

Workshop Volume



GERM
Workshop
2006

May 29-31

Columbia University

<http://earthref.org/GERM>

GERM Workshop

Manhattan, USA
May 29-31, 2006

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Welcome to the Fifth Geochemical Earth Reference Model (GERM) Workshop in Manhattan

We are very pleased to welcome you at the Fifth Geochemical Earth Reference Model workshop at Columbia University in the City of New York.

With this GERM workshop, we are celebrating our tenth anniversary. These ten years brought us five stimulating Workshops, Special Sessions at AGU meetings and the associated Conference Volumes that include many influential papers. Over the last ten years, GERM made much progress in improving the geochemistry science infrastructure: GERM developed the GERM/EarthRef.org website that is widely used in research and education, with close to 8,000 independent visitors per month, and GERM was instrumental in development of a first rate electronic journal, G-cubed. This journal is now in its sixth successful year since its inception during the third GERM Workshop in 1998 and amongst the premier scientific journals in geochemistry, geophysics and paleoclimate studies. GERM is working closely with Editors and Publishers on issues of data publication, through inception of the Editor's Roundtable at the GERM Workshop in 2003, and through publications of technical papers on data publication.

The NYC GERM Meeting continues this quest of advancing our understanding of the chemical composition and evolution of the Earth through promotion of science contributions and by advancing the geochemistry science infrastructure. Both of them are important and require some hard work and commitment to succeed. We have a great Science Program that spans from the deep earth to the biosphere, and we have five breakout sessions that address key science infrastructure issues. We also have an exciting social program, where we have the NY Symphony orchestra playing "for us" in the Cathedral Church of St. John the Divine, right next to Columbia University, we will have a twilight river cruise on the Hudson, and a final Barbecue on the grounds of Lamont Doherty Earth Observatory in Palisades NY.

Join us, enjoy the scientific and social programs, and please help us to continue to progress on our science infrastructure efforts in the breakout sessions. NSF embraced Cyberinfrastructure as a major funding effort, and it is up to us to make these efforts effective and assure that this money is well spent.

Thanks for coming to New York !!!

Hubert Staudigel and Steve Goldstein

For the GERM Steering Committee

Thank You

GERM and this workshop were funded by the National Science Foundation (NSF-EAR), the Lamont-Doherty Earth Observatory and industry sponsors, in particular, Elsevier Science Publishers, Nu Instruments, Thermo Finnegan and GV Instruments. We thank Patty Keizer for her tireless organization of almost any aspect of this meeting, and, last, not least, we want to thank you, the conference participants for spending a few days of your busy professional lives with us and other supporters of GERM for giving us a chance to make all this work.

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Fifth GERM Workshop Program

May 28 2006	May 29 2006	May 30 2006	May 31 2006	
	8:30 – 10:00	8:30 – 10:00	8:30 – 10:00	
	<u>INTRODUCTION TO MEETING</u> Steve Goldstein Kerstin Lehnert Hubert Staudigel	Early Life and Volcanoes Neil Banerjee Oliver Rouxel Susan Brantley (DL)	Microbes and Water Katrina Edwards Ruth Blake Emi Ito (DL)	
	Coffee Break			
9:30 – 12:00	10:30 – 12:00	10:30 – 12:00	10:30 – 12:00	
<u>GERM SHORT COURSE I</u> U-Series Modeling Marc Spiegelman	Element Cycling: Rivers, Erosion and Weathering Jerome Gaillardet Peter Raymond Bernhard Peucker-Ehrenbrink (DL)	Mantle Veining and Melting Alex Sobolev Marc Hirschmann Al Hofmann (DL)	Volatiles and Crust-Mantle Recycling Erik Hauri Brad Hacker Bill White (DL)	
Lunch Break			Brown Bag Lunch	
13:30 – 16:30	13:00 – 14:00	13:00 – 14:00	12:00 – 13:30	
<u>GERM SHORT COURSE II</u> MELTS Marc Hirschmann Mark Ghiorso	<u>BREAKOUT SESSIONS</u> River Databases (Bernhard Peucker-Ehrenbrink) Geoinformatics for Geochemistry (Kerstin Lehnert) GERM – The Next 4 Years (Hubert Staudigel, Anthony Koppers) Editor's Round Table (Vincent Salters, Steve Goldstein) From GERM to LEPER (Marc Hirschmann, Mark Ghiorso)		<u>BREAKOUT SESSIONS</u> <u>PLENARY DISCUSSION</u> What lies in the Future of GERM ... ~13:30 END OF MEETING	
	14:00 – 15:00	14:00 – 15:00		
	<u>POSTERS I + Coffee Break</u>			<u>POSTERS II + Coffee Break</u>
	15:00 – 16:00	15:00 – 16:00		
	Composition of the Depleted Mantle Charles Langmuir Jun Korenga (DL)	Biosphere-Lithosphere Connections: The Science of the Critical Zone Susan Brantley Lou Derry (DL)		
14:00 – 17:00	16:00 – 17:30	16:00 – 17:30		
<u>WORKSHOP REGISTRATION</u> Putting Up the Posters	Tracers and Trace Elements in the Oceans: GEOTRACES Jim Moffett Jess Adkins Robert Anderson (DL)	Plumes or No Plumes Jason Phipps Morgan Guust Nolet Cornelia Class (DL)		
17:30				
<u>ICE BREAKER RECEPTION</u>				

Breakout Sessions

Breakout sessions address key infrastructure issues in geochemistry, in particular, how GERM can work with the geochemistry community to help developing a geochemical network, what tools, databases or features are needed to bridge the gaps between the geochemical sub-disciplines, and how to facilitate open access to all types of geochemical data. This will be done in five separate sessions.

During the final wrap-up plenary session there will be a 15 minute discussion time slot for each breakout group to discuss what has been accomplished, to ask for input from workshop participants who had to attend other sessions, and to plan future activities.

1. Generation of a Rivers Database

Convener: Bernhard Peucker-Ehrenbrink (WHOI)

Panelists: Blake, Gaillardet, Grossman, Moffett, Raymond

Room: 551 in Schermerhorn Extension

This breakout session focuses on the understanding and potential resolution of important limitations in our understanding of land-to- sea transport. Those may include infrastructure issues (lack of a database), observational limitations (lack of time-series observations) or conceptual complexities such as ground-water vs. surface runoff, physical erosion, the role of climate change, or anthropogenic effects. Our goal is to identify the most critical impediments and devise strategies to overcome these problems.

2. Geoinformatics for Geochemistry

Convener: Kerstin Lehnert (LDEO)

Panelists: Edwards, Hart, Helly, Koppers, Langmuir, Mogk, Shaw, Staudigel

Room: 506 in Schermerhorn Hall

Over the past decade, advances in information technology have created a new paradigm for conducting research. Geoinformatics is creating new research environments for the Geosciences, offering new "computational, collaborative, data acquisition, and management services that become available to researchers through high-performance networks" (Report of the NSF Blue-Ribbon Advisory Panel on Cyberinfrastructure, Atkins et al. 2003). In this breakout session, we will explore and identify opportunities, needs, requirements, and approaches to advance the application of Geoinformatics to support Geochemistry research in general and, more specifically, the GERM.

3. GERM: Planning the Next Four Years

Conveners: Hubert Staudigel (UCSD) and Anthony Koppers (UCSD)

Panelists: Hofmann, Ito, McDonough, Mogk, Shaw

Room: 555 in Schermerhorn Extension

Over the last three years, GERM has made substantial progress in improving its website and providing a wide range of computational and "Reference Data" resources that provide a widely used cyber-resource in geochemistry research and education. The GERM website developers and designers seek feedback

from the science community on these developments and advice on the next priorities in GERM website development. GERM also seeks advice on its work with the geochemistry science and education communities. Such activities include, for example, the integration of GERM with other geochemistry database activities (e.g. EarthChem), its activities in GERM-related publications, the organization of workshops like this one, and how to support geochemistry education at all levels, ranging from primary and secondary schools to university-based education.

4. Geochemical Editor's Roundtable: How Should we Publish Geochemical Data in the Future?

Conveners: Vincent Salters (Florida State) and Steve Goldstein (LDEO)

Panelists: Adkins, Brantley, Veenstra, White

Room: 561 in Schermerhorn Extension

With the rapid progress in information technology, the Geoscience community has started building a digital data system that dramatically advances the sharing and integration of data across disciplines and borders. For example, data management systems for igneous rock geochemistry have made global geochemical datasets readily accessible for broad audiences. The new opportunities for archiving, discovery, accessing and analysis of geochemical data require us to rethink the way data is published. This breakout session will discuss how geochemical data publication should be structured in the future, to best take advantage of these new opportunities.

5. From GERM to LEPER (Library of Experimental Phase Relations)

Conveners: Marc Hirschmann (U Minn) and Mark Ghiorso (OFM Resources, Inc.)

Panelists: Hacker, Hauri, Helly, Koranaga, Spiegelman

Room: 559 in Schermerhorn Extension

Alongside large scale databases of geochemical analyses, there is increasing need for comprehensive community libraries of data collected in experimental laboratories. This session will be an opportunity to introduce to the GERM community our initial efforts to develop LEPER, a database of experimental data pertaining to magmatic phase equilibria. This project is an outgrowth of ongoing efforts to improve the MELTS algorithm. The session will introduce the scope of data and metadata included in LEPER, as well as a prototype web interface for serving LEPER data to the community. This session may interest potential producers and consumers of data for LEPER, as well as those interested in discussing the needs and challenges for developing experimental databases. The discussion may also extend to other types of experimental data (metamorphic phase relations, trace element partitioning, hydrothermal data, thermodynamic data, transport properties, etc.) and thermodynamics data that can/should/might be incorporated into LEPER or to other future database efforts.

Social Program

An exciting social program is offered to all GERM Workshop participants: The NY Symphony Orchestra is playing “for us” in the Cathedral Church of St. John the Divine, right next to Columbia University; a Dinner Cruise on the Hudson River lets you enjoy the famous NY Skyline; and a final Barbecue brings you to the grounds of Lamont Doherty Earth Observatory in Palisades, NY.

And, of course, don’t miss the GERM Icebreaker on Sunday !!!

May 28, 2006

Icebreaker Reception

Bistro Ten 18, 110th St. and Amsterdam Ave
5:30-7 PM

May 29, 2006

New York Philharmonic Concert

Cathedral Church of St. John the Divine
112th St and Amsterdam Ave
8 PM
Free admission

May 30, 2006

Harbor Lights Cruise

Hudson River
8-10 PM

May 31, 2006

Barbecue

Lamont-Doherty Earth Observatory
from 4 PM



New York Philharmonic

Lorin Maazel Music Director

Memorial Day Concert

DATES AND TICKETS

Mon, May 29, 2006, 8:00 PM

PROGRAM

Verdi: *La Forza del Destino Overture*

Tchaikovsky: *Symphony No. 5*

FEATURED ARTISTS

Xian Zhang, Conductor



Xian Zhang

PERFORMANCE INFORMATION

FREE concert at the Cathedral Church of St. John the Divine,
Amsterdam Avenue at 112th Street

Seating is on a first-come, first-served basis. The doors will open at 7:00 p.m. Additional seating will be available, weather permitting, on the Pulpit Green adjacent to the Cathedral. For more information, please call the Cathedral’s Visitors’ Center at (212) 316-7540.

Notes

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Abstracts

Listing in alphabetical order

Some successes and some unrealized potential in reconstructing the past deep ocean circulation

Adkins, J

As the repository of most of the climate system's heat capacity and carbon, the deep ocean can play a critical role in both glacial-interglacial cycles and rapid climate shifts. It is the only climate reservoir with a "time constant" long enough to account for the 1-3,000 year time lags seen in the Antarctic and Greenland temperature records. Indeed, a leading hypothesis to explain the causes of rapid climate changes in the past, the "bi-polar seesaw", is based on abrupt variations in the deep ocean overturning strength. In the modern ocean, we often use geochemical tracers to probe the patterns and integrated rate of this deep ocean ventilation. Passive tracers such as temperature, salinity, and PO₄* have been combined with time dependent tracers like radiocarbon and CFCs to measure the volumes and fluxes of NADW and AABW. From radiocarbon alone we know that the mean overturning time of the modern deep ocean is ~800 years. Based on the same principles, past reconstructions of deep overturning should also be straightforward, but now we need two separate clocks; one to tell the time of the past and one to use as the age tracer. Several ingenious solutions have been proposed to solve this problem, all of which are based on trace elements and isotopes in the water column. I will focus on two of the most promising techniques to date, paleo-radiocarbon measurements and ²³¹Pa/²³⁰Th ratios. While progress with these two tracers has been fantastic, quantitative calculations of the fluxes in Sverdrups and their associated error bars are limited by our understanding of the tracers' behavior and by an ability to trace water mass mixing ratios independent of other process. To some degree this is the problem of "everything is correlated with everything" in the modern ocean and GEOTRACES is being designed with this specific problem in mind.

Lava Life: Microbial Alteration Of Oceanic Crust And The Search For Early Life On Earth

Banerjee, N R

Petrographic analysis of basaltic glass preserved in modern pillow rims or within volcanoclastic rocks invariably reveals the presence of microbial alteration textures produced by etching of glass during microbial colonization [1-4]. Detailed SEM imaging of the microbial alteration textures reveals the presence of delicate filament-like structures and material resembling desiccated biofilm. X-ray element maps show elevated levels of C, N, P, and K associated with the microbial alteration features. Disseminated carbonate in pillow-rim basalt glasses show differences in C isotope ratios from those of the adjacent crystalline cores that likely relate to microbial activity during alteration. Ophiolites and greenstone belts provide an opportunity to prospect for evidence of microbial alteration in oceanic basalts of much greater age than found in the modern oceans. Recently discovered biosignatures in the formerly glassy rims of ~3.2 to ~3.5 billion-year-old pillow lavas from both the Barberton Greenstone Belt [5,6], South Africa (BGB) and the Pilbara craton, W. Australia (PWA) suggest they were colonized by microbes early in Earth's history. Micron-sized tubular structures mineralized by titanite are present in the for-

merly glassy rims and interpillow hyaloclastites of the BGB and PWA pillow lavas. Based on their similarity to textures observed in recent glassy pillow basalts, we interpret these structures to represent ancient mineralized traces of microbial activity formed during biogenic etching of the originally glassy pillow rims and hyaloclastites as microbes colonized the glass surface. X-ray mapping reveals carbon and to a lesser extent nitrogen, along the margins of the tubular structures in both the BGB and PWA interpreted as residual organic material. Disseminated carbonates within the microbially altered BGB pillow rims have C-isotope values depleted by as much as -16‰ , which is consistent with microbial oxidation of organic matter. Petrography, overlapping metamorphic and magmatic ages from the pillow lavas, as well as direct dating of the titanite within microbial tubules by in situ laser ablation multi-collector-ICP-MS all demonstrate that the titanite is of Archean age. We suggest microbial alteration proceeded immediately after pillow formation, in a similar fashion to what invariably can be observed in pillow lavas of modern ocean crust. Both the BGB and PWA pillow lavas likely hosted similar microbial communities ~ 3.2 to ~ 3.5 billion-years-ago.

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Boron isotopic fractionation by land plants of a forest ecosystem under temperate climate : consequences for boron global biogeochemical cycles

Bouchez, J; Gaillardet, J; Chetelat, B; Gerard, F

To assess the possible influence of land plants on boron biogeochemical cycle, several samples from a forest ecosystem (rain, litter, litter solution, soil, soil solution, pine needles, stem...) were analyzed for boron concentration ([B]) and isotopic compositions ($\delta^{11}\text{B}$).

The forest ecosystem is an experimental set-up, situated in Morvan (central France, in the Seine catchment), ran by the French Institut National pour la Recherche Agronomique (INRA), divided into seven pieces of land, each containing one species of tree. In this study we focus on samples taken from the spruce and beech pieces. The existing data (Ranger et al, 2002) on precipitation, runoff, and organic matter transfers about this site allows us to quantify the fluxes of boron from, to and into the ecosystem. Boron isotopes ratios were analyzed by MC-ICPMS, after separation on ion-exchange resin Amberlite (Lemarchand et al, 2002a) and a micro-sublimation step (Gaillardet et al, 2001), with an external reproducibility of $0,7\text{‰}$, mainly due to the variations of mass discrimination magnitude on MC-ICPMS over time.

Rainfall is poorly concentrated in boron (1,5 ppb), and shows $\delta^{11}\text{B}$ values of approximately 15‰ , consistent with previous measurements in this area (Chetelat et al, 2005). Bulk soil profile do not show vertical variations, neither in concentration nor in isotopic composition, yielding values close to bedrock values ([B] $\approx 30\text{ppm}$, $\delta^{11}\text{B} \approx -20\text{‰}$) and showing that the loss of boron during weathering is small, as already been shown in previous studies (Spivack et al, 1987). The living organic matter and litter exhibit high values of [B] and $\delta^{11}\text{B}$ (around 10ppm and 30‰ respectively).

The litter solution boron, although not containing much boron (1,5ppb), seems to be influenced by organic matter remineralization, rather by boron coming from bedrock weathering and/or rainfall, as its isotopic composition (30‰) is close to the ones of living organic matter and litter. The possibility of boron adsorption onto organic matter inducing an isotopic fractionation on residual boron in solution (Lemarchand et al, 2005) is also pointed out.

We quantify these features by establishing a simple steady-state model of the ecosystem, and we finally show that the litter solution is probably isotopically very different from the soil solution underneath, and that its contribution to the water drained out from the soil profile to the river of the basin is probably small. Nevertheless, in catchments for which biological material forms a large part of the suspended load, we predict that the dissolved boron isotopic composition reflects the biological composition (Lemarchand et al, 2002b).

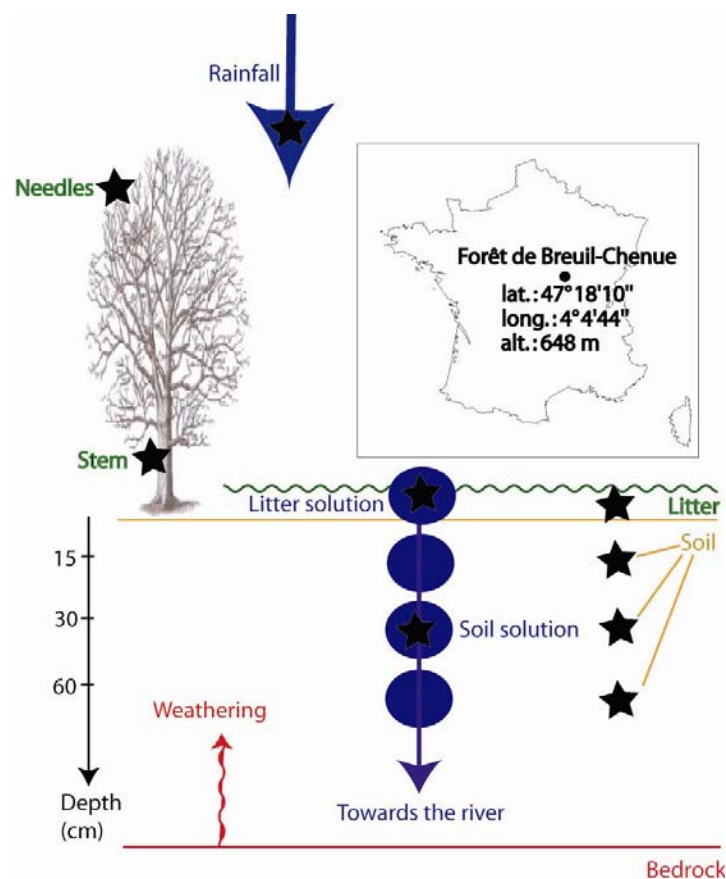


Figure 1. Location and sketch of the ecosystem. Black stars indicate samples, analyzed for boron concentration and/or isotopic composition.

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Exploration of the Critical Zone: Assessing Rates of Earth Surface Processes across Environmental Gradients

Brantley, S L

Introduction. At the Earth's surface, a complex suite of chemical, biological and physical processes combine to create the engine that transforms bedrock into soil (Figure 1). This weathering engine provides nutrients to nourish ecosystems and human society, controls the transport of toxins to water resources, creates flow paths for water that erode and weaken bedrock, and contributes to the evolution of landscapes. At the longest timescales, the weathering engine sequesters CO₂, thereby influencing long-term climate change.

Despite the fact that soils are second only to water and air as resources nurturing human populations, our knowledge of soil formation and transformation is limited due to the extraordinary complexity of the weathering engine. Furthermore, while soils are clearly a globally important resource, no international initiative has promoted a systems approach to investigation of weathering science across geology, soil science, ecology, climatology and hydrology. The time for such an approach has arrived to answer the following question:

How does Earth's weathering engine break down rock to nourish ecosystems, shape terrestrial landscapes, and control carbon dioxide in the global atmosphere?

Only with a systems approach will we be able to predict how weathering rates in the so-called "Critical Zone" respond to climatic, tectonic, and anthropogenic forcings over all temporal and spatial scales.

What is CZEN. The Critical Zone Exploration Network (CZEN) (<http://www.wssc.psu.edu/>) is an interdisciplinary systems approach to investigations of Critical Zone processes (Figure 2). The network encompasses people, sites, tools, data, and ideas.

First, we have initialized funding for a network of field sites to investigate weathering worldwide. The network will be defined by a relatively small number of permanent, highly instrumented, hierarchically nested field sites designed to investigate Critical Zone processes at the soil profile, catchment, and watershed scales, and a larger number of sites to be analyzed for Critical Zone processes over a range of scales but not to be permanently instrumented and monitored. These latter sites will be chosen so as to

explore the effect of environmental variables across natural or disturbed gradients (Figure 2). Parameters to be measured at all sites include bedrock, soil, water, and biological analyses. CZEN is thus promoting the inter-comparison of properties and processes within the Critical Zone across a variety of lithologies, ecosystems, topographies, and climate zones. A worldwide distribution of sites to probe climate, ecosystem, and geologic regimes globally is envisioned.

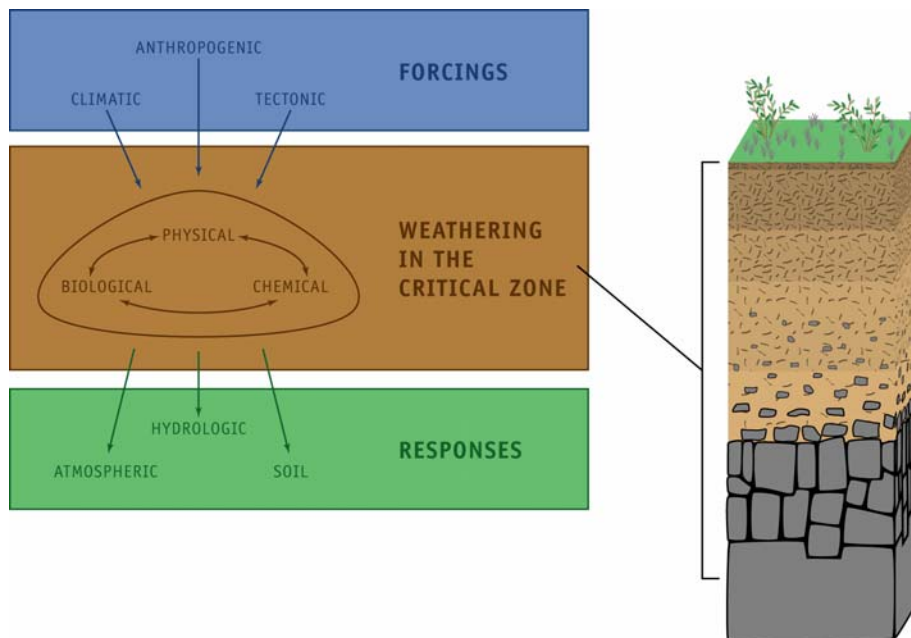


Figure 1. The weathering system.

Second, to enable intercomparison of weathering data, CZEN will provide technical support to instrument or sample sites similarly, and is starting a coordinated data management system and a sample storage system. Data and samples will be accessible to all scientists, allowing new and emerging methodologies to be tested on well-characterized samples as projects unfold.

Critical Zone Exploration Network

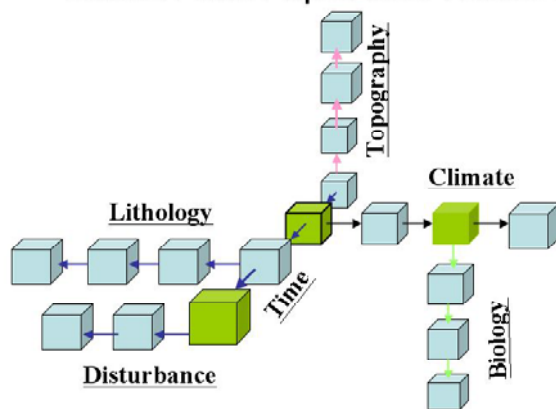


Figure 2. The Critical Zone Exploration Network. Examples of environmental gradients are shown.

Third, and perhaps most importantly, CZEN is promoting the integration of these efforts through a variety of community- and network-building approaches including conferences, fellowships, seed grants, integrative disciplinary centers, cyberinfrastructure, and workshops aimed to stimulate the use of reaction transport and soil and ecosystem models to create new understanding of the rates and mechanisms of processes within the Critical Zone.

Scientific Approach. The gradient approach shown schematically in Figure 2 can be used to address how the rates of Critical Zone processes vary as a function of environmental variables such as rainfall, temperature, duration of weathering, lithology, and relief. For example, the rates of dissolution of primary minerals, precipitation of secondary minerals, net sequestration or degradation of soil organic carbon, and rates of creation of surface area at the bedrock-saprolite interface all vary across environmental gradients. At present, only simplistic governing equations are available to predict the rates of these processes as a function of the important environmental variables, and the coupling between processes as environmental variables change still remains obscure. In cases such as the formation of saprolite from bedrock, conceptual models are still needed. A conceptual model for saprolite formation during spheroidal weathering of bedrock will be discussed, along with some modeling approaches for weathering as a function of environmental variables.

Constraints from helium in ocean island basalts on the plume debate

Class, C; Goldstein, S L

Mid-ocean ridge basalts (MORB) away from bathymetric anomalies show a restricted range in their $^3\text{He}/^4\text{He}$ ratios of about $8 \pm 1 R_A$ ($^3\text{He}/^4\text{He}$ relative to the atmospheric ratio) consistent with a degassed and well-mixed upper mantle. In contrast, the elevated $^3\text{He}/^4\text{He}$ ratios $\gg 9 R_A$ in some oceanic island basalts (OIB) has been considered the primary evidence for the contribution of a less-degassed reservoir in the lower mantle which retained relatively more primordial ^3He than the upper mantle. Thus, helium isotope ratios have been considered an important indicator for the existence of deep mantle upwellings, so-called mantle plumes. Recently the existence of mantle plumes has been questioned based on the failure of many plumes to satisfy all the different characteristics that have been suggested to verify their existence. For example, only few OIB have very high $^3\text{He}/^4\text{He}$ ratios $> 15 R_A$, many actually show MORB-like helium isotope ratios and some are even characterized by $^3\text{He}/^4\text{He} < 7 R_A$. Whether OIB are formed from deep mantle plumes or from shallow sources is of immediate relevance to GERM as OIB have been taken as our primary source of information on the composition of deep reservoirs in the mantle. Here we address the question of what noble gas characteristics are indicative of a deep mantle upwelling.

In our recent global data compilation relating helium isotopes of OIB and MORB to Sr-Nd-Pb isotopes and trace element abundances (Class and Goldstein, 2005; Class et al., 2005) based on data from the online GEOROC and PetDB databases, we divided oceanic islands into $^3\text{He}/^4\text{He}$ groups based on the maximum or minimum $^3\text{He}/^4\text{He}$ ratios measured in mineral separates or glass: (1) “high” ($^3\text{He}/^4\text{He}_{\text{max}} > 15 R_A$); (2) “moderately high” ($9-15 R_A$); (3) “MORB-like” ($8 \pm 1 R_A$); (4) or “low” with $^3\text{He}/^4\text{He}_{\text{min}} < 7 R_A$. This approach is justified by the global presence of MORB-like helium in OIB suites (Fig. 1), that is, the helium in OIB is a mixture of MORB-like helium and a high- or low- $^3\text{He}/^4\text{He}$ component. Strong evidence for this is that MORB-like helium forms a lower limit for “high $^3\text{He}/^4\text{He}$ OIB” and an upper limit for “low $^3\text{He}/^4\text{He}$ OIB”. These global systematics suggest a major contribution of helium from the

aesthenospheric MORB mantle to OIB magma sources. The OIB $^3\text{He}/^4\text{He}$ groups filter out the effects of the ubiquitous upper mantle $^3\text{He}/^4\text{He}$ signal, and allow extraction of information on the composition of sources other than the shallow asthenospheric MORB mantle.

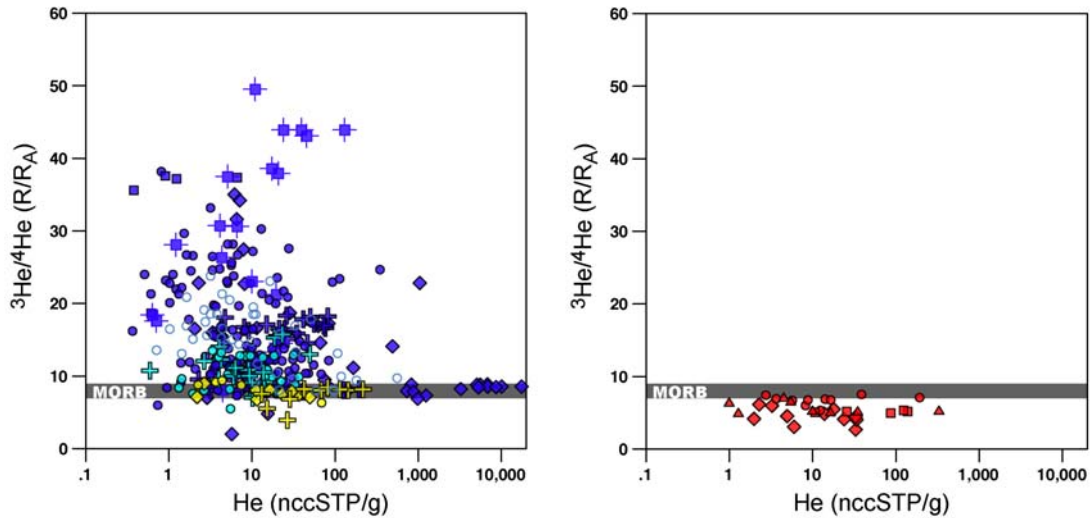


Figure 1. Global compilation of $^3\text{He}/^4\text{He}$ versus He content in all OIB showing that MORB-like helium seems to be present in all OIB and forms (a) a lower limit for OIB with maximum $^3\text{He}/^4\text{He}$ ratios $>$ MORB, or (b) an upper limit for OIB with minimum $^3\text{He}/^4\text{He}$ ratios $<$ MORB. To identify the helium contribution from sources other than the MORB source, OIB are grouped based on their extreme $^3\text{He}/^4\text{He}$ ratios relative to MORB: “high” ($^3\text{He}/^4\text{He} > 15$ RA), dark blue symbols; “moderately high” (9-15 RA), turquoise symbols; “MORB-like” (8 ± 1 RA), yellow symbols; or (b) “low” with $^3\text{He}/^4\text{He} < 7$ RA, red symbols. Samples clearly identified in the literature as contaminated by radiogenic ^4He were excluded.

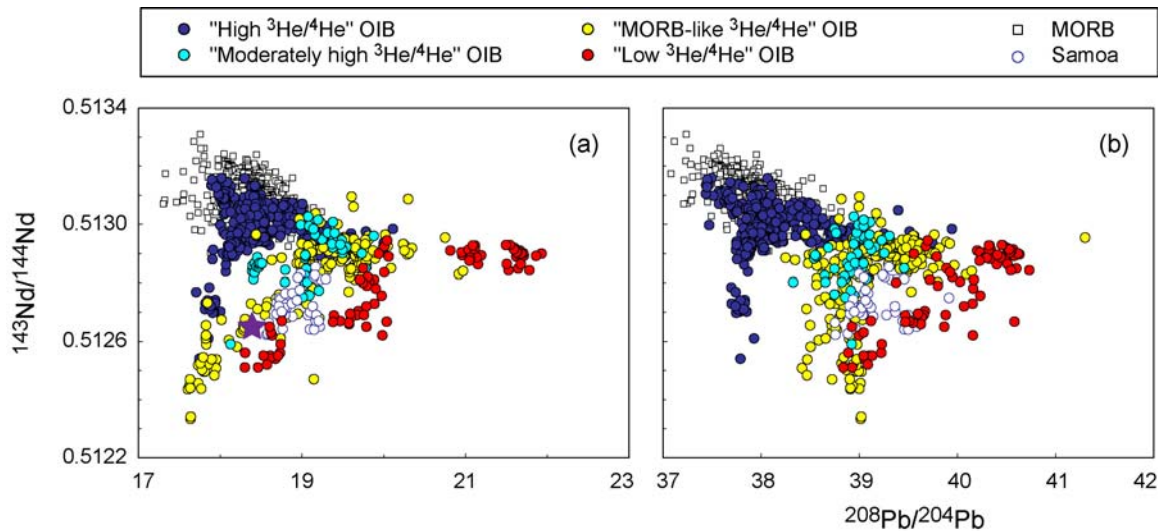


Figure 2. Nd-Pb-He isotopes of OIB and MORB. High $^3\text{He}/^4\text{He}$ OIB have the most MORB-like Nd and the lowest Pb isotope ratios. $^{206}\text{Pb}/^{204}\text{Pb}$ (a) and $^{208}\text{Pb}/^{204}\text{Pb}$ (b) vs. $^{143}\text{Nd}/^{144}\text{Nd}$. OIB and MORB data are from the GEOROC (<http://georoc.mpch-mainz.gwdg.de/>) and PetDB (www.petdb.org) databases, respectively.

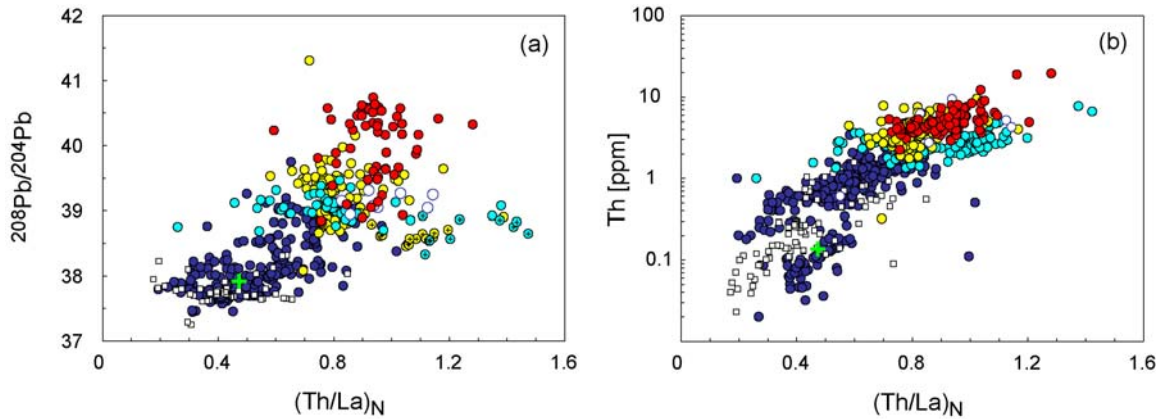


Figure 3. Th, Th/La and helium isotope ratios of OIB and MORB. High $^3\text{He}/^4\text{He}$ OIB have MORB-like $(\text{Th}/\text{La})_N$ ratios and Th contents. (a) $^{208}\text{Pb}/^{204}\text{Pb}$ and (b) Th content vs. Th/La normalized to primitive mantle in OIB and MORB. For Th, only samples with $5\text{wt.}\% < \text{MgO} < 15\text{wt.}\%$ are shown. Symbols and data sources are as in Fig. 2.

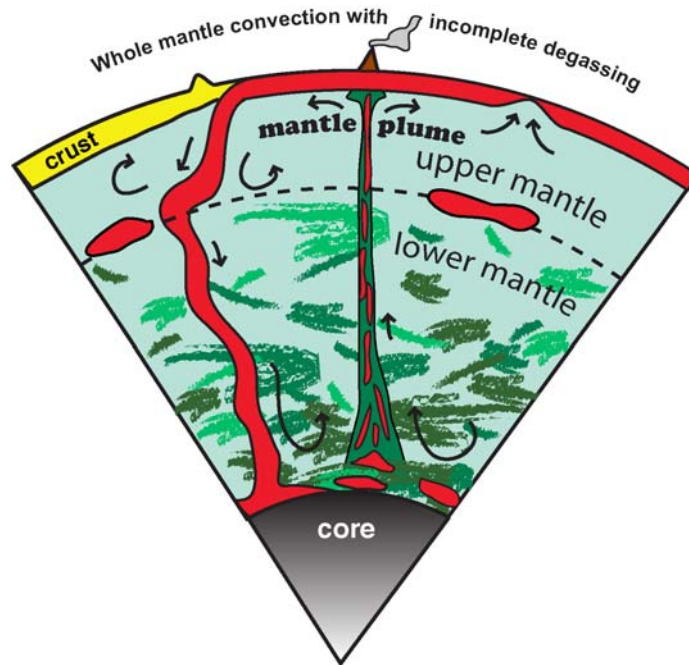


Figure 4. Schematic diagram illustrating the Class and Goldstein (2005) mantle model where mantle plumes are formed from ‘old depleted mantle’ characterized by high $^3\text{He}/^4\text{He}$ and recycled material dominating the radiogenic ^4He budget.

The compositions of the four He-groups of OIB show the following systematics (Fig. 2, 3): (i) lower $^{143}\text{Nd}/^{144}\text{Nd}$ ratios are associated with lower $^3\text{He}/^4\text{He}$, (ii) at a constant $^{143}\text{Nd}/^{144}\text{Nd}$ ratio, higher Pb isotope ratios are associated with lower $^3\text{He}/^4\text{He}$, and (iii) low $^3\text{He}/^4\text{He}$ ratios are accompanied by high Th, U abundances independent of partial melting effects. The compilation shows there is a global relationship between the $^3\text{He}/^4\text{He}$ groups and Th+U contents of OIB. There is ample evidence that OIB sources contain recycled oceanic crust and sediment that affect their Sr-Nd-Pb-Hf isotope ratios and contribute trace elements such as Th and U. The recycled component cannot provide significant primordial ^3He , as

helium is degassed during oceanic crust formation, alteration and subduction, but it would contain radiogenic ^4He produced after crust formation by Th+U decay. The global relationship between $^3\text{He}/^4\text{He}$ ratios and Th (and U) contents (Fig. 3) indicate that OIB sources contain both a primordial helium component and extra radiogenic ^4He from Th+U in recycled oceanic crust (i.e. basalt \pm sediment).

These global systematics are based on the majority of OIB, and therefore we conclude that these systematics can be used to generalize about the nature of OIB sources. Island groups displaying the strongest primordial $^3\text{He}/^4\text{He}$ signal are the ones that are chemically (e.g. low Th and Th/La, Fig. 3) and isotopically (i.e. Sr, Nd, Pb) most like mid-ocean ridge basalts (although we emphasize that we do not mean they are the DM end-member). This indicates that like MORB, OIB sources have become depleted in incompatible elements through processing by plate tectonics over geological time. This shared history still allows a distinction from MORB sources, and is consistent with the concept of “FOZO” as a source of the high $^3\text{He}/^4\text{He}$ OIB. Class and Goldstein (2005) showed through modeling that helium isotopes in the mantle can be explained through continuous, incomplete degassing by continent and ocean crust formation. It appears that the high $^3\text{He}/^4\text{He}$ component in plume sources is compatible with whole mantle convection and represents “old” depleted mantle, isolated from convection and upper mantle degassing for 1-2 billion years. Such isolation seems the most likely to be possible in the lower mantle (Fig. 4). Thus, the global Nd-Pb-He isotope and Th systematics suggests that the majority of OIB are formed by upwellings from sources in the lower mantle.

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Geomicrobiology in oceanography: Mineral-microbe interactions in the deep sea

Edwards, K J; Santelli, C M; Banning, E; Toner B; Rogers, D R

At mid ocean ridge (MOR) spreading centers and seamounts, the ocean crust is exposed to oxygenated seawater and microbes. On a global basis the MOR systems represents a $\sim 600,000 \text{ km}^2$ continuous rock-colonizing ('endolithic') community of microbes, ranking it the largest endolithic microbial ecosystem on Earth. Fluid circulation at ridge flanks and seamounts may “inoculate” the subsurface, extending this ecosystem hundreds of meters into porous basement. In theory, microbes can propagate where water, nutrients, and energy are available, and temperatures permit. However, few studies have empirically examined the nature of deep-sea endolithic microbial ecosystems in any detail. Consequently, fundamental questions remain to be addressed, such as, what is the abundance and activity of endolithic deep-sea microbial communities? What ‘types’ of microbes – from a phylogenetic and physiological standpoint – comprise deep-sea endolithic communities? And importantly, what role, if any, does this biosphere play in important geochemical processes such as rock weathering and elemental exchange between ocean and crust?

To answer these questions, we are studying deep-sea microbial communities at the Lo’ihi seamount, Hawaii, and at the East Pacific Rise 9°N (a RIDGE 2000 Integrated Study Site) on a long-term, time-series basis. A multi-disciplinary approach for studying microbial communities colonizing rocks and

minerals at these sites will be discussed. Our work applies microbiological and geochemical methods for ‘full-circle, spatially-resolved geomicrobiology’: a suite of integrative, iterative approaches designed to link specific microbes and microbial communities with biogeochemical processes. The microbiological techniques involved include culturing, physiological studies, and both 16S rDNA and genomic sequencing to determine the composition and function of these communities. In-situ experiments with rock substrates, in tandem with examination and analysis of environmental samples, are being assessed using 16S rDNA phylogenetic approaches, fluorescence and electron microscopy, and synchrotron-based mineralogical and chemical methods. Our specific goals are to establish definitive roles for microbes in ocean crust weathering in the deep sea; however, in principal these types of approaches can be applied in an integrative fashion to study mineral-microbe interactions in a variety of Earth environments.

Rivers and the weathering factory

Gaillardet, J

The weathering factory is transforming material of the Earth’s surface into secondary products, either soluble or solids, that rivers are exporting to the ocean, the ultimate sink. This factory has been functioning for several billion years and has allowed the atmosphere, ocean and sedimentary reservoir to acquire their present day chemical composition.

Over the last decades, considerable efforts have been made by the geochemical community to fully understand the weathering factory. Experimental and field work has been developed and chemical or isotopic tools have been set up to understand the sensitivity of the different minerals and rocks to chemical weathering, the rates of weathering and the fate of weathering products in the ocean. The global picture proposed by Garrels and Mackenzie (1972) has given rise to an abundant literature on the relationships between weathering and climate evolution through geological time.

Here, we review the main characteristics of the weathering factory that have recently been deduced from the geochemistry of rivers. Rivers integrate the diversity of weathering processes and allow the calculation of material fluxes. They allow to trace the origin and pathways of weathering products on continents and to estimate the rates at which the weathering factory is working. Finally, river geochemistry allows to identify the key factors that regulate the weathering factory.

1. What does the factory produce?

The factory produces solids and dissolved elements. However, in particular for solids, the production is not constant through time, and peaks of production occur. The relationship between basin hydrology and chemical exportation is of crucial importance. The solids that are being produced by the weathering reactions do not have a single grain size and mineralogy. A wide range of particle size and mineralogical type is observed in rivers. This has important implication for the sampling and monitoring of river products.

2. What are the different primary materials that the factory consumes?

Chemical and isotopic investigation of rivers clearly show that all kind of rocks and minerals are being weathered when they are in contact with water and a source of acidity. However, the source of acidity may be variable, even if the major source is the dissolution of soil CO₂ (of biogenic origin) in water. Recent data have shown that sulfuric acid, and nitric acid in agricultural watersheds are a significant source of acidity.

3. The factory has different regimes.

Rivers do not support the conventional and simplistic view that chemical weathering is occurring in soils. It remains difficult to assess the global role of soils for chemical weathering reactions, but some of the major fluxes of chemically weathered material occur in regions where soils do not even exist! Weathering can be surficial or can affect the whole mineral. Groundwaters can provide in some cases a major contribution to rivers.

4. The factory is recycling its material.

One of the features of the weathering factory is that most of the material that is processed in the factory has already been weathered in the past. This results in a loss of efficiency for the weathering factory and gives a great importance to regions where rocks have never been weathered such as basaltic or andesitic provinces. New isotopic developments confirm that most of river material are recycled and allow to constrain the timescale of chemical weathering products within a drainage basin.

5. What is the production rate?

River chemistry shows that the weathering rates are very variable on Earth. This is a result of a combination of environmental factors, such as temperature, runoff, lithology and physical denudation processes. Basalts weather 10 times faster than granite in certain conditions. Limestones weather even more rapidly.

6. Is the factory a source or a sink of atmospheric CO₂?

The conventional view is that only silicate weathering is a net sink of atmospheric CO₂ over long time-scales can no longer be held if carbonate and silicate are weathered by sulfuric acid. This acid is derived from the oxidative weathering of pyrite, and transformation of old sedimentary organic matter into CO₂. Some recent results from the Mackenzie river basin show that diverse microbial metabolisms, depending on the hydrological conditions are responsible for a huge amount of sulfuric being produced and being available for carbonate weathering.

7. The factory needs fresh mineral surfaces and high temperatures.

The comparison of river chemistry in different weathering environments has shown that temperature and water abundance are key factors for determining weathering rates. Basalt weathering for example obeys to an Arrhenius-type law. However, the production of fresh mineral surfaces appears as a limiting factor. This can be shown with variable examples. In the Amazon basin, for example, the weathering factory is active in the mountains of the Andes, but not in the plain, however submitted to warm and humid conditions. In the Mackenzie basin, the exactly opposite result is obtained. In both cases, mechanical and chemical weathering rates are coupled.

8. The river geochemistry toolbox.

A toolbox including isotopes and chemical elements concentrations has been developed by the different groups. Tracers of sources (carbonate vs. silicate), tracers of timescales, tracers of groundwater inputs or of the sources of acidity are actively used. The development of new isotopic tracers is clearly promising.

9. What do we need to sample?

Because the chemical weathering factory is complex we need to simplify nature to identify the key factors. A network of weathering sites is being constructed that will help the geochemical community to calibrate the different tracers. As our world is changing in response to anthropogenic activities and in-

creasing energy demand, we think that a major challenge of the weathering community is to monitor rivers seriously. Rivers are observatories of the way the surface of our planet is changing, of the way the soils formation and destruction is evolving, of the way the ecosystems are going to adapt to global changes, and of the way the water resource is going to evolve both in quantity and quality.

CHRONOS: Transforming Earth History Research By Seamlessly Integrating Stratigraphic Data And Tools

Grossman, E L; McArthur, J; Cervato, C; Fils, D; Bohling, G; Bowring, S; Diver, P; Greer, D; Lambi, B; Ogg, J; Reed, J; Sadler, P; Tang, X

Geologic time is the intellectual theme that connects a wide variety of research endeavors in geoscience – missing is the corresponding cyberinfrastructure that allows the resources of all these endeavors to be pooled. CHRONOS (www.chronos.org) is a community facility that addresses the geoinformatics needs of sedimentary geology, paleochemistry, and paleobiology, especially emphasizing global correlation and time-series analysis. CHRONOS's purpose is to transform Earth history research by seamlessly integrating stratigraphic databases and tools into a virtual on-line stratigraphic record. CHRONOS provides an open, community-based geoinformatics platform for storing, accessing, and analyzing sedimentary geological, geochemical, and paleobiological data. This effort directly supports cutting-edge research on evolution and the diversity of life, climate change, geochemical cycles and global change, and many other aspects of the Earth system.

Numerous discussions at workshops and meetings have underscored community needs: convenience, quality control, and cost containment. These needs have lead to the following guiding principles for CHRONOS development:

- Provide an architecture that is flexible, open, and searchable;
- Give users a choice of data-entry pathways;
- Allow linked databases to maintain autonomy;
- Integrate time and stratigraphy;
- Develop tools and data services together;
- Distribute and share costs with research opportunities.

The full CHRONOS system includes a core Information Technology (IT) facility and databases, a global network of federated databases, tools, targeted development projects, and education/outreach activities. CHRONOS and its partners cooperate to: 1) link existing databases and other geoinformatics components into a single interoperable network, 2) provide primary databases to capture relevant data types, 3) offer tool sets for data analysis, and 4) create working groups and organize workshops to ensure that the needs of the community are met. Whereas no single facility can encompass all the data types needed for all of Earth sciences, nor provide all the analytical tools necessary to work with and synthesize these data, we are developing a facility that addresses many of these needs, that interoperates with other data collections, and is connected to a national geoinformatics and computational grid (GEONGrid).

The CHRONOS database HERMES (named after the Greek name of Mercury, messenger of the gods and first alchemist) is a relational database for geochemical and geochronological data running under Postgresql. HERMES is specifically designed to meet the needs of chemostratigraphers and paleocean-

ographers, and is closely tied with CHRONOS's Neptune database, age model database, and age/depth plotting tool. The geochemical component of the schema has been designed by Pat Diver with the assistance of Ethan Grossman and John MacArthur, and has built upon lessons learned from EarthRef, PaleoStrat, PetDB, JANUS (IODP), and the USGS. It utilizes valuable feedback from 27 attendees of the CHRONOS sedimentary geochemistry workshop in San Antonio, TX (June 2004) and the advice of CHRONOS's Sedimentary Geochemistry Working Group. HERMES is tailored to include data quality and sample quality metadata. Data quality metadata include sample handling, sample treatments, analytical methods, standardization method, and precision. Sample quality metadata for fossils include mineralogy, microstructure preservation, cathodoluminescence, trace element content, and conodont alteration index. For whole sediment studies, % CaCO₃ and % organic carbon are important metadata entries. Using metadata, users will be able to set criteria for sample quality in their legacy data compilations.

Paleochemists and chemostratigraphers will shortly be able to download their spreadsheets into the HERMES database, or connect to remote databases and data repositories (e.g. Pangaea, PaleoStrat, SedDB) and retrieve attributed data compilations without physically copying the data into HERMES. CHRONOS will provide tools for plotting, modeling, stratigraphic correlation, time scale development, age modeling, standardization, normalization, and more. Many of these tools are now available online. Ultimately, by augmenting and connecting community databases and giving them an unprecedented level of interoperability, CHRONOS will provide a virtual, on-line, electronic stratigraphic record - a means to increase the tempo and scope of integrative geoscience.

Dehydration and Intermediate-Depth Seismicity in Subducting Slabs

Hacker, B

Thermal–petrologic models of subduction zones show a correlation between the patterns of intermediate-depth seismicity and the locations of predicted hydrous minerals: earthquakes occur in subducting slabs where dehydration is expected, and they are absent from parts of slabs predicted to be anhydrous. A subducting oceanic plate can consist of four petrologically and seismically distinct layers: 1) hydrated, fine-grained basaltic upper crust dehydrating under equilibrium conditions and producing earthquakes facilitated by dehydration embrittlement; 2) coarse-grained, locally hydrated gabbroic lower crust that produces some earthquakes during dehydration but transforms chiefly aseismically to eclogite at depths beyond equilibrium; 3) locally hydrated uppermost mantle dehydrating under equilibrium conditions and producing earthquakes; and 4) anhydrous mantle lithosphere transforming sluggishly and aseismically to denser minerals. Fluid generated through dehydration reactions can move via at least three distinct flow paths: percolation through local, transient, reaction-generated high-permeability zones, flow through mode-I cracks produced by the local stress state, and post-seismic flow through fault zones.

Water in the Earth's Mantle; Intro and Outro

Hauri, E H

Most of the hydrogen in the Earth's upper mantle is dissolved in nominally anhydrous minerals such as olivine, orthopyroxene, clinopyroxene and garnet [e.g. 1]. Compared to its abundance, water has a disproportionately large influence on mantle properties such as solidus temperature, rheology, diffusivity, electrical conductivity and seismic velocity, so it is important to understand both the distribution of wa-

ter among mantle phases and the mass transfer processes that influence water distribution in the Earth's mantle. Despite the important role of water in the mantle, experimental determinations of the equilibrium distribution of trace amounts of hydrogen among coexisting silicate phases remain extremely limited. Improved analytical techniques have recently paved the way for quantitative investigations of water partitioning and abundances in nominally anhydrous mantle minerals [e.g. 2]. Several studies of submarine glasses have revealed correlated increases in incompatible elements and water contents along segments of mid-ocean ridges approaching hotspots [e.g. 3,4], and variably hydrated and dehydrated regions of the mantle have been postulated to account for these variations. New experimental water partitioning data illuminate these differences.

Hydrogen isotope ratios vary in submarine glasses from ocean ridges, back-arc basins and hotspots, and in hydrous phases from arcs and hotspots, suggesting significant hydrogen isotopic variability in the mantle, which may be related to the subduction of water. Water clearly enters the upper mantle at subduction zones, however the full water budget for any single subduction zone is highly uncertain [e.g. 5]. This uncertainty in the water budget at convergent margins indicates that we do not even know whether the present-day net flux of water is into or out of the Earth. This talk will highlight areas of both knowledge and ignorance on the origin and distribution of water in the Earth's mantle.

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Petrologic considerations of pyroxenite heterogeneities in basalt source regions

Hirschmann, M; Kogiso, T; Pertermann, M

Key questions regarding the role of heterogeneous lithologies in oceanic basalt source regions include (1) What is the spectrum of heterogeneity compositions and what is their origin? (2) What are the processes that occur when heterogeneous mantle undergoes partial melting and (3) How does melt extraction and transport modulate the signatures of heterogeneous partial melts?

Pyroxenitic domains in basalt source regions are likely to have a wide spectrum of compositions, in part because of diverse origins of the domains and in part because of modifications of the domains during ~1-2 Ga residence in the mantle. Experiments investigating sub-solidus diffusive interactions at 3 GPa between quartz eclogite and garnet peridotite show vigorous modification of both domains (Fig. 1). Regions of quartz eclogite are converted to garnet pyroxenite and regions of garnet lherzolite proximal to the margin are converted to garnet orthopyroxenite or garnet websterite. These interactions are of potential importance for several reasons: (1) Partial melting models in basalt source regions may need to account for partial melting behavior of orthopyroxene-rich lithologies, which are poorly known. (2) Major element, trace element, and isotopic signatures of recycling may be decoupled depending on the prevailing effective diffusivity of different elements and isotopes. (3) Heterogeneities entering basalt source regions may be surrounded by orthopyroxene-rich septa, which may inhibit interactions between partial melts of pyroxenites and surrounding peridotite.

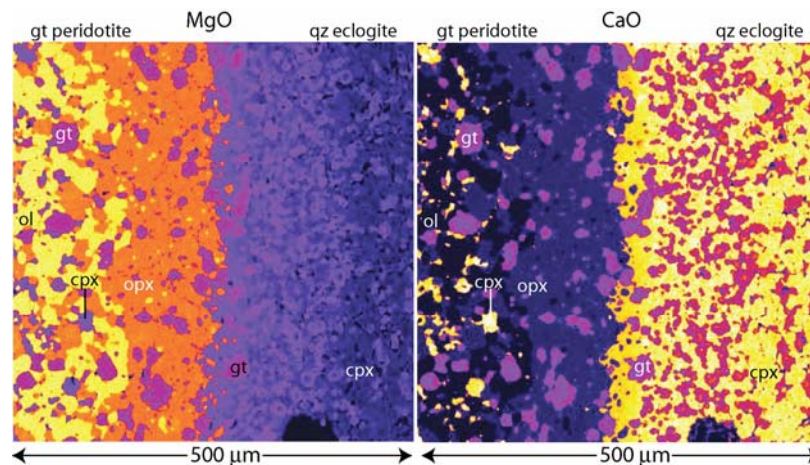


Figure 1. X-ray element maps of subsolidus reaction between garnet peridotite and quartz eclogite at 3 GPa, 1200 °C for 96 hours. Olivine and cpx dissolve in peridotite, producing a thick (~100 micron) garnet orthopyroxene skarn.

Quartz eclogites originating from subducted oceanic crust are likely to be transformed into bimineralic quartz eclogite, either by (a) loss of fluids or melts during subduction dehydration (b) diffusive interactions with surrounding peridotite and/or (c) removal of small amounts of melt deep in basalt source regions. It is widely assumed that bimineralic lithologies will be refractory compared to more mineralogically complex peridotite. However, experimental data, including new experiments on bimineralic eclogite conducted at 3 and 5 GPa, show that this is unlikely to be true. Compatible or modestly incompatible behavior of Na in eclogitic cpx at high pressure creates residues that remain more fertile than peridotite to high degrees of melting. Moreover, partial melts of bimineralic eclogite at 3-5 GPa are alkalic basalts.

Probably the most knotty question regarding the effect of partial melts of heterogeneities is their fate once they are extracted from their source domains. The simplest process is that the melts are extracted with little interaction with peridotite and are mixed with partial melts of peridotite at shallow levels. This idea is widely disparaged because it is difficult to imagine how partial melts of mantle heterogeneities fail to react with surrounding peridotite. However, the viability of this model clearly depends on the trade off between the length scale of pyroxenitic domains and the distance between the domains and available fast paths (channels or dikes) through the overlying lithosphere. Further, effective extraction of melts from pyroxenites to shallow levels is consistent with geochemical evidence (chiefly from Os isotopes) that blending of melts from different components in OIB source regions occurs by melt-melt mixing, rather than by melt-rock interaction. Such a process may be no less surprising than that required by eruption of any highly alkalic basalt, which demonstrate that some melts are transported from ~80-100 km depth with minimum interaction with the mantle. Alternatively, partial melts of pyroxenite may interact extensively with surrounding peridotite, leading to a model of metasomatism and refertilization, as advocated by Yaxley and Green (1998) and as will be discussed in greater detail at this meeting by Sobolev. This model has many appeals, though it is unclear whether it can account for previously inferred melt-melt mixing trends.

GeoReM: A Geochemical Database for Reference Materials and Isotopic Standards

Jochum, K P; Nohl, U; Sarbas, B

Jochum et al. (2005) developed the GeoReM database (<http://georem.mpch-mainz.gwdg.de>) for reference materials of geological and environmental interest, such as rock powders, synthetic and natural glasses as well as mineral, isotopic, river water and seawater reference materials. GeoReM is a relational database, which strongly follows the concept of the three EARTHCHEM databases GEOROC, PetDB and NAVDAT. It contains published analytical and compilation values (major and trace element concentrations, radiogenic and stable isotope ratios), important metadata about the analytical values, such as uncertainty, uncertainty type, method and laboratory. Sample information and references are also included.

Queries are possible now by: (1) Sample names or material types, (2) Chemical criteria, (3) Bibliography, and (4) Methods and institutions.

Querying by sample names the database provides ranges of published data for concentrations and isotope ratios. To get more detailed information, all primary data and metadata can be shown and downloaded. It is also possible to query by material type (powder, glass, solution, mineral, gas, metal) and material (e.g., basalt, komatiite, seawater).

To query by chemistry, element concentrations and isotope ratios can be selected. As a result, a list of suitable reference materials fulfilling all selected chemical criteria is shown. The database provides tables with all analytical data for these samples or data only for the selected items. Furthermore, the number of analytical data can be reduced by selecting one or more materials, material types and/or methods. Four bibliographic queries are possible, by author or coauthor(s), journal, keywords, and by GeoReM number. The GeoReM number, which unambiguously assigns to the reference, may be useful for citation purposes.

The query by methods and institutions provides lists of methods used in selected institutions, and lists of institutions using certain techniques. For example, it is possible to list all LA-ICPMS, SIMS or MC-ICPMS laboratories stored in GeoReM, and to find out analytical techniques used in selected institutions including detailed information about the elements, the isotope ratios measured and the reference materials analyzed.

GeoReM currently contains more than 1000 geological reference materials, 8000 individual sets of results and references to 1000 publications.

New developments are in progress to link references of GEOROC and GeoReM databases to each other. This means that the quality of published geochemical data for ocean island basalts, flood basalts and intraplate volcanic rocks available in GEOROC can be better controlled taking advantage of the much more specific analytical information supplied by GeoReM.

References

Jochum et al. (2005), *Geostandards and Geoanalytical Research*, 29, 333-338.

Universal kimberlite exploration system (the “spiderweb”)

Kryvoshlyk, I

Each successful exploration company has to have a reliable exploration strategy. This should provide information to make following steps forward logical and so avoid exploration within wrong areas. Even the best exploration techniques will provide unsatisfactory result if it applied to barren areas. My Kimberlite Exploration System includes four main parts: Kimberlite Provinces, Large Diamond Mine Locator, Diamond Grade Grid, and Garnet-Ilmenite Geochemical Program.

The Kimberlite Provinces program displays the law of spatial distribution of the areas with highest volcanic activity on the Earth. Within mobile belts, this program indicates locations of “hot spots”. Within ancient platforms, it indicates locations of kimberlite provinces. For instance, in Northern Hemisphere locations of two major “hot spots” (Alaska and Iceland) along with all three known kimberlite provinces (Slave, White Sea and Yakutia) create equilateral five-pointed star within the same radius from North Pole.

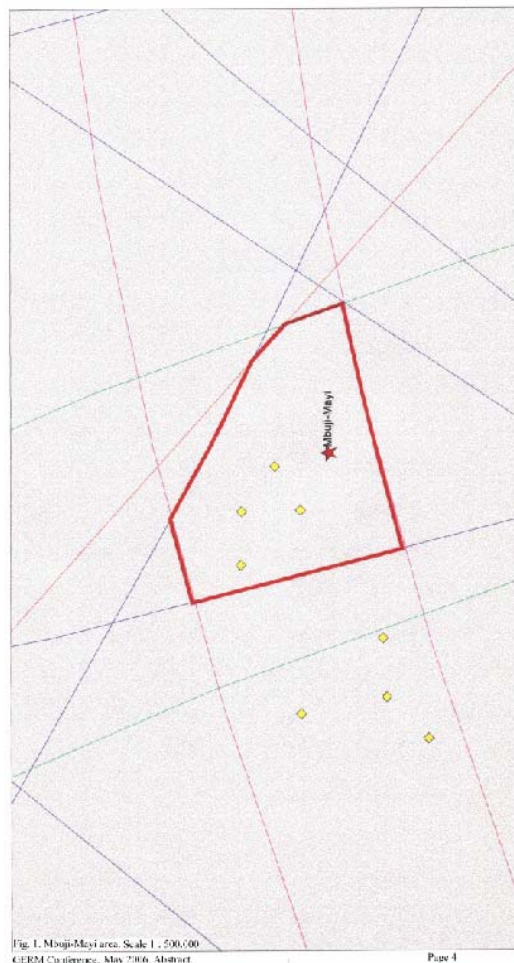


Figure 1.

The Large Diamond Mine Locator (LML) was designed to describe mathematically calculated distribution of large diamond mines on the earth’s surface. LML was created to aid in selection of large (hun-

dreds of square km) exploration areas, which can contain economically profitable diamond mine. LML has to aid to focus company's effort to get maximum result with minimum expense.

LML looks like a multiple combination of stereometrical complexes. Each complex consists of about two dozen concentric conical figures. On the earth surface, they look like a group of concentric circles. The main parameters and geographical location of these were calculated with the same set of mathematical formulas. The absolute values of the complexes's dimensions create mathematical series (sequences).

Intersections of complexes indicate the areas (polygons) of the highest chance to contain large diamond mine. The higher number of intersection at each particular polygon (double, triple or quadruple) indicates the higher probability of the presence of large diamond mine within that intersection (Fig. 1). Statistically almost all known large diamond mines are located within such polygons. In other words, there are no large diamond mines outside these areas. Therefore, there is no reason to waste time and budget for exploration between polygons.

Diamond Grade Grid (DGG) also can be used as a Small Diamond Mine Locator. It has to aid in evaluation within state, province or territory of the local small size areas (tens of square km) displaying the distribution of the kimberlites with high (greater than 30 cpht), moderate (10 – 30 cpht) and poor (less than 10 cpht) diamond grade on the mantle level of their origin.

DGG looks like a composite planimetric figure, which have clear geographical accordance with major local tectonic structures. DGG orientation is different for different regions (provinces). For example, within James Bay Lowlands (Northern Ontario) DGG has an azimuth N.W. 326. This is very close to orientation of the Lake Timiskaming Rift Zone (“Diamond Corridor”) – N.W. 325 (JML Resources) or – N.W. 330 (Northern Shield Resources) or – N.W. 327 (Moorhead et al, 2003?). Within central part of the Slave Province DGG has an azimuth N.E. 27. Approximately the same angle we can get if to measure the direction of the longest axis of the Slave Craton, if to approximate its shape to ellipse.

DGG within Africa continent has azimuth E.S.E. 97 for Cape Province, which is close to direction of “the seismically slow regions of the northern Kaapvaal Craton” (Shirey S.B., et al, 2003). DGG azimuth N.E. 50 for Gibeon Province roughly coincides with direction of the close located Damara Mobile Belt (by Boroukaev C.B., Elizariev U.Z., et al, 1976). Approximately the same azimuths we can find in publication by R.H.Mitchell (1986, Fig. 30): E.S.E 94.5 for Cape Province, and N.E. 43-45 for Namibia.

The Diamond Grade Grid was built based on Garnet-Ilmenite Geochemical Program calculations for pyropes and ilmenites.

Garnet - Ilmenite Geochemical Program (GGP). “A diamond junior's first task is to find a diamondiferous kimberlite. The next and very important step is to provide a convincing arguments as to why this kimberlite deserves a more expensive mini bulk sample to establish carat grade” - (John Kaiser, Nvest@groups.msn.com 3/19/2002).

GGP is a quick and statistically confirmed way to convert chemical composition of garnets into reliable value of the diamond grade for each separated kimberlite (Table 1), bearing in mind the existence of three sources of diamonds: one peridotitic and two eclogitic (ECL-1 and ECL-2, perhaps, one of them – for igneous eclogites and another one – for metamorphic eclogites (Kryvoshlyk, 2003). GGP is based on the file with more than 55,000 of individual garnet analyses and ca. 25,000 of ilmenites. GGP was cre-

ated with about a dozen of standard geochemical formulas and several newly found mathematical equations.

It can be useful in selection of the best exploration activity, and preliminary evaluation of diamond mine before expensive traditional feasibility study, which includes intensive drilling, sampling, processing, etc. “To find a kimberlite pipe is like finding “a needle in a haystack”. The collective expenditure on exploration [using traditional technique – I.K.] to locate one kimberlitic diamond mine is estimated to be in the vicinity of \$500 million.” - (Features Archive, May 26, 2000). It is quite possible, that “The Spiderweb” will decrease that number significantly.

Kimberlite	Estimated (feasibility study, before the end of mining)			Recovered (after mining)	Calculated (present research)
Marsfontein M-1 Pipe S.Africa 1999	335 Rangold Explor. Press Release 1998	308 Small Mines Field Excurs. 7 th IKC, 1998	242 S.Collingridge Wordsmith 1999	148.58 Southernera Annual Report 2000	151.09 based on 356 PYR, 7 ECL-1 & 59 ECL-2
Klipspringer: South Africa 2000	47 Badger Mining & Cons. Aug. 2000 (Southernera, 2002)			42 Annual Meeting May 2003 (Southernera, 2003)	44.20 based on 15 ECL-2
Kimberley “Big Hole” South Africa	No Data Available			63.88 Generic Template Diamonds of Africa	64.23 based on 241 PYR
Roberts Victor South Africa	No Data Available			up to 100 Flinders Diamonds Annual Report 2004	100.06 based on 44 PYR & 9 ECL-2
Udachnaya Siberia Russia	120 Miller, P. “Diamonds” Yorkton Sec., 1995	100 First Strike Diamonds Inc. Web Site		60 Eberle, J.M. “Diamant: panorama minier mondial Part 2.” Feb. 2003	60.44 based on 31 PYR 1998
D0-27 NWT Canada	1.3 (Kennecott, 1994) Dentonia Res. “Microdiamonds” 2005	1 Boxer, G.L. 2002	36..... 89.88 NE lobe....South. lobe Peregrine Diamonds June 14, 2005	No Data Available	71.42 based on 58 PYR 2000

Table 1. Kimberlite diamond grade (cpht). Comparison of Calculated grade by “Spiderweb” against Recovered or Estimated by regular methods.

References

John Kaiser. Nvest@groups.msn.com 3/19/2002.

Kryvoslyk I. 2003. Garnet & Ilmenite Geochemical Computer Program For Exploration For Diamonds. 8th IKC, Victoria, B.C.

Composition of the Interactive Mantle and Origin of the Depleted Mantle

Langmuir, C; Jun Su, Y

As a community we have inherited a kind of mental paradigm where there is a "depleted upper mantle" and then enriched reservoirs, usually considered to be deeper. This "DM" composition has been most often modeled to be the complement to the continental crust, although recent work has pointed out that the fit is not perfect. We suggest a separation of the words "depleted" and "upper", because of course all volcanism comes from the upper mantle, and therefore the upper mantle, sampled today, encompasses the entire range of observed reservoirs. In addition, there is the question of what "upper" represents, because we do not have direct constraints on the depth of these reservoirs sampled by basalts. Several years ago we put together the average composition of the mantle sampled by ocean ridges, making sure to take into account both sampling and interlab biases. Subsequently we have made use of more than 500 ICP-MS analyses to try to get accurate values for the highly incompatible elements. This provides the fundamental data for evaluating the mantle reservoir sampled by volcanism. We are currently calling this composition the "interactive mantle" (IM) since it represents the mantle that interacts with the surface in observable ways. This IM composition has interesting characteristics-- it is the only mantle composition that fits as the complement to continents. The size is roughly 80% of the entire mantle--certainly not just the upper mantle. The composition is also identical to the mean source of huge flood basalt provinces such as the Ontong Java Plateau. Aside from such provinces, oceanic volcanism rarely samples this composition. Instead, plate recirculation has operated upon it to create mantle heterogeneity.

How is mantle heterogeneity created from this composition? Continent extraction creates IM-but otherwise shows little contribution to mantle heterogeneity. In fact, there is a remarkable lack of apparent influence of subducted continental crust on mantle compositions. Recycled ocean crust does not create enriched reservoirs--- the recycled crust model is inconsistent with both isotope and trace element evidence. Instead, enriched and depleted reservoirs are created by the movement of low degree melts of various flavors in various settings. Enriched reservoirs are created by the addition of low degree melts. The depleted mantle is the residue from extraction of low F melts from IM. Such a model is required by the trace elements, and is also required by the global isotope variations of Sr-Nd-Hf, and is not bad for Atlantic and Pacific Pb. Hence depleted mantle is a two step process (1) extraction of the continents from a large fraction of the total mantle; (2) extraction of low degree melts from IM. A very promising candidate for the fertile component of the depleted mantle is recycled eclogite from which low degree melt has been removed. In general, isotope evolution models need to be reconsidered to generate IM as the consequence of continent extraction through earth history, not "DM. "

Exploring the relationships between trace metals and the N and P cycles in the oceans

Moffett, J

The distribution and chemistry of several biologically active trace metals are closely linked to the nitrogen and phosphorus cycling in the oceans. In part, these relationships arise because the metals are required for metalloenzymes that catalyze key steps in the N and P cycles. Factors that control the spatial and temporal variability of key metals like Fe can influence the boundaries of various biogeochemical oceanic regimes on a global scale, with important implications for the carbon and nutrient cycles. Yet

among the most important factors controlling metals are the nutrient cycles themselves and the “functional groups” of microorganisms that control nutrient cycles. This leads to a variety of interrelationships and feedback scenarios that are poorly understood. In this presentation, I will show how the large database envisioned in the GEOTRACES program is absolutely necessary to understanding these relationships, drawing on several examples from my own research.

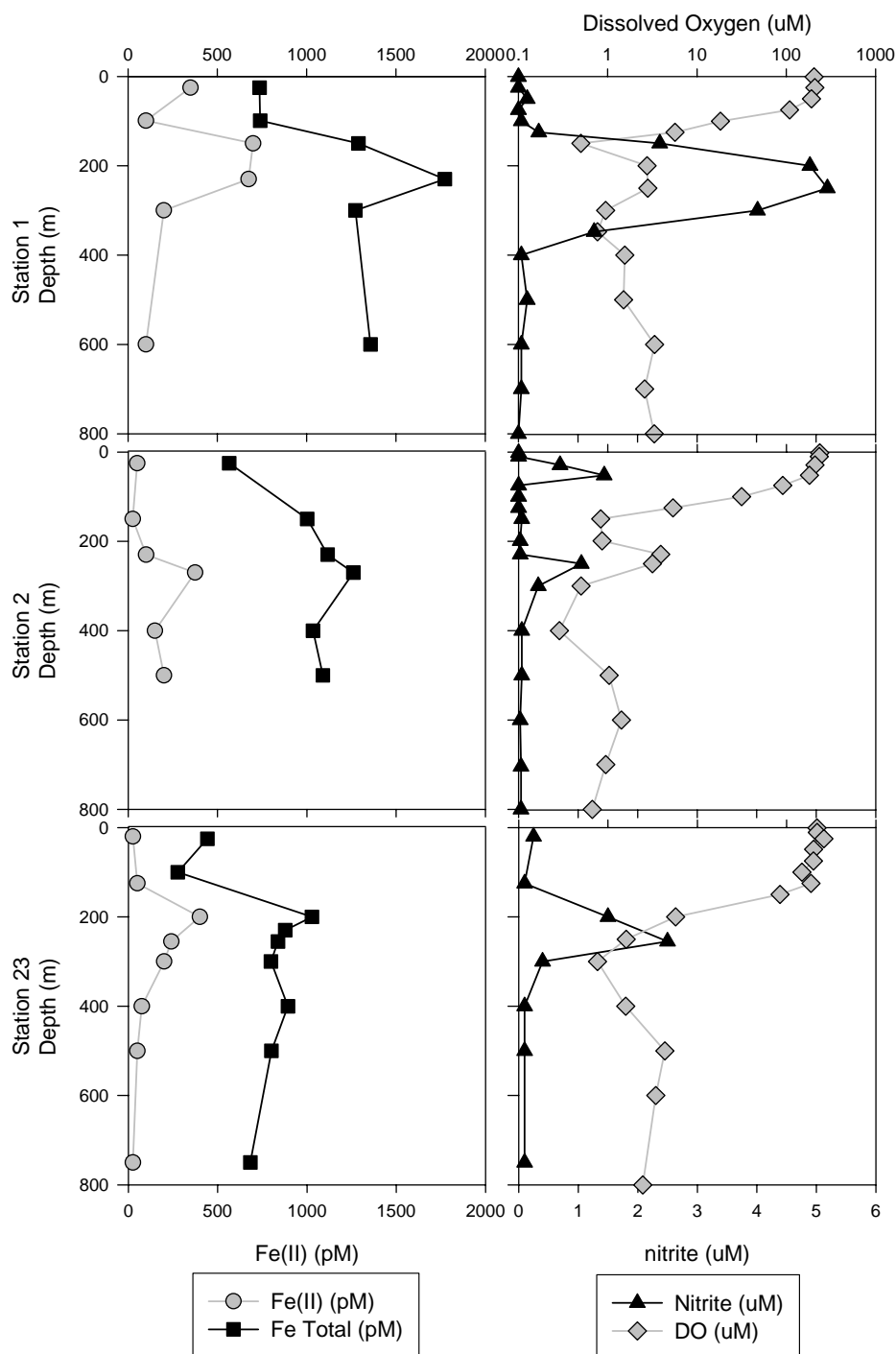


Figure 1. Fe(II), total dissolved Fe, nitrite and oxygen at three stations in the Arabian Sea.

Oxygen minimum zones in the eastern tropical Pacific and Arabian Sea are the major regions for denitrification in the world's oceans. While the zones are several hundred meters thick, most denitrification occurs in a very narrow band at the top of the OMZ defined by a sharp nitrite maximum and a local maximum in particle density associated with a rich microbial community. Here we show that this band is enriched in Fe, possibly through in situ reduction by denitrifying bacteria, which need Fe for denitrification (Figure 1). In the Arabian Sea, this results in a vast subsurface lens of water, depleted in oxygen and enriched in Fe and nitrite. In the eastern tropical Pacific, this deep nitrite maxima may be an important horizon for isopycnal transport of Fe from the Fe rich shelf waters of the Peruvian Coast. High resolution profiling is required to understand the mechanism which can maintain this structure, and sections are important to determine where this Fe ends up. Radioisotopes, particularly radium and Th isotopes are important to understand the source of the Fe (reminerzalization versus horizontal transport) and the importance of internal recycling.

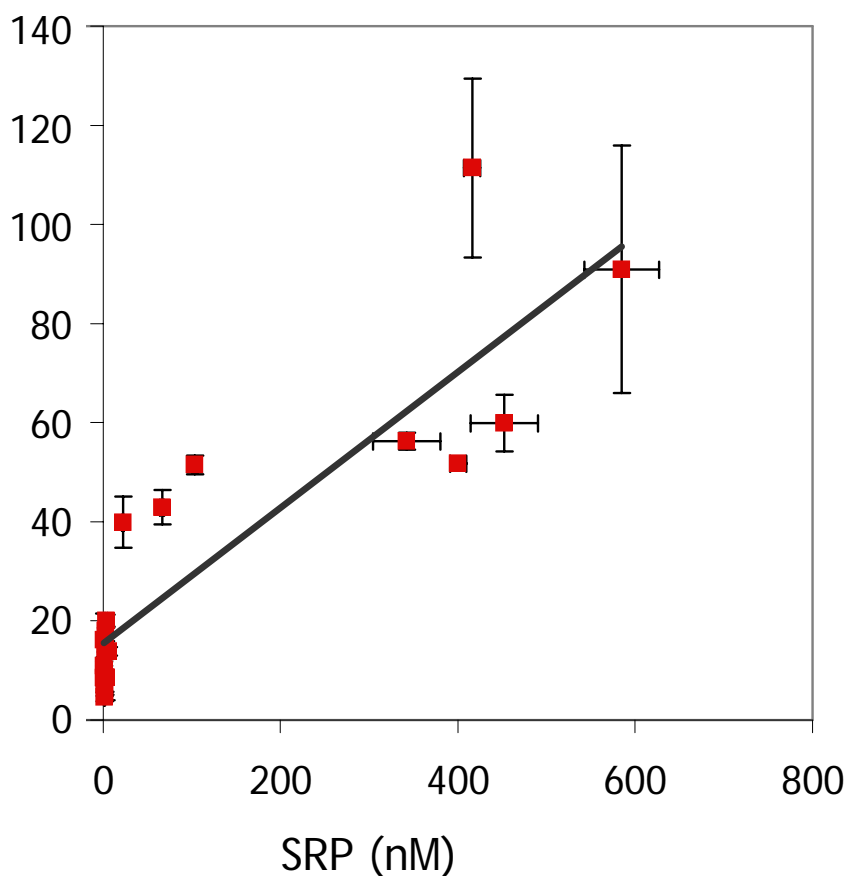


Figure 2. Cobalt versus P on a section in the NW Atlantic Ocean.

Keith Moore, Jim Christian and others have modeled the global distribution of Fe in surface waters incorporating data for atmospheric transport, internal cycling and removal and existing field data, and have been reasonably successful in simulating the open ocean distributions of Fe. They have used these results to predict the boundaries of Fe-limited HNLC regions. However, in boundary regions and marginal seas, the models don't work as well. A good example is the Arabian Sea. A biogeochemical model by Wiggert and coworkers predicts a very strong draw down of Fe during the SW monsoon to values

lower than 50pM, throwing the whole regime into Fe limitation. Measurements made by me, and by Chris Measures, show draw down, but not too these very low values. We argue that the sources of Fe have been underrepresented (perhaps by ignoring local features like the Shamal wind), or the extent of dust dissolution has been underestimated, or the modest data sets for Fe available to date are inadequate in light of the complex physical regime.

Moore and others have also modeled the linkage between Fe and nitrogen fixation associated with the high Fe requirement of nitrogenase enzymes, and simulated the Fe – controlled distribution of N-fixation in the global ocean. One way to test their model is to develop molecular diagnostics of Fe limitation in the N – fixing organisms, to see if they are truly stressed and to evaluate – and potentially re-define – the regional boundaries in Moore’s model output. Eric Webb has developed two such methodologies in recent years. Molecular biomarkers enable one to assess the physiological status of a key functional group (like N-fixers) without lengthy growout or incubation experiments that are at odds with the sectional and survey nature of GEOTRACES cruises.

Recent advances in detection limits for the determination of P in surface waters enable us to study the relationship between P and “nutrient-like” metals in oligotrophic gyres. Such measurements are particularly important in the NW tropical Atlantic, where dissolved inorganic P can be in the nanomolar range, and P limitation is likely to be important. Many elements show a tight correlation with P, but the relationship at low P can be obscured by high P detection limits, making it difficult to determine the slope or intercept. High quality P data reveals previously undetected trends. Figure 2 shows the relationship between Co and P in the Sargasso Sea. The positive y-axis intercept implies that Co only gets drawn below concentrations of 20pM when inorganic P has run out. One interpretation, based on process studies and incubations in my lab, is that under these conditions, phytoplankton synthesize a Co-containing alkaline phosphatase to utilize organic phosphorus, and this additional Co demand draws concentrations down to lower values. This mechanism provides a linkage between P limitation and metal geochemistry previously unrecognized. GEOTRACES provides an opportunity to examine metal – phosphorus linkages with the benefit of these newer analytical methodologies.

The role of plumes in the cooling of the Earth

Nolet, G

Mantle plume images using finite frequency tomography for both P and S waves agree that a large number of mantle plumes extend deeply in the lower mantle. The diameter of the images of velocity anomalies is large - in fact most plumes would not be resolvable at depth if it wasn't for their size. Yet, several plumes show signs of resistance at the 670 km discontinuity: although not a perfect barrier, widening of plumes just below 670 km depth indicates that the phase transition from ringwoodite to perovskite plus magnesiowuestite resists plume passage into the upper mantle.

Translating the P velocity anomalies - for which the plume diameter is better constrained than for the S waves - and applying the Stokes equation across well-resolved cross-sections we obtain a quantitative estimate of the heat and volume flux for several plume sections in mid-mantle. The actual flux through the plumes is narrower than the velocity anomaly would suggest, but even the plume flux width is of the order of 500 km or more.

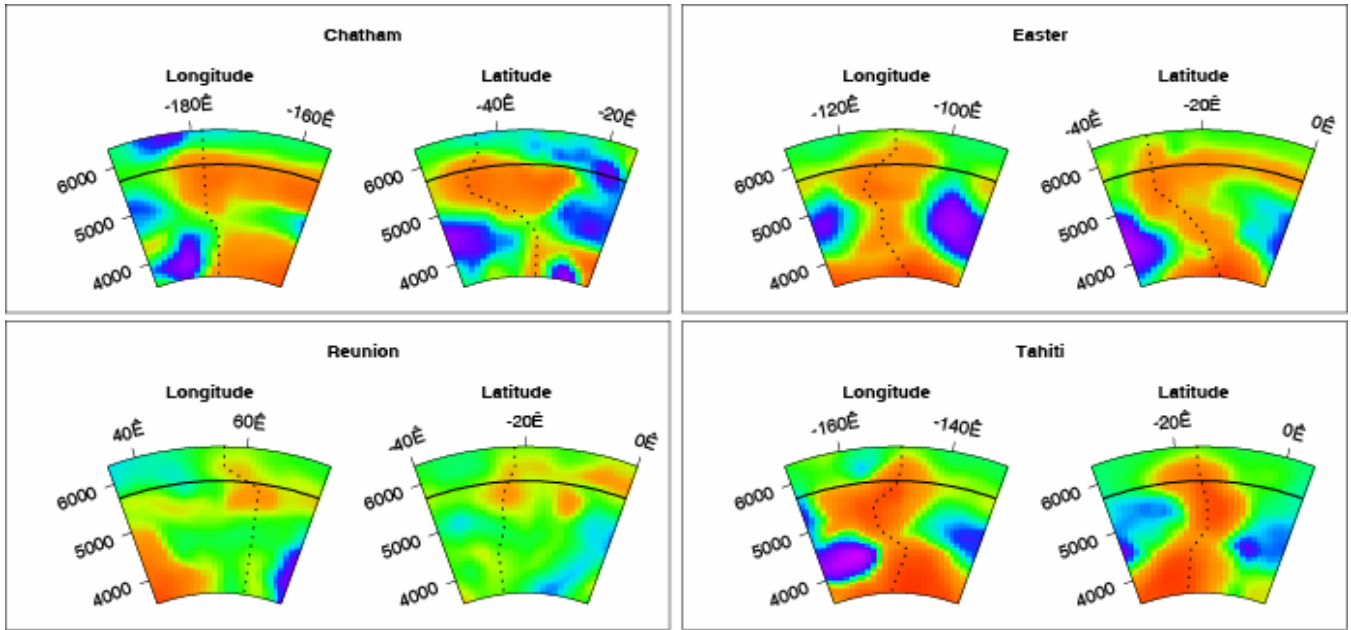


Figure 1. Four examples of plumes that widen or even get stuck below the 670 km discontinuity. The colour scale indicates temperature, with maximum temperature anomalies in the plumes about 350K.

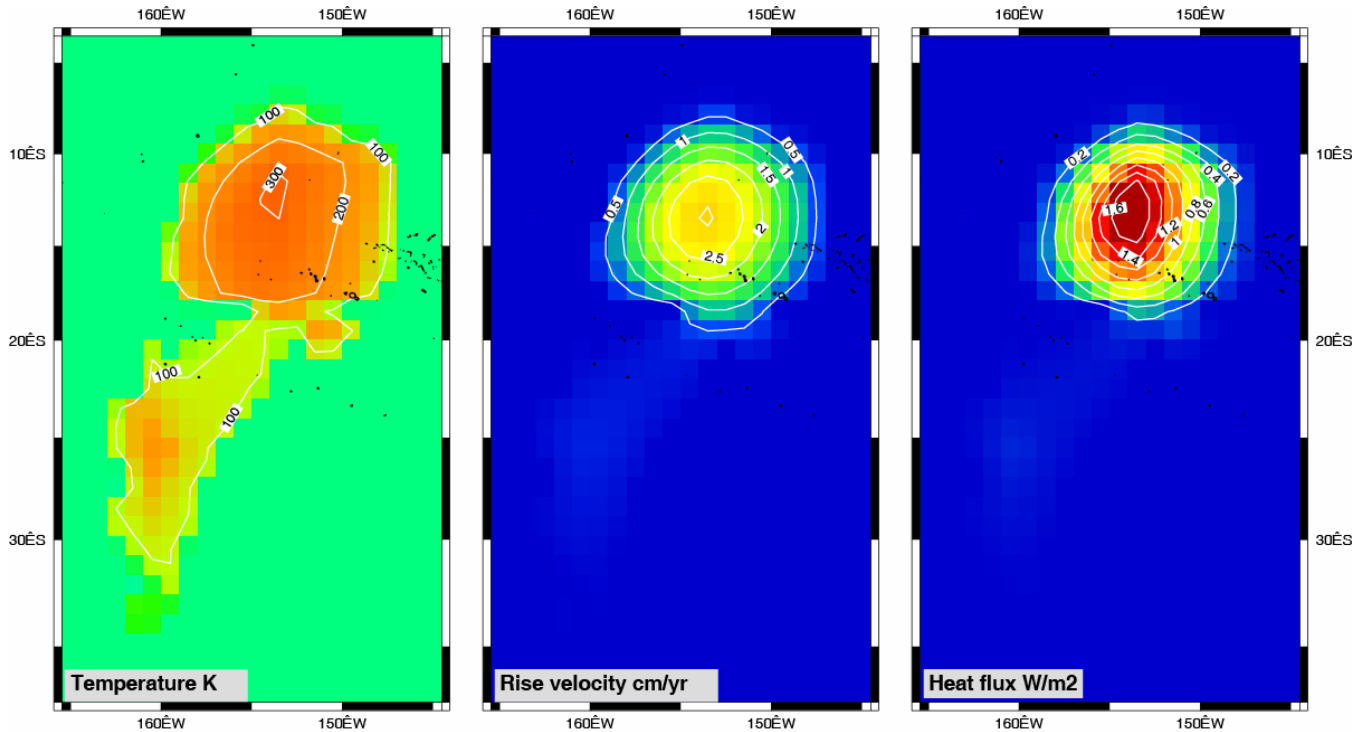


Figure 2. Illustration, from left to right, of the most important steps in the heat flux analysis, for the Tahiti plume at a depth of 1600 km. (left) The P-velocity anomaly as determined by a finite-frequency inversion of delay times is converted to a temperature anomaly. Temperature contours in Kelvin. (center) Solving Stokes' equation, assuming a balance between the buoyancy force and the viscous drag, yields the rise velocity of plume. Velocity contours in cm/yr. (right) Finally, we compute the heat flux Q .

Estimated heat- and volume flux for individual plumes at mid-mantle depths is greater than predicted by surface observations of buoyancy flux, even for very high viscosity. Although uncertainties are large, this high inferred flux for plumes at midmantle depth contradicts the common view that plumes play only a minor role in the Earth's heat budget, and is even compatible with the view that plumes are responsible for all upward advective heat transport in the lower mantle that eventually breaks through into the upper mantle, and with the view that the phase transition at 670 impedes mass transport except for the powerful fluxes from slabs and plumes, perhaps 200 cubic km per year not counting flood basalts.

Bedrock Geology and River Chemistry

Peucker-Ehrenbrink, B; Miller, M W

Project goals:

The interaction of rainwater with soils and underlying bedrock determines the chemical composition of runoff and exerts a strong influence on the chemistry of seawater. Since 2002 we have been working towards a quantitative characterization of the lithologic composition and age structure of continental bedrock. We specifically focus on the characterization of bedrock geology in individual river drainage basins in order to quantitatively evaluate links between bedrock geology and the chemical composition of river water. Here we present a progress report on our activities and show that the lithologic composition and age structure of river drainage basins is strongly correlated with the radiogenic isotope signature of riverine dissolved and particulate matter.

Global Bedrock Geology:

A Geographic Information System analysis of the Geological Map of the World at 1:25,000,000 scale (2nd edition, CGMW, 2000) reveals that 62.9% (93.76 million km²) of the mapped continent surface is covered by sedimentary rocks, whereas endogenous (plutonic and metamorphic) rocks and extrusive volcanic rocks cover 19.2% (28.69 Mkm²) and 7.9% (11.72 Mkm²), respectively. The remaining surface area is covered by glaciers (9.4%, 14.02 Mkm²), lakes (0.6%, 0.91 Mkm²), and unidentified areas (0.42%, 0.62 Mkm²). The age structure of these large lithologic units is quite distinct: Sedimentary rocks have an average stratigraphic age of 246 ± 42 Myr (1 SD) that reflects the cannibalistic recycling of older sedimentary units. Endogenous (plutonic and metamorphic) rocks and extrusive volcanic rocks have average ages of 1749 ± 269 Myr (1 SD) and 335 ± 52 Myr (1SD). Global bedrock, averaged according to area, has an average age of 576 ± 69 Myr (1 SD).

Large-Scale Drainage Basins:

Nineteen large-scale drainage basins covering the entire continental bedrock vary considerably in their geologic makeup. Basins dominated by sedimentary bedrock such as the Black Sea (84.4%, 247 ± 23 Myr), the Russian Arctic (80.4%, 454 ± 44 Myr) and the North American Arctic (79.9%, 836 ± 62 Myr) have average bedrock ages that are intermediate between ages of drainage basins dominated by volcanic rocks, such as the West coasts of North (35.4%, 231 ± 31 Myr) and South America (37.3%, 144 ± 22 Myr), and basins dominated by endogenous rocks, such as West (34.4%, 901 ± 128 Myr) and East (33.6%, 804 ± 128 Myr) Africa and the Red (45.7%, 734 ± 282 Myr) and Baltic (41.5%, 826 ± 180 Myr) Seas.

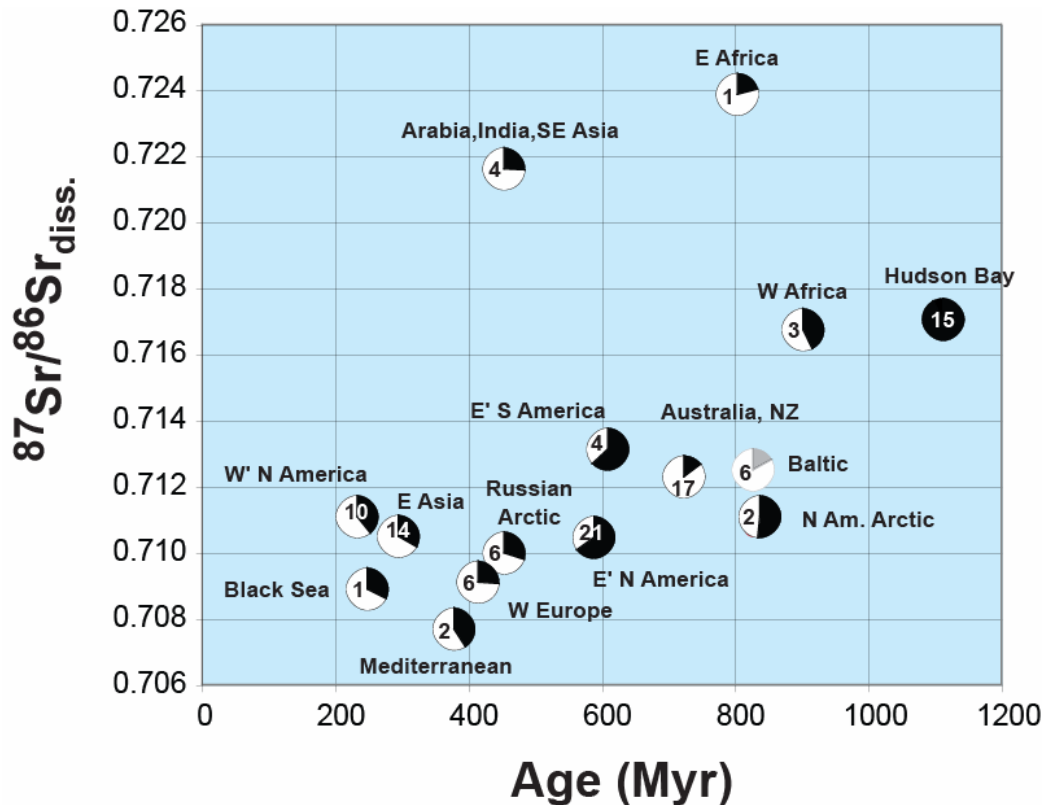


Figure 1.

Global Runoff:

A compilation of global runoff (GLORI Database, Meybeck & Ragu, 1996) from these 19 large-scale drainage basins reveal that runoff into the central Atlantic from the East coast of South America (9,365 km³ yr⁻¹) and the West coast of Africa (2,080 km³ yr⁻¹) accounts for about one third of the continental runoff. We emphasize that high-standing tropical islands with small drainage basins are currently underrepresented in our database. Inclusion of smaller drainage basins in areas with high rainfall (East Asia, West coast of South America) may thus yield slightly different results. However, our database currently includes rivers that account for 28,332 km³ yr⁻¹, or 75%, of the global runoff of about 37,400 km³ yr⁻¹. The runoff-weighted average bedrock composition of the continental area connected to the oceans is composed of 68.0% sedimentary, 10.3% extrusive volcanic, and 20.8% endogenous rocks with an average age of 538 Myr.

Global Strontium Runoff:

A reevaluation of the global runoff of strontium indicates that the average ⁸⁷Sr/⁸⁶Sr is 0.7124. This number is slightly biased to more radiogenic values because chemical analysis of young drainage basins along the West coast of South America and East Asia are sparse. We are working towards improving the global database that currently consists of 112 rivers. We also observe a positive correlation between average age of the drainage basins and dissolved ⁸⁷Sr/⁸⁶Sr (Figure 1, black areas and numbers in pie charts represent the percentage of runoff and number of rivers analyzed for ⁸⁷Sr/⁸⁶Sr). This correlation agrees well with more detailed analyses of the Fraser and Mississippi River basins that also show striking linear correlations between bedrock age and dissolved ⁸⁷Sr/⁸⁶Sr. The correlations can be interpreted as binary mixtures of young volcanic and sedimentary contributions on one hand and old

plutonic and metamorphic rocks on the other hand. Given the age distribution for these broad lithologic units discussed above the correlations can also be viewed as the effect radiogenic ingrowth of ^{87}Sr since the last resetting had on the Sr isotopic composition of runoff. Correlations between age and the dissolved Nd isotopic composition of runoff will be less pronounced, because the Sm-Nd system is less affected by weathering and erosion than the Rb-Sr system (e.g., Goldstein, 1988). We hypothesize that the U-Pb and Re-Os isotope systems will be more akin to the Rb-Sr system, whereas the Lu-Hf systematics of global runoff will be more similar to the Sm-Nd system.

The Marine $^{87}\text{Sr}/^{86}\text{Sr}$ Record:

Since the discovery of submarine hydrothermal vents in 1977 the marine $^{87}\text{Sr}/^{86}\text{Sr}$ record has been viewed primarily as the balance between unradiogenic hydrothermal inputs and radiogenic continental runoff. This view neglects temporal variations in the makeup of the continental crust, that were viewed as the main driving force of changes in the marine $^{87}\text{Sr}/^{86}\text{Sr}$ before the discovery of hydrothermal vents (e.g., Brass, 1976). We argue that changes in the composition and age structure of the continental crust that contribute dissolved solids to continental runoff are an important driving force of secular changes in the marine $^{87}\text{Sr}/^{86}\text{Sr}$. We suspect that a paleo-bedrock reconstruction throughout the Phanerozoic (e.g., Ronov et al., 1989; Bluth & Kump, 1991) coupled with reconstructions of past runoff distribution using GCMs will reveal that the marine $^{87}\text{Sr}/^{86}\text{Sr}$ has been influenced primarily by changes in the chemical composition of continental runoff. We present a first attempt to cast the Ronov et al. reconstructions in the context of the changing age structure of the continental crust and argue that first-order variations in the marine $^{87}\text{Sr}/^{86}\text{Sr}$ since the Cambrian are consistent with a continental driving force.

Mantle Plumes: Not just heads or tails, maybe burls, shoots & restite roots

Phipps Morgan, J

The idea that hotspot volcanism is only made by melting near the top of a narrow core-to-surface pipe has long been superseded, except to those who wish a simple straw horse to flog. Modern variants of the plume hypothesis keep the basic idea of plumes as concentrated pipes of mantle upwelling that are the return flow counterpart to subducting slabs. However, they introduced (starting with Morgan [JGR, 1978]) several other mechanisms for plumes and lateral asthenosphere flow from plumes to induce hotspot volcanism in addition to the classical expression of plume stem-top melting as the source of main-stage hotspot island volcanism. Here I will review this conceptual progress and potential resolutions to several ongoing debates in plumology.

In my opinion, the worst myth about plumes is the mistaken ‘factoid’ that plumes only bring up ~10% of the heat lost through the seafloor. Although embedded in modern literature and thinking, this ‘observation’ is actually poorly based and depends highly on an implicit assumption about the origin of hotspot swell relief — it depends on interpreting a hotspot swell as reflecting the entire upwelling buoyancy flux of its associated plume. If hotspot swells reflect the fraction of the plume-buoyancy flux that is ‘trapped’ to move with the lithosphere by the increase in viscosity due to dehydration associated with hotspot melt-extraction from the hottest central core of a plume, then measured swell relief provides only a lower bound to upwelling plume fluxes (See Phipps Morgan, Morgan, and Price [JGR, 1995] for a detailed presentation of the restite-root mechanism, in which it is estimated that 1/3 of the buoyancy of hotspot swells comes from basaltic intrusions, 1/3 from the trapped heat of the swell’s $\sim 3 \times 10^{20}$ Pa-s restite root, and 1/3 from the melt-extraction-induced compositional buoyancy of the restite

root. The key theoretical concept in this scenario is that melt-extraction from the peridotite fraction of upwelling plume mantle can sometimes desiccate the hottest part of the plume so that this buoyant material increases in viscosity enough to ‘stick to’ overriding lithosphere instead of flowing away from the plume-top to become typical plume-fed asthenosphere)

The high plume upwelling fluxes recently inferred by Nolet and coworkers are completely consistent with the restite-root hypothesis for the formation of hotspot swells, and the restite-root hypothesis, coupled with the same mechanism of partial melt-extraction at mid-ocean ridges creating a ~70km-thick and $\sim 3 \times 10^{20}$ - 10^{21} Pa-s compositional lithosphere underlying young seafloor, can also explain the apparent absence of focused high-relief hotspot swells on young seafloor as well as the formation of the broader and lower-relief South Pacific ‘Superswell’ — beneath young seafloor restite-root swells will naturally spread into much broader and lower-relief structures.

I also briefly review mantle energetics constraints on possible mechanisms that may heat plume material near the base of the mantle. It seems likely that ~9TW of heat is being conducted out of the core along the core adiabat. A further ~13TW of heat is presently being generated by viscous dissipation induced by subducting slabs, and much of this heat could be dissipated in a low-viscosity plume-source region connected to upwelling plume stems. Perhaps these sources of ‘bottom heating’ are enough to stabilize deep mantle plumes — to test this we still need to explore credible numerical experiments of compressible mantle convection that incorporate a temperature-temperature dependent rheology. The only ‘hard’ bound that currently exists on upwelling plume fluxes is that over time, on average, the net upwelling plume flux can’t be higher than the downwelling flux of subducting slabs.

Another possibly mistaken factoid about plumes is that starting plumes have a broad plume-head that is followed by a much narrower plume-stem. Recent numerical and lab experiments suggest that in a high-viscosity mantle with a highly temperature-dependent viscosity, it is often difficult for the mantle to ‘neck down’ after passage of the plume head. Two interesting consequences result from this; first the plume-head consists almost entirely of deep plume-source material because it is relatively ‘easy’ for plume source material to ascend up a broader plume-stem, so that the stirring and folding like that seen in the classical Griffiths-Campbell experiments can also be produced by internal stirring within a plume head, and second that plume heads and tails entrain little surrounding mantle into the hot regions of the plume so that upward plume flow consists almost entirely of laminar upwelling of deep plume-source material. (This effect is commonly seen in many recent numerical experiments.)

Lateral flow from upwelling plumes has also been linked to volcanism at fracture zones & continental margins. This mechanism for ‘away-from-plume-stem’ plume-linked hotspot volcanism is reviewed in the context of potential plume-linked continental margin volcanism in the Arctic, E. Australia, and E. Asia, and also in potential oceanic intraplate volcanism associated with fracture zones and plume-to-ridge asthenosphere flow. I will also briefly review why I feel that the edge-effect argument for continental margin volcanism championed by Anderson is wrong, and why this is somewhat hidden by the over-idealized melting scenarios explored by Anderson and King.

Finally, I will discuss a conceptual ingredient that may explain the apparent existence of ‘episodic hotspot clusters’ linked to a single deeper upwelling plume, e.g. in French Polynesia. The idea is rheological, and again based upon the concept that water tends to lower the viscosity of nominally anhydrous mantle minerals, so that somehow ‘extracting’ the water from these minerals will lead to a

geodynamically significant increase in viscosity. If the mantle transition zone between 410-660km is a region where P-T conditions allow stable hydrous phases as suggested by lab experiments, then mantle viscosity may be significantly higher in this region as water has been ‘extracted’ from anhydrous phases to reside in low-volume fraction hydrous minerals. If a deep upwelling plume’s viscosity increases when its material rises above 660km, then, to maintain the same upward mass flux for the same buoyancy, it will need to have a larger diameter conduit. This will induce a tendency to spread beneath 660km (an effect maybe noted by Nolet and coworkers?). Above the transition zone there would be a sudden drop in viscosity that would be consistent with a much narrower fast-rising plume stem. The region where the broad slowly upwelling stem transforms into a narrow plume-stem has intrinsic instability; numerical experiments that several unstable plume-shoots can form and transiently exist above a broad transition zone ‘burl’ of upwelling plume material.

Climatic Controls on C export from 3 major US watersheds

Raymond, P

The export of carbon from watersheds has important implications to both terrestrial and oceanic biogeochemical budgets. Various factors, including land use, precipitation, temperature, watershed hydrology, soil C stocks, terrestrial productivity, and increasing atmospheric CO₂ can be critical factors controlling carbon export. Many of these factors influence each other and operate on different time scales.

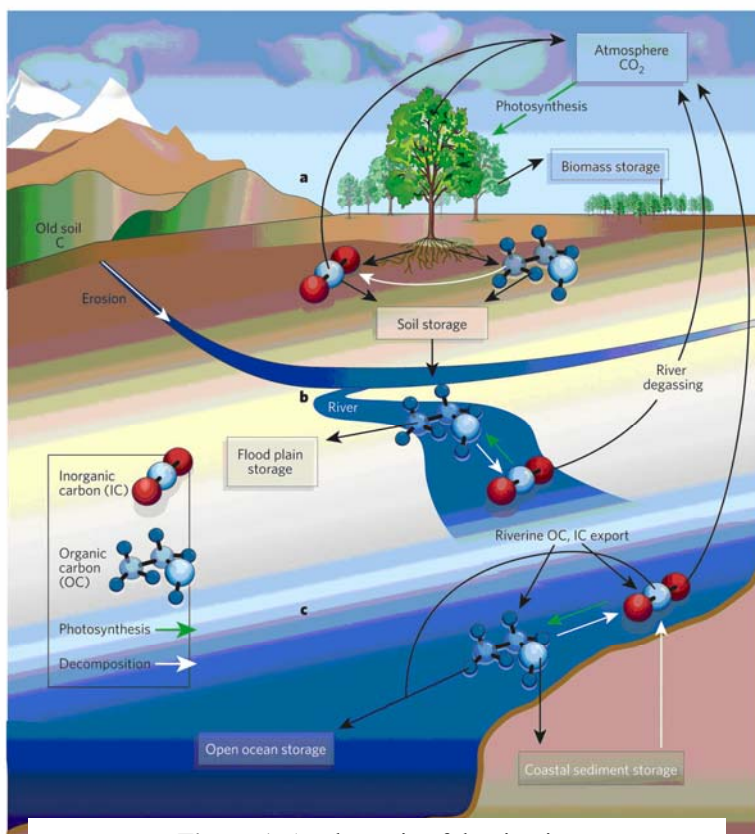


Figure 1. A schematic of the riverine

It has long been recognized that across system variation in the flux of carbon from watersheds is strongly correlated with precipitation. Within a watershed, annual variation in precipitation is also a driver of the annual export of carbon. One major change that is predicted with global warming is an accelerated hydrologic cycle, although regional areas of decreased precipitation are also predicted.

Large scale changes to the hydrologic cycle are in fact already being reported, as are associated changes in riverine carbon export. Future changes in climate will undoubtedly alter the riverine carbon export flux. There are however, feedbacks within the hydrologic and carbon cycle that make it difficult to predict the net change of C export under accelerated precipitation scenarios. The purpose of this talk is to investigate empirical relationships between

precipitation and C export (DOC, DIC, POC) from three large US watersheds over a relatively short time period when land use change was minimal.

The environmental impact of life on Early Earth : Using Iron and Sulfur Isotopes as tracers of redox changes in Proterozoic Oceans

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Redox conditions on a hierarchy of scales are controlled by, and influence, the presence of life. Locally, redox conditions associated with biological activity might be faithfully recorded by mineralogical or geochemical indicators and can serve as potential biosignatures. On a global scale, the redox evolution of Earth's atmosphere and ocean from an essentially anoxic condition to the present oxygen-rich state are undoubtedly rooted in biological activity. Since life creates and takes advantage of redox boundaries to fuel metabolic reactions, isotope composition of redox sensitive elements such as S, Fe, Se, Cu and Mo that are fractionated during redox cycling may preserve information about redox conditions in past surface environments and may help to determine the potential of life to adapt to different environments. Past studies of sulfur and iron isotope records in sedimentary sulfides over geological time have placed important constraints on the biogeochemical cycle of sulfur and the evolution of ocean chemistry during the rise of atmospheric oxygen (e.g. [1-3]). Sedimentary sulfides older than ca. 2.47 Ga have small range of $\delta^{34}\text{S}$ values and generally display non-mass dependent fractionation of S isotopes, whereas younger sedimentary sulfides have larger range of $\delta^{34}\text{S}$ values and lack non-mass dependent fractionation [1,2]. Recently the record of Fe isotope composition of pyrite in black shales have been investigated to identify a direct link between the rise of atmospheric oxygen and changes in the Fe ocean cycle and provided new insights into the past ocean redox state [3]. However, the ocean redox state after 1.8 Ga is still a matter of controversy since the disappearance of major BIFs is thought to indicate that the deep ocean became either oxic or euxinic ([4, 5]).

Here, I will present two alternative approaches to further examine redox changes in Paleoproterozoic oceans based on (1) an integrated study of Fe and S isotope fractionations in black shales, which permit to evaluate the biogeochemical cycles of Fe and S in ancient marine systems and the effects of Fe-limitation and S-limitation for pyrite formation and (2) coupled rare earth elements (REE) and Fe isotope systematics of deep-marine hematitic cherts (jasper) and iron formations (IF) in association with volcanogenic massive sulfide (VMS) deposits, which provide a window into deep ancient oceans. Three major stages of the Earth's redox history will be discussed: Stage 1 (>2.32 Ga) is when the atmosphere and ocean were anoxic with local 'oxygen oases' in the shallow ocean; Stage 2 (2.3-1.8 Ga) is after the rise of atmospheric oxygen when the deep ocean remained at least episodically anoxic but not sulfidic; Stage 3 is after deposition of the last Paleoproterozoic banded iron formations at ~ 1.8 Ga when Fe oxides were no longer soluble in the deep ocean due to either higher oxygen or H₂S content in the deep ocean.

Results of coupled Fe and S isotope analysis in black shales confirmed that after the rise of atmospheric oxygen by ca. 2.3 Ga, Paleoproterozoic ocean became stratified and gradually affected by an increase of seawater sulfate concentration in an Fe-limited system whereas pre-2.3 Ga ocean was S-limited and characterized by extensive Fe-oxide precipitation and Fe redox cycling.

The study of 1.74 Ga old jasper and IF from the Jerome mining district in Arizona revealed the occurrence of hematite together with REE patterns displaying positive to small negative Ce anomalies that have been interpreted to reflect suboxic conditions in the deep ocean at 1.74 Ga [6]. Fe isotope compositions show significant variability which are within the range for Archean BIFs but are unlike those of modern hydrothermal plume fallout that generally have moderately negative $\delta^{56}\text{Fe}$ values reflecting the composition of the hydrothermal fluids. Positive $\delta^{56}\text{Fe}$ values are found in jasper and IF deposited proximally and distally to the VMS deposits, respectively, and suggest slow Fe oxidation rates in the non-buoyant part of the hydrothermal plume. Both Fe isotope and REE data are thus consistent with a suboxic redox state for deep seawater at 1.74 Ga.

Although large fractionations in Fe isotopes were originally interpreted as potential biosignatures for Early Earth [7], subsequent studies have shown that Fe isotopes are affected by non-biological processes in low temperature settings [8]. By demonstrating the utility of Fe isotopes coupled to other geochemical tracers, such as S isotopes and REE, this study provides a framework to identify biosignatures and to advance the understanding of environmental impacts of key biological processes on Early Earth.

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Dissolved Trace Metal and Organic Matter Relationships over Various Fluvial Scales

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The fluvial mobilization of many dissolved trace elements is affected by dissolved organic matter, primarily through complexation. We have examined the metal-DOC relationship through various means including: a) metal-DOC comparisons over large scales, b) metal-DOC comparisons between watersheds of differing landscapes, and c) an incubation experiment designed to see how changing DOC composition affects metal speciation. Our compilation of data includes time series samples from the lower Mississippi River, the Loch Vale Watershed, the Pearl River (MS), and the Yukon River as well as short time series and grab samples from a wide variety of streams and rivers in the Yukon Basin. When pooled together, overall relationships between DOC and the concentrations of certain trace elements (e.g., Fe, Cu, Zn) are observed. In many cases this probably reflects competition between adsorption and organic complexation and suggests the possibility that complexation and adsorption constants in these systems vary less than the amounts of organic matter and adsorbing surfaces. In other words, it

may be possible to develop a simple one-site, one-ligand model to approximately (or, at least, conceptually) describe fluvial trace element behavior.

We also observe, when comparing watersheds of the Yukon River Basin, differences in both DOC and associated dissolved metal concentrations. If DOC is truly a master variable for these trace elements, then prediction of how climate change will affect DOC mobilization from various environments will lead to predictions of dissolved trace elements will also be affected. However, some caution is required for these generalizations. Because DOC tends to vary inversely with pH and conductivity on global fluvial scales, the importance of other controlling factors cannot be ignored.

To further investigate DOC metal relationships we have also used column partitioning methods to examine metal speciation during a photo-incubation experiment. The experimental results are indicative of a release of organically-complexed trace elements during the photo-degradation of the organic matter. Our results indicate that as fluvial DOM becomes more photo-refractory upon exposure to sunlight, there will be a transfer of certain trace elements from strongly complexed forms to adsorbed or weakly complexed forms. This can involve both decreased metal complexation as DOC is degraded as well as increased adsorption onto ferric colloids freshly precipitated by the release of complexed iron. Thus, there may be fundamental differences in metal speciation, transport, and bioavailability between low-order streams with photo-fresh allochthonous DOM inputs and floodplain rivers dominated by photo-refractory DOM.

Overall our results delineate several key points: a) for certain trace elements, there may be roughly “universal” relationships with DOC over a wide range of catchments, b) co-variance of DOC with other likely master variables remains a major uncertainty in interpreting field data when speciation data are unavailable, and c) processes that transform DOC during fluvial transport likely have an important but as yet poorly understood impact on the physical-chemical partitioning of trace elements.

Recycled crust in sources of mantle-derived melt: how much?

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Oceanic crust of basaltic composition is a common component of subducted oceanic lithosphere. At pressures higher than around 2.5 GPa, typical oceanic crust transforms completely to eclogite (clinopyroxene + garnet) with a free SiO₂ phase [1-3]. In the ascending mantle (e.g recycling in a mantle plume or upstream flow of convecting mantle, [4]) this assemblage starts to melt at higher pressures than peridotite, producing high silica melt [5]. This melt reacts with olivine from peridotite, producing pyroxenes and garnet [5,6]. Previously it has been suggested that this reaction only partially replaces olivine and thus creates refertilized peridotite enriched in pyroxenes [5,7]. This predicts various mixing proportions of ingredients (eclogite derived high-Si melt and peridotite) drastically different in composition. Such a combination will create highly nonlinear correlations of ¹⁸⁷Os/¹⁸⁸Os and ⁸⁷Sr/⁸⁶Sr isotopic ratios, which is contradicted by the strong linear correlations observed in Hawaiian basalts [8,9]. However it was shown [6] that, under conditions of local equilibrium, the reaction between high-Si eclogite derived melt and peridotite in fact produces a sharp replacement front (as explained long ago by D.S. Korzhinskii, 1970 [10]), and thus creates olivine-free lithology enriched in clinopyroxene. This was then proved by direct sandwich experiments, where natural oceanic gabbro melted and reacted with peridotite (see Fig 1). This fundamentally differs from a partial reaction because it leads to a stable pyroxenite lithology

generated by roughly fixed proportions of high-Si melt and peridotite (between 0.4-0.6 fractions of melt [6]) irrespective of the initial proportions of the reaction ingredients. Mixing of partial melts from pyroxenite and peridotite can indeed create linear correlations between $^{187}\text{Os}/^{188}\text{Os}$ and $^{87}\text{Sr}/^{86}\text{Sr}$, observed on Hawaii [6]. The other predicted geochemical consequences of replacement of olivine by pyroxene are a significant decrease of the bulk distribution coefficient between crystals and melt (K_d) for Ni [6,7] and a decrease in the ratio of bulk coefficients of Mn and Fe [11]. This occurs because olivine is the major silicate phase in peridotite concentrating Ni and the only silicate phase in peridotite preferring Fe over Mn. In addition, because pyroxene has significantly higher $K_d(\text{Ca})$ compared to olivine, the bulk $K_d(\text{Ca})$ in pyroxenite should significantly increase compared to peridotite. All these changes in bulk K_d s will increase Ni and decrease Ca and the Mn/Fe ratio of pyroxenite-derived melt compared to partial melts from peridotite. The other predicted differences between these lithologies are higher melting rates for pyroxenite than peridotite, and higher Si and lower Mg in pyroxenite-derived melt [6,12].

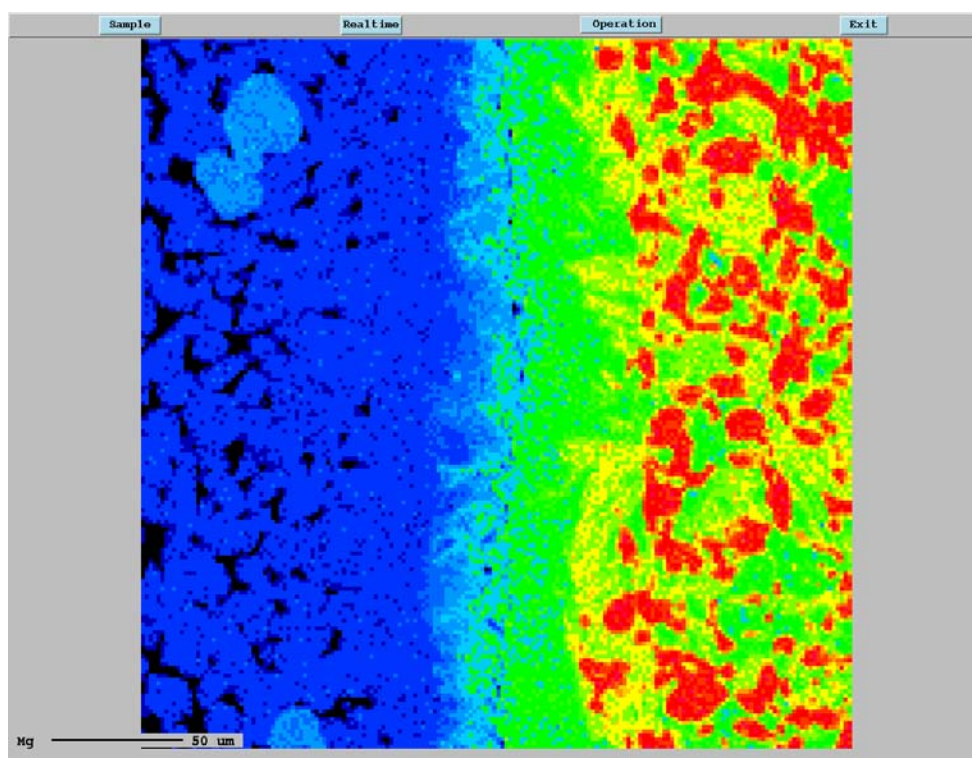


Figure 1. Mg concentration map of sandwich, (eclogite (left) and peridotite (right)) experiment at 3.5 GPa and 1500 C. Red- olivine, yellow –orthopyroxene, green-Mg-rich clinopyroxene and garnet, blue- Mg-low clinopyroxene or garnet, black- SiO_2 -rich partial melt from eclogite. Reaction between eclogite-derived melt and peridotite creates olivine free pyroxenite zone on the boundary of eclogite and peridotite.

We have tested these predictions by experimental melting of a model reaction pyroxenite from Sobolev et al, 2005[6], Table S2 column 50% at pressure 3.5 GPa and temperatures between 1400-1570 °C in a conventional 1.27cm piston-cylinder apparatus at the Australian National University[5]. These results confirm the Ni and Mn relationships predicted above. From these data, we calculate equilibrium olivine compositions at low pressure [13-15]. We use these results along with experimental data for peridotite melting [16] to calculate mixing proportions of melts derived from the two end-member sources (pyroxenite and peridotite) for the olivine datasets representing different geodynamic settings. The calculated mixing trajectory is superimposed on the natural olivine data shown in Fig. 2. Olivines from the within

plate magmas emplaced on thick (> 70 km) lithosphere (WPM-THICK group of basalts) including suites from Hawaii with seamounts, North Atlantic Province without Iceland, Reunion, Canaries, Afar, Siberian flood basalts, Emeishan, and Karoo yield average around 60% of pyroxenite derived component, similar to results derived from Ni data in Hawaiian basalts and olivines only[6]. The olivines from some continental LIPs (Siberia, Karoo, Etendeka) indicate almost purely pyroxenitic sources. Corresponding results for the other groups are: within plate magmas emplaced on thin (50-10 km) lithosphere (WPM-THIN -Iceland, Detroit Seamount, Azores) – 20-30%, MORB – 5-10%. Because of the uncertainties involved in estimating the end-member compositions, the differences between groups are better constrained than the absolute numbers. We also note that although MORB contain the lowest proportion of pyroxenite-derived melt (close to zero on average), the spread of MORB data is significant and many samples do contain substantial amounts of pyroxenite derived component. A single, highly unusual MORB sample of andesitic composition from the Southern Atlantic [17] indicates essentially 100 % pyroxenite-derived component.

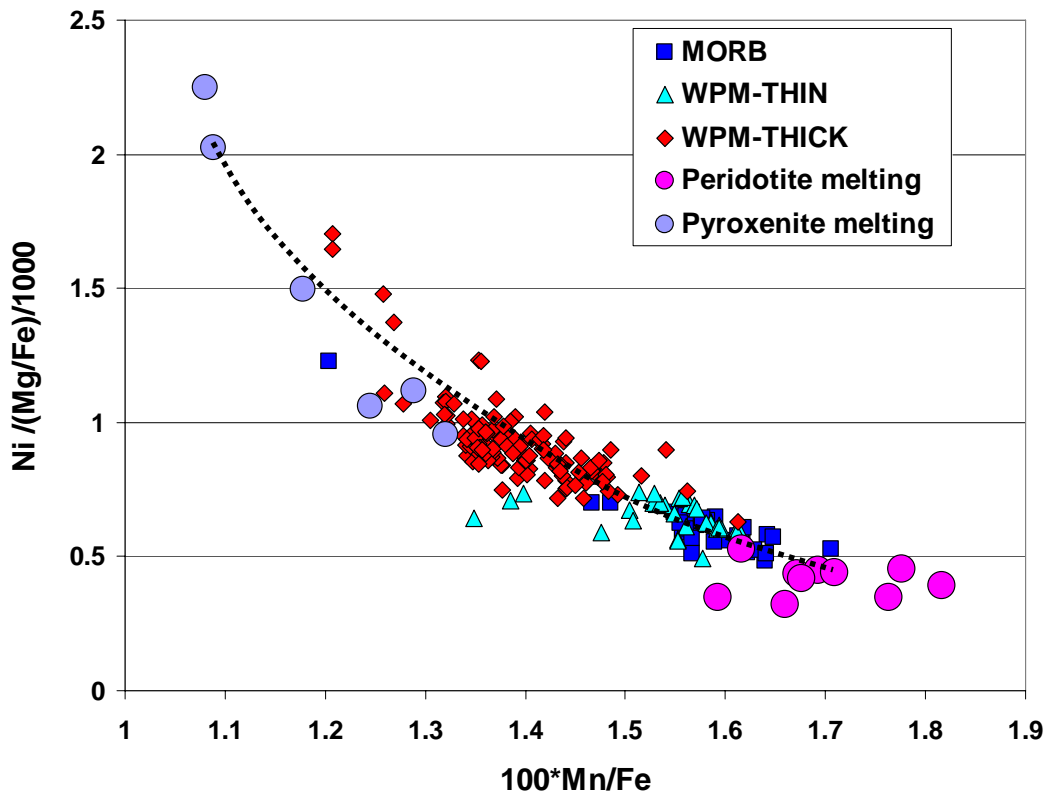


Figure 2. Average compositions of most Mg-rich olivine phenocrysts from 200 samples from different OIBs, LIPs and MORBs. Superimposed are calculated compositions of olivine equilibrium with partial melt of high pressure (3-4 GPa) experiments with fertile peridotite [16] and reaction pyroxenite (this paper). For groups definitions see text. All elements are in ppm.

A final step is to estimate the actual amount of recycled oceanic crust (X_{crc}) from the above results. This quantity is linked to the proportion of pyroxenite-derived melt (X_{px}) by the degree of melting of eclogite (F_e), the amount of eclogite-derived melt needed to produce pyroxenite from peridotite (X_e), and the degrees of melting of peridotite (F_{pe}) and pyroxenite (F_{px})[6]: Following assumption of Sobolev et al, (2005)[6], we propose that the F_e reaches a maximum of 50%. The amount of X_e is prescribed by the stoichiometry of the reaction, which also yields proportions of the reactants of close to 50:50[6]. The F_{px}

can be estimated at low pressure (1-2 GPa by modeling using MELTS software [18]), yielding a maximum of about 60 % for batch melting at 1 GPa and 1320 to 1350 °C. At higher pressures (3.5 GPa) we must rely on the (unpublished) experimental data of Yaxley et al., which also yield a maximum melt fraction of about 50-60% for batch melting for 1550-1570 °C. These values will be significantly lower for fractional melting [19], for the same reason as discussed for eclogite melting (i.e. early Na removal). Adopting an amount of 50-60 % pyroxenite melting will therefore result in a minimum estimate in the amount of recycled crust present. Finally, we estimate F_{pe} using published results [13] for MORBs (10%), Iceland, as a proxy for the WPM-THIN group (20%), Hawaii, as proxy for the WPM-THICK group. This yields the following average estimates for the amounts of recycled oceanic crust in the mantle sources: few % for MORB, 10% for WPM-THIN group and 15-20% for WPM-THICK group. These results suggest that amount of recycled oceanic crust in the convecting mantle is probably high and is likely controlled by the potential mantle temperature which is highest for WPM-THIN and lowest for MORB [13].

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Immobilization of Groundwater Arsenic in River Bank Sediment from the Ganges-Brahmaputra-Meghna River Delta

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In the Ganges-Brahmaputra-Meghna River delta, elevated concentrations of As prevalent in the Holocene shallow aquifers has been attributed to mobilization of natural As present in the aquifer sediments under reducing conditions. Recently, groundwater As concentrations is found to increase with groundwater age determined by $3\text{H}/3\text{He}$ dating in the shallow aquifer. This leads to the question about the fate of groundwater As when the reducing groundwater reaches the point of discharge at a hydrologic boundary such as the river bank. There, the sediment is likely to be more oxic and may act as a trap to immobilize discharging As. We present two sets of data in support of the redox trapping of discharging groundwater As.

In January 2003, 2-m long sediment push cores and 0.5-m surface sediment auger samples were obtained at 12 sites along the Meghna River bank from upstream to downstream coastal area. Concentrations of As were found to range from close to crustal level of < 1 mg/kg, to highly elevated level of ~ 10,000 mg/kg in subsurface sediment samples. Analysis using XANES confirms that the downstream samples are mostly arsenite while the upstream and midstream samples are mixture of arsenite and arsenate. Mineralogy of Fe determined by EXAFS confirm that downstream and midstream samples are mostly of magnetite with a mixed Fe II and III, with two upstream samples showing characteristic spectrum of goethite. Sorption capacity of these Fe-minerals would be sufficient to account for the elevated As found in the sediment.

In January 2006, we chose two areas, one with regionally high groundwater As concentrations located in the downstream area of the Meghna River, another with regionally low groundwater As concentrations (< 10 ug/L) located in the upstream area of the Brahmaputra River, for As concentration analyses in sediment cores collected along the river bank. Several, but not all of the river bank sediment cores in the high groundwater As area were found to have hundreds of mg/kg As. In contrast, none of the 5 river bank sediment cores in the low groundwater As area had elevated sedimentary As. Our results illustrate the importance of biogeochemical gradient at the groundwater-river interface in influencing elemental distribution and fluxes.

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