high-pressure polymorph of olivine that is expected to be a dominant mineral in the Earth’s transition zone from 410 km to 520 km depth. Wadsleyite can incorporate variable amounts of water up to 3.3 wt %. With graduate student Zhu Mao, we have recently measured the single-crystal elastic constants of hydrous wadsleyite with water contents between 0.4 wt % and 1.7 wt % using Brillouin spectroscopy at ambient conditions. We found that both the bulk and shear modulus of hydrous wadsleyite decrease strongly with water content. Compared with anhydrous wadsleyite, 1 wt % of water will lead to 7% decrease in the bulk modulus and 11% decrease in the shear modulus. The olivine to wadsley-
ite phase transition is believed to be the origin of the major seismic discontinuity near 410 km. Using these new results, we are examining the potential effects of water content on the seismic signature at this depth. With post-doctoral fellow Fuming Jiang, we are also carrying out parallel measurements on the elastic properties of hydrous forsterite. The next step for both materials is to measure the elastic properties as a function of pressure to conditions approaching the 410-km discontinuity. This work is being carried out in collaboration with colleagues from the University of Colorado and Northwestern University.

Seismological observations of the lowermost mantle (the D” region) have revealed a region of incredible complexity that includes a seismic discontinuity, strong lateral heterogeneity and regional seismic anisotropy. We are carrying out a number of studies to assess the role of the phase transition in (Mg,Fe)SiO3 from perovskite to a post-perovskite (CaIrO3-type) phase. The existence of a CaIrO3-type phase under deep lower mantle conditions was a surprising finding as this is a very rare type of layered structure. Together with colleagues from Berkeley and Chicago, we have carried out deformation experiments to examine development of lattice preferred orientation in (Mg,Fe)SiO3 post-perovskite as well as two analog materials (MgGeO3 and CaIrO3). Using our observations together with convection and deformation modeling, it appears that observed slip planes could explain some observations of seismic anisotropy in the D” region. Our other studies of post-perovskites are focusing on determination of equation of state, compressibility, and structural response in different compositions for silicates and germanates at conditions exceeding 1 Mbar and 2000 K.

Two-Year Bibliography

Books:

Refereed articles:


Jiang, F., S. Speziale, and T. S. Duffy, Single-crystal elasticity of brucite, Mg(OH)2, to 15 GPa by Brillouin scattering, American Mineralogist, 91, 1893-1900, 2006.


Other miscellaneous publications:

Articles in press or submitted:
How are mountains and continental crust made? This is the major question driving my research and teaching, I interpret the pressure-temperature-time-strain history of rocks in the context of the tectonic processes operating on the continental crust. My contributions are based on direct observation of the products of mountain building. I have forged collaborations with people in other disciplines, and I work over a wide range of disciplines with the objective to achieve results unattainable by focusing on only one or two disciplines.

This approach led to the article that Chris Andronicos and I wrote (Hollister & Andronicos, 2006), which brought together results from the 1993-2000 multidisciplinary project ACCRETE into a hypothesis for formation of continental crust. (see comments from T. Pavlis, below).

My current research is on three fronts: the origin of the Coast Mountains of British Columbia, the origin of the Himalayas in Bhutan, and the application of lamellar magnetism for resolving the Baja British Columbia controversy. In addition, I play a critical role for obtaining permits for a controlled source seismic experiment, now scheduled for fall 2007. I coordinate with the other PIs, with the granting agencies, with the ship scheduling, and with the consultants; and I help in communications with the public.

1) BATHOLITHS. My biggest research commitment now and for the next few years (funded 2003-2008) is the multidisciplinary collaboration, called BATHOLITHS, which proposes to resolve the continental crust composition paradox: although continental crust begins as accreted island arcs, the average composition of continental crusts is more silicic than that of island arcs. Before becoming stable continental crust, the original island arc composition is modified by processes that are not understood. This is a fundamental problem in the earth sciences, and was a topic of a special conference convened in June 2006 in Valdez, Alaska, and the subject of the article by Hollister & Andronicos (2006).

The disciplines of BATHOLITHS include active and passive source seismology, geochemistry, structural geology, and petrology. Most of these endeavors are underway, but the active source seismology experiment has been delayed due to ship scheduling problems. The delays in ship scheduling may have actually helped because of evolving complexities in obtaining Canadian environmental permits.

For information on the permitting process, see http://www.eos.ubc.ca/research/batholiths/. In addition, the BATHOLITHS team has been involved in debate in public forums in Canada. An op-ed I had published in the Seattle Post-Intelligencer is found at: http://seattlepi.nwsource.com/opinion/279541_seismicrebut01.html.

NOTE: The future of controlled source seismic imaging of coastal areas of the world will be affected by how our project fares in the arena of public and governmental policy.

Comments by Terry Pavlis on the Hollister and Andronicos (2006) manuscript:

From: tpavlis <tpavlis@uno.edu>
Date: April 27, 2006 11:01:05 AM EDT
To: “Lincoln S Hollister (linc@Princeton.edu)” <linc@Princeton.edu>
Subject: EPSL paper

Hey, I just finished reviewing the best paper I’ve read all year--actually for several years. It was by a pair of yahoos from the northeast--I think it was a guy named Hollister and this guy with a name I can never spell--Andronicos?

I am actually serious. I really like this paper; I got a real epiphany reading it thinking about general problems of how the crust evolves in time. I wrote in my review that is should be required reading for all tectonics classes...

Terry

Below are the review comments of Pavlis:

Reviewer #2: General comments

This is an absolutely fabulous paper that could be virtually published as is. It outlines a fascinating new hypothesis for how continental crust is assembled from amalgamation of collided blocks (arcs and plateaus). Most importantly, I think, is the conclusion that unlike the type of models usually developed by isotope geochemists (i.e. overly simplified) this paper proposes a geologically realistic model of how metamorphic, igneous, and structural processes all combine into a three-dimensional flow system that reforms the crustal section into to what we call continental crust. This paper should become required reading for all students studying tectonics because it nicely summarizes a lot of key data on a wide range of topics into a clean concise story that explains a lot of the geophysical complexity of continental crust.

2) Bhutan. With my colleague Djordje Grujic at Dalhousie University, we have defined a process in mountain building, based on our studies in Bhutan. This process involves the rapid extrusion of a low viscosity, partially melted orogenic channel from lower crustal depths. It was published in 2002. In 2005 we completed an article on pulsed channel flow in Bhutan (Hollister & Grujic, 2006). This article rationalizes seemingly contradictory field data to the theoretically based channel flow model of Beaumont and others. I have helped recruit two Bhutanese students to study geology in USA. They recently received MS degrees at University of Texas, El Paso, and one,
Tobgay Tobgay, who arrived at Princeton Sept. 2006, is beginning his studies toward a Ph.D.

3) Lamellar Magnetism. Following up on our hypothesis (Hollister, et al, 2004) that reheating of ilmenohematite may explain anomalous remanent magnetization in rocks along the west coast of North America, I am collaborating on a NSF proposal funded through UC Berkeley to test the hypothesis. I wrote most of the proposal, but it is funded through Berkeley because we do not have the facilities for doing the project at Princeton. The graduate student who is working on the project is one of our former undergraduate students (Sarah Brownlee). A consequence of this study may be a solution to the Baja British Columbia controversy; the controversy is whether or not parts of western Canada traveled from latitudes corresponding to Baja California during the latest Cretaceous.

Two-Year Bibliography
Refereed articles:

Gerta Keller
Professor
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During the past two years my research project on the Cretaceous-Tertiary boundary impact and mass extinction, done in collaboration with an international team of scientists, has culminated in spectacular success with the coming together of empirical evidence from sedimentology, stratigraphy, paleontology, mineralogy, geochemistry, and paleomagnetic stratigraphy. The environmental history revealed by all of these disciplines indicates that the 25-year-old impact mass extinction theory can no longer be supported. The Chicxulub impact, commonly believed to be the cause for the KT mass extinction, predates this mass extinction by 300,000 years. A second impact together with major Deccan volcanism is the likely cause for the mass extinction. Our research results have caused further controversy and calls for confirmation or refutation of our results. As a result, we obtained NSF funding to drill new KT sequences in Texas and Brazil, localities at 1000 km and 7,800 km from the Chicxulub impact location. Drilling was completed between the fall of 2005 and January 2006.


Other publications:


The new results from the Texas localities were presented at AGU in Baltimore and GSA in Philadelphia in 2006 and received wide media attention, with press releases by NSF and GSA of our work, an invitation to give a public evening lecture at GSA to present the results, and two invitations to present talks at special symposia. The results obtained from the Brazos, Texas, provide support for the earlier findings of the pre-KT age of the Chicxulub impact and also revealed that this impact caused no extinctions. A website is maintained on the research.

The Chicxulub Debate:
http://geoweb.princeton.edu/people/faculty/keller/chicxulub.html

Our new theory and its supporting evidence has been carried by news outlets all over the world and more than 100 news articles have appeared in international magazines, including top journals like Nature, The Economist (G.B), La Recherche (France), Der Spiegel (Germany), Focus (Switzerland), Facts (Austria), National Geographic, etc., and the Geological Society of London sponsored a debate on my team's work. Our work was included in six documentary films, including ABC Australia, the History Channel, Swiss TV, and the American Museum of Natural History in New York. In addition, our work was the main feature in a special BBC Horizon documentary (“What didn’t kill the Dinosaurs”), and a 45-minute TV interview with Alexander Kluge for German Film, TV and Media.

Two-Year Bibliography
Refereed articles:


**Articles in press or submitted:**


Adam Maloof  
Assistant Professor  
Ph.D., 2004, Harvard University  
email: maloof@princeton.edu

My research continues to involve using sedimentary and volcanic rocks to extract information about Earth’s ancient magnetic field and the relative motion of continents, perturbations to the global carbon cycle, climate change, and processes related to small meteorite impacts.

During January 2006, I completed the second and final field season at Lunarr Crater in India. Lunarr Crater is young (~40 kyr old) and formed in layered basalts, and therefore represents a fairly pristine terrestrial analogue to craters on Mars. Currently, I am writing the paper that presents the digital topography and the geology of the crater and ejecta blanket. I am also a contributing author to papers currently in preparation at Harvard and MIT on shock remagnetization of basalt and remanence acquisition in impact generated glass, respectively.

In the winter of 2006, I completed a third field season on the Holocene carbonate platform of Northwestern Andros Island, Bahamas. The purpose of this study is two-fold. First, I hoped to document the source of magnetization in modern carbonate muds as an analogue for ancient carbonate rocks that we use for paleomagnetic study. This project has already led to one publication (Kopp et al. 2006), and I am currently preparing a comprehensive manuscript on the topic. Second, I conducted a digital topographic, and stratigraphic survey of the tidal flat to determine the nature and origin of facies variation in carbonate parasequences (in other words, is it sea level variation or tidal channel migration that controls the architecture of ancient carbonate rocks?). In fact, students in my new course, GEO 450, will conduct a 10-day research project on this topic during Spring break. I expect to submit these results for publication before the summer.

During the summer of 2006, my new graduate student (Swanson-Hysell) and I spent two months in Australia testing the true polar wander hypothesis for global change 800 million years ago. The hypothesis was first published in GSA Bulletin in September 2006, and has generated a small amount of public interest (News Item 1: http://geoweb.princeton.edu/people/maloof/). Currently, Swanson-Hysell, a team of three Princeton freshman and I are preparing Australia samples for isotopic, trace element and paleomagnetic analysis. We will return to Australia this summer for at least two months, to continue the true polar wander project and to begin a new project in 2.7 Ga basalts with my prospective graduate student, Catherine Rose.

For his first year project, graduate student Swanson-Hysell is conducting a paleomagnetic and geochronological study of 1.1 Ga basalts from Ontario. These rocks were thought to contain some of the only evidence in Earth
history for non-dipole contributions to the geomagnetic field. Swanson-Hysell presented our findings at the annual Geological Society of America Meeting this fall and will be preparing the results for publication this spring.

In collaboration with Prof. Sam Bowring (MIT) and graduate student David Fike (MIT/Caltech), I have expanded on work published in 2005 in the Canadian Journal of Earth Sciences on the Early Cambrian of Morocco. We have added strontium and sulfur isotopic analyses and new uranium-lead geochronology to the published record of physical stratigraphy and carbon isotopes to better constrain models for the evolutionary radiation of macroscopic animals. I have compiled this data in a proposal to NSF to (1) support David Fike as a postdoctoral fellow at Princeton, (2) contribute to analysis costs at the geochronology laboratory at MIT, and (3) fund a new field season in Morocco.

During the next month, I will be concentrating on preparing lecture notes and problem sets for GEO 450, Earth Surface Processes.

Two-Year Bibliography
Referred articles:


Articles in press or submitted:

Halverson, G.P., A.C. Maloof, M. and Hurtgen, Stratigraphy and geochemistry of an 800 Ma negative carbon isotope stage in northeast Svalbard; Chemical Geology, in press.

The 1960’s and 1970’s heralded in a revolution in earth-science thinking. Scientists realized that the outer shell of the earth is composed of a mosaic of 15 irregular sections or plates. Initial tenants of plate tectonics assume that these plates are rigid and deform along narrow zones at plate boundaries. In the 40 years following, we have learned that when the boundary of a plate is a continent, the resulting deformation, or “orogen,” can be very broad and diffuse. The interaction of plates, at plate boundaries, generates large (magnitude 6-9) earthquakes that have recurrence intervals of 50 years to 500,000 years depending on the width of the deforming boundary. These earthquakes along narrow plate boundaries (Sumatra) or diffuse (Iran) emphasize the importance in understanding how plates are currently deforming as well as how plate boundaries have evolved through time. My research focuses on the kinematic evolution of mountain belts, which are the continental expression of fundamental plate boundaries. Research projects start with structurally based field studies, the goal of which is to produce new geologic maps at finer scales and higher resolutions than previously available. New geologic mapping is essential because the intersection of 3-dimensional topography and geologic structures on a 2-dimensional geologic map provides one of the few ways we can understand the geometry of structures at depth. Using the geological mapping as a foundation, the projects expand to include the creation and sequential restoration of geologic cross sections as well as new mineral cooling ages to determine the distribution, magnitude and rate of deformation. The overarching questions that drive my research include: 1) When and why is deformation plate like or diffuse? A specific question that illustrates this is: “Can motion along the boundary between the North American plate and Pacific plate (the San Andreas fault, California) cause motion along faults 1000 km to the east (Wasatch front fault, Utah)?” 2) How and why do rates of deformation along faults vary depending on the window of observation (10$^4$, 10$^5$ or 10$^7$ years)? 3) Does focused precipitation or erosion change the way in which mountain ranges deform? The physiographic expression of mountain ranges is a function of plate interactions as well as climate, which redistributes material through erosion. Thus, 4) what are the primary controls on the topographic evolution of mountain ranges? My research addresses these big questions as described in the following section.

Integrating Rates of Deformation Across an Orogen
With the advent of global positioning systems (GPS), precise displacement fields of continental deformation are becoming increasingly more exact and available across continents.
These displacement fields provide an unprecedented view of modern (the last 10 years) deformation occurring at plate boundaries, but provide only a geologically instantaneous snapshot of plate behavior. Displacement histories over much longer scales (10^7-10^10 years) are required for addressing questions of how the lithosphere responds to major changes in plate geometry and kinematics, or to understand what portion of the modern strain recorded by GPS networks will result in permanent deformation. For many regions on earth the detailed geologic history necessary for long-term displacement fields is just not available. In the last few years, I have focused on acquiring and compiling displacement information in Bolivia and western North America.

In Bolivia my collaborators and I have determined cooling ages on minerals and collected structural data that have been combined in a preliminary kinematic model depicting how the fold-thrust belt has developed through time (Barnes et al., 2006, McQuarrie et al., in rev.) (http://geoweb.princeton.edu/pub/mcquarrie/Bolivia_NFTB.mov). We have used new mapping to construct a balanced cross section across the Andean plateau from the volcanic arc to the undeformed foreland. The restored cross section was imported into 2D MOVE (a cross-section restoration program), and the displacement along folds and faults was forward modeled providing a quantitative description of the kinematics (displacement, velocity, velocity change) of fold-thrust belt deformation. Cooling ages of minerals sampled throughout the region provide age constraints for long-term rates of deformation and erosion. The cooling ages, combined with the simulated velocity field, will be used to link uplift and erosion to an evolving thermal field through 2D and 3D thermo-mechanical models. This will allow us to test the range of permissible deformation rates that can produce the cooling history recorded in apatite fission track and apatite and zircon (U-Th)/He sample ages.

In western North America more is known about timing, amount, and spatial variations of deformation than any other comparable region. Compiling all of the available data on the timing and magnitude and direction of fault displacement into an Arc GIS (global information systems) format, we can sequentially restore deformation through western North America with time, creating a series of palinspastic maps from 36 million years ago to present. The data from these maps are displayed in a variety of ways, including computer animations, that highlight not only the areas where the reconstructions are accurate, but more importantly where the reconstructions are inaccurate (implying problems with existing models and signaling where more field-based data are needed) (http://geoweb.princeton.edu/pub/mcquarrie/WestUS_GES016.mov). The maps can also be displayed as velocity fields over 2-5-10 m.y. increments that can be compared to the modern GPS strain field (McQuarrie and Wernicke, 2005). The power of these sequential reconstructions come from: 1) highlighting areas that are not strain compatible and require additional field research on the timing, magnitude and style of deformation (Lease et al., in rev.), 2) restoring other data sets of interest, such as the volcanic eruptive centers through the Basin and Range, 3) comparing robust features of the reconstruction velocity field with the latest GPS velocity field such as the counterclockwise rotation of the Sierra Nevada Mountains, California.

Evaluating the Primary Controls on the Topographic Evolution of Mountain Ranges

The topographic expression of modern mountain ranges is the combination of a prior deformational history, active deformation, which is currently raising the mountain range and erosional processes, which remove material and act to lower the elevation of mountain ranges. Quantifying the feedbacks between lithology, tectonics, and climate on multiscale morphologies of mountain ranges is at the forefront of current geologic research. One of the main objectives to this research is to understand the magnitude of control climate and the associated erosion rates have on the formation and development of orogens. The Andes Mountains extend over 8000 km along the western side of the South American continent and are the result of a common tectonic process—subduction of the Nazca plate under the South American plate. This shared tectonic regime, combined with significant along strike changes in morphology, structure, and zonal climate regimes, make the South American Andes an ideal location to look at the factors that control topographic expression of deformation. One of the first order changes in the morphology of the Andes Mountains along strike is variation in width of high elevations. Interestingly, the widest portion of the high elevation Andes, between 12° and 27° S, is also the driest, suggesting limited erosion is an important factor in the construction of broad (350-550 km) high (4-5 km) continental plateaus. We are looking at the topographic evolution of the Andes in 3 locations: 1) the Central Andean plateau in Bolivia where an impressive high elevation plateau spans a pronounced switch in hemisphere-scale Hadley precipitation regimes at ~17°-18° S (Barnes et al., 2006, McQuarrie et al., in rev.), 2) the northern edge of the plateau in Peru where a wide zone (~350 km) of high topography with minimal vertical relief transitions abruptly into a significantly narrower (150 km) mountain range with a narrow drainage divide, and 3) the Ecuadorian Andes, which is one of the most narrow zones of high elevation topography along the 8000 km long mountain chain.

Active Projects

COCA: Climate-Orogenic Coupling in the Andes. One of the most abrupt along strike changes in morphology of the Andean Mountains is in Peru. Along the northern edge of the Andean plateau in Peru a west-stepping, right-angle bend in topography is mimicked in the structural elevation (i.e. stratigraphic erosion level) of lower Paleozoic rocks. Nicole Gotberg (Princeton graduate student) has initiated mapping as part of a multidisciplinary project (geophysics, structural geology, sedimentology, stable isotope geochemistry, thermochnronology, climate, and geodynamical modeling) and is constructing balanced cross sections to quantify the minimum and maximum shortening estimate across the pronounced change in mountain width.
Structural Architecture and Kinematics of the Himalayan Orogen in Bhutan. The Tibetan-Himalayan orogenic system is the archetype of continent-continent collision, and tectonic models born in the Himalaya are invoked to explain orogenesis all around the world. Yet, encompassing a region greater than 2.5x10^6 km², and only accessible to geologic field research in the last 20-30 years, the Tibetan-Himalayan orogen may be one of the more incompletely mapped and thus least understood orogens. The Bhutan Himalaya has traditionally been an area of limited access. However, through formal collaborations with the Department of Geology and Mines of the Kingdom of Bhutan, specifically with the help of Tobgay Tobgay, a geologist in the Department of Geology and Mines who is pursuing his Ph.D. at Princeton University, we can gain access to previously restricted areas. To determine the first-order framework of the eastern Himalaya in Bhutan, and to constrain the kinematic history of deformation, we plan on: 1) mapping the frontal, unexplored portion of the Bhutan Himalayas; 2) integrating new mapping with existing maps of the hinterland regions; 3) creating balanced crustal-scale structural cross sections along two transects; and 4) restoring these sections sequentially using new ⁴⁰Ar/³⁹Ar ages to elucidate regional cooling patterns and ages of synkinematic mineral growth to date fault motion. Graduate students Tobgay Tobgay and Sean Long are compiling preliminary and existing mapping, determining U-Pb ages and εNd concentrations in our initial rock samples and analyzing white mica in fault rocks to ascertain ⁴⁰Ar/³⁹Ar ages of synkinematic minerals.

Elevation Versus Deformation. Traditionally the topographic history of mountain ranges has been thought to mimic the deformational history. Thus, as compressive forces shorten and thicken the continental crust, the buoyancy forces associated with a thicker, lighter crust raises the surface elevation of mountain ranges. Recent analytical advances that capitalize on systematic changes in the ratios of stable isotopes with elevation, particularly the ratio of O¹⁸/O¹⁶, suggest that the deformation history of a mountain range may be decoupled in time from the elevation history. We have two projects determining the deformation and elevation history of the Andes in Bolivia and Ecuador. In these regions, much of the deformation occurred between 40-30 Ma, implying long-lived elevations, however youthful topography and low temperature thermochronometers suggest young (10-5 Ma) uplift and exhumation. This discrepancy needs to be reconciled or understood, which will likely involve new plate tectonic-deformation paradigms. Postdoctoral researcher Andrew Leier is combining sedimentology, U-Pb ages of detrital zircons, and O¹⁸/O¹⁶ isotope ratios to compare the timing of isotopic changes in areas of unknown elevation (the Bolivian Altiplano today) to timing of isotopic changes in areas of known elevation (the Amazon Basin). Graduate student Sarah Johnston is combining detailed structural mapping of the Ecuadorian Andes with cooling ages from multiple thermochronometers to document the history of deformation (when faults moved) and exhumation (when minerals cooled) and to model the elevation history of the mountain range through time.

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Marine phytoplankton are responsible for about half of the global primary production and, by exporting organic matter to the deep sea, they maintain a low concentration of CO₂ in surface waters and in the atmosphere. What physical and chemical factors control the growth and activity of phytoplankton in the sea is the overarching question addressed in my research group. Ongoing projects include: the acquisition of carbon and iron by diatoms, the storage of iron by nitrogen fixing cyanobacteria, the acquisition of phosphorus from organic compounds by coccolithophores, and the biological role of cadmium in the sea. A separate long-term project addresses the biogeochemical cycling of mercury. All theses projects involve some aspects of the chemistry, biochemistry, and geochemistry of trace metals in aquatic systems.

Iron Uptake by Diatoms. Iron is known to limit the growth of phytoplankton, particularly diatoms, in large regions of the oceans. Old laboratory data from our group have shown that diatoms take up the free iron (i.e., the iron that is not bound to strong chelating agents) from solution. But, according to field data, the free iron in surface seawater is too low to support the growth of these dominant primary pro-
ducers. Both new and old laboratory data show that diatoms can obtain their iron by reducing Fe(III) in some chelates. We have established that Fe(III) reduction at the diatom surface is an essential step in the uptake of iron in all cases and developed a model for uptake kinetics that reconciles all available data (Shaked et al. 2005). This model provides a chemical framework to quantify the bioavailability of Fe in seawater. In the course of this study, we have also shown that diatoms produce an abundant quantity of superoxide (O$_2^-$), by extracellular reduction of oxygen (Kustka et al. 2005). Superoxide is an extremely reactive radical able to reduce and oxidize many solutes, including Fe, in seawater. To obtain a more mechanistic understanding of the iron uptake system of diatoms, we have now studied the effect of Fe availability on the expression of genes coding for the proteins that are thought to be responsible for the reduction of Fe(III) and the transport of Fe in the two diatoms whose full genomes have been sequenced (Kustka et al. in press). Recently, we have established that diatoms and other marine phytoplankters are able to acquire Fe from iron storage proteins such as ferritins and Dps proteins (Castruita et al. submitted). These proteins may thus play an important role in the biological cycling of iron in surface seawater (see below).

**Iron Storage in Cyanobacteria.** In addition to directly limiting primary production in some oceanic regions, iron is thought to limit it indirectly in many other regions by controlling the input of fixed nitrogen. This is because the nitrogenase enzyme, which is responsible for dinitrogen (N$_2$) fixation, requires a lot of Fe. The most important nitrogen fixer in the sea is the cyanobacterium *Trichodesmium* which thrives in tropical and subtropical regions where iron inputs from atmospheric dust are highly episodic. We have thus been studying the mechanism of Fe storage in *Trichodesmium*. As a first step, we have identified, isolated, over-expressed and partially characterized a Dps protein (DNA-binding protein from starved cells) from this organism (Castruita et al. 2006). This protein, the first Fe storage protein isolated from a marine microbe, is able to store vast quantities of Fe; it is also able to bind to DNA and protect it from degradation. This second attribute may be important to protect the genetic material of the organism during periods of dormancy when nutrient concentrations are low or other environmental conditions are unfavorable.

**Inorganic Carbon Acquisition by Diatoms.** A few years ago, we reported that diatoms growing under present-day atmospheric conditions function as unicellular C$_4$ plants, i.e., that they concentrate carbon by accumulating an intermediate C$_3$ organic compound before CO$_2$ fixation in their chloroplast. This work, which implies that CO$_2$ may limit the productivity of diatoms, has been controversial. Our ongoing work shows that, in accord with our previous findings, specific inhibitors of the two enzymes involved in the formation of the C$_3$ intermediates and the release of CO$_2$ from them (PEPC and PEPSCK) inhibit photosynthesis in diatoms but not in well-characterized C$_3$ microalgae (McGinn et al. in prep.). This project, in concert with our work on cadmium-carbonic anhydrase, indicates that a particularly effective carbon acquisition system may be in part responsible for the ecological success of diatoms in the oceans.

**Use of Organic Phosphorus Sources by Coccolithophores.** Coccolithophores are calcite precipitating phytoplankton that are dominant in many oligotrophic gyres of the oceans and they can form massive blooms visible from space. They owe part of their ecological success to their ability to obtain phosphorus from organic compounds when inorganic P concentrations are vanishingly low. This is achieved through the activity of the zinc enzyme alkaline phosphatase which cleaves phosphate from various organic substrates. We have studied the activity of this enzyme in the ubiquitous species *Emiliania huxleyi* and demonstrated that very small enzyme (and thus zinc) concentrations are necessary to provide the phosphate necessary for growth (Shaked et al. 2006). We have now isolated and partially characterized this enzyme, which has no homology to other known alkaline phosphatases (Xu et al. 2006). This work provides the basis for studying the expression of alkaline phosphatase, and, hence, the extent of P limitation, in the field.

**The Biological Role of Cadmium.** Cadmium, an element which has been thought to be only toxic to organisms, behaves exactly like a nutrient in the sea. Because of its excellent correlation with phosphate, cadmium is used as a paleotracer for nutrients. Over the past several years, we have demonstrated that cadmium is an important micronutrient for marine phytoplankton. In particular, we have discovered that diatoms possess a Cd-carbonic anhydrase, which is involved in the acquisition of inorganic carbon for photosynthesis. We have obtained the full DNA sequence for this enzyme, characterized its active center by X-ray spectroscopy and shown its induction upon Cd addition (Lane et al. 2005). We have also now shown that many diatom species possess closely homologous versions of this Cd enzyme and that it is induced under CO$_2$ and Zn limitation (Park et al. 2006). Recently, we have been able to over-express an active form of the enzyme (the first known Cd enzyme) and, in collaboration with Yigong Shi’s group in MOLBIO, obtain its crystal structure (Xu et al. in prep).

**Mercury Methylation.** Our continuing work on the biogeochemistry of mercury is presently focused on mercury methylation. Since methyl-mercury is the species accumulated in fish via the food chain, this is a key transformation in determining human exposure to mercury. Yet it has received surprisingly little attention over the past 20 years. The two questions we are trying to answer are: 1) where is methylation occurring in the ocean and by what mechanism? and 2) what controls the rate of methylation by sulfate reducing bacteria in freshwater systems? On the basis of previous field data, we have proposed that methyl mercury in the open ocean may originate from the deep sea, perhaps from hydrothermal vents. We have indeed measured significant concentrations of methylmercury in some hydrothermal samples and shown that mercury methylation can be effected chemically at high pressure and temperature by reaction with yet unidentified trace organic compounds (Eileen Ekstrom’s...
doctrinal systems, we know that mercury methylation is effected by sulfate reducing bacteria. Using cobalt limitation as a means to modulate the activity of vitamin B12, we have shown that the acetyl-CoA pathway is responsible for Hg methylation in sulfate reducing bacteria that oxidize their substrate to CO2 (as commonly believed), but not in others (Ekstrom et al. submitted).

Two-Year Bibliography

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Water is essential for the origin and survival of life on our planet and perhaps plays an important role on the existence of life on other planetary bodies as well. In several different forms, water mediates the physical and chemical interactions between various components of the Earth’s surface environment, which includes mineral oxides, biota and their byproducts, and the atmosphere. One of the challenges in environmental sciences is to gain a better understanding of interactions between these different components in nature, and to use it to predict a variety of biogeochemical processes such as elemental cycling, biological chemistry of elements, and the fate and transport of contaminants in the environment. This area of research is gaining importance, and researchers from different disciplines began conducting studies to explore these interactions in greater detail. I am interested in exploring one of these fundamental interactions, which include the evaluation of the chemical state of water in different geologic media and how this modifies the biogeochemical behavior of different inorganic and organic moieties in the natural systems. I am also interested in evaluating the chemical state(s) of important geochemical species to develop predictive patterns for explaining their macroscale behavior.

A summary of my current research projects, and accomplishments in the last one-year are provided below.

Speciation of Aluminum and Iron in Aqueous Solutions and in Solid Phases

Aluminum and iron are among the most abundant elements in the Earth’s crust and form common minerals of all soils and sediments. The oxides and oxyhydroxides of these elements are highly reactive towards aqueous contaminants and nutrients and play an important role in the geochemical cycling of several elements. However, several oxides and oxyhydroxides of Al3+ and Fe3+ exist in the form of amorphous and poorly crystalline precipitates and aqueous polymers, whose genesis, structure, composition, and reactivity are poorly understood. These metastable phases occur as nanosize particulates, and convert to crystalline phases if given enough time. The rates of trans-
formation depend on several physicochemical variables in the environment, and vary from a few hours to several months. My research focuses on the structural chemistry of these metastable phases, and on the influence of different environmental variables that modify their transformation. My group members, Laura Harrington and Michael Hay, are participating in this investigation.

We use different x-ray scattering and spectroscopy techniques to evaluate the coordination environment of $\text{Al}^{3+}$ and $\text{Fe}^{3+}$ in the stable and metastable phases, and vibrational spectroscopy to understand the coordination environment of bridging and terminal hydroxyls. We also use x-ray spectroscopy and microscopy to evaluate the heterogeneity in size and composition of these phases. In collaboration with Dr. Ann Chaka at the National Institute of Standards and Technology, we are conducting quantum chemical calculations to complement the experimental investigations.

The formation of different oxyhydroxides of $\text{Al}^{3+}$ and $\text{Fe}^{3+}$ in the environment is influenced by the speciation of these ions in aqueous solutions. It is well understood that these ions exist as hexa-aqua complexes (e.g. $\text{Al(H}_2\text{O)}_{6}^{3+}$) in highly acidic solutions and hydroxylated species (e.g. $\text{Al(OH)}_m(\text{H}_2\text{O})^{3+}$) at all other pH values, and exhibit least solubility at near neutral pH. The chemical behavior of these two ions in aqueous solutions is significantly altered by their hydroxylation; however, the changes in the electronic state of these ions responsible for this enhanced reactivity is not well understood. We built a new synchrotron experimental chamber to evaluate the electronic states of the hydrated, and hydroxylated species of these ions in aqueous solutions.

**Chemistry of Natural Organic Molecules**

Organic molecules are found everywhere on the surface of the Earth, and their composition, molecular structure and concentration modifies the biogeochemical processes in the environment. One of the bottlenecks in our understanding of the elemental cycles is related to the speciation of $\text{C}$, $\text{N}$, and $\text{S}$ associated with the organic molecules, and their variation in the environment. For the past several years, my research group has been developing and using X-ray spectroscopy and spectromicroscopy methods for studying the chemistry of natural organic molecules in their pristine state (Rev. Mineral., 2002). Using these methods, I am investigating the:

- Functional group composition and macromolecular structure of natural organic molecules in soils and sediments,
- Role of minerals in the retention and fractionation of organic molecules in the environment,
- Chemistry of natural organohalogenes in the environment: coordination chemistry, rates of formation in the environment and their role in various biogeochemical reactions, and
- Reactions at the microorganism-water interfaces.

To investigate the biogeochemical processes involved in organic molecule halogenation in terrestrial systems and their rates in detail, we built a field station in the Princeton University campus. In addition, we are monitoring the speciation of $\text{C}$, $\text{N}$, and $\text{S}$ in organic molecules to evaluate the association of these elemental cycles with the halogen-cycle. We found several interesting results on these systems, and some of the highlights are as follows.

**Chemistry of natural organohalogenes.** While manmade organohalogenes are widely distributed throughout the biosphere and are characterized by varying degrees of persistence and toxicity, natural production of organohalogen compounds is gaining recognition as a significant contributor to the organohalogen burden in the environment. With the help of my research group members, I made significant progress in understanding the chemistry of natural organohalogenes in the past 3-4 years. Using x-ray spectroscopy, I directly showed that the formation of organochlorines and their speciation variations in soils are directly related to the weathering of plant material. Dr. Deshmukh (postdoctoral scholar) conducted a detailed speciation of organochlorines in the O-horizons of soils, and his studies indicated that a majority of chlorinated organic molecules in weathering plant material are associated with the soluble polyphenol fraction, but not with stable lignins, as thought by several previous investigators. Specific molecules identified in our investigation are chlorinated xanthones (probably associated with lichens), and several other aliphatic and aromatic chlorinated molecules (sources uncertain at this stage). The X-ray microscopy studies conducted by Ms. Leri (graduate student) indicated a heterogeneous distribution of organochlorines in weathering leaves, which we are attributing to the differences in organic molecule halogenation processes. Senior, Ms. Jevon Harding, and Leri are currently evaluating the dynamics of natural organochlorines in soil systems.

Researches conducted by Ms. Hakala (senior) and Leri have shown that organobromines, like organochlorines, are common in terrestrial and marine environments. Since they are present at high concentrations in marine systems, we are planning detailed studies on their formation in the photic zone of ocean water, and their accumulation and dehalogenation in sediments. Although iodine is present at trace concentrations, we are finding that iodide and iodate present in soils react with naturally occurring organic molecules and form organoiodines in short time. The presence of $\text{Ca}$ is significantly affecting the sensitivity of X-ray spectroscopy methods in detecting organoiodines in all natural samples. However, we found that the reactions of inorganic iodine with organic molecules are slow, and take about a week to reach equilibrium in laboratory microcosms. Rachel Zwilling, a senior in my research group, conducted these investigations.

**Reactive Carboxylic Acids in Natural Organic Molecules.** Carboxylic acid groups are one of the most important reactive groups in naturally occurring organic molecules. It has been widely assumed that a majority of these carboxylic acids are present as aromatic carboxylic acids (such as in salicylic acid). However, a combination of multidimensional nuclear magnetic resonance and infrared spectroscopy studies indicated that a majority of carboxylic groups in natural organics are associated with the aliphatic fraction, and have an electron withdrawing group on the adjacent C-atom (in the $\alpha$- and
β-positions). The presence of such groups makes the carboxyl group much more reactive and promotes the formation of strong complexes (chelation) with aqueous metals and mineral surfaces. This information is important in understanding the reactivity of common stable biomacromolecules and their origin in aquatic systems.

In summary, my research group is developing into a diverse and interdisciplinary research group to address the fundamental biogeochemical processes in the environment.

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The past year was characterized by the arrival of two new postdocs that I supervise together with Tony Dahlen: Mark Panning and Huub Douma. With Tony's illness casting a shadow over the researchers on the third floor of Guyot, both Mark and Huub's considerable enthusiasm, together with Tony's own efforts at keeping research going as usual, helped much to keep a positive spirit among the geophysicists.

With Mark I have started to investigate how his approach to seismic tomography can be incorporated in the “Princeton” vision; the data he uses are complementary to ours. With him I have also started to revamp the Powerpoint approach to seismic tomography can be incorporated in the math department, I have been working at the testing of wavelet-based regularization algorithms for application I seismic tomography.

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Guust Nolet

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My two students, Yue Tian and Karin Sigloch, are close
to finishing a major effort at remeasuring seismic data from
the digital networks in the past twenty years. Existing
measurements of delay times and amplitudes were not suitable
for application in finite-frequency tomography. I expect this
to lead to a whole new suite of tomographic models of the
Earth in the next two or three years, starting with a P-wave
model that should make up the major part of Karin’s thesis
next year. With Yue, I have also been working at making
finite-frequency software sufficiently user-friendly for
distribution, thereby eliminating one of the major obstacles
for this theory – developed at Princeton and first applied
here – to become accepted widely. The success of this effort
is confirmed by the fact that one of the articles that resulted
from this, Montelli et al., Science, 2004, reached the number
two spot in ScienceWatch’s list of ten most cited papers in
the geosciences over the past two years, a rare distinction for
a paper in the field of solid earth geophysics.

Much of my own efforts in the past year have gone to the
writing of a new book on seismic tomography. In the Fall of
this year, I have taught most of the chapters in GEO558 and
I hope to finish the book by September 2007. On the basis
of a first draft, Cambridge University Press has already accepted
it for publication. During the writing I have obtained some
new results, but lack of time has so far prevented me from
writing these up in separate publications, and if that situation
does not improve I may end up leaving them simply in the
book.

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NAI for coring into deep permafrost in the Canadian Arctic
was funded in June, and I had six weeks to get a field team
on site. Despite transport difficulties, I did manage to get 4
investigators, including myself, to High Lake for 3 weeks, dur-
ing which we successfully captured 200 meters of permafrost
and subpermafrost core from Archean metavolcanic strata. We
were able to utilize core liners, fluorescent microspheres and
perfluorocarbon compounds added to the drilling water with
an HPLC pump during the coring. These protocols assured
us of being able to obtain high-quality cores for microbial
analyses and of being able to assess the level of contamination.
We were also able to obtain some moderately contaminated
samples of the subpermafrost saline water before the borehole
froze. Cores were processed on site in a cleaned, anaerobic
glove bag, and samples were sealed in vacuum canisters for
pore gas analyses, frozen in a -20°C freezer for DNA and lipid
analyses, and were sealed in Mason jars and kept in ice coolers
for activity measurements and enrichments. We were able to
obtain dry ice through shipments from Calgary, which permitted
us to transport samples back to the USA. Unfortunately,
new regulations from the Dept. of Homeland Security exacer-
bated our transport efforts, and many samples arrived unfrozen or exposed to air. From Princeton, the salvaged core samples were shipped out to five other investigators for characterization of their geophysical, microbial, and geochemical properties. At Princeton, $^{35}$SO$_2$ microautoradiography experiments are being performed to locate regions within the rock core that harbor sulfate reducing bacteria. These experiments are being performed at 4°C as opposed to the -6 to 2°C in situ temperatures.

Another good development for this research is the publication of a new amplification procedure last year known as Multiple Displacement Amplification (aka MDA). This has the potential of being much more sensitive than the PCR technique that is commonly utilized. Daniel McGown has been testing this procedure in our lab, and it appears to be successfully amplifying DNA from Lupin Mine filters for where no PCR product had been formerly derived. This was an important step forward for Daniel's thesis research, which is to perform environmental genomic analyses of the Lupin Mine subpermafrost saline water. With the ability to clone this amplified product, we can now use PCR to amplify specific genes, such as functional genes, to identify the metabolic capabilities of the subpermafrost community and, with our colleagues at LBL, obtain complete sequence data, perhaps yielding almost complete genome sequences for our low diversity and extremely low biodiversity environments. The MDA procedure will be essential for analyses of the core samples collected at High Lake, which, based upon prior experiences, typically yield no PCR product except from the contaminated portions. The use of this procedure requires extreme care in maintaining a DNA-free laboratory environment.

Our group has continued to focus upon methane as a potential biomarker for Martian life since the discovery of methane in the Martian atmosphere in 2004 by several investigators. This discovery led to a plethora of papers speculating on its abiogenic or biotic origin, including my own paper published this year in Astrobiology Journal. One thing that is certain is that the methane is emanating from the subsurface of Mars today, but whether it is related to the modern gully deposits is not known. No instruments are currently flight ready that are capable of performing C and H isotopic analyses of methane, which is critical to determining the origin of the methane. John Kessler, a postdoctoral research fellow in our laboratory, however, has succeeded in constructing a near-IR Cavity Ringdown Spectrometer (CRDS), which currently has a reproducibility of 0.03%, better than has ever been published for CRDS devices to date, and he has been measuring trace gases in the lab air. Now that he has obtained sufficient precision for Martian methane gas concentrations, he is modifying the instrument to measure the C and H isotopic composition of methane in the lab air, at which point he'll be ready to publish his first paper on the instrument.

The bad news is that NASA has cut funding for the NASA Astrobiology Institute, which means that our fourth and fifth year funding will be reduced from what was promised. As a result, John Kessler submitted two proposals to NSF equipment programs to acquire support to complete the development of the near-IR CRDS and to support a mid-IR CRDS using a Quantum Cascade Laser in collaboration with Prof. Clair Gmachl at PRISM, who is the Director of the MIRTHE Facility. NASA also eliminated support for their ASTID and ASTEP programs, which meant that the proposals we submitted this year concerning Planetary Protection of Martian Rovers are in limbo. Nevertheless, thanks to support from Princeton University and our IPTAI grant we were able to support an undergraduate, David Smith, to go to Kennedy Space Center this summer, where he tested the survivability of psychrotolerant aerobic bacteria on Mars by utilizing a Mars Simulation Chamber with the assistance of Dr. Andrew Schuerger of the University of Florida.

### The South African Deep Microbiology Project and NELSAM

The discovery by my former graduate student, LiHung Lin, of an environment in the deep subsurface of South Africa, which is dominated by one sulfate reducing bacterial species that has been sustained for millions of years by radiolysis of water and sulfide was published in *Science* this year. It was quite an achievement because it not only required DNA and S isotopic analyses of the fracture water, but also S isotopic analyses of the fracture mineralogy, the latter of which he performed as a postdoctoral research associate at the Carnegie Institute. This publication is timely as a recent review paper published in *Nature* citing LiHung's earlier papers on radiolytic reactions is proposing the same mechanism may be supporting deep subseafloor microbial life.

The DNA obtained from this same site was completely sequenced by the Joint Genomics Institute and the annotation that was completed this year indicates that it appears to represent the complete genome of one microbial species. This organism, which hasn't been successfully cultured and is the dominant species below a depth of 2 km in South Africa, represents a new genus of *Firmicutes* with genetic capabilities that are surprising when compared to what we thought were the characteristics of deep subsurface organisms. It is capable of both autotrophic and heterotrophic metabolisms, of $N_2$ fixation, and of chemotactic motility. In a manuscript that is almost ready for submission to *Science*, we are proposing to name this organism, *Desulforudis audaxviator*. It is the first complete genome assembled from environmental DNA and exhibits an incredibly low number of small nucleotide polymorphisms, which implies either a surprisingly low number of doublings in this ancient environment or a remarkably low mutation rate compared to ocean planktonic species. It also contains evidence of multiple lateral gene transfers including from Archaea and from viruses.

This year we completed coring and installing a packer in what has been named the DABFIO borehole hole located at 3.7 km depth in Tau Tona mine as part of an NSF funded project to monitor earthquake seismicity. This borehole will enable us to relate ongoing mining-induced seismicity activity to geochemical and microbial fluctuations and now represents the deepest site in the world for long term observation of subsurface phenomena. This was truly an international effort as the ICDP has paid for the acquisition of pristine cores from...
the site, the German government is supporting a group from Univ. of Potsdam to investigate changes in gas chemistry and the South African NRF is supporting our colleagues from the Univ. of Free State to run the site. Having the capability for long term in situ studies will hopefully lead to an understanding of some of the mysterious relationships we’ve been observing with spot samples over the past six years. In the coming year, we may have to modify the packer system because of the deformation that occurred in the borehole during the interval of time separating the completion of coring and installation of the packer. We will also be analyzing the cores for sulfate reducing activity and extracting and sequencing the DNA (again using the MDA methodology). In a related laboratory activity, Mark Davidson, my graduate student, has for the first time, successfully completed a retentostat experiment under thermophilic, anaerobic conditions using a model sulfate reducing bacterium that is phylogenetically similar to Desulfurococcus australis. The retentostat enables him to test the metabolic physiology of the organism under zero growth conditions, and thus represents a more accurate laboratory simulation of subsurface conditions than a chemostat experiment where growth is continuous. Once the packer system has been tested in South Africa, the plan is to set up an in situ retentostat experiment and monitor changes in the biodiversity and microbial community structure.

This year, in a trip to a Pt mine in South Africa, I was successful in recovering biofilm samples containing the star-shaped microbe that had been seen in samples collected four years ago. In January ‘07 we’ll try to determine the phylogeny of this organism. I also collected samples of some of the most bizarre biofilms I’ve ever seen from dripping boreholes.

I have been working with Bianca Mislowack to complete her Ph.D. thesis during several visits she made to my office over the past year. She has completed a manuscript that is ready for submission to Environmental Microbiology and which represents the first chapter of her thesis. We plan to submit this in early January ‘07. Her goal is to complete two more chapters during ‘07 and submit her thesis.

Deep Underground Science and Engineering Laboratory (DUSEL)

This year we completed the “glossy” report on DUSEL entitled DEEP SCIENCE: A Deep Underground Science and Engineering Initiative, which will be released in January ‘07. The two candidate sites for DUSEL are submitting their S3 proposals to NSF in January ‘07 along with a competing proposal from the University of Washington for a site located in the Cascades. One site will be awarded funds for further characterization and the development of a plan for construction, which will then be submitted to Congress for FY09.

The As Remediation Project (SERDP)

My laboratory technician, Eric Chan, successfully completed the laboratory phase of this investigation which demonstrated that As could be successfully removed from groundwater under sulfate reducing conditions and that the solid phase As was stable under aerobic conditions. This is being prepared for publication as we await the decision of SERDP to fund a field demonstration of our process in Florida this year.

Two-Year Bibliography

Refereed articles:


The overarching theme of my research is the question of what constitutes a dangerous level of climate change. More specifically, I have explored particular outcomes or impacts of climate change that might have important consequences for people and societies, and therefore could produce useful benchmarks for policy makers on an appropriate approach for limiting the greenhouse gas emissions that are causing warming. Specific studies have focused on the effect of warming on 1) Antarctic and Greenland ice sheets, 2) coral reef ecosystems, and 3) the nitrogen biogeochemical cycle. In each case, attempts are being made to use modeling, observations, and paleoclimatic data to provide bounds on the probability of various outcomes for given levels of warming. The most important outcome has been recognition that a warming in excess of two degrees Celsius is likely to lead to outcomes that would be widely recognized as dangerous.

More recently, I have begun to focus on the issue of decision making under uncertainty under expectations of future learning. I have developed the concept of “negative learning” which involves flows of errant information from scientists to policy makers resulting from a mismatch of decision and learning timeframes. We have employed a Bayesian decision model to explore the economic consequences of negative learning, which are substantial.

Major Research Themes, 2007 and 2008
My research will continue to focus on the West Antarctic and Greenland ice sheets, a global assessment of coral reef ecosystems, and construction of a nitrogen sub-model within the Geophysical Fluid Dynamics Laboratory’s Earth System Mode. In cooperation with GFDL, I am also catalyzing the development of a state-of-the-art ice sheet model. An area of expanding interest will be the development of new decision making models appropriate to global change problems, including the detailed exploration of “negative learning.” Of particular importance will be the development of new approaches to scientific assessment that minimize the impact of negative learning on societal decisions. The relation between negative learning and precautionary approaches to decisions will be explored within a formal framework, and particular case studies of learning will also be investigated.

Two-Year Bibliography

Unrefereed Articles, Reports, Meeting Abstracts
The Latest Myths and Facts on Global Warming (with James D. Wang), Environmental Defense, 2005.
Future of Sea Level Rise and the New Jersey Coast: Assessing Potential Impacts and Opportunities (with M.J.P. Cooper and M. Beevers) November 16, 2005.
Linked Regimes to Solve the Timing Problem for Global Warming (with A. Petsonk), Prepared for the conference on Nesting and Overlapping Institutions, Woodrow Wilson School, Princeton University, 24 February 2006.

Published books, chapters in books
These geological records show that the present is an unusual moment in the recent history of our planet. Superimposed on the global cooling that started some 50 million years (Ma) ago when polar temperatures were close to 10°C are periodic oscillations that were modest in amplitude up to ~3 million years but then started to amplify, culminating in dramatic fluctuations between prolonged ice ages that persisted for some 100,000 years, and brief temperate interglacials. (Variations in $^{18}$O in seafloor cores, the top panel, are a measure of polar temperatures.) Our species took advantage of the current interglacial – it started 10,000 years ago – to advance rapidly, from the invention of farming to industrial activities that are causing a rapid rise in the atmospheric concentration of greenhouse gases. This rise, the vertical upper bar in the lower panel which shows measurements from Antarctic glaciers, is occurring at a time when those concentrations are at a natural maximum. That it is also occurring in an era, the past 1 Ma, of great climate sensitivity, follows from the cause of the recurrent ice ages: very modest, periodic variations in the distribution of sunlight because of periodic variations in orbital parameters such as the tilt of the Earth’s axis. To anticipate what will happen next, it will be helpful to understand what had happened in the past.

Two sets of processes determine the climate variations described above. One associated with the drifting of continents (which affects the frequency of volcanic eruptions and hence the composition of the atmosphere) is mainly responsible for the long-term global cooling. The other is associated with the Milankovitch cycles, the periodic variations in sunlight. The global cooling affected the response to relatively constant Milankovitch forcing by introducing feedbacks at certain times. For example, the global cooling led to the appearance of northern glaciers around 3 Ma, bringing into play the ice-albedo feedback. (White glaciers reflect sunlight, thus promoting the growth of glaciers by depriving the Earth of heat.) This mechanism has been studied extensively in connection with ice ages, but many puzzles remain. One concerns the recent discovery that fluctuations in equatorial sea surface temperatures are highly correlated with, and lead by a few thousand years, those in global ice volume. Our research explores how changes in the oceanic circulation, and in interactions between the ocean and atmosphere, contribute to the tropical signature of the Ice Ages.

Equatorial sea surface temperature patterns depend on the winds and in turn influence the winds. This implies that interactions between the ocean and atmosphere amount to positive feedbacks. Their impact on the global climate is evident during El Niño episodes when the atmospheric concentration of the powerful greenhouse gas water vapor increases significantly. Sea surface temperature patterns depend critically on the subsurface thermal structure of the ocean, especially the depth of the thermocline, the interface between the shallow layer of warm surface waters and the much colder water at depth. El Niño corresponds to changes in the slope of the equatorial thermocline as in the sketch on the left (below). Changes in the spatially averaged depth of the thermocline, as in the sketch on the right, also alter sea surface temperatures, by means of entirely different (diabatic) processes that involve changes in the heat budget of the ocean.

A balanced heat budget implies that a decrease in the heat loss in high latitudes is accompanied by a decrease in the heat gain in low latitudes. The latter depends on the degree to which the depth of the thermocline allows cold water to rise to the surface. Hence a decrease in heat gain means a deeper tropical thermocline. A warming of the extra-tropical atmosphere does this directly. Alternatively, a freshening of the surface waters that decreases surface salinities and makes the water buoyant does this indirectly by inhibiting the meridional overturning of both the deep, slow thermohaline, and the shallow, swift wind-driven components of the oceanic circulation. The two components respond very differently: in one case surface waters cool in high latitudes; in the other case equatorial waters warm. A climate model can favor either response depending on its treatment of turbulent, diffusive, oceanic
processes, and of ocean-atmosphere interactions. Simulations of the Earth's current climate are insufficient to determine which models are realistic so that studies of past climates are of central importance for the understanding and prediction of future global warming.

The climate records in the first figure provide several stringent tests for climate models. One is related to conditions up to 3 million years ago when the equatorial Pacific was as warm in the east as in the west. El Niño was in effect a permanent rather than intermittent phenomenon. Another is the climate response to periodic variations in sunlight (the Milankovitch forcing) especially those associated with the tilt (obliquity) of the Earth's axis. Discrepancies between the observations and the simulations with climate models indicate a need for reducing uncertainties and eliminating inconsistencies in measurements, and a need to improve models.

For the past few years I have been studying earthquake physics observationally, theoretically, and most recently experimentally. The primary impetus for this work has been the advent of waveform cross-correlation as a tool for obtaining precise relative locations of microearthquakes. Because the number of earthquakes increases exponentially with decreasing magnitude, earthquakes near the detection threshold of existing seismic networks represent a potential wealth of data for both structural geologists and seismologists. A major impediment to exploiting these datasets has been that location errors are typically ~1 km, a value that exceeds both the earthquake dimensions (tens of meters for magnitude 1 events) and the length scales of significant structures within fault zones. By cross-correlating the seismograms of “similar” earthquakes (those with similar locations and focal mechanisms), it is possible to determine relative arrival times with errors that are less than one-tenth the sampling rate. From such measurements I and students and postdocs working with me have relocated many thousands of microearthquakes recorded by seismic networks in California and Hawaii. In most of our study regions we have reduced errors in relative location to meters to tens of meters for events separated by tens to hundreds of meters. This increased resolution allows us to image fault-zone structures that previously were invisible, and to obtain catalogs of many thousands of events in which relative location errors are much smaller than the earthquakes themselves. For studies of earthquake interaction, which can be conducted sensibly only in a statistical sense, such large numbers are essential and cannot be obtained from standard catalogs.

For the past year most of my research has been devoted to developing a theoretical understanding of earthquake nucleation, a spin-off of one of our ongoing projects designed to study the very asymmetric distribution of earthquake aftershocks in our central San Andreas fault catalog. The modern view of fault friction is that it depends upon both the fault sliding velocity and the evolving physical or chemical state of the fault surface, which together comprise the “rate” and “state” aspects of “rate-and-state” friction. Despite the fact that the standard rate-and-state equations have been around for over 20 years, their implications for earthquake nucleation on elastically-deformable faults (meaning any fault in the Earth, as opposed to small laboratory versions) have remained elusive. The interest in this topic stems from the fact that if nucleation occurred on large enough temporal and spatial scales, precursory signals could be detected and interpreted prior to damaging earthquakes. While the observational record in this regard has not been promising, there have been numerous suggestions of “nucleation events,” occurring on timescales of fractions of a second to hours before the main dynamic earthquake phase, that scale with the ultimate size of the earthquake.

It is sad but accurate to say that the constitutive laws for the evolution of the fault “state” are essentially empirical. Two versions are in common use. In one, termed the “aging” law, the fault state increases linearly with time when the surfaces are in stationary contact, but in the other, termed the “slip” law, the state does not evolve unless the surfaces are sliding. In the last decade the aging law has become the clear favorite of numerical modelers. We have, for the first time, succeeded in obtaining analytic expressions for the size and temporal evolution of the earthquake nucleation zone under this law. This has led to two significant realizations. First, nucleation near the base of the seismogenetic zone should take the form of an expanding crack that under some conditions would be detectable using surface instruments. Second, the

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Two-Year Bibliography
Refereed articles or book chapters:
aspect of this law that leads to such large nucleation zones (possibly hundreds of meters across) is an aspect that is not supported by existing laboratory friction experiments. Under the “slip” law, in contrast, nucleation takes the form of much smaller “pulses” that migrate in one direction only and that would be much less likely to be detected from the surface. Our analytic results allow this difference in behavior to be ascribed to the different responses of the fault surface to large, abrupt increases in sliding velocity as the edge of the nucleation zone sweeps by.

In fact, such “velocity-stepping” experiments have been a staple of the experimental community for decades, but these typically have been limited to jumps of a single order of magnitude, both because larger jumps are difficult to stabilize and because it was unclear that such large jumps would be geologically relevant. With Chris Marone at Penn State we have succeeded in stabilizing velocity jumps of 2 to 3 orders of magnitude, and find them to be clearly consistent with the slip law and inconsistent with the aging law. In addition, our work has shown that the “slide-hold-slide” experiments that captured the imagination of the modeling community as favoring the aging law really point to a failure of both laws. Future work with Chris Marone and Nick Beeler at the USGS will be designed to sort this out. The good news is that the failure of the slip law appears to be restricted to very low sliding speeds, so low that they might be only marginally relevant to nucleation.

Several recent discoveries of “new” kinds of earthquakes make this an exciting time to study nucleation. The first of these are quasi-periodic “slow” earthquakes in many subduction zones around the world, comparable to magnitude 7 earthquakes in terms of area, that reach slip speeds of only 10–100 times the background plate tectonic rate. The second is the close association of these events with “subduction tremor,” which apparently consists of large numbers of small earthquakes deficient in high-frequency radiation (and which plausibly represent just much faster, but still slow, earthquakes). Both the slow slip events and the tremor migrate at rates of 1–10 km/day. Our analytic results for the aging law provide a possible explanation for these periodic events, and our more general results represent the only existing model for interpreting the observed migration velocities. While this does not mean that our models are “correct” in any micromechanical sense, the increased understanding that comes with analytical results often transcends the precise form of the equations studied, and can be immensely useful in pointing out what sorts of studies (observational, experimental, and theoretical) are needed to get at the heart of the matter.

Two-Year Bibliography

Refereed articles:

Articles in press:
Pritchard, M.E., A.M. Rubin, and C.J. Wolfe, Do flexural stresses explain the mantle fault zone beneath Kilauea volcano?, in press.

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The most important research accomplishment of the past year was the publication of my book Ocean Biogeochemical Dynamics by Princeton University Press, which I authored together with Nicolas Gruber. One of the nicest compliments I have received on the book so far was from Wally Broecker who said: “A superb book. Goodbye Tracers in the Sea.” This has been a productive year for other research as well, with seven articles published as of the time of this writing, three of them in Nature; seven papers in press, one of them in Science and another in Nature; and three articles submitted. The new journal articles published and in press during 2006 can be categorized into three broad areas:

Ocean Biogeochemical Processes and Modeling (published references 1 and 3 and in press references 1, 2, and 7): I am particularly excited by the Deutsch et al. (in press) paper (reference 2), which describes a new global estimate of nitrogen fixation at the ocean surface. We demonstrate in this paper that fixation occurs in close association with areas of denitrification, which implies that negative feedbacks on the fixed nitrogen cycle occur on century rather than multi-millennial time scales. We conclude that major excursions of the ocean fixed nitrogen pool, such as have been suggested by some authors, are unlikely.

Modeling and Observational Constraints on Carbon Sinks (published references 2, 6, and 7, and in press references 3, 4, and 5): These papers represent the culmination of several long-term projects, aimed at understanding the global carbon cycle. Crevoisier et al. (2006; published reference 6) describes a new method we developed to estimate highly resolved terrestrial CO$_2$ fluxes over North America using new data being obtained as part of the North American Carbon Project (NACP). Mikaloff-Fletcher et al. (published reference 6 and in press reference 5) and Jacobson et al. (in
press references 3 and 4) describe our newest estimates of the air-sea CO$_2$ flux and our detailed examination of the implications of these air-sea fluxes for our understanding of terrestrial CO$_2$ fluxes. We demonstrate in these papers that there does not appear to be a CO$_2$ sink in the tropics, which was one of the few remaining places where it was still thought that there might be a CO$_2$ fertilization sink. The implications for the future growth of atmospheric CO$_2$ are huge, as all carbon models up to now have assumed that such a fertilization sink would make a major contribution to reducing the rate of atmospheric CO$_2$ growth in the future.

**Southern Ocean Circulation and Biogeochemistry** (published references 4 and 5, and in press reference 6): Understanding the critical role of the Southern Ocean in controlling ocean biogeochemistry and its carbon cycle is an ever-deepening interest to which I am planning to dedicate greater effort over the next few years, particularly as it looks like the US oceanography community may finally be returning their with major field research. Published reference 4 (Marinov et al., 2006) demonstrates that there is a clear separation in the Southern Ocean between regions that control the air-sea balance of CO$_2$ (confined primarily to high latitude regions of deep-water formation), and regions that control the return of nutrients from the deep ocean to the surface (lower latitude areas where Subantarctic Mode Water forms). In Mignone et al., (2006, published reference 5), we show that major differences in the representation of Southern Ocean circulation can be explained as resulting from differences in the representation of wind forcing and mixing in the ocean models. These differences have major consequences for the rate of CO$_2$ uptake estimated by these models. In Sarmiento et al. (in press reference 6), we examine how the Southern Ocean cycling of silicic acid and nitrate determines the deep distribution of these two nutrients.

As regards the future, many of the papers that were published this year, particularly those on ocean biogeochemistry and the global carbon cycle, represent the culmination of many years of research that has begun to reach closure. I have spent much of my time this fall planning and trying to obtain funding for the next years of research, which I hope to continue during my sabbatical next year. I recently heard from NSF that our latest proposal on Southern Ocean processes received high ratings and will be funded depending on what their budget finally turns out to be. Another proposal I submitted to NOAA to form a Climate Process Team (CPT) on Southern Ocean biogeochemical processes also reviewed well and will be funded if the budget permits. I am hoping to leverage the CPT project into a larger one with DOE support. As regards the global carbon cycle, my group is focusing now on the tropical carbon balance using satellite and other observations of CO$_2$, CO and CH$_4$. We have new support from DOE for our work in North America, but are trying to obtain support for our research on the tropics.

Finally, I have been exploring how we could develop a new set of models to predict the effect of global warming on fisheries. I am one of the leaders of a consortium of investigators who submitted a letter of intent to the North Pacific Research Board for a multimillion dollar project to develop a model for the eastern Bering Sea fisheries. Our letter of intent was well received and we are one of two teams who have been invited to prepare a full proposal. I am very excited by this project, as I suspect the impacts of global warming on fisheries will be very large and I believe we are in a position to make substantial contributions to our understanding of what these might be.

**Two-Year Bibliography**

**Books:**


**Refereed articles or book chapters:**


**Articles in press:**
Sarmiento, J. L., J. Simeon, A. Gnanadesikan, N. Gruber, R. M. Key, and R. Schlitzer, Deep ocean biogeochemistry of silicic acid and nitrate, Global Biogeochem. Cycles in press.

**Articles submitted:**
Dunne, J. P., J. L. Sarmiento, and A. Gnanadesikan, submitted.
A synthesis of global particle export from the surface ocean and cycling through the ocean interior and on the sea floor, Global Biogeochem. Cycles, submitted.

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My group members and I are focused on two distinct but complementary research goals. First, we use the isotopic composition of dissolved nitrogen species (such as nitrate (NO$_3^-$) and dissolved organic nitrogen) to provide integrative constraints on nitrogen cycle processes in modern environments, mostly in the ocean but also in terrestrial systems and the atmosphere. Second, we treat the past, as recorded in marine sediments and glacial ice, as an archive of natural experiments from which the underlying controls on the physical and biogeochemical fluxes of the environment can be determined; we study the past N cycle both in its own right and as an indicator of broader environmental change.

A unifying goal of this work is to understand the role of plant nutrients in the interaction between life and the environment. Two sets of questions, focused on the ocean, have most centrally motivated our studies:

The polar oceans are special domains in the ocean where the “major nutrients” nitrogen (N) and phosphorus (P) are not completely consumed by algal growth. What factors control the physical conditions and nutrient status of the polar surface ocean? Over the ice age/interglacial cycles of the last three million years, how have the characteristics of the polar ocean affected other regions of the ocean, atmospheric carbon dioxide, and climate?

What terms and rates compose the budgets of “fixed” (biologically available) N in the modern ocean, on land, and in the atmosphere? What are the sensitivities of the different inputs and outputs? How have the N budgets in these systems changed over climate cycles, and how have these changes affected the fertility of ocean and land? What has been the role of such changes in the global carbon cycle?

My research activities over the past year are summarized below under the following headings: (1) isotope method development, (2) laboratory studies of isotope discrimination, (3) studies in the modern ocean, (4) studies in the terrestrial biosphere, the atmosphere, and ice cores, (5) paleoceanographic studies, and (6) model studies of past ocean changes. My group’s body of work in these areas represents our effort to progress from the introduction of new measurements, to the development of the background information needed to make those measurements useful, to their application to important questions, and finally to a quantitative consideration of the findings in a broader environmental context. The citations below refer to manuscripts listed in the publications section of the annual review form.

**Isotope Method Development**
In 2006, we published a manuscript on our method for the removal of nitrite (NO$_2^-$) from aqueous samples [Granger et al., 2006]. Our goal for this method is to prevent this species from contaminating the isotopic analysis of nitrate (NO$_3^-$).
This method is particularly relevant to Granger's culture studies of denitrifying bacteria (see below), in which there were large accumulations of nitrite. However, it has also proven critical in the analysis of low-nitrate water samples from some regions of the surface ocean. Nitrite is unstable and converts partially to nitrate during its degradation. For this reason, this method is becoming an integral part of the water collection process at sea.

An on-line method for the coupled analysis of $^{17}\text{O}/^{16}\text{O}$ and $^{18}\text{O}/^{16}\text{O}$ of nitrate in natural waters, developed by Jan Kaiser and Meredith Hastings, is in press [Kaiser et al., in press]. This method couples our previously described method for nitrate $^{15}\text{N}/^{14}\text{N}$ and $^{18}/^{16}\text{O}$ analysis, which converts nitrate to $\text{N}_2\text{O}$ gas, with pyrolysis of the $\text{N}_2\text{O}$ to $\text{N}_2$ and $\text{O}_2$, allowing for $^{16}\text{O}/^{15}\text{O}/^{18}\text{O}$ determination of the $\text{O}_2$. $^{17}\text{O}/^{16}\text{O}$ is a useful fingerprint for atmospheric nitrate, and Kaiser's technique is orders of magnitude more sensitive than previous methods, allowing for extension of this analysis to a diversity of sample types and environments. An application of the method is described in a manuscript in review on the origin of atmospheric nitrate in Antarctica, first-authored by Joel Savarino of CNRS, France [Savarino et al., in review].

On the basis of previous work on dissolved organic N by Angie Knapp in our lab, collaboration among Moritz Lehmann, Ben Houlton, and Masha Prokopenko has resulted in the development of a high-sensitivity method for measuring the $^{15}/^{14}\text{N}$ of dissolved ammonium ($\text{NH}_4^+$). Data using this method are described in a manuscript in review first-authored by Houlton [Houlton et al., in review].

Also building upon Knapp's dissolved organic N method, Becky Robinson and Brigitte Brunelle have previously established, improved, and tested a new technique for the $^{13}/^{14}\text{N}$ of diatom microfossil-bound N, for paleoclimate studies [Robinson et al., 2004, 2005]. In 2006, Brigitte's first-authored manuscript, which includes a description of important improvements and an informative set of method tests, was accepted for publication [Brunelle et al., in press]. With Brunelle's updated protocol, we are producing more precise measurements than previously, reducing the amplitude of the signal that can be recovered from the sedimentary record.

**Laboratory Studies of Isotope Discrimination**

The utility of isotopic distributions in the environment is premised on knowledge of the magnitudes of isotope discrimination by individual biogeochemical reactions, which is most often gained through lab studies of cultured organisms. The focus of Julie Granger's thesis was on the isotope effects of nitrate-consuming processes, in particular, nitrate assimilation by algae (central to studies of nutrient supply and uptake in the surface ocean) and denitrification by heterotrophic bacteria (central to studies of the global ocean's input/uptake in the surface ocean) and denitrification by heterotrophic algae (central to studies of nutrient supply and consumption of nitrate-consuming processes, in particular, nitrate as a nutrient source). The focus of Julie Granger's thesis was on the isotope effects of nitrate-consuming processes, in particular, nitrate assimilation by algae (central to studies of nutrient supply and uptake in the surface ocean).

In 2006, we submitted a manuscript describing our first results with denitrifiers [Granger et al., in review]. In brief, the denitrifiers show remarkable similarity to nitrate assimilators with respect to N-to-O isotope coupling, with the exception of a strain that possesses only the auxiliary periplasmic nitrate reductase Nap. The $1:1$ N-to-O isotope coupling of normal respiratory denitrification provides a critical constraint for interpreting isotope distributions in the environment. While the expression of Nap is likely minimal in most environments, the finding of its unique isotopic behavior indicates the potential for computational chemists to test enzyme mechanism using coupled N-to-O isotope constraints. Finally, the results also offer mechanistic insight into the controls on the amplitude of the coupled N and O isotope effects of denitrification.

**Studies in the Modern Ocean**

The isotopes of nitrate represent a potentially powerful constraint on the internal cycling of fixed N in the ocean, with implications for ocean circulation and the carbon cycle. My strongest interest in this regard is in the supply, transport, and consumption of nitrate in regions of the polar ocean, the Southern Ocean in particular. Combined nitrate concentration and isotope data, interpreted with a numerical model, allowed Peter DiFiore to quantify the different physical mechanisms of nitrate supply, the rate of biological export production, and the isotope effect of nitrate assimilation in the Subantarctic Zone of the Southern Ocean [DiFiore et al., 2006]. Among other observations, DiFiore found that the isotope effect of nitrate assimilation is greater in the Subantarctic than in the seasonal sea ice zone of the Antarctic. Based on our previous culture work, we suggest that this is due to the limited availability of light in the Subantarctic, where summer mixed layers are deeper than in the Antarctic. These studies of the modern polar ocean provide needed constraints for our paleoceanographic studies [Robinson et al., 2005; Robinson and Sigman, in review].

Nitrate N and O isotope data are also contributing to our understanding of fixed N loss from the ocean. In 2006, Moritz Lehmann submitted his first-authored manuscript describing porewater nitrate N isotope analyses from Bering Sea basin and margin. This large data set and its analysis are a major part of our long-term goal to develop a mechanistic understanding of the expression (and under-expression) of isotoically fractionating N reactions in sediments and other media. This goal is central to the use of the N isotopes to constrain N budgets, in the ocean (e.g., [Sigman et al., 2005; Lehmann et al., 2005]) and on land (e.g., [Houlton et al., 2006]).

**Studies in the Terrestrial Biosphere, the Atmosphere, and Ice Cores**

Recent Ecology and Evolutionary Biology graduate student Ben Houlton has measured the isotopic composition of nitrate, dissolved organic N, and ammonium in cloud water, rainfall, soil extracts, soil water, and streams across a well-constrained rainfall gradient on the island of Maui. The resulting N isotope budgets for these forests indicate an important and rainfall-dependent role for denitrification in tropical systems [Houlton et al., 2006]. Associated with changes in the forest N budget across the rainfall gradient, we found a remarkably abrupt transition in the form of N fuel-
ing plant growth, from nitrate to ammonium with increasing rainfall [Houlton et al., in review]. The Maui gradient suggests that the plants in these forests are not so much driving the N fluxes as finding a solution for their N demand that is consistent with the redox-driven activity of soil microbes.

**Paleoceanographic Studies**

My collaborators and I continue to pursue the evidence for reduced vertical exchange (i.e. “stratification”) in the halocline-bearing polar ocean regions under colder climates of the past 3 million years. A major motivation for this focus is that the reconstructed polar ocean changes have the capacity to affect atmospheric CO$_2$ in the observed sense of its glacial/interglacial oscillation. In 2006, graduate student Brigitte Brunelle’s first-authored manuscript on ice age conditions in the Bering Sea of the Subarctic North Pacific, mentioned above with regards to its methodological advances, was accepted for publication [Brunelle et al., in press]. This paper reports diatom-bound N isotope and export flux proxy data indicating reduced nutrient supply from below during the last ice age, strengthening the case for a bipolar (Antarctic and North Pacific) increase in stratification during ice ages. These data constrain the cause for this change, which is under investigation, to a mechanism that applies to both of these regions.

**Model Studies of Past Ocean Changes**

We have recently begun to consider a physical mechanism for the apparent climate/polar stratification link mentioned above. This mechanism involves the reduced sensitivity of seawater density to temperature at low temperatures: in the case of a globally colder ocean, temperature gradients become less important in polar ocean density structure, reducing their opposition to the stratifying effect of the net atmospheric deposition of fresh water on polar ocean regions. Recent AOS postdoctoral researcher Agatha de Boer has used a general ocean circulation model to investigate this effect [de Boer et al., in press]. The results provide proof of concept for a direct effect of whole ocean temperature change on the rate polar ocean overturning. They also point to interactions among the polar regions of the different ocean basins. In a second manuscript, de Boer has demonstrated that the density/temperature effect described above fits into a common theoretical framework with the ocean’s response to changes in southern hemisphere winds and in low-to-high latitude water vapor transport [de Boer et al., in review]. She describes a “haline” end member state (where salinity has a dominant effect on the relative densities of the polar ocean regions), in which deep ocean overturning is weak and focused in the North Atlantic, and a “thermal” state, in which overturning is strong and distributed among the different polar ocean regions. The inter-basin interactions that she has described, when combined with other processes, have led us toward a more complete hypothesis for the role of polar ocean stratification in the Pleistocene cycles in CO$_2$ and climate [Sigman et al., in review].

**Two-Year Bibliography**

*Referred articles:*


In the past year I have made research progress on a few different fronts.

First, I have continued the development of algorithms for the automatic detection and discrimination of teleseismic earthquake phases onboard autonomous oceanic divers, and applied these to data collected by our prototype MERMAID float. My Princeton colleague Guust Nolet and myself published a paper with coauthors from the Scripps Institution of Oceanography on this topic in the Transactions of the American Geophysical Union (EOS). The main news to report was the discovery of a relatively small (magnitude 6) earthquake detected at a relatively large (about 5,000 km) distance by our hydrophone on one of its experimental runs. “Seismologists detect earthquake” could have been our title, but for obvious reasons we chose to focus on the more weighty consequences of this first very promising step. In “A future for drifting seismic networks” we describe how we believe that the next generation of seismic networks will be autonomous, and floating. Our technology has the potential to definitively address the coverage gap in whole-Earth seismic tomography by putting intelligent earthquake recorders afloat the two thirds of the Earth’s surface that are covered by oceans. Much of our progress in the coming years will depend on the continued involvement of the engineers at Scripps in what is at this point still only a small pilot study.

Even if we can’t get all of Scripps’s engineers’ attention all the time, I have shown that the development of intelligent algorithms to analyze earthquake time series fits right into a much wider scheme: that of earthquake early warning. My Princeton colleague Guust Nolet and myself published a paper with coauthors from the Scripps Institution of Oceanography on this topic in the Transactions of the American Geophysical Union (EOS). The main news to report was the discovery of a relatively small (magnitude 6) earthquake detected at a relatively large (about 5,000 km) distance by our hydrophone on one of its experimental runs. “Seismologists detect earthquake” could have been our title, but for obvious reasons we chose to focus on the more weighty consequences of this first very promising step. In “A future for drifting seismic networks” we describe how we believe that the next generation of seismic networks will be autonomous, and floating. Our technology has the potential to definitively address the coverage gap in whole-Earth seismic tomography by putting intelligent earthquake recorders afloat the two thirds of the Earth’s surface that are covered by oceans. Much of our progress in the coming years will depend on the continued involvement of the engineers at Scripps in what is at this point still only a small pilot study.

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In all of this, somehow the bulk of my research has still been concerned with the problem of studying “processes” (like topography, or the gravity or magnetic fields) that live on spherical surfaces, my fourth main area of interest. Much of the above involved “signal processing” – one-dimensional wavelet analysis, two-dimensional coherence analysis – a dirty word to some, but absolutely vital to answer the geophysical questions (listening to distant earthquakes in the oceans, measuring an earthquake’s magnitude before the main shaking comes in, studying the mechanical properties of the lithosphere) I have continued to be interested in. It is only logical, then, that I have wanted to get ready for the study of any such questions on the surface of the sphere, such as will be vital in the analysis of any data where the curvature of the Earth’s surface cannot be safely neglected, or, more generally, of observations made on other planets in the solar system (the latter mostly of global extent and made by satellites). “Spatiospectral localization on the sphere” is the name of this game, and, ever since Mark Wieczorek (of IPG Paris) and I started getting interested in this in 2003, I haven’t been able to quit playing it. My Princeton colleague Tony Dahlen (who is now rivalling me in not being able to get this out of his mind, I suspect) and I spent much of 2004 on a generalization of this so-called concentration (or Slepian’s) problem (the eponymous paper came out this year in SIAM Review, whose cover was graced by one of our figures), and much of 2005 and part of 2006 on one very particular special case. In this year’s paper “Spherical Slepian functions and the polar gap in geodesy” Tony and I “localize” spherical harmonic functions to the equatorial area between two equal-size polar caps. We thereby construct a natural basis for the analysis of global potential fields that have been measured at an altitude by satellites, in the presence of noise, but, more importantly, that are, as is commonly the case, suffering from “polar gaps” – small areas on the North and South pole without tracks and where no data has been collected. In a submitted paper called “Minimum variance multitaper spectral estimation on the sphere,” Mark and I use spherical Slepian functions to derive power spectral estimates and their error bars… and for the last few months Tony and I have been working on what we’ve provisionally called “Spectral estimation on a sphere.” The short title suggests that we think we’re “covering” this problem from all possible angles: I will report on this next year, when it should have been submitted for publication.

All of our work on this fourth subject has been theoretical (paired with numerics and the attendant extensive development of computer code, all of which I am making freely available on the Web), except for a first application about which Shin-Chan Han (now at NASA’s Goddard Space Flight Center) and Chris Jekeli from the Ohio State University, and myself, have submitted a manuscript entitled “Spatiospectral localization of global geopotential fields from GRACE reveals the coseismic gravity change due to the 2004 Sumatra-Andaman earthquake.” The title probably reveals it all, except my great enthusiasm for the direction our “esoteric form of signal processing” seems to have entered. GRACE is a pair of satellites that collects global data on Earth’s time-variable gravity field. GRACE data are noisy, and spherical, and collected at an altitude, over incomplete portions of the globe, and expressed in spherical harmonics… and from this we want to extract local information – about Earth’s changing mass balance due to the hydrological cycle, ocean currents, the melting of ice caps, anthropogenic factors, … and now also large earthquakes. That we are able to do this at all is in no small way dependent on spherical data analysis, and I expect that myself and my collaborators will continue to develop methods to do this ever better, in the next year and beyond.

Two-Year Bibliography

**Refereed articles:**


**Other miscellaneous publications**


I was on a one-year sabbatical AY2005-2006, spending six months as a Visiting Professor of Tectonics at Caltech and six months at the Ludwig Maximilians University in Munich. The stay in Germany was the first part of a total of one year of sojourn supported by an honorific award from the Alexander von Humboldt Foundation.

I have spent much effort on conference volumes associated with a July 2005 “International Conference on Theory and Application of Fault-Related Folding in Foreland Basins” that I organized. This 10-day conference included a logistically ambitious field trip for ~70 international experts to remote areas of far western China to observe many examples of actively growing anticlines, which was the phenomenon of interest to this conference. Two major collections of papers are in process: one is a Memoir of the American Association of Petroleum Geologists and the other a special section of the Journal of Geophysical Research. I am involved in many papers and with the editing. So many of my former students and friends are contributing that it could be considered a festchrift.

However, my main current focus is completing a major monograph on fault-related fold theory to be published by Princeton University Press. In addition, I have obtained a surprising result in critical-taper wedge theory which allows one to determine absolute fault strength from wedge taper data, independent of significant assumptions about material properties. This is an important contribution to the long-standing controversy over the strength of major plate-boundary faults. Results using this new theory indicate very weak faults in Taiwan, Japan, and the Niger Delta. Furthermore, this work shows that the upper crust is relatively strong, which raises the fundamental question of how a crust containing weak faults is able to be strong.

Two-Year Bibliography

Books:

Articles in press or submitted:
(with Li-Fan Yue and Jih-Hao Hung) Structural geology of a classic thrust belt earthquake: the 1999 Chi-Chi earthquake Taiwan (M7.6), Journal of Structural Geology, v. 27, 2058-2083, 2005.

Other miscellaneous publications:
(with Dengfa He) Guidebook for field trip in south and north Tianshan foreland basin, Xinjiang Uygur Autonimous Region, China: International Conference on Theory and Application of Fault-Related Folding in Foreland Basins, 78 pp, 2005.

Articles in press or submitted:


My research concerns the marine and global nitrogen cycle, using molecular and immunological probes for marine bacteria and bacterial processes (especially nitrification and denitrification), and measuring the rates of N transformation processes. We have ongoing research on 1) denitrification in several suboxic zones of the world ocean (Arabian Sea, Eastern Tropical North and South Pacific) and in Chesapeake Bay; 2) the genes involved in nitrogen assimilation by phytoplankton and the diversity of functional guilds of bacteria involved in the nitrogen cycle of aquatic systems; 3) genomic studies of nitrifying and denitrifying bacteria.

Microbes control many of the important biogeochemical processes that occur in the oceans as well as on land. They contribute to the trace gas cycles that influence climate; they utilize and produce nutrients that are involved in eutrophication; and they are even capable of cleansing the environment by degrading a vast variety of chemical compounds, both naturally occurring and anthropogenically produced. My research focuses on the nitrogen cycle and the microorganisms involved in transformations of inorganic and organic nitrogen in the ocean and in sediment environments. This research makes use of technical approaches that range from molecular biology to stable isotope biogeochemistry. The two main bacterial groups we study are the nitrifiers, autotrophs that oxidize ammonium to nitrite and nitrate, and the denitrifiers, heterotrophs that can respire nitrate in the absence of oxygen. The linked activities of these two groups can be crucial in determining the chemical form and supply of nitrogen to planktonic communities and in determining the net nitrogen budget of ecosystems.

A new project on phytoplankton nitrogen dynamics now makes the link between the carbon and nitrogen cycles explicit, by investigating the potential for N assimilation to control the composition of photosynthetic planktonic assemblages.

Ward lab has a web page where all of this is described. [http://geoweb.princeton.edu/research/ecomicrobio/ecomicrobio.html](http://geoweb.princeton.edu/research/ecomicrobio/ecomicrobio.html)

1. Denitrification and Anammox: In previous work (Granger and Ward, 2003), we showed that denitrification by cultured bacteria in the lab could be limited by copper availability, leading to the accumulation of denitrification intermediates in the medium. We hypothesized that copper availability in OMZs might be quite low, low enough in fact to limit denitrification at the nitrous oxide reduction step, thus leading to accumulation of nitrous oxide. We have now completed three major cruises in the last three years, one each to the three major oxygen minimum zones of the world ocean. Using chelators and various carbon and nutrient additions to manipulate the natural communities in trace metal clean incubations, we have shows that carbon is probably the most important limitation in these systems, that denitrification is very episodic (probably dependent upon C supply), and that Cu(I) rather than Cu(II), as had been supposed, is the Cu species available to microbes. The most interesting finding is the denitrifying bacterial assemblages appear to exhibit bloom dynamics, analogous to those observed in surface phytoplankton communities. In the early stages of denitrification, the assemblage is quite diverse, but is gradually dominated by a small number of phylotypes as denitrification intensifies. The implication is that most of the actual work of denitrification is performed by a small number of different types of microbes, depending on initial conditions and episodic carbon supply. Variable conditions probably ensure continued diversity in the background community. These observations provide an explanation both for observed patterns in oceanic denitrification and for the maintenance of diversity in functional groups.

Anammox (anaerobic ammonium oxidation) is a recently discovered step in the N cycle, that performs essentially the same role as denitrification. We have made some of the first measurements of this process in Chesapeake Bay, and in the OMZ regions of the ocean (Jeremy Rich). Contrary to the first reports by Danish and German investigators, we find the anammox occurs in both sediments and the water column, but is not the dominant process. We hypothesize that our methods, which were designed to minimize artifacts we perceived in the original methods, may be responsible for the different conclusions. This is a very controversial area in which we are keenly involved and plan to continue working; a new NSF proposal was recently funded to allow us to investigate the relative importance of denitrification and anammox in the Arabian Sea, avoiding some of the artifacts common in the methods used by others for the measurements.

2. Diversity of Functional Guilds: Molecular biological methods have revealed a truly incredible range of diversity in natural microbial assemblages, which now begs the question of whether this diversity matters to ecosystem function. We approached the problem first by assessing the diversity of important functional groups (e.g., denitrifying bacteria, nitrifying bacteria) and using the sequence database that we obtained to design DNA microarrays. The microarrays provide a high throughput method for community composition and activity (gene expression) analysis. Several array projects are moving forward, but publication has been slower than we had hoped. Array projects nearing completion include the study of nitrifying assemblages in Chesapeake Bay on the basis of amoA genes, seasonal and composition patterns in phytoplankton in the English Channel on the basis of nitrate
reductase and rubisco genes, and denitrifiers in Chesapeake Bay on the basis of nitrite reductase genes. We have recently succeeded in analyzing messenger RNA from sediments, not a trivial problem, and have therefore been able for the first time to evaluate differential gene expression by different members of the assemblage, using the microarray.

3. Economic Studies: We’ve been involved at a low level in the analysis of several nitrifier genomes and have had the genomes of two marine denitrifying isolates completed to draft stage. Although fascinating, this work is underfunded (agencies tend to support the actual sequencing, but not the analysis of the data!).

Two-Year Bibliography

Refereed articles:


Articles in press:


Articles submitted:


Song, B. K., E. Chyun, P. Jaffe and B. B. Ward, Molecular detection and quantification of uncultured dissimilatory arsenate respiring bacteria (DARB) in Chesapeake Bay sediments, *Microbial Ecology*.


