Guyot Science 2004
A Summary of the Research Progress and Accomplishments
Made by the Faculty Members of the
Department of Geosciences During the Year 2004

Last year, January-December 2004, was a year of transition for the Princeton Department of Geosciences. In June Jason Morgan retired from active service as a faculty member, after a distinguished 44-year career as a geoscientist at Princeton, and in July we were delighted to welcome the newest member of the geosciences faculty, Nadine McQuarrie. A second new faculty member, Adam Maloof, will join us approximately one year from now, following the completion of his postdoctoral fellowship at MIT. Nadine is a structural geologist who studies mountain building and other active tectonic processes, whereas Adam applies paleomagnetism and other tools to the study of the ancient earth. As usual, a number of geosciences faculty members received outside honors and awards in recognition of the excellence of their research. George Philander was elected a Member of the National Academy of Sciences, raising the departmental membership to four, and Bess Ward was elected a Fellow of the American Academy of Arts and Sciences, raising the departmental membership to three. Jorge Sarmiento was elected a Fellow of the American Association for the Advancement of Science; he is the first Princeton geoscientist to be so honored. Danny Sigman received the 2004 Macelwane Medal of the American Geophysical Union, which recognizes significant contributions to the geophysical sciences by an outstanding young scientist. Danny is the first member of the geosciences department to receive this coveted award; he also received a prestigious Friedrich Wilhelm Bessel Research Award of the Humboldt Foundation. François Morel will be the next recipient of the Maurice Ewing Medal of the American Geophysical Union and the U.S. Navy, “for his leadership in the revolution in low-temperature aqueous geochemistry that has resulted in a new field of studies at the interface between marine chemistry and biology.” Finally, Allan Rubin was elected a Fellow of the American Geophysical Union; this is a prestigious honor restricted to no more than 0.1 percent of the membership each year. More than half of the faculty members in the Department of Geosciences are now Fellows of the AGU. 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, 2003–2004, is appended to each narrative report.
The activities of my laboratory focus 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.

They 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; these models predict that there should be a relatively large maximum in the atmospheric $O_2/N_2$ ratio in air over the tropical Pacific.

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, and net production 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.

Supplementing the $O_2$ studies are studies of Ar. 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.

**Highlights of our research of last year include:**

1. Completing data interpretation and preparing papers summarizing the following studies:

   (a) Measurements of atmospheric $O_2/N_2$ variations since 1991, and their implications for land and ocean $CO_2$ sequestration (and its interannual variability). We show that the oceans take up twice as much $CO_2$ as the land biosphere between 1993-2002, and confirm previous conclusions that the land biosphere is a major $CO_2$ source during El Nino events. (paper in review)

   (b) The meridional gradient in the annually averaged $O_2/N_2$ ratio of air. This work, led by my former postdoc Mark Battle (Bowdoin College), finds that the gradient is similar to recent model predictions, with a large equatorial maximum due to ocean outgassing in the tropics. (paper still in preparation)

   (c) Studies of the isotope geochemistry of $O_2$ in the tropical Pacific. This paper, led by former postdoc Melissa Hendricks, shows that the triple isotope composition of $O_2$ in the tropical Pacific reflects rates of all the metabolic and water mass mixing processes relevant to regional carbon fluxes and the nutrient supply, which can therefore be quantified from the data. (paper in review)

   (d) Studies of the triple isotope composition of $O_2$ in surface waters of the Southern Ocean. This work, led by Matt Reuer, gives far more data than heretofore available on rates of net and gross production in the upper water column of the Southern Ocean, and show that rates of net and gross production increase to the north, contrary to our general understanding of controlling factors. (paper still in preparation)

2. Other significant developments:

   (a) Jan Kaiser’s instrument for continuously measuring the $O_2/Ar$ ratio along cruise tracks was deployed on two additional equatorial Pacific cruises. His extensive data set allows continuous estimates of net oceanic production and gives a great deal of new information about the regional variations in this rate, and factors controlling them.

   (b) Bruce Barnett has completed the 400 ka record of the triple isotope composition of $O_2$ based on analyzing trapped gases in the Vostok ice core. The preliminary interpretation is that photosynthesis rates of the global biosphere were about 15% lower during glacial times and vary strongly with ice volume and the atmospheric $CO_2$ concentration.

   (c) Makoto Suwa participated in an Antarctic expedition led by Jeff Severinghaus (Scripps) that advanced our understanding of the processes by which gases are trapped in glacial ice.

   (d) We have installed automated air samplers at nearly all of our air sampling sites; the last one will go in this coming March. We hope for a significant improvement in the quality of our atmospheric $Ar/N_2$ ratio measurements, in particular.

   (e) John Dunne has put the isotopes of O into his GFDL model of ocean biogeochemistry, a key step in quantitatively interpreting our data on this property.

   (f) Experiments with a postdoctoral fellow of Chuck.
Dismukes, Department of Chemistry, showed that less than 1 part in 105 of photosynthetic O₂ production is from bicarbonate; water is the main source.

(g) We have constructed a vacuum line for doing He/U dating of speleothems. Speleothems are emerging as the most exciting new climate archive, and He/U dating would allow us to study samples that are too old to be dated by current methods (> 400,000 years).

(h) We have established a collaboration with Dave Marchant, Boston University, to study samples of glacial ice from the Dry Valleys, Antarctica, that are believed to be as old as Miocene. These samples could represent a major new climate archive but it remains to be demonstrated that their gas records are properly preserved.

Two-Year Bibliography

Refereed articles:

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Last year in this report, I described the first success of my longstanding collaboration with Gust Nolet, to account for finite-frequency wavefront healing effects in global seismic traveltime tomography: the successful imaging of deep-mantle thermal convection plumes by then graduate student Raffaella Montelli. Raffa’s P-wave velocity images (Science 2004) show at least six well-resolved plumes — Ascension, Azores, Canary, Easter, 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. Raffa successfully defended her Ph.D. dissertation in September 2003, and has been working since that time as a postdoctoral fellow in the Department of Geosciences. In 2004 she has gone to invert S-wave traveltimes using finite-frequency sensitivity kernels, in order to provide an independent check on her very exciting P-wave results. In fact, Raffa’s recently obtained S-wave images confirm the presence of the six well-resolved deep-mantle plumes listed above, as well as the existence of 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. This strong confirmation of her earlier P-wave results is significant not only because the raypath coverage differs, but also because the off-path sensitivity of finite-frequency S waves is different from that of P waves.

Research on finite-frequency seismic tomography also proceeded on a number of other fronts in 2004. Graduate student Ying Zhou completed her Ph.D. dissertation project, in which she developed and 3-D sensitivity kernels for the measured phases, arrival angles, and amplitudes of waves that travel along the earth’s surface rather than through its interior. The off-great-circle sensitivity that is accounted for by Ying’s surface-wave kernels enables a significant improvement in the imaging and resolution of small-scale structural features in the upper mantle. Her upper-mantle S-wave velocity model, obtained by inversion of a relatively small global phase-delay dataset collected by Gabi Laske at the Scripps Institution of Oceanography, is comparable in quality to recent ray-theoretical inversions of much larger datasets, with denser crossing-path coverage. Ying has moved on to a postdoctoral position, working with Jeroen Tromp, at Caltech.

Third-year graduate student Tarje Nissen-Meyer has made substantial progress on his dissertation project, to compute exact waveform and traveltime sensitivity kernels in a background spherical earth model, using an axially symmetric spectral element method. The method should also 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 codes are required for the monopole, dipole and quadrupole components of the source. At the present time, these three source types have been successfully implemented in the simple case of an earth model lacking a fluid outer core. The next steps are to account for the core using a displacement potential representation, and to parallelize the code, for implementation on a small cluster.
My research program focuses on understanding the large-scale behavior of Earth and other planets through experimental study of geological materials directly under extreme pressure and temperature conditions. The study of planetary interiors is currently progressing rapidly as a result of observational advances including new three-dimensional images of the deep Earth. These new observations have the potential to answer fundamental questions about the Earth’s origin, evolution, and structure. Progress in this area is dependent on coupling the new observations with a detailed knowledge of the physical and chemical properties of the materials composing the region. We are using the diamond anvil cell together with laser-heating techniques to produce pressures and temperatures comparable to the deep mantle. Using these tools, we are exploring crystal structures, phase relations, elasticity, and other fundamental properties at ultrahigh pressure conditions. Some examples of current research projects are listed below.

**Elastic properties of minerals.** The elastic properties of minerals serve as a link between the observed seismic velocity structure of the Earth and its physical constituents at high pressures and temperatures. Elastic properties also provide insights into structure, bonding, and phase transitions. Brillouin scattering is a method whereby one can measure the complete elastic tensor by recording the frequency shift induced in scattered laser light by thermally generated sound waves. We have recently used this technique to investigate the elastic properties of a variety of upper mantle minerals to pressures corresponding to ~300-400 km depth. Global seismological and geodynamic models require an assessment of not only thermal effects on seismic velocities but also compositional effects. We have used this new data together with selected values from the literature to comprehensively

**Two-Year Bibliography**


evaluate the sensitivity of seismic velocity to composition, pressure, and temperature for major upper mantle minerals. As an example of the conclusions drawn from this type of study, we find that the very different responses of olivines and garnets to iron substitution gives rise to significant variations in the sensitivity of different rock types to iron concentration in accordance with their garnet content. Velocities in mid-ocean ridge basalts are thus much affected by variations in iron content than other rock types such as harzburgite.

**Crystal structures at ultrahigh pressures.** The recent discovery of a post-perovskite phase in MgSiO$_3$ may have profound implications for understanding the Earth's deep mantle and, in particular, the D" region near its base. Using the laser-heated diamond anvil cell, we investigate the physical properties of the post-perovskite (CaIrO$_3$-type) phase synthesized from a natural pyroxene composition with Fe content (9 mol.%) close to that expected for the lower mantle. Our measured equation of state is consistent with theoretical calculations for the Fe-free endmember, suggesting compressibility is not strongly sensitive to iron content. The transition pressure, on the other hand, is greatly lowered in iron content than other rock types such as harzburgite.

Two-Year Bibliography

**Books**


**Refereed articles:**


**Other miscellaneous publications**


How are mountains and continental crust made? These are the major questions 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 work in an interdisciplinary mode where the objective is to achieve results unattainable by individual investigators. I also continue to work on ways to help students use the power of making observations in the field.

Currently, my 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.

Batholiths
My biggest research commitment for the next five years is a new multidisciplinary collaboration 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.

The new project is located in the Coast Mountains of British Columbia. It is called BATHOLITHS. The name comes from the hypothesis that the formation of batholiths is a major factor in making typical continental crust. Our toolbox of techniques includes active and passive source seismology, geochemistry, structural geology, and petrology.

Bhutan
With my colleague Djordje Grujic at Dalhausie 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.

With my colleagues at the University of Texas, El Paso, I helped establish a temporary seismic network in Bhutan in order to determine the whole crustal structure under the Himalayas and in order to assess earthquake hazard potential. The network operated for a year and we are now interpreting the results. This includes rationalizing fault plane solutions with convergence of India against Asia and with geologic features exposed at the surface.

Lamellar magnetism
With the late Robert Hargraves, I worked on using properties of lamellar magnetism for interpreting discordant paleomagnetic inclinations of plutons in western British Columbia. We submitted a paper prior to Robert’s death; it was published in 2004. In the paper, we propose a solution to the origin of enigmatic paleomagnetic data pertaining to the on-going Baja British Columbia controversy.

Two-Year Bibliography
Referred articles:

Articles in press or submitted
Hollister & Grujic, Channel flow in Bhutan; submitted to Quarterly Journal of Geological Society of London.
Velasco and others. High seismicity rate in the Bhutan Himalaya determined from a temporary seismic network. GRL.
During the past year the 10-year-long research project on the Cretaceous-Tertiary boundary impact and mass extinction 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 current impact mass extinction scenario 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 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, La Recherche, Der Spiegel, Focus, Facts etc. and the Geological Society of London has sponsored a debate on my team’s work (Geoscientist, November, 2003).

Six documentary films have been made over the past year, including BBC Horizon (released in October 2004 in the UK), ABC, the History Channel, Swiss TV (released Nov. 24), The New York Museum of Natural History, (to be released May 2005) and TV interview with Alexander Kluge for German Film, TV and Media to be released in January 6 and February (2005).

A 2000 word summary of our results is published in the Geoscientist and can be downloaded at http://www.geolsoc.org.uk/template.cfm?name=NSG2349857238495

Two-Year Bibliography
Referred articles:

Other miscellaneous publications

Articles in press or submitted
My principal research interests include the structural and geodynamic evolution of mountain belts and orogenic plateaus. I use structurally based field studies, in conjunction with a variety geophysical and geochemical data sets to understand and quantify tectonic processes such as the growth and collapse of orogenic plateaus, development of fold-thrust belts, kinematics of continental collision, flow of the lower crust and the kinematics and dynamics of diffuse continental extension. Current projects I have been working on include: 1) how extension varies is space and time within the western United States over the last 36 m.y., 2) what controls the lateral extent of the Andean Plateau in Peru and 3) the interaction between erosion and deformation in fold-thrust belts both in Bolivia and Ecuador.

Basin and Range, Western U.S. The Basin and Range province of western North America is the classic example of large magnitude diffuse deformation. More is known about timing, amount, and spatial variations of extension within the Basin and Range Province than any other comparable region. Thus, the western United States is the best natural laboratory available to look at the driving forces behind large magnitude diffuse deformation such as the interplay between body and plate boundary forces. The critical body of data required to evaluate the dynamics of continental extension is the detailed kinematic history of the region of interest. Reconstructing the strain history of the province as a whole requires knowing both the extension rate and width of extending regions as a function of time. Although in some areas of the Basin and Range this information is very well known, the kinematics of the province as a whole is not. To reconstruct the strain history of the Basin and Range, I have created a GIS (global information systems) database of timing, magnitude and direction of extension for areas within the Basin and Range of North America in which the kinematics are well documented. This database is accessed by an ARC GIS script that sequentially restores the extension and allows me to determine possible extensional histories for areas that are not as well documented. The end results of this work are a series of palinspastic maps that show a sequentially restored Basin and Range from 36 million years ago to present. The data from these maps can be displayed in a variety of ways that highlight not only the areas where the reconstructions are accurate, but more importantly where the reconstructions are inaccurate (implying where more field-based data are needed). The maps can also be displayed as a movie that illustrates how extension varies with time and as velocity fields over 2-5-10 m.y. increments that can be compared to the modern GPS strain field.

This work has provided the background for two senior theses. Margee Prat is integrating the ARC GIS database of extension in the central Basin and Range with the NAVDAT (North American Volcanic) Database. The geochemistry of volcanic rocks in the NAVDAT data set is related to the lithospheric thickness at the time the rocks were formed. The palinspastic maps allow us to know where the rocks were located as they were erupting. Together these data sets have the potential to show how mantle lithospheric thickness has evolved with time in conjunction with crustal thinning. Richard Lease is conducting field research to constrain the amount and timing of fault offset in the Mojave portion of the Eastern California Shear Zone (ECSZ). The ECSZ is a region east of the San Andreas fault that accommodates a significant portion of the Pacific/North American plate boundary and has been the site of several large (M 6-7), recent earthquakes. The model suggests large fault displacements are needed in this region, but the geologic data to support model offsets are unavailable. Richard found a unique marker offset along the fault, which suggests 25 km of offset (15-25 km more than previous estimates).

Controls on orogen width. The formation of high elevation plateaus has been linked to a wide variety of processes including: shortening magnitudes, pre-existing sedimentary or structural architecture, plate convergence rates and directions, subducting plate geometry and climate. Although the Andes mountains extend over 8000 km along the western side of the South American continent, only the segment between 12° and 27° S houses a high elevation plateau. The 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 orogen width. One of the most abrupt along strike changes in morphology of the Andes is along the northern edge of the Andean plateau in Peru. Here 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. This west stepping, right angle bend in topography is mimicked in the structural evolution (i.e. stratigraphic erosion level) of lower Paleozoic rocks. This significant change in topographic and structural width provides a unique opportunity to evaluate the factors that govern the width of orogens.

This last summer I conducted a pilot field study along the northern border of the Andean plateau in central Peru. The goals of the study were to (1) evaluate road access and safety, (2) understand the level of rock exposure (quality of outcrops) especially on the wet, eastern side of the orogen, (3) decipher the Paleozoic stratigraphy, (4) make a pre-
liminary strip map across one of the proposed transects, (5) collect and evaluate quality of samples for thermochronology, and (6) establish collaborations with Peruvian Scientists. The preliminary data was incorporated into a collaborative NSF grant that was submitted to the Tectonics panel. My colleague and I proposed to evaluate the first order controls on plateaux formation through mapping lithological, structural, and erosional changes along four structural transects that cross the entire orogen, constructing modern, crustal-scale balanced cross sections, and quantifying the timing and rates of exhumation and erosion with low-temperature thermochronometry. Documenting the 3D kinematic history of the northeastern Andean plateau enables an evaluation of the relative importance of several features (climate, erosion, pre-existing stratigraphy, pre-existing structure and regional tectonics) that are commonly cited as exerting a major control on orogen width.

Interaction between erosion and deformation in fold-thrust belts. Quantifying the interactions of lithology, tectonics and climate on multi-scale morphologies of mountain ranges is at the forefront of current geological research. One of the central facets to this research is the magnitude of control climate and the associated erosion has on the formation development of orogens. Projects in both Bolivia (collaborative research with Dr. Todd Ehlers and graduate student Jason Barnes at University of Michigan) and Ecuador will use low-temperature thermochronometry, field-constrained structural analysis, and numerical models to delineate the kinematic evolution of the fold-thrust belts, and the impact of erosional variations on their formation. In Bolivia we have obtained preliminary cooling ages and structural data for balanced cross sections. During the following year we will integrate the cross sections in to 2-D MOVE (a cross section restoration program) that allows deformation to be forward modeled providing a quantitative description of the kinematics (displacement, velocity, velocity change) of fold-thrust belt deformation. The simulated velocity field will be the input into 2D and 3D thermo-mechanical models that link uplift and erosion to an evolving thermal field. This thermal history is used to calculate and predict apatite fission track and apatite and zircon (U-Th)/He sample ages. Numerical modeling allows a physically based evaluation of the plausible range of structural and erosion histories that could produce an observed suite of ages. Thus, our approach to interpreting thermochronometer ages is not to determine the solution that satisfies a set of observations, but rather the range of solutions.

In Ecuador our approach will be similar. Preliminary field work this summer in Ecuador allowed us to sample rocks suitable for low temperature thermochronology across a thrust sheet composed entirely of granite rocks. Although the thrust sheet contains no traditional markers to determine the amount of fault offset, we propose that a robust set of cooling ages can help limit permissible amounts of fault offset and provide insight to erosion magnitudes. If this is possible we will be able to use a suit of thermochronometers to describe the relative contributions of uplift, translation and erosion to the exhumation history of the Ecuadorian fold-thrust belt.

Two-Year Bibliography

Refereed articles:

Articles in press or submitted
and developed a model for uptake kinetics that reconciles all available data (Shaked et al. submitted). 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. in press). Superoxide is an extremely active radical (able to reduce and oxidize many solutes including Fe) but we have, so far, not been able to establish a physiological role for its production by diatoms.

**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. submitted). 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$_4$ 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. In a recent paper (Reinfelder et al. 2004) we have now provided strong supporting evidence for the C$_4$ pathway: i) specific inhibitors of the enzymes involved in the C$_4$ pathway effectively stop oxygen evolution under low (i.e., atmospheric) pCO$_2$; ii) addition of the C$_4$ intermediates drastically lowers inorganic carbon uptake but not photosynthesis; iii) the carbon accumulated in the cells in very short duration experiments is an organic rather than an inorganic compound as previously thought. 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 now studied the activity of this enzyme in the ubiquitous species Emiliana huxleyi and demonstrated that very small enzyme (and thus zinc) concentrations are necessary to provide the phosphate necessary for growth (Shaked et al. in prep). We have also shown that the activity of this extracellular enzyme is enhanced by association with the calcite laths of the organism. We are in the process of purifying and characterizing the enzyme.

**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. In fact 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 now obtained the full DNA sequence for this enzyme (the first Cd enzyme discovered), over-expressed it in a bacterial host, characterized its active center by X-ray spectroscopy and shown its induction upon Cd addition (Lane et al. submitted). 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. in prep.). These results make it now possible for us to design experiments that will test the presence and induction of this Cd–carbonic anhydrase in the field.

**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? New data on the concentration of mercury in tuna caught off Hawaii show that this concentration has not changed in thirty years. Mercury in tuna thus does not respond to the increase in mercury in the atmosphere and in the surface of the oceans caused by anthropogenic inputs (Kraepiel et al. 2003). We thus propose that methyl mercury in the open ocean may originate from the deep sea, perhaps from hydrothermal vents. An ongoing Bachelor thesis (April Brown ’05) indicates that methylation might be effected chemically by methane at high pressure and temperature. In terrestrial systems, we know that mercury methylation is effected by sulfate reducing bacteria. Our biochemical work with these organisms has shown that, contrary to what is commonly believed, the acetylCoA pathway is not necessary for Hg methylation (Ekstrom et al. 2003). We are now trying to elucidate what enzymes are actually involved in methylation and what control their activity.
Water is essential for the origin and survival of life on our planet and perhaps plays a pivotal 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 research projects and accomplishments in the last one year are provided below.

**Molecular Studies on Water and Aqueous Systems**

The goals of this research project are to evaluate H-bonding environment in liquid water, and how this modifies ion solvation and complex formation in aqueous solutions and at natural interfaces. Results from previous studies and collaborations have been published or to be submitted for a publication, and these are,

- H-bonding interactions in liquid water (J. Phys. 2002),
- Chemical state of ion-solvated water (J. Phys. Chem. 2003), and
- Dissolved ion influence on the H-bonding networks in bulk water (to be submitted shortly)

Experimental studies on the nature of solvated hydrogen and hydroxyl ions have been conducted and we are waiting for contributions from the ab initio calculations in interpreting the structural environments of these ions. My studies on water will continue, and the future emphasis will
be on the nature of water at the mineral-water interfaces as a function of water-film thickness and pH, and the nature of surface hydroxyls. We built a new synchrotron experimental chamber to conduct these studies both in vacuum and under ambient conditions. Using this new facility, we hope to understand hydration of mineral surface functional groups, and how surface hydration changes with variations in the composition of water films, and how this further modifies ion interactions at mineral-water interfaces. Michael Hay and Laura Harrington, graduate students in my group, will focus on these studies.

Our recent studies on solvation focused on the structure and speciation of Al$^{3+}$ in aqueous solutions. Aluminum is an important element that forms a majority of stable minerals in weathering environments. A majority of them are amorphous and nanocrystalline, whose chemistry is poorly understood. Although Al-speciation in aqueous solutions and precipitates is well studied using the NMR spectroscopy, variations in the structural environment of Al in these systems are not well understood. Using a combination of X-ray spectroscopy and NMR spectroscopy we are evaluating the variations in the chemical state of Al$^{3+}$ associated with these structural variations. This information is important in predicting the behavior of aqueous and solid phase Al in the weathering environments. Michael Hay, a graduate student in my group, and Juraj Majzlan, a former post-doctoral scholar in my group, are working on this project.

Iron (especially in ferric state), which is also an important rock forming element in terrestrial systems and an important nutrient to living organisms, follows the chemistry of Al closely. We are investigating the structure and chemistry of Fe$^{3+}$ in aqueous solutions and in precipitates. Since Fe$^{3+}$ exhibits stronger interactions with sulfate, and both of them occur together in several natural systems, our initial studies focused on Fe$^{3+}$-sulfate interactions. Our studies (a combination of infrared, Raman and X-ray spectroscopy) on these systems provided unequivocal evidence for the occurrence of H-bonding complexes of sulfate with Fe-oxyhydroxide polymers. These studies unravel the mystery of solution and solid phase speciation of Fe$^{3+}$ in acidic environments (Environ. Sci. Technol. In press). My former post-doctoral scholar (Dr. Juraj Majzlan) and one of the current graduate students (Laura Harrington) are continuing these studies, and the future emphasis will be on the understanding of the structural environments of soluble Fe$^{3+}$-polymers in aquatic and biological systems (e.g. ferritins).

**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 C, N, and S associated with the organic molecules, and their variation in the environment. For the past several years, my research group has been using and developing X-ray spectroscopy and specromicroscopy methods for studying the chemistry of natural organic molecules in their pristine state (Rev. Min-

• 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 (Science, 2002)

• Using haloperoxidase enzymes common to all soils and sediments, we have successfully halogenated plant materials. The products of these reactions are similar to those found in naturally weathered plant material, which implicates their role in extensive organohalogenation in the nature (Rachel Reina, M. Eng Thesis; Environ. Sci. Technol, 2004).

• Detailed speciation of organochlorines, conducted until recently, 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 are flavones (derived from weathering plant material), and xanthones (probably from the lichens). (Dr. Ashish Deshmukh, a post-doctoral scholar in my group, is conducting this investigation).

• We also found 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. (Jacqueline Hakala, a senior in my group, began this work. Alessandra Leri, a graduate student in my group, is currently working on this system).

• 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 Ca
is significantly affecting the sensitivity of X-ray spectroscopy methods in detecting the organohalides in all natural samples. However, we find that the reactions of inorganic iodine with organics are slow, and take about a week to reach equilibrium in laboratory microcosms. Rachel Zwilling, a senior in my research group, began this project this year and will submit a senior thesis next year.

To investigate the biogeochemical processes involved in organic molecule halogenation in soil systems and their rates in detail, we built two field stations in Pine Barrens (NJ) and in Princeton University campus. We are also monitoring the speciation of C, N, and S in organic molecules to evaluate the association of these elemental cycles with the Cl-cycle.

**Functional Group Chemistry of Natural Organic Molecules.** To understand the chemistry of complex natural organic molecules, we are investigating the functional group chemistry of small chain model organic ligands and their metal complexes in aqueous solutions and at the mineral-water interfaces (Geochim. Cosmochim. Acta 2004). Graduate students, David Edwards and Wei Jiang, are examining the chemistry of selected biomacromolecules (Langmuir 2004; Geochim. Cosmochim. Acta, In review); and Michael Hay and Dr. Deshmukh are investigating the types of carboxylic acid groups associated with biomacromolecules found in aquatic and soil systems using infrared, NMR, and X-ray spectroscopy methods. A summary of these studies are as follows:

- Carboxylic groups, which are important reactive groups in biomacromolecules, occur as aliphatic carboxylic acids, as opposed to the assumed aromatic carboxylic acids (such as salicylic acid). We also find that a majority of carboxylic groups have an electron withdrawing group on the adjacent C-atom (in the - and -positions), which makes the carboxyl group much more reactive and promotes the formation of strong complexes (chelates) with aqueous metals and mineral surfaces. This information is useful to predict the light scattering and water absorption characteristics of aerosols. I am also extending these investigations to evaluate the organic molecule composition and mineralogical variation of aerosols trapped in ice cores (in collaboration with Dr. Lonnie Thompson, Ohio State University). We began these studies very recently. We hope to obtain information on natural organohalogenes associated with the modern and ancient aerosols and their impact on the ozone depletion.

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

**Two-Year Bibliography**

**Referred articles:**


**Articles in press or submitted**


White SJO, Hay M., Marcus M., Lanzirotti A., Myhnen SCB. Constraints for sequestering CO2 in geologic formations (Submitted for consideration as a research article in Environ. Sci. Technol.).


With Raffaella Montelli and Tony Dahlen, we continued the exploration of the effects of finite frequency – introduced by us four years ago – into the imaging of the Earth's interior. An investigation of long period S, ScS and SS waves led to a spectacular confirmation of the earlier results that showed a number of mantle plumes reach deep down into the lower mantle. This finding has important implications for the geodynamics of the Earth, and I am exploring the consequences of that with Raffaella Montelli and Shun Karato (Yale). It seems that we are for the first time able to directly infer the speed by which plumes rise in the mantle, that we can put constraints on the lower mantle viscosity and it also seems likely the lower mantle is enriched with a heavy element, probably iron. With Nick Arndt (Grenoble) and Claude Herzberg (Rutgers) we are exploring the consequences of the observed plume temperatures for the petrology of ocean island basalts.

Also with Raffaella Montelli, we put the parameterization of tomographic models on a surer footing in the theory of nonlinear optimization. We are now able to adapt the node density of models to the local resolution.

With Frederik Simons and Jeff Babcock (Scripps), we did a second test of the MERMAID diver, designed to record earthquakes while floating autonomously at a depth of 1000 m or more in the oceans. We were able to recognize clearly the signal of a magnitude 6.1 earthquake at teleseismic distances. This is a great success, and we hope to use it to obtain funding for further development of this prototype. Though Simons has left Princeton for a faculty position at UC London, he will remain strongly involved.

Karen Sigloch has completed and perfected new software to measure arrival times and amplitudes of complicated P and S waves from shallow earthquakes. She is ready to start applying this.

See geoweb.princeton.edu/people/faculty/nolet/research.html for up-to-date information on equally interesting as well as less spectacular results.

Two-Year Bibliography
Referred articles:

Articles in press or submitted
During the spring I also organized and ran a seminar series on Extrasolar Planets and Astrobiology with some support from our department. The seminar primarily tapped faculty and research staff from Princeton and Rutgers universities who were actively involved in many facets of this topic from mass spectrometers for Mercury to deep sea robotic vessels.

During the reunions, I joined engineering faculty (Kasdin) and astrophysics faculty (Turner) in a 1 hour presentation to the alumni on searching for life in the universe. During the spring and summer I worked with Ed Turner (AST) primarily and with Laura Landweber (EEB), Chuck Dismukes and Ed Stiefel (Chem) on a proposal to the Sophomore Initiative for a new sophomore level course in Astrobiology called Life in the Universe (GEO/AST/EEB 255). The proposal was funded. We used most of the funds to support a field trip to Yellowstone National Park and to cover the acquisition of a telescope and microscope. The department kicked in additional funds for a digital camera that can be mounted on the microscope. As a result we now have a field microscope with sufficient resolution to image microbes that can be used for other GEO and PEI courses. I also organized the syllabus, selected the texts, organized the field trip, taught 6 of the 24 lectures, graded the mid-terms and field notebooks and developed and graded four problem sets.

The intention of the spring seminar series, the presentation to the alumni and GEO/AST/EEB 255 course was to determine the level of interest among the Princeton University students, faculty and alumni in the topic of astrobiology. The response to all three venues has been very enthusiastic and has convinced Turner, Kasdin and I to pursue submission of a proposal to Provost for the support and development of Princeton University Planets and Life Institute. This institute would foster interdisciplinary research in the areas related to the search for extrasolar planets and exobiology and the origin of life. It would provide certificates in Astrobiology to undergraduate and graduate students. Proposals to NASA for the Terrestrial Planet Finder Mission Science Center and to NASA’s Astrobiology Institute would be among the principal funded initiatives. If the former is successful, then a new building would be required to house the institute in order to support the ~100 FTE’s required to process the satellites data.

Over the past year as part of our IPTAI astrobiology effort we performed a reconnaissance of an arctic Au mine, Lupin Mine, that accesses brine situated beneath 500 meters of permafrost and rock. The geochemical and microbial analyses from the survey revealed conditions that indicate it represents the most accessible, Mars-like environment on Earth. The subpermafrost brines are rich in methane and with the discovery of methane in the Martian atmosphere this past year, makes the site even more relevant to Mars exploration. The investigators involved in research at this site will be gathering this January to share the results of this first reconnaissance and plan a drilling campaign for this coming spring. The lead IPTAI investigator, Prof. Pratt of Indiana University, and I are preparing a proposal to the NAI to support the drilling. This campaign will be the first of several designed to develop the technology required for locating subsurface brines beneath deep permafrost on Mars, for retrieving samples of permafrost and brine with little organic or microbial contamination, for performing life detection experiments on these same samples in the field or in the borehole and to determine how sensitive the organic and inorganic constituents are to the thermal histories that Martian samples will be subjected to upon their return from Mars be robotic craft. It is anticipated that such a mission would take place in the 2013-15 time frame and none of the technology required has reached flight capability as of yet. No progress was made on the development of a down hole instrument for life detection as this was not supported by Princeton University for an MRI proposal. IPTAI is, however, planning to submit a proposal to NASA’s ASTEP Astrobiology Science and Technology Engineering Program in July 05 to initiate this activity. We have also developed a proposal to NASA’s ASTID, Astrobiology Science and Technology Instrument Development, program for perfecting the means of contaminant removal on the surface of Mars by Mars rovers that will be submitted later this year.

During the past two years I developed the concept of free energy flux or FEF in calculating the maximum amount of energy available to microbial cells for the production of ATP (published in Onstott, 2004). This simple calculation combines the concentrations and diffusivities of gaseous and aqueous geochemical species determined for the environment with ~80 microbial redox reactions to determine which microbial phenotype should be dominant in that environment. This calculation for the first time effectively couples the geochemical characterization of the environment with the phylogenetic characterization from analyses of the environmental DNA using the 16SrDNA gene. In applying this approach to the results from ~200 sites in South Africa I observed that the biodiversity and phenotype predicted by the genetic analyses was comparable to that predicted by FEF analyses. Surprisingly, however, the magnitude of FEF increased with depth while the biomass diminished. In other words, the deeper you go in the crust the greater the bioavailable energy and the less the microbial biomass. Furthermore, the FEF is so high that it is unsupportable over the 10’s of...
million year lifetimes of the environments we sampled in South Africa. This apparent contradiction in observations may be due to one or all of the following possibilities:

1. Most of the biomass is located within the rock matrix and not within the fissure water and energy substrates are slowly diffusing from the fissure water into the rock matrix.
2. Most of the biomass was recently introduced into the environment by mining activity (which is not consistent with the gaseous geochemical results or the DNA of the mining contaminants).
3. Most of the gaseous and aqueous geochemical constituents were recently introduced into the fractures by mining activity or specifically due to fracture propagation into the rock matrix.
4. Some other factors inhibit the utilization of the abundant energy resources by the organisms within this environment.

Recent analyses of core samples retrieved from 2.0 kmbls in South Africa by my graduate students, Mark Davidson and Bianca Mislowack, do not support the first possibility. DNA analyses of these rock cores are in progress to further test the second possibility. The third possibility is consistent with the observed elevated concentrations of energy nutrients within the rock matrix, but we have no direct observations that fracture propagation leads to enhanced fluences of energy substrates into the fracture or whether microbial communities are affected by such fluxes if they occur. For this reason we submitted a proposal to NSF in conjunction with geophysicists interested in monitoring crustal seismicity in South Africa to core across an active fault zone at a depth of 3.7 km. The boreholes resulting from this activity would be instrumented not only with motion detectors and strain gauges, but one borehole will be devoted to monitoring gaseous and aqueous geochemical fluctuations and changes in microbial communities during a magnitude 3-4 earthquake that is anticipated along the fault zone during the next 2 years of mining operations. This NSF proposal was successful and plans for development of the site during the spring of ’05 are underway. The observations obtained from this site will hopefully provide conclusive evidence regarding the third possibility. To examine the fourth possibility, my graduate student, Mark Davidson, has been developing a “retentostar” the low metabolic activities and growth rates in an apparently nutrient rich environment are reproducible in the lab. This device will enable him to monitor the population density and genetic composition of a thermophilic sulfate reducing bacteria under in situ conditions as he alters the nutrient flux.

The maximum extent to which the biosphere penetrates the crust is presumably based upon the maximum temperature limit for life, currently 123°C for laboratory isolates. The general perception based primarily upon the absence of petroleum biodegradation in reservoirs above 80°C is that hyperthermophiles do not exist in the subsurface. Their absence is attributed to the lack of sufficient energy resources to maintain cell integrity at such high temperatures. Our results on the energy flux in South Africa do not support such a presumption. The search for hyperthermophiles in the deep subsurface, however, requires access to samples with in situ temperatures of ~100°C. For this reason we submitted a proposal to NSF’s Earthscope Program to obtain microbial samples from the San Andreas Fault where drilling and coring at depths of 3 kilometers accesses rock and fluid at such temperatures. This proposal to NSF is still pending but results based upon samples collected by Mark Davidson during the stage 1 drilling appear promising. If funded, this research project, the monitoring program in South Africa and a project being carried out by my former graduate student, Li-Hung Lin, in Taiwan where they are coring into an active fault zone will be the first projects to examine the relationships between tectonic activity and subsurface microbial density, diversity and activity predicted by my former graduate student, Hsin-Yi Tseng in 1996.

My interactions with the SAFOD program and our development of a drilling program for the Canadian permafrost environment have reinforced my perception, one shared by many of my colleagues, that many subsurface processes cannot be adequately characterized by boreholes drilled from the surface. Subsurface processes operate at spatial scales ranging from microns to 100’s of meters and time scales of minutes to years. In performing deep subsurface experiments using kilometer long boreholes it is virtually impossible to examine the short time and length scale mechanisms. To do so would require having a deep underground cavity from which several km3 blocks of crust can be characterized and instrumented in 4D. Such an experimental cavity can only rarely exist within operating mines because they require years of dedicated time and isolation. For these reasons we have joined forces with the high energy physicists and astrophysicists that have been developing a proposal for a program within NSF funded at the congressional level for a Deep Underground Science and Engineering Laboratory (DUSEL). Currently I am one of six P.I.’s (3 physicists and 3 earth scientists) supported by phase 1 of an NSF program to select a site and fund the installation of the DUSEL. Our role at this initial phase of the projects is to promote the concept to our communities and hold workshops to develop the infrastructure requirements, the priority experimental clusters and monetary requirements for DUSEL. The factors will be used by NSF to select from among 6 candidate DUSEL sites.

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Two-Year Bibliography
Refereed Articles:
The West Antarctic Ice Sheet and Long Term Climate Policy (with R.B. Alley), Climatic Change, 64, 1-10, 2004.
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Two-Year Bibliography
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Response (to comments on, On past temperatures and anomalous late-20th century warmth, with 12 co-authors), Eos, 84, 473-4, 2003.
Published (or in review) chapters in books:

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Two-Year Bibliography
Books
Our Affair with El Niño (How we transformed an Enchanting Peruvian Current into a Global Climate Hazard) Princeton University Press, 2004

Refereed articles:

On past temperatures and anomalous late-20th century warmth (with 12 co-authors), Eos, 84, 256-8, 2003.
Response (to comments on, On past temperatures and anomalous late-20th century warmth, with 12 co-authors), Eos, 84, 473-4, 2003.
Published (or in review) chapters in books:

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Two-Year Bibliography
Books
Our Affair with El Niño (How we transformed an Enchanting Peruvian Current into a Global Climate Hazard) Princeton University Press, 2004

Refereed articles:


Other miscellaneous publication

Articles in press or submitted:
Because the number of earthquakes increases exponentially with decreasing magnitude, earthquakes near the detection threshold of a given seismic network represent a potential wealth of data for both structural geology and seismology. A major impediment to exploiting such datasets in the past 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 post-docs working with me have relocated many thousands of microearthquakes recorded by the USGS Northern California Seismic Network. Errors in relative location are only 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. The most impressive of these structures are the slip-parallel “streaks” of seismicity, up to kilometers in length and as little as 100 m and 10 m in height and width, that seem to be ubiquitous along creeping faults in central California.

The high-precision catalog also allows us to study earthquake interaction on an unprecedented scale, resulting in new and surprising insights into the mechanics of rupture. Because of the obvious implications for seismic hazards, geologists have long asked how earthquakes stress or de-stress the nucleation zones of potential future earthquakes. However, location errors previously restricted such studies to earthquakes larger than magnitude 5 or 6, of which only a modest number exist in any given region on a timescale of a few decades. We now have a catalog of many thousands of earthquakes with errors in relative location that are a small fraction of the rupture dimensions. Because these are mostly magnitude 1-3 events each may have only a few (or zero) catalogued aftershocks, but by “stacking” all the aftershocks robust statistics are easily obtained.

Along the NW-SE trending San Andreas fault in central California, we have found that the nearest aftershocks of microearthquakes are nearly three times more likely to occur to the northwest of the mainshock than to the southeast. This asymmetry disappears for mainshock-aftershock distances larger than about twice the mainshock radius, and for mainshock-aftershock time lags greater than ~1 day. For a vertical, planar fault in a homogeneous medium there is no mechanism for generating such asymmetry. However, there is a 10%-20% contrast in seismic velocity across the central San Andreas fault, with the North American rocks being the slower. This introduces a symmetry-breaking heterogeneity, to which we ascribe the asymmetry in aftershock occurrence. Consistent with this, the nearby Calaveras fault exhibits essentially no across-fault velocity contrast and no aftershock asymmetry.

Over the last year we have pursued this topic using both numerical models and additional observations. On the numerical front, we have been modeling elastodynamic ruptures on an interface separating differing materials. Such models demonstrate a pronounced tendency for the ruptures to propagate preferentially in one direction, that being the direction of motion of the more compliant rocks abutting the fault (for the San Andreas this would be the SE-moving North American plate located to the NE). The cause is a large reduction in fault-normal compression near the SE-propagating rupture front, an effect that is absent in a homogeneous body. While this result is not new, no previous modeling efforts have been directed toward understanding what happens when such ruptures stop. This is the central issue for understanding the aftershock asymmetry, and this asymmetry remains the best observational evidence to date of an effect of a material contrast.

We have identified two processes that could be responsible for the dearth of aftershocks to the SE. First, as the SE-propagating front is slowed and stopped by a barrier, for a wide range of conditions a slip “pulse” detaches from the main rupture and continues to the SE before dying. This slip pulse “smooths” the stress field and leaves the region immediately to the SE of the rupture farther from failure than the region immediately to the NW. Second, as the slip pulse dies, the propagating pulse of reduced normal stress that sustained it continues along the fault. Conceivably, this pulse could trigger slip on any patch of fault close enough to failure to otherwise have produced an aftershock, making it instead part of the mainshock.

These models have identified an additional observation that could help constrain the modeling and distinguish between the above scenarios. As the rupture front slows and stops, the region to the SE experiences its peak stress essentially instantaneously (with the arrival of the local normal stress reduction), while the region to the NW must wait until the stopping phases from the opposite side of the rupture arrive. This introduces much larger delays for potential “immediate aftershocks” located to the NW. No aftershocks triggered by stress waves arriving from the mainshock can be identified by the seismic network, because their signals would be buried in the mainshock coda. However, the signature of any such aftershocks is still present in the archived waveforms. Because the waveforms of both mainshocks and aftershocks would be essentially identical to those of other nearby earthquakes, it is possible to identify the aftershocks by
The primary focus of my research is on the global carbon cycle, with particular attention to the role of the ocean in controlling atmospheric carbon dioxide levels. My recent publications can be categorized into three broad areas: (1) modeling and observational constraints on ocean and land carbon sinks for anthropogenic carbon; and (2) stabilization of atmospheric carbon dioxide; (3) ocean biogeochemical processes and modeling. Each of these areas is discussed below, with attention primarily to papers published during 2004.

**Modeling and Observational Constraints on Carbon Sinks** One of the major research directions that my group has taken in the past years is estimation of the magnitude, spatial distribution, and temporal variability of carbon sources and sinks by inverse modeling of atmospheric and oceanic CO2 observations and by evaluation of models with the major new data sets that were gathered by global surveys during the last decade. This work has culminated during the past two years in several papers that converge on an estimate for the oceanic carbon sink of $2.0 \pm 0.4$ Pg C yr$^{-1}$ for the 1990’s (e.g., Gloor et al., 2003; McNeil et al., 2003; Matsumoto et al., 2004; and Jacobson et al., in preparation). The uncertainty is half that which we would have given for the oceanic carbon sink estimate a decade ago. My group is now working hard to explore the implications of this oceanic constraint for our estimates of land carbon sources and sinks. A paper in preparation by Jacobson et al. suggests that the large CO$_2$ fertilization sink postulated to exist in the tropics might in fact be nonexistent. The absence of this CO$_2$ fertilization sink has major negative implications for the future growth rate of atmospheric CO$_2$.

**Stabilization of carbon dioxide.** We wrapped up several projects on enhancing the uptake of anthropogenic carbon by the ocean either by iron fertilization or by deep-sea...
sequestration. Gnanadesikan et al. (2003) examined a new scenario for iron fertilization that involves small-scale patch fertilization. We found that patch fertilization was extremely inefficient (only a tiny fraction of the organic carbon exported from the surface ocean comes from the atmosphere) and probably impossible to verify due to the small size of the signal relative to natural variability. Irina Marinov’s Ph.D. thesis completed in December of 2004 examined the fundamental processes that control the air-sea balance of CO$_2$ and how removal of nutrients might affect biological production in lower latitudes. Mignone et al. (2004) examined deep sequestration of carbon, with the main emphasis being on how the large differences in ocean circulation models lead to correspondingly large variations of a factor of 2x or more in sequestration efficiency. Edmonds et al. (2004) used a combination of integrated assessment and carbon cycle models to examine some of the major issues that would need to be resolved in order to stabilize atmospheric carbon dioxide.

**Ocean Biogeochemical Processes and Modeling.** My research in this area has two major goals, the first being to develop an understanding of what controls ocean biogeochemistry, and the second related goal being to develop the capability to predict the response of ocean biogeochemistry to climate change. The major accomplishment of 2004 was the final completion of the textbook I have been working on for 10 years (Sarmiento and Gruber, *Ocean Biogeochemical Dynamics*, in press, Princeton University Press). The book will likely appear in early 2005. Another important milestone was the publication in *Nature* of Sarmiento et al. (2004), which describes a major new insight about how nutrients are returned from the deep ocean to the main thermocline. This supply of nutrients to the thermocline of the world ocean, which occurs by formation of Subantarctic Mode Water, appears to be responsible for about three-quarters of the biological productivity in the global ocean to the north of the Southern Ocean.

As regards the development of a prediction model, over the past few years, my group has collaborated with GFDL to develop and test a new model of ocean biogeochemistry, including iron delivery by dust from the atmosphere (Gao et al., 2003) and ecosystem models for biological production and export of organic matter from the surface of the ocean (e.g., Gnanadesikan et al., 2004). Meanwhile, I undertook an independent study to analyze 6 global warming predictions of the next century from which I hoped to be able to infer how biology might change in response to global warming. As part of this study we developed a new empirical modeling approach to predict ocean biology and applied it to the climate warming simulations from the 6 models (Sarmiento et al., 2004, Global Biogeochemical Cycles).

My group participated in an ocean carbon model inter-comparison study (OCMIP), results from which are now starting to be published (Watson et al., 2003; Doney et al., 2004; see also Matsumoto et al., 2004). I also was asked to write two overview papers on modeling ocean biogeochemistry, which I wrote with two members of my group (Greenlatt and Sarmiento, 2004; Marinov and Sarmiento, 2004).
In order to develop a predictive understanding of the Earth’s environment, new disciplines have arisen that seek to be quantitative in both measurement and theory. Biogeochemistry represents one such discipline, in which environmental processes are generalized and abstracted in terms of underlying chemistry and elemental mass balance. To succeed, biogeochemistry and related disciplines must overcome two fundamental challenges. First, the environment is spatially and temporally complex, obscuring integrated fluxes. Second, it is exceedingly difficult to quantify the sensitivities of biogeochemical fluxes to the point of developing a predictive understanding of how the fluxes interact. Much of my research has involved the development of subject-specific solutions to these broad challenges. With regard to the first, I have advanced the use of the isotopic composition of dissolved N species in the ocean (nitrate ($\text{NO}_3^-$) and dissolved organic N in particular) to provide integrative constraints on N cycle processes. With regard to the second, I am among those who treat the sediment record as an archive of natural experiments from which the underlying controls on the N cycle can be determined; I seek to derive information from the N isotopic composition of sediments and organic matter bound within sedimentary microfossils.

Laboratory studies of biological transformations of nitrogen. Ongoing studies in my lab and in collaboration with graduate students Julie Granger and Joe Needoba from University of British Columbia make use of laboratory culture experiments to characterize the isotope discriminations caused by specific biological transformations of nitrogen. This is a necessary starting point for isotope studies of the environment, and it has also yielded insights into the transformations themselves. Measuring the changes in N and O isotope composition of nitrate in the medium of growing algal cultures and comparing the isotopic composition of the medium nitrate with the nitrate inside the cells of these algae, we have built on earlier work to develop a model for the controls on the isotope effect expressed during nitrate assimilation by algae. In this model, the dominant isotope discriminating process is the reduction of nitrate within the cell, and the degree of isotope discrimination actually observed in the environment is controlled by the fraction of nitrate that is taken up into the cell, witnesses the isotope discrimination associated with nitrate reduction, but then leaks back out into the environment. The fraction of back-leakage to gross nitrate uptake appears to depend on what properties are limiting algal growth, with the largest fraction of leakage when algae are limited by light. Such a dependency is consistent with a physiological strategy in which algae up-regulate nitrate uptake in the darkness to be prepared for any future increase in the availability of light; light availability in the ocean can be extremely variable, so such a strategy is plausible. Looking forward, this offers the possibility that we can use the amplitude of isotope fractionation (an index of nitrate back-leakage) to identify light limitation in the ocean (as opposed to other limitations on growth, such as from iron). However, the above model regarding light limitation arises from observations of only a single cultured species of diatom. Thus, they may not apply broadly among oceanic phytoplankton.

Another important observation from this culture work is
of a constant ratio of O-to-N isotope fractionation by enzymatic nitrification. This invariance is observed at various amplitudes of isotope fractionation, over a range of growth conditions for a given algal species, for a number of algal species (both eukaryotic and prokaryotic), and in both nitrate assimilating and nitrate respiring organisms. This raises the O-to-N isotope fractionation ratio as an important constraint on the enzyme mechanism of nitrate reductases and suggests that, with regard to the chemical properties that set the N and O isotope effects, diverse nitrate reductases operate via the same basic chemical mechanism. We have only begun to explore the direction; nevertheless, it is a promising one.

**Studies of the modern nitrogen cycle.**

My group's measurements of the modern environment have involved diverse materials, such as samples from the ocean water column, sediment pore waters, soil and stream waters, rain waters, surface snow, and glacial ice cores. Most of these studies are relevant for both the modern ocean and the interpretation of the geologic and glacialologic records. The following is a summary list of recently completed studies, for which there is a manuscript published, submitted, or in a late stage of preparation.

Graduate student Meredith Hastings has completed the first thorough study of nitrate N and O isotopes in surface snow, which she conducted on a sample suite that she collected at the summit of the Greenland ice cap, from which important ice core records have been retrieved. Meredith's study provides a basis for downcore nitrate isotope studies to reconstruct past changes in the reactive N chemistry and oxidation state of the atmosphere, indicating that the isotopic composition of nitrate being deposited at the snow surface is preserved as the snow is buried. This study also reveals a seasonal cycle in the N and O isotopic composition of nitrate deposited on the Greenland ice cap, which she uses to test ideas regarding seasonal changes in nitrate source and atmospheric processing. Hastings is in the process of writing up two other major projects: (1) a downcore study of nitrate isotopic composition in Greenland ice cores indicating dramatic changes in the past, and (2) a year-long data set of nitrate N and O isotopic composition ($^{15}\text{N}/^{14}\text{N}$, $^{18}\text{O}/^{16}\text{O}$, and $^{17}\text{O}/^{16}\text{O}$) in Princeton rain water collected at the top of Fine Tower.

Angela Knapp is measuring the N isotopic composition of dissolved organic matter and the N and O isotopic composition of nitrate in the tropical/subtropical Atlantic and Pacific, and she has one manuscript in press and one in preparation on her Atlantic results. Dissolved organic nitrogen is the dominant form of bio-available nitrogen in the nutrient-poor low-latitude ocean, but its role in biological productivity has been a mystery. Her work to date suggests that much of the DON pool is so recalcitrant that it is homogenized by the upper ocean circulation in large regions of the subtropical gyres. At the same time, her combined nitrate N and O isotope data indicate that much of the nitrate above 500 m in the tropical Atlantic has recently been added to the ocean, through cyanobacterial N$_2$ fixation and its subsequent oxidation to nitrate.

Postdoc Moritz Lehmann has completed the analysis of a large nitrate N and O isotope sample set from the Bering Sea. These data indicate that a previously recognized nitrate deficit in the deep Bering Sea is due to nitrate respiration (also known as denitrification) by bacteria in the deep seafloor sediments; denitrification is the dominant loss of biologically available N from the ocean. Combining this observation with other constraints on circulation, Lehmann estimates extremely high rates of denitrification, much higher than is normally measured by direct methods for deep sea sediments. We suggest that the extremely steep slopes of the Bering basin channel organic matter into the deep sea, driving these high rates. This study may reconcile a standing discrepancy among different approaches to estimating sedimentary denitrification rates in the ocean.

EEB graduate student Ben Houlton (advisor: Lars Hedin) has analyzed Hawaiian rain waters, soil waters, soil extracts, and stream waters for the isotopic composition of nitrate and dissolved organic N. In a submitted manuscript, he combines his results with simple steady state models of the terrestrial nitrogen cycle to argue that denitrification is an under-appreciated mechanism of bioavailable N loss in tropical forest ecosystems; previous paradigms have focused on loss by surface and ground water flow.

I will soon submit a manuscript describing a large nitrate N and O data set from the water column of the eastern North Pacific. This data set reveals with remarkable clarity an anomaly in nitrate $^{18}\text{O}/^{16}\text{O}$ and $^{15}\text{N}/^{14}\text{N}$ from the covariance expected from our culture studies of the denitrification process. While it is too early in the development of this field to definitively explain this anomaly, it may well be the result of a previously unrecognized input of (low-$^{15}\text{N}/^{14}\text{N}$) nitrate from recent and local cyanobacterial N$_2$ fixation. This would run against the current paradigm for where one expects to find high N$_2$ fixation in the ocean, but there are good geochemical arguments for its plausibility.

My collaborators and I recently published a study of the N isotope dynamics in the Cariaco Basin, an O$_2$-deficient marine basin off the coast of Venezuela. The Cariaco is one of the best studied O$_2$-deficient basins and is thus an important model system for redox reactions and their influence on the N cycle and the N isotopes. Coring in the basin has also provided a remarkable sedimentary record of the past, but downcore studies of N isotopes are in need of groundtruthing in the modern ocean. We observe that the sharp depth transition to O$_2$ deficiency in the deep Cariaco basin leads to complete consumption of nitrate at the transition where denitrification occurs. As a result, in this system, the normally highly isotope-fractionating process of denitrification has no isotopic impact. This informs models that use the N isotopes of nitrate to describe and quantify denitrification in the global ocean.

On the basis of seasonally distributed water column sampling, we have developed a seasonal picture of the $^{15}\text{N}/^{14}\text{N}$ of nitrate across the Subantarctic Zone of the Southern Ocean, south of Australia. Despite only modest seasonal changes in surface nitrate concentration ([NO$_3^-$]), nitrate $^{15}\text{N}/^{14}\text{N}$ increases dramatically from winter to summer. The nitrate
A relationship of the Antarctic surface to the south of the Subantarctic surface is very different from that of the Subantarctic thermocline below the Subantarctic surface. Thus, the seasonal change in Subantarctic surface nitrate $^{15}$N/$^{14}$N indicates a winter/summer difference in the source of nitrate to the Subantarctic surface, with vertical mixing supplying nitrate from the Subantarctic thermocline during the winter and Ekman transport supplying Antarctic nitrate from the south during the summer. At the same time, the completeness of the apparent wintertime “reset” of the Subantarctic surface to thermocline characteristics introduces the surface salinity of the Subantarctic as a constraint on the amount of Antarctic nitrate input during the summer. For the nitrate isotope data to be consistent with the salinity constraint, the isotope effect for nitrate assimilation in the Subantarctic must be significantly higher than we observe in the seasonally ice-covered Antarctic. A higher isotope effect in the Subantarctic is also suggested by our studies of sinking N [Lourey et al., 2003]. When combined with other regional studies from the Subarctic Pacific and equatorial Pacific, these data argue that the Subantarctic Zone is home to a uniquely high isotope effect for algal nitrate assimilation. This may be due to a uniquely important role for light limitation of algal growth in this region (see summary of culture work above).

**Earth history studies.**

Based on Angie Knapp’s work on dissolved organic nitrogen, postdoc Becky Robinson Graham and graduate student Brigitte Brunelle have developed a method for the N isotopic analysis of organic matter trapped within microfossils that are buried in deep sea sediments. This is a specialized measurement, but it offers the potential to expose changes in nutrient cycling through Earth history. Our work to date has focused on sediment cores from polar ocean regions, where the nutrient status of the surface has a major effect on atmospheric CO$_2$.

Becky Robinson Graham has demonstrated that previous bulk sediment and diatom-bound N isotope records from the Antarctic have major flaws. Based on her results, changes in the surface nitrate concentration of the Antarctic were much more modest than the previous records suggested, with some evidence for spatial variations. These results fit with studies suggesting that significant iron fertilization of the Antarctic by enhanced dust transport is difficult to achieve even during the peak of the last ice age, partially because glacial dust deposition is expected to occur mostly in the lower latitude Subantarctic Zone, which shares a common latitude range with expected dust sources. While the data continue to support a previous hypothesis of Antarctic stratification during glacial times, which would have reduced the escape of deep-sequestered CO$_2$ to the atmosphere, the new data suggest a less important role for Antarctic nutrient drawdown in glacial/interglacial CO$_2$ changes. Given the limited evidence for patchiness in glacial nutrient drawdown, this study suggests that each of the zonal sectors of the Antarctic must be studied to get an adequate view of nutrient status during the last ice age.

Becky has also generated three downcore records of diatom-bound N isotope composition from the Subantarctic Zone, the region to the north of the Antarctic in the Southern Ocean. Surprisingly, the records indicate the opposite sense of change that had been inferred from bulk sediment N isotope measurements in the Subantarctic. The most robust explanation for the records is that the degree of nitrate consumption was much higher in the Subantarctic during the last ice age than today, most likely because of iron fertilization during ice ages, an established but unproven hypothesis. Unfortunately, we currently cannot rule out an alternative potential explanation for the glacial/interglacial N isotope change, a northward migration of Antarctic conditions lowering the isotope effect of nitrate assimilation. Because of the potential importance of a glacial change in Subantarctic nutrient conditions, resolving this uncertainty in our interpretation is a focus of ongoing activity.

As our collaboration with the lab of Gerald Haug at GFZ Potsdam continues, we are developing a progressively stronger case for a link between climate cooling and polar ocean stratification over the last three million years of Earth history. I have recently become interested in a new physical mechanism for this link that involves the reduced temperature sensitivity of ocean density at low temperatures, which I describe in the context of new evidence in a 2004 manuscript. The motivation for this new interest is that our data in hand indicate that (1) the Antarctic in the Southern Ocean and the Subarctic North Pacific show the same response of upper ocean stratification to climate cooling, and (2) there appears to be a relatively linear response of upper ocean stratification to climate in both of these regions. These observations are difficult to explain by other (e.g., sea ice- or wind-related) mechanisms, which are likely to have different effects in the two hemispheres and to cause threshold responses.

Postdoctoral researcher Agatha DeBoer has been performing model experiments to test the potential role of the non-linear dependence of density on temperature in the observed link between climate and polar ocean overturning. In order to carry out these long time scale experiments, she has adapted a computationally efficient model developed by GFDL’s Robbie Toggweiler, the “water planet” model, which has simplified bathymetry and basin geometry and is coupled to a simple energy balance model of the atmosphere. DeBoer has recently obtained extremely encouraging results for our cooling-driven stratification hypothesis. These involve model experiments in which we “lie” to the density calculation protocol in the model, such that density and its gradients in the model are calculated as if the ocean were homogeneously warmer or colder than it really is. This has proven to be an effective strategy for isolating the temperature effects on density structure from the other effects that temperature change has in a model. In the “pseudo-warming” experiments, we find a remarkable spin-up of polar ocean overturning. In the “pseudo-warming” experiments, polar ocean overturning decreases markedly. Follow-up experiments are currently being run to improve our understanding of these results and to compare the strength of this effect with other likely influences on polar ocean overturning that arise in the context
of climate change (most critically, changes in the poleward water vapor transport in the atmosphere). A manuscript is in preparation.

Lastly, recent Ph.D. graduate Curtis Deutsch (advisor: Jorge Sarmiento) and I have modeled the expected effects of hypothesized glacial/interglacial changes in the nitrogen cycle on the isotopic composition of oceanic nitrate. Comparison of his model results with sedimentary nitrogen isotope data suggest that negative (stabilizing) feedbacks in the ocean nitrogen cycle have prevented large changes in the oceanic nitrogen reservoir over the last glacial/interglacial transition.

Method development.
The foundation for nearly all of the ongoing analytical work in my lab is the method we developed for measurement of the isotope ratios of nitrogen (15N/14N) and oxygen (18O/16O) in nitrate (NO3-) dissolved in diverse aqueous solutions (e.g., freshwater, seawater, sediment porewater, culture media). Nitrate in itself is a central part of the nitrogen cycle, especially in the ocean. Moreover, other forms of nitrogen can be converted to nitrate in the lab, so that their isotopic composition can also be determined. In previous years, I have described the nitrate method and our derivative methods for measuring dissolved organic N and the organic N bound within sedimentary microfossils. We have added two new analytical capabilities this year. Graduate student Ben Houlton and postdoc Moritz Lehmann developed a technique to measure the 15N/14N of ammonium in natural samples with roughly 100 times higher sensitivity than previous methods. Postdoc Jan Kaiser and graduate student Meredith Hastings developed a new technique to measure the 18O/16O of nitrate, with probably a 1000-fold improvement in sensitivity relative to previous methods and a major reduction in the labor requirements of the measurement.

Two-Year Bibliography

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Articles in press or submitted:


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We are working to understand the rich variety of processes by which the upper crust deforms, particularly by studying actively deforming mountain belts such as Taiwan, the Tianshan of western China and the Transverse Ranges of southern California. For the first 150 years of Geology the study of active deformation moved rather slowly because of “data starvation” caused by difficulties in seeing into the complex deforming interiors of mountain belts. The subject finally began to take off about 1980 because of improved seismic imaging. Since then my students and I have been at the forefront of a successful effort to use these new data to develop fault-related fold theory which has shown, surprisingly, that the vast richness of deformed structures that we observe are formed by simple processes of displacement and propagation of non-planar faults. In the last few years we have made breakthroughs in insight, developing shear fault-bend folding and detachment folding theories, which explain in detail large classes of previously misunderstood structures.

I am working hard at completing a book on fault-related fold theory to be published by Princeton University Press and I have joined with former students John Shaw at Harvard and Chris Connors at Washington & Lee to write and edit a major volume on interpretation of seismic images in light of fault-related fold theory, which about to be published with AAPG. In addition I am a co-organizer of a major international conference on Theory and application of Fault-related folding in Foreland Basins which will be held in China this summer. It is an unusual conference because the list of participants includes a very large number of well-known scientists from diverse fields ranging from structural geology, to active tectonics to petroleum geologists. We will have three days of meeting in Beijing after which we all fly to western China for a one-week field trip to see actively growing structures in the Tianshan Mountains.

I feel that Active Tectonics in the midst of a new acceleration of understanding driven by new data that can be brought to bear on upper crustal deformation, especially: [1] precise earthquake locations, [2] dense geodetic data, [3] tectonic geomorphology (which provides an integral of deformation of the land surface over the last 10,000-100,000 years), and [4] seismic imaging. We are engaged in a number of projects that are at the forefront of using all these new data for new insight, working in areas of active deformation in southern California, Taiwan and the Tianshan mountains of western China.

For example, graduate student Lifan Yue has combined a detailed 3D image he has developed of the classic thrust fault of the major Chi-Chi earthquake in Taiwan with an equally detailed coseismic displacement field to get an unparalleled image of the relationships between complex earthquake slip and complex fault geometry in a major earthquake. The Chi-Chi earthquake is a unique opportunity because it is the best instrumented earthquake ever and for unusual reasons we are able to independently map the fault in detail in 3D. Furthermore we have shown that borehole measurements of pore-fluid pressures surrounding this fault are entirely hydrostatic in contrast with the classic hypothesis of Hubbert & Rubey (1959) that high pore-fluid pressures are the solution to the problem of fault weakness. Also 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 longstanding controversy over the strength of major plate-boundary faults because they have been largely inaccessible to measurement. Results using this new theory indicate very weak basal detachments in Taiwan, Japan and Niger delta.

Graduate student Ramon Gonzalez is making significant advances in the understanding of detachment folding based on precise analysis of well-imaged examples from the Tianshan, Nankai trough, Cascadia accretionary wedge and Niger delta.

I am finishing with former postdoc Aurelia Hubert-Ferrari of University of Neuchatel a major paper on “the link between the surface and the subsurface” in active tectonics, in which we have been able to establish close relationships between surface deformation and geomorphology and the subsurface structure in the Tianshan of western China. With Dr. Dengfa He I have been working on what may be the longest active intact thrust sheet in the world which is on the northern margin of Tibet and extends ~250km out into the Tarim basin to the north. In addition I went to China last summer to initiate a new multiyear project on active deformation in the Junggar basin on the northern margin of the Tianshan.

Two-Year Bibliography

Books

Referred articles:


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 denitrification in Antarctica and the Arabian Sea, the genes involved in nitrogen assimilation by phytoplankton, diversity of functional guilds of bacteria involved in the nitrogen cycle of Chesapeake Bay, and the role of metals in nitrogen redox biogeochemistry. Some of the main projects are summarized explicitly below.

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 denitifiers, 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.

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

Summary of Progress During the Past Year on Each Project:

1. "Biocomplexity of Aquatic Microbial systems: Relating diversity of Microorganisms to Ecosystem Function" (O’Mullan, Adhitya) (http://geoweb.princeton.edu/research/biocomplexity/index.html)

2004 was the fourth year of this collaborative project, involving several other institutions, all working in Chesapeake Bay and coordinated through Princeton as the lead institution. Microbial biogeochemical cycling of the elements regulates a dynamic environment in which the cycles of different elements are linked through the physiology of microorganisms. Our present understanding of ecosystem function has been gained through physical/chemical approaches to measurement and modeling of the net transformations. These approaches necessarily rely on gross simplifications about the role and regulation of the various functional groups (guilds) involved. Recent advances in molecular microbial ecology have shown the microbial world to contain immense diversity and complexity at every level: redundancy and duplication of functional genes within a single organism; molecular di-
versity among functional genes that encode the same process in different organisms; large genetic diversity among different organisms apparently engaged in the same biogeochemical function within single communities; great variability in the species composition of different communities that apparently perform equally well.

The goal of this project is to investigate the functional relationship between complexity in microbial communities and the physical/chemical environment at a range of biological and ecological scales. Previously, such analysis was technologically limited by the inability to assay large numbers of samples simultaneously for a large number of genes and phylotypes. Using gene array technology, we will be able to detect the distribution and differential expression of functional genes in natural systems. The results of this study will constitute the first step towards application of DNA chip technology for gene expression of “exotic” (i.e., not of biomedical importance) processes and organisms in the environment. The gene arrays, along with a full suite of ecosystem process measurements, are deployed along a transect that spans the eutrophic - oligotrophic gradient from the inland waters of the Chesapeake Bay out to the Sargasso Sea. Experiments and functional gene studies focus on key transformations in the carbon and nitrogen cycles (C fixation, N fixation, nitrification, denitrification, urea assimilation). The diversity of guilds will be interpreted in terms of ecosystem function, assessed using geochemical data and tracer experiments. In addition to field studies designed to investigate and dissect the natural system, we have also performed perturbation experiments using mesocosms. The goal of these experiments is to determine how microbial species diversity affects the major energy and nutrient flows within ecosystems, and to assess the degree of stability or instability associated with changes in redundancy within guilds of microorganisms responsible for major nitrogen and carbon pathways.

To date, about 20 field trips/research cruises have been completed in Chesapeake Bay, the Choptank River and the Sargasso Sea. Both microarrays (using 70-bp oligomer probes) and macroarrays (using ~350 bp PCR products) derived from functional genes, which we extracted from Chesapeake Bay sediments, plus a few representative genes from cultured organisms. The first generation microarrays containing oligos for nitrite reductase genes (nirS) were characterized in terms of their specificity and sensitivity using simple and complex mixtures of known genes, and complex environmental samples from Chesapeake Bay (Taroncher-Oldenburg et al., 2003). Sequence differences of 13-15% can be distinguished and the detection limit is 107 copies of a particular target. These results appear to be robust for all genes, due to the uniform behavior of oligomer probes. A similar microarray, containing oligo probes for ammonia monooxygenase (amoA) genes has been used to characterize sediment and water column samples along the complete transect from April 2001.

The second generation of microarrays employed a new labeling protocol and a new quantification procedure. Genes encoding the essential enzymes RuBiSCO (rbcL) and nitrate reductase (NR) in eukaryotic phytoplankton were used in the first successful second generation array to analyze phytoplankton communities in the English Channel. This array detected both community composition (DNA) and gene expression (mRNA) in natural assemblages and demonstrated the power of the approach. Papers are in prep and submitted. The second generation version of the nirS and amoA arrays have been constructed and will be deployed in the coming year.

The macroarray project is based at UCSC (Zehr lab); the first macroarrays were tested with nitrogenase genes (nifH) and found to have discriminatory power and sensitivity similar to that of the microarrays (Steward et al., 2004; Jenkins et al., 2004). Both kinds of arrays are able to distinguish different community compositions of denitrifiers, nitrifiers or nitrogen fixers, respectively, in sediment and water samples from different stations.

2. “What limits denitrification and bacterial production in Lake Bonney, Antarctica?” (Tuit)
The second three-year period of this project initially focused on experiments with denitrifying laboratory cultures grown under trace metal clean denitrifying conditions in trilaminate bags. The ongoing experiments are designed to test the copper hypothesis, which grew out of our previous work on this project. The copper hypothesis suggests that lack of Cu can limit denitrification and lead to build up of inorganic nitrogen intermediates in the water column. Field work in the dry valley lakes of Antarctica is planned for 2004 and 2005. During the first season (ongoing at the time of this writing), we developed and tested a series of flow cytometric assays for bacterial abundance and physiological state in the lake samples.

3. “Center for Environmental Bioinorganic Chemistry”
(Jayakumar, Tuit)
The two forms of dissimilatory (respiratory) nitrite reductase, the cd-NiR (nirS gene) and Cu-NiR (nirK gene), are distributed across the Bacterial and Archaeal domains in a great diversity of microorganisms. Because trace metal availability can limit denitrification in the lab, we hypothesized that metal distributions might influence the type of nir found in natural marine assemblages. The first step in addressing this hypothesis is to describe the distribution and diversity of nir genes in marine systems. One paper (Jayakumar, Francis and Ward, 2004) describes the diversity and distribution of nirS genes in the low oxygen coastal waters of the Arabian Sea in the continental shelf region of India. The sequences found here are the first reported for a water column environment, and are quite different from those previously reported from sediment environments. Jayakumar and Tuit participated in a month long cruise in Nov-Dec 2003 in the Eastern Tropical North Pacific which visited the strong oxygen minimum zone in that region. They conducted Cu perturbation experiments and hope to detect a response by the indigenous denitrifying community based on nitrous oxide production. Samples were also collected for analysis of both nirS and nirK genes. The only definitive results of the cruise experiments were that 1) denitrification rates were overall very low and 2) denitrifica-
tion rates were stimulated by the addition of organic carbon but not by the addition of Cu, Fe or Cu chelators.

4. “Draft Level Sequencing of a Selection of Nitrifying Bacteria” (O’Mullan) and “Microbial genome sequencing: The complete genome sequence of a mini consortium of marine ammonia oxidizers”

DOE has agreed to sequence the entire genome of five ammonia- and nitrite-oxidizing bacteria. Nitrobacter hamburgensis 14X was grown in our lab and I extracted the DNA that was used for sequencing. Ward lab is the lead on the N. hamburgensis genome and annotation is currently underway. In the NSF project, we are sequencing two additional ammonia oxidizers, including Nitrosococcus oceanica. The Moore foundation microbial genome project has agreed to sequence another N. oceanica genome, and we are growing the cells for that project.

5. “Diversity and distribution of denitrifying bacteria in relation to chemical distributions in the oxygen minimum zone of the Arabian Sea” (Jayakumar, Tuit, Rich)

The Arabian Sea is one of three regions in the open ocean where significant denitrification occurs in the water column. Nitrous oxide is an intermediate in the denitrification pathway, and is also produced during aerobic nitrification at low oxygen tensions. It is very effective as a greenhouse gas, and what controls its production and release from marine systems is not well understood. Nitrous oxide accumulates in a characteristic pattern in oxygen minimum zones (OMZs), such as that found in the Arabian Sea. 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. Copper limitation might also lead to accumulation of nitrite in denitrifying bacteria that possess the copper type nitrite reductase, rather than the iron enzyme. Thus, if copper limitation were a fact of life in the OMZ, we might expect that the iron NiR should be more common than the copper NiR.

In September 2004, Carrie Tuit, Amal Jayakumar, and Jeremy Rich participated in a month long cruise in the Arabian Sea in collaboration with Indian colleagues on the Indian research vessel Sagar Kanya. Preliminary results indicate that, unlike the Eastern Tropical North Pacific where similar experiments were performed in November 2003, denitrification was NOT carbon limited. Nitrate disappeared from the bags over the course of a few days, and the entire denitrification sequence was observed in most bags. We suspect that a large, basin-wide dinoflagellate bloom may have supplied organic matter to the OMZ at an unusually high rate. The results suggest that denitrification rates can be very variable and episodic, implying that conventional areal and annual denitrification rate estimates may be unreliable.

Anammox (Jeremy Rich), denitrification (Al Devol, University of Washington) and trace metal distributions (Jim Moffett, WHOI) were also investigated on the cruise. Our samples for DNA and RNA will be analyzed to determine the kinds of denitrifying genes present, and to investigate their patterns of expression under different conditions.

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Submitted


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Guyot Hall, front entrance.